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1988 Arctic Survey, Diurnal Study (Sunrise and Sunset) and Peak Altitude (22 km) Flights for the In Situ Detection of ClO and BrO from the NASA ER-2 Aircraft

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Two critical areas of research were addressed successfully by this research. The first involves NASA ER-2 airborne observations of ClO and BrO radical destruction of ozone within the arctic vortex. The second involves the analysis of diurnal variations in ClO, to test the production and loss rates of ClO that constitutes the test for coupling reactions between the chlorine and nitrogen systems. We discuss results from this research in order.

Destruction of ozone within the arctic vortex:

In January and February 1989, large abundances of ClO were observed inside the arctic polar vortex during fourteen flights of the NASA ER-2 aircraft from Stavanger, Norway (59°N, 6°E) to 80°N latitude. Flights were conducted at altitudes between 14–20 km, when the solar zenith angle was between 79°–101°. Data are reported for three flights—January 6, January 16, and February 10—that represent the main features observed during the mission. ClO mixing ratios were typically less than 50 parts per trillion by volume (pptv) outside the vortex and exceeded 100 pptv inside the vortex for all flights. ClO mixing ratios were more than 500 pptv for four days in a row in early February, reaching 1130 pptv on February 10, at an altitude of 19 km (potential temperature of 450 K). Peak ClO mixing ratios in early February were ~ 100 times larger than those observed at mid latitudes for all altitudes surveyed between 15–19 km. These data, comparable to those obtained in the antarctic ozone hole, indicate that the springtime arctic polar vortex was extensively perturbed by heterogeneous chemistry and contained enough ClO to catalytically destroy ozone rapidly.

Mixing ratios of BrO also were measured in the arctic lower stratosphere. Observations during the fourteen flights defined BrO mixing ratios within the arctic vortex of 4±2 pptv at a potential temperature of 400 K, rising to 8±2 pptv at 470 K. These values are twice as large as values found at equivalent potential temperatures at lower latitudes, and are comparable to the mixing ratios found inside the antarctic polar vortex. Within the statistical uncertainty of the measurements, no BrO was observed in darkness at any time, either inside or outside of the vortex, indicating that active bromine was sequestered in long-lived reservoirs, probably $BrONO_2$ and BrCl. These measurements, in conjunction with measurements of ClO, demonstrate that the interaction of bromine and chlorine could represent a major sink for ozone in the presence of sunlight.

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 10–15% at altitudes inside the polar vortex where polar stratospheric clouds had occurred. These local losses can translate into 5–8% 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.

Diurnal variations of ClO:

The abundances of ClO have been measured in situ in the lower stratosphere during sunrise and sunset. Measurements were made with an instrument mounted on the NASA ER-2 aircraft, which was flown at an altitude of 20 km and latitudes between 35°–47°N during a morning and an evening flight. The abundances of ClO were observed over a dynamic range of 20 from a detection threshold of ~ 1 pptv. These data confirm the sunrise variation of the photolysis of chlorine nitrate that is predicted by a zero-dimensional photochemical model. They also suggest that the absolute photolysis and termolecular formation of chlorine nitrate occur at rates consistent with nominal $ClONO_2$ and NO_2 concentrations.

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IN SITU OBSERVATIONS OF ClO IN THE ARCTIC STRATOSPHERE: ER-2 AIRCRAFT RESULTS FROM 59°N TO 80°N LATITUDE

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Abstract. Large abundances of ClO were observed inside the arctic polar vortex during 14 flights of the NASA ER-2 aircraft from Stavanger, Norway (59°N, 6°E) to 80°N latitude. Flights were conducted at altitudes between 14 and 20 km when the solar zenith angle was between 79° and 101°. Data are reported for three flights, January 6, January 16, and February 10, that represent the main features observed during the mission. ClO mixing ratios were typically less than 50 parts per trillion by volume (pptv) outside the vortex and exceeded 100 pptv inside the vortex for all flights. ClO mixing ratios were more than 500 pptv for four days in a row in early February, reaching 1130 pptv on February 10, at an altitude of 19 km (potential temperature of 460 K). Peak ClO mixing ratios in early February were $\sim$ 100 times larger than those observed at mid-latitudes for all altitudes surveyed between 15 and 19 km. These data, comparable to those obtained in the antarctic ozone hole, indicate that the springtime arctic polar vortex was extensively perturbed by heterogeneous chemistry and contained enough ClO to catalytically destroy ozone rapidly.

Introduction

The dramatic depletion of ozone in the antarctic polar vortex has been shown to result from the presence of highly elevated abundances of ClO. While no such massive depletion has been observed in the Arctic, the potential for ozone loss in the arctic vortex needs to be understood. Substantial amounts of ozone can be lost by halogen catalysis only if the mixing ratios of ClO remain high ($\geq$ 1000 pptv) for at least two to three weeks. Thus for the Arctic we must, first, determine if ClO levels are elevated and, in addition, if BrO is present; second, quantify the rates of ozone loss using the observed levels of ClO and BrO; and, finally, see if the conditions in the Arctic are similar to those observed in the Antarctic. In the absence of observed ozone loss, elevated abundances of ClO are the strongest signature of potential ozone depletion.

We discuss here in situ measurements of ClO made as part of the Airborne Arctic Stratospheric Experiment (AASE) during January and February, 1989. Measurements of BrO are described in a companion letter [Toohey et al., 1990]. The instrument was mounted on the NASA ER-2 high-altitude aircraft, which was flown from Stavanger, Norway, toward the arctic polar vortex on 14 flights. Observations from three of those flights are described. Unlike measurements in the Antarctic in 1987, which were all made when air in the vortex was sunlit, those in the Arctic were often made when the sun was below the horizon. The observed ClO abundances depend on the position of the vortex, the solar zenith angle (SZA), and the history of temperatures and sunlight along the trajectory of the air masses. We will use these three flights to illustrate the main features of ClO formation and evolution during the six-week mission.

Experiment

The basic goals of the AASE mission were to determine if the wintertime arctic stratosphere is perturbed, as is the antarctic stratosphere, and to learn more about the perturbing mechanisms. The AASE mission consisted of 14 flights from Stavanger, Norway, toward the arctic polar vortex, and four transit flights, two each direction, between Moffett Field, California, and Stavanger. The 14 flights from Stavanger were conducted on the following dates: January 3, 6, 7, 12, 16, 19, 20, 24, 25, 30, and February 7, 8, 9, and 10. The transit flights were flown on December 29 and 31, and, for the return, on February 20 and 21. Data are reported in this letter for the flights on January 6 and 16, and February 10.

The Harvard University ClO-BrO instrument was mounted in a pod under the left wing of the NASA ER-2, and was part of the 15-instrument complement. Fairly detailed discussions of this instrument have been presented [Brune et al., 1989], and a brief summary is presented here. ClO and BrO are detected simultaneously as the free air stream is decelerated from 200 m sec^{-1} to 20 m sec^{-1} and passes in a laminar stream through the instrument. ClO is not detected directly, but rather is chemically converted to Cl atoms by a reaction with reagent NO that is added near the inlet to the measurement flow tube. These chlorine atoms are then detected by resonance fluorescence [Brune et al., 1989]. The ClO concentration is proportional to the difference between the signal when NO is added to the flow and the signal when it is not. Nitric oxide is added during a 32-s cycle, and ClO levels of 2 pptv can be detected at a signal-to-noise ratio of two for each of these cycles. The absolute calibration is estimated to be $\pm25\%$ at the 2σ confidence level. ClO abundances in this paper reflect the most recent understanding of our calibrations. ClO data reported by other investigators involved in the AASE mission have typically not been updated, and may be 10–35% different.

The ER-2 was usually flown on isentropic surfaces between 420 and 500 K to and from the arctic vortex, which was most often located north of Stavanger (59°N, 6°E). A rapid descent to $\sim$ 380 K followed by a rapid ascent to often another constant potential temperature surface was included on the return leg, usually just south of the solar terminator. This pattern was not the only one used, but it was used for all the flights described here.

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Results

January 6, 1989. The first flight to penetrate the arctic polar vortex occurred on January 6, 1989. The ER-2 was flown up the Norwegian coast, over the sea to (74°N, 21°E), and back again. Contained in Figures 1*a-c* are the SZA, the potential temperature at the aircraft (denoted as theta), and the observed ClO abundance. At a potential temperature of ~ 470 K, ClO mixing ratios were less than 30 pptv, even for SZAs less than 90°. As the aircraft penetrated the wall of the vortex, at ~ 70°N for this flight, the ClO abundance rose rapidly to more than 250 pptv. The SZA for maximum ClO was 92.5°, which was also the SZA at which the sun was 2° above the horizon at 20 km altitude. Most of the elevated values of ClO were observed in the dark and decreased as the aircraft flew further into polar night. Shortly after the aircraft was turned south, the pilot executed a dive to the 390 K surface at 15 km altitude, and then rose to a constant 410 K surface for the remainder of the flight. ClO changed a factor of six between the 460 and 390 K surfaces inside the vortex, and fell off to values of ~ 10 pptv just outside the vortex. The slow rise in ClO for the remainder of the flight, outside the vortex, agrees with the change in ClO expected from the exchange of chlorine between ClO and $ClONO_2$ reservoirs [Brune et al., 1990].

