

MLS observations of ClO and HNO₃ in the 1996–97 Arctic polar vortex

M. L. Santee, G. L. Manney, L. Froidevaux, R. W. Zurek, and J. W. Waters

Jet Propulsion Laboratory, California Institute of Technology, Pasadena

Abstract. Microwave Limb Sounder (MLS) measurements of lower stratospheric ClO and gas-phase HNO₃ are presented for the 1996–97 Arctic winter. The horizontal and vertical extent of enhanced ClO were smaller in 1997 than in 1996, as was the degree of enhancement. This is consistent with differences in the evolution and vertical structure of temperatures in the two years. Gas-phase HNO₃ abundances, which increased in early winter due to diabatic descent, exhibited a decreasing trend from mid to late winter in all six Arctic winters observed by MLS, probably due to increasing HNO₃ photolysis throughout this period.

Introduction

As pointed out by Zurek *et al.* [1996], the northern hemisphere (NH) winters since the launch of the Upper Atmosphere Research Satellite (UARS) have been characterized by lower temperatures and a stronger, more isolated vortex in the lower stratosphere – and thus conditions more conducive to chemical ozone depletion – than most of the NH winters dating back to 1978. This continued to be the case for the two most recent winters. In particular, the 1995–96 winter was the coldest and the most persistently cold [Manney *et al.*, 1996; Naujokat and Pawson, 1996]. Daily minimum temperatures inside the vortex on the 465 K potential temperature surface (~18 km, 50 hPa) were below 195 K (the approximate existence threshold for crystalline polar stratospheric clouds (PSCs)) continuously for 80 days and below 188 K (the nominal ice frost point for lower stratospheric conditions) for a total of 28 days. Low temperatures extended over a larger geographic area and up to higher altitudes than during any of the previous 17 NH winters [Manney *et al.*, 1996].

In Fig. 1 we compare the area within which United Kingdom Meteorological Office (UKMO) [Swinbank and O'Neill, 1994] temperatures were below 195 K during the winters of 1996–97 and 1995–96. The early onset and large areal extent of the lower stratospheric cold region in 1995–96 is evident. In contrast, the 1996–97 early-winter lower stratosphere was unusually warm, with temperatures at 465 K remaining above 195 K until early January, and was also distinguished by the weakest vortex in the past 18 NH winters [Coy *et al.*, 1997]. However, at levels near 600 K in mid-January the area of low temperatures in 1997 briefly approached that of 1996. In February the region of low temperatures covered a slightly smaller vertical range and a less extensive geographic area in 1997 than in 1996.

There have been other warm years with a small, weak vor-

tex in the lower stratosphere. What makes the 1996–97 NH winter remarkable is that 465 K minimum temperatures eventually dropped quite low (hovering just above 188 K from mid-February to early March) and then rose slowly, defining new record low values for late March [Coy *et al.*, 1997]. In fact, 465 K minimum temperatures continued to be less than 195 K approximately two weeks later than in 1995–96 (Fig. 1) and approximately one week later than in any of the previous 18 NH winters [cf. Zurek *et al.*, 1996]. Since crystalline PSCs would have endured as long as temperatures stayed below ~195 K, the later persistence of low temperatures in 1997 possibly prolonged heterogeneous processing into a period of greater exposure to sunlight than in previous years. In addition, the vortex remained substantially intact in the lower stratosphere into early May, exhibiting unprecedented longevity [Coy *et al.*, 1997; Manney *et al.*, 1997; Manney *et al.*, 1994].

