The Potential for Ozone Depletion in the Arctic Polar Stratosphere

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The nature of the Arctic polar stratosphere is observed to be similar in many respects to that of the Antarctic polar stratosphere, where an ozone hole has been identified. Most of the available chlorine (HCl and $ClONO_2$) was converted by reactions on polar stratospheric clouds to reactive ClO and Cl_2O_2 throughout the Arctic polar vortex before midwinter. Reactive nitrogen was converted to HNO_3, and some, with spatial inhomogeneity, fell out of the stratosphere. These chemical changes ensured characteristic ozone losses of 10 to 15% at altitudes inside the polar vortex where polar stratospheric clouds had occurred. These local losses can translate into 5 to 8% losses in the vertical column abundance of ozone. As the amount of stratospheric chlorine inevitably increases by 50% over the next two decades, ozone losses recognizable as an ozone hole may well appear.

THE SPECTACULAR LOSS OF STRATOSPHERIC O_3 IN THE Antarctic O_3 hole results primarily from halogen-catalyzed chemistry in air parcels that have been exposed to low temperatures (*1*). Most of the chlorine compounds involved have entered the stratosphere after having been released as anthropogenic chlorofluorocarbons at the surface of Earth. Because the increasing loss of O_3 over Antarctica during the last decade has been linked in part to the corresponding increase in the abundance of stratospheric chlorine and because this chlorine abundance will continue to increase into the future, we need to know how susceptible the rest of the stratosphere is to this destructive chemistry.

The Arctic stratosphere is in many ways similar to the Antarctic stratosphere, but O_3 loss in the Arctic on the scale of that over Antarctica has not been observed. Yet a downward trend in the O_3 vertical column abundances of −2% per decade has been detected for the Northern Hemisphere at latitudes greater than 30°N in wintertime (*2*). At least part of this trend may be related to O_3 losses in the lower stratosphere of the Arctic that result from the increasing amounts of chlorine in the atmosphere. In this article, we examine the chemical state of the Arctic lower stratosphere in wintertime by analyzing data obtained in January and February 1989 during the Airborne Arctic Stratospheric Experiment (AASE) (*3*) and by comparing data from this experiment to data obtained in the Antarctic O_3 hole in 1987. We do not discuss the role of chlorine chemistry in the observed O_3 decline during the wintertime in the Northern Hemisphere, because the number of unresolved issues makes quantitative calculations difficult. Instead, we focus on the question: Will an O_3 hole that is similar to the Antarctic O_3 hole form over the Arctic?

Mechanisms for O_3 Loss over Antarctica

Before we can consider the potential for O_3 loss in the Arctic, we must understand the mechanisms for O_3 loss that are occurring over Antarctica (*4*). The primary mechanism for O_3 loss in the Antarctic stratosphere is the rapid, catalytic photochemical destruction of O_3 by chlorine and bromine. These reactions involve the chlorine monoxide (ClO) and bromine monoxide (BrO) radicals. The primary reaction sequence (*5*) is:

$$ClO + ClO + M \rightarrow Cl_2O_2 + M$$

$$Cl_2O_2 + \text{sunlight} \rightarrow Cl + ClOO$$

$$ClOO + M \rightarrow Cl + O_2 + M$$

$$2(Cl + O_3 \rightarrow ClO + O_2)$$

where M is molecular nitrogen and oxygen. This reaction sequence involves ClO alone, but a second important sequence involves BrO as well (*6*):

$$ClO + BrO \rightarrow Cl + Br + O_2$$

$$Cl + O_3 \rightarrow ClO + O_2$$

$$Br + O_3 \rightarrow BrO + O_2$$

Other reaction sequences contribute, but these two are thought to dominate in the springtime polar regions (*1*). Both mechanisms require sunlight in the near-ultraviolet to visible part of the spectrum, because at night ClO recombines to form Cl_2O_2, which is not reactive toward O_3, and BrO reacts to form BrCl and $BrONO_2$. The loss of O_3 is greatest when the exposure to sunlight is longest, at lower latitudes and later in the spring.

These mechanisms can be the cause of the observed O_3 loss over Antarctica only if two conditions are met. The first condition is that

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ClO and Cl_2O_2 abundances must be a large part of the available chlorine (7) abundances of 2000 to 3000 parts per trillion by volume (pptv $= 10^{-12}$) in air and the BrO abundances must be a large part of the available bromine abundances of 15 to 20 pptv. When the ClO and BrO abundances exceed 1200 and 5 pptv, respectively, these mechanisms are sufficient to explain the observed rate of O_3 destruction, which approaches 2% per day of the initial O_3. However, this rate of O_3 loss must be maintained for more than a month in the springtime sun to account for the observed cumulative O_3 loss. Thus, a second condition for halogen photochemistry to be responsible requires that ClO and BrO have large abundances for at least a month in the spring.