We can draw three conclusions from these observations. First, the air inside the vortex, even in early January, had already been perturbed, presumably by a sequence of PSC activity followed by sunlight to create these large levels of ClO. Second, the amount of NO_2 inside the vortex was substantially less than that of ClO. Otherwise, at these high SZAs, ClO would combine with NO_2 to form $ClONO_2$ in less than an hour. Such low values of NO_2 are confirmed by the measurements of NO [Fahey et al., 1990]. And third, the total amount of chlorine converted from HCl and $ClONO_2$ into more reactive chlorine was more than the 250 pptv of ClO observed at the vortex edge, since, at these SZAs, much of the reactive chlorine would be in the form of the ClO dimer, Cl_2O_2.

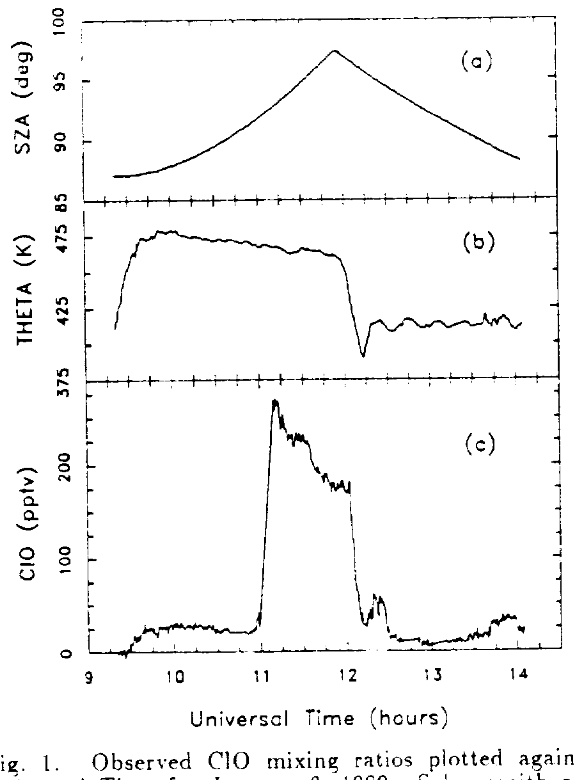

Fig. 1. Observed ClO mixing ratios plotted against Universal Time for January 6, 1989. Solar zenith angle (degrees), potential temperature (K), and ClO mixing ratio (pptv) are plotted in Figures 1*a*, 1*b*, and 1*c*, respectively.

January 16, 1989. The sharp rise in the ClO mixing ratio at the edge of the vortex followed by a slow decrease north of the terminator is more evident on January 16, when the flight path extended to 78°N, over Spitzbergen Island. The SZA, potential temperature, and observed ClO mixing ratios are shown in Figures 2*a-c*, respectively. The SZA varied from 90° to 100°, and the potential temperature was a constant 445 K until the dive to the 380 K surface at 12:45 UT. The peak ClO mixing ratio was 175 pptv at a SZA of 93° and a potential temperature of 445 K, entirely consistent with the value observed during the January 6 flight at the same potential temperature.

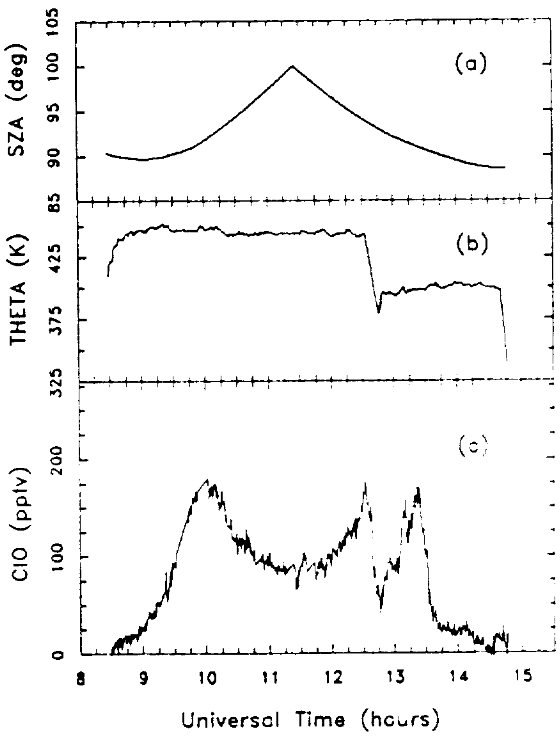

Fig. 2. Observed ClO mixing ratios plotted against Universal Time for January 16, 1989. Individual graphs are as in Figure 1.

ClO dropped by a factor of four between the 445 and 380 K surfaces inside the vortex, from 175 to 45 pptv, but recovered to 160 pptv at the 400 K surface an hour later. This asymmetry in the "dog dish" profile for ClO has two causes. First, the time constants for exchange of chlorine between ClO and the other chlorine reservoirs are almost a day. Second, the total exposure of the air to sunlight increases during the day at a given latitude. So, for the same SZA, ClO will be greater in the afternoon, when more of it has been shifted from its nighttime reservoirs into ClO, than in the morning.

A striking feature of the ClO profile is that substantial ClO, 80 pptv, was observed even when the SZA was 100°. Trajectory analyses from the U. K. Meteorological Office show that the air sampled at the highest latitudes could not have been exposed to sunlight at a SZA of less than 96° for the previous 40 hours (R. L. Jones, private communication). This observation of ClO in the dark is even stronger proof than the results of January 6 that, inside the vortex, NO_2 was very low and that ClO was being exchanged with the ClO dimer. And, since this air mass had remained at high SZAs for almost two days, the ClO could exist in observable amounts only if it was in thermal equilibrium with the dimer.

The amount of dimer (Cl_2O_2) in thermal equilibrium with the observed ClO can be determined if the temperature of the air parcel is known. However, the temperature at the time of observation may not be the appropriate one if the air parcel had experienced temperature variations during the previous day, because the time for ClO and the dimer to establish thermal equilibrium after a temperature change is ~ 20 hours. By using a photochemical model that is moved along the trajectory, we can find the temperature that was experienced by the air parcel prior to our observation, and for which the dimer and observed ClO concentrations were effectively in thermal equilibrium. The effective equilibrium temperature so determined is 189.7 K, which is 0.6 K lower than the observed temperature obtained at the ER-2 simultaneously with the ClO observation. The ClO dimer mixing ratio implied from the ClO concentration (1.6×10^8 molecules cm^{-3}) and the equilibrium constant of Cox and Hayman [1988] is 910 pptv. Thus, the total chlorine in ClO and the dimer is 1900 pptv. An error of 1 K in the derived temperature would alter this value by 400 pptv.

ClO was observed inside the vortex at SZAs exceeding 94.5° on eight other flights, and the total chlorine in ClO and the dimer derived from the observed levels of ClO and temperatures exceeded 1100 pptv for all of them. While the temperature histories along the trajectories and the photolysis rates for the ClO dimer at high SZAs must be known to derive more exact numbers, the consistently high values for ClO and the dimer indicate either that much of the inorganic chlorine was shifted into ClO and the dimer as early as January 6, or that, in fact, the mixing ratios for the dimer were lower, and thus the equilibrium constant is lower than that determined by Cox and Hayman [1988]. If chlorine was converted to ClO and the dimer in early winter, then ozone loss could occur earlier than currently thought. If the equilibrium constant is lower, perhaps by a factor of two, then more Cl_2O_2 would thermally dissociate, and less would be photolyzed than is currently calculated for arctic stratospheric temperatures. As a result, less ozone would be destroyed by the dimer mechanism in the early spring. We are conducting studies to see if the dimer was detected in our instrument during some thermal diagnostic tests that were periodically performed during flight, and if absolute Cl_2O_2 values can be determined.

In late January, temperatures were low enough for the formation of water ice PSCs (Type II), and these PSCs were pervasive over Scandinavia and Siberia (R. L. Jones, private communication). The peak ClO mixing ratios for the final five flights, January 30 and February 7, 8, 9, and 10, all exceeded 500 pptv. These observations were made inside the vortex with the SZA less than 90°. The first four of these flights were to Spitzbergen Island at 78°N and back. ClO has the same features on these four flights that it did on January 16: a sharp rise at the vortex edge, evening values higher than morning values for the same SZA, and a decrease toward the northern latitudes and higher SZAs. The ClO mixing ratios outside the vortex edge are typically less than 50 pptv, but show some rapid increases to more than 100 pptv for short intervals. These small features may represent vortex air that was spun off of the vortex, and had not yet mixed with the surrounding air that was advected from mid-latitudes. The elevated levels of ClO on the last four consecutive days confirm that the vortex was extensively perturbed by the second week in February.

February 10, 1989. All previous flights had been flown to the north of Stavanger, toward polar night. However, in early February, the vortex was becoming distorted and, by February 10, was actually closer to Stavanger in the west-northwest direction than to the north. The flight trajectory on February 10 was across Iceland to Greenland, up the coast of Greenland, and returned by the same path. Thus the northernmost latitude sampled was 72°N, but the vortex was encountered for roughly half the flight. The vortex edge, defined by elevated ClO, was crossed as the aircraft passed over Iceland. The observed vortex air was illuminated during the entire flight, since the SZA was always less than 89°. Under sunlit conditions, the conversion of reservoir chlorine to radical chlorine could be better determined, since more chlorine would be in ClO and less in the nighttime reservoirs, particularly the ClO dimer.

