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

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Abstract

Microwave Limb Sounder (MLS) measurements of lower stratospheric ClO and gas-phase HNO₃ are presented for the 1996–97 Arctic winter. The magnitude and vertical extent of, and the portion of the lower stratospheric vortex filled by, enhanced ClO were smaller in 1997 than in 1996, 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.

uid 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 have formed, 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 HNO_3 maps the UKMO temperature contours of 195 K and 192 K, as well as 188 K (the approximate water ice frost point). Contours of PV derived from the UKMO analyses are also included to indicate the approximate 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 HNO_3 and strong HNO_3 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 vortex than in 1996. Uniformly high values of gas-phase HNO_3 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- HNO_3 regions in the 20 and 26 February 1997 maps are coincident with low-temperature regions; S96 showed that similar pockets of depleted gas-phase HNO_3 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 the winds are strongest, in 1997 they were situated near the vortex center. Thus less air may have undergone chemical processing in 1997 than in 1996. Temperatures at 465 K rose above the existence threshold for crystal line PSCs in late March, halting further chlorine activation. By the beginning of the next north-viewing period on 10 April, the chlorine was almost

completely deactivated.

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 proportion of the vortex throughout the lower stratosphere in 1997, consistent with the patterns in the 465 K maps discussed above.

Time series of vortex-averaged ClO at 465 K and 585 K are shown in Fig. 5 for all six NH winters observed by UARS to date. ClO enhancement in late December 1995 was greater than in any of the previous UARS years, especially at 465 K. Although no measurements were obtained in late December 1996, since temperatures were still relatively high, extensive chlorine activation was not expected. Vortex-averaged ClO in mid-February 1996 was about as high as ever observed in the Arctic; in February 1997 the vortex-averaged ClO was considerably lower at 585 K and slightly lower at 465 K, consistent with the different shape and location of the low-temperature areas relative to the vortex in the two years as discussed above. As seen in Fig. 2, the ClO was substantially deactivated by 10 April.

Fig. 5 also shows time series of vortex-averaged HNO_3 . A general anticorrelation between vortex-averaged ClO and HNO_3 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 higher PV persisted after the erosion of the main vortex. We have included averages within these regions in Fig. 5. At 585 K vortex-averaged HNO_3 exhibited a general decreasing trend throughout the winter; a similar decline at 465 K started in late February or early March in most years (see also Fig. 2). Since this gradual reduction in HNO_3 mixing ratios took place even in years when PSC activity was minimal and continued well past the time of ongoing PSC activity in every year, it is unlikely to have been caused by denitrification. Rather, it probably resulted from increasing amounts of sunlight leading to a greater degree of HNO_3 photolysis. This explanation is consistent with an increasing trend in NO_x abundances

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

Figure 2. Maps of 465 K MLS CIO (left, ppbv) and HNO₃ (right, ppbv) for selected days during the 1996-97 Arctic winter period. 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 CIO; the thick black contour on the CIO 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 represent the approximate edge of the winter polar vortex at this level and to indicate 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 thresholds for the existence of various types of PSCS (see text for details).

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

Figure 4. MLS CIO 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 CIO values), in PV/ θ space. PV is expressed as equivalent latitude (the latitude enclosing the same area as a given PV contour). Two PV contours, corresponding to the ones used to demark the vortex boundary in Fig. 2 but scaled to give similar values throughout the 0 domain, are overlaid in white.

Figure 5. Time series of area-weighted vortex averages of MLS CIO and gas-phase HNO₃ at (a) 585 K and (b) 465 K for the 1995-96 (cyan triangles) and 1996-97 (magenta squares) winters. Daily vortex averages for the previous four NH winters observed by UARS are represented by gray circles; specific results for CIO for each of these years are depicted in *Santee et al.* [1996]. Large data gaps in January/early February every year correspond to periods when MLS was viewing southern high latitudes; smaller gaps in some years represent times when the instrument was turned off. The low CIO values in February/March each year occur during a brief interval in the middle of every observing period when MLS is measuring in darkness.

