Chlorine Chemistry on Polar Stratospheric Cloud Particles in the Arctic Winter

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Simultaneous in situ measurements of hydrochloric acid (HCl) and chlorine monoxide (ClO) in the Arctic winter vortex showed large HCl losses, of up to 1 part per billion by volume (ppbv), which were correlated with high ClO levels of up to 1.4 ppbv. Air parcel trajectory analysis identified that this conversion of inorganic chlorine occurred at air temperatures of less than 196 ± 4 kelvin. High ClO was always accompanied by loss of HCl mixing ratios equal to $1/2(ClO + 2Cl_2O_2)$. These data indicate that the heterogeneous reaction $HCl + ClONO_2 \rightarrow Cl_2 + HNO_3$ on particles of polar stratospheric clouds establishes the chlorine partitioning, which, contrary to earlier notions, begins with an excess of $ClONO_2$, not HCl.

A cornerstone of our understanding of polar ozone loss (*1*) is the heterogeneous conversion on particles of polar stratospheric clouds (PSCs) (*2*) of inorganic chlorine from its less reactive components hydrochloric acid (HCl) and chlorine nitrate ($ClONO_2$) to photochemically labile Cl_2 and HOCl (*3*). Conversion is believed to occur on surfaces of both type I nitric acid trihydrate (NAT) and type II (water ice) PSC particles that form in the lower stratosphere at temperatures at or below about 196 K and 188 K, respectively, when sufficient amounts of HNO_3 and H_2O condense on sulfate aerosol particles (*2*). The principal reactions (*4*) are:

$$HCl + ClONO_2 \xrightarrow{\text{Type I,II PSC}} Cl_2 + HNO_3 \quad (1)$$

$$ClONO_2 + H_2O \xrightarrow{\text{Type II PSC}} HOCl + HNO_3 \quad (2)$$

$$HOCl + HCl \xrightarrow{\text{Type I,II PSC}} Cl_2 + H_2O \quad (3)$$

The fast reaction rate of HOCl with HCl (*5*) means that reactions 2 and 3 together are indistinguishable from reaction 1 for unlimited amounts of available reactants. Springtime polar ozone loss through catalytic cycles involving ClO (*6*) and BrO (*7*) is associated with the maintenance of high amounts of ClO and its dimer (Cl_2O_2) in the sunlit atmosphere produced by reactions initiated by photolysis of the reaction products Cl_2 and HOCl (*8, 9*).

Verification of the occurrence of the above reactions requires direct atmospheric observations of key reactants or products and stoichiometry. Because Arctic temperatures rarely fall low enough for type II PSC formation, it is possible that inorganic chlorine conversion will be driven by reactions 1 and 3, which should terminate once either of the reactants is gone. It is therefore particularly important to know the initial relative abundance of HCl and $ClONO_2$. Measurements of the total HCl and $ClONO_2$ column amounts from ground-based and aircraft (DC-8) platforms (*10*) have been limited by the absence of simultaneous measurement of ClO, and earlier in situ studies of PSC chemistry (*8, 11–13*) have without measurements of either HCl or $ClONO_2$ been unable to identify the reaction responsible for the high ClO production. In this report we describe in situ measurements of stratospheric HCl made simultaneously with those of ClO in air processed and unprocessed by PSC chemistry, made from the ER-2 payload for the second Airborne Arctic Stratospheric Expedition (AASE II).

