Ground-based measurements of ClO from Mauna Kea and intercomparisons with Aura and UARS MLS

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[1] The ground-based measurements of upper stratospheric ClO, made with a ground-based millimeter wave instrument at Mauna Kea, Hawaii (19.8°N, 204.5°E) starting in 1992, are compared with UARS (Upper Atmosphere Research Satellite) MLS ClO measurements (1991–1998) and the Aura MLS ClO measurements (2004–2009). The ground-based measurements are made as part of the Network for the Detection of Atmospheric Composition Change (NDACC). Intercomparisons between the ground-based measurements and the Aura MLS measurements show that both instruments retrieve similar seasonal variations over Mauna Kea. The seasonal variation in ClO is also compared with measurements of variations in stratospheric CH_4, which affects the partitioning of total inorganic chlorine. Using the ground-based instruments as a transfer standard, we find that the agreement between UARS and Aura MLS ClO measurements near the peak of the mixing ratio profile is within ~1%. Combining the uncertainties in the biases calculated from the coincident ground-based and satellite measurements, we find that using the ground-based data as a transfer standard allows us to provide a 2σ limit to the bias between the UARS and Aura measurements of 3%–4% near the peak of the ClO profile. Given agreement between UARS and Aura MLS of ~1% ± 4%, there is no reason to apply any bias correction in order to use the UARS and Aura MLS ClO measurements as a single data set.

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1. Introduction

[2] ClO is the molecule most directly involved in the depletion of the Earth's ozone layer due to the input of man-made CFCs [*Molina and Rowland*, 1974]. Most of the active chlorine in the stratosphere resides in ClO. As part of the Network for the Detection of Atmospheric Composition Change, we operate two ground-based millimeter wave spectrometers for the purpose of measuring and long-term monitoring of stratospheric ClO. The instruments measure the pressure-broadened line shape of the thermally excited rotational emission line of stratospheric ClO at 278 GHz (wavelength = 1.1 mm), from which the ClO altitude profile can be retrieved. One instrument, located on Mauna Kea, Hawaii (19.8°N, 204.5°E), has monitored the ClO altitude profile from 1992 to the present with some gaps due to equipment problems. A predecessor instrument was used at the same site for a small number of ClO measurements, beginning in 1982 [*Solomon et al.*, 2006]. The other instrument, located at Scott Base, Antarctica, records the rapid changes in ClO during the formation and breakup of the Antarctic ozone hole every year since 1996 [*Solomon et al.*, 2000, 2002; *Connor et al.*, 2007], providing important constraints on chlorine chemistry and tests of stratospheric models, particularly in the lower stratosphere.

[3] Here we will compare the ground-based measurements from Mauna Key with ClO measurements taken by Upper Atmosphere Research Satellite (UARS) MLS (1991–1998) [*Barath et al.*, 1993] and Aura MLS (since 2004) [*Waters et al.*, 2006]. In this paper, we will study the temporal variations in these data sets, and we will use the ground-based data to determine if there are measurable systematic differences between the two MLS satellite data sets.

2. Measurements and Retrievals

[4] The ground-based instrument consists of a cooled heterodyne receiver operating at 278.6 GHz and a spec-

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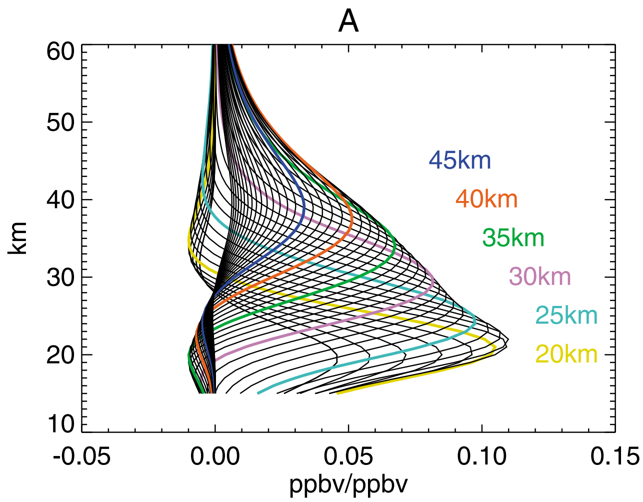

Figure 1. Averaging kernels for a typical "weekly" ground-based ClO retrieval. Each curve represents the response of the retrieval at the indicated altitude (shown for 20–45 km) to 1 ppmv perturbations from 15 to 60 km.

trometer with a total bandwidth of 506 MHz. The channels of the spectrometer are 5 MHz wide in the line wings and 1 MHz wide near line center. The instrument is indoors and observes through a Teflon window in the wall of the building. With the exception of the operating frequency and the distribution of the filters, this instrument is nearly identical to the millimeter wave ozone instruments operating at Mauna Loa and at Lauder, New Zealand. These instruments are described in detail by *Parrish* [1994].

[5] The sensitivity of the measurements is strongly affected by the opacity of the troposphere, which varies with the amount of water vapor. Thus, measurements are best made from high dry sites, and Mauna Kea, at 4200 m, provides the best site in the United States. Because the instrument operates continuously and automatically, it is able to take maximum advantage of very dry observing conditions whenever they occur. Excellent conditions tend to occur more frequently in the winter and early spring, although in some years, there are excellent periods throughout the entire year. The best days tend to come in clusters, and the data set analyzed here consists of 170 "weekly" averages of spectra from periods of 7–12 days each from January 1992 through June 2009. The retrieval requires atmospheric temperature and pressure profiles, and these are obtained from the National Center for Environmental Prediction (NCEP). A single a priori ClO profile is used in all of the retrievals shown here for Mauna Kea.