The observed abundances of ClO are greater than 1100 pptv on the 470 K potential temperature surface, well inside the vortex, as shown in Figure 3. The sharp boundary at the vortex edge still persists, and the profile shows both vertical and horizontal structure. This profile for ClO looks very similar to those obtained over Antarctica during the Airborne Antarctic Ozone Experiment in August and September, 1987, which were obtained with similar flight altitude profiles [Brune et al., 1989]. For ClO levels to be this elevated, about one half of the total inorganic chlorine must have been in the form of ClO.

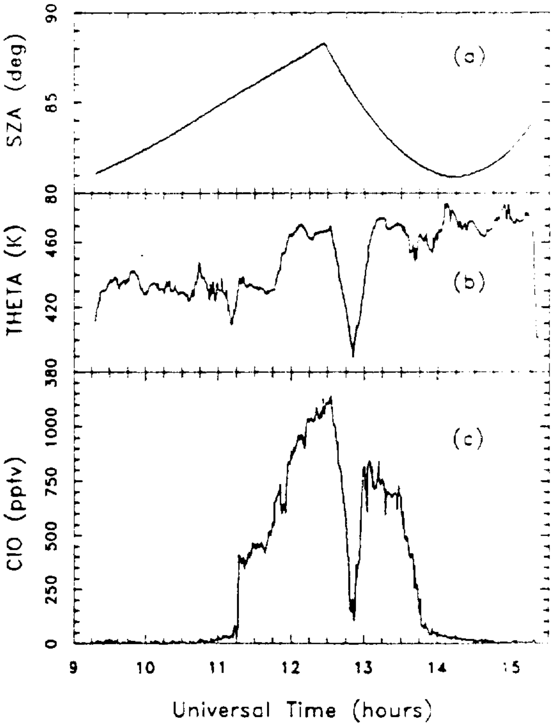

Fig. 3. Observed ClO mixing ratios plotted against Universal Time for February 10, 1989. Individual graphs are as in Figure 1.

The vertical distribution of ClO, taken during the dive inside the vortex on February 10, is shown in Figure 4. In addition, vertical distributions are shown for the flights of August 28, 1987, and February 13 and 19, 1988. The profile from August 28 was measured inside the antarctic polar vortex at 71°S. The profile from February 19 was obtained over Moffett Field, California, and is representative of mid-latitude profiles for that time of year. The

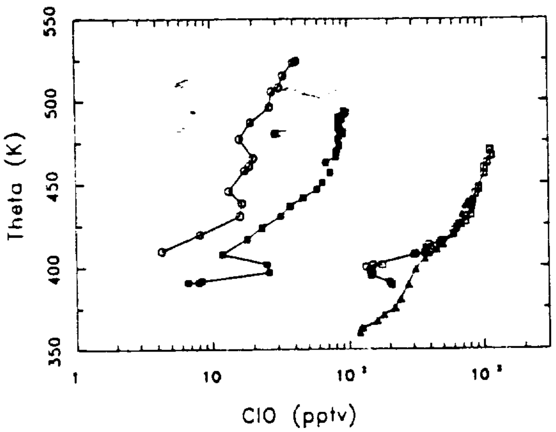

Fig. 4. ClO mixing ratio versus potential temperature for four flights. Data are shown for February 10, 1989, 70°N, inside the vortex (open squares); February 13, 1988, 61°N, outside the vortex (solid squares); February 19, 1988, 35°N, a typical mid-latitude profile (open circles); and an Antarctic flight on August 23, 1987, 72°S, inside the vortex (triangles).

profile from February 13 was obtained at 61°N, in a region slightly outside the arctic vortex. (The ClO levels for February 13 are ~ 30% larger than reported in Brune et al. [1988] because of an improved calibration.)

We draw four conclusions from these profiles. First, the ClO mixing ratios inside the arctic polar vortex are ~ 100 times larger than the mid-latitude abundances at all altitudes. Second, the ClO mixing ratios observed in the arctic vortex above a potential temperature of 400 K are comparable to those observed in the antarctic vortex. Thus, for chlorine, the arctic polar vortex appears to be as perturbed in 1989 as the antarctic vortex was in 1987. Third, the ClO mixing ratio decreases more rapidly at lower potential temperatures in the arctic than in the antarctic. These differences reflect the generally higher altitude of formation of PSCs in the northern hemisphere [McCormick et al., 1988]. Finally, the observed ClO mixing ratios for February 13, 1988, which are more than 80 pptv, were produced by heterogeneous chemistry on PSCs in the arctic polar vortex, and did not result from wintertime, high latitude gas-phase photochemistry [Brune et al., 1988]. The ClO mixing ratios observed outside the polar vortex during the AASE mission, which were typically less than 50 pptv, indicate how much ClO that gas-phase chemistry alone can produce.

Summary

The ClO mixing ratios exceeding 1000 pptv and the sharp edges in the elevated ClO distributions are strong evidence that heterogeneous processes have altered the partitioning of species in the chlorine and odd-nitrogen chemical families. The sequencing of heterogeneous conversion followed by exposure to sunlight was capable in early 1989 of perturbing a large portion of the arctic polar vortex, extending from above the ER-2 flight altitudes down to 15 km. Evidence of heterogeneous processes was found on the first flight that penetrated the vortex, January 6, and on all subsequent flights that sampled vortex air. The arctic vortex was extensively perturbed, both horizontally and vertically. Such large abundances of ClO in concert with BrO, HO_2, and O, are capable of depleting ozone at rates comparable to those observed over Antarctica, ~ 1% per day [see, for example, Anderson et al., 1989], and some small loss of ozone must certainly have occurred.

Acknowledgments. A mission of this scale is possible only by the dedication and hard work of a large number of people. Excellent support and advice were given by members of the Atmospheric Research Project at Harvard University, particularly those who worked in Norway—Nate Hazen, Maria Mueller, and Norton Allen—but also Joyce Makrides, Joe Demusz, Elliot Weinstock, Bob Heroux, and others. The pilots, crews, and management of the NASA ER-2 were always helpful and performed well in less-than-ideal circumstances. Estelle Condon and Steve Wegener were always available to smooth logistical tangles, and members of the NOAA Aeronomy Laboratory provided excellent facilities. We also acknowledge the many thoughtful discussions with the other scientists on this mission. This work was supported by the NASA Upper Atmospheric Program under grants NASW 3960 and NAGW 1465.

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THE SUNRISE AND SUNSET VARIATION OF ClO IN THE LOWER STRATOSPHERE

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Abstract. The abundances of ClO have been measured, in situ, in the lower stratosphere during sunrise and sunset. Measurements were made with an instrument mounted on the NASA ER-2 aircraft, which was flown at an altitude of 20 km and latitudes between 35°N and 47°N during a morning and an evening flight. The abundances of ClO were observed over a dynamic range of 20 from a detection threshold of ~ 1 part per trillion volume (pptv). These data confirm the sunrise variation of the photolysis of chlorine nitrate that is predicted by a zero-dimensional photochemical model. They also suggest that the absolute photolysis and termolecular formation of chlorine nitrate occur at rates consistent with nominal $ClONO_2$ and NO_2 concentrations.

Introduction

Stratospheric chlorine, with an abundance of ~ 3 parts per billion volume (ppbv), causes 15-40% of the catalytic destruction of ozone above 35 km [WMO, 1986]. In the lower stratosphere below 25 km, chlorine is held in check by the more abundant (5-15 ppbv) odd-nitrogen chemical family, primarily by the termolecular reaction between ClO and NO_2 that forms chlorine nitrate, $ClONO_2$. If the level of inorganic chlorine approaches that of odd-nitrogen, as it may in the future and does in the polar regions in winter, then the control is removed because ClO can "titrate" nitrogen oxides from the atmosphere. Ozone can then be depleted at an ever increasing rate for a given incremental addition of chlorine. A key photochemical link for our understanding about the behavior of chlorine in the atmosphere is one that connects chlorine to odd-nitrogen.

A measurement of the diurnal variation of the ClO abundance in the lower stratosphere provides an excellent test of the coupling between the chlorine and nitrogen chemical families. In the lower stratosphere, the interaction between the two chemical families involves the formation and photolytic destruction of chlorine nitrate, $ClONO_2$. The formation of $ClONO_2$ occurs by the termolecular reaction coupling ClO and NO_2:

$$\mathrm{ClO} + \mathrm{NO_2} + M \rightarrow \mathrm{ClONO_2} + M \qquad (1)$$

The destruction of $ClONO_2$ involves photolysis at ultraviolet wavelengths, mainly producing Cl atoms:

$$\mathrm{ClONO_2} + h\nu \rightarrow \mathrm{Cl} + \mathrm{NO_3} \qquad (2)$$

which is followed by the rapid reaction:

$$\mathrm{Cl} + \mathrm{O_3} \rightarrow \mathrm{ClO} + \mathrm{O_2} \qquad (3)$$

that regenerates ClO. The NO_2 abundance is only slightly affected by exchange between $ClONO_2$ and NO_2, but the ClO abundance varies dramatically. At night, with no photolysis, the abundance of ClO is very small, and the inorganic Cl is partitioned between HCl and $ClONO_2$, with a small amount in HOCl. Thus, at sunrise the abundance of ClO increases from virtually nothing to its peak value near midday, and then decays with a one-hour time constant at sunset.