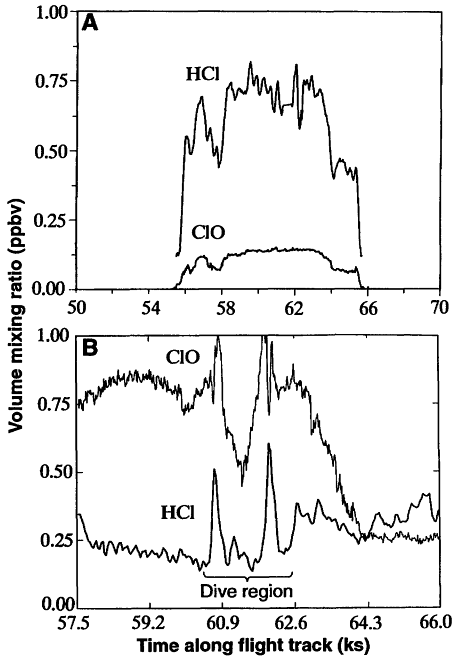

Fig. 1. Examples of flight data recorded by the ALIAS instrument (HCl) and the resonance fluorescence instrument (ClO) in two flights from Bangor, Maine, over the northeastern United States. **(A)** Data from 8 December 1991, in which the lowest N_2O levels reached were about 180 ppbv. Solar zenith angles ranged from 67.5° to 76.6°. **(B)** Data from the dive region of the flight of 13 February 1992. Over the portion shown, N_2O values ranged from 190 to 65 ppbv.

The aircraft laser infrared absorption spectrometer (ALIAS) instrument on the ER-2 was a scanning tunable diode laser spectrometer capable of measuring HCl, N_2O, and CH_4 simultaneously by way of high-resolution laser absorption at wavelengths from 3 to 8 μm (*14, 15*). The ClO measurements were made by detecting Cl atoms resulting from chemical conversion of ClO by injected NO (*8*). The December and February flight data (Fig. 1) illustrate the widely differing HCl and ClO amounts encountered over the period of inorganic chlorine conversion. Uncertainties in measured ClO and HCl levels are typically ±25 and ±15%, respectively. The minimum detectable HCl amount is about 0.04 ppbv.

We obtained data from 14 flights of the ER-2 out of Bangor, Maine, from December 1991 through March 1992. The aircraft

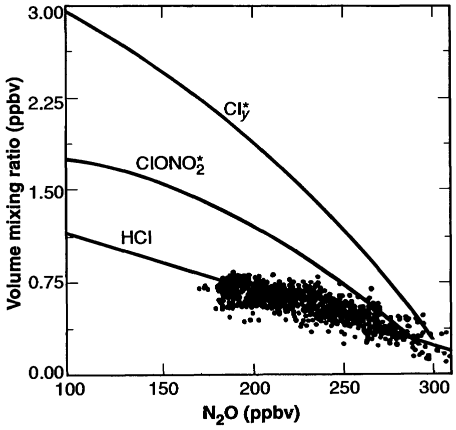

Fig. 2. Baseline relationships of Cl_y^*, HCl, and $ClONO_2^*$ with N_2O, used for assessing change in reservoir chlorine with PSC processing. The HCl data is from flights of 8, 12, and 14 December 1991 and 15 and 22 March 1992. Although some curvature of the HCl/N_2O data is evident, a linear relation was used of the same slope as the gas-phase model HCl/N_2O over the region 170 ppbv N_2O to lower values.

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attained a maximum pressure altitude of about 50 mbar, and covered a latitude range of about 45° to 69°N for northerly flights, and about 45° to 22°N in the three southerly flights. The strategy was generally to fly deep into the vortex to the highest potential vorticity (*16*), and have the aircraft dive to pressures of ~120 mbar. Air that was sampled in the vortex interior in winter resulted from dynamical descent from much higher altitudes. Although descent brings chemically processed air down from above for study, analysis of HCl loss is restricted by the limited ability to sample this same air outside the vortex. Air containing PSCs was not sampled (*17*) but rather air that in some cases had earlier contained PSCs and undergone subsequent chemical processing.

In order to remove the contribution of atmospheric dynamics to the observed variations of HCl and ClO, we ratioed the mixing ratios to those of N_2O, a conserved long-lived dynamical tracer. Data from several flights either before or outside PSC processing yielded an empirical relation of

$$\mathrm{HCl} = 1.56 - 0.0046\mathrm{N_2O} \qquad (4)$$

for N_2O mixing ratios > 100 ppbv (all equations are written in units of parts per billion by volume). We used this relation as a baseline (*18*) with which to identify HCl change in and out of PSC-processed regions (Fig. 2). This baseline must be extrapolated to the lower N_2O values typical of the descending vortex interior (*19*), because the lowest N_2O values reached were only ~170 ppbv during the aircraft flights outside the vortex or before it formed.

