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Latitudinal distribution of upper stratospheric ClO as derived from space borne microwave spectroscopy

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Abstract. Latitudinal distributions of upper stratospheric ClO measured by MAS during the three ATLAS missions are presented for northern hemisphere (NH) spring equinox in 1992, southern hemisphere (SH) early fall in 1993, and NH fall in 1994. The MAS ClO results are shown along with correlative MLS observations. The results of both instruments consistently show the same latitudinal features. The ClO maximum in the NH spring occurs at mid latitudes, whereas the latitudinal ClO maximum in both the NH and SH fall occurs at high latitudes. The volume mixing ratio maxima were significantly higher in the fall (0.7–0.8 ppbv) than in spring (0.5–0.6 ppbv). Qualitatively, these results are consistent with calculations of several 2–D models.

Introduction

Chlorine monoxide (ClO) is the predominant form of reactive chlorine in the stratosphere. Knowledge of the stratospheric ClO distribution, and an understanding of its chemistry, are of great interest because ClO is a key constituent in ozone (O_3) depletion. The large springtime loss of lower stratospheric O_3 over Antarctica is largely driven by a chlorine catalytic cycle in which the formation of the ClO dimer (Cl_2O_2) is the rate limiting step [Molina and Molina, 1987]. The ClO abundance is also important in controlling the O_3 distribution in the upper stratosphere, where it participates in a catalytic cycle that destroys O_3 very effectively [Molina and Rowland, 1974].

Because of interest in the ozone hole and polar O_3 depletion in general, there has been a great deal published over the past few years about the distributions of enhanced ClO in the lower stratosphere during photochemically perturbed conditions. These studies have used ground–based [e.g. de Zafra et al., 1989], air–borne in–situ [e.g. Anderson et al., 1991], or space–based [e.g. Santee et al., 1995] measurements. However, less has been published [e.g. Crewell et al., 1995] on the latitudinal distribution of ClO in the upper stratosphere. Uncertainties regarding Cly partitioning [Michelsen et al., this issue] can be addressed by such upper stratospheric observational studies in conjunction with HCl and CH_4 measurements [Solomon and Garcia, 1984].

In this paper we present measurements of the vertical and latitudinal distribution of ClO measured by the Millimeter–wave Atmospheric Sounder (MAS) [Croskey et al., 1992], with special emphasis on the ClO abundance in the upper stratosphere in the vicinity of the mixing ratio peak. MAS is part of the NASA Atmospheric Laboratory for Application and Science (ATLAS) spacelab shuttle mission. Stratospheric ClO measurements obtained from 24 March–2 April 1992 (ATLAS 1), from 8–17 April 1993 (ATLAS 2), and from 3–4 November 1994 (ATLAS 3) are presented along with correlative observations from the Microwave Limb Sounder (MLS).

MAS ClO Observations and Analysis

The signal strength of the upper stratospheric ClO emission line at 204 GHz is very weak and provides double side band (DSB) brightness temperature amplitudes of the order of only 0.5 K for limb sounding observations. To reduce the effect of measurement noise on the retrieved ClO profiles, extensive radiance averaging of about 1000 s per retrieval were performed [Aellig et al., 1993]. ClO also exhibits a distinct diurnal variation, which is especially pronounced at pressures higher than about 5 mb where virtually all ClO reacts with NO_2 to form $ClONO_2$ at night [Ko and Sze, 1984]. Therefore, only daytime ClO spectra with solar hour angles (SHA) between -60^0 and $+60^0$ were used for the ClO retrievals.

The measured radiances were first binned in latitude bands of ten degrees on a pressure grid between 80 and 1 mb, using 30 grid points vertically spaced at approximately 1 km. (Pressure was provided by simultaneous measurements of O_2 lines near 60 GHz [Langen et al., 1994].) These spectra are affected by blending of lines from other species, which increases with pressure. In the ATLAS 1 and 2 measurements, there are also persistent instrumental baseline artifacts over the entire pressure range. (The long term baseline stability, how-