Chlorine is being exchanged with other reservoirs as well. Cl atoms are exchanged with ClO in minutes to seconds, and the abundance of Cl atoms is at most a few percent of the abundance of ClO. HCl is exchanged with ClO over days and weeks, and so is virtually constant over a diurnal cycle. HOCl, like $ClONO_2$, is coupled to ClO with time constants of ~ 1 hour, but in the lower stratosphere its maximum abundance is less than that of ClO and the exchange is small compared to that of $ClONO_2$. To first order then, the variation of ClO is given by the rate expression:

$$d[\mathrm{ClO}]/dt = J_2[\mathrm{ClONO_2}] - k_1[M][\mathrm{NO_2}][\mathrm{ClO}] \qquad (4)$$

The measurement of the abundance of ClO during sunrise and sunset presents a unique opportunity to study the interactions between the chlorine and nitrogen chemical families that are relatively free from the interferences of other interactions.

The diurnal variation of ClO, primarily above 30 km, has been observed before in total column measurements of millimeter-wave emission [Solomon et al., 1984; Waters et al., 1981; Froidevaux et al., 1985; Waters et al., 1988]. For these observations, the total column is affected not only by the interchange between the ClO and $ClONO_2$ reservoirs but also by the interchange between ClO and HOCl in the middle to upper stratosphere as well. The ground-based [Solomon et al., 1984] and early balloon-borne [Waters et al., 1981; Froidevaux, 1985] millimeter-wave column measurements are in fair agreement with the results of computer simulations, but tend to have a slower morning rise than predicted [Ko and Sze, 1984; Froidevaux et al., 1985]. The cause of this difference is not understood, but it cannot be explained by the uncertainties stated for the rate constants and photolysis cross sections [Froidevaux, 1985]. However, balloon-borne measurments of ClO made in 1985 and 1986 [Waters et al., 1988] do not clearly support the earlier observations of the slow morning rise.

We report here observations of the variations of the abundances of ClO in the midlatitude lower stratosphere during sunrise and sunset. In situ measurements were made with an instrument mounted on the NASA ER-2 high altitude aircraft which was flown in the lower stratosphere at 20 km altitude. The measured ClO abundances are compared to results from a computer model simulation.

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Experiment

The NASA ER-2 aircraft, flown from its base in Moffett Field, California, had an instrument complement that included the Harvard University ClO-BrO instrument, the Ames Research Center ozone photometer, and the navigational aides that are a normal part of aircraft operation. The ClO-BrO and ozone instruments have been described elsewhere [Brune et al., 1989; Brune et al., 1988, Starr and Vedder, 1989], although the ClO-BrO instrument is described briefly here as well. The ClO-BrO instrument, mounted in the left wing pod of the aircraft, allowed the detection of ClO in a laminar airstream that was decelerated from 200 meters s^{-1} to 20 meters s^{-1}. The ClO abundances were measured when reagent nitric oxide (NO), added to the ambient airstream, converted the molecules to their respective halogen atoms. The Cl atoms were then detected by resonance fluorescence. The difference between the signals when NO was added and when it was not is proportional to the ClO concentration. The accuracy of the laboratory calibration is ±25%, and a ClO mixing ratio of 2.5 pptv could be detected at 20 km altitude with a signal-to-noise ratio of two in a 32 s period.

The sunrise and sunset flights were made on two separate days, February 12 and 16, 1988, respectively. Each flight was four to five hours long, and spanned times when the solar zenith angle was between 60° and 110°. The flight altitude was chosen to be a constant altitude near 20 km, and this condition was maintained for both flights to within 0.1 km, except for an hour at low solar zenith angles during the both flights. The flight paths were chosen to sample air masses with similar trajectories while avoiding the possibility of sampling air contaminated by the aircraft exhaust. The winds at 50 and 70 mb pressure levels, by the NMC analysis, were from the northwest at speeds of 10–40 knots for both days. The flight paths were set at slight angles to the wind direction. For the sunrise flight, the trajectory was along the 122° longitude, from a latitude of 37°N to 49°N. For the sunset flight on February 16, the trajectory was along a line running roughly from 35°N, 119°W to 45°N, 125°W. The air temperature was approximately 215 K for both flights, and few clouds were below the aircraft on either flight.

Results

The measured abundances of ClO are shown as a function of Universal Time (UT) for the sunrise and sunset flights in Figures 1 and 2, respectively. Each 32 s cycle constitutes a measurement of ClO, and nine of these are averaged to produce each data point. The resulting typical $\pm 1\sigma$ statistical uncertainties are approximately ±0.7 pptv. Despite some variability associated with sampling of different air masses, the data points define quite well the rise of ClO at sunrise and the fall of ClO at sunset.

Some of the variability of the data can be removed by considering tracers of atmospheric motion, such as ozone. This adjustment is particularly important for the sunrise data taken from 17.0–17.5 hours UT, when the aircraft was diverted to 21 km, and the ClO abundance doubled due to its substantial altitude gradient in the lower stratosphere [Brune et al., 1988]. These data can be corrected by considering the variability in ozone, the variation of ClO with ozone near midday, and the observed ClO abundance at that time. The variation of ClO with ozone at the lowest solar zenith angles is fitted to a straight line with a slope and an intercept. The expression for making the correction becomes:

$$[ClO]_c = [ClO]_{obs} \times ([ClO]_{avg}/[ClO]([O_3]_{obs})) \qquad (5)$$

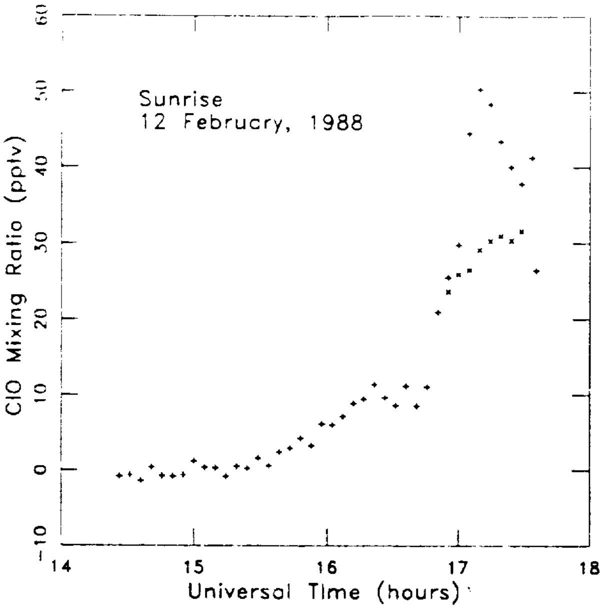

Fig. 1. The sunrise variation of the ClO mixing ratio with respect to Universal Time. The observations are indicated by +, and the data corrected for a change in altitude by ×.

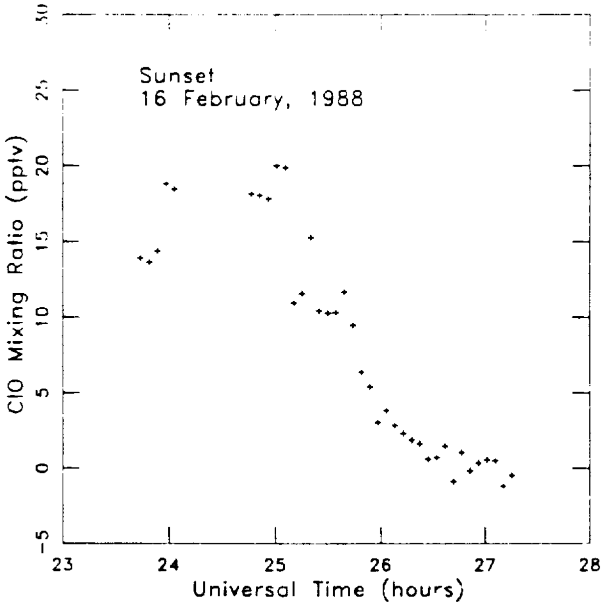

Fig. 2. The sunset variation of the ClO mixing ratio with respect to Universal Time.

where $[ClO]_c$ is the corrected abundance, $[ClO]_{obs}$ is the observed abundance, $[ClO]_{avg}$ is the calculated [ClO] at high solar zenith angles for an average abundance of ozone, and $[ClO]([O_3]_{obs})$ is the value for [ClO] determined from the straight line fit to the ClO–O_3 data and the observed value of ozone. In effect, we are correcting ClO abundances to those we expect in the average air mass defined by ozone. The agreement between the corrected and uncorrected points at 17.5 hours UT validates this correction process.

For most other sections of the sunrise flight, and for all of the sunset flight, the differences between the corrected ClO abundances and the observed ClO abundances was less than 15%. Between 16.5 and 17.0 hours UT, during the sunrise flight, the ClO abundances appear to be too low. The values obtained with equation (5) would be ~ 35% higher, because ozone was much lower than average during this time. However, the correction precedure used for ClO is really only valid for variations induced by changes in altitude, and not for variations induced by changes in ozone at a constant altitude; so the correction was applied only between 17.0 and 17.5 hours UT during sunrise. We note that the observed sunrise variation of ClO does not depend on the corrected data, since data before and after the altitude change give the same shape to the ClO rise.

