

In situ measurements of chlorine monoxide, bromine monoxide, and ozone were extrapolated globally, with the use of meteorological tracers, to infer the loss rates for ozone in the Arctic lower stratosphere during the Airborne Arctic Stratospheric Expedition II (AASE II) in the winter of 1991–1992. The analysis indicates removal of 15 to 20 percent of ambient ozone because of elevated concentrations of chlorine monoxide and bromine monoxide. Observations during AASE II define rates of removal of chlorine monoxide attributable to reaction with nitrogen dioxide (produced by photolysis of nitric acid) and to production of hydrochloric acid. Ozone loss ceased in March as concentrations of chlorine monoxide declined. Ozone losses could approach 50 percent if regeneration of nitrogen dioxide were inhibited by irreversible removal of nitrogen oxides (denitrification), as presently observed in the Antarctic, or without denitrification if inorganic chlorine concentrations were to double.

Loss rates for O₃ were estimated for the lower stratosphere during AASE II in 1991–1992. We computed distributions of reactive chlorine ([Cl*] ≡ [ClO] + 2 × ([ClO]₂)) and bromine ([Br*] ≡ [BrO] + [BrCl]) (where brackets denote concentration) along the flight track of the ER-2 airplane by assimilating in situ observations of ClO and BrO with a simple model. Relations between potential vorticity (PV) and potential temperature (Θ), meteorological tracers (1, 2), and Cl* and Br* were developed to compute O₃ loss rates for the north polar region, accounting for the influence of insulation, temperature, and pressure as air circulates around the polar vortex (3, 4). Seasonal changes observed for ClO (5), NO (6), HCl (7), and O₃ (8) were investigated with the use of a photochemical model constrained by meteorological observations (9) and measured surface areas for sulfate aerosol (10); factors regulating chemical removal of O₃ in the Arctic were examined with this model.

Reactions on the surfaces of polar stratospheric clouds (PSCs) (11), which are composed of condensed phases of H₂O and HNO₃ (12), catalyze the rapid conversion of HCl and ClONO₂ to labile species of inorganic chlorine in the polar vortex during winter (13, 14). Three catalytic cycles involving halogens account for ~95% of photochemical loss of O₃ in the vortex.

1) The self-reaction of ClO forming its dimer, (ClO)₂, followed by photolysis

\[ \text{ClO} + \text{ClO} + \text{M} \rightarrow (\text{ClO})₂ + \text{M} \] (1)

\[ (\text{ClO})₂ + hν \rightarrow \text{ClOO} + \text{Cl} \]

\[ \text{ClOO} \rightarrow \text{Cl} + \text{O}_2 \]

2(\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2) \]

Net: 2\text{O}_3 \rightarrow 3\text{O}_2

catalyzes the recombination of two \text{O}_3 molecules with the use of one photon (with energy hν) (15). Thermal decomposition of (ClO)₂, short-circuits this cycle, regenerating ClO without producing Cl atoms or recombing \text{O}_3.

2) The reaction of BrO and ClO and the photolysis of BrCl

\[ \text{BrO} + \text{ClO} \rightarrow \text{Cl} + \text{Br} + \text{O}_2 \] (2a)

\[ \rightarrow \text{Br} + \text{OCIO} \] (2b)

\[ \rightarrow \text{BrCl} + \text{O}_2 \] (2c)

\[ \text{BrCl} + hν \rightarrow \text{Br} + \text{Cl} \]

\[ \text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2 \]

\[ \text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \]

Net (2a, 2c): 2\text{O}_3 \rightarrow 3\text{O}_2

catalyzes recombinations of O₃ (13). Photolysis of OCIO produces O atoms; therefore, reaction 2b does not destroy O₃ (16).

3) The reaction sequence

\[ \text{BrO} + \text{ClO} \rightarrow \text{Cl} + \text{Br} + \text{O}_2 \] (2a)

\[ \rightarrow \text{Br} + \text{OCIO} \] (2b)

\[ \rightarrow \text{BrCl} + \text{O}_2 \] (2c)

\[ \text{BrCl} + hν \rightarrow \text{Br} + \text{Cl} \]

\[ \text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2 \]

\[ \text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \]

Net (2a, 2c): 2\text{O}_3 \rightarrow 3\text{O}_2

catalyzes recombinations of O₃ (13). Photolysis of OCIO produces O atoms; therefore, reaction 2b does not destroy O₃ (16).