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ever, was for all missions generally less than 0.05 K, which is approximately 10 % of the DSB amplitude.) Therefore, in order to minimize retrieval error resulting from the atmospheric and instrumental baseline, in the ATLAS 1 and 2 retrievals, nighttime (11 p.m.– 4 a.m.) measurements (binned on the same pressure grid) have been subtracted from the daytime spectra over the entire pressure range. Prior to ATLAS 3, the ClO receiver was replaced, significantly reducing the instrumental baseline compared to that obtained in the two previous missions. Therefore, in the ATLAS 3 retrievals, the day–night spectral subtraction was performed only at pressures higher than 5 mb. The approach used in the ATLAS 3 retrievals is appropriate, and causes little retrieval bias because there is virtually no ClO at pressures higher than 5 mb at night, according to theory [Ko and Sze, 1984]. Above 5 mb, however, nighttime ClO becomes increasingly abundant. Therefore, the day–night subtraction does produce a significant retrieval bias in the ATLAS 1 and 2 retrievals above 5 mb. This bias is constant with latitude for each mission because the same night spectra were used for all latitudes. ClO mixing ratios were retrieved from these averaged and differenced spectra on six layers, each of a thickness of about 6 km, using an optimal estimation approach described in Aellig et al. [1993]. To account for the bias in the ATLAS 1 and 2 retrievals introduced by the difference of day and night spectra, estimated ClO night profiles were then added to the ATLAS 1 and 2 retrievals. Using correlative Atmospheric Trace Molecule Spectroscopy (ATMOS) experiment measurements [Gunson et al., this issue] as constraints, ClO night time estimates were derived from 1–dimensional photochemical model calculations.

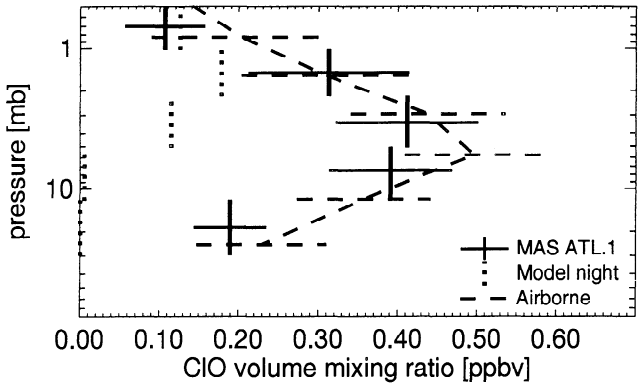

Figure 1. Comparison of MAS and correlative airborne ClO observations. The MAS measurements are zonal means between 25 and 35 N, averaged between 24 March and 2 April 1992. The model night profile was already added to the MAS retrievals to obtain the values shown. The airborne measurements were obtained on a flight from the Azores (39 N) over Teneriffe (28 N) to Lisbon (39 N) on 29 March 1992. The range of solar hour angle is 32^0 to 42^0 for MAS and -30^0 to 105^0 for the aircraft observations. Discrepancies in the results due to unequal diurnal sampling are believed to be 10 % or less between 20 and 1 mb.

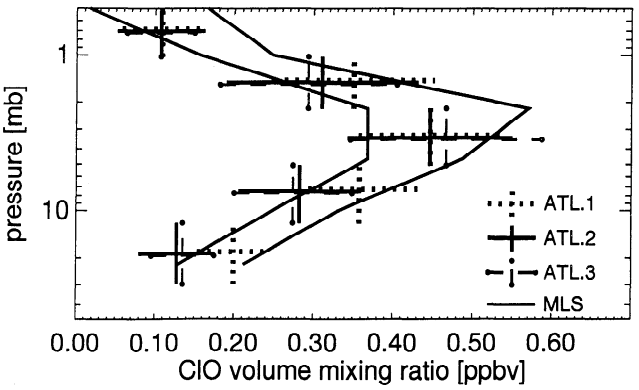

Figure 2. Comparison of MAS and MLS ClO version 3 (scaled by 0.92, see text) measurements. The MAS measurements are zonal averages for ATLAS 1 (20–40 N), ATLAS 2 (20–40 S), and ATLAS 3 (25–35 N). MLS results represent the range of ClO monthly means averaged between 20 and 40 N [Waters et al., 1996].

Validation of MAS Observations

As a part of the MAS validation campaign, correlative airborne measurements of ClO at 649 GHz were performed during ATLAS 1 by the Max Planck Institute for Aeronomy and by the University of Bremen. A description of the sub-mm instrument used and the results of earlier measurements can be found in Wehr et al. [1995]. A comparison of MAS and airborne ClO profiles obtained at similar latitudes is shown in Figure 1. The two profiles are in good agreement within the error bars (1σ), which represent the total retrieval errors. The estimated retrieval precision of MAS ClO is of the order of 0.05 parts per billion by volume (ppbv) at the ClO vmr peak, which is significantly better than the total retrieval error.

Comparisons of MAS ClO with MLS ClO version 3 climatology were also performed. (An error in the data processing caused the MLS ClO version 3 retrievals to be too large by 8%. Thus, these retrievals need to be multiplied by 0.92 to correct for this systematic error. This correction was made for all MLS ClO version 3 data shown in this Letter. The estimated MLS ClO version 3 bias uncertainties are 0.15–0.2 ppbv (2σ) and the estimated scaling error is 15–20 % (2σ). See Waters et al. [1996] for validation of the MLS ClO version 3 data.) As pointed out by Waters et al. [1996], zonal averages in the region between 20 N and 40 N are meaningful for comparisons because the seasonal variation is small in this latitude band. We therefore compared MAS data averaged on the same or on similar latitude bands with MLS monthly means. It can be seen in Figure 2 that the MAS ClO measurements for all missions are generally within the range of the MLS measurements.

