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Validation of stratospheric ClO measurements from the Millimeter-wave Atmospheric Sounder (MAS)

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Abstract. During three missions in 1992, 1993, and 1994, the Millimeter-wave Atmospheric Sounder (MAS) measured volume mixing ratio profiles of stratospheric chlorine monoxide (ClO) at 204 GHz from the space shuttle. Owing to the space shuttle orbit, measurements were restricted to tropical and midlatitudes. We compared zonal mean profiles to correlative ClO measurements by an airborne 649 GHz radiometer, a ground-based 278 GHz instrument on Mauna Kea, Hawaii, and Version 4 ClO profiles by the Microwave Limb Sounder (MLS) on the Upper Atmosphere Research Satellite (UARS). The agreement between MAS and all the other instruments was well within the combined error bars over a pressure range of 0.4–40 hPa. Further comparisons of MAS and MLS day-night difference profiles produced an agreement of typically better than 0.1 ppbv. A detailed analysis proved that this agreement was independent of the a priori information that was used for the retrieval of the different data sets.

1. Introduction

Chlorine monoxide (ClO) is a very important trace gas because it is the key species in the catalytic destruction of stratospheric ozone [*Anderson et al.*, 1989] by anthropogenic chlorine compounds [*Molina and Rowland*, 1974]. However, ClO is difficult to measure, and most available data sets are sparse either in temporal or spacial coverage. ClO measurements have typically been made in situ (e.g., by *Anderson et al.* [1977], *Brune et al.* [1988], *Avallone et al.* [1993a], and *Toohey et al.* [1993]) or with remote sensing techniques from the ground (e.g., by *Parrish et al.* [1988]), from aircraft (e.g., by *Wehr et al.* [1995]), from balloons (e.g., by *Stachnik et al.* [1992]), and from space (e.g., by *Waters et al.* [1993] and *Aellig et al.* [1996]). Most observations were made in the Arctic [*de Zafra et al.*, 1994; *Crewell et al.*, 1994; *Raffalski et al.*, 1998; *Ruhnke et al.*, 1999] or Antarctic [*de Zafra et al.*, 1995; *Shindell and de Zafra*, 1996; *Klein et al.*, 1996] because of the heterogeneous chemistry that takes place at high latitudes. Observations at tropical or midlatitudes [*Carli et al.*, 1988; *Avallone et al.*, 1993b; *Gerber and Kämpfer*, 1994; *Ricaud et al.*, 1997] are sparse. Global or near global measurements of ClO exist only from the Microwave Limb Sounder (MLS) [*Barath et al.*, 1993] and the Millimeter-wave Atmospheric Sounder (MAS) [*Croskey et al.*, 1992].

MAS is a limb-scanning radiometer that measured microwave spectra of atmospheric constituents from the space shuttle during the ATLAS 1 (March/April 1992), ATLAS 2 (April 1993), and ATLAS 3 (November 1994) missions [*Hartmann et al.*, 1996]. From the measurements, latitudinal distributions of stratospheric ClO [*Aellig et al.*, 1996], as well as stratospheric and mesospheric profiles of O_3 and H_2O have been derived [*Bevilacqua et al.*, 1996; *Daehler et al.*, 1998]. It should be pointed out that the MAS observations did not aim at the high latitudes. The mission goals for MAS, first near-global measurements of O_3, H_2O, and ClO as well as pressure and temperature especially in the upper atmosphere, had already been defined [*Schanda et al.*, 1986] when the severe ozone loss in the Antarctic vortex was first discovered by *Farman et al.* [1985]. At that time, only the homogenuous chemistry processes involving ClO, which were expected to be most effective in the upper stratosphere, were known.

In this article, we attempt to validate the MAS ClO observations by comparing them to ClO measurements from airborne and ground-based instruments and, in particular, Version 4 ClO profiles from MLS. These comparisons do not cover the high latitudes because the space shuttle orbit did not allow ClO measurements beyond 70° latitude. This study is a continuation of an earlier attempt to validate the MAS ClO data product [*Feist et al.*, 1998]. The major improvements are the use of MLS Version 4 instead of Version 3 as the reference data set, improved consideration of different vertical resolutions, and the elimination of systematic errors by comparing day-night-difference profiles.

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2. MAS ClO Observations and Analysis

MAS observed emission lines of stratospheric ClO at 204.352 GHz. To reduce noise in the spectra of these very weak transitions, we applied extensive radiance averaging over time and latitude. For the retrievals the radiances of an entire mission were averaged over latitude bands of 10°. The typical integration time for each latitude and altitude binned spectrum was in the range of 200–1000 s. These zonal mean spectra were used in this study.

The MAS profiles that were retrieved from these spectra represent mean volume mixing ratios (vmr) of ClO in vertical layers of a thickness of about 6 km. The error bars represent the total estimated retrieval error. They include statistical as well as systematic components. The measurement and retrieval method for MAS ClO as well as a detailed error analysis for limb-sounding instruments have been published earlier by *Aellig et al.* [1996, 1993].

The MAS ClO spectra for ATLAS 1 and 2 suffered from strong baseline artifacts. It was necessary to subtract a night spectrum from the measured day spectra to eliminate these artifacts. The night spectrum was an average spectrum of all night measurements from 45°S to 45°N over the entire mission. The retrievals were then performed on the resulting day-night difference spectra. This approach caused only little bias at low altitudes (pressures above 5 hPa) because according to *Ko and Sze* [1984] there is virtually no nighttime ClO at these altitudes in the latitude range observed by MAS. At higher altitudes a bias is introduced from residual nighttime ClO. To account for this bias, model night profiles, which are shown in Figure 1, were added to the retrieved profiles. Different night profiles were used for ATLAS 1 and 2, but the same night profile was used for the retrieval at all latitudes. *Aellig et al.* [1996] describe this process in greater detail.