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reaction. Removal rates attributable to reaction 1 decline at temperatures above 220 K, the fraction of (ClO)₂ is therefore not considered here. By column measurements of HOC₁ (I 9) and HO₂, which is very stable at low sun angle (< 80°) at 52°N, the descent and ascent in sunlight (solar angle < 80°) at 52°N, and NO₃, normally important at mid-latitudes, are negligible in the winter polar stratosphere (18). The catalytic cycle involving NOx, normally important at mid-latitudes, are negligible in the winter polar stratosphere (18). The catalytic cycle involving reaction of CIO with HO₂ represents less than 5% of the total loss of O₃ on the basis of calculated values for HO₂, corroborated by column measurements of HOCl (19) and is therefore not considered here.

The photochemical loss rate of ozone is

\[
\frac{d[O_3]}{dt} = -2[k_{CIO+ClO} + k_{ClO+HClO}] |ClO|^{2}
\]

where \( k \) is the rate coefficient for the specified reaction, M denotes an air molecule, and \( R \) is

\[
J(\text{ClO})_2|\text{ClO}_2| + k_{CIO+ClO} + k_{ClO+HClO}] |ClO|^{2}
\]

the fraction of (ClO₂) that photolyses, where \( J \) is the photolysis frequency for the specified reaction. Removal rates attributable to reaction 1 decline at temperatures above 220 K, where \( R \rightarrow 0 \) (20). Loss of O₃ requires sunlight to photolyze (ClO₂), BrCl (the nighttime reservoir for BrO), and O₃ (to generate O atoms).

Equation 4 allows us to compute instantaneous rates for O₃ loss along a flight track directly from measured radicals (5, 21), apart from \( R \) and \( [O] \), which are calculated with Eqs. 5 and 7 below. To determine global loss rates of O₃, we must infer radical concentrations throughout the polar vortex from observations along the flight track, and the loss rate must be integrated over 24 hours (3).

The diurnal variations of ClO, BrO, and O₃ are governed by

\[
\frac{d[ClO]}{dt} = J_{BCl}[ClO] - k_{BrO}[BrO][ClO] + k_{ClO+Cl}[O][ClO]
\]

\[
\frac{d[BrO]}{dt} = J_{BrCl}[BrCl] - k_{ClO+Cl}[ClO][BrCl]
\]

\[
\frac{d[O]}{dt} = J_{O}[O] - k_{ClO+Cl}[O][ClO] - k_{O+O}[O][ClO]
\]

Equation 5 balances production and loss of (ClO₂). Eq. 6 balances production and loss of BrCl, and Eq. 7 balances production of O₃ with recombination of ClO and O₃; each process has a relaxation time shorter than 1000 s. We determined the concentration of reactive chlorine corresponding to each measurement of ClO by matching observations to diurnal calculations with Eq. 5. Concentrations of BrO were about twice as high inside the vortex than outside, with little change during the winter; hence, a fixed relation was adopted between Br* and \( \Theta \) (22).

Concentrations of ClO began to increase dramatically in late December after concentrations of CIO peaked in late January and then declined slowly in February and March. On 20 January 1992, the ER-2 aircraft departed Bangor, Maine (44°47'N, 68°47'W), at 1500 GMT, flew north at -18-km altitude (\( \Theta = 460 \) K), and turned south to return at -19 km (\( \Theta = 490 \) K), with brief descents to 15 km at 65° and 52°N. Figure 1A shows data for ClO and HCl and inferred values of CI⁺ and total inorganic chlorine, CI⁻, computed from observations of N₂O and organochlorine gases (23). A steep decline in N₂O and an increase in CIO were observed just north of Bangor (Fig. 1A) at the edge of the polar vortex (PV = \( 2.1 \times 10⁻^5 \) K m² kg⁻¹ s⁻¹). Mixing ratios for ClO rose to 0.8 parts per billion by volume (ppbv) (1 ppbv = \( 10⁻^9 \) mole fraction in air) near the vortex edge, increasing to 1.2 to 1.4 ppbv further inside; less than 15% of CI⁺ was converted to CI⁺ outside the vortex, 60% near the edge, and 75 to 85% in the interior (24). Figure 1B shows loss rates of ozone along the flight track, computed by integrating Eq. 4 over 24 hours. Removal rates exceeded 1.4% per day: 50% attributed to reaction 1, 35% to 2, and 15% to 3.

