CHAPTER 4

Stratospheric Processes: Observations and Interpretation

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SCIENTIFIC SUMMARY

The primary cause of the Antarctic ozone hole is firmly established to be halogen chemistry. Increased confidence in this mechanism results from analyses using reevaluated field measurements, new laboratory data, and modeling studies.

The year-to-year fluctuation in the area and depth of the ozone hole over the last decade, which has been attributed to dynamical effects, is not fully explained. The apparent lack of variability in recent years—extensive ozone holes have been observed in four of the last five years—may imply that halogen chemistry is becoming dominant over dynamically-induced fluctuations in Antarctic ozone depletion.

High concentrations of CIO between 16 and 20 km have been observed in wintertime in the Arctic lower stratosphere. These observations have been incorporated into diagnostic models that have calculated localized ozone depletions of about 10 percent at these altitudes over a period of about 1 month, which are consistent with concurrent ozone measurements.

Should an unusually cold and long winter occur in the Arctic polar vortex, the appearance of clearly detectable ozone depletions there will be more likely.

Limited observations suggest that the abundance of CIO in the lower stratosphere at mid-latitudes is greater than that predicted by current models containing only gas phase chemistry, and the observed seasonal and latitudinal dependences are opposite to those predicted. Some new studies that incorporate currently known heterogeneous processes provide an improved simulation for some observed gases, such as CIO and nitric acid.

There is not a full accounting of the observed downward trend in global ozone. Plausible mechanisms include heterogeneous chemistry on sulfate aerosols and the transport of chemically perturbed polar air to middle latitudes. Although other mechanisms cannot be ruled out, those involving catalytic destruction of ozone by chlorine and bromine appear to be largely responsible for the ozone loss and are the only ones for which direct evidence exists.

The potential importance of ozone loss in the lower stratosphere due to bromine, through bromine-chlorine interaction, is significantly increased by the widespread enhanced CIO abundances.

Because heterogeneous processes are important and the levels of chlorine in the stratosphere are increasing, volcanic injections into the stratosphere could have a substantial effect on global ozone.

Increasing levels of atmospheric chlorine and bromine are expected to lead to significantly more ozone depletion.
4.1 INTRODUCTION

Explaining the observed ozone trends discussed in Chapter 2 and predicting future trends requires an understanding of the stratospheric processes that affect ozone. Stratospheric processes occur on both large and small spatial scales and over both long and short periods of time. Because these diverse processes interact with each other, only in rare cases can individual processes be studied by direct observation. Generally the cause and effect relationships for ozone changes have been established by comparisons between observations and model simulations. Increasingly, these comparisons rely on the developing, observed relationships among trace gases and dynamical quantities to initialize and constrain the simulations.

The goal of this chapter on stratospheric processes is to describe the causes for the observed ozone trends as they are currently understood. At present, we understand with considerable confidence the stratospheric processes responsible for the Antarctic ozone hole but are only beginning to understand the causes of the ozone trends at middle latitudes. Even though the causes of the ozone trends at middle latitudes have not been clearly determined, it is likely that they, just as those over Antarctica, involve chlorine and bromine chemistry that has been enhanced by heterogeneous processes.

This chapter generally presents only an update of the discussions and observations that have occurred for stratospheric processes since the last assessment (WMO, 1990), and is not a complete review of all the new information about stratospheric processes. It begins with an update of the previous assessment of polar stratospheres (WMO, 1990), followed by a discussion on the possible causes for the ozone trends at middle latitudes and on the effects of bromine and volcanoes.

4.2 ANTARCTIC OZONE DEPLETION

Significant advances in our understanding of the processes of the lower stratosphere have come from our attempts to understand the Antarctic ozone hole. We know that the ozone loss each spring over Antarctica is in large part caused by chlorine and bromine catalysis, that the enhanced chlorine catalysis results from the alteration of the chemical environment near and inside the Antarctic polar vortex by heterogeneous processes, and that these processes occur in the meteorological conditions of the winter-time stratosphere at high latitudes (Solomon et al., 1986; McElroy et al., 1986a; Toon et al., 1986; WMO, 1990).

The basic catalytic cycles responsible for most of the observed ozone loss are (Molina and Molina, 1987):

\[
\begin{align*}
\text{ClO} + \text{ClO} + \text{M}^* & \rightarrow \text{Cl}_2\text{O}_2 + \text{M} \\
\text{Cl}_2\text{O}_2 + \text{sunlight} & \rightarrow \text{Cl} + \text{ClO} + \text{O}_2 \\
\text{ClO} + \text{M} & \rightarrow \text{Cl} + \text{O}_2 + \text{M} \\
\text{Cl} + \text{O}_3 & \rightarrow \text{ClO} + \text{O}_2
\end{align*}
\]

and (McElroy et al., 1986b):

\[
\begin{align*}
\text{ClO} + \text{BrO} & \rightarrow \text{Br} + \text{Cl} + \text{O}_2 \\
\text{Cl} + \text{O}_3 & \rightarrow \text{ClO} + \text{O}_2 \\
\text{Br} + \text{O}_3 & \rightarrow \text{BrO} + \text{O}_2
\end{align*}
\]

*M represents N$_2$ and O$_2$

Other catalytic cycles, one containing the reaction ClO + HO$_2$ → HOCl + O$_2$ (Solomon et al., 1986) and another containing ClO + O → Cl + O$_2$, make smaller contributions.