The partitioning of inorganic chlorine between its reservoir and reactive forms must be related to the total inorganic chlorine available ($\mathrm{Cl_y = Cl + ClO + 2Cl_2O_2 + HCl + ClONO_2 + HOCl}$) in a given air parcel characterized by its specific N_2O mixing ratio. The relation between Cl_y and N_2O has been established (*20*) on the basis of whole-air sampling of chlorine-containing compounds (*21*). Chlorine in the troposphere is mainly organic compounds, whereas in the stratosphere it resides mainly in inorganic forms. The total available chlorine level has been estimated as 3.4 ppbv for the 1991–1992 Arctic stratosphere (*22, 23*). The stratospheric inorganic chlorine is:

$$\mathrm{Cl_y} = 3.4 - \mathrm{CCl_y} \qquad (5)$$

where the organic chlorine component, CCl_y, is calculated from the observed dependence on N_2O, according to (*20*):

$$\mathrm{CCl_y} = 2.867 \times 10^{-5}(\mathrm{N_2O})^2 + 1.59 \times 10^{-3}(\mathrm{N_2O}) + 0.126 \qquad (6)$$

The total available inorganic chlorine (Cl_y^*) may in this way be calculated along the ER-2 flight track with the use of measured N_2O levels (Fig. 2).

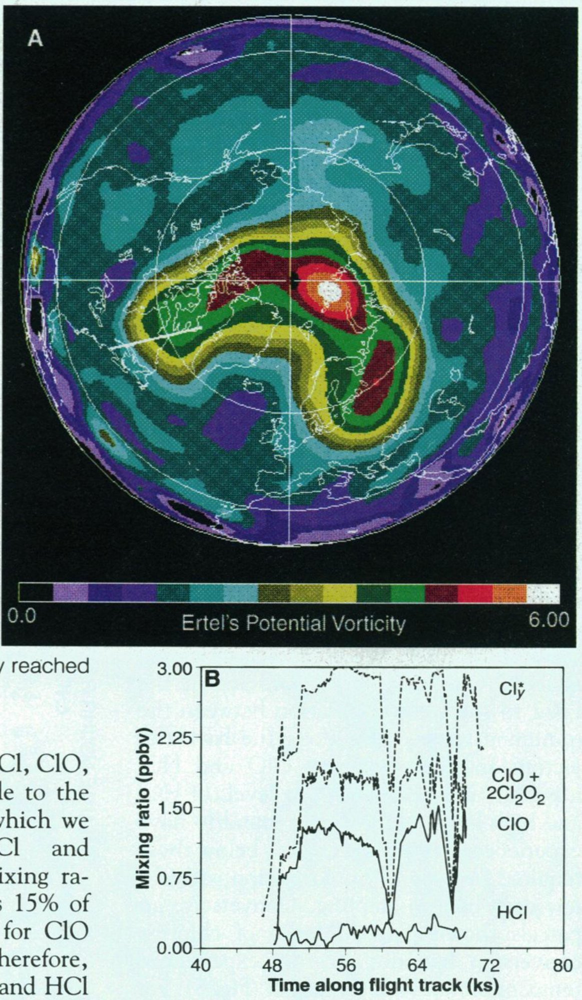

Fig. 3. (**A**) A polar view of Ertel's potential vorticity map at noon (UT) on 20 January 1992 for the 440 K potential temperature surface (*16*), with the ER-2 aircraft flight track marked in white. The proximity of the vortex edge to both Maine and to Europe is the result of planetary wave activity, which distorts the vortex symmetry about the pole, coupled with a blocking high-pressure system near Iceland. (**B**) Corresponding flight data for ClO and HCl along the flight track for 20 January 1992 and the calculated values of the available inorganic chlorine, Cl_y^* calculated measured CFC-11 mixing ratios (*18*) and the sum ClO + $2Cl_2O_2$ (*26*). The dimer amount is calculated from an assumption of steady-state balance between its three-body production from ClO + ClO + *M*, and its loss through both photolysis and thermal decomposition (*26*). The vortex edge was over northeast Canada and the United States, and easily reached from Bangor, Maine.

