

Severe chemical ozone loss inside the Arctic polar vortex during winter 1999-2000 inferred from *in situ* airborne measurements

E. C. Richard^{1,2}, K. C. Aikin^{1,2}, A. E. Andrews³, B. C. Daube, Jr.³, C. Gerbig³, S. C. Wofsy³, P. A. Romashkin^{2,4}, D. F. Hurst^{2,4}, E. A. Ray^{2,4}, F. L. Moore^{2,4}, J. W. Elkins⁴, T. Deshler⁵, and G. C. Toon⁶

Abstract. Lower stratospheric *in situ* observations are used to quantify both the accumulated ozone loss and the ozone chemical loss rates in the Arctic polar vortex during the 1999-2000 winter. Multiple long-lived trace gas correlations are used to identify parcels in the inner Arctic vortex whose chemical loss rates are unaffected by extra-vortex intrusions. Ozone-tracer correlations are then used to calculate ozone chemical loss rates. During the late winter the ozone chemical loss rate is found to be -46 ± 6 (1σ) ppbv/day. By mid-March 2000, the accumulated ozone chemical loss is 58 ± 4 % in the lower stratosphere near 450 K potential temperature (~ 19 km altitude).

Introduction

Over the past decade, records of ozone observations in the northern polar region between February and April have shown variable decreases in lower stratospheric ozone [Newman *et al.*, 1997; WMO, 1999]. Like the large-scale ozone losses observed in the Antarctic [Farman *et al.*, 1985; Solomon *et al.*, 1986], these decreases have been directly linked to anthropogenic chlorofluorocarbons (CFCs) and halons. Ultimately, in polar regions in winter, heterogeneous chemical processing on polar stratospheric clouds (PSCs) liberates active chlorine that chemically destroys ozone through catalytic cycles [Solomon, 1999]. The magnitude and areal extent of the ozone loss in the Arctic vary considerably more from year-to-year than in the Antarctic, primarily a consequence of greater wintertime interannual variability of Arctic stratospheric temperatures [Zurek *et al.*, 1996; Manney *et al.*, 2000]. Due to higher temperatures resulting from fundamental dynamical differences between the hemispheres, the Arctic has not in general witnessed ozone depletion to the extent observed in the Antarctic.

For the 1999-2000 Arctic vortex, unusually low stratospheric temperatures persisted over a larger area and longer duration than ever recorded in the previous 21 years, thus setting the stage for potentially large areas of PSC activation [Manney *et al.*, 2000; Voigt *et al.*, 2000]. Because total organic chlorine plus bromine (CFCs + halons) is dropping at a very small rate in the atmosphere (less than 1 % per year) [Montzka *et al.*, 1999],

accurate ozone loss observations supported by precise model calculations are needed to follow the recovery of the ozone layer over the next half century.

Although progress has been made in recent attempts to model the observed chemical ozone loss in the Arctic polar vortex, substantial disagreements with observations remain. During the previous years with large springtime chemical loss, observed ozone depletion in the lower stratosphere is 30-40% greater than computed by some chemical model simulations [Deniel *et al.*, 1998; Becker *et al.*, 2000]. Major complications in quantifying chemical ozone loss in the Arctic polar vortex are associated with the difficulties in quantifying descent over the winter and/or estimating transport influencing the degree of vortex isolation [Chipperfield and Jones, 1999]. Here we make use of appropriate long-lived tracer relationships to accurately remove the effects of large-scale diabatic descent and differentiate between the influences of transport and chemistry on ozone losses within the 1999-2000 Arctic vortex. We are then able to quantify accurate ozone chemical loss rates during the late winter-early spring.

Observations and Results

The observational results presented here involve *in situ* O₃, N₂O, CCl₃F (CFC-11) and CO₂ measurements from the NASA ER-2 high-altitude aircraft [Proffitt and McLaughlin, 1983; Elkins *et al.*, 1996; Boering *et al.*, 1994] and measurements from the Observations of the Middle Stratosphere (OMS *in situ* and remote) [Ray *et al.*, 1999; Toon, 1991] and Halogen and Ozone (HALOZ) [Deshler *et al.*, 1990] balloon platforms. These measurements were obtained during the joint SAGE III Ozone Loss and Validation Experiment (SOLVE) and Third European Stratospheric Experiment on Ozone 2000 (THESEO 2000) campaigns based out of Kiruna and Esrange, Sweden (near 68°N, 20°E) between November 1999 and March 2000. ER-2 flights during SOLVE sampled deeper into the Arctic polar vortex than ever before and also traversed the vortex edge region, providing detailed, extensive coverage of the activated Arctic polar vortex from the exterior to the deep interior both before and after the onset of photochemical ozone loss.