Our confidence in the validity of these processes, which were postulated with little initial support from laboratory and field measurements, has continually increased as laboratory and field studies have been completed. At the time of the last assessment (WMO, 1990), most of the reaction rate constants and the reaction products were known for the catalytic cycles. The products of the photolysis of ClOOCI, previously unknown, have now been identified as Cl and ClOO (Molina et al., 1990). Although, in 1989, heterogeneous reactions affecting chlorine and nitrogen were known to be fast, computer models using these data were hard pressed to simulate features of the ozone hole (Rodriguez et al., 1989; Prather, 1991). Laboratory data taken since 1989 indicate that chlorine nitrate reactivity with H$_2$O is slow on nitric acid trihydrate, that the reaction between HOCl and HCl is fast on ice surfaces, and that chlorine and nitrogen chemistry occurs on cold liquid sulfate aerosols that exist in the polar regions prior to the onset of polar stratospheric clouds (PSCs) (see Chapter 3 for details and references). These heterogeneous reactions lead to more mechanisms for converting chlorine from reservoir to reactive forms than were previously known.
4.2.1 Quantitative Estimates of Ozone Loss

The observed increase in the reactive CIO and the concurrent decrease in ozone as measured from outside to inside of the chemically perturbed region over Antarctica (Figure 4-1) gave a strong indication that the proposed chlorine chemistry was involved in the ozone loss (Anderson et al., 1989a). However, at the time of the 1989 assessment (WMO, 1990), the ozone loss calculated using the observed abundances of CIO and BrO and measured reaction rate constants produced expected ozone losses that were somewhat less than the ozone losses that were concurrently observed. (Anderson et al., 1989b; deZafra et al., 1989; Sander et al., 1989). These calculations all assumed that abundances of CIO and BrO were zonally symmetric, and that the vortex edge restricted the flow of polar air to middle latitudes, thus forming a "containment vessel." Other model calculations that did not depend upon the observed CIO abundances and simple assumptions about halogen radical distributions were capable of reproducing the observed ozone destruction because they calculated CIO abundances that were larger than those observed (Jones et al., 1989; Austin et al., 1989; Ko et al., 1989). These models, however, were not definitive because of the uncertainties in the spatial and temporal distributions of PSCs and heterogeneous chemistry. As a result, a number of other catalytic ozone loss mechanisms involving chlorine were proposed.

Recent calculations of ozone loss (Anderson et al., 1991) using reevaluated in situ CIO and BrO measurements show that the observed ozone loss can be described completely by chlorine and bromine catalysis, to within experimental errors, for a zonally symmetric air flow within a containment vessel (Figure 4-2). This reevaluation resulted from additional, careful laboratory calibrations of the pressure and temperature dependences of the instrument used to measure CIO and BrO from the National Aeronautics and Space Administration (NASA) ER-2 aircraft during the Airborne Antarctic Ozone Experiment (AAOE) campaign (Anderson et al., 1991). As a result, the measured in situ values of CIO and BrO are larger than was earlier reported, and the calculated rate of ozone destruction is increased, particularly for potential temperatures below 400 K (Murphy, 1991).

Agreement between observed and calculated ozone loss is also obtained from other data. An analysis of OCIO column abundances and diurnal variations from McMurdo, Antarctica, during September 1987 shows that the observed ozone loss can be accounted for by the catalytic mechanisms involving Cl2O2 and CIO + BrO (Solomon et al., 1990). In another study, model calculations using ground-based and in situ CIO measurements and aircraft HCl and ClONO2 column measurements were used to synthesize the expected CIO abundances well inside the Antarctic vortex (Rodriguez et al., 1990). Visual agreement was obtained between the observed and the calculated ozone decline.

Verification, with even less uncertainty, of the processes that cause the Antarctic ozone hole will require additional information (Solomon, 1990). The temporal and spatial distribution of CIO and BrO should be mapped globally. The amount of air that flows through the vortex in winter—whether the vortex is a flowing processor (Tuck, 1989; Proffitt, 1989) or a containment vessel (Hartmann et al., 1989; Schoebel and Hartmann, 1991)—needs to be definitively settled. The mixing of air parcels must be better understood. The characteristics of the large PSCs,
composed mainly of water ice, and the amount of cloudiness in the troposphere over Antarctica need to be quantified, so that the radiative effects of PSCs, which may be small on average, can be better understood (WMO, 1990; Rosenfield, 1991).