For the second condition to be satisfied, the affected air parcel must have most of its NO_x (NO_x is the sum of NO, NO_2, and N_2O_5) removed. If NO_x is present in the air parcel, then chlorine can be shifted from reactive forms back into the reservoir forms, $ClONO_2$ and HCl, by the reactions:

$$ClO + NO_2 + M \rightarrow ClONO_2 + M$$

and

$$ClO + NO \rightarrow Cl + NO_2$$

$$Cl + CH_4 \rightarrow HCl + CH_3$$

The formation of $ClONO_2$ takes only a few hours if enough NO_2 is available, and the formation of HCl takes somewhat longer, at least weeks or months (*8*). Similar reactions occur with bromine.

The stratospheric abundance of total reactive nitrogen, called NO_y (*9*), is 4,000 to 15,000 pptv (*10*), and HNO_3 is the largest part throughout much of the lower stratosphere. However, enough is in the form of NO_x that the halogens are maintained in their reservoir forms, HCl and $ClONO_2$. Even if all NO_x were shifted into HNO_3, it would be reformed when HNO_3 was exposed to ultraviolet sunlight:

$$HNO_3 + \text{ultraviolet sunlight} \rightarrow OH + NO_2$$

This process takes weeks to months in the springtime polar regions because the ultraviolet light is rapidly attenuated through the large air mass present at low sun elevation angles, but some photolysis does occur (*11*). For large, cumulative O_3 losses, either reactive nitrogen must be continually shifted back into HNO_3 approximately every week or reactive nitrogen must be removed from the air parcel. Both of these processes are accomplished by heterogeneous reactions of chlorine and reactive nitrogen with polar stratospheric cloud particles (*12*).

Polar stratospheric clouds (PSCs) form below an altitude of ~25 km when sufficient water vapor and reactive nitrogen are exposed to the low temperatures of the polar winters (*13*). At temperatures lower than about −78°C, about 4° to 7°C above the water vapor frost point, water vapor and HNO_3 cocondense as $HNO_3 \cdot 3H_2O$ on background sulfate aerosol particles (*14*). As temperatures fall below the water vapor frost point, PSC particles may also grow by the condensation of water vapor (*15*). The conversion of chlorine occurs within a few hours of exposure to PSCs, mainly by the reaction of $ClONO_2$ with HCl that is adsorbed onto PSCs:

$$ClONO_{2(gas)} + HCl_{(solid)} \rightarrow HNO_{3(solid)} + Cl_{2(gas)}$$

Only a few hours of sunlight are required to convert Cl_2 to chlorine atoms. At the same time, any N_2O_5, the nighttime reservoir for NO_x, is rapidly incorporated as HNO_3 on the PSC particles (*16*).

These PSC particles may grow large enough to fall to lower altitudes in a few days if HNO_3 and H_2O cocondense on only a few of the background aerosol particles or if HNO_3 condenses on ice particles (*17*). HNO_3 may also condense on ice particles that have fallen from higher altitudes (*18*). In all three mechanisms, reactive nitrogen is actually removed from one region of the stratosphere and deposited in another lower region of the atmosphere, a process called denitrification. The Antarctic stratosphere is sufficiently cold over the entire depth of the lower stratosphere that ~80% of the reactive nitrogen and a large part of the water vapor were removed from the stratosphere in 1987 (*19*).

As a result of all these processes, an encounter of an air parcel with PSCs (Fig. 1) produces large abundances of reactive chlorine that begin to rapidly destroy O_3. It also produces negligible abundances of NO_x, and possibly reduced abundances of NO_y. If all the reactive nitrogen were removed, then the catalytic destruction of O_3 could continue without hindrance until these air parcels were mixed with other air containing reactive nitrogen.

Air parcels that have been exposed to PSCs must remain relatively isolated from mid-latitude air that contains NO_x in order to maintain the large abundances of ClO and BrO. The wintertime polar vortex, which is a pattern of high-speed, circumpolar winds, establishes the necessary isolation. Over Antarctica, the polar vortex begins forming in April or May and remains intact until October or November. It then breaks up (*20*), and the polar air and mid-latitude air mix.

The rapid reduction of O_3 is observed in the Antarctic stratosphere until the middle of October, a month past the spring equinox. Elevated abundances of ClO and BrO that cause this rapid O_3 loss are maintained by occasional exposure to PSCs that persist into early October (*21*). Because ClO abundances were observed to be enhanced in the Antarctic stratosphere beginning in mid-August (*22*) and may have been enhanced even earlier, O_3 could be almost completely removed from the lower stratosphere (14 to 24 km) by mid-October, as was observed (*23*). The removal of O_3 between these altitudes resulted in a one-half to two-thirds reduction of the total vertical column abundance of O_3.