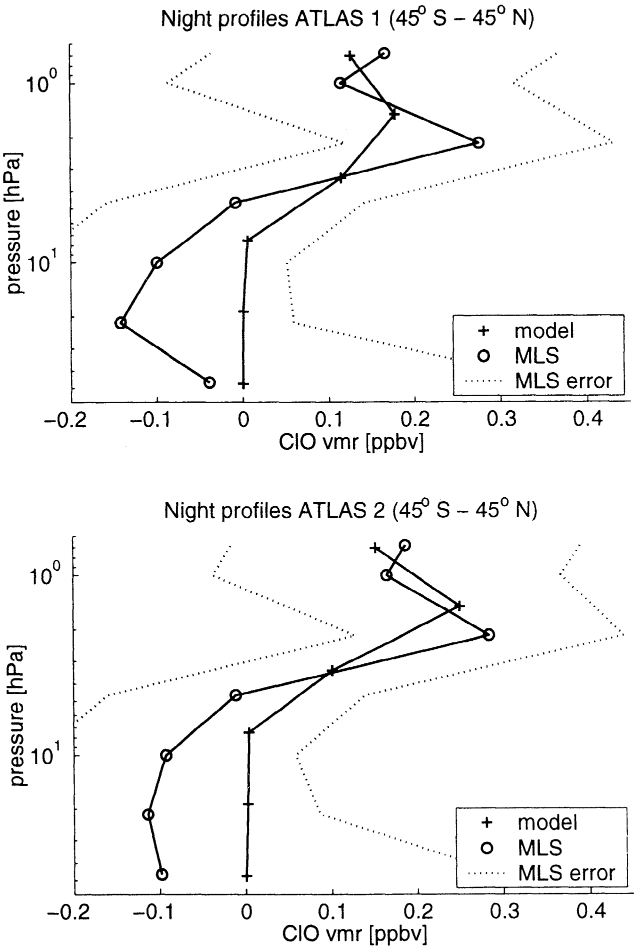

Figure 1. Comparison of model night profiles used for ATLAS 1 (March 24 – April 2, 1992) and ATLAS 2 (April 8–17, 1993) with nighttime Version 4 L3AT profiles measured by MLS. The MLS data are zonal means over 45°S to 45°N, averaged from March 14–23, 1992 for ATLAS 1 and April 6–15, 1993 for ATLAS 2. Several thousand MLS profiles were averaged for this plot.

Table 1. Time and Latitude Ranges Covered by the Data Sets Used for Comparison

Instrument	Time	Latitude
MAS ATLAS 1	March 24 to April 2, 1992	0°–70°N
UARS-MLS 1992	March 14 to 23, 1992	30°S–80°N
Mauna Kea 1992	March 21 to 31, 1992	20°N
Airborne	March 29, 1992	28°–38°N
MAS ATLAS 2	April 8 to 17, 1993	0°–70°S
UARS-MLS 1993	April 6 to 15, 1993	80°S–10°N
MAS ATLAS 3	Nov. 3 to 4, 1994	30°N–70°S
UARS-MLS 1994	Nov. 15 to 29, 1994	80°S–60°N
Mauna Kea 1994	Nov. 24 to Oct. 20, 1994	20°N

The space shuttle orbit with a typical flight altitude of 300 km and an inclination in the range of 57° limited the MAS observations to an effective latitude range of 72°S to 72°N. Because of the Sun-synchronous orbit, the majority of daytime measurements took place on one hemisphere, while most of the nighttime measurements were made on the other hemisphere. This separation of daytime and nighttime measurements to different hemispheres increased with latitude. Most daytime measurements were made on the northern hemisphere during the ATLAS 1 and 3 missions and on the southern hemisphere during ATLAS 2.

MAS was not able to observe ClO in the Arctic or Antarctic vortex like MLS [*Santee et al.*, 1996] because it was looking at the autumn hemisphere during ATLAS 2 and 3 (see Table 1). During ATLAS 1 (northern hemisphere spring), only a few measurements were made at high latitudes. If enhanced ClO were observed during this mission, its impact on the zonal mean profile would be expected to be very small, since the vortex should only occasionally reach below 70°N and chlorine activation in the northern hemisphere would not have been as strong as in the antarctic vortex in 1992. Note that the day-night differencing discussed above should not have taken out the effects of enhanced ClO since the night spectra were all taken from low latitudes where no chlorine activation could be expected at any time.

3. Available ClO Data Sets

During the ATLAS missions, only very few measurements of stratospheric ClO took place in the latitude range observed by MAS. However, measurements were available from the ground, from an airborne instrument, and from space. All of these measurements relied on microwave remote sensing techniques. Table 1 provides an overview of the temporal and latitudinal coverage of these measurements.

3.1. Ground-Based Measurements of ClO From Mauna Kea, Hawaii, at 278 GHz

The State University of New York at Stony Brook has been observing the 278.632 GHz emission line of stratospheric ClO from Mauna Kea, Hawaii (latitude 20°N, altitude 4300 m above sea level), since 1982 [*Solomon et al.*, 1984]. During 1982–1988, observations were conducted for a few weeks each year; since 1992 (as part of the Network for the Detection of Stratospheric Change (NDSC)) observations have been continuous, weather and equipment problems permitting (P. M. Solomon, Research summaries 1994–1996, in NASA Upper Atmosphere Research Program Summaries, p. 89, 1997). Typically, an average of several days' data during good observing conditions yields a spectrum with a signal-to-noise ratio sufficiently high for successful deconvolution. There have been approximately 30 periods of good observing conditions, that is, periods of 5–7 days with very good weather resulting in an average zenith opacity of less than 0.1, since 1992. One ClO profile has been retrieved during each such period. Two of these periods overlap with the ATLAS 1 and ATLAS 3 mission, respectively (see Table 1).

In this paper, we present ClO profiles obtained from spectra that were measured from March 21–31, 1992, and October 24 to November 20, 1994 (P. M. Solomon et al., data deposited in the NDSC database, 1997). These measurements cover the ATLAS 1 and 3 missions (Table 1). The profiles were retrieved from true daytime observations (0900–1700 hours local time) that were averaged over several consecutive days. A singular value decomposition (SVD) method was used to retrieve profiles from the spectra. The profiles represent mean values of ClO vmr over layers of a thickness of approximately 3 km. This is not equivalent to the true vertical resolution which is rather around 7 km, a typical value for this uplooking observation geometry. However, the altitude of the peak mixing ratio is determined to ±1.5 km. The error bars indicate a 1 σ deconvolution error and an estimated 15% calibration error. The results were converted to the MAS pressure grid by linear interpolation over log(pressure) for this comparison.

3.2. Airborne Measurements of ClO at 649 GHz

During ATLAS 1, correlative ClO measurements at 649 GHz were performed with an airborne submillimeter-wave radiometer. A description of the instrument and earlier results have been published by *Crewell et al.* [1995]. The ClO profile for this comparison resulted from a flight from Teneriffe (28°N) to Lisbon (38°N) on March 29, 1992.

Altitude profiles of ClO were retrieved from the submillimeter spectra with the Optimal Estimation Method (OEM) [*Rodgers*, 1976, 1990; *Marks and Rodgers*, 1993]. Figure 2 shows the averaging kernels that were generated for this retrieval. The averaging kernel functions represent the smoothing of the retrieved profile due to the observational method. The a priori profile was taken from [*Stachnik et al.*, 1992]. The profile in Figure 3 represents daytime ClO vmr on an evenly spaced altitude grid of 5 km, averaged over the entire flight. The error bars indicate the 1 σ retrieval error caused by measurement noise and smoothing (null-space) error as well as an estimated systematic error caused by the aircraft window and spectral contamination from several ozone lines.

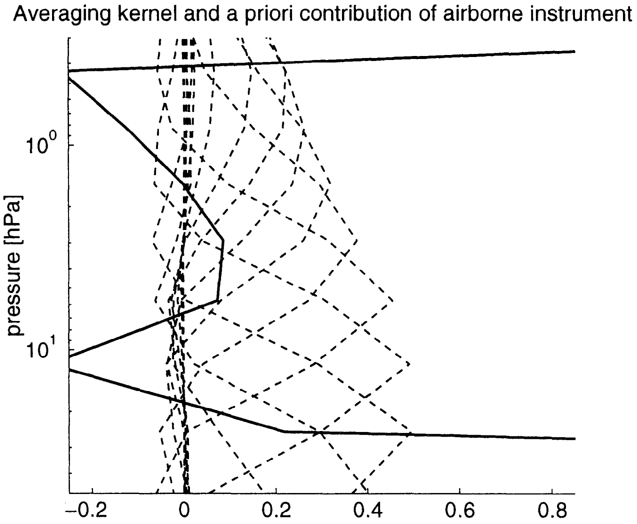

Figure 2. The dotted lines show the averaging kernel functions for the airborne radiometer. The solid line is the relative a priori contribution according to equation (2). The original 5-km spaced retrieval grid was converted to pressure coordinates for this plot.