Nonetheless, since the first observations of the ozone hole, we have been able to state to within the uncertainties of the laboratory and field measurements and the models that the ozone hole is caused largely by halogen chemistry. The difference between this assessment and the previous one (WMO, 1990) is that the uncertainties in our knowledge of stratospheric processes have been reduced by the reevaluated field measurements, new laboratory data, and modeling studies. We now have greater confidence that the ozone hole is caused by halogen chemistry.

4.2.2 Year-to-Year Variability in the Severity of the Ozone Hole

The fundamental mechanisms that determine the interannual variability of the severity of the Antarctic ozone hole have so far not been identified. Evidence has been presented for a correlation between one dynamical effect, the tropical quasi-biennial oscillation (QBO), and total ozone amounts in the extratropics, although the relationship is not well understood (Garcia and Solomon, 1987; WMO, 1990; Gray and Ruth, 1991; Lait et al., 1989; Angell, 1990). The QBO may modulate the transport of inorganic chlorine and reactive nitrogen or may modulate the propagation of planetary waves, thus affecting the temperatures and winds associated with the polar vortex. The modulation of the observed total ozone loss may be related to others factors as well. These dynamical couplings are complex, and attempts to establish connections on the basis of simple correlations have not been successful (Dunkerton and Baldwin, 1991; Angell, 1990).

In three of the last four years, the ozone hole has been as extensive and as intense as the ozone hole in 1987. The correlation of the easterly phase of the QBO and a less intense ozone hole was observed in 1988 but has not been observed in 1991 (Figure 4-3). This diminished effect of the QBO on ozone loss may result from the shift in the phase of the QBO cycle (a period of 22 to 34 months) relative to the austral winter over the course of several years (Gray and Ruth, 1991). On the other hand, this recent series of deep ozone holes may be an early indication that the fluctuating dynamical effects on the stability, temperatures,
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Figure 4-3 Year-to-year variations of the mean ozone observed in the southern polar region for October (R.S. Stolarski, private communication). Satellite and ground-based measurements of the October mean total ozone show the development of the Antarctic ozone hole. The measurements are by the Dobson Instrument at Halley Bay (plusses); the Nimbus 7 TOMS satellite instrument, processed as Version 6 on a 2° latitude by 5° longitude grid (asterisks with a dashed line); and the Nimbus 4 Backscatter Ultraviolet instrument for the first 3 years (triangles).

and thus annual ozone loss of the Antarctic polar vortex may not moderate ozone loss in the future.

As the chlorine loading of the stratosphere increases in the future, the amount of time required for significant ozone depletion by these chemical mechanisms will decrease. Under these circumstances, significant ozone depletion would eventually occur even for a warmer, shorter-lived vortex that might be expected in the easterly phase of the QBO. Although it is plausible that this chemical control has already begun, such speculation must be quantified and verified by continued observations of yearly, intense ozone holes.

4.3 THE PERTURBED CHEMISTRY AND OZONE LOSS IN THE ARCTIC

4.3.1 Observations of the Arctic Polar Vortex

No ozone decline similar to the Antarctic ozone hole has yet been observed in the Arctic. Yet the observations of the Arctic polar vortex in January and February 1989 indicate that the Arctic polar vortex was almost as chemically perturbed as the Antarctic polar vortex (Figure 4-4) (see Geophys. Res. Lett., 17, No. 4, 1990, special issue on the Airborne Arctic Stratospheric Experiment (AAOE); Geophys. Res. Lett., 18, No. 4, 1991, Chemistry of Ozone in the Polar Stratosphere, special section on CHEOPS-III). First of all, enhanced abundances of CIO were observed near and inside the Arctic polar vortex (Brune et al., 1988, 1990) with values inside the vortex at altitudes of 16 to 20 km as large as those observed over Antarctica. Estimates of the amount of available chlorine indicate that inside the Arctic polar vortex, the amount of chlorine in the forms of CIO or Cl2O2 was at least 85 percent of the total amount of available chlorine (Figure 4-5) (Kawa et al., 1990).

Figure 4-4 Comparison of Antarctic and Arctic in situ data taken during the AAOE in 1987 and the AASE in 1989 (Brune et al., 1991). Arctic data are represented by solid lines; Antarctic data by dashed lines. The dot-dash line represents the NOy abundances predicted by the measurement of N2O and the empirical relationship between N2O and NOy, called NOy* (Fahey et al., 1990c). The Arctic abundances shown are about 1,000 pptv larger than the Antarctic abundances. All data have been averaged over the flights except for CIO over the Arctic, which are only from one flight on Feb. 10, 1989. In relation to the spring equinox for the respective hemispheres, the Arctic mission (Jan. 3–Feb. 10) ended before the Antarctic mission (Aug. 17–Sept. 23) started. Error bars are the variability (+1σ) of the results for all flights. The CIO abundances observed in the Antarctic vary little from flight to flight and were similar to the abundances observed in the Arctic. The Antarctic abundances of NOy had large variability, as shown by the error bars at 430 K and 370 K.
1991; Brune et al., 1990, 1991; Salawitch et al., 1990; McKenna et al., 1990). Measurements of the depleted HCl reservoir (Mankin et al., 1990; Adrian et al., 1991) and the increased column abundances of ClONO\textsubscript{2} near the edge of the vortex and decreases inside (Mankin et al., 1990) are consistent with widespread conversion of chlorine to reactive forms. The abundances of BrO were also found to be similar to those observed over Antarctica (Toohey et al., 1990; Wahner et al., 1990a).