These observations are compared to the results of a zero-dimensional model from the Naval Research Laboratory [Anderson and Lloyd, 1989], which uses the parameters listed in Table 1. The values for the rate constants and absorption cross sections are all taken from the JPL evaluation (87-41) [DeMore et al., 1988]. This model is designed to accurately calculate the photochemical photolysis rates (J-values) at twilight for solar zenith angles as large as 95°. The longitudes and latitudes chosen for the model correspond to the average positions of the aircraft. The slight difference between observed and modeled solar zenith angle ($< 2°$) has an effect on the comparison between the data and the model if variations of ClO are plotted against local time. However, the choice of the average position for the model calculations is not important if the data and model results are plotted against solar zenith angle. We have calculated the variation of ClO with solar zenith angle for the latitudes 35°N and 47°N, and find that it is not significantly different from the variation calculated at the average positions.

The abundances of NO_2 and $ClONO_2$ should be measured simultaneously with ClO if we are to critically test the exchange between ClO and $ClONO_2$ and thus quantify the coupling between chlorine and the oxides of nitrogen. Without measurements of NO_2 and $ClONO_2$, we can only determine consistency between modeled and observed ClO, using reasonable abundances for the other crucial species. Since this effort is the first attempt to measure the diurnal variation of ClO in situ, the consistency acts as a check on the gross features of the sunrise and sunset variability. The model values for $ClONO_2$ (0.25 ppbv) and NO_2 (0.50 ppbv, at sunset and a solar zenith angle of 91.5°) are similar to those observed by the ATMOS experiment [Russell et al., 1988], which at 19.5 km were measured to be 0.3 ± 0.3 ppbv and 0.6 ± 0.1 ppbv, respectively. Using the model parameters in Table 1, we are able to achieve agreement with the observations shown in Figures 3 and 4, in which the ClO concentration is plotted as a function of solar zenith angle at sunrise and sunset, respectively. With these reasonable values for $ClONO_2$ and NO_2, the agreement between observed and modeled ClO is good for both sunrise and sunset.

Table 1. Flight and Model Parameters

Averaged Parameter	Sunrise[†]
density (molecules cm^{-3})	$(1.94 \pm .05) \times 10^{18}$
temperature (K)	215 ± 3
altitude (km)	$19.9 \pm .1$
potential temperature (K)	483 ± 4
ozone (ppmv)	$2.1 \pm .2$
latitude	45°N (39°N)
longitude	122°W
ozone column density (D.U.)	280 (325)
model $[NO_2]$ (pptv)	380
model $[ClONO_2]$ (pptv)	250 (230)
$k_1[M]$ (cm^3 $molecule^{-1}$ s^{-1})	9.0×10^{-13}
J_2 (s^{-1}) @ 90°	9.06×10^{-6}
J_2 (s^{-1}) @ 85°	2.9×10^{-5}
J_2 (s^{-1}) @ 80°	3.6×10^{-5}

[†] If sunset data are different from sunrise data, they are shown in parentheses.

The most striking difference between the previously observed column measurements of ClO and the results of photochemical models was that ClO appeared to rise more slowly in the morning than predicted by photochemical models. We cannot address this issue specifically because the column measurements pertain to ClO mainly above 30 km, whereas our observations are at 20 km. However, our data test the rise in ClO at 20 km without substantial uncertainty from the unmeasured abundances of $ClONO_2$ and NO_2 for two reasons. In the production term for ClO in equation (4), the abundance of $ClONO_2$ is effectively constant. Also, in the destruction term the abundance of NO_2 undergoes its most rapid diurnal change before ClO does, since the photolysis of NO_2 begins earlier and is 1000 times greater than the photolysis of $ClONO_2$. When the solar zenith angle is between 90° and 75°, the variation in NO_2 is less than 30%. The only remaining variables are ClO and the photolysis rate of $ClONO_2$. While the photochemical system is simple, the calculation of the photolysis rate, or J-value, remains complex for large solar zenith angles near 90°. Multiple scattering and the sphericity of Earth become important in determining the correct value [Anderson, 1983; Anderson and Lloyd, 1989]. We see in Figure 3 that the growth in ClO predicted by the model matches that observed as ClO changes by over a factor of 20. Thus the

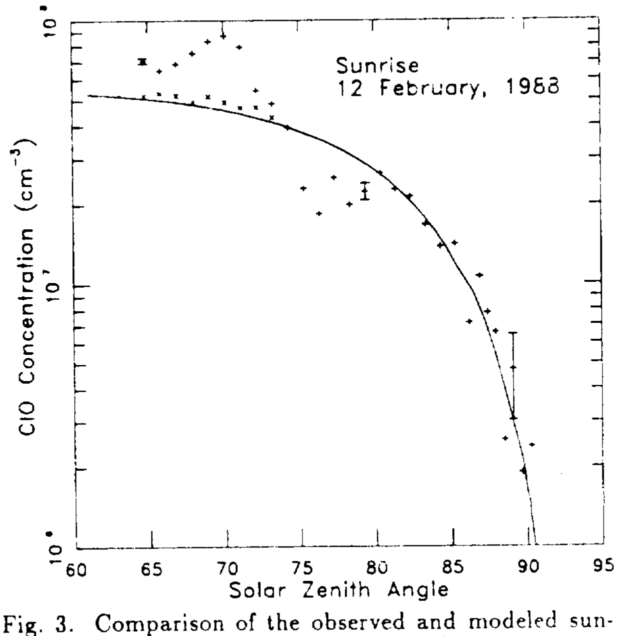

Fig. 3. Comparison of the observed and modeled sunrise variation of the ClO concentration. Observations are indicated by +, corrected data by ×. Error bars are ±1σ.

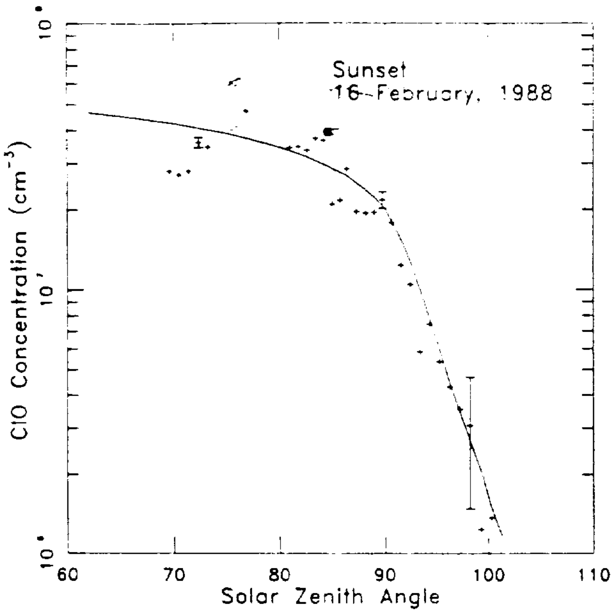

Fig. 4. Comparison of the observed and modeled sunset variation of the ClO concentration. Error bars are ±1σ.

observed variation of ClO verifies the model calculations, and unlike previous measurements, no apparent discrepancy exists.

At sunset, the most rapid change in the ClO levels occurs at solar zenith angles between 90° and 100°, unlike the change at sunrise that occurs between 80° and 90°. This asymmmetry reflects the chemical formation time of $ClONO_2$, which is typically 1 hour near 20 km in the lower stratosphere. In fact, when the solar zenith angle is greater than 92°, the production of ClO from $ClONO_2$ photolysis is very small, and the rate equation for ClO becomes:

$$d(ln[ClO])/dt = -k_1[M][NO_2] \quad (6)$$

If we make the reasonable assumption that the reaction rate constant for the formation of $ClONO_2$ is correct, we can derive the average abundance of NO_2 near sunset, at solar zenith angles exceeding 92°. Nitric oxide is fully converted to NO_2 at solar zenith angles $< 92°$, so NO_2 is nearly invariant with solar zenith angle during the period of ClO decay. The observed change in the natural logarithm of ClO with solar zenith angle is given in Figure 4. With these data, we determine by a linear least squares fit that the time rate of change of the ClO abundance implies an NO_2 abundance of $\sim$ 390 pptv at a solar zenith angle of 92°. The model, which has 500 pptv of NO_2 at sunset, yields ClO concentrations as a function of solar zenith angle, shown in Figure 4 superimposed on the observations. Observed decay rates of ClO cannot be distinguished from the calculated rates.

In summary, the solar zenith angle dependence of the photolysis rate of $ClONO_2$ has been confirmed by the sunrise observations. Further, the observed formation and decay rates for ClO are consistent with results from the NRL model that is initialized with acceptable abundances of NO_2 and $ClONO_2$. Nevertheless, the unequivocal identification of the mechanism coupling chlorine with the oxides of nitrogen in the lower stratosphere is so fundamental to predictions of secular trends in ozone column resulting from increasing levels of chlorine that simultaneous, in situ measurements of ClO, NO_2, $ClONO_2$ and the radiation field are essential.

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IN SITU MEASUREMENTS OF BrO IN THE ARCTIC STRATOSPHERE

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Abstract. Mixing ratios of BrO have been measured in the arctic lower stratosphere with an instrument mounted on the NASA ER-2 aircraft. Observations from fourteen flights above the Arctic Circle in January and February of 1989 defined mixing ratios within the vortex of 4 ± 2 parts per trillion by volume (pptv) at a potential temperature of 400 K, rising to 8 ± 2 pptv at 470 K. These values are twice as large as values found at equivalent potential temperatures at lower latitudes, and are comparable to the mixing ratios found inside the antarctic polar vortex. Within the statistical uncertainty of the measurements, no BrO was observed in darkness at any time either inside or outside of the vortex, indicating that active bromine was sequestered in long-lived reservoirs, probably $BrONO_2$ and BrCl. These measurements, in conjunction with measurements of ClO, demonstrate that the interaction of bromine and chlorine could represent a major sink for ozone in the presence of sunlight.