Outside PSC-processed regions Cl, ClO, Cl_2O_2, and HOCl contribute little to the inorganic chlorine budget (*31*), which we assume is predominantly HCl and $ClONO_2$. Chlorine monoxide mixing ratios may be approximated (*24*) as 15% of the observed HCl mixing ratios for ClO mixing ratios below 200 pptv. Therefore, by differencing the curves of Cl_y^* and HCl shown in Fig. 2, and making allowance for the small amount of ClO, we developed a relation for the budget residual inorganic chlorine, identified it as chlorine nitrate, and labeled it $ClONO_2^*$.

The relationships of HCl and $ClONO_2^*$ with N_2O, plotted in Fig. 2, represent the unperturbed conditions with which to assess the behavior of the chlorine partitioning during any flight. These relations imply that, contrary to earlier notions, HCl is not the principal reservoir of inorganic chlorine in the lower stratosphere at northern latitudes, as it represents only about 40% of Cl_y in the region up to about 20 km. Thus before chemical processing by the reaction of HCl + $ClONO_2$ on PSCs begins, the atmosphere has $ClONO_2$ in excess.

After the atmosphere cooled below 196 K (*25*), so that type I PSCs formed, significant

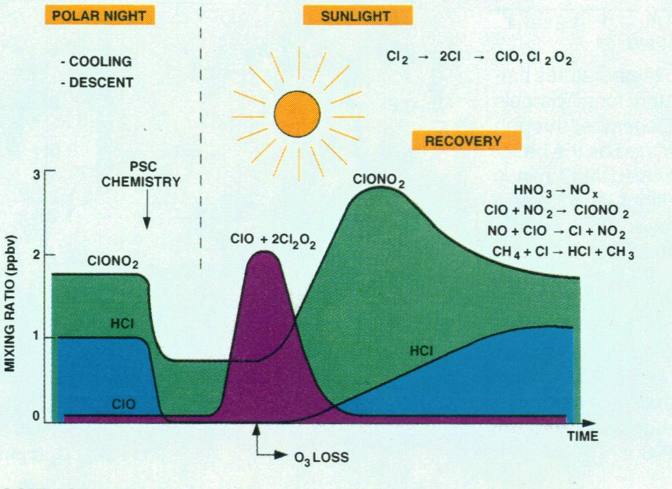

Fig. 4. Schematic of the time evolution of the chlorine chemistry, illustrating the importance of the initial HCl/$ClONO_2$ ratio, the sudden formation of ClO with returning sunlight, the way in which $ClONO_2$ levels can build up to mixing ratios in excess of its initial values, and the slow recovery of HCl levels.

loss of HCl was seen in early December and coincided with high ClO values to 0.5 ppbv. By early January, ClO levels regularly approached 1 ppbv. On 20 January near complete loss of HCl (>95% in some air parcels) was observed, corresponding to removal of about 1 ppbv HCl. This loss was accompanied by large increases in ClO of up to 1.4 ppbv. The observed reversal in the relative amounts of HCl and ClO is attributed to chemical repartitioning within the vortex. The data of Fig. 3B show that 65% of the available inorganic chlorine has been converted to ClO + $2Cl_2O_2$, with the remainder in $ClONO_2$ left over from the PSC processing or formed during recovery (Fig. 4).

Because of planetary wave activity at northern high latitudes, the Arctic winter vortex is characterized by temperatures higher than that of the more stable, more symmetric, and more persistent Antarctic polar vortex (*27*), and occurrences of type II PSCs are rarer. We used back trajectory analysis on air parcels encountered by the ER-2 to study the correlation between the minimum temperature along the back trajectory and the measured ClO and HCl loss. All air parcels with low levels of HCl and high levels of ClO were found to have experienced temperatures at or below those required for type I PSC formation within a few days before sampling. Conversely, air parcels showing no evidence of chlorine conversion had not recently experienced temperatures of PSC formation (Fig. 5). For HCl loss between 0.2 and 1.2 ppbv, back trajectories usually passed through regions with temperatures cold enough for NAT formation. Exceptions are all within 3.5 K of the NAT formation temperature, which is within the uncertainty of the trajectory calculation and the NMC (National Meteorological Center)-analyzed temperature field.