At altitudes between 16 and 20 km inside the Arctic polar vortex, these observed, enhanced abundances of reactive chlorine and bromine in the presence of sunlight dictate the instantaneous rate of ozone loss. The integrated amount of ozone loss by

![Diagram](image)

**Figure 4-5** Fractional partitioning that is derived for reactive chlorine in the Arctic during AASE at three potential temperatures (Kawa et al., 1991). Photochemical stationary steady state is assumed to determine ClONO\textsubscript{2} and Cl\textsubscript{2}O\textsubscript{2} abundances from observations of ClO and NO. Data are averaged for several flights, for which the maximum wind has been used to define the vortex edge at 0° latitude. Positive values of the latitude are inside the vortex. The values of ClO are low because the illumination of the vortex was weak during much of this mission. Note that ClO and Cl\textsubscript{2}O\textsubscript{2} make up essentially all of the total available chlorine for potential temperatures below 470 K at 5° to 10° latitude inside the vortex.
chlorine and bromine catalysis, however, is also dictated by the abundances of \( \text{NO}_x \), which control CIO and BrO through the formation of ClONO\(_2\) and BrONO\(_2\). Inside the Arctic polar vortex, the amounts of the reactive nitrogen species NO\(_2\) (Mount et al., 1988; Pommereau and Goutail, 1988; Mankin et al., 1990; and Wahner et al., 1990b) were very low, and the amount of NO was unmeasurable (<10 pptv) by in situ techniques (Fahey et al., 1990a). The Arctic polar vortex was only occasionally observed to be denitrified, and then, usually only partially so (Arnold and Knop, 1989; Kawa et al., 1990; Fahey et al., 1990b; Schlager and Arnold, 1990; Mankin et al., 1990; Kondo et al., 1990). This amount of denitrification is significantly different from the almost complete denitrification observed over Antarctica. This difference in denitrification means that more HNO\(_3\) was available to be photolyzed into NO\(_2\) in the Arctic, thus speeding the chemical conversion of CIO into ClONO\(_2\), and slowing the halogen catalytic destruction of ozone.

### 4.3.2 Estimates and Observations of Ozone Loss in the Arctic Polar Vortex

Diagnostic models based on the observations of CIO, BrO, and NO\(_x\) suggest that losses of ozone at altitudes between 16 and 20 km inside the Arctic polar vortex in 1989 were about 10 percent for the 35 days between January 6 and February 10 (McKenna et al., 1990; Salawitch et al., 1990). These local losses are consistent with the analyses of the ozone losses deduced from the ozone observations made concurrently (Proffitt et al., 1990; Browell et al., 1990; Schoeberl et al., 1990; Hofmann et al., 1989). Additional local losses that might have occurred in mid-February were estimated to be about 2 percent per day (McKenna et al., 1990; Murphy, 1991; Brune et al., 1991).

Total ozone loss can be estimated from calculated and measured local ozone loss rates by integrating through the region affected by polar stratospheric clouds. The effects of PSCs on reactive chlorine and reactive nitrogen were observed for altitudes below 20 km and must be estimated for higher altitudes where no measurements of reactive chlorine and bromine exist. However, losses in the total ozone for 60°N to 70°N in 1989 have been calculated to be 5 percent to 8 percent by two-dimensional models (Isaksen et al., 1990; Chipperfield and Pyle, 1990; Pitari and Visconti, 1991). These losses of total ozone are roughly consistent with the observations and calculations of the local ozone losses discussed above, although these calculations are sensitive to the characteristics and chemistry of PSCs. Ozone changes of this magnitude can be determined when data are averaged over large spatial and temporal scales but are difficult to separate from the natural, seasonal ozone fluctuations when the ozone changes are observed for only one to two months.

A difference between the Arctic polar vortex and the Antarctic chemically perturbed region is that the Arctic vortex does not get as cold and thus is not as denitrified. Further, the Arctic vortex often breaks up a month before the spring equinox, whereas the Antarctic polar vortex breaks up 1 or 2 months or after the spring equinox. However, the observations show that even the rather limited number of PSCs of the Arctic polar vortex is sufficient to activate the reactive chlorine. In 1989, the vortex was as cold as had been observed in January in 30 years of records, but rapidly warmed in mid-February (Nagatani et al., 1990). The breakup of the vortex in early March restricted the amount of ozone loss. However, the Arctic polar vortex was more stable and colder in the winters of 1966–1967 and 1975–1976 (Nagatani et al., 1990). If the conditions of these years were repeated, with the increased amount of stratospheric chlorine that exists today (Zander et al., 1987; Wallace and Livingston, 1991), then an Arctic ozone hole, probably smaller and less intense than an Antarctic ozone hole, would most likely occur. This probability will increase as the amount of stratospheric chlorine increases from 3.5 to 4.1 parts per billion by volume (ppbv) in the near future.