The Microwave Limb Sounder (MLS) on UARS made measurements of O₃, ClO, and gas-phase HNO₃ in the Arctic on selected days in December 1996, late January and February 1997, and April 1997. In this paper we examine the MLS ClO and HNO₃ data in relation to chlorine activation and

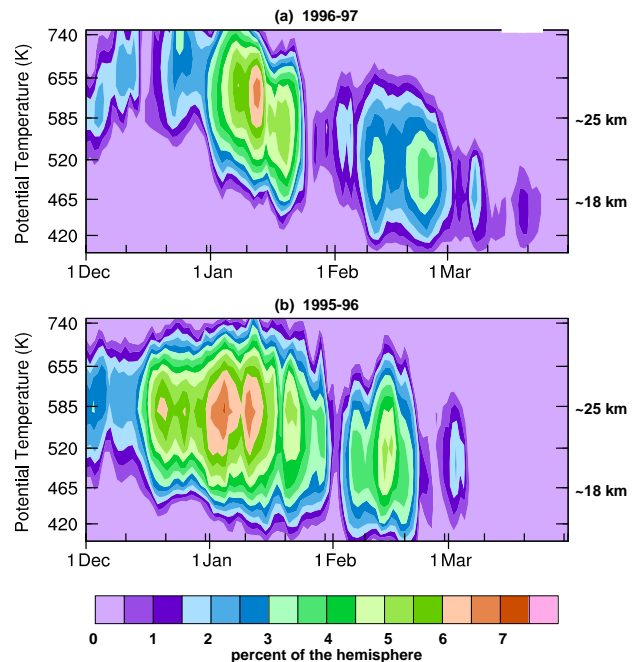


Figure 1. The area in percent of the hemisphere within which UKMO temperatures in the region poleward of 30°N were below 195 K, as a function of potential temperature (θ) and time for the Arctic winters of (a) 1996–97 and (b) 1995–96.

PSC formation under the unusual meteorological conditions during the 1996–97 NH winter, providing a context for the MLS observations of O₃ discussed by *Manney et al.* [1997].

Measurement Description

MLS Version 3 ClO data and validation are described by *Waters et al.* [1996]. Version 4 data are now available and are used here; some of the differences in Arctic ClO between Versions 3 and 4 are discussed by *Santee et al.* [1996] (hereafter S96). Version 4 ClO data have an estimated single-profile precision and accuracy of 0.4 ppbv and 10%, respectively, at 46 hPa. Gas-phase HNO₃ is also retrieved in Version 4. Preliminary validation studies indicate that MLS HNO₃ data are scientifically useful on the 100, 46, and 22 hPa retrieval surfaces, where the estimated single-profile precisions are approximately 2.0, 3.0, and 4.5 ppbv, respectively. MLS measurements of gas-phase HNO₃, and their correlation with low temperatures and PSC formation, are discussed for the 1995–96 Arctic winter by S96 and for the 1992–1996 Antarctic winters by *Santee et al.* [1997]. Averaging individual measurements reduces the noise contribution to the uncertainties; thus the vortex averages presented below have an estimated precision of ~ 0.03 ppbv for ClO and ~ 0.2 ppbv for HNO₃ at 465 K.

Analysis and Discussion

Maps of MLS ClO and gas-phase HNO₃ are presented in Figs. 2 and 3 for selected days during the 1996–97 Arctic winter. Daily MLS data were gridded and then vertically interpolated to the 465 K and 585 K isentropic surfaces using UKMO temperatures. A recent analysis of MLS 465 K gas-phase HNO₃ measurements obtained at the beginning of five southern hemisphere winters (1992–1996) indicates that most of the MLS data are consistent with the initial formation of liquid ternary solution PSCs as temperatures drop below ~ 192 K, followed by a gradual conversion to more stable crystalline forms after exposure to low temperatures for several days [*Santee et al.*, 1997]. Once crystalline PSCs form, they remain present at 465 K up to temperatures as high as 195 K [*Hanson and Mauersberger*, 1988]. Therefore we have overlaid on the 465 K HNO₃ maps the UKMO temperature contours of 195 K, 192 K, and 188 K. Contours of UKMO potential vorticity (PV) are also shown to indicate the extent and strength of the polar vortex.