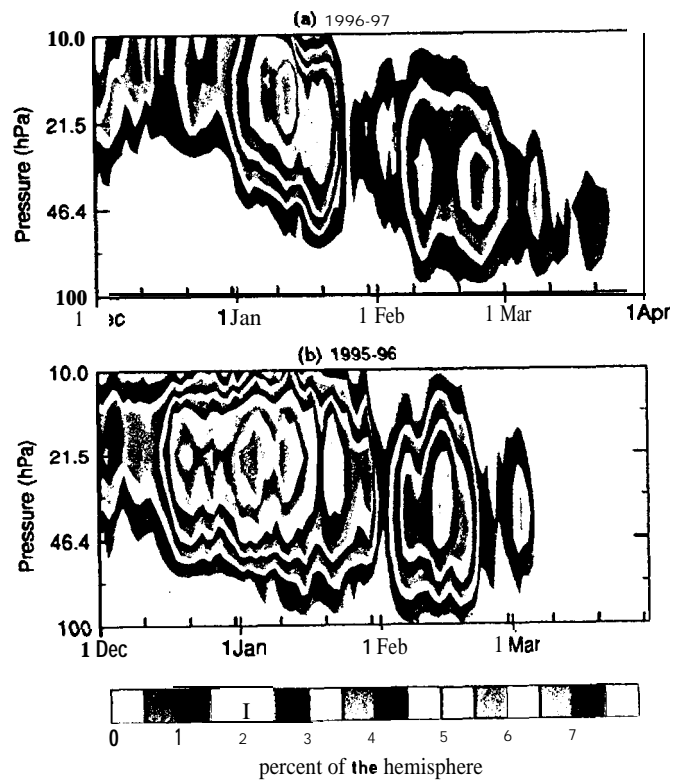


Figure 1

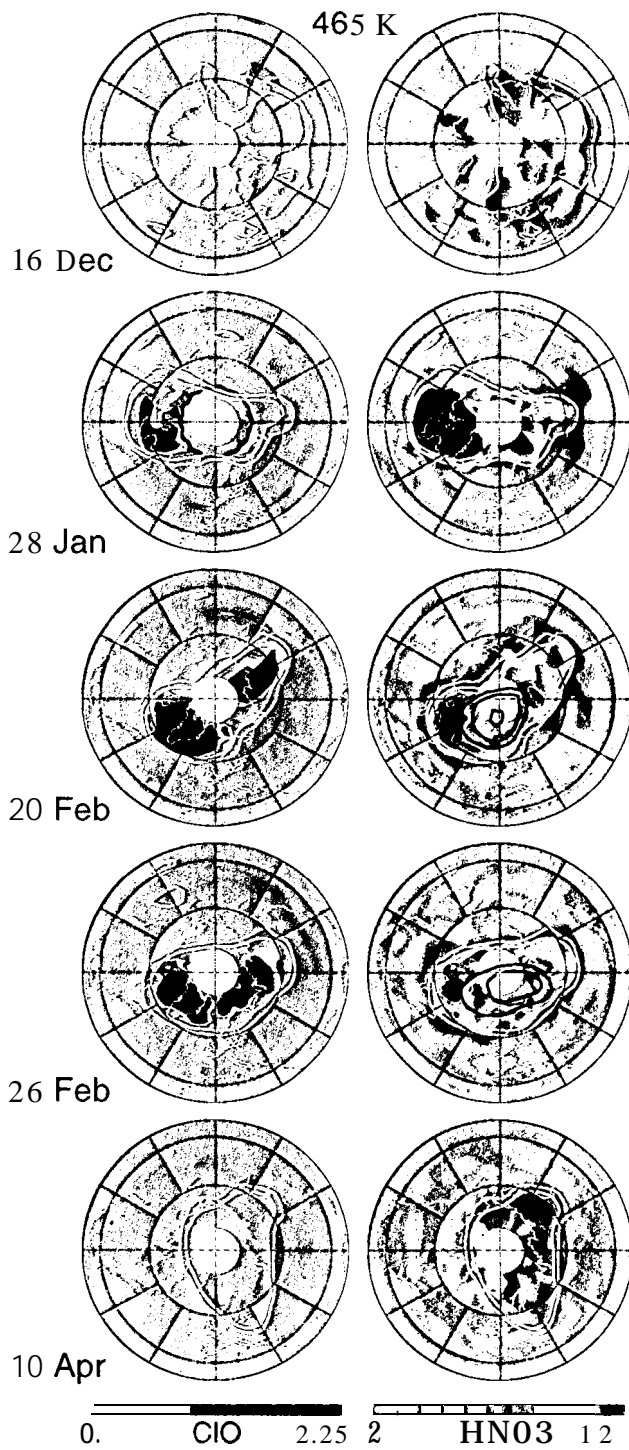


Figura 2

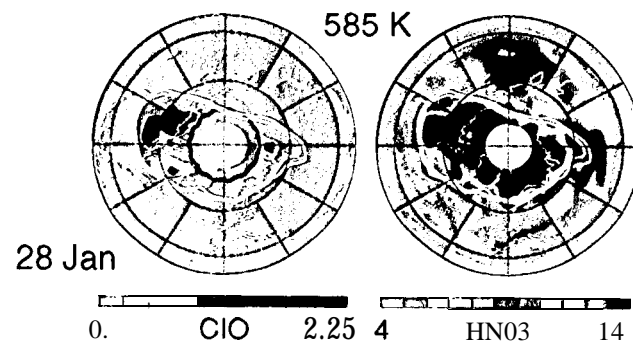