[6] In addition to the ClO line at 278.631 GHz, the spectrometer bandwidth also contains lines due to ozone and NO_2, as well as baseline curvature of instrumental origin. These additional lines and artifacts must be removed from the spectrum to recover the ClO line shape. ClO has a strong diurnal cycle, with a very weak and narrow nighttime signal originating from residual ClO mainly near the stratopause. This line is removed from the nighttime spectrum by interpolation across ±25 MHz around the line center. A daytime ClO spectrum with instrumental baseline and interfering lines removed is obtained by subtracting the modified nighttime spectrum from the adjacent daytime spectrum [*Solomon et al.*, 1984]. The same definitions of "Day" and "Night" are used year-round, namely 0900–1700 and 2200–0500 Hawaiian Standard Time, respectively. The region of the difference spectrum near the center of the strongest of the interfering ozone lines (278.521 GHz) contains a residual ozone signal and is not used in the retrieval. Daytime altitude profiles of ClO are then retrieved from these spectra using a modified Rodgers optimal estimation algorithm [*Solomon et al.*, 2000].

[7] A characterization and error analysis for the Mauna Kea ClO retrievals appeared in the work of *Solomon et al.* [2006]. The ClO profile is retrieved between 20 and 45 km. In this study, we will focus on retrievals at 35 and 40 km, where the vertical resolution given by the full width at half maximum (FWHM) of the averaging kernels is ~16 km. Precision of individual profiles is 0.02–0.03 ppbv, depending on altitude, and the formal accuracy is 0.03–0.04 ppbv. The averaging kernels for these measurements are shown in Figure 1.

[8] Since the publication of *Solomon et al.* [2006], we have implemented corrections to the treatment of the hyperfine splitting and to the vibrational partition function which have resulted in a slightly revised data set for ClO at Mauna Kea. These corrections have reduced the values retrieved near the upper stratospheric peak by ~0.05 ppbv and cause a small increase (~0.02 ppbv) at ~30 km. These corrections have little impact on the long-term temporal variation derived from the data set.

[9] UARS MLS data shown here is from the version 5 (v5) retrievals using the 204.4 GHz ClO line [*Livesey et al.*, 2003]. Aura MLS data shown here are from the version 2.2 retrievals using the 649.5 GHz ClO line [*Santee et al.*, 2008]. Just as for the ground-based retrievals, only the daytime data (0800–1600 local time) is shown here. The nighttime values (2000–0400 local time) at pressure >10 hPa are subtracted from the daytime data in both the UARS MLS and Aura MLS data sets as recommended by *Santee et al.* [2008]. *Livesey et al.* [2003] give an estimated accuracy for the UARS MLS v5 retrievals (2σ) of 0.1 ppbv + 15% at 4.6 hPa (~36 km) and above and 0.05 ppbv + 15% at 6.8 hPa (~34 km) and below. *Santee et al.* [2008] show a 2σ bias uncertainty for the Aura MLS retrievals of ~0.03 ppbv +10% from 22 to 1.5 hPa. Unless otherwise indicated, the MLS data shown here has been convolved with the averaging kernels calculated for the ground-based measurements.

3. Coincident Ground-Based and MLS Measurements

[10] The ground-based retrievals are compared both with UARS MLS data from 1992 to 1998 and with Aura MLS data from 2004 to 2009. For the Aura coincidence comparisons, we use Aura MLS profiles at all longitudes within ±2° latitude, ±30° longitude, and ±7 days from the average time of the ground-based retrieval. For the UARS measurements, we apply the same temporal coincidence criteria (which are comparable to the ground-based integration time), but since this data set is both sparser and noisier, we found that looser spatial coincidence criteria of ±5° latitude and all longitudes both increased the number of available coincidences and reduced the standard deviation of the differences. These coincidence criteria result in 26 ground-based/UARS coincidences and 75 ground-based/Aura coincidences.