Ozone loss rates in the polar vortex (Fig. 2) were uniform for 420 < \( \Theta < 500 \) K (16 to 20 km), declining at lower \( \Theta \). The mixing ratios of CIO, Cl⁺, CI⁻, and N₂O versus PV for \( \Theta = 470 \pm 10 \) K are shown in Fig. 3. Monotonic increases of the CI⁺ value on an isentropic (constant \( \Theta \)) surface were derived for 8 of the 10 flights in the polar vortex; similar values for CI⁻ were observed for a given PV on flights a few days apart. These results imply a heterogeneous distribution for CI⁺ in the polar vortex, extending over more than 4 km in the vertical and as far north as 70°N. Values of CI⁺ versus PV were similar in 1989 and 1992 (3).

We computed distributions of CI⁺ and daily loss rates for O₃ throughout the vortex using global meteorological fields for PV and the observed relation between CIقود and PV (4). Regions with elevated CI⁺ were exposed to sunlight in lobes of the vortex that extended to 45°N, one of which was sampled by the ER-2. The mean ozone loss rate for the vortex region (PV > \( 2.1 \times 10⁻^5 \) K m² kg⁻¹ s⁻¹) was 0.4% per day, notably lower than rates along the flight track (Fig. 1B). This difference illustrates the importance of assimilating aircraft observations in a tracer model account for distortion of the polar vortex from axial symmetry (2, 3). Ozone loss rates found here are similar to those inferred from...
measurements of CIO in the Arctic lower stratosphere made between 1 and 13 January 1992 by the Microwave Limb Sounder on the Upper Atmosphere Research Satellite (25).

After 1 February, minimum temperatures in the vortex exceeded the threshold for PSCs (5, 9), ending PSC processing. Little or no denitrification was observed (26), and CP and rates for ozone destruction began to decline (Fig. 5). The influence of illumination is evident in Fig. 5B. Loss rates were larger for given Cl* at lower latitudes (lower PV). However, elevated Cl* persisted longer at high latitudes, and O3 losses integrated over the winter were similar for a wide range of latitudes. About 0.7 part per million by volume (ppmv) (1 ppmv = \(10^{-9}\) mole fraction in air) of O3 (~15 to 20%) was removed by reactions 1 through 3 at \(\Theta = 470 \pm 10\) K in the Arctic polar vortex in 1991–1992, similar to losses for 1988–1989 (3, 27).

The ozone loss rates in Fig. 5B represent snapshots of an isentropic surface on which air parcels move adiabatically (28). Non-adiabatic processes, such as radiative cooling, can significantly modify PV and \(\Theta\) over time scales of a month, with changes in \(\Theta\) of about \(-70\) K over the winter (29). The seasonal integral at \(\Theta = 470\) K nevertheless may approximate net ozone removal at \(-18\) km because O3 loss rates are uniform in both vertical \((420 < \Theta < 500\) K) (Fig. 2) and horizontal (Fig. 5B) dimensions. Transport of O3 to \(\Theta = 470\) K during the winter makes it difficult to detect net chemical removal of 0.7 ppmv (8). Analysis of temporal variations of N2O and O3 suggest reduction of 15 to 20% of O3 at 17 km (8) and 10 to 15% between 10 and 12 km (30), consistent with chemical loss rates computed here.

Season-long observations during AASE II provide a unique opportunity to test ideas about the photochemical processes regulating radical concentrations in the polar vortex. We calculated production and loss of O3 and the evolution of CIO, HCl, NO, and HNO3 from 15 December 1991 to 30 March 1992 for a hypothetical air parcel at \(\Theta = 470\) K, 65°N (PV = \(2.8 \times 10^{-5}\) K m kg\(^{-1}\) s\(^{-1}\)), assumed to circulate around the vortex every 8 days, by solving time-dependent equations (31) with a comprehensive set of chemical reactants, reaction rates, and photolysis cross sections (20). Data from the ER-2 in December were adopted to define initial concentrations of total nitrogen oxides (NOy) (6), HCl (7), O3 (8), H2O, CH4, temperature (9), and the surface area of sulfate aerosols (10) on 15 December. Values of Cl were inferred from measured N2O (23, 26). The reaction efficiency for hydrolysis of N2O3 on surfaces of sulfate aerosols was assumed to be 0.10 (32).

Mean temperatures within the vortex (~210 K in January, ~230 K in March) were adopted from meteorological analyses for 1991–1992 (9). Temperatures below the PSC threshold were assumed to occur 1 day out of 8, from 9 to 25 January (9). Production of Cl* by reaction of HCl and ClNO3 on PSC surfaces was assumed to be rapid and stoichiometric (5, 7). Complete return of HNO3 to the gas phase was assumed upon PSC evaporation, consistent with observations for 1991–92 (26).