3.3. ClO Data From MLS on UARS at 204 GHz

The Microwave Limb Sounder (MLS) on the Upper Atmospheric Research Satellite (UARS) currently provides the most complete data set on stratospheric ClO. Measurements have been taken since 1991. The data set is distributed by the Goddard Space Flight Center's (GSFC) Distributed Active Archive Center (DAAC). Level 3 data (altitude profiles) are available in the form of time ordered (L3AT) as well as latitude ordered (L3AL) data sets. The L3AL data sets are interpolated onto a evenly spaced latitude grid. All altitude profiles are provided as volume mixing ratio on a standard pressure grid that is used for all UARS measurements. Version 3 of the ClO data product has been validated by *Waters et al.* [1996]. The most recent version on the GSFC-DAAC is Version 4. Version 5, which uses nonlinear retrieval techniques, is currently in production. These MLS Version 5 data have day-night ClO differences at mid and low latitudes which differ by 0.03 ppbv or less from the MLS Version 4 data used here.

In this comparison we used Version 4 data which was made publicly available in 1997. MLS Version 4 data corrects the known 8% scaling error in Version 3 [*Waters et al.*, 1993]. A programming error that caused some Version 3 Level 3AL profiles before April 15, 1993 to be too large by a factor of 1.32 because an isotopic correction was applied twice (MLS Version 4 Quality Document distributed with the UARS data) has also been fixed. L3AT profiles of Version 3 and 4 were never affected by this error. The negative bias errors of 0.1 to 0.2 ppbv for ClO in the 10–46 hPa range of MLS Version 3 data still exist in Version 4. Day-night differences should be taken to eliminate these errors.

For the comparison with MAS we used L3AT ClO profiles that covered roughly the same time periods as the ATLAS missions. We averaged them over the same latitude bands that were used for the MAS profiles. Roughly every 36 days, UARS performs a yaw maneuver that shifts the main field of view from one hemisphere to the other. Therefore MAS and MLS did not always look at the same latitude range during the ATLAS missions. The best coincidence was achieved during ATLAS 2, when both instruments were looking at the southern hemisphere during daytime.

The MLS profiles in this article represent ClO vmr on standard UARS pressure levels. The error range indicates the total error consisting of noise, scaling, and bias uncertainties as defined by *Waters et al.* [1996]. The profiles were averaged over several days to reduce the noise contribution below the combined scaling and bias uncertainty. We used only MLS ClO profiles with QUALITY_CLO=4 and MMAF_STAT='G' and only data points with positive quality values. That is the suggested procedure for using MLS Version 4 ClO. Whether the profiles represented day or night measurements was determined from the REF_SOLAR_ILLUM-Flag in the Level 3TP file that corresponded to the Level 3AT file that contained the ClO profiles. For a description of these terms and files, see *Waters et al.* [1996] and the MLS Version 4 Quality Document that is distributed in electronic form with the MLS data by the GSFC DAAC.

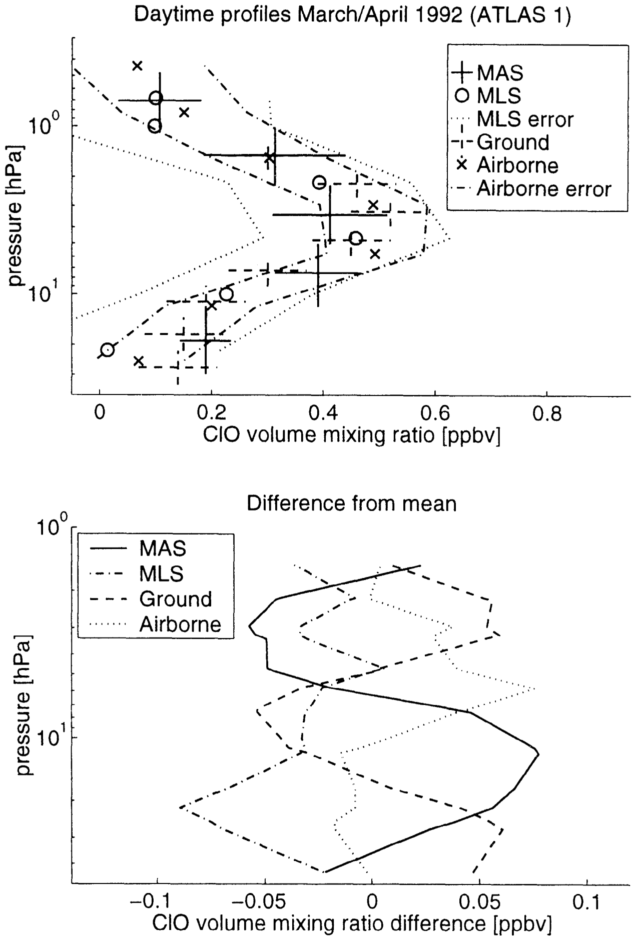

Figure 3. (top) Correlative spaceborne, airborne, and ground-based measurements in the spring of 1992 at 30°N. The MAS results are zonal means between 15° and 25°N averaged from March 24 to April 2, 1992. MLS data are zonal means (15°–25°N) of Version 4 daytime L3AT profiles, averaged from March 14–23, 1992. The ground-based measurements are true daytime observations at 278 GHz from Mauna Kea, Hawaii (20°N), averaged from March 21–31, 1992. The airborne submillimeter data were taken on a flight from Teneriffe (28°N) to Lisbon (38°N) on March 29, 1992. (bottom) Difference of all profiles from their common mean.

4. Results of Comparisons

4.1. Direct Comparisons of All Available Data Sets

During the ATLAS 1 mission, measurements were available from all the above instruments. Figure 3 shows a comparison of the ground-based and airborne ClO measurements in the tropics and subtropics as well as zonal means derived from the MAS and MLS data sets. All measurements were put onto a common pressure grid by linear interpolation over log(pressure). The measurement periods and latitude ranges were chosen to provide the best overlap of the available data with as little additional averaging as possible. In particular, the 20°–30° range was chosen for MAS and MLS because it covered the ground-based measurements as well as the part of the flight track with the highest solar zenith angle. The top plot includes the error bars that were provided with the data sets. Because the MAS and ground-based profiles represent vertical means, they are plotted as vertical lines with horizontal error bars. The MLS and airborne profiles are intercepting points of piecewise linear functions and are plotted as points with an enveloping error range. The bottom plot shows the difference from the common mean of all profiles.