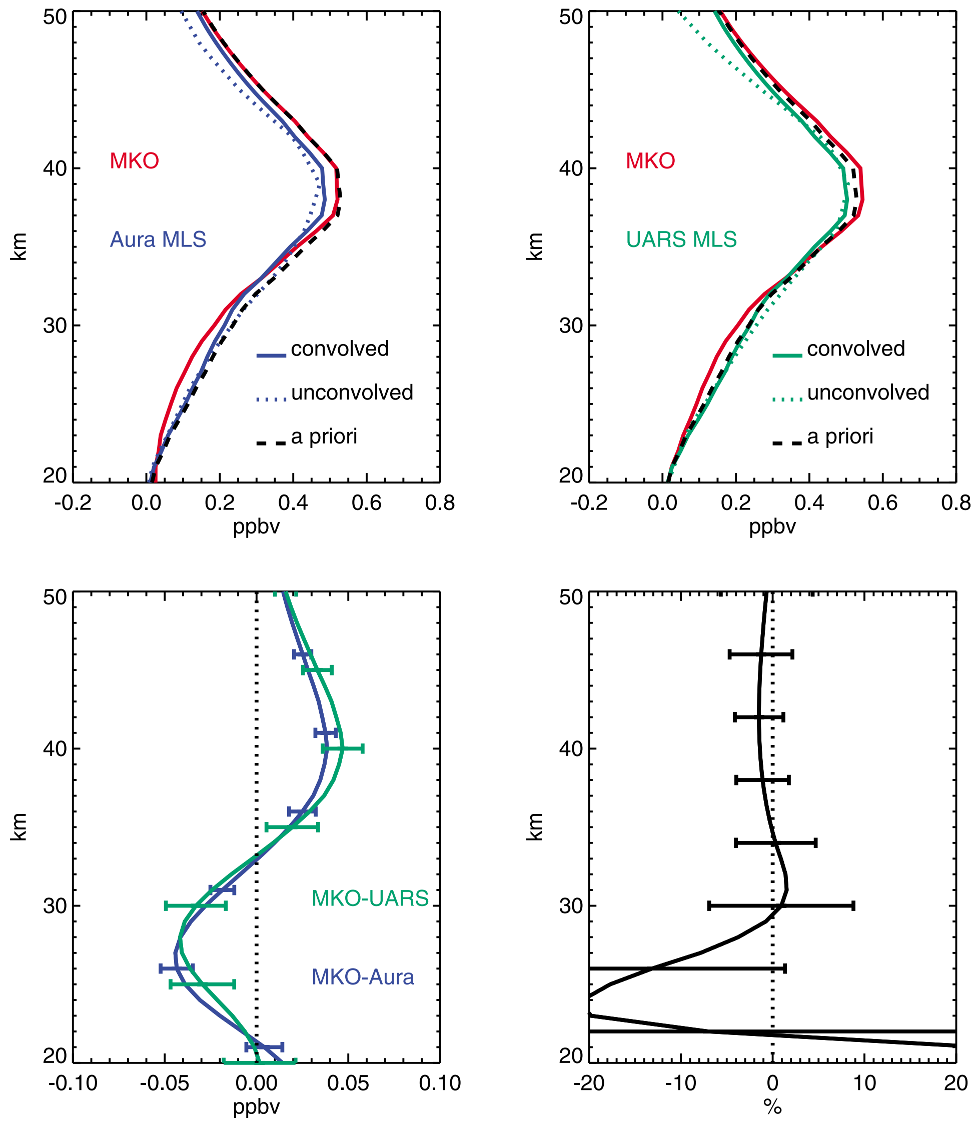

Figure 2. (top left) Overall average profiles for 75 ground-based (MKO)/Aura MLS coincidences. The Aura average is shown both for convolved and unconvolved data. Also shown is the a priori used in the ground-based retrievals and in the convolution of the satellite data. (top right) Overall average profiles for 26 ground-based/UARS MLS coincidences. (bottom left) Difference between the ground-based and satellite comparisons for UARS (light blue) and Aura (dark blue). Also shown is the uncertainty in the bias from the coincident measurements ($2\sigma/n^{1/2}$). (bottom right) Percentage difference between Aura and UARS (expressed as Aura-UARS) measurements using the ground-based data as a transfer standard. Error bars are root sum squares of the error bars in the bottom left, converted to percentages.

The results of this comparison are shown in Figure 2. In the following comparisons, the ground-based results are labeled as MKO.

[11] Figure 2 shows that, in both the UARS and Aura comparison, the ground-based measurements have higher mixing ratios than the satellite measurements in the upper stratosphere and lower mixing ratios in the lower stratosphere. At the peak of the profile (~40 km) the ground-based/satellite differences are ~7%–8%. The error bars in Figure 2 show the uncertainty in the bias from the coincident measurements, $2\sigma/n^{1/2}$, where σ is the standard deviation of the difference between the number of measurements (n).

[12] The average coincident differences between the ground-based instrument and each satellite instrument can be compared to the estimated biases in these measurements. *Solomon et al.* [2006] give fixed errors (1σ) for the ground-based measurements. These are smallest in the 25–34 km altitude range (~0.012 ppbv) and larger near the lower and upper stratosphere (0.031 ppbv at 20–24 km and 0.032 ppbv at 40–44 km). In addition to these fixed errors, there are possible long-term baseline errors in the ground-based measurements, which contribute uncertainties of ~0.02 ppbv. Average coincident differences between the UARS MLS and MKO measurements shown in Figure 2 are within 1σ over

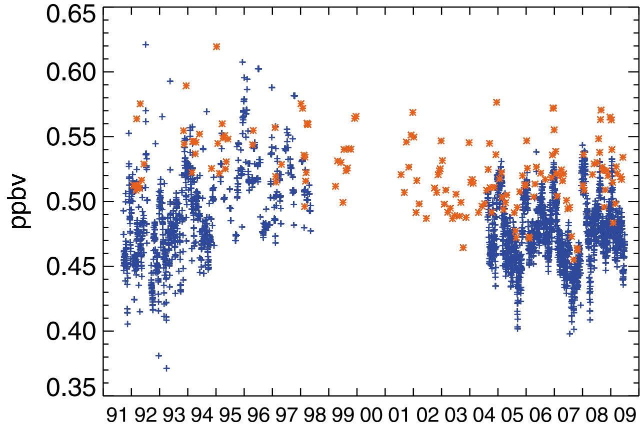

Figure 3. Ground-based microwave retrievals at 40 km from Mauna Kea (red) and daily averaged convolved MLS measurements (blue) near the Mauna Kea site from 1991 to 2009.

the entire altitude range. The average differences between the ground-based measurements and the Aura MLS measurements are within 1σ over most of the altitude range shown in Figure 2 and are within 2σ everywhere.