The region of greatest O_3 destruction does not fill the entire Antarctic polar vortex, which extends to latitudes as far north as 55°S, but instead is restricted to regions near or directly over the

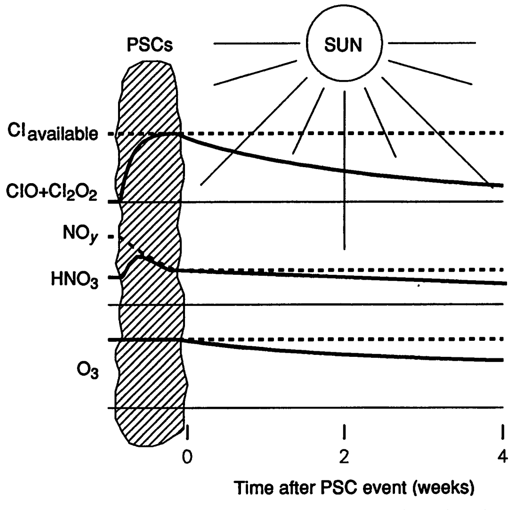

Fig. 1. Diagram illustrating how PSCs and sunlight alter the abundances of trace gases and O_3 in the polar vortex. Dotted lines indicate the available chlorine, reactive nitrogen, and initial O_3; the solid lines indicate reactive chlorine (ClO and Cl_2O_2), HNO_3, and O_3. Ozone is rapidly destroyed by reactive chlorine after all available chlorine becomes reactive chlorine (ClO and Cl_2O_2) by heterogeneous reactions on PSCs. NO_y is reduced by denitrification, and HNO_3 becomes the major component of NO_y by heterogeneous reactions. When the PSCs evaporate, HNO_3 again becomes gaseous and is slowly photolyzed into NO_2, which reduces reactive chlorine. The time constants for these processes are hours to days for the conversion of chlorine and reactive nitrogen, days to weeks for denitrification, and weeks for gas-phase photochemistry.

Antarctic continent itself (*20*). This region of rapid O_3 loss is called the "chemically perturbed region" (CPR). Although the CPR must be relatively isolated from the rest of the vortex, some exchange occurs. As a result of this exchange and the occasional formation of PSCs outside the CPR, some small O_3 loss due to enhanced chlorine catalysis does occur outside the CPR. Thus, enhanced O_3 loss occurs throughout the polar vortex but is greatest inside the CPR.

Observations in the Arctic Stratosphere in Early 1989

The formation of PSCs at low temperatures is the first step leading to the chlorine-catalyzed destruction of O_3. The minimum temperatures in the Arctic stratosphere are almost always higher than the maximum temperatures in the Antarctic stratosphere for the same season (*24*). As a result, fewer and less frequent PSCs are formed over the Arctic. Secondly, the Arctic vortex (Fig. 2) is smaller, more asymmetric, and less stable than the Antarctic vortex, sometimes breaking up in midwinter, and usually warming above temperatures for the formation of PSCs in February, a month before the spring equinox (*25*). Because the initiation of the halogen-catalyzed destruction of O_3 is so dependent on the presence of PSCs, these differences in the meteorology (*26*) provide a simple qualitative picture for the differences in the observed loss in the O_3 vertical column abundances in the two polar regions.

The temperatures in the Arctic stratosphere in January 1989 were the lowest in the last 26 years (*27*), although the February temperatures rose rapidly, and the presence of widespread PSCs is well documented (*28*). Indeed, observations by instruments flown on NASA aircraft during the AASE in January and February 1989 verify that the Arctic polar vortex was primed for O_3 destruction (Fig. 3) (*29*). The key measurements for understanding the potential for O_3 loss are the abundances of ClO and BrO, which dictate the rate of O_3 loss, and the abundances of NO and NO_y, which, by controlling ClO and BrO, dictate the total amount of O_3 loss.

The most dramatic change observed over this period was the change in the ClO abundance, which rose from relatively small values (<50 pptv) outside the polar vortex to as high as 1150 pptv inside (Fig. 3C). The sharp edges in ClO coincide with the boundary of the polar vortex at ~70°N, and on the return a sharp spike in the ClO abundance at 69°N is evidence that part of the vortex had split off, as is constantly occurring. These large observed abundances of ClO indicate that chlorine had been extensively shifted from HCl and $ClONO_2$ into ClO and Cl_2O_2.

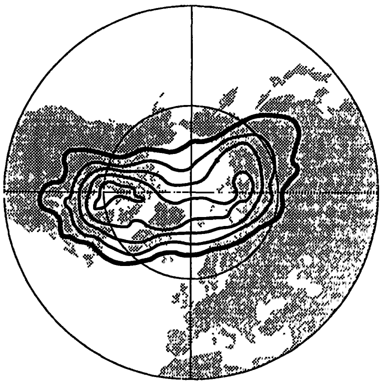

Fig. 2. The Arctic polar vortex for 7 February 1989 for the 460 K potential temperature surface (*39*). Unlike the boundary for the Antarctic polar vortex, which is much larger than its CPR, the boundary for the Arctic polar vortex coincides with the boundary for its CPR. Thus the heavy line that encircles the polar vortex also encircles the region containing increased amounts of reactive chlorine and reduced amounts of NO_x. Note the areal extent, which is about half of the size of the Antarctic CPR, and distortion, which is a common feature for the Arctic vortex. Note also that one of the two lobes extends over Canada and the United States. The heavy line is a potential vorticity (*20*) contour that has a value of 2.4×10^{-5} K m^2 kg^{-1} s^{-1}, and the lighter contours are progressively larger by 0.8×10^{-5} K m^2 kg^{-1} s^{-1}. Not apparent in this figure are the small pieces of the vortex that are continually being shed by the vortex into the midlatitude air.