Our chemical ozone loss analysis relies on referencing changing O₃ mixing ratios to two independent long-lived atmospheric trace gases (N₂O and CO₂). An empirically determined winter reference is established for each of these conserved tracers representative of the vortex O₃:N₂O and O₃:CO₂ mixing ratio relationships prior to the onset of ozone chemical loss. Figure 1 shows the evolution of the O₃:N₂O and O₃:CO₂ relationships derived from simultaneous measurements, representative of the 1999-2000 Arctic polar vortex. The profiles include measurements from the ER-2 aircraft, OMS-MkIV (19991203) and HALOZ (20000127) balloon platforms spanning a time period from early winter (December) to late winter (March) 2000. Ozone mixing ratio increases in altitude (θ), maximizing near 34 km (~ 850 K) at high latitudes during winter. Thus, in the absence of chemical loss, isolated descent resulting

¹NOAA Aeronomy Laboratory, Boulder, CO.

²Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder.

³Division of Applied Sciences and Department of Earth and Planetary Sciences, Harvard University, Cambridge MA.

⁴NOAA Climate Monitoring and Diagnostics Laboratory, Boulder, CO.

⁵Department of Atmospheric Sciences, University of Wyoming, Laramie, WY.

⁶Jet Propulsion Laboratory, Pasadena, CA.

Copyright 2001 by the American Geophysical Union.

Paper number 2001GL012878.
0094-8276/01/2001GL012878\$05.00

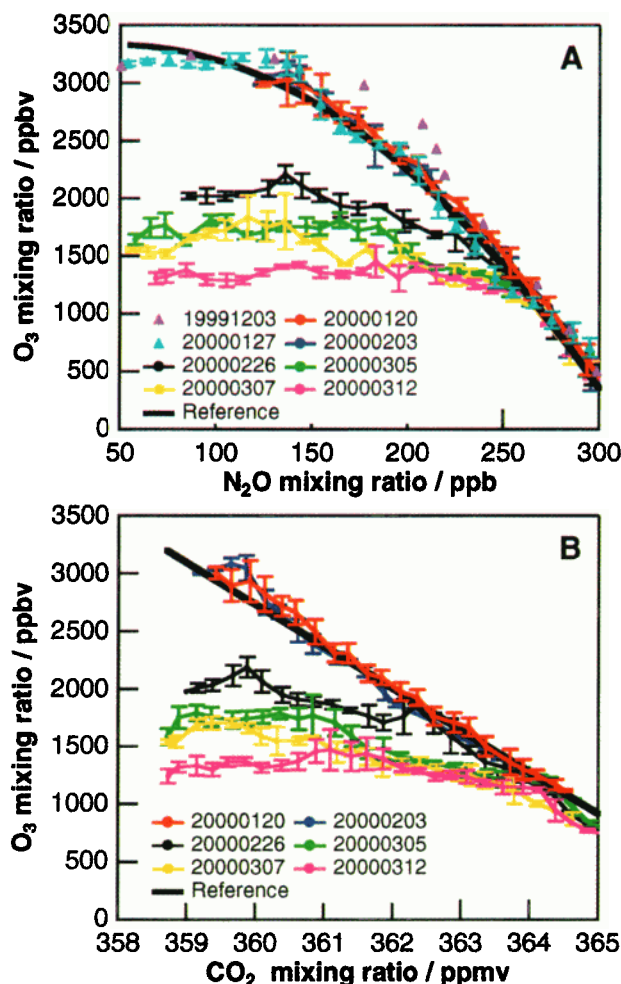


Figure 1. The evolution during the SOLVE campaign of (A) the vortex $O_3:N_2O$ relationship as measured from the ER-2 aircraft (dots) and balloon platforms (triangles) and (B) the vortex $O_3:CO_2$ relationship measured from the ER-2 aircraft (Color-coding represents flight date in YYYYMMDD format).

from diabatic cooling would increase O_3 mixing ratios at ER-2 sampling altitudes in the lower stratospheric vortex, but would not alter initial ozone-tracer relationships [Proffitt et al., 1993].