Introduction

The suggestion that bromine compounds released at the earth's surface could destroy ozone in the stratosphere was first made in 1975 [Wofsy et al., 1975]. During the following decade, while research efforts focussed on quantifying the effects on ozone of chlorine atoms released by photolysis of chlorofluorocarbons in the stratosphere, bromine largely remained ignored. Only recently, after massive seasonal losses of ozone over Antarctica were reported, has this disparity been reduced. A renewed interest in bromine chemistry was initiated in part by the suggestion [McElroy et al., 1986] that bromine oxide (BrO) in the presence of enhanced concentrations of chlorine oxide (ClO) within the antarctic polar vortex could lead to substantial losses of ozone through the catalytic cycle

$$\begin{aligned} ClO + BrO &\rightarrow Cl + Br + O_2 && (1a)\\ Br + O_3 &\rightarrow BrO + O_2 && (2)\\ \underline{Cl + O_3} &\underline{\rightarrow ClO + O_2} && (3)\\ net: O_3 + O_3 &\rightarrow 3O_2. \end{aligned}$$

In contrast with the knowledge of chlorine chemistry obtained from fifteen years of in-situ and laboratory studies [WMO Report 16, 1986], analogous processes involving bromine remain poorly understood. Although the reactivities of related bromine and chlorine species are often similar, there are some important differences. Consequently, BrO represents a large fraction of the total inorganic bromine budget [Yung et al., 1980], which is estimated to be less than 15 pptv [Brune and Anderson, 1986]. Yet these concentrations of BrO are small and pose a serious challenge to both ground-based and in-situ instruments.

The presence of BrO in the antarctic vortex was inferred from ground-based spectroscopic observations of OClO from McMurdo Station in 1986 [Solomon et al., 1987]. OClO, formed in the atmosphere primarily by the reaction

$$ClO + BrO \rightarrow OClO + Br, \qquad (1b)$$

was observed during twilight and in total darkness. The observed slant-column depths were consistent with enhanced abundances of ClO and the upper limit of 15 pptv of BrO established by midlatitude balloon measurements.

The first successful in-situ measurements of BrO in the stratosphere were made in the southern hemisphere during the AAOE campaign of 1987 [Brune et al., 1989a]. These observations showed that BrO mixing ratios within the southern polar vortex, ranging from 5 to 7 pptv, were somewhat enhanced compared to values found outside the vortex. Complementary ground-based studies of BrO and OClO during the same season [Solomon et al., 1989] provided additional strong evidence for occurrence of reaction (1) as well as information regarding the importance of a long-lived reservoir of BrO at night. From the slant-column measurements and a photochemical model, a mixing ratio of ≈ 7 pptv was derived for BrO, and it was concluded that photolysis of $BrONO_2$ in the morning twilight was more consistent with the observations than was photolysis of BrCl, a species formed by yet another channel of reaction (1),

$$ClO + BrO \rightarrow BrCl + O_2, \qquad (1c)$$

which represents about 10% of the overall reaction in laboratory studies [Toohey and Anderson, 1988; Friedl and Sander, 1989]. The ER-2-based observations, which were carried out in daylight, were unable to address this photochemical issue. However, they did demonstrate that a significant fraction ($\approx 20\%$) of the ozone depletion observed over Antarctica in 1987 was due to the catalytic cycle rate limited by the reaction of ClO with BrO [Anderson et al., 1989].

Several experiments were carried out in early 1988 to examine bromine and chlorine within the arctic vortex. Ground-based observations of OClO provided strong evidence again for the presence of BrO and enhanced concentrations of ClO inside the vortex [Solomon et al., 1988], while an in-situ study with the ER-2-based ClO-BrO instrument detected evidence of perturbed halogen chemistry outside the vortex [Brune et al., 1988].

We report here the results of recent measurements of BrO obtained during the AASE mission to the arctic stratosphere in January and February of 1989. As in the

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companion paper that reports ClO observations [Brune et al., this issue, a], we will focus on three of the fourteen flights from Stavanger, Norway, across the Arctic Circle that occurred over the period from January 3 to February 10, 1989. In addition, we will draw upon measurements obtained on December 29, 1988, during a transit flight which passed over the continental United States. These results will be compared to previous measurements of BrO obtained over Antarctica and Canada in 1987 and 1988.

Experiment

The ClO–BrO instrument, which was mounted in a pod on the left wing of the NASA ER-2 aircraft, has been described in detail elsewhere [Brune et al., 1989b]. Detection of BrO is accomplished through addition of nitric oxide to a flow of air which is decelerated to ≈ 20 m s^{-1} with a double-ducted flow system. The reaction of BrO with NO is greater than 95% complete within 10 to 15 ms at the NO concentrations added ($\approx 10^{13}$ molecules cm^{-3}); the bromine detection system is positioned approximately 25 ms downstream of the NO injector. Bromine atoms formed by this reaction are then detected by resonance fluorescence with a density-dependent sensitivity ranging from $\approx 10^{-6}$ cts s^{-1}/(Br atom cm^{-3}) at the highest flight altitudes achieved, to $\approx 3 \times 10^{-7}$ cts s^{-1}/(Br atom cm^{-3}) at the minimum altitude the aircraft could sustain to allow for sufficient signal averaging. For background signals (which were also density dependent) of 5000 cts s^{-1}, a detection limit of $\approx$ (2–3) cts s^{-1} was obtained for signal averaging of one hour at most altitudes. Thus, BrO mixing ratios of 6 pptv could be detected with typical signal-to-noise ratios of 3 to 5.

The bromine lamp employed for the first half of the campaign was the same lamp as that used during the AAOE flights, the February flight series based at Moffett Field [Brune et al., 1988], and all test flights. This system has been calibrated at four separate instances. Both the absolute calibration (when scaled to the total background signal at an air density of 2.6×10^{18} molecules cm^{-3}) and the pressure dependence have varied less than 10% over more than 200 hours of operation in the stratosphere and in the laboratory. Calibrations used the rapid reaction of a measured amount of chlorine atoms with molecular bromine, and is described elsewhere [Brune et al., 1989a].

After the flight of January 30, 1989, this lamp was removed. The replacement lamp was calibrated after the flight series, and concentrations of bromine measured with this lamp over the last seven flights of the campaign were in good agreement with values observed during the first half of the flight series. Therefore, although the laboratory calibrations for the two lamps were different, there appears to be no significant systematic difference between bromine concentrations determined with the two systems.

Upon addition of nitric oxide to convert BrO to Br there is a small absorption of the background nonresonant scatter. By reproducing flight conditions in the laboratory, this correction to the bromine signal has been measured to be smaller than 10^{-17} cm^2 (molecule NO)$^{-1}$ for the lamps employed in these flights. In practice, accounting for this absorption leads to a positive offset of less than 1.5 pptv. Overall, it is estimated that the uncertainty in the BrO calibration is ±35% at the 2σ confidence level.

Observations

A typical ER-2 flight track consisted of a rapid ascent to maximum altitude, a hold at some potential temperature between 440 and 470 K while flying up the Norwegian coast and then toward Spitzbergen, a turn-around at approximately local noon with a dive for a vertical scan, and finally a return leg at a different potential temperature back to Stavanger. These flight tracks were similar to those employed out of Punta Arenas, Chile, during the AAOE mission [Tuck et al., 1989]. We have selected three flights that illustrate key features of the bromine observations that were evident on most of the fourteen flights. Taken together, the flights of January 6, January 16, and February 10, sampled both inner- and outer-vortex air, and sampled inner-vortex air that was both illuminated and in total darkness. In addition, these flights, which span the entire series, serve to define the temporal evolution of BrO during the mission.

The BrO measurements for three flights appear in Figures 1 through 3, overlaid by the measurements of ClO. While these latter measurements are described in detail elsewhere [Brune et al., this issue, a], there are some important points that deserve review here. First, throughout the mission, every flight into the polar vortex revealed highly perturbed concentrations of ClO. Clearly, a significant fraction of the vortex air had been processed by polar stratospheric clouds (PSCs), at least at altitudes accessible to the ER-2. Both ClO and BrO are sensitive to concentrations of NO_2, which were significantly depleted within the vortex [Fahey et al., this issue]. The observations of high concentrations of ClO in air that has been in total darkness for at least 20 hours leads to the conclusion that a considerable fraction of ClO was bound up in a form other than $ClONO_2$. It is likely that the less stable species ClOOCl represents the major nighttime reservoir of ClO. Finally, as the mission progressed, the mixing ratios of ClO rose from several hundred pptv to over 1100 pptv by February 10. This increase was most likely due to increasing solar illumination with continued processing of air by PSCs.