The decrease in ClO abundances farther into the vortex reflected the increase in solar zenith angle (SZA) to 94°, so that more of the ClO was in the nighttime reservoir, which is Cl_2O_2 when the NO_x abundance is low. Some ClO remained, however, even after the air parcel containing it had been in darkness for 24 hours because thermal equilibrium was established between ClO and Cl_2O_2 (*30*). To determine what fraction of chlorine had been shifted from reservoir to reactive forms, we need to know the abundances of ClO and Cl_2O_2. Only ClO was measured, but we can determine the abundances of Cl_2O_2 from the thermal equilibrium that it establishes with the measured ClO abundances in darkness. The results of this analysis (Fig. 4), and other analyses (*31*), show that inside the Arctic polar vortex, away from the edge, essentially all of the available chlorine was shifted to reactive forms between the potential temperatures of 390 and 470 K (approximately 16 and 20 km). The observations of elevated amounts of reactive chlorine as early as 6 January indicate that some enhanced chemical destruction of O_3 by chlorine and bromine began before midwinter, 2 months before the spring equinox.

The BrO abundance (not shown in Fig. 3) (*32*) increased from 2 to 5 pptv outside the vortex to typically 4 to 8 pptv in the sunlit (SZA < 93°) part of the vortex, although individual measurements as large as 14 pptv were recorded during the flight of 8 February. The change in BrO is less dramatic than the change in ClO because the total abundance of bromine in the stratosphere is smaller (~15 to 20 pptv) and bromine chemistry causes ~50% of bromine to

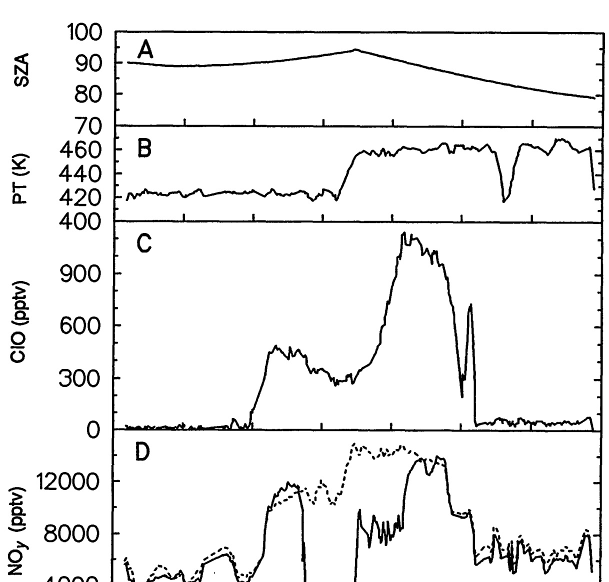

Fig. 3. In situ data taken from the 7 February flight of the ER-2 high-altitude aircraft from Stavanger, Norway, to over Spitzbergen (78°N), and back. (**A**) Solar zenith angle (*43*), (**B**) potential temperature (*44*), (**C**) the ClO mixing ratio (*45*), and (**D**) the NO_y mixing ratio (*46*) are plotted against latitude. The most northern latitude was 78°N, which was reached near local noon. The shorter exposure time to sunlight and lower altitude of the observation make the morning side of the ClO profile lower than the afternoon side. The calculated NO_y^* mixing ratio [dotted line in (D)] is the amount of NO_y that is expected to be present. It is derived from measurements of N_2O (*47*) and a well-documented relation between NO_y and N_2O (*10*). The difference between NO_y^* and NO_y indicates the amount of reactive nitrogen that was removed from the sampled air parcels.

reside as BrO even at midlatitudes.

The reactive nitrogen trace gases were also altered inside the Arctic polar vortex . The NO_y abundances (Fig. 3D, solid line) show variability and structure observed during this and other flights. Abundances range from 2,000 to 14,000 pptv. Although some of this variability is associated with sampling of air parcels from different altitudes and trajectories, some is associated with the spatially inhomogeneous removal of NO_y by aerosol sedimentation, or denitrification. Denitrification was observed to vary from 0 to 80% (Fig. 3D). Partial denitrification was observed on many flights, although only a little NO_y removal was observed in early January, and removal became more pronounced in late January and early February. However, unlike the Antarctic polar vortex, where denitrification is accompanied by intense dehydration, the Arctic polar vortex, at ER-2 aircraft flight levels, experienced partial denitrification and only slight dehydration (*33*).