In mid-December 1996 the lower stratospheric vortex was not yet well-developed [*Coy et al.*, 1997], and the high vortex HNO₃ and strong HNO₃ gradients across the vortex boundary that result from diabatic descent within a confined area were not yet apparent (Fig. 2). Since temperatures were still relatively high at this time the chlorine had not yet been activated, in contrast to the mid-December 1995 observations presented by S96. By 28 January, when MLS observations of the northern high latitudes resumed, 465 K temperatures had been below 195 K for 20 days and below 192 K for 12 days, facilitating the heterogeneous activation of chlorine on PSC particles [e.g., *Solomon*, 1990] as evidenced by the enhanced ClO in the sunlit portion of the vortex. ClO was also significantly enhanced at 585 K (Fig. 3), where temperatures had been very low throughout January. However, comparison with the 29 January 1996 map in S96 indicates that in 1997 the 465 K ClO abundances were smaller and the enhanced ClO filled less of the sunlit portion of the vortex than

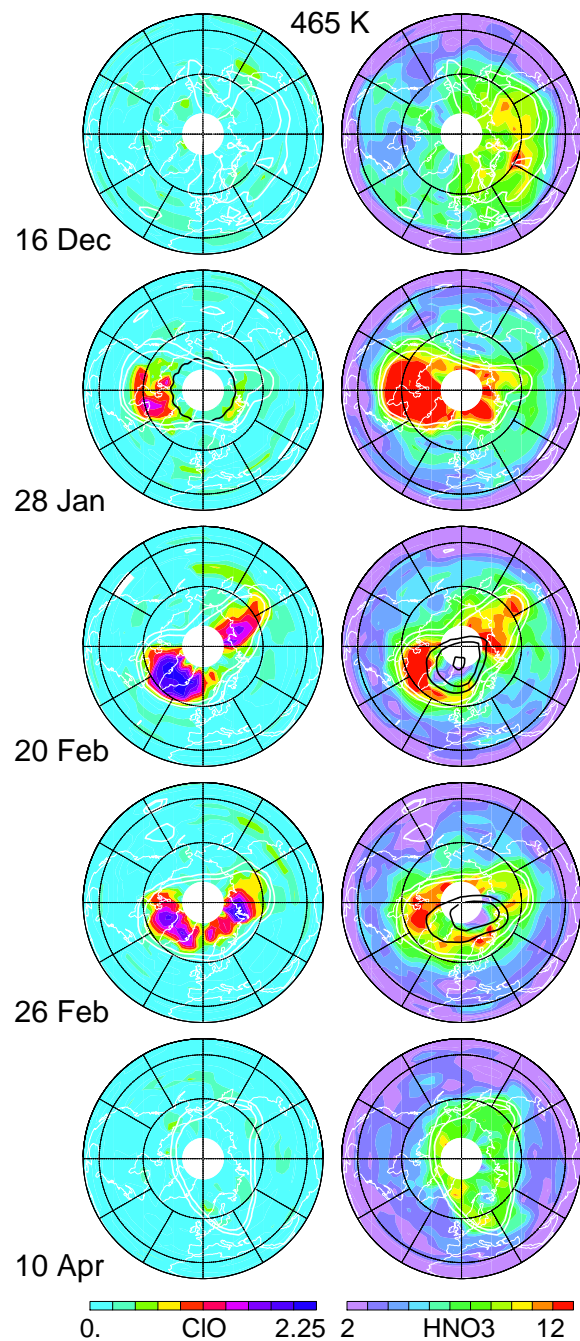


Figure 2. Maps of 465 K MLS ClO (left, ppbv) and HNO₃ (right, ppbv) for selected days during the 1996–97 Arctic winter. These are orthographic projections, with 0° longitude at the bottom and dashed black circles at 30°N and 60°N; blank spaces represent data gaps or bad data points. Only data from the “day” side of the orbit are shown for ClO; the thick black contour on the ClO maps denotes a solar zenith angle of 94°, which represents the approximate edge of daylight for the measurements. Superimposed in white are the 0.25×10^{-4} and $0.30 \times 10^{-4} \text{ Km}^2 \text{ kg}^{-1} \text{ s}^{-1}$ UKMO PV contours to indicate the approximate edge of the polar vortex and the steepness of the PV gradient. Superimposed in black on the HNO₃ maps are the 195, 192, and 188 K UKMO temperature contours to represent various PSC existence thresholds (see text).