The principal action of sunlight on air parcels that have undergone heterogeneous conversion on PSC particles is twofold: first, to produce labile chlorine, and second, to photolyze HNO_3, thereby continuously replenishing NO_x levels and beginning the healing process of tying up the reactive chlorine in the temporary reservoir $ClONO_2$. In this way (Fig. 4), the vortex recovery period of February to March 1992 was expected to be characterized by diminishing ClO amounts, some ozone loss, increasing $ClONO_2$, and low HCl showing only slow recovery through the Cl + CH_4 reaction responsible for HCl production (*28*).

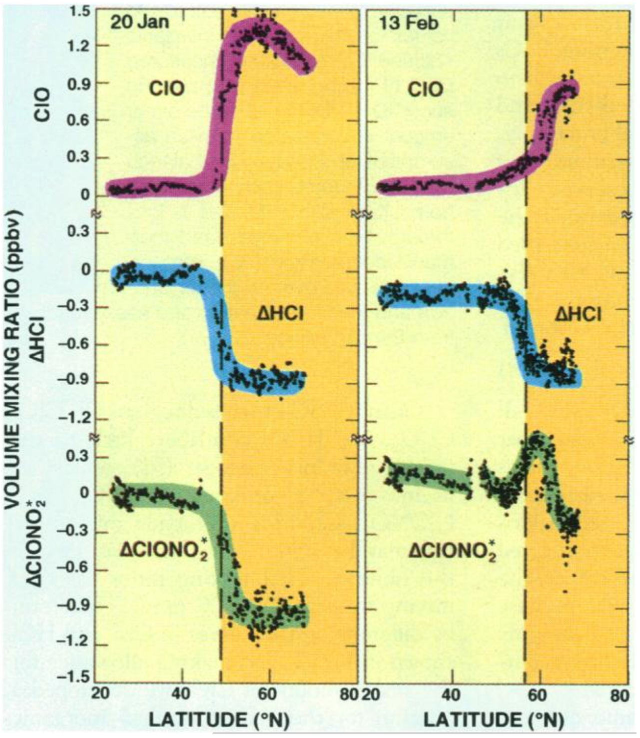

Fig. 6. Volume mixing ratios of ClO, ΔHCl, and $\Delta ClONO_2^*$ as function of latitude for flights of 20 January and 13 February 1992. See Fig. 5 and text for definition of ΔHCl and $\Delta ClONO_2^*$. Data for latitudes below 42°N is from the southerly flight of 22 February 1992. The dotted vertical lines indicate the position of the vortex edge, as defined by the maximum value of the mean zonal wind measured (*30*) aboard the ER-2. The vortex edge is therefore located at 49°N, and 57°N, respectively, for each flight.

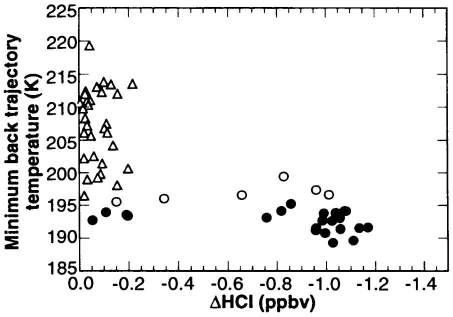

Fig. 5. Minimum atmospheric temperatures calculated along the back trajectory for air parcels sampled during flights from December through March 1992, versus ΔHCl, defined as the baseline HCl expected from observed N_2O minus the HCl measured in the flight. Full circles identify minimum temperatures <196 K, whereas open triangles and circles identify those temperatures >199 K and <199 K, respectively. Back trajectory lengths are typically 10 days, with those of February being 30 to 40 days. Vortex edge parcels have been eliminated. The few points showing minimum temperatures <196 K for which ΔHCl is small limit the ability of back trajectory analysis to identifying the NAT temperature, which is 196 ± 4 K.