The results for the first flight to encounter highly perturbed ClO, on January 6, appear in Figure 1. The potential temperature and solar zenith angles (SZA) for the entire flight track are shown by Brune et al. [this issue, a]. Interestingly, BrO was highest where ClO was low, and there was no BrO where ClO was highly perturbed. However, upon consideration of the SZA, we note that regions in which no BrO was observed were at very high angles, in this flight greater than 92°. Inversely, portions of the January 6 flight where BrO mixing ratios were high occurred where the ClO was low. The mixing

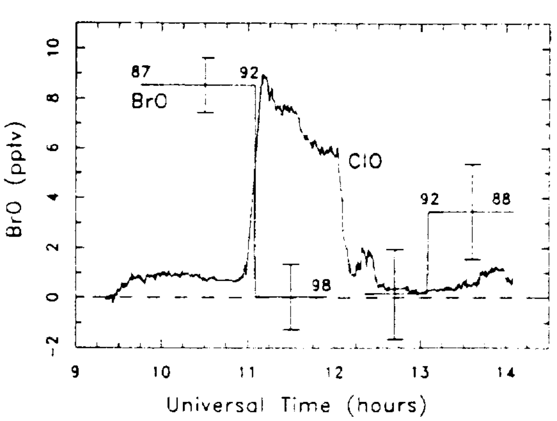

Fig. 1. Overlay of BrO and ClO mixing ratios for the flight of January 6, 1989. Horizontal bars represent time over which signal was averaged to obtain the 1σ statistical uncertainties represented as vertical bars. Numbers indicate solar zenith angles corresponding to various positions along the flight track. ClO axis units are unspecified.

ratio of BrO was 8.5±1.2 pptv along the outbound leg, which was flown at a potential temperature of 475 K, and 3.5±2 pptv along the inbound leg flown at 413 K. Even at this early stage in the flight series these BrO values were greater than values observed at comparable altitudes at midlatitudes and were similar to values observed within the antarctic vortex [Brune et al., 1989a]. Although ClO mixing ratios were relatively low at the start and the end of the flight, these outer-vortex values (25 pptv) were still considerably larger than values measured at midlatitudes at comparable altitudes and SZA [Brune et al., this issue, b], and thus represent a perturbation from typical midlatitude values.

The results obtained on January 16 were similar to those of January 6, and are shown in Figure 2. The mixing ratios of ClO were highly perturbed throughout the entire flight, while the behavior of BrO was identical to that for the flight of January 6. Once again, no BrO was observed at SZA greater than 92° and BrO values in sunlight were moderately high, even at a potential temperature of 400 K on the inbound leg. Within the statistical uncertainties of the measurements (typically ±1.5 pptv), at no time during any flight was BrO observed at solar zenith angles greater than 94°. At SZA greater than 90°, photolysis rates of $BrONO_2$ and BrCl decrease rapidly as the sun approaches the horizon (which is near 94° SZA at maximum ER-2 flight altitudes) [Solomon et al., 1989]. Thus, in darkness, BrO was likely sequestered in $BrONO_2$ or BrCl, or both. These observations also indicate that destruction of ozone by the catalytic cycle rate limited by the BrO + ClO reaction was terminated in darkness, even though ClO remained at moderate concentrations. In addition, the observations of zero BrO are important because they add confidence that the small offset due to absorption by NO is valid.

Results of the last arctic flight of the AASE campaign, on February 10, are summarized in Figure 3. The ER-2 flew over Iceland and Greenland staying in sunlight for the entire flight. Here, both the BrO and the ClO profiles strongly resemble those obtained over Antarctica [Brune et al., 1989a]. Within the arctic vortex the BrO mixing ratio was 8±2 pptv at 470 K. However, values outside the vortex were low (1-4 pptv), similar to those observed at midlatitudes. The mixing ratios of ClO early in the outbound leg and late in the return leg were the lowest values measured in sunlight during the latter half of the campaign. Indeed, meteorological analysis indicated that this outer-vortex air was drawn from significantly lower latitudes than earlier in the mission (D. S. McKenna, personal communication, 1989).

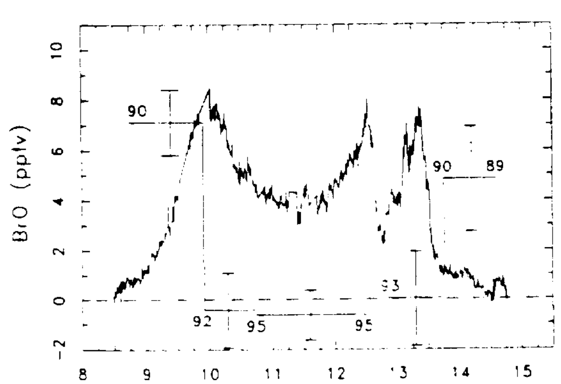

Fig. 2. Overlay of BrO and ClO mixing ratios for the flight of January 16, 1989. Data are represented as described in Figure 1 caption.

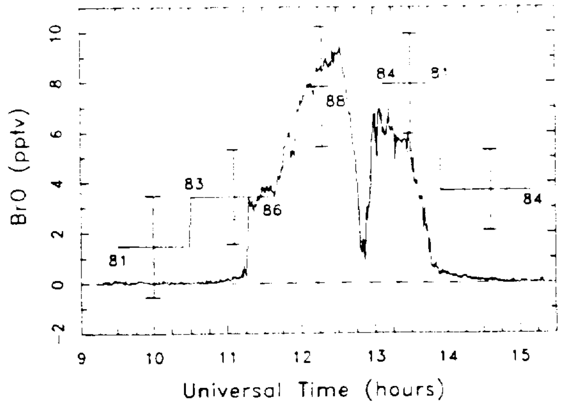

Fig. 3. Overlay of BrO and ClO mixing ratios for the flight of February 10, 1989. Data are represented as described in Figure 1 caption.

Near the end of the campaign, a number of measurements within sunlit portions of the vortex yielded values of 6 to 8 pptv (independent of SZA when SZA was less than 90°), while measurements obtained when ClO mixing ratios were observed to be low yielded values of 2 to 4 pptv. To highlight these differences, and also to compare to the measurements of BrO from over Antarctica, we plot the measurements as a function of potential temperature in Figure 4. Data obtained in air that had ClO mixing ratios typical of those found at midlatitudes are plotted as open symbols. Also included are data from the transit flight of December 29, 1988, which passed over the continental United States. There was indeed BrO enhancement within the two vortices, but much less than corresponding enhancements of ClO. BrO mixing ratios within the vortex were about twice as large as values at midlatitudes. This is consistent with the notion that BrO represents a major inorganic bromine species and reaches a maximum value with only a small reduction in NO_2 concentration.

Although there was a slight increase in mixing ratios of BrO over the course of the flight series, more likely

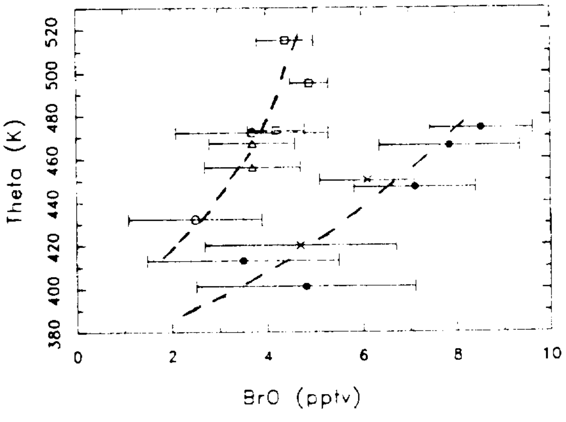

Fig. 4. Observed BrO mixing ratios for a number of flights as a function of potential temperature. Circles are from AASE flights, inner-vortex values represented by closed circles. × represent values from antarctic observations of Brune et al. [1989a], squares are from February 13, 1988, a flight over Canada [Brune et al., 1988], and triangles are from the transit flight of December 29, 1988, which passed over the continental US at midday. Dashed lines are for emphasis only.

this was due to the ability of the aircraft to reach higher potential temperatures as the vortex warmed than to any real temporal trend in the total burden of inorganic bromine or in its partitioning. While ClO concentrations rose markedly (as solar zenith angles decreased), BrO mixing ratios at a fixed potential temperature in sunlight remained fairly constant over the six-week period. This is consistent with observations from over Antarctica [Brune et al., 1989a]. If the partitioning of bromine was perturbed, as suggested by the significant perturbation in ClO, the burden of inorganic bromine in the stratosphere likely does not exceed 10 to 15 pptv, in contrast to a recent far-infrared emission mearurements at midlatitudes which found 25 pptv of HBr [Park et al., 1989]. However, a strong conclusion cannot be drawn until we know the details of heterogeneous reactions of HBr and $BrONO_2$ on PSC particles.

We can use the simultaneous measurements of BrO and ClO to estimate the rate of ozone loss due to reaction (1). Using a value of 1 part per billion of ClO in sunlight, consistent with the observations late in the mission, a rate of roughly 6×10^5 s^{-1} is derived for ozone loss, or equivalently, 0.5% each 12 hours of solar illumination. This loss rate is comparable to that observed within the Antarctic Ozone Hole. Therefore, should the arctic vortex remain stable into springtime, the interaction of bromine and chlorine could represent a significant sink for ozone in the arctic stratosphere.

Summary

Mixing ratios of BrO observed within the arctic lower stratosphere during daylight in January and February of 1989 were found to be enhanced by a factor of 2 over values normally found at midlatitudes. These observations are similar to those made over Antarctica in September, 1987. Values as large as 8 ± 2 pptv were observed late into the mission when more than a part per billion of ClO was measured. Within the statistical significance of the measurement, no BrO was observed at any time in complete darkness, indicating that BrO was tied up at night in long-lived reservoirs, most likely $BrONO_2$ and BrCl. These observations demonstrate the potential for significant loss of ozone, especially if vortex air masses were to experience significant solar illumination.