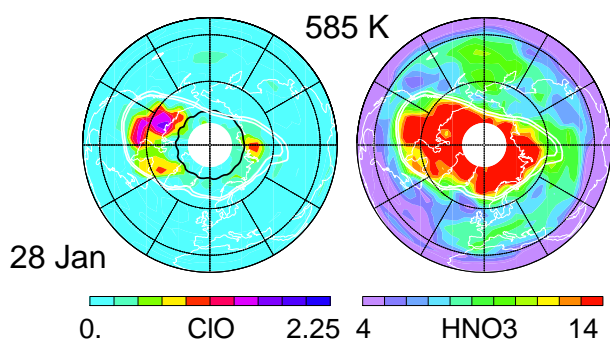


Figure 3. As in Fig. 2, for 585 K (with UKMO PV contours of 0.70×10^{-4} and $0.80 \times 10^{-4} \text{ K m}^2 \text{ kg}^{-1} \text{ s}^{-1}$).

in 1996. Uniformly high HNO₃ mixing ratios were observed inside the vortex on 28 January 1997, when UKMO minimum temperatures at 465 K briefly exceeded 195 K and any PSCs present would have evaporated. Low-HNO₃ regions in the 20 and 26 February 1997 maps are coincident with low-temperature regions; S96 showed that similar pockets of depleted gas-phase HNO₃ on 20 February and 3 March 1996 were caused by PSC formation. Whereas in 1996 the cold PSC-formation areas extended along the vortex edge [S96] where winds are strongest, in 1997 they were situated near the vortex center where winds are weak. The location of the cold regions away from the jet core may have caused less air to undergo chemical processing in 1997 than in 1996. Temperatures at 465 K rose above the existence threshold for crystalline PSCs in late March, halting further chlorine activation. By the beginning of the next north-viewing period on 10 April, chlorine abundances had dropped below the MLS detection limit.

Significant ClO enhancement extended over a larger vertical range in February 1996 than had been observed in previous NH winters [S96]. The vertical extent of enhanced ClO was somewhat smaller in February 1997 (Fig. 4), although the largest ClO values reached to lower altitudes. This is in keeping with the slightly smaller vertical extent of low temperatures in mid-February 1997 (Fig. 1). In addition, the enhanced ClO filled a smaller portion of the vortex throughout the lower stratosphere in 1997, consistent with the patterns in the 465 K maps discussed above.

Vortex averages (area-weighted averages within a PV contour representative of the vortex edge) of ClO at 465 K and 585 K are shown in Fig. 5 for the six NH winters observed by UARS. Vortex-averaged ClO in mid-February 1996 was the highest ever observed in the Arctic. In February 1997, vortex-averaged ClO was considerably lower at 585 K and slightly lower at 465 K than in 1996, consistent with the different shape and location of the low-temperature areas relative to the vortex in the two years as discussed above.

Fig. 5 also shows time series of vortex-averaged HNO₃. A general anticorrelation between vortex-averaged ClO and HNO₃ is evident during early and mid winter at both levels. Because the vortex typically dissipates in the lower stratosphere in late March or early April [Manney *et al.*, 1994], defining a vortex average for the previous years to compare to the mid-April 1997 values is problematic [Manney *et al.*, 1997]. However, in some years small remnants of high PV persisted after erosion of the main vortex. We included aver-