[13] While the ground-based/satellite differences are ~7%–8% near the peak of the profile, the difference between the UARS and Aura MLS data sets at this altitude is much smaller. The consistency of the UARS and Aura measurement is highlighted in Figure 2 (bottom), which shows the difference between the MKO-UARS fractional difference and the MKO-Aura fractional difference. As is indicated in Figure 2, the agreement between UARS and Aura MLS measurements near the peak of the profile is within ~1%. Combining the uncertainties in the biases calculated from the MKO-UARS and MKO-Aura coincident comparisons, we find that using the ground-based data as a transfer standard allows us to provide a 2σ limit to the bias between the UARS and Aura MLS measurements of 3%–4% near the peak of the ClO profile. Given agreement between UARS and Aura MLS of ~1% ± 4%, there is no reason to apply any bias correction in order to use the UARS and Aura MLS ClO measurements as a single data set.

[14] There are three major possible sources of error which could change the bias in the ground-based instrument: beam efficiency, window opacity, and sideband ratio. We have measured these parameters and can limit the change in the bias resulting from each one to <1% over the period of these comparisons. The formal (2σ) uncertainty estimated from these three possible sources of error is thus similar to the 3%–4% uncertainty derived from the ground-based/satellite coincidences. In Figure 3, we show the ground-based data record at 40 km for Mauna Kea since 1991, as well as daily average UARS MLS and Aura MLS measurements spatially coincident (as defined above for each satellite instrument) with Mauna Kea. As expected from Figure 2, the ground-based retrievals are somewhat higher than the satellite retrievals at this altitude, but this high bias is similar in both

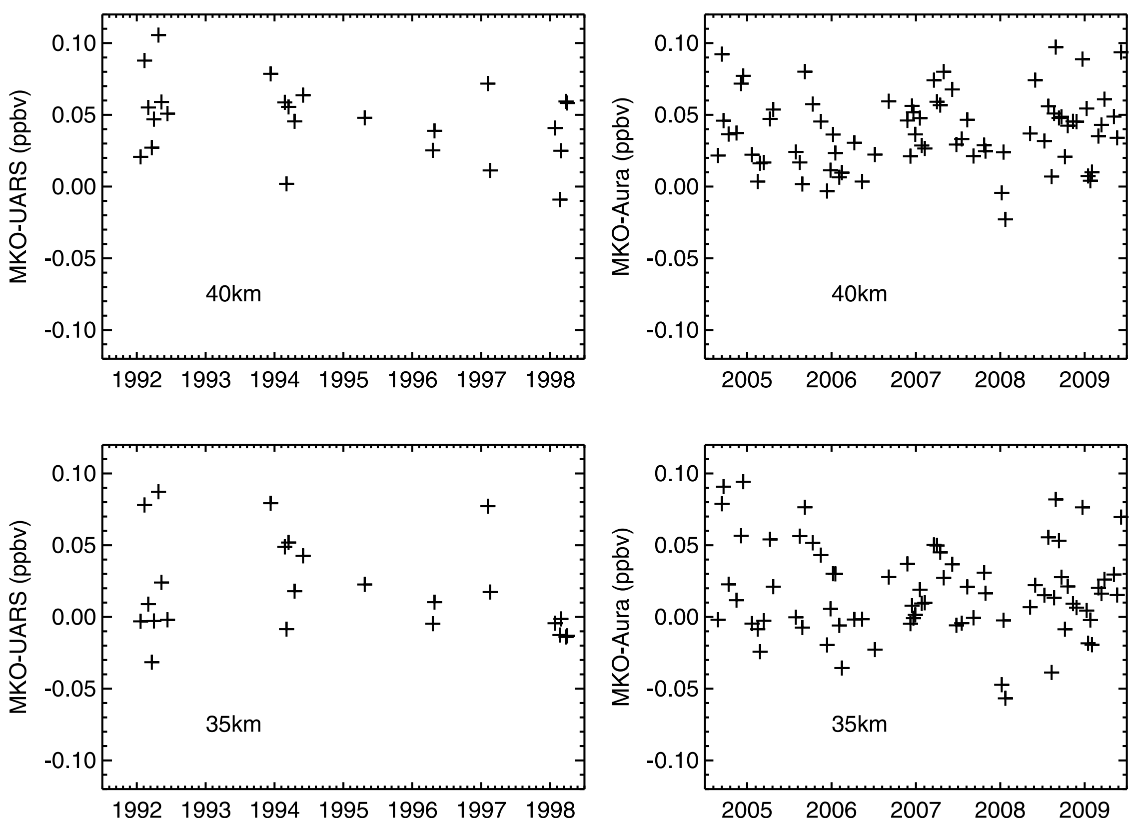

Figure 4. The difference between individual ground-based/MLS coincidences at (top) 40 km and (bottom) 35 km. The left-hand plots show the comparisons during the UARS time frame, while the right-hand plots show coincidences during the Aura mission.

Table 1. Significance of Ground-Based and MLS Difference Variations

MKO-MLS	1992 Average Difference (ppbv)	1998 Average Difference (ppbv)	1992–1998 Linear Fit of Difference (ppbv/yr)	2004–2009 Linear Fit of Difference (ppbv/yr)
40 km	0.057 (0.010)[a]	0.038 (0.011)	−0.0034 (0.0025)	0.0017 (0.0020)[b]
35 km	0.020 (0.015)	−0.010 (0.003)	−0.0039 (0.0029)	−0.0024 (0.0025)

[a]1992 and 1998 average difference errors represent bias errors ($\sigma/n^{1/2}$).
[b]Slope errors are 1σ.

ground-based/satellite data comparisons. Despite the coarse temporal sampling of the ground-based instrument, there appears to be good agreement in the temporal variability during the Aura time period, with both instruments showing minima in mid-2005 and mid-2007.