As can be seen there is relatively little change in the ER-2 $O_3:N_2O$ and $O_3:CO_2$ relationships over the two week period between 20 January and 3 February 2000. Additionally, the $O_3:N_2O$ profiles are found to be similar to the early winter vortex balloon profiles which allow extension of the relationships to regions above the ER-2 flight altitudes thus defining the chemical composition of air that later descends to ER-2 sampling altitudes (18–21 km). During this time period of polar night the inner, lower stratospheric Arctic vortex was predominantly in darkness. With the exception of regions near the vortex edge sampled by a few later flights during this phase, relatively small changes in the $O_3:N_2O$ and $O_3:CO_2$ relationships for the inner vortex were observed. Therefore, these relationships allow for the establishment of a winter vortex reference to quantify O_3 chemical loss occurring during late February/early March 2000. The reference curve for $O_3:N_2O$ was generated using all early phase ER-2 vortex flights and the HALOZ profile. A quadratic fit to this data yields the following: $O_3(\text{ppbv}) = 3227.6 + 4.378(N_2O) - 0.046(N_2O)^2$ ($50 \text{ ppb} \leq N_2O \leq 275 \text{ ppb}$). For the $O_3:CO_2$ reference a line was generated using all early phase ER-2 vortex flights: $O_3(\text{ppbv}) = 1.3303 \times 10^5 - 361.97(CO_2)$ ($358.6 \leq CO_2 \leq 365.0 \text{ ppmv}$).

While there is little change in the early winter to mid-winter ozone-tracer correlations dramatic decreases in ozone are observed in the late winter/early spring flights from 26 February through 12 March 2000, a time period during which the polar vortex received greater solar exposure. Figure 1 shows that in tracer-space these O_3 losses occur over a large range of N_2O and CO_2 mixing ratios, indicating substantial depletion over a broad altitude range (390–460K) within the 1999–2000 Arctic vortex during later winter/early spring.

Identifying the Effects of Mixing

There has been considerable debate recently regarding the use of ozone-tracer correlations to infer chemical ozone change [Plumb et al., 2000; Michelsen et al., 1998; Waugh et al., 1997]. A particular concern is whether such relations can be used to make quantitative estimates of chemical loss in the presence of transport. Several studies have found that ozone-tracer relationships can be changed significantly by transport events alone and have questioned their utility to make quantitative estimates of chemical ozone loss [Plumb et al., 2000; Michelsen et al., 1998]. Both vertical and horizontal mixing processes can modify the vortex correlations, independent of chemistry. Differential descent combined with horizontal mixing within the