Calculated changes of CIO, HCl and NO (Table 1, case A) correspond closely to observations (Fig. 6), indicating accurate simulation of rates for key processes regulating ClO after the cessation of PSCs: photolysis of HNO3, which regenerates ClNO3, and reaction of Cl with CH4, which regenerates HCl. A study that included detailed air parcel trajectories to examine recovery from PSC processing reached similar conclusions (33). The integrated removal of O3 was ~19%, similar to empirical values from the ER-2 data discussed above.

What conditions would allow high concentrations of Cl* to persist into spring, as observed in the Antarctic (34)? If PSC processing persisted for another month, O3 losses would increase modestly (Table 1, case B): Photolysis of HNO3 accelerates rapidly as the season progresses, limiting

![Fig. 4. Distribution of the 24-hour mean loss rate for O3 (percent per day) in the north polar vortex for the 470 ± 10 K isentrope, derived with global fields of PV and the relation between Cl* and PV shown in Fig. 3, as described in the text. Contours of PV (in units of \(10^{-5}\) K m2 kg\(^{-1}\) s\(^{-1}\)) and the flight track of the ER-2 (black line, with circle denoting Bangor, Maine) are shown. Latitude circles 60° and 30°N and a map of the continents are denoted by green lines.](image)

![Fig. 5. (A) Calculated mixing ratio of Cl* (41) and (B) 24-hour mean loss rate for ozone on the \(\Theta = 470 \pm 10\) K isentropic surface, plotted as a function of PV and day of the year for the Arctic polar vortex in 1991–1992. Day 1 is 1 January 1992, and negative numbers refer to 1991.](image)

<table>
<thead>
<tr>
<th>Case</th>
<th>Model conditions</th>
<th>O3 removal* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>PSCs every 8 days until 25 January</td>
<td>19</td>
</tr>
<tr>
<td>B</td>
<td>PSCs every 8 days until 26 February</td>
<td>26</td>
</tr>
<tr>
<td>C</td>
<td>Case A plus 90% denitrification at first PSC event</td>
<td>44</td>
</tr>
<tr>
<td>D</td>
<td>Case A plus twice the present Cl*</td>
<td>48</td>
</tr>
</tbody>
</table>

*Stated relative to a model without PSCs (see Fig. 6).
loss of O₃ after each PSC encounter. Extremely cold temperatures throughout the vortex (<195 K) in March could produce larger losses of O₃ if HNO₃ were sequen-
teated in an aerosol phase. If HNO₃ were irreversibly removed by the sedimentation of PSCs (denitrification), Cl* would remain
elevated until equinox, and O₃ losses would increase significantly (31, 35) (Fig. 6 and Table 1, case C). Much of the Antar-
tic polar vortex is denitrified because of pervasively cold temperatures (36), but only sporadic denitrification has been ob-
erved in the Arctic (26, 36). Large-scale denitrification could occur in the Arctic if there were an anomalously cold winter or if ice cloud formation were enhanced by in-
creased concentrations of stratospheric H₂O. Cooling of the polar vortex could occur as a result of increasing CO₂ (37) or
decreasing concentrations of O₃ (38). Large ozone reductions would also be expected in the Arctic without denitrification if con-
centrations of inorganic chlorine were to double beyond present-day values (Table 1, case D). This scenario appears unlikely if present revisions (39) to the Montreal Pro-
ocol of 1987 (40) are effective in reducing inputs of chlorocarbons and bromocarbons to the atmosphere.

REFERENCES AND NOTES

1. Potential temperature, θ, is the temperature that an air parcel would reach if it were compressed adiabatically to 1000 mbar. Potential vorticity, PV, is a measure of the ratio of the absolute vorticity of a fluid layer to its depth [B. J. Hoskins, M. E. McIntyre, A. W. Robertson, Q. J. R. Meteorol. Soc. 111, 877 (1985)]. For the polar stratosphere, θ and PV are conserved typically over time scales of several weeks.


7. M. H. Proffit et al., ibid., p. 1150.

8. F. A. Newman et al., ibid., p. 1143.

9. J. C. Wilson et al., ibid., p. 1140.


11. M. H. Proffit et al., ibid., p. 1150.


20. M. H. Proffit et al., ibid., p. 1150.


22. J. C. Wilson et al., ibid., p. 1140.


26. Montreal Protocol on the Substances that Deplete the Ozone Layer and Amendments and Corrections Made Here to This Protocol.