[15] Figure 4 shows comparisons between individual ground-based retrievals and the average of the satellite retrievals (as defined above for each satellite instrument) coincident with each of these measurements at 35 and 40 km. As is shown in Figure 2, mixing ratios tend to drop rapidly above 40 km and below 35 km at this latitude. Figure 1 shows that the ground-based and convolved satellite measurements at these two altitudes are not independent, but we nevertheless show in Figure 4 measurements at both altitudes, since there are small differences in the comparisons at these two altitudes, which can result in slightly different interannual variations in ClO. Figure 4 shows that the ground-based/satellite differences are generally consistent throughout each mission and between missions. The differences at both 35 and 40 km are slightly smaller at the end of the UARS measurements than at the beginning, but at 40 km, this is primarily caused by the drop in the difference from 1992, while at 35 km there is a decrease in the difference from 1997 to 1998. Slightly different biases may have occurred in the UARS MLS retrievals because of the switch off of the 63 GHz radiometer (retrieving temperature and tangent pressure) after 14 June 1997 [*Livesey et al.*, 2003], and this may have contributed to slight differences in the MKO-UARS MLS results.

[16] In Table 1 we use two methods to quantify the significance of the variations and their uncertainties between the ground-based and UARS MLS measurements from 1992 to 1998. We compare the average difference between the ground-based and UARS instruments in 1992 and 1998, and we find that the average difference does not significantly change (at the 2σ level) between the 1992 and 1998 data at either 35 or 40 km. We also show the calculated linear fit of the difference over the UARS and Aura time periods and find again that, at the 2σ level, there is no significant variation in the differences between the ground-based and MLS measurements. Hence, from the coincident ground-based and MLS measurements, we conclude not only that there was no significant variation (at the 2σ level) between the UARS and Aura measurements but also that there was no significant variation between ground-based and MLS measurements within the UARS and Aura measurement time periods.

4. Variations in Ground-Based and MLS Measurements

[17] Almost all of the ground-based measurements during the UARS time period were taken in the winter and early spring, with no measurements available from May through August. Since 2001, however, there have been some extended periods of low tropospheric optical depth during other seasons. We will therefore use ground-based data since 2001 to estimate seasonal and quasi-biennial oscillation (QBO) variations. We shall compare the variations in this ground-based data set to those from the Aura measurements within ±2° latitude and ±30° longitude of Mauna Kea from 2004 to 2009.

4.1. Time-Dependent Fits to Data Since 2001

[18] Both the ground-based and Aura MLS volume mixing ratio measurements are fit using singular value decomposition to the equation

$$\mathrm{vmr}(t) = a_o + a_1 \sin(2\pi t) + a_2 \cos(2\pi t) + a_3 \sin(4\pi t) + a_4 \cos(4\pi t) + a_5\ \mathrm{qbo}\ 30(t) + a_6\ \mathrm{qbo}\ 50(t), \quad (1)$$

where t is in years and qbo30(t) and qbo50(t) represent the monthly 30 and 50 mb QBO anomalies obtained from www.cpc.noaa.gov/data/indices. The data and the fits at 40 km are shown in Figure 5.

[19] As can be seen in Figure 5, the ground-based and Aura measurements show similar variability on seasonal and QBO time scales. The amplitude of the annual and semiannual cycles from ground-based measurements is 0.010 ± 0.004 and 0.012 ± 0.004 ppbv, respectively, while for the Aura measurements, the fit to these cycles is 0.0129 ± 0.0009 and 0.0163 ± 0.0009 ppbv, so the differences are just slightly greater than 1σ. Both instruments show a positive correlation with the 30 mb wind anomalies. The a_5 and a_6

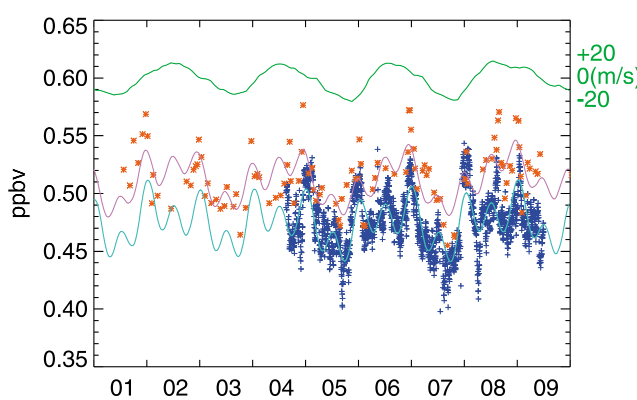

Figure 5. Ground-based microwave measurements (red) and daily averaged convolved Aura MLS measurements (blue) at 40 km from 2001 to 2009. Also shown are fits to the ground-based measurements (magenta) and Aura MLS measurements (cyan). The 30 mb QBO wind anomalies are indicated in green, with the scale on the right-hand axis.