Figure 4 is very similiar to Figure 3, except that it shows the available data sets for the ATLAS 3 mission. There were no aircraft measurements during that mission. In general, the temporal overlap of the available data sets was not as good for that mission as for ATLAS 1.

Figures 3 and 4 clearly show that the results of all instruments were well within their combined error bars. In general, their agreement is better than 0.1 ppbv. Especially near and above the volume mixing ratio peak, MAS and MLS values are very close. The MLS profiles reach the lowest values at pressures above 10 hPa, a result of the well known systematic bias of -0.1 to -0.2 ppbv at higher pressures in the MLS data. The selected latitude range is very useful for

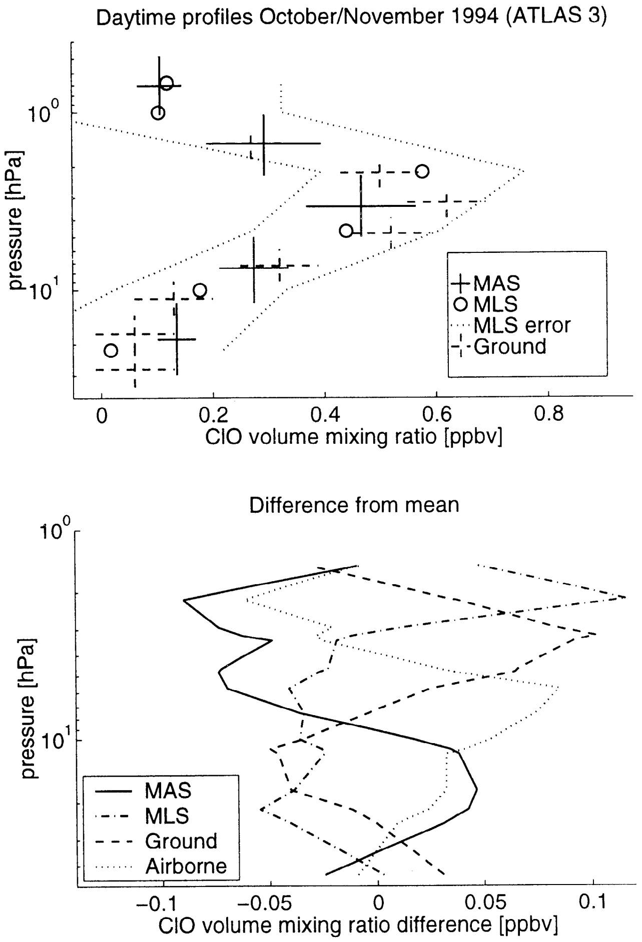

Figure 4. Similar to Figure 3 for the fall of 1994. MAS data were taken from November 3–4, 1994 (ATLAS 3), MLS data were taken from November 15–29, 1994, and Mauna Kea data were taken from October 24 to November 20, 1994. Airborne measurements were not available for that mission.

intercomparisons of this kind since the natural variability of the ClO abundance is typically smaller than 0.1 ppbv over a range of 20°–40°N independent of season, see *Waters et al.* [1996] (their Figure 22).

4.2. Vertical Resolution and A Priori Information

Tsou et al. [1995] and *Connor et al.* [1995] have pointed out that vertical resolution has to be taken into account when measurements of different vertical resolutions are compared. The reason is that microwave measurements have typical vertical resolutions in the range of a few kilometers. The eigenvectors of the retrieval process may also not be localized. Speaking in the terms of *Rodgers* [1976], this means that the averaging kernels of the retrieval may not be well peaked and may have significant contributions from several retrieval layers.

This problem can be avoided when the higher-resolution measurements are degraded by convolution with the averaging kernels of the lower-resolution measurement. The idea is that a high-resolution profile x_h is convoluted with the averaging kernel $\mathbf{A}$ and the a priori profile $\mathbf{x}_a$ to produce a profile $\mathbf{x}_c$ that has the same vertical resolution as the microwave profile [*Tsou et al.*, 1995]:

$$\mathbf{x}_c = \mathbf{x}_a + \mathbf{A}(\mathbf{x}_h - \mathbf{x}_a) \tag{1}$$

Figure 5 shows the results of applying this procedure to the ClO data sets in Figure 3. The averaging kernel and a priori profile were taken from the airborne ClO measurements during ATLAS 1. They are provided in Figures 2 and Figure 5 (top), respectively. This data set was chosen because it had a lower vertical resolution than the limb-sounding profiles and it was produced with the Optimal Estimation Method.

The agreement of the convoluted data sets in Figure 5 was slightly better than the agreement of the unconvoluted profiles in Figure 3. It appeared that all the profiles were rather close to the a priori profile that was used for the airborne measurements. However, Figure 6 shows clearly that very different a priori profiles were used for the retrieval of the ClO profiles in Figures 3 and 5. The discrepancy between the a priori profiles was 3–4 times larger than the discrepancy between the retrieved profiles.

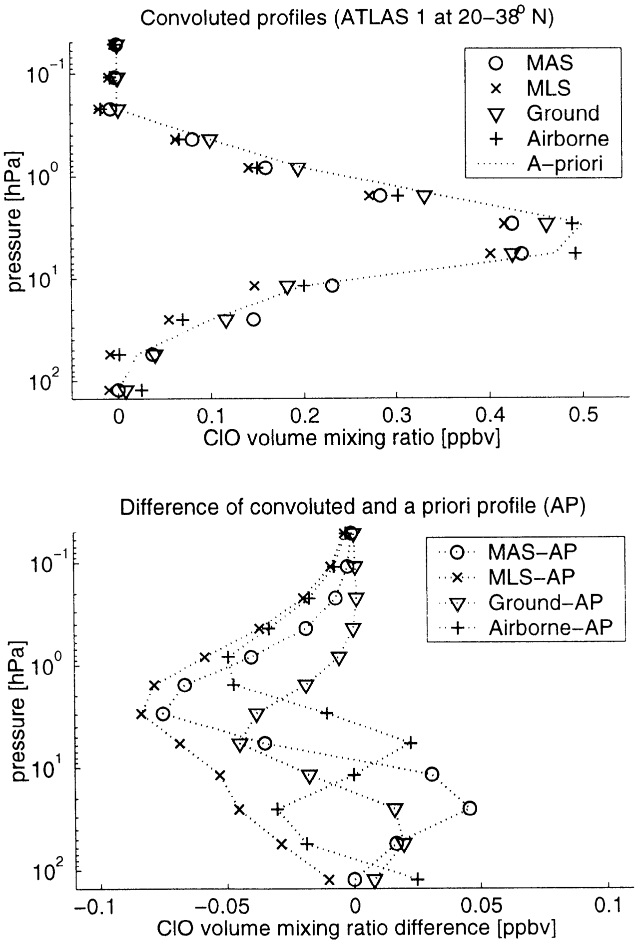

Figure 5. (top) Similiar to Figure 3, but taking into account the different vertical resolutions. The profiles were convoluted using the a priori profile in the top panel and the averaging kernel in Figure 2. (bottom) Difference from the a priori profile for each convoluted profile.