### 4.3.3 Dynamics of the Arctic Polar Vortex

The issue of the amount of air that is exchanged between the polar vortex and middle latitudes, previously examined for the Antarctic, has now been examined for the Arctic (Proffitt et al., 1990; Tuck et al., 1991; Schoeberl et al., 1991). The amount of air transported between the polar vortex and middle latitudes affects not only the actual ozone loss within the vortex, but also that in middle latitudes. The effects on ozone in middle latitudes will be examined in the next section.
The polar vortex could be viewed as a flowing processor of air. The diabatic cooling that produces transport from the vortex exterior to the interior has been used to explain the observed distributions of N₂O from the AASE mission (Proffitt et al., 1990). In addition, high-resolution analyses of potential vorticity from the European Center for Medium-Range Weather Forecasts (ECMWF), in combination with trajectory calculations, have been used to support the notion that air may be chemically processed within the Arctic polar vortex and then transported to the middle latitudes (Tuck et al., 1991) (Figure 4-6). Measurements of water vapor near the Antarctic and Arctic polar vortices may also indicate a substantial flow of air through the polar vortices (Kelly et al., 1990).

However, the polar vortex may also be viewed as a leaky containment vessel. Plumb (1990) contends that the large meridional flow proposed by Proffitt et al. (1990) is probably inconsistent with the angular momentum budget. Schoeberl et al. (1991) have combined data analyses, trajectory calculations, and radiative transfer computations to diagnose the residual polar circulation. They conclude that the polar vortex is essentially isolated from the middle latitudes. Their model of the vortex has rather rapid mixing outside the vortex, weak mixing across the vortex boundary, and modest mixing inside the vortex (Figure 4-7). However, rapid radiative cooling due to large PSCs, even if it occurs infrequently, may affect these conclusions. In support of the concept of weak mixing from inside to outside the vortex, three-dimensional model calculations using assimilated data fields (Rood et al., 1991) indicate that only a small amount of the chemically perturbed polar air passes from inside the vortex to the middle latitudes. This model has only modest spatial resolution, however, and so may not quantitatively represent the transport of the observed small-scale polar air parcels to the middle latitudes.

4.4 OZONE DEPLETION AT MIDDLE LATITUDES

The ozone loss at the middle latitudes has well-defined characteristics that must be explained by any proposed stratospheric processes (see Chapter 2 for details). The decadal trend is greatest at high latitudes and in winter and spring, although significant trends occur as far south as 30°N and in summer. Further, the observed ozone decreases predominantly occur in the lower stratosphere below 25 km. Computer models containing only the currently understood gas phase chemistry cannot reproduce these characteristics of the observed ozone trends (see Chapter 8). As a result, some other chemistry or dynamics that are not properly represented in these models must be involved.

Isolating the causes of this decadal change in ozone at middle latitudes is considerably more difficult than establishing the link between stratospheric chlorine and the Antarctic ozone hole. While the ozone decreases in the Antarctic ozone hole are measured in percent per day, the ozone decreases at middle latitudes are measured in percent per decade. Subtle changes in either the dynamics or chemistry could possibly cause such ozone changes.

At present, the only proposed cause of the downward trends in total ozone at middle latitudes that can satisfy most current observations involves enhanced chlorine and bromine catalysis that is initiated by heterogeneous chemistry. These processes based on halogen photochemistry are appealing as the cause for a couple of reasons. First, they occur in the lower stratosphere where both PSCs and stratospheric aerosols are concentrated, precisely at the altitudes where the observed ozone trend is occurring. Second, the observed increases in stratospheric chlorine and bromine that have occurred over the last few decades could, by these processes, result in the observed ozone trend.