The measured abundances of NO (not shown) (*34*) were near the detection level of the instrument (15 to 20 pptv) inside the Arctic polar vortex. They only provide confirmation that NO_x was depleted inside the polar vortex. Just outside the vortex, the abundances of NO were lower than predicted by photochemical models and may have been affected by either the shedding of vortex air or reactions on particles that occurred outside the vortex.

A comparison of data taken with the same instruments over the Arctic during the AASE in 1989 and over Antarctica during the Airborne Antarctic Ozone Experiment (AAOE) in 1987 shows that (Fig. 5) the ClO abundances reached ~1200 pptv in both CPRs, but highly enhanced ClO abundances were distributed over a slightly greater depth over Antarctica. An analysis of these ClO measurements indicates that ClO and Cl_2O_2 comprise more than 80% of the available chlorine for 10 February in the Arctic between the potential temperatures ~410 and 470 K, and more than 60% for the Antarctic between 380 and 460 K. The BrO abundances varied from 4 pptv at the 420 K potential temperature surface to 8 pptv at 460 K inside both CPRs. The NO abundances (not shown) were small (<20 pptv) inside both CPRs.

A striking difference between the Arctic and Antarctic was observed for NO_y. The CPR over Antarctica was heavily denitrified, with 70 to 86% NO_y removal consistently observed, whereas on average only 13% of the NO_y was removed above the 420 K surface in the Arctic polar vortex. The average denitrification observed in the Arctic polar vortex during three flights in early February was 35%. However, the spatial inhomogeneity of denitrification was so great (Fig. 3D) that 35% may not be representative of the entire vortex. Another difference between the Antarctic and the Arctic stratospheres is that NO_y was completely removed from the stratosphere over Antarctica but on average settled only to lower altitudes still in the stratosphere over the Arctic (Fig. 5).

Assessment of O_3 Loss in the Arctic Polar Vortex for 1989

Data obtained in 1989 show that the most perturbed regions of the Arctic polar vortex had the same potential for O_3 loss as the Antarctic CPR. Ozone loss rates that were calculated from the observed Arctic ClO and BrO abundances were 3×10^6 molecules cm^{-3} s^{-1} between altitudes of 16 and 20 km when the SZA was less than 85°. This loss rate was about 1.2% per day for mid-February at 70°N latitude. To translate these O_3 loss rates into cumulative O_3 losses, we need to know the total exposure to sunlight, the frequency of PSC events, and the rate at which NO_x was reintroduced either by the photolysis of HNO_3 or by the mixing with mid-latitude air that contains NO_x.

To determine how the exposure to sunlight and variation in temperature and pressure affect the O_3 loss in an air parcel that remains inside the polar vortex, we used a photochemical box model integrated forward in time along isentropic trajectories. A calculation for data taken during the last flight of the AASE mission on 10 February serves as an example. Trajectories were computed with winds and temperature fields analyzed by the United Kingdom Meteorological Office (*35*) for 10 days forward and backward in

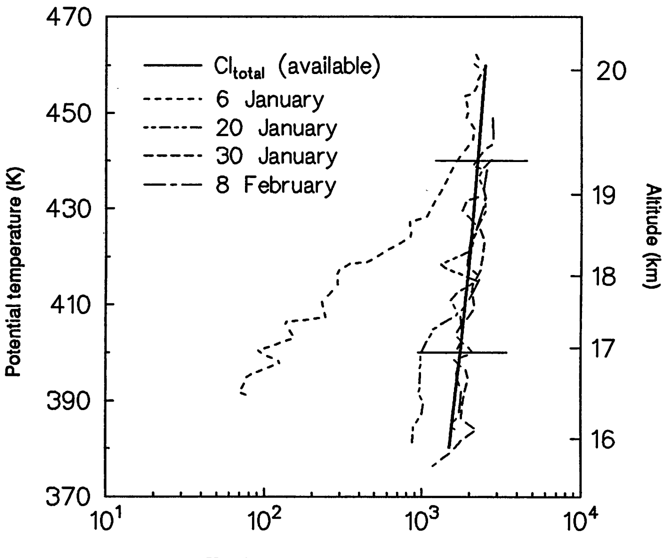

Fig. 4. Calculated total reactive chlorine (ClO + 2 × Cl_2O_2) plotted against potential temperature for four Arctic flights. Cl_{total} (available) is the available chlorine estimated from the measurements of Heidt (*48*). For data obtained after 6 January, most of the available chlorine was converted into reactive ClO and Cl_2O_2 in the interior of the polar vortex. Uncertainty (±1σ) in the calculations is a factor of 2. Altitudes are only approximate.