Figure 3

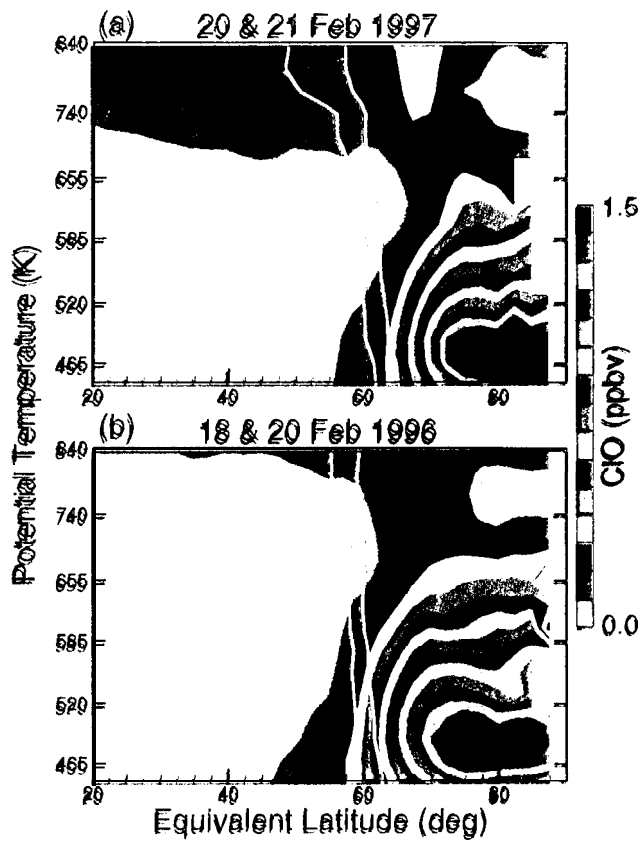


Figure 4

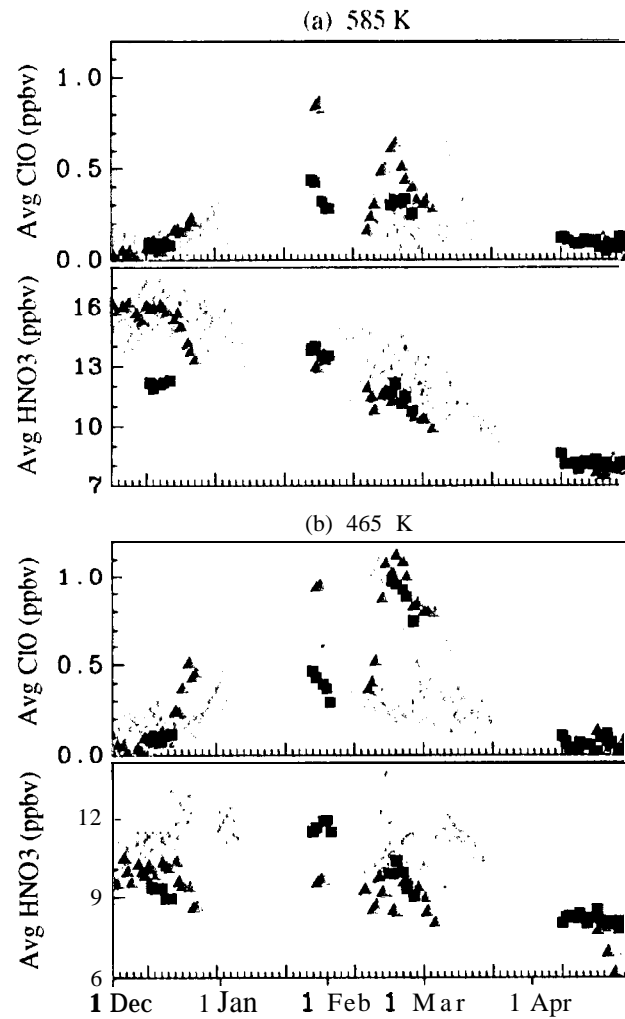


Figure 5