

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 insolation, 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.

Fig. 1. Observations and reconstructions for 20 January 1992. (A) Observed mixing ratios of ClO and HCl, inferred mixing ratios for Cl* and Cl₂, and (B) the 24-hour mean loss rates for ozone, computed using Eq. 4 and Cl* shown in (A). The total recombination rate and contributions from the ClO-ClO, BrO-ClO, and ClO-O₂ catalytic cycles (reactions 1, 2, and 3) are shown. All measurements taken along the ER-2 flight track, plotted against universal time (GMT). Corresponding latitudes are indicated at the top of the figure.

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

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

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

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

Net: 2O₃ → 3O₂
catalyzes the recombination of two O₃ molecules with the use of one photon (with energy hν) (15). Thermal decomposition of ClO, short-circuits this cycle, regenerating ClO without producing Cl atoms or recombing O₂.

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

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

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

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

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

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

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

Net (2a, 2c): 2O₃ → 3O₂
catalyzes recombinations of O₃, ClO, and HNO₃ (12), and also leads to decomposition of BrCl, as shown.

3) The reaction sequence

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

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

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

Net: 2O₃ → 3O₂

...

reaction, $M$ denotes an air molecule, and where $k$ is the rate coefficient for the specified reaction 1 decline at temperatures above 220 K, and $O_3$ (to generate O atoms).

Equation 4 allows us to compute instantaneous rates for $O_3$ 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 $O_3$, 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 $O_3$ are governed by

$$\frac{d[ClO]}{dt} = 2J(ClO)_1 + k(ClO)_1 R[M][ClO]^2 - 2ClO + O_3 + M[ClO]^2$$

$$\frac{d[BrO]}{dt} = J_{br}[BrCl] - k[ClO] + Br[BrO][ClO]$$


where $k$ is the rate coefficient for the specified reaction, $J$ denotes an air molecule, and $R$ is

$$J(ClO)_1, [ClO]^2$$

the fraction of ClO$_2$ 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 $R \to 0$ (20). Loss of $O_3$ requires sunlight to photolyze ClO$_2$, BrCl (the nighttime reservoir for BrO), and $O_3$.
measurements of ClO 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 Cl* 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). Nonadiabatic 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 ClO, HCl, NO, and BrO from 15 December 1991 to 30 March 1992 for a hypothetical air parcel at $\Theta = 470$ K, 65°N (PV $\approx 2.8 \times 10^{-8}$ K m^2 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 reactions, reaction rates, and photolysis cross sections (20). Data from the ER-2 in December were adopted to define initial concentrations of total nitrogen oxides (NOx) (6), HCl (7), O3 (8), H2O, CH4, temperature (9), and the surface area of sulfate aerosols (10) on 15 December. Values of ClI 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).

Meantempatures 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 ClI 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 ClO, 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: photochemical decomposition 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 ClI 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
loss of $O_3$, after each PSC encounter. Extremely cold temperatures throughout the
vortex (<195 K) in March could produce larger losses of $O_3$ if HNO$_3$ were seques-
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Fig. 6. Calculated seasonal evolution (day 1 corresponds to 1 January) of CIO, HCI, NO, and $O_3$ at noon for a hypothetical air parcel cir-
culating at 18 km altitude, 65° latitude, pro-
cessed periodically by PSCs as described in the

1. Potential temperature, $\Theta$, 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. J. Robertson, Q. R. Meteorol Soc 111, 877 (1985)]. For the polar stratosphere, $\Theta$
and PV are conserved typically over time scales of
several weeks.


4. A vortex circulation forms in the stratosphere over each pole in winter. Air cools radiatively and descends within the vortex, creating steep gradients for tracers across the vortex boundary (M Lowenstein, J. R. Prospero, K. R. Chan, S. E. Strahan, J. Geophys. Res. Lett. 17, 477 [1990]). Temperatures below the threshold for the formation of polar stratospheric clouds are pervasive in the Antarctic vortex and more localized in the

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REFERENCES AND NOTES

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following the first PSC event), and a parcel with no PSC processing are shown by the solid, dotted,
and dashed lines, respectively. Reductions in $O_3$
During March in the absence of PSC pro-
cessing occurs because of reactions involving
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deviation of observations for $\Theta = 470 \pm 30 K$
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