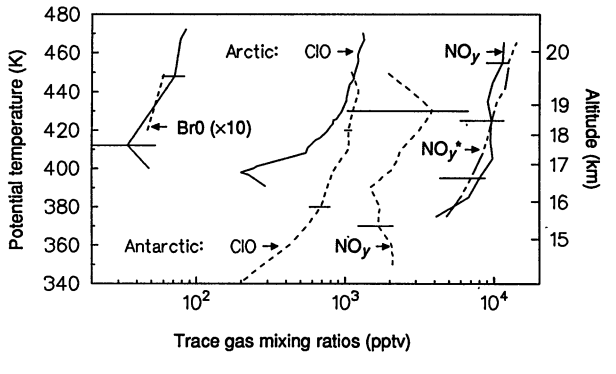

Fig. 5. Comparison of Antarctic and Arctic in situ data, taken during the AAOE in 1987 and the AASE in 1989, respectively. Arctic data are represented by solid lines, Antarctic data by dashed lines. The dot-dash line represents the NO_y^* mixing ratios for the Arctic, which are ~1000 pptv smaller for the Antarctic. All data have been averaged over the flights except for ClO over the Arctic, which are data only from a flight on 10 February 1989. In relation to the spring equinox for the respective hemispheres, the Arctic mission ended before the Antarctic mission started, because the AASE flights were from 3 January to 10 February, whereas the AAOE flights were from 17 August to 22 September. Error bars are the variability (±1σ) of the results for all the flights. The ClO abundances observed in the Antarctic varied little from flight to flight and were very similar to the ClO abundances observed in the Arctic. The greater depth of the ClO distribution over the Antarctic than the Arctic resulted from the greater range of altitudes over which PSCs formed. The Antarctic abundances of NO_y, with error bars at potential temperatures of 430 K and 370 K, had large variability.

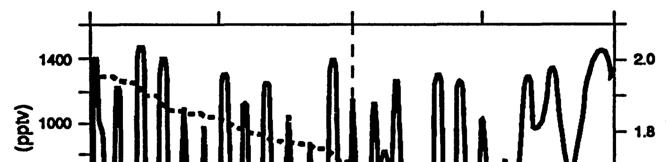

Fig. 6. Calculated ClO mixing ratio variations and O_3 destruction for an air parcel observed on 10 February 1989. The solid line shows the variation of ClO over 20 days centered on 10 February; the dotted line shows the expected change in O_3 for the same 20 days. The ClO abundance depends strongly on the latitude of the air parcel during solar illumination, and O_3 is chemically destroyed only during these sunlit periods.

time from the aircraft locations on the morning of 10 February (*36*). In order to match the levels of ClO and NO observed on 10 February, the simulation was initialized on 31 January with over 80% of the chlorine converted to ClO and Cl_2O_2 and with 90% of the NO_y removed.

During the 21-day run (Fig. 6) beginning on 31 January, the air parcel circled the pole four times and had excursions in latitude from 80°N to 50°N. The assumption of extreme denitrification meant that no PSCs were formed even though temperatures were occasionally low enough for the formation of PSCs in the absence of denitrification. It also meant that the mixing ratio of ClO in sunlight was greater than 1000 pptv throughout the simulation. These high levels of ClO, coupled with the wide swings to lower latitudes where the amount of sunlight was greater, resulted in substantial O_3 loss along the trajectories.

The decline in O_3 was not uniform along the trajectory because the amount of sunlight received varied greatly. The net loss was 23% in 20 days, and the average loss rate was 1.1% per day. However, O_3 losses of 2 to 3% per day were apparent on individual days when air parcels were at low latitudes because the vortex was distorted and oblong. From these simulations, 70% of the O_3 loss was caused by the catalytic cycle involving Cl_2O_2 and 20% was due to the catalytic cycle involving both ClO and BrO (*37*). For this air parcel, O_3 would continue to decline until the reaction between Cl and CH_4 reformed HCl or the air parcel was mixed with mid-latitude air.

For other air parcels observed in the Arctic polar vortex, in which more NO_y remains, a competition develops between the rate of O_3 destruction by the ClO catalytic cycles and the rate of reintroduction of NO_x by photolysis of HNO_3. To learn how the amount of NO_y remaining in the air parcel effects O_3 loss in that air parcel, we use a zero-dimensional model (*40*) to calculate the change in O_3 over a 21-day period. We assume zonal flow but perform the calculations at four latitudes to examine the range of O_3 losses encountered by an air parcel that traverses a range of latitudes. These calculations were made for 10 January. We can determine the O_3 loss for other days by noting that the solar declination (the angle that the direction to the sun makes with the plane of the equator) changed by ~5° from 10 January to 2 February, and another 5° by 18 February and became 0° on 22 March. Thus, the calculated loss appropriate for 45°N on 10 January was equivalent to that at 55°N on 18 February. We also assume that, after a PSC event, all chlorine is initially in the form of ClO and Cl_2O_2 and all the NO_y is in the form of HNO_3. These assumptions of complete chemical conversion by PSCs are consistent with the observations and calculations of the heterogeneous chemistry conversion rates.