ClO Latitudinal Distributions

Figure 3 is a contour plot of northern hemisphere ClO zonal mean volume mixing ratios (vmr) measured by MAS (a) along with MLS (b) results, both taken within

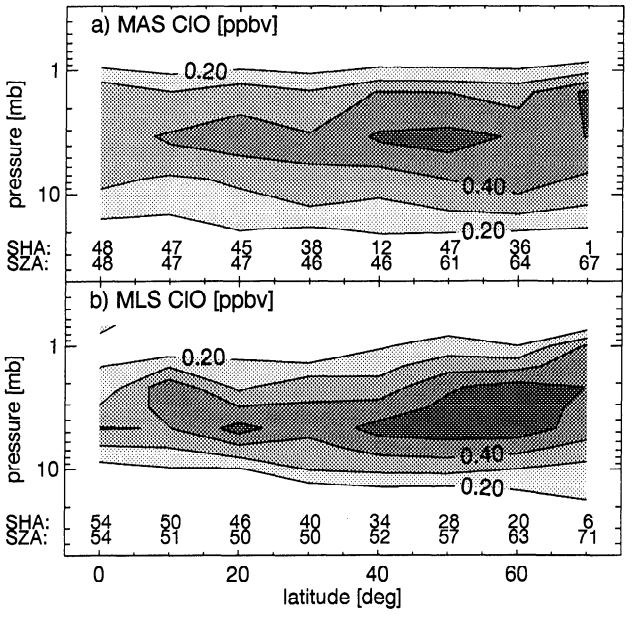

Figure 3. a) MAS ATLAS 1 ClO distributions in ppbv measured between 24 March and 2 April 1992. b) MLS daytime ClO version 3 (scaled by 0.92, see text) in ppbv taken between 16 and 19 March 1992. Only MLS data with `DATA_QUALITY_UARS=0.4`, `DATA_QUALITY_PI=0.4`, and positive data quality numbers were used. Contour levels are 0.1 ppbv, which is about twice the retrieval precision (1σ) of the MAS and MLS results shown. Average solar hour angle (SHA) and solar zenith angle (SZA) in degrees are indicated as a function of latitude for both MAS and MLS.

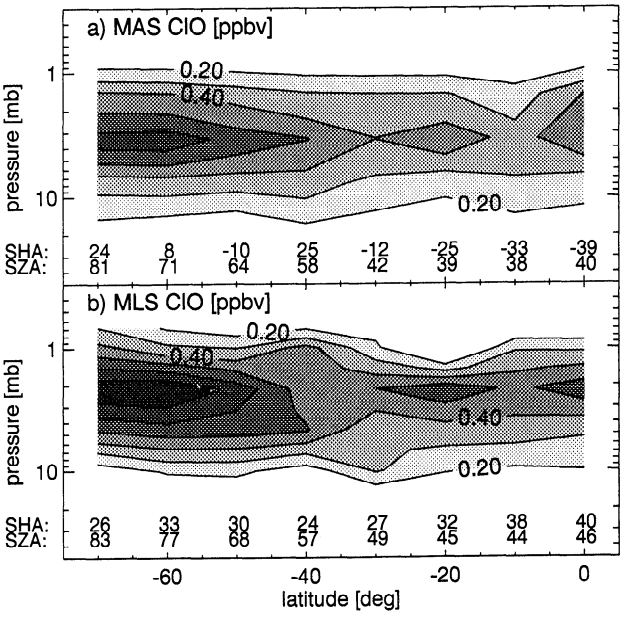

Figure 4. Similar to Figure 3, but for ATLAS 2 (13–15 April 1993). MLS measurements were taken between 10 and 22 April 1993.