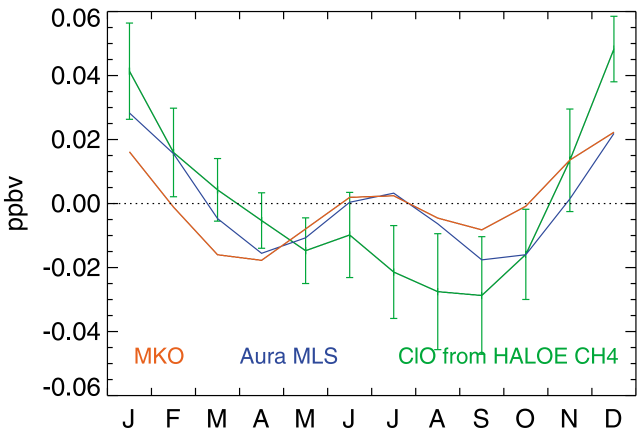

Figure 6. Annual and semiannual variation of ClO at 40 km calculated from fits to 2001–2009 ground-based (red) and the convolved MLS/Aura data (blue). Also shown is the expected change in ClO (green; see text) calculated from a convolved HALOE CH4 climatology for 15°N–25°N. Error bars on the HALOE data indicate $2\sigma/n^{1/2}$, where n is the number of years for which HALOE measurements were available for a specific month.

terms, representing the fits to the 30 and 50 mb standardized QBO anomalies, respectively, are 0.011 ± 0.003 and 0.000 ± 0.002 ppbv for the ground-based measurements and 0.0093 ± 0.0005 and −0.0025 ± 0.0005 ppbv for the Aura MLS measurements, so these fits both agree at the 1σ level. The good agreement in these measures of variability between the ground-based and Aura MLS measurements is encouraging for the application of these data to trend studies.

[20] Having established seasonal and QBO variations from the Aura measurements and from the ground-based measurements from 2001 to present, we subtracted these variations from the 1990s data in order to simplify the interpretation of the longer-term variations which occurred in the 1990s. We found, however, that the fit which works so well in removing QBO variability in the data from 2001 to June 2009 accentuates the QBO-like variations when applied to the 1990s data. In particular, we note that the late 1992 minimum in UARS ClO corresponds to a period when the 30 mb winds are strongly westerly (positive), in contrast to the easterly 30 mb winds coincident with the 2005 and 2007 minima in the Aura MLS data. Since the subtraction of a QBO fit from the measurements is difficult to interpret, we will henceforth work with only the first five terms from (1). We note that the fit to the calculated values for terms a_1–a_4 is very similar (within ±0.001) whether or not they are calculated using (1), or just the first five terms from (1).

4.2. The Seasonal Effect of CH_4 on ClO

[21] Variations in CH_4 make an important contribution to variations in ClO. In their study of UARS MLS ClO, *Froidevaux et al.* [2000] focused primarily on multiyear changes in ClO and found that much of the ClO upper stratospheric variability could be explained by changes in CH_4. Here we will use HALOE CH_4 measurements to better understand the annual cycle of ClO and CH_4. CH_4 data from both HALOE (through 2005) and from the Atmospheric Chemistry Experiment (ACE) [*De Mazie're et al.*, 2008] are invaluable for the interpretation of MLS ClO data, but ACE data are not used here because the sampling is quite sparse at the latitude of the Mauna Kea ground-based measurements.

[22] Annual changes in CH_4 are primarily caused by changes in age-of-air, with older air having experienced more methane oxidation. While Mauna Kea is near the tropics, where the CH_4 mixing ratio in the upper stratosphere peaks near January [*Wrotny et al.*, 2010], studies have shown that in the upper stratosphere and mesosphere this latitude shows seasonal variations characteristic of a Northern midlatitude site [e.g., *Nedoluha et al.*, 2007]. We therefore would expect the lowest CH_4 (and hence high ClO) values in the upper stratospheric air in winter when the air is older than in the summer.

[23] In Figure 6 we show, for the ground-based and convolved MLS data, the variation calculated from a fit to the first five terms in (1). These fits can be compared to the variations in ClO expected based on a chemical box model [*Siskind et al.*, 1998], which shows that the influence of small changes in CH_4 mixing ratio on the change in ClO mixing ratio can be expressed as

$$d[\mathrm{ClO}]/d[\mathrm{CH_4}] = -0.42 \times 10^{-3}. \qquad (2)$$

We apply this relationship to the monthly CH_4 data from HALOE (validated by *Park et al.* [1996]) values from 15°N–25°N. The ground-based ClO measurement resolution is much coarser than that of the HALOE CH_4 measurements (which have a vertical resolution of ~4.5 km [*Wrotny et al.*, 2010]), so we need to take into account how the finely resolved CH_4 changes affect the coarsely resolved ground-based ClO measurements. Since the ClO in (2) responds linearly to changes in CH_4, and since the convolution procedure is linear, it is appropriate to convolve the HALOE CH_4 data with the ClO averaging kernels as shown in Figure 1. Since we are studying the effects of changes in CH_4, we use an average CH_4 value as the a priori. This allows us to directly compare the coarse resolution ground-based and convolved MLS ClO measurements with the expected variation in coarse resolution ClO caused by variations in the fine resolution CH_4.

[24] Figure 6 shows that the seasonal variations in ClO calculated from (2) are at least qualitatively in agreement with the observed variations in ClO. There is a minimum in CH_4 in December and January, and this corresponds to the maximum in the ClO measurements. The CH_4 does show an indication of a semiannual cycle, which should result in a local maximum in ClO in June, but the semiannual cycle is more clearly apparent in the ClO measurement. Also the calculated annual variation based on the HALOE CH_4 is clearly somewhat larger than in the measured annual ClO variation.