4.4.1 Transport of Polar Air to the Middle Latitudes

One reasonable postulate for the total ozone decrease at middle latitudes is that the chemically perturbed polar air is being transported to middle latitudes in the lower stratosphere. In the Southern Hemisphere, the mixing of the polar air, depleted of ozone, with the middle latitude air (the dilution effect) (Chipperfield and Pyle, 1988; Sze et al., 1989; Prather et al., 1990; Cariolle et al., 1990) would cause ozone loss at the middle latitudes at the breakup of the vortex in November or December. A second effect, which can occur in both hemispheres, is the transport to middle latitudes of air that has enhanced levels of reactive chlorine and deplet-
Figure 4-6  The potential vorticity (PV) map at the 475 K potential temperature surface for Feb. 20, 1989, from the European Center for Medium-Range Weather Forecasts (ECMWF) analysis model run at the T63 resolution (horizontal resolution of 210 km) (Tuck et al., 1991). PV contours are marked every $6 \times 10^{-6}$ K kg$^{-1}$ m$^2$ s$^{-1}$, and the area between the PV contours of $30 \times 10^{-6}$ and $36 \times 10^{-6}$ K kg$^{-1}$ m$^2$ s$^{-1}$ has been shaded. This band corresponds to a conservative view of the Arctic polar vortex edge. Arrows mark the direction and relative speed of the horizontal wind. The butterfly shape of the polar vortex is evident, and small features of high PV are scattered over the map. The heavy line indicates the flight track of the NASA ER-2 aircraft from Stavanger, Norway, to Wallops Island, VA.
The Polar Vortex

Figure 4-7 A schematic diagram of the circulation and mixing associated with the generic polar vortex, based on mixing rate estimates and radiative transfer computations (Schoeberl et al., 1991). Thin lines show the zonal contours; J indicates the jet core. Double arrows indicate mixing, with the longer arrows representing larger mixing rates. Mixing rates vary from $10^4$ m$^2$ sec$^{-1}$ or less inside the vortex to greater than $10^6$ m$^2$ sec$^{-1}$ outside. Single arrows indicate flow directions, with the lengths approximately indicating magnitude. Maximum poleward flow (on the order of 0.1 m sec$^{-1}$) occurs equatorward of the wind jet. The largest descent zone (with vertical velocities of about 0.05 cm sec$^{-1}$) is roughly coincident with the jet core. Long-lived tracer isopleths are shown by thick lines. This picture of the polar vortex is relevant to the Arctic midwinter period or the Antarctic early spring. Approximate altitudes and pressures (in mb) are given along the ordinate.
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ed levels of reactive nitrogen (called chemical propagation) (Prather and Jaffe, 1990). In these air parcels, the reactive chlorine would be constantly depleting ozone at an accelerated pace until the CIO is converted to CIONO₂ and HCl by gas phase chemistry. This conversion occurs over a period of weeks either by photolysis of any nitric acid remaining in the air parcel or by mixing of the polar air with middle latitude air.

The mixing of the polar air with the middle latitude air at the breakup of the vortices in the late winter and early spring can explain some of the ozone loss at the middle latitudes for these times. However, significant flow of air through the vortex, as proposed by Tuck et al. (1991) and Proffit et al. (1990), is required if the ozone losses during the winter are to be explained mainly by this mechanism. Tuck et al. (1991) estimate that 5 percent to 25 percent of the area north of 30°N consists of air that has come from the vortex. Conflicting results are reported from a three-dimensional model study capable of reproducing the observed CIO abundances at modest resolution (Douglass et al., 1991; Kaye et al., 1991). This study indicates that the transport of polar air masses contributes little to the ozone change at middle latitudes. In addition to any ozone loss that may be caused by transport of polar air, some ozone loss occurs in air parcels that come from the middle latitudes and pass through cold regions, in which PSCs form, that are outside the Arctic polar vortex (Jones et al., 1990; Lefèvre et al., 1991). The amount of ozone that is being removed by all these processes at middle latitudes during winter and after the vortex breakup, perhaps even into summer, needs to be quantified.

The chemical signatures of air parcels from the vortices are enhanced levels of reactive chlorine, low levels of NOₓ, and possibly NO₂, low levels of long-lived tracers such as N₂O, and high values of the dynamical tracer, potential vorticity. In the Southern Hemisphere after mid-September, these air parcels would also exhibit low levels of ozone. Such air masses, with spatial extents of 10 to 100 km, have been observed outside of both polar vortices (Tuck et al., 1991, and references therein; Atkinson et al., 1989), as is shown for outside the Arctic polar vortex in 1989 (Figure 4-8). The observations of spikes of chemically perturbed air imply that some ozone is being lost at middle latitudes by the transport of polar air.

4.4.2 Photochemistry of the Sulfate Aerosol Layer

A newly proposed mechanism for explaining at least part of the observed ozone trends at middle latitudes involves heterogeneous reactions occurring on the global sulfate aerosols, as discussed in Chapter 3. In the current theory, the rapid reaction,

\[
N_2O_5(g) + H_2O(aerosol) \rightarrow 2 \times HNO_3(g)
\]

happens on the sulfate aerosol, and its reaction efficiency, \( \gamma = -0.1 \), is independent of temperature. The direct conversion of the reservoir chlorine species on sulfate aerosols by the reactions, CIONO₂ + H₂O → HOCl + HNO₃ and CIONO₂ + HCl → Cl₂ + HNO₃, is thought to be unimportant for most of the stratosphere (Watson et al., 1990; Mather and Brune, 1990; Rodriguez et al., 1991), except perhaps near the polar vortices where the temperatures are lower than 205 K (Wolff and Mulvaney, 1991; Drdla et al., 1991), or after large volcanic eruptions (Hofmann and Solomon, 1989; Brasseur et al., 1990; Pitari et al., 1991).