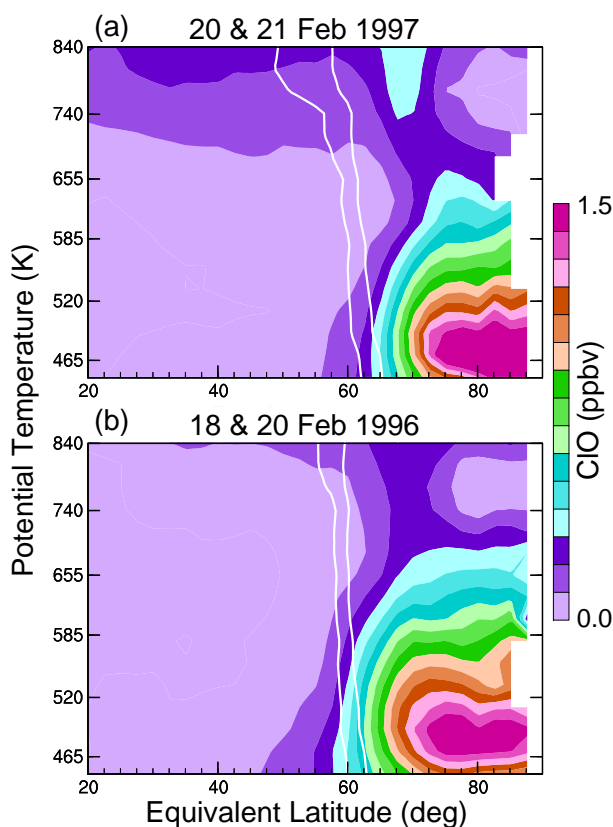


Figure 4. MLS ClO averaged over (a) 20 and 21 February 1997 and (b) 18 and 20 February 1996 (the two days in each year when MLS observed the highest 465 K ClO values), in PV/ θ space. PV is expressed as equivalent latitude (the latitude enclosing the same area as the PV contour). PV contours corresponding to those in Fig. 2 but scaled to give similar values throughout the θ domain are overlaid in white. The ClO values (except at the highest equivalent latitudes) are averages of ~ 20 – 40 points and thus have uncertainties less than ~ 0.1 ppbv.

ages within these regions in Fig. 5. At 585 K vortex-averaged HNO₃ exhibited an overall decreasing trend from early winter onward; at 465 K a similar decrease started somewhat later in most years. Since the gradual decline in HNO₃ occurred even in years with minimal PSC activity and continued well past the PSC season in every year, it is unlikely that denitrification was the main cause. Rather, the reduction probably resulted from increasing sunlight leading to greater HNO₃ photolysis, which in polar winter occurs on a timescale exceeding a month [Austin *et al.*, 1986]. This explanation is consistent with an increasing trend in vortex NO_x abundances measured by the UARS Halogen Occultation Experiment [Pierce *et al.*, 1997] in March 1997. For a more definitive answer, we plan to undertake detailed modeling of HNO₃ photochemistry and transport effects.

Acknowledgments. We thank the UKMO for meteorological data and our MLS colleagues for their many contributions. Work at the Jet Propulsion Laboratory, California Institute of Technology, was done under contract with the National Aeronautics and Space Administration.