4.3. Annual Averages

[25] In Figure 7 we show the annual averages of the ground-based and MLS measurements. Since Figure 2 shows that the UARS and Aura MLS measurements have no significant relative bias, we shall henceforth treat all of the MLS data as a single data set. We show results both for a simple average, and for an average modified by subtracting the seasonal variation (terms a_1–a_4) from a fit using the

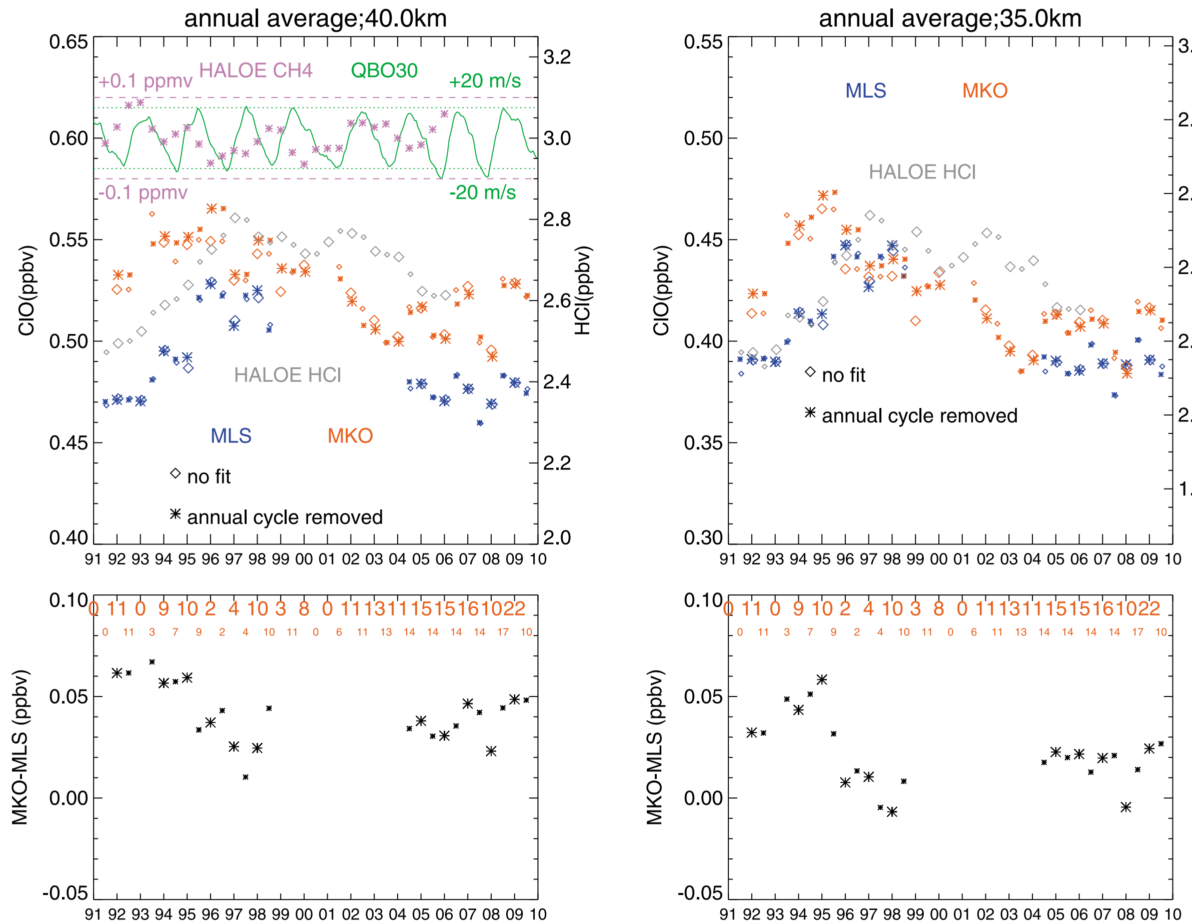

Figure 7. (top) Annual average mixing ratios at (left) 40 km and (right) 35 km. Results are shown for ground-based microwave measurements (red) and MLS (blue). Diamonds indicate raw average annual mixing ratios, and stars indicate mixing ratios with annual cycle removed (see text). Also shown are the HALOE HCl annual average mixing ratios (gray) with the scale on the right. These have been scaled to exactly 5 times the values of the ClO measurements at 40 km and 5.5 times the ClO measurements at 35 km, so fractional changes in ClO and HCl are directly comparable. The variation in HALOE CH4 annual average mixing ratios are shown only at 40 km (magenta). The green line indicates the 30 mb QBO wind anomaly. (bottom) The difference between MLS and MKO mixing ratios for each year. The numbers at the top of each of the bottom indicate the numbers of ground-based measurements included in the average. The larger symbols and numbers indicate July-June averages, while the smaller symbols indicate January-December averages.

terms in (1). Since the MLS measurements tend to sample evenly over the entire year, the difference between the raw average and the seasonally corrected average is generally small. The correction is largest for ground-based measurements in the 1990s, when the measurements tended to cluster in winter and early spring.