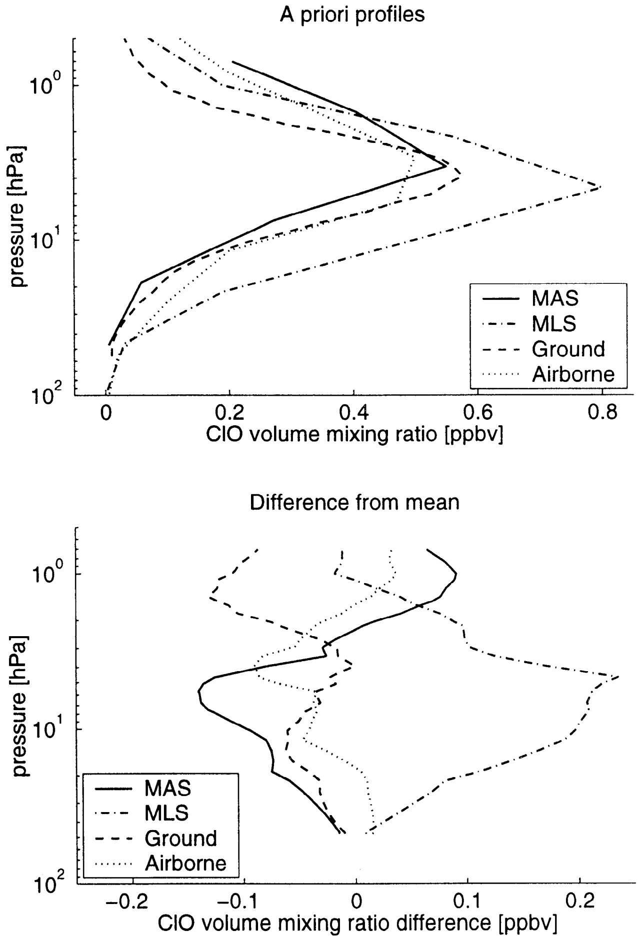

Figure 6. A priori profiles for the time and latitude range in Figure 3 (ATLAS 1). Since the MAS a priori profiles were actually day-night difference profiles, they were corrected with the model night profile in Figure 1 (top) to produce equivalent daytime a priori profiles.

Connor et al. [1995] define another way to estimate the dependence of a measurement on a priori information. The relative contribution of the a priori profile $\mathbf{c}_a$ to the retrieved profile $\mathbf{x}$ can be defined as

$$c_i = \frac{\mathbf{A}_i \mathbf{x}_a}{x_i}. \tag{2}$$

The index i represents the ith row of each vector or matrix. The solid line in Figure 2 shows the result for the airborne instrument. A value in the range of 10% or less in the range of the volume mixing ratio peak (4-5 hPa) is typical for an uplooking measurement geometry. For a limb-sounding geometry the averaging kernels are much closer to a unity matrix and the a priori contribution drops to almost zero. In the case of MAS (Figure 7) this is further enhanced by the extensive vertical averaging and the fact that the profiles were retrieved on only six levels. The averaging kernels for MLS [*Waters et al.*, 1996] (their Figure 2) show a very similiar behavior. A similiar plot for the ground-based instrument was not possible because a different retrieval technique was used.

4.3. Comparisons of Day-Night Differences

The large amount of MLS data allowed a more detailed comparison between MAS and MLS. For a direct comparison of MAS and MLS data it appeared to be more useful to compare day-night differences instead of daytime profiles. The main reason was that the known biases in the MLS profiles are expected to disappear when taking day-night difference profiles [*Waters et al.*, 1996]. In addition to that, the MAS profiles were originally derived from day-night difference spectra. As mentioned before, the model night profiles shown in Figure 1 were then added to the retrieved profiles to produce the published daytime profiles of ATLAS 1 and 2 [*Aellig et al.*, 1996]. For each mission, the same night profile was added to every zonal mean profile.

Day-night difference profiles for MAS were produced by simply subtracting the ATLAS 2 model night profile in Figure 1 from the ATLAS 2 daytime profiles. That produced the MAS profiles that had been derived from the day-night difference spectra. For MLS, night profiles from 45°S to 45°N, the same latitude range that had been used to produce the MAS night spectra, were averaged for the ATLAS 1 and 2 mission. The MLS night profiles clearly show the known bias of -0.1 to -0.2 ppbv at low altitudes (pressures above 10 hPa) which was also present in the MLS Version 4 day profiles. These profiles were then subtracted from the daytime MLS profiles to produce day-night difference profiles for MLS.

Figure 8 shows comparisons of these day-night differences for all overlapping latitude bands during the ATLAS 2 mission. The MLS error range is much smaller in this plot than in Figures 3 and 4 because the large systematic components were removed as a result of the day-night subtraction.

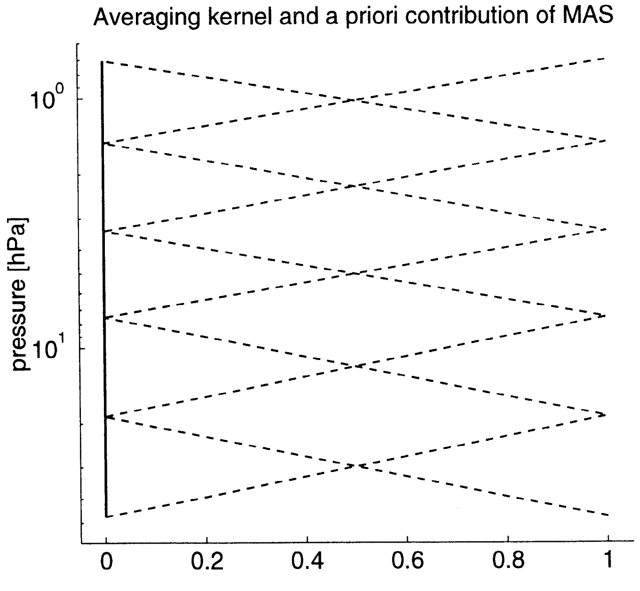

Figure 7. Similiar to Figure 2, but for MAS. Because of the limb-sounding geometry and the fact that the MAS profiles were only retrieved on six altitude levels, the averaging kernel matrix is practically equal to unity, and the relative a priori contribution is nearly zero.