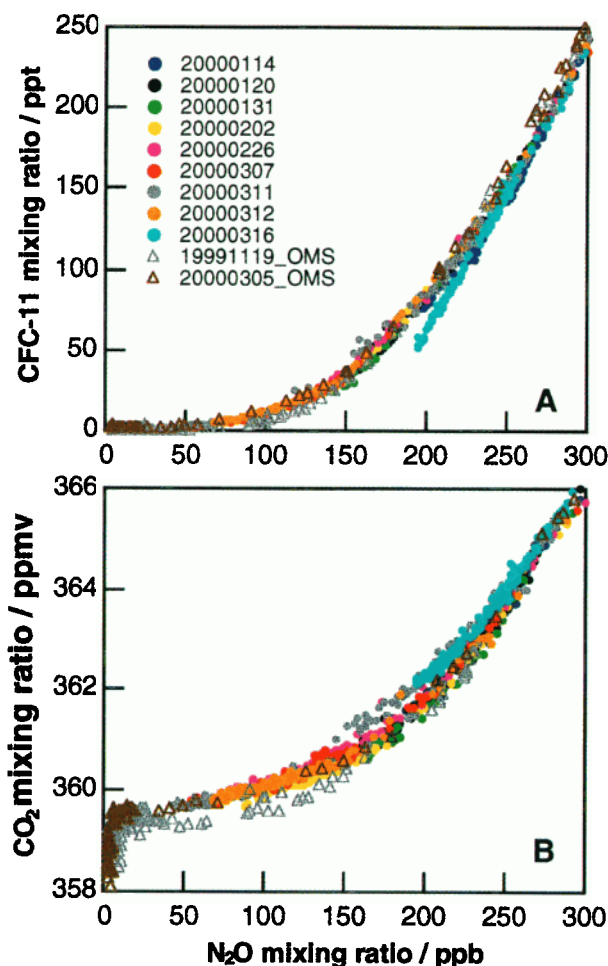


Figure 2. Tracer-tracer correlation plots for (A) CFC-11: N_2O and (B) $CO_2 : N_2O$ for selected ER-2 flights (dots) and the early and late winter OMS balloon profiles (triangles). In addition to ER-2 vortex flights, the ER-2 transit flights that sampled predominantly extra-vortex air on 14 January and 16 March 2000 are shown.

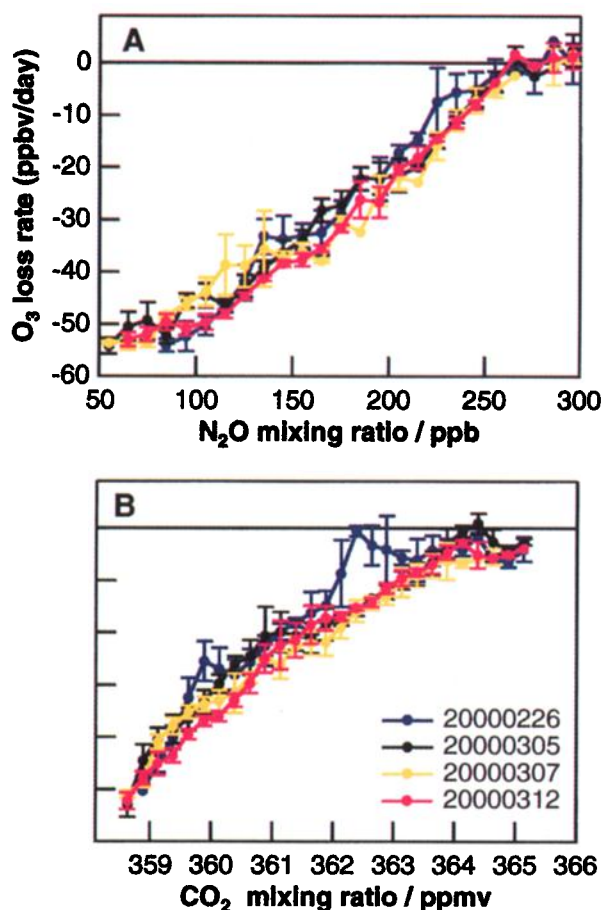


Figure 3. Calculated loss rates for (A) N_2O and (B) CO_2 for the four vortex flights following 3 February 2000 referenced to their respective winter reference relations shown in Figure 1. N_2O is binned by 10 ppb and CO_2 by 0.25 ppmv.

inner vortex can result in changing O_3 mixing ratios along a given isentrope. However, because of the near linear ozone-tracer relationships present, this will result in little change from the original inner vortex relationships. This is not the case, however, with mixing across the vortex edge that can change the vortex correlations significantly. By using at least two long-lived tracers correlated to each other as well as with respect to ozone we are able to identify and reject parcels which have been affected by horizontal mixing across the vortex edge. Therefore, we are able to address questions concerning how mid-latitude mixing of ozone into the vortex inhibits the quantitative estimates of chemical ozone loss inferred from such ozone-tracer correlation techniques. In quantifying chemical ozone loss from ozone-tracer relationships, we use long-lived tracer correlations to identify and eliminate transport-induced changes from the analysis. In this respect, our analysis differs from previous efforts quantifying chemical ozone loss in the polar vortex [Proffitt *et al.*, 1991, 1993; Müller *et al.*, 1997].

In order to differentiate between recent transport induced and chemical ozone change, we examine both the $\text{CFC-11: N}_2\text{O}$ and $\text{CO}_2\text{:N}_2\text{O}$ correlation plots for ER-2 vortex flights and both the early winter and late winter OMS profiles shown in Figure 2. Because they display distinct curvilinear relationships in tracer space, their tracer relationships can be used to identify mixing processes. The region of maximum curvature coincides with the spatial location of largest chemical ozone loss, providing a sensitive indicator for dynamical influence. We exploit the differences in the curvature of these tracer-tracer relationships.