For these air parcels, the fractional O_3 loss (Fig. 7) from an initial O_3 abundance of 2.25 parts per million by volume (ppmv) in air is initially greatest at the lowest latitudes, but, as NO_2 is reintroduced into the air parcel from the photolysis of HNO_3, the greatest loss is shifted to higher latitudes. The amount of reactive nitrogen remaining in an air parcel had the greatest effect at low latitudes and only small effects at the highest latitudes. In the northernmost air parcels, the photolysis of HNO_3 is so slight in January that O_3 loss proceeds at a rate of ~0.4% per day and the ClO abundance decreases only slightly. Even higher losses of O_3 than shown are thus possible in such air parcels as they move southward into more intense sunlight.

In 1989, the air inside the Arctic polar vortex was located north of 55°N for most of the time until mid-February (*39*). Thus the calculated O_3 losses at 45°N to 55°N are representative of the O_3 losses expected after a single encounter with PSCs. For the amount of denitrification observed inside the Arctic polar vortex, 10 to 15% of the O_3 between 15 and 25 km would have been destroyed in 14 days after an encounter with PSCs. The O_3 loss after 1 month is only 30 to 40% higher, so that the value at 14 days may be regarded as a "characteristic" O_3 loss. These numbers also apply to almost the entire polar vortex after mid-January. Air inside the vortex probably encountered PSCs more than once, and much of the chlorine and reactive nitrogen were probably reinitialized to ClO + Cl_2O_2 and HNO_3, respectively. Any O_3 loss would have been cumulative.

These O_3 losses calculated from the trajectory and simple photochemical models are consistent with the trend in O_3 amounts observed during the AASE mission in 1989. Analyses of O_3 data from 3 January to 10 February indicate a downward O_3 trend of 0.4% per day (*38*), or a 15 ± 10.5% loss over the 35 days analyzed. These analyses also agree with other model calculations of O_3 loss that occurred during the mission (*31*).

When the vortex breaks up, as it did in early March 1989, the catalytic cycles of ClO can be curtailed by mixing of polar air with mid-latitude air. One estimate (*40*) for the time constant for this mixing process is 5 to 20 days. From observations and calculations, the air parcels remain chemically isolated from mid-latitude air while they erode and become totally mixed in the vertical dimension first. Thus, even in these eroding air parcels, the characteristic O_3 loss of

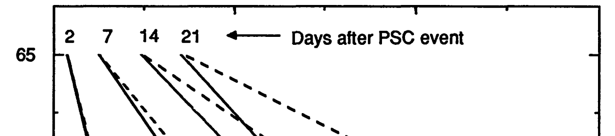

Fig. 7. Latitudinal dependence of the fractional O_3 loss at an altitude of 18 km. The initial conditions include a temperature of 205 K, an altitude of 18 km, an air density of 2.4×10^{18} molecules cm^{-3}, an O_3 abundance of 2.3 ppmv (5.6×10^{12} molecules cm^{-3}), and a total chlorine abundance of 2000 pptv. The lines are the calculated fractional O_3 loss that occurs 2, 7, 14, and 21 days after a PSC event. Solid lines are for an NO_y abundance of 12,000 pptv, dashed lines are for 2,000 pptv. Calculations for other altitudes between 16 and 24 km give similar results, although the losses for 16 km are about 0.5 of the losses at 18 km for the case with NO_y of 2000 pptv.

10 to 15% will occur before the parcels are completely mixed with mid-latitude air.

Slower, additional O_3 loss will continue for weeks until all the chlorine is shifted from $ClONO_2$ into the mid-latitude partitioning of $ClONO_2$ and HCl. This O_3 loss may in part be responsible for the downward trend in the wintertime vertical column abundances of O_3 in the Northern Hemisphere (*2*). Other contributions may come from the mixing of the air parcels that are continually being shed from the Arctic polar vortex and from heterogeneous chemical conversions on PSCs and background sulfate aerosols outside the polar vortex. Because the heterogeneous chemical conversions may not be complete in these air parcels that are always outside the polar vortex, the expected local O_3 loss would be less than that calculated for air parcels inside the Arctic polar vortex.

Depletions of the vertical column abundance of O_3 inside the Arctic polar vortex for 1989 are calculated to be 5 to 8%, based on the characteristic local O_3 losses of 10 to 15% between 15 and 25 km. This number agrees with the result of another model calculation (*41*). Because PSCs were not observed after early February, the number of "effective" cycles of a PSC encounter followed by 14 days of sunlight was probably one to two. This predicted loss in the vertical column abundance of O_3 could not be identified in the satellite data because of the dynamic variability of 10 to 20% in the vertical column abundance of O_3.

The Potential for Large-Scale O_3 Loss in the Arctic

The Antarctic polar stratosphere has such widespread, persistent cold regions that the exact details of the formation and chemistry of PSCs may not be essential for understanding the O_3 loss. The Arctic stratosphere, on the other hand, is often only marginally cold enough for PSCs to form, although they have been observed in most years (*13*). As a result, a complete understanding of PSC formation and chemistry is required if we are to predict future O_3 loss. We do not yet have this complete understanding and do not know if the widespread, large abundances of ClO and BrO and the denitrification that were observed in 1989 also occur in years during which the winter temperatures are higher than in 1989 and the PSCs are less prevalent.