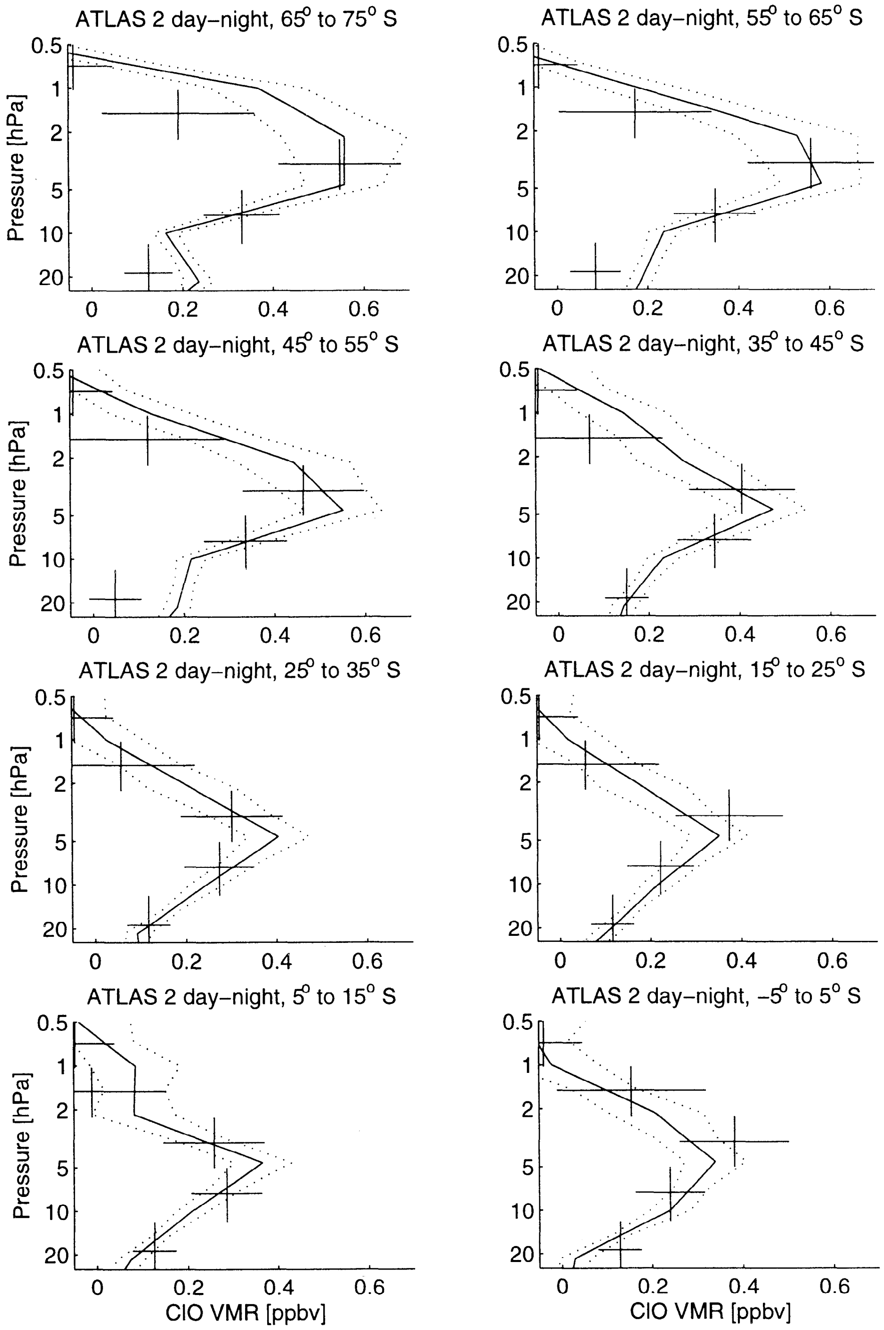

Figure 8. Comparison of day-night difference profiles for MAS and MLS during ATLAS 2. The crosses represent MAS profiles, while the solid lines are MLS results. The dotted lines give the MLS error range. We used the original MAS profiles without the added model profiles (see Figure 1). For the MLS profiles we subtracted the MLS night profile in Figure 1 from the zonally averaged day profiles of April 8–17, 1993. The MLS error range only includes scaling and statistical errors, since the day-night subtraction should remove the bias components.

Figure 9 shows the residuals of subtracting the MLS profiles in Figure 8 from the corresponding MAS profiles.

The agreement between both instruments on this level was typically better than ±0.1 ppbv. In the 10–20 hPa range the agreement was even better than ±0.05 ppbv for most latitudes. Larger differences of up to 0.2 ppbv exist near the 2 hPa level at higher latitudes. However, beyond 50°S there were hardly enough MLS profiles for a meaningful comparison. In general, there was no strong latitudinal structure in the residuals. The agreement appeared to improve toward low latitudes. This was not unexpected, since the stratospheric conditions should be more stable at lower latitudes. Therefore differences that arise from the observation of different regions or time periods should subside with decreasing latitude. The ATLAS 2 mission was used here because it was the only mission with truly coincident measurements by both instruments. That means that both instruments were looking at overlapping latitude ranges at daytime during the

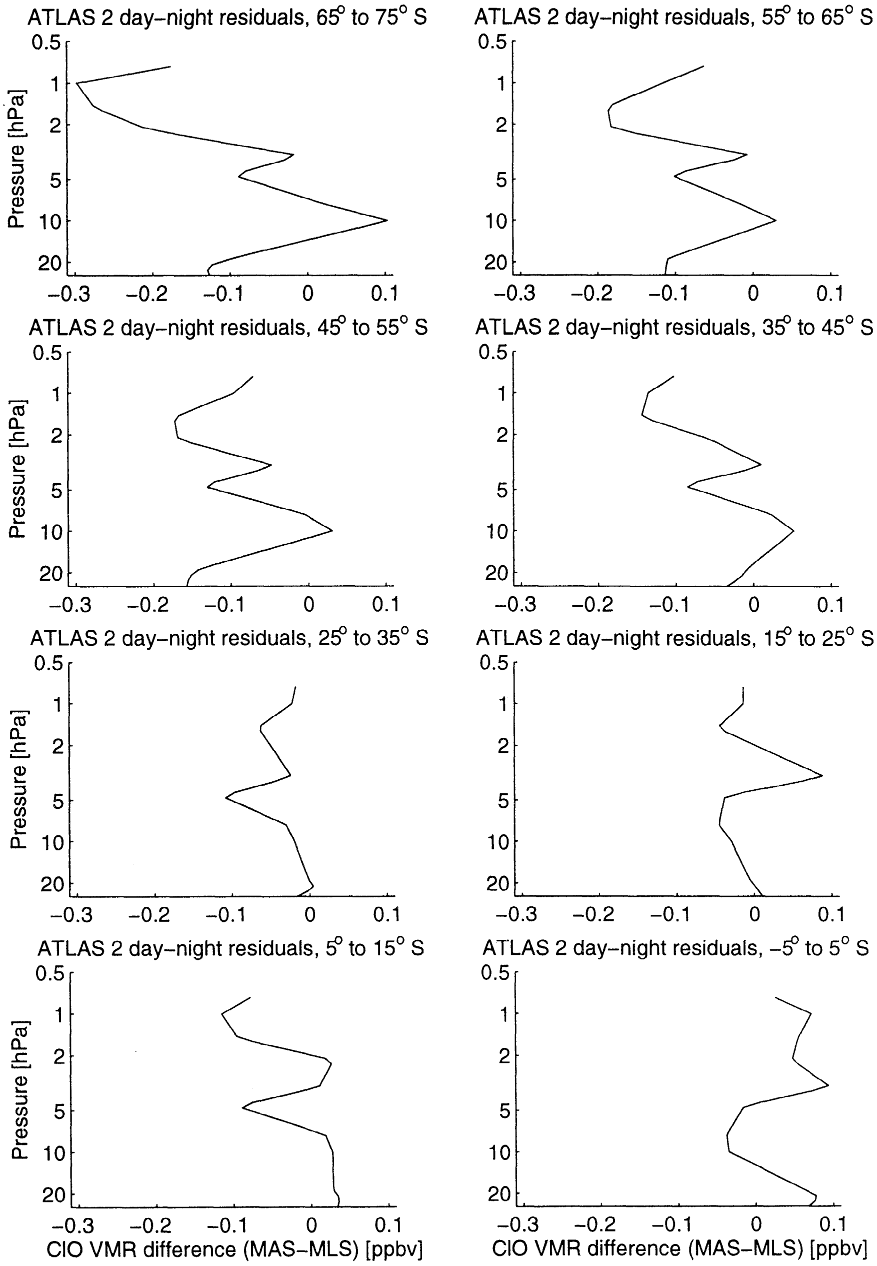

Figure 9. Residuals of the day-night differences in Figure 8. The MLS profiles were subtracted from the MAS profiles after interpolating both onto a common pressure grid.