[26] As was shown in Figure 5, the interannual 40 km ClO variations from 2002 to 2009 seem to correlate with the QBO winds. This might suggest that QBO winds are driving changes in CH_4, which are in turn driving changes in ClO. At Figure 7 (top), we therefore show the 30 mb QBO winds and the monthly convolved HALOE CH_4 values. The annual cycle has been removed from the CH_4 measurements. The CH_4 variations are notable for the lack of any clear correlation with the QBO winds. We note that such a correlation is present in the tropical (10°S–10°N) HALOE CH_4 measurements [*Wrotny et al.*, 2010] but as was the case for the annual cycle, the QBO variations in CH_4 at Mauna Kea do not follow the tropical cycles. The absence of a clear correlation between the QBO winds and the CH_4 variations, coupled with the presence of clear correlation between QBO winds and ClO variations, suggests that perhaps another dynamically driven species, besides CH_4, may also be playing a role in the repartitioning of chlorine compounds. However, *Siskind et al.* [1998] found that, while the Cl/HCl ratio is dependent upon OH, CH_4, H_2, HO_2, and H_2CO, the CH_4 and H_2CO (which is produced from CH_4) terms account for 75% of the Cl loss from 35 to 50 km. Hence, it seems surprising that variations in any species besides CH_4 would cause such large QBO-like variations in ClO.

[27] While the relationship between ClO and CH_4 is clearly complicated, we can nevertheless use (1) to estimate the effect of long-term changes in CH_4 on ClO. During the early 1990s, there was a decrease in stratospheric CH_4

[*Nedoluha et al.*, 1998] and, as was pointed out by *Siskind et al.* [1998] and *Froidevaux et al.* [2000], the decrease in CH_4 from 1991 to 1997 contributed to the observed increase in ClO over that time period. Using (1), the effect of the CH_4 changes from 1991 to 1997 is to cause an increasing trend in ClO at these altitudes of ~2%/yr. Similarly, from 1997 to 2005, there was an overall increase (albeit with large year-to-year variations) in CH_4 which, based on (1), should contribute a decrease in ClO of ~−0.5%/yr over that time period.

[28] *Egorova et al.* [2005] modeled the effect of the 11 year solar cycle on changes in ClO. Their model showed, at the latitude of Mauna Kea, a ~2% increase from solar min to solar max at 35 km, and a ~1% increase at 40 km. Periods of high solar flux occurred in 1989–1992 and 2001–2002, with a minimum in 1996 and a prolonged period of low solar flux since ~2005 (data available from Lasp Interactive Solar Irradiance Datacenter [*Woods et al.*, 2000]), so from the effects of the solar cycle alone we might expect a minimum in ClO in 1996. While the effects of the solar variation are small when compared to the ~2%/yr effect of CH_4 from 1991 to 1997, they become particularly significant during more recent years when changes in ClO are small.

[29] We also show in Figure 7 the annual averages of the monthly HALOE HCl values [*Anderson et al.*, 2000], which have been convolved using the averaging kernels in Figure 1 (using the same method as for the CH_4). No annual cycle fit has been applied to these values. The right-hand scale has been chosen so that the HCl values are 5 times larger than the ClO values at 40 km, and 5.5 times larger than the ClO values at 35 km; hence, the fractional changes of ClO and HCl are directly comparable. Figure 7 shows clearly the increasing ClO until the mid-1990s and a clear decrease from the mid-1990s until ~2004. Since ~2004, both the Mauna Kea ground-based and coincident MLS Aura data sets appear to show a leveling off in the decline of ClO. We note that, while the measured ClO increases did qualitatively follow the large HCl increase observed until ~1996, the subsequent decrease in HCl has been much slower. *Froidevaux et al.* [2006] calculate a decrease of HCl of ~0.027 ppbv/yr for 2004–2006, which, at 40 km, represents a trend of ~1%/yr in HCl. Such a small trend is easily masked by the large year-to-year variations of as much as 7% in the annual ClO measurements, and we do not suggest that the leveling off in the decline of ClO is related to a change in the well measured decreasing HCl trend.

5. Conclusions

[30] The ground-based microwave measurements at Mauna Kea have been compared with UARS MLS and Aura MLS ClO measurements. Coincident measurements, using the ground-based measurements as a transfer standard, show that the UARS and Aura MLS ClO measurements agree to within 1% ± 4% near the peak of the ClO profile in the upper stratosphere. Thus, our analysis indicates that, within the uncertainties provided by the ground-based measurements, the UARS and Aura MLS measurements can be considered as a single unified data set, with no bias corrections between them needed. Coincident measurements within the UARS and Aura time periods also show no significant relative trend between the ground-based and satellite measurements.

[31] The Aura MLS and ground-based measurements also show good agreement in terms of seasonal and QBO variations. The seasonal variations in ClO are qualitatively consistent with the changes expected based on a box model and on the observed changes in CH_4 as measured by HALOE. The ground-based measurements from Mauna Kea, as well as the coincident satellite measurements, show an increase in ClO from ~1991 to 1996 and a decrease from ~1997 to 2009, with the decrease leveling off from ~2004 to 2009.

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References

Anderson, J., J. M. Russell III, S. Solomon, and L. E. Deaver (2000), Halogen Occultation Experiment confirmation of stratospheric chlorine decreases in accordance with the Montreal Protocol, *J. Geophys. Res.*, *105*(D4), 4483–4490, doi:10.1029/1999JD901075.

Barath, F. T., et al. (1993), The upper atmosphere research satellite microwave limb sounder instrument, *J. Geophys. Res.*, *