For example, the $\text{CO}_2\text{: N}_2\text{O}$ correlation is sensitive to mixing from mid-latitude to the vortex edge, whereas the $\text{CFC-11: N}_2\text{O}$ displays curvature in a region most sensitive to mixing from the vortex edge to the inner vortex (where CFC-11 mixing ratios approach zero).

Of particular importance here are the 19 November 1999 OMS $\text{CFC-11: N}_2\text{O}$ and $\text{CO}_2\text{:N}_2\text{O}$ correlations that establish the initial vortex relationships. This balloon profile occurred during the early stages of the vortex and provides a unique opportunity to trace the vortex from its formation. For the later ER-2 flights, continuous descent and isentropic mixing in the vortex produces interior vortex relationships that are distinct from the early vortex relationships, but still compact and curvilinear and also differ significantly from the extra-vortex relationships (e.g. see 20000114 and 20000316 transit flights).

Throughout the January-March period, both the $\text{CFC-11: N}_2\text{O}$ and the $\text{CO}_2\text{:N}_2\text{O}$ correlations remain compact and curvilinear, and essentially invariant. Exceptions occur during the flights in the vicinity of the vortex edge where filaments are visible as deviations on the concave side (cf. Fig 2B). This is apparent on the flights of 26 February, 7 March 2000 and to a greater extent on 11 March 2000 for N_2O values of 150–250 ppb. The fact that few similar deviations occur for the inner vortex air ($\text{N}_2\text{O} < 150$ ppb) shows that in spite of recent mixing at the vortex edge, intrusions into the inner vortex were not significant during this time period. Where visible deviations in the tracer-tracer correlations appear, the data are excluded, thus restricting data used for a chemical loss calculation to regions unaffected by mid-latitude intrusions. Overall, a comparison between the *in situ* tracer correlations from all the ER-2 flights demonstrates that throughout the mid-winter to the late winter the lower stratospheric inner vortex was relatively well isolated from mid-latitude intrusions.

Ozone Loss Analysis

We focus now on chemical ozone loss occurring within the inner vortex. The calculations are restricted to regions where the $\text{CFC-11: N}_2\text{O}$ and $\text{CO}_2\text{:N}_2\text{O}$ correlations are compact and mid-latitude intrusions have been filtered out. We use both N_2O and CO_2 as dynamical tracers for referencing O_3 chemical rates of change over the late winter phase from 26 February through 12 March. Losses are referenced to 3 February 2000 using the winter vortex reference curve. As shown in Figure 1, the changes in O_3 between 20 January 2000 (day 20) and 3 February 2000 (day 34) were small and most likely a consequence of atmospheric variability rather than to photochemical loss processes. Overall, changes in O_3 in the inner vortex during this time of larval isolation are within $\pm 5\%$ of the early vortex reference. This can be seen in Figure 1, which shows the good agreement between the early vortex reference and the data from 3 February 2000 (the last ER-2 flight before the observation of substantial ozone loss).

Figure 3 shows the results of the calculated ozone loss per day relative to N_2O and CO_2 for the late winter. The calculations have been performed for each of the four vortex flights 26 February 2000 (day 57), 5 March 2000 (day 65), 7 March 2000 (day 67) and 12 March 2000 (day 72). For these calculations we have incorporated all theta levels between 390 K (bottom of ER-2 aircraft dive) to 450 K (typical ER-2 aircraft cruise altitude). The results show there is excellent consistency between the loss rates calculated for each flight with respect to both N_2O and CO_2 mixing ratio, independently. This indicates an approximate constant chemical loss rate for ozone resulting in a linear decrease of ozone over the two week period between late February and mid-March 2000 (day 57 through day 72).