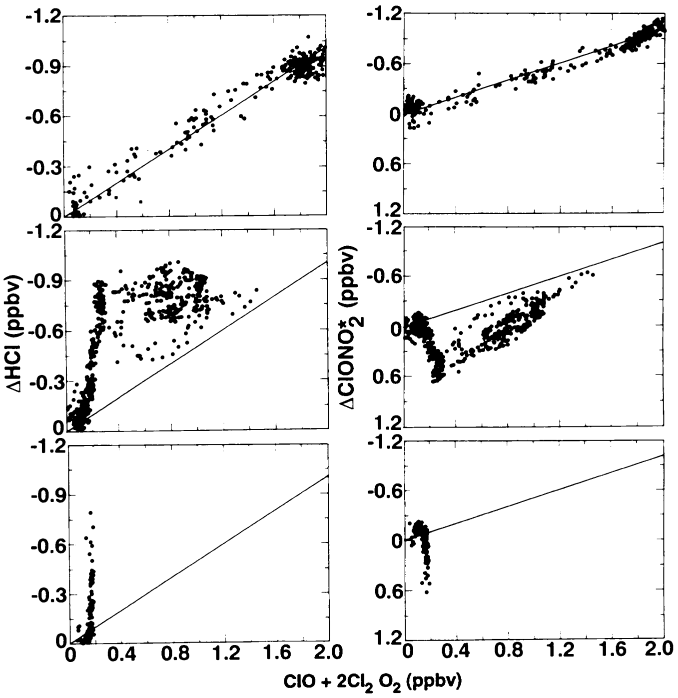

Fig. 7. ΔHCl (ppbv) and $\Delta ClONO_2^*$ (ppbv) plotted against the sum ClO + $2Cl_2O_2$ (ppbv) for the following flights: top panels, 12 December and 20 January; middle panels, 13 and 17 February; bottom panels, 18 March. The slopes drawn are the 1:2 slopes for comparison with the data. A large fraction of the sum ClO + $2Cl_2O_2$ is measured ClO, and differences in the Cl_2O_2 absorption cross section used (*26*) affect the sum by only ~13%.

Following a minor warming event in late January, temperatures of the vortex rose above the PSC threshold (*25*), and high ClO mixing-ratios began to decline just inside the vortex. Flights in February (Fig. 6) showed ClO and ClONO$_2$* behavior different from that of January, whereas the HCl loss appeared to be similar: the edge of the region of loss still maintained coincidence with the maximum in the wind field defining the vortex edge. The ClO data now showed a more gradual change across the vortex edge, characteristic of the vortex recovery. Most interesting was the collar of high ClONO$_2$* levels just inside the vortex edge (*10*). Deeper into the vortex at the highest latitudes reached, air depleted in ClONO$_2$ was still present. The springtime decline of ClO mixing ratios, and the resulting formation of ClONO$_2$ to amounts larger than its initial values arose from the production of NO$_2$ from photolyzed HNO$_3$ released from PSC's as sunlight returned.

ClO amounts seen in February and March generally decreased, with low HCl air masses still observed on most flights, some correlated with high ClO values. For example, in the lower trace of Fig. 1, the large spikes in HCl amounts correspond with downward spikes in ClO amounts, and are associated with transit through a layer of air in the aircraft dive which had not seen PSC processing. Flights in February and March often encountered air masses of low HCl and low ClO amounts (see the lower trace of Fig. 1); the chlorine budget calculations show large amounts of ClONO$_2$, as expected. The data of Fig. 6 show that ClO quickly lost its value as an indicator of the vortex edge, whereas the slow recovery of HCl made this gas an excellent indicator of both the vortex edge and of air that has at some time undergone PSC processing.