whole ATLAS 2 mission. Comparisons for the other missions, where MLS profiles shortly before or after the respective ATLAS mission had to be used, still produced very similiar results. The reader should consult *Aellig et al.* [1996] for an interpretation of the zonal mean profiles measured by MAS.

5. Conclusions

ClO measurements by MAS from all three ATLAS missions were compared to correlative ground-based, airborne, and spaceborne measurements. In general, MAS was in good agreement with all the other instruments, always lying within the combined error bars. Considering the different measurement geometries and temporal and spacial ranges covered by the four instruments, their agreement was satisfactory. Since the agreement between all the instruments was comparable to the natural variablility of ClO in the considered latitude range, it appeared that there were no obvious systematic errors in the data sets. Unfortunately, it was not possible to compare with nonmicrowave data sets or under conditions of enhanced ClO in the Arctic or Antarctic vortex.

Comparisons of day-night difference profiles between MAS and MLS produced a good agreement of typically better than 0.1 ppbv over the whole latitude and altitude range. No further systematic differences between MAS and MLS were encountered. The much larger discrepancies of up to

0.3 ppbv between MAS and MLS Version 3 L3AL (latitude-ordered) day profiles [*Feist et al.*, 1998] did not appear in the MLS Version 4 L3AT (time-ordered) profiles that were used in this study. Those discrepancies have now been identified. They were caused by a programming error in the production of some of the Version 3 L3AL profiles. This error has never affected the more commonly used L3AT profiles.

When all the measurements were compared at an equivalent vertical resolution, the agreement was even slighty better than for the direct comparison. The retrieved profiles were very close to the a priori profile of the airborne radiometer. However, very different a priori profiles had been used for retrieving the different data sets. The a priori contribution for the airborne instrument was in the range of 10%, a typical value for uplooking measurements, while the a priori contribution for MAS was practically zero. The MLS data set, which uses the same a priori information for all profiles, has proved before that it depends only very little on a priori information, for example, when ClO profiles in the Arctic or Antarctic vortex were retrieved. Since the differences between the a priori profiles were much larger than the differences between the retrieved profiles, it rather appears that all instruments saw a similiar true profile which was close to the a priori profile of the airborne instrument. Since the expected natural variablility of ClO is small in the considered latitude range and all the measurements contain a considerable amount of averaging, it is not surprising that the true distribution of ClO would resemble climatological profiles.

The data from MLS, MAS, and the Mauna Kea instrument have been submitted to databases and are available for scientific use. With this study, we hope to have established and improved credibility in the MAS data set as well as the others that were used in this study. Credibility is equally important for the measured values as well as the error bars, both of which have proved to be realistic for all instruments. This is important to secure the intepretations that have been or will be made using these data sets. For this study, independent ClO measurements with a good spatial and temporal coverage were absolutely essential. Therefore such measurements should be continued at all latitudes and altitudes in the future.

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References

Aellig, C. P., N. Kämpfer, and R. M. Bevilacqua, Error analysis of ClO, O_3, and H_2O abundance profiles retrieved from millimeter wave limb sounding measurements, *J. Geophys. Res.*, *98*, 2975–2983, 1993.

Aellig, C. P., et al., Latitudinal distribution of upper stratospheric ClO as derived from space borne microwave spectroscopy, *Geophys. Res. Lett.*, *23*, 2321–2324, 1996.

Anderson, J. G., J. J. Margitan, and D. H. Stedman, Atomic chlorine and the chlorine monoxide radical in the stratosphere: Three in situ observations, *Science*, *198*, 501–503, 1977.

Anderson, J. G., W. H. Brune, and M. H. Proffitt, Ozone destruction by chlorine radicals within the Antarctic vortex: The spatial and temporal evolution of ClO–O_3 anticorrelation based on in situ ER-2 data, *J. Geophys. Res.*, *94*, 11,465–11,479, 1989.

Avallone, L. M., D. W. Toohey, W. H. Brune, R. J. Salawitch, A. E. Dessler, and J. G. Anderson, Balloon-borne in situ measurements of ClO and ozone: Implications for heterogeneous chemistry and mid-latitude ozone loss, *Geophys. Res. Lett.*, *20*, 1795–1798, 1993a.

Avallone, L. M., D. W. Toohey, M. H. Proffitt, J. J. Margitan, K. R. Chan, and J. G. Anderson, In situ measurements of ClO at mid-latitudes: Is there an effect from Mt. Pinatubo?, *Geophys. Res. Lett.*, *20*, 2519–2522, 1993b.

Barath, F. T., et al., The Upper Atmosphere Research Satellite Microwave Limb Sounder instrument, *J. Geophys. Res.*, *98*, 10,751–10,762, 1993.

Bevilacqua, R. M., et al., MAS measurements of the latitudinal distribution of water vapor and ozone in the mesosphere and lower thermosphere, *Geophys. Res. Lett.*, *23*, 2317–2320, 1996.

Brune, W. H., E. M. Weinstock, and J. G. Anderson, Midlatitude ClO below 22 km altitude: measurements with a new aircraft-borne instrument, *Geophys. Res. Lett.*, *15*, 144–147, 1988.

Carli, B., F. Mencaraglia, M. Carlotti, B. M. Dinelli, and I. Nolt, Submillimeter measurement of stratospheric chlorine monoxide, *J. Geophys. Res.*, *93*, 7063–7068, 1988.

Connor, B. J., A. Parrish, J.-J. Tsou, and M. P. McCormick, Error analysis for the ground-based microwave ozone measurements during STOIC, *J. Geophys. Res.*, *100*, 9283–9291, 1995.

Crewell, S., K. Künzi, H. Nett, T. Wehr, and P. Hartogh, Aircraft measurements of ClO and HCl during EASOE 1991/92, *Geophys. Res. Lett.*, *21*, 1267–1270, 1994.

Crewell, S., R. Fabian, K. Künzi, H. Nett, T. Wehr, W. Read, and J. Waters, Comparison of ClO measurements by airborne and spaceborne microwave radiometers in the arctic winter stratosphere 1993, *Geophys. Res. Lett.*, *22*, 1489–1492, 1995.