For a typical sulfate aerosol surface area of 0.5 \( \mu \text{m}^2 \text{ cm}^{-3} \), the time constant for the conversion of \( N_2O_5 \) to nitric acid is \( \sim 5 \) days. The immediate result is that NOₓ is diminished, particularly at the high latitudes in seasons when the sunlight is too weak to photolysis the nitric acid significantly. Due to the coupling among the chlorine, nitrogen, and hydrogen families, concentrations of reactive chlorine and HOₓ increase. As a result, the negative ozone trends calculated by models that include the heterogeneous conversion of \( N_2O_5 \) on sulfate aerosols increase by almost a factor of two, not only for high latitudes in winter, but also at middle latitudes in summer (Rodriguez et al., 1991; see also Chapter 8). These models simulate the observed ozone trends substantially better than models with only gas phase chemistry (see the discussion in Chapter 8).

Preliminary evidence exists for the conversion of \( N_2O_5 \) to nitric acid on the global sulfate aerosols and the subsequent enhancement of CIO. First of all, from a limited set of measurements (King et al., 1991; Toohey et al., 1991), the observed abundances and latitudinal gradient of CIO are better simulated by models containing heterogeneous chemistry on sulfate aerosols than by models with only gas phase
**Figure 4-8** Measurements of trace gases from the NASA ER-2 aircraft versus longitude, taken on Feb. 20, 1989, along the flight track shown as a heavy line in Figure 4-6 (Tuck *et al.*, 1991). Measurements are: (a) ClO (pptv); (b) O₃ (ppmv); H₂O (ppmv); (d) N₂O (ppbv); and (e) NOₓ (ppbv). Superimposed on each plot is the potential temperature along the flight track. Note that sharp increases in ClO, O₃, NOₓ, and H₂O occur simultaneously with sharp decreases in N₂O in the spikes. These chemical signatures indicate that the air in the spikes has been altered by heterogeneous chemistry and comes from the polar vortex.
chemistry (Figure 4-9) (King et al., 1991; Toohey et al., 1991). This conclusion appears to be robust despite the inability of the models to simulate the downwelling of the stratosphere (Heidt et al., 1989; Loewenstein et al., 1990; Schmidt et al., 1991). Some observations of reactive nitrogen gases, when compared with model results, also indicate that these heterogeneous processes on sulfate aerosols are occurring. These observations include nitric acid measurements from the Limb Infrared Monitor of the Stratosphere (LIMS) (Austin et al., 1986; Jackman et al., 1987; Rood et al., 1990) and Atmospheric Trace Molecule Spectroscopy Experiment (ATMOS) (Natarajan and Callis, 1991), N2O5 measurements (Natarajan and Callis, 1991; Evans et al., 1985), and the high-latitude column measurements of NO2 (Pommereau and Goutail, 1988; Solomon and Keys, 1991).

On the other hand, some discrepancies between model results and observations suggest that more work is required to understand all the processes that affect the abundances of reactive chlorine and nitrogen in the lower stratosphere. First, the observed abundances of ClO at low latitudes (<30°N) are better represented by the model with only gas phase chemistry (Figure 4-9). Second, the abundances of ClO obtained in summertime during only a few observations at 40°N latitude are smaller than predicted by models with heterogeneous chemistry on sulfate aerosols. Also, studies of in situ NO measurements (Considine et al., 1991; Kawa et al., 1991) indicate that the observed NO levels may be higher than predicted by models containing the N2O5 + H2O reaction but are smaller than predicted by models containing gas phase chemistry only.

**4.4.3 Halogen Photochemistry as a Cause of the Observed Ozone Decline**

Comparisons between observations and model results will become more definitive in establishing the role of heterogeneous chemistry on sulfate aerosols when more measurements are made and the models are improved. In addition, the impact of new laboratory data, such as the measurements of smaller, temperature-dependent absorption cross sections for HNO3 (Rattigan et al., 1991), must be carefully assessed. Nevertheless, the characteristics of the ozone trends and of the ClO and HNO3 abundances place tight constraints on any proposed mechanism. Thus, although proposed dynamical mechanisms might explain the observed ozone changes in the lower stratosphere, they would also have to simultaneously explain the observed abundances of ClO, NOx, and HNO3. The assertion that dynamics alone is probably not responsible for the observed ozone trend is supported by an analysis of total ozone in the Southern Hemisphere for July–September from 1963 to the present (Lehmann et al., 1991). In this study, the changes in the tropopause height and the transient eddy heat flux, used to represent dynamical influences, explain the interannual variability, but not the
observed negative trend in total ozone over the last decade.