For the current levels of stratospheric clorine and bromine, an Arctic O_3 loss can be substantial enough to be detected in the vertical column abundance by satellites only if the Arctic polar vortex is colder and more stable than the climatological average. The increased and prolonged PSC activity produced by the extended colder conditions would lead to greater denitrification and longer isolation from midlatitude air, more like the Antarctic chemically perturbed region, thus allowing the halogen mechanisms more time to destroy O_3. Such cold winters and springs do occur, as in 1975 to 1976 when stratospheric temperatures were below the PSC formation temperature until early March (*27*), but they occur rarely. Thus, O_3 losses that are much larger than those already observed are possible but not likely with current amounts of chlorine and bromine.

The possibility of substantial O_3 loss in the Arctic polar vortex will increase in the future, however, because stratospheric chlorine will inevitably increase from ~3200 to ~5000 pptv in the next two decades. Bromine may increase as well. Even total international compliance with a recent agreement to stop the production and use of most chlorofluorocarbons and Halons by 2000 cannot prevent these increases (*42*). As chlorine increases, the increased rate of chlorine-induced O_3 destruction will cause more O_3 to be lost during the lifetime of the polar vortex. Also, the effectiveness of reactive nitrogen for slowing halogen-induced O_3 loss will be diminished as the abundance of chlorine approaches that of reactive nitrogen. As a result, the destruction of O_3 by chlorine will increase by a factor of 1.5 to 2, and losses in the vertical column abundances inside the Arctic polar vortex may become 10 to 20% by the year 2010. These estimates are based on the assumptions that climate will not change radically and that we can estimate the future increases in other stratospheric gases by projecting the current rates of change. If climate does change in response to the increases in greenhouse gases such as CO_2 and CH_4, then the lower stratosphere would be expected to cool. Lower temperatures will lead to more frequent and widespread PSCs, which ultimately will lead to even greater O_3 destruction. Thus, an Arctic O_3 hole, smaller and less intense than the Antarctic O_3 hole, is possible in the near future.

The potential for substantial O_3 depletion in the Arctic polar stratosphere no longer depends simply on atmospheric dynamics. It also increasingly depends on the international policies that govern the use of long-lived chlorine and bromine compounds and that moderate the anthropogenic effects on climate.

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The Response of Electrons to Structural Changes

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The properties of a molecule are determined by the distribution of its electrons. This distribution can be described by the charge density, which is readily obtained from the wave functions derived by ab initio molecular orbital calculations. The charge density may be analyzed in a number of different fashions to give information about the effects of substituents, structural changes, and electronic excitation on the properties of molecules; one common procedure makes use of projection density or charge difference plots. Charge density also may be partitioned among atoms, and by numerical integration over appropriate volume elements one may obtain atomic charges, dipoles, kinetic energies, and other properties of the atoms in a molecule. Many chemical phenomena have been analyzed in terms of charge densities.

ELECTRONS ARE THE GLUE THAT HOLDS MOLECULES TOgether. This is readily seen if the total energy of a molecule is decomposed into its components

$$E = T + V_{nn} + V_{ee} + V_{ne}$$

where T is the kinetic energy of the electrons, V_{nn} is the nuclear-nuclear repulsion, V_{ee} is the electron-electron repulsion, and V_{ne} is the nuclear-electron attraction. The first three terms are destabilizing, and V_{ne} must dominate the total energy if the molecule is to be stable. It then seems appropriate to consider intra- and intermolecular interactions in terms of changes in the charge density (ρ) distribution. The charge density, $\rho(r)$, is readily obtained from the wave functions derived from ab initio molecular orbital (MO) calculations because for real wave functions, $\rho(r) = \psi(r)^2$. This distribution is experimentally accessible from x-ray crystallography and there is good agreement between the experimental charge densities and those derived from calculations (*1*). Further, all of the properties of a molecule that may be calculated from its molecular wave function can equally well be obtained from the charge density distribution (*2*).

A common way in which to examine intermolecular and intramolecular interactions makes use of MO theory, and the simplest approach of this type, frontier orbital theory (*3*), has become popular. A procedure that correlates all of the orbitals of the interacting units will, of course, give the correct result because the total wave function contains all of the information inherent in the charge density distribution. However, when only small subsets of MOs are used, or when some of the interactions, such as electron repulsion, are left out, one cannot be sure that a correct interpretation has been achieved. The charge density serves to describe all of the electrons in a molecule, and analyses of ρ have inherent advantages over MO studies that use less than a complete set of MOs. In addition, there are useful ways in which charge densities may be examined that have no simple counterparts in the use of MOs. In this article we illustrate some of the ways in which the charge density may be used in studying chemical phenomena.

There are two approaches that may be used. In the first, distribu-

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