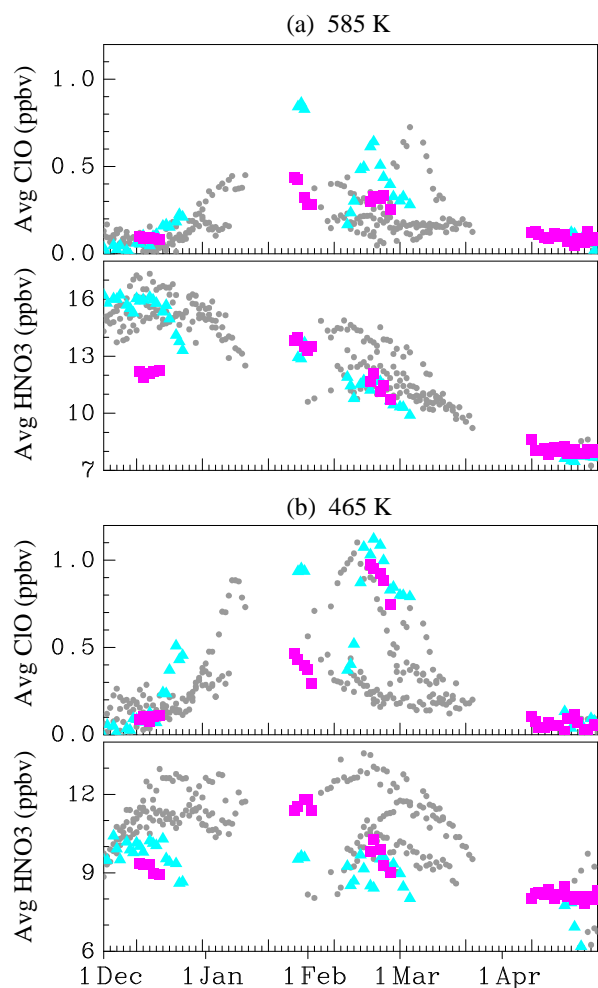


Figure 5. Time series of vortex-averaged ClO and HNO₃ at (a) 585 K and (b) 465 K for the 1995–96 (cyan triangles) and 1996–97 (magenta squares) winters. Values for the previous four NH winters observed by UARS are represented by gray circles; the ClO for each of these years is depicted in Santee *et al.* [1996]. Large data gaps in January/February and March/April each year correspond to periods when MLS was viewing southern high latitudes; smaller gaps represent times when the instrument was turned off. Low ClO values are recorded during a brief interval in the middle of every observing period when MLS measures in darkness.

References

- Austin, J., et al., On the atmospheric photochemistry of nitric acid, *J. Geophys. Res.*, *91*, 5477–5485, 1986.
- Coy, L., E. R. Nash, and P. A. Newman, Meteorology of the polar vortex: Spring 1997, *Geophys. Res. Lett.*, this issue, 1997.
- Hanson, D., and K. Mauersberger, Laboratory studies of the nitric acid trihydrate: Implications for the south polar stratosphere, *Geophys. Res. Lett.*, *15*, 855–858, 1988.
- Manney, G. L., et al., The anomalous Arctic lower stratospheric polar vortex of 1992–1993, *Geophys. Res. Lett.*, *21*, 2405–2408, 1994.
- Manney, G. L., et al., Polar vortex conditions during the 1995–96 Arctic winter: Meteorology and MLS ozone, *Geophys. Res. Lett.*, *23*, 3203–3206, 1996.
- Manney, G. L., et al., MLS observations of Arctic ozone loss in 1996–97, *Geophys. Res. Lett.*, this issue, 1997.
- Naujokat, B. and S. Pawson, The cold stratospheric winters 1994/1995 and 1995/1996, *Geophys. Res. Lett.*, *23*, 3703–3706, 1996.
- Pierce, B., et al., HALOE observations of the Arctic vortex during the 1997 spring, *Geophys. Res. Lett.*, this issue, 1997.
- Santee, M. L., et al., Polar vortex conditions during the 1995–96 Arctic winter: MLS ClO and HNO₃, *Geophys. Res. Lett.*, *23*, 3207–3210, 1996.
- Santee, M. L., et al., UARS MLS HNO₃ observations: Implications for Antarctic PSCs, Submitted to *J. Geophys. Res.*, 1997.
- Solomon, S., Progress towards a quantitative understanding of Antarctic ozone depletion, *Nature*, *347*, 347–354, 1990.
- Swinbank, R. and A. O’Neill, A stratosphere-troposphere data assimilation system, *Mon. Weather Rev.*, *122*, 686–702, 1994.
- Waters, J. W., et al., Validation of UARS Microwave Limb Sounder ClO measurements, *J. Geophys. Res.*, *101*, 10,091–10,127, 1996.
- Zurek, R. W., et al., Interannual variability of the north polar vortex in the lower stratosphere during the UARS mission, *Geophys. Res. Lett.*, *23*, 289–292, 1996.

L. Froidevaux, G. L. Manney, M. L. Santee (mls@praxis.jpl.nasa.gov), J. W. Waters, and R. W. Zurek, Jet Propulsion Laboratory, Mail Stop 183–701, 4800 Oak Grove Drive, Pasadena, CA 91109.

(Received May 9, 1997; revised August 8, 1997; accepted September 3, 1997.)