The proposed enhanced halogen catalysis that is initiated by heterogeneous chemistry currently appears to be the most likely cause of the declining ozone trend at middle latitudes. The summer trends and about one-half of the winter trends in ozone are simulated by models with heterogeneous chemistry on sulfate aerosols; the other half of the winter trend may result from transport of chemically-processed polar air to middle latitudes (see Chapter 8). If halogen chemistry is the cause, then as the atmospheric abundances of chlorine and bromine increase in the future, significant additional losses of ozone are expected not only in the Arctic, but also at middle latitudes.

4.5 BROMINE PHOTOCHEMISTRY

This current assessment (in Chapter 6), as well as the last assessment (WMO, 1990), has pointed to the greater potential of bromine than chlorine per molecule to destroy stratospheric ozone. This greater ozone depletion potential for the lower stratosphere happens because ~50 percent of the available bromine is in the reactive forms (Br and BrO), compared with chlorine, which has only a few percent in the reactive ClO form. Moreover, BrO primarily reacts synergistically with ClO in the fast catalytic cycle already shown to destroy ozone, even in the absence of oxygen atoms. Finally, bromine catalysis is most efficient in the lower stratosphere where the ozone concentration is largest. Thus, as the abundances of chlorine increase throughout the stratosphere, ozone destruction by bromine catalysis will increase proportionally to the increases in the abundances of both stratospheric chlorine and bromine.

Reactive bromine has been detected directly in the stratosphere, particularly inside the Antarctic chemically perturbed region and the Arctic polar vortex (Toohey et al., 1990; Wahner et al., 1990a; Carroll et al., 1989). Direct measurements of the reaction of BrO with ClO in these polar regions come from the ground- and aircraft-based measurements of OCIO (Solomon et al., 1988; Wahner et al., 1989; Perner et al., 1991), for which the only known source is the reaction between BrO and ClO. Analyses of these measurements indicate that the BrO + ClO catalytic cycle is responsible for roughly 25 percent of the observed total ozone loss in the Antarctic ozone hole, with the ClO2 mechanism responsible for roughly 70 percent. Outside the polar vortices, or when the ClO abundances are only a few hundred pptv, the BrO + ClO catalytic cycle is more important, relative to the ClO2 cycle, than when ClO abundances exceed 1,000 pptv.

4.6 EFFECTS OF VOLCANIC Eruptions ON OZONE

A large increase in the aerosol surface area caused by the injection of gas and debris from El Chichón in 1982, and the subsequent heterogeneous reactions may have lead to a decrease in the total ozone in the years that followed (Hofmann and Solomon, 1989; Brasseur et al., 1990). The ozone depletion resulted from chlorine catalysis that followed heterogeneous reactions on sulfate aerosols in the El Chichón cloud (see Chapter 3). Direct evidence for heterogeneous conversions—the shifts in the trace gas concentrations in the El Chichón cloud—has been collected (Arnold et al., 1991). Such eruptions could have a large impact in the future as the chlorine and bromine content of the stratosphere continue to increase.

Mt. Pinatubo in the Philippines erupted violently in June 1991, injecting a cloud of sulfur into the stratosphere. Analysis of early satellite observations suggest that Mt. Pinatubo injected two to three times as much sulfur into the stratosphere as El Chichón (Bluth et al., 1992). In the following few months, the aerosols from the eruption were observed as far north as Wyoming (Deshler et al., 1992, Sheridan et al., 1992), and a thick cloud encircled the Earth equatorward of 30° latitude (McCormick and Veiga, 1992).

The potential impact of the Mt. Pinatubo eruption on total ozone has been modeled. The calculated decline in total ozone is predicted to be in the range of 3 to 12 percent in the northern middle latitudes between 30°N and 60°N, depending on which model was used (J.M. Rodriguez, private communication; G.P. Brasseur, private communication). At high latitudes (>70°N) in February, these models predict maximum ozone losses in the range of 8 to 24 percent. Ozone reductions of 2 percent or less result from chlorine chemistry that is initiated by the reaction of N2O5 + H2O on the sulfate aerosols. The largest impact appears to result from chlorine chemistry that
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is initiated by the reactions of ClONO$_2$ + H$_2$O on the volcanic sulfate aerosols. The rates of these latter processes depend heavily on the temperature and the water vapor mixing ratio and are thus somewhat uncertain. However, the assessment models do indicate that volcanic injections into the stratosphere could have a substantial effect on global ozone, at least for one or two years.

A positive aspect of the volcanic injection into the stratosphere is that it presents an opportunity to study these processes on sulfate aerosols. Sharp gradients in aerosol abundances that are present in the early stages of the spread of the volcanic plume are excellent for testing theories about chemical processes that occur on time scales of less than a few weeks. They also present an excellent opportunity to test theories about the motion and mixing of air parcels in the lower stratosphere. These studies will help shape our understanding of the heterogeneous processes that are occurring on sulfate aerosols and will give us greater predictive capability of the future trends of total ozone.

REFERENCES


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