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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

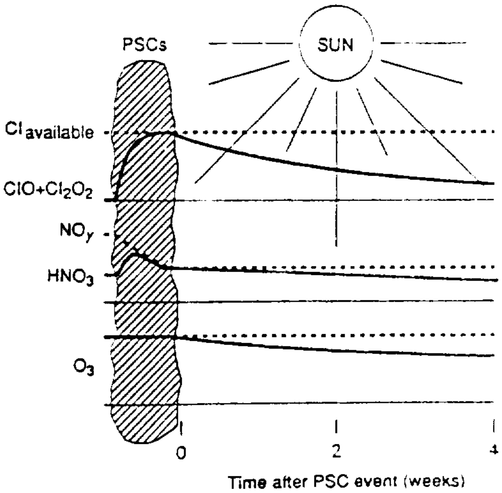

Fig. 1. Diagram illustrating how PSCs and sunlight alter the abundances of trace gases and O_3 in the polar vortex. Dotted lines indicate the available chlorine, reactive nitrogen, and initial O_3; the solid lines indicate reactive chlorine (ClO and Cl_2O_2), HNO_3, and O_3. Ozone is rapidly destroyed 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.

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

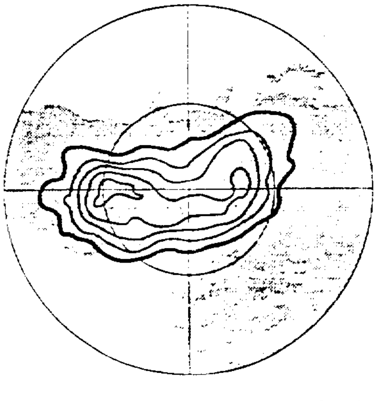

Fig. 2. The Arctic polar vortex for 7 February 1989 for the 460 K potential temperature surface (*39*). Unlike the boundary for the Antarctic polar vortex, which is much larger than its CPR, the boundary for the Arctic polar vortex coincides with the boundary for its CPR. Thus the heavy line that encircles the polar vortex also encircles the region containing increased amounts of reactive chlorine and reduced amounts of NO_y. 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.

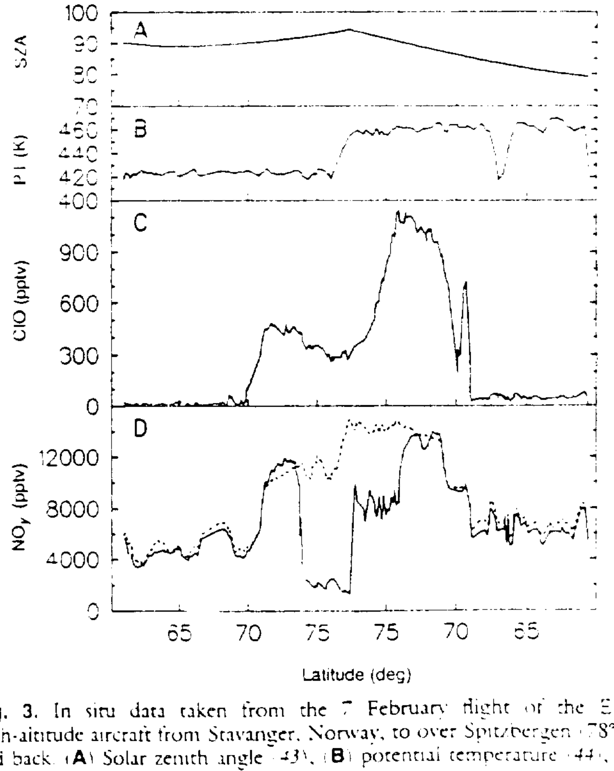

Fig. 3. In situ data taken from the 7 February flight of the ER-2 high-altitude aircraft from Stavanger, Norway, to over Spitzbergen (78°N), and back. (**A**) Solar zenith angle (*43*), (**B**) potential temperature (*44*), (**C**) the ClO mixing ratio (*45*), and (**D**) the NO_y mixing ratio (*46*) 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 (*48*). 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

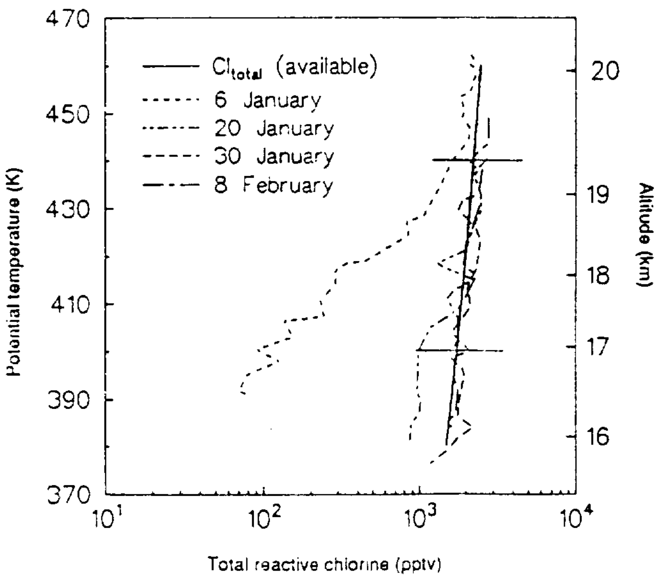

Fig. 4. Calculated total reactive chlorine (ClO + 2 × Cl_2O_2) plotted against potential temperature for four Arctic flights. Cl_{total} (available) is the available chlorine estimated from the measurements of Heidt (*48*). For data obtained after 6 January, most of the available chlorine was converted 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.

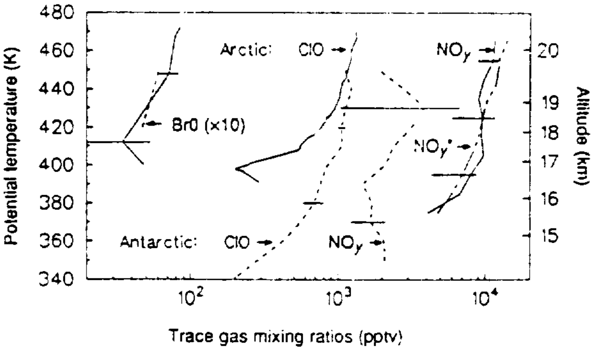

Fig. 5. Comparison of Antarctic and Arctic in situ data, taken during the AAOE in 1987 and the AASE in 1989, respectively. Arctic data are represented by solid lines, Antarctic data by dashed lines. The dot-dash line represents the NO_y^* mixing ratios for the Arctic, which are ~1000 pptv smaller for 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

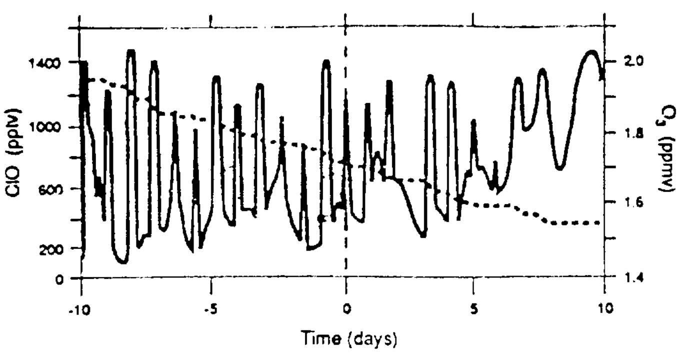

Fig. 6. Calculated ClO mixing ratio variations and O_3 destruction for an air parcel observed on 10 February 1989. The solid line shows the variation of ClO over 20 days centered on 10 February; the dotted line shows the expected change in O_3 for the same 20 days. The ClO abundance depends strongly 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

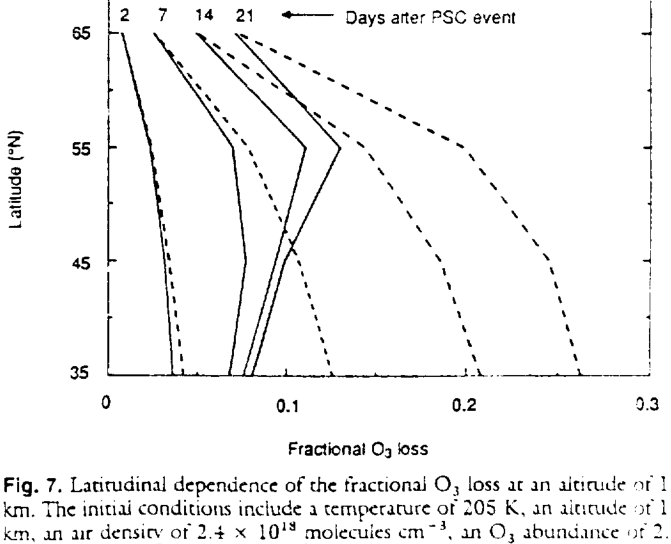

Fig. 7. Latitudinal dependence of the fractional O_3 loss at an altitude of 18 km. The initial conditions include a temperature of 205 K, an altitude of 18 km, an air density of 2.4×10^{18} molecules cm^{-3}, an O_3 abundance of 2.3 ppmv (5.6×10^{12} molecules cm^{-3}), and a total chlorine abundance 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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