During the early stages of inorganic chlorine conversion, it can be seen (Fig. 7) that for both HCl and ClONO$_2$* loss, the data lie close to the 1:2 line predicted from the reaction stoichiometry, especially for higher ClO + 2Cl$_2$O$_2$ amounts. Even during the January flights, however, some recovery was still taking place for air parcels processed weeks earlier, and we identify data above and to the left of the 1:2 line with recovery, where the ClO levels have declined, and the HCl remained depleted to some extent. The counterpart is seen in the change in ClONO$_2$* levels where recovery corresponds to increased amounts of ClONO$_2$*. In February and March, when the recovery was well under way, the data indicate a shift in chlorine from ClO and its dimer into the temporary reservoir chlorine nitrate.

These data imply that reactive chlorine (ClO + 2Cl$_2$O$_2$) production: (i) occurs at mixing ratios double those lost from HCl, supporting a reaction in which one molecule of HCl reacts with another (different) molecule containing one chlorine atom, identified as ClONO$_2$ (*31*); (ii) occurs suddenly at temperatures below 196 ± 4 K, with little if any production at warmer temperatures; and (iii) does not occur without HCl loss, even after virtually all the HCl is gone. For example, for HCl loss maximized at 0.9 ppbv, further production of ClO + 2Cl$_2$O$_2$ is not observed. No evidence is found for the occurrence of the ClONO$_2$ + H$_2$O reaction, which, following HCl depletion, would have continued to produce reactive chlorine through production of HOCl.

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16. Potential vorticity is usually defined as $PV = -g(f + \zeta)d(\theta)/dp$ where g is the acceleration due to gravity, and θ is the potential temperature. Potential temperature is the temperature of an air parcel brought adiabatically to the surface. For an air parcel at −80°C and 50 mbar pressure, its potential temperature is about 180°C (453 K). P and V are the pressure and volume; f and ζ are the planetary and relative vorticity.
17. Actually a single, brief encounter with air containing PSCs occurred on the flight of 6 January 1992 from Bangor, ME, to Greenland, as inferred from high NO$_y$ observations using particle-sensitive sampling.
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had been depleted. This is not observed.

32. We thank team members of the AASE-II mission, including J. G. Anderson, M. J. Kurylo, E. Condon, the ER-2 pilots, and the aircraft and mission operation staff. Field operations support of ALIAS was by M. Tuchscherer and C. Trimble. Part of the research described in this paper was carried out by the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration.

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The Seasonal Evolution of Reactive Chlorine in the Northern Hemisphere Stratosphere

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In situ measurements of chlorine monoxide (ClO) at mid- and high northern latitudes are reported for the period October 1991 to February 1992. As early as mid-December and throughout the winter, significant enhancements of this ozone-destroying radical were observed within the polar vortex shortly after temperatures dropped below 195 k. Decreases in ClO observed in February were consistent with the rapid formation of chlorine nitrate ($ClONO_2$) by recombination of ClO with nitrogen dioxide (NO_2) released photochemically from nitric acid (HNO_3). Outside the vortex, ClO abundances were higher than in previous years as a result of NO_x suppression by heterogeneous reactions on sulfate aerosols enhanced by the eruption of Mount Pinatubo.

Ozone destruction in the stratosphere by chlorine compounds occurs at a rate that is proportional to the abundance of ClO (*1*, *2*). Large enhancements of this reactive form of inorganic chlorine were observed in the Arctic polar vortex in the winter of 1989 during the first Airborne Arctic Stratospheric Expedition (AASE I), but, because the measurements were limited to a 6-week period, one much shorter than the life cycle of the vortex, the total amount of ozone destroyed by chlorine was unknown. In this report we present in situ observations of ClO taken from the NASA ER-2 high-altitude aircraft from October 1991 through February 1992 during AASE II. These results, which were obtained before the appearance of perturbed chemistry in the vortex and during recovery in springtime, illustrate the main features of the seasonal variation of ClO inside and outside the Arctic polar vortex and provide the basis for numerical estimates of ozone loss (*2*, *3*).