Croskey, C. L., et al., The Millimeter Wave Atmospheric Sounder (MAS): A Shuttle-based remote sensing experiment, *IEEE Trans. Microwave Theory Tech.*, *40*, 1090–1100, 1992.

Daehler, M., et al., Validation of Millimeter-wave Atmospheric Sounder (MAS) ozone measurements, *J. Geophys. Res.*, *103*, 19,615–19,640, 1998.

de Zafra, R. L., L. K. Emmons, J. M. Reeves, and D. T. Shindell, An overview of millimeter-wave spectroscopic measurements of chlorine monoxide at Thule, Greenland, February–March, 1992: Vertical profiles, diurnal variation, and longer-term trends, *Geophys. Res. Lett.*, *21*, 1271–1274, 1994.

de Zafra, R. L., J. M. Reeves, and D. T. Shindell, Chlorine monoxide in the Antarctic spring vortex, 1, Evolution of midday vertical profiles over McMurdo Station, 1993, *J. Geophys. Res.*, *100*, 13,999–14,008, 1995.

Farman, J. C., B. G. Gardiner, and J. D. Shanklin, Large losses of total ozone in Antarctica reveal seasonal ClO_x/NO_x interaction, *Nature*, *315*, 207–210, 1985.

Feist, D. G., et al., Comparison of MAS stratospheric ClO measurements with spaceborne, airborne, and ground-based experiments, in *Atmospheric Ozone: Proceedings of the Quadrennial Ozone Symposium 1996*, edited by R. D. Bojkov, and G. Visconti, vol. 2, pp. 499–502, Int. Ozone Commission, L'Aquila, Italy, 1998.

Gerber, L., and N. Kämpfer, Millimeter-wave measurements of chlorine monoxide at the Jungfraujoch Alpine Station, *Geophys. Res. Lett.*, *21*, 1279–1282, 1994.

Hartmann, G. K., et al., Measurements of O_3 , H_2O, and ClO in the middle atmosphere using the Millimeter-wave Atmospheric Sounder (MAS), *Geophys. Res. Lett.*, *23*, 2313–2316, 1996.

Klein, U., S. Crewell, and R. L. de Zafra, Correlated millimeter wave measurements of ClO, N_2O, and HNO_3 from McMurdo, Antarctica, during polar spring 1994, *J. Geophys. Res.*, *101*, 20,925–20,932, 1996.

Ko, M. K. W., and N. D. Sze, Diurnal variations of ClO: Implications for the stratospheric chemistries of $ClONO_2$, HOCl, and HCl, *J. Geophys. Res.*, *89*, 11,619–11,632, 1984.

Marks, C. J., and C. D. Rodgers, A retrieval method for atmospheric composition from limb emission measurements, *J. Geophys. Res.*, *98*, 14,939–14,953, 1993.

Molina, M. J., and F. S. Rowland, Stratospheric sink for chlorofluoromethanes: Chlorine atom-catalysed destruction of ozone, *Nature*, *249*, 810–812, 1974.

Parrish, A., R. L. de Zafra, P. M. Solomon, and J. W. Barrett, A ground-based technique for millimeter wave spectroscopic observations of stratospheric trace constituents, *Radio Sci.*, *23*, 106–118, 1988.

Raffalski, U., U. Klein, B. Franke, J. Langer, B.-M. Sinnhuber, J. Trentmann, K. F. Künzi, and O. Schrems, Ground-based millimeter-wave observations of arctic chlorine activation during winter and spring 1996/97, *Geophys. Res. Lett.*, *25*, 3331–3334, 1998.

Ricaud, P., J. de La Noë, R. Lauqué, and A. Parrish, Analysis of stratospheric chlorine monoxide measurements recorded by a ground-based radiometer located at the Plateau de Bure, France, *J. Geophys. Res.*, *102*, 1423–1439, 1997.

Rodgers, C. D., Retrieval of atmospheric temperature and composition from remote measurements of thermal radiation, *Rev. Geophys. Space Phys.*, *14*, 609–624, 1976.

Rodgers, C. D., Characterization and error analysis of profiles retrieved from remote sounding measurements, *J. Geophys. Res.*, *95*, 5587–5595, 1990.

Ruhnke, R., W. Kouker, T. Reddmann, H. Berg, G. Hochschild, G. Kopp, R. Krupa, and M. Kuntz, The vertical distribution of ClO at Ny-Ålesund during March 1997, *Geophys. Res. Lett.*, *26*, 839–842, 1999.

Santee, M. L., G. L. Manney, W. G. Read, L. Froidevaux, and J. W. Waters, Polar vortex conditions during the 1995–1996 Arctic winter: MLS ClO and HNO_3, *Geophys. Res. Lett.*, *23*, 3207–3210, 1996.

Schanda, E., et al., Millimeter wave atmospheric sounding from space shuttle, *Acta Astronaut.*, *13*, 553–563, 1986.

Shindell, D. T., and R. L. de Zafra, Chlorine monoxide in the Antarctic spring vortex, 2, A comparison of measured and modeled diurnal cycling over McMurdo Station, 1993, *J. Geophys. Res.*, *101*, 1475–1487, 1996.

Solomon, P. M., R. de Zafra, A. Parrish, and J. W. Barrett, Diurnal variation of stratospheric chlorine monoxide: A critical test of chlorine chemistry in the ozone layer, *Science*, *224*, 1210–1214, 1984.

Stachnik, R. A., J. C. Hardy, J. A. Tarsala, J. W. Waters, and N. R. Erickson, Submillimeterwave heterodyne measurements of stratospheric ClO, HCl, O_3, and HO_2: first results, *Geophys. Res. Lett.*, *19*, 1931–1934, 1992.

Toohey, D. W., L. M. Avallone, N. T. Allen, J. N. Demusz, J. N. Hazen, and J. G. Anderson, The performance of a new instrument for in situ measurements of ClO in the lower stratosphere, *Geophys. Res. Lett.*, *20*, 1791–1794, 1993.

Tsou, J. J., B. J. Connor, A. Parrish, I. S. McDermid, and W. P. Chu, Ground-based microwave monitoring of middle atmosphere ozone: Comparison to lidar and Stratospheric and Gas Experiment II satellite observations, *J. Geophys. Res.*, *100*, 3005–3016, 1995.

Waters, J. W., L. Froidevaux, W. G. Read, G. L. Manney, L. S. Elson, D. A. Flower, R. F. Jarnot, and R. S. Hartwood, Stratospheric ClO and ozone from the Microwave Limb Sounder on the Upper Atmosphere Research Satellite, *Nature*, *362*, 597–602, 1993.

Waters, J. W., et al., Validation of UARS Microwave Limb Sounder ClO measurements, *J. Geophys. Res.*, *101*, 10,091–10,127, 1996.

Wehr, T., S. Crewell, K. Künzi, J. Langen, H. Nett, J. Urban, and P. Hartogh, Remote sensing of ClO and HCl over northern Scandinavia in winter 1992 with an airborne submillimeter radiometer, *J. Geophys. Res.*, *100*, 20,957–20,968, 1995.

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