ten days of spring equinox in 1992. MLS data shown in this and the following figures were obtained from the Distributed Active Archive Center (DAAC). Single daytime profiles (SHA: -45^0 to $+60^0$) were binned into 10^0 latitude zones. SHA and SZA (solar zenith angle) for both MAS and MLS measurements are also indicated in Figure 3. The SHA shows that MAS and MLS measurements were taken in similar diurnal periods over the entire latitude region. Therefore, no substantial discrepancies due to unequal diurnal sampling are expected. In fact, diurnal model results have shown that the discrepancies in the ClO observations due to unequal diurnal sampling of MAS and MLS are 5% or less for all observation periods near the ClO peak at 2–4 mb. A latitudinal gradient of 0.1–0.2 parts per billion by volume (ppbv) in the ClO distribution between the tropics and northern mid latitudes is evident in both the MAS and MLS measurements in NH spring. MLS clearly observed a ClO vmr maximum at higher mid latitudes. MAS also observed a ClO vmr maximum at mid latitudes, and also high vmr at high latitudes. The difference in the peak ClO vmr measured by MAS and MLS is less than 0.1 ppbv, well within the combined error bars. In Figure 4, ClO zonal mean vmr measured by MAS and MLS in mid April 1993 between 70 S and the equator are displayed. These are fall results taken roughly three weeks after equinox. These southern fall observations show a distinct ClO vmr maximum at high latitudes, unlike the northern spring observations displayed in Figure 3. For both the MAS and the MLS measurements, the magnitude of the maximum is higher than that of the mid latitude maximum measured in the spring by about 0.1–0.3 ppbv. In fact, the latitudinal gradients observed with the two instruments are remarkably consistent. In both measurements, a distinct ClO gradient of 0.2–0.3 ppbv occurs between mid and high latitudes, but no significant gradient is evident between low and mid latitudes. While the MAS and MLS latitudinal gradients and the approximate gradients of

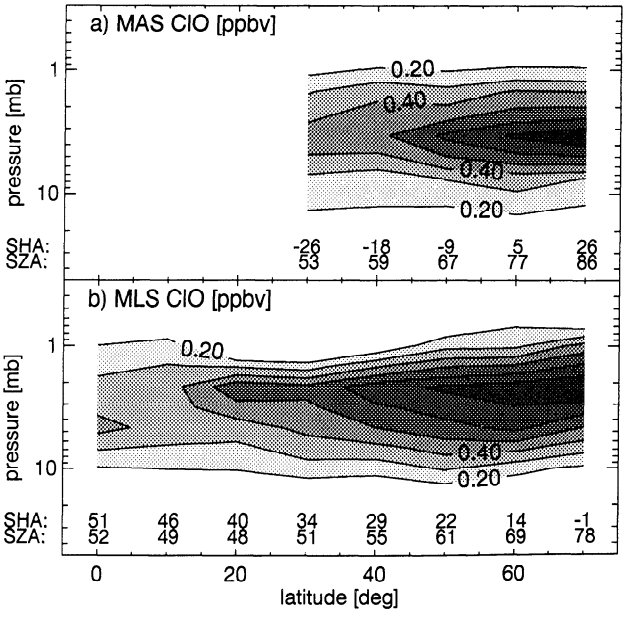

Figure 5. Similar to Figure 3 and 4, but for ATLAS 3 (3–4 November 1994). MLS measurements were taken between 12 and 23 October 1994.

the peak mixing ratios are consistent, the MAS/MLS comparison indicates that the altitude of the mixing ratio peak measured by MAS is lower (3–4 mb) than measured by MLS (2–3 mb). Figure 5 displays the northern ClO latitudinal distribution measured in early November 1994 by MAS, and in mid October 1994 by MLS. These are also fall measurements taken 6 weeks (MAS) and 3–4 weeks (MLS) after equinox. The MAS measurements cover only the region between 30 and 70 N, because of the short measurement period during ATLAS 3. These northern fall measurements show similar features to those observed in the southern hemisphere fall results displayed in Figure 4. Maximum ClO mixing ratios of 0.7–0.8 ppbv occur at high latitudes. The altitude of the mixing ratio peak measured by MAS is somewhat lower than measured by MLS, similar to the southern fall results shown in Figure 4a and 4b.

Model calculations of the latitudinal distribution of ClO in the stratosphere for solstice conditions have been presented and discussed by Solomon and Garcia [1984]. Their model results indicate a mid–latitude maximum in winter, and a high latitude maximum in summer. The increase of ClO from the equator to higher latitudes obtained in the model calculations for both seasons is explained mainly by the decrease of CH_4 towards high latitudes. The reaction $CH_4 + Cl \rightarrow HCl + CH_3$ converts reactive chlorine ($Cl + ClO = Cl_x$) into the inert HCl. In the winter polar region, however, the reduced conversion of Cl_x into HCl is expected to be balanced by the slow production of Cl_x from all chlorine reservoir gases (HCl, $ClONO_2$, and HOCl), resulting from the lack of sunlight.

A compilation of 2–dimensional model calculations of the stratospheric ClO distribution was published by Jackman et al. [1989]. The March results of several models feature the ClO maxima at mid latitudes in the NH and at high latitudes in the SH, similar to the March/April measurements in 1992 and 1993. The AER and GSFC2 model results in Jackman et al. in particular exhibit higher ClO distributions in the SH fall than in the NH spring, in agreement with the MAS and MLS measurements. For a more quantitative data–model comparison, up–to–date stratospheric chlorine loading and chlorine chemistry need to be applied.

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