At mid-latitudes, below 20 km, ClO is normally present at abundances under 50 parts per trillion by volume (pptv) (*4*), representing less than 5% of the chlorine available (*5*). The relatively unreactive species HCl and $ClONO_2$ are the most abundant forms of inorganic chlorine and are produced by the reactions $ClO + NO \rightarrow Cl + NO_2$ followed by $Cl + CH_4 \rightarrow HCl + CH_3$, and the termolecular recombination reaction $ClO + NO_2 \rightarrow ClONO_2$. In daytime, photochemical production of ClO is limited by slow photolysis of $ClONO_2$, whereas at sunset ClO is tied up into $ClONO_2$ by a surplus of NO_2 present from photolysis of the more abundant NO_x-containing compounds HNO_3 and N_2O_5. Observations in October 1991 illustrate this normal photochemical exchange between ClO and NO_x in sunlight and between ClO and $ClONO_2$ in darkness (Fig. 1A). Within air masses that were ultimately entrained within the vortex ClO was present at less than 100 pptv. In sunlight, NO (and consequently NO_x) was in excess of ClO, such that the disappearance of ClO at latitudes poleward of 82°N was due to its recombination with NO_2 to form $ClONO_2$, because this region was in total darkness. The dominant forms of inorganic chlorine were HCl and $ClONO_2$ from 40°N to the pole before winter (*6*).

By 12 December (Fig. 1B), temperatures within the polar vortex had decreased below 195 K, the threshold for co-condensation of HNO_3 and water at 20 km (*3*). The abundance of ClO had risen abruptly in the vortex, while that of NO had dropped to near the detection threshold. On the basis of back trajectory analyses, the air masses with high ClO abundances had been below 195 K, whereas air masses that had remained above this temperature for the previous 2 weeks appeared "normal." Although NO_2 was not observed directly, had it been present to any great extent at the northernmost portion of the flight track ClO would have been nearly undetectable because photolysis of $ClONO_2$ is slow at these high solar zenith angles (*7*). Therefore, a significantly different type of chemistry, one dominated by reactive chlorine rather than by NO_x, occurred in the cold vortex air. As corroborated by observations of HCl loss, reactive chlorine formed at the expense of both HCl and $ClONO_2$ (*6*).

During January 1992, the abundance of

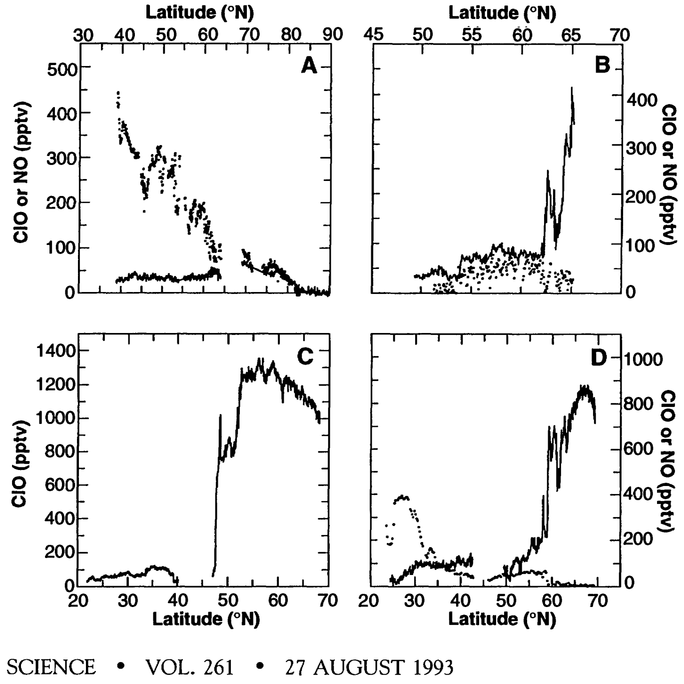

Fig. 1. Mixing ratios of ClO and NO (in parts per trillion by volume) plotted versus latitude for selected flights of the NASA ER-2 aircraft during the AASE II mission: (**A**) 12 and 14 October 1991; (**B**) 12 December 1991; (**C**) 12 and 20 January 1992; (**D**) 13 and 22 February 1992. For each panel ClO data are represented as a solid line and NO data as discrete points.

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