Finally, we can use the tracer referenced results to generate the vertical distribution of the observed ozone loss rates over the ER-

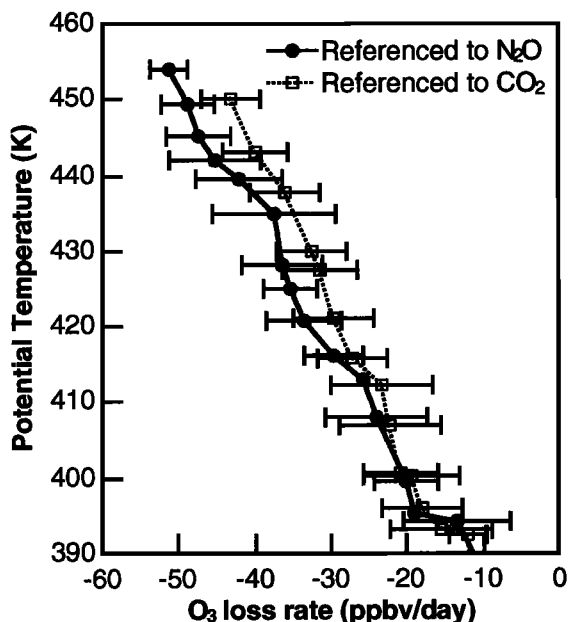


Figure 4. Potential temperature dependence of loss rates relative to N_2O (solid circles) and CO_2 (open squares). Error bars denote the 1σ error in propagating errors from the calculated average loss rates generated from Figure 3.

2 sampling altitudes. Figure 4 shows the vertical distribution of the observed loss rate generated by binning the N_2O and CO_2 mixing ratios into potential temperature intervals. Despite the large differences in the vertical gradients between N_2O and CO_2 mixing ratios, there is excellent agreement (within 1σ) between the calculated loss rate from each tracer over a large range of potential temperatures. The maximum observed chemical loss rate (relative to day 34) is -51 ± 3 ppbv/day with a tracer averaged maximum loss rate of -46 ± 6 ppbv/day at 450 K potential temperature (~ 19 km altitude). Over the 38 days of these measurements this represents an accumulated chemical ozone loss of $\sim 1.8 \pm 0.3$ ppmv ($\sim 58\%$) at 450 K potential temperature. While the last ER-2 vortex flight occurred on 12 March 2000, elevated ClO concentrations and a significant level of denitrification remained past this date resulting in continued ozone depletion. The results of ozone sonde observations at Ny-Ålesund, Spitsbergen (79°N , 12°E) between November 1999 and April 2000 show total ozone losses of ~ 2.5 ppmv ($\sim 70\%$) near 450 K by the end of March 2000 [Sinnhuber et al. 2000]. However, for late March/early April it is unclear from these sonde observations what contribution extra-vortex intrusions played in the observed ozone decreases.

Acknowledgments. We wish to acknowledge the contributions of the NASA ER-2 pilots J. Barrilleaux, J. Nystrom, and D. Porter and the tireless efforts of the NASA ER-2 crew during the SOLVE campaign. We thank A. Engel and U. Schmidt for providing us their TRIPLE O_3 and N_2O data and L. Lait and P. Newman for providing us their equivalent latitude data. We also wish to thank R. Müller and R. Salawitch for valuable comments and suggestions. This research is supported by the NASA Upper Atmosphere Research Program.

References

- Becker, G. et al., Ozone loss rates in the Arctic stratosphere in the winter 1991/92: Model calculations compared with Match results, *Geophys. Res. Lett.*, 25, 4325-4328, 1998.
- Boering, K. A. et al., Tracer-tracer relationships and lower stratospheric dynamics: CO_2 and N_2O correlations during SPADE, *Geophys. Res. Lett.*, 21, 2567-2570, 1994.
- Chipperfield, M. P. & Jones, R. L. Relative influences of atmospheric chemistry and transport on Arctic ozone trends, *Nature*, 400, 551-554, 1999.
- Deniel, C., Bevilacqua, R. M., Pommereau, J. P. & Lefèvre, F. Arctic chemical ozone depletion during the 1994-1995 winter deduced from POAM II satellite observations and the REPROBUS three-dimensional model, *J. Geophys. Res.*, 103, 19,231-19,244, 1998.
- Deshler, T., Hofmann, D. J., Hereford, J. V., and Sutter, C. B., Ozone and temperature profiles over McMurdo Station Antarctica in the spring of 1989, *Geophys. Res. Lett.*, 17, 151-154, 1990.
- Elkins, J. W. et al., Airborne gas chromatograph for in-situ measurements of long-lived species in the upper troposphere and lower stratosphere, *Geophys. Res. Lett.*, 23, 347-350, 1996.
- Farmen, J. C., Gardiner, B. G. & Shanklin, J. D., Large losses of total ozone in Antarctica reveal seasonal ClO_x/NO_x interaction, *Nature*, 315, 207-210, 1985.
- Manney, G. L. & Sabutis, J. L. Development of the polar vortex in the 1999-2000 Arctic winter stratosphere, *Geophys. Res. Lett.*, 27, 2589-2592, 2000.
- Michelsen, H. A., Manney, G. L., Gunson, M. R., Rinsland, C. P. & Zander, R., Correlations of stratospheric abundances of NO_y , O_3 , N_2O , and CH_4 derived from ATMOS measurements, *J. Geophys. Res.*, 103, 28,347-28,359, 1998.
- Montzka, S. A. et al., Present and future trends in the atmospheric burden of ozone-depleting halogens, *Nature* 398, 690-694, 1999.
- Müller, R. et al. Severe chemical ozone loss in the Arctic during the winter of 1995-96, *Nature* 389, 709-712, 1997.
- Newman, P. A., Gleason, J. F., McPeters, R. D. & Stolarski, R. S., Anomalous low ozone over the Arctic, *Geophys. Res. Lett.* 24, 2689-2692, 1997.
- Plumb, R. A., Waugh, D. W. & Chipperfield, M. P., The effects of mixing on tracer relationships in the polar vortices, *J. Geophys. Res.* 105, 10,047-10,062, 2000.
- Proffitt, M. H. & McLaughlin Fast-response dual-beam UV-absorption ozone photometer suitable for use in stratospheric balloons, *Rev. Sci. Instrum.*, 54, 1719-1728, 1983.
- Proffitt, M. H. et al., Ozone loss in the Arctic polar vortex inferred from high-altitude aircraft measurements, *Nature*, 347, 31-36, 1990.
- Proffitt, M. H. et al. Ozone loss inside the northern polar vortex during the 1991-1992 Winter, *Science*, 261, 1150-1154, 1993.
- Ray, E. A. et al., Transport into the Northern Hemisphere lowermost stratosphere revealed by in situ tracer measurements, *J. Geophys. Res.*, 104, 26565-26580, 1999.
- Scientific Assessment of Ozone Depletion: 1998 (Rep. 44, World Meteorological Organization, Geneva, 1999).
- Sinnhuber, B.-M., et al., Large loss of total ozone during the Arctic winter of 1999/2000, *Geophys. Res. Lett.*, 27, 3473-3476, 2000.
- Solomon, S., Garcia, R. R., Rowland, F. S. & Wuebbles, D. J., On the depletion of Antarctic ozone, *Nature*, 321, 755-758, 1986.
- Solomon, S. Stratospheric Ozone Depletion: A Review of Concepts and History, *Rev. Geophys.* 37, 275-316, 1999.
- Toon, G. C., The JPL MkIV Interferometer, *Optics and Photonics News* 2, 19-21, 1991.
- Voigt, C., et al., Nitric Acid Trihydrate (NAT) in polar stratospheric clouds, *Science*, 290, 1756-1758, 2000.
- Waugh, D. W. et al. Mixing of polar vortex air into middle latitudes as revealed by tracer-tracer correlations, *J. Geophys. Res.*, 102, 13,119-13,134, 1997.
- Zurek, R. W., Manney, G. L., Miller, A. J., Gelman, M. E., & Nagatani, R. M. Interannual variability of the north polar vortex in the lower stratosphere during the UARS mission, *Geophys. Res. Lett.* 23, 289-292, 1996.
- E. C. Richard and K. C. Aikin, NOAA Aeronomy Laboratory, Boulder, CO, and Cooperative Institute for Research in Environmental Sciences (CIRES), University of Colorado, Boulder.
- A. E. Andrews, B. C. Daube, Jr., C. Gerbig, and S. C. Wofsy, Division of Applied Sciences and Department of Earth and Planetary Sciences, Harvard University, Cambridge, MA.
- P. A. Romashkin, D. F. Hurst, E. A. Ray, F. L. Moore, and J. W. Elkins, NOAA Climate Monitoring and Diagnostics Laboratory, Boulder, CO, and Cooperative Institute for Research in Environmental Sciences (CIRES), University of Colorado, Boulder.
- T. Deshler, Department of Atmospheric Sciences, University of Wyoming, Laramie, WY.
- G. C. Toon, Jet Propulsion Laboratory, Pasadena, CA

(Received January 18, 2001; accepted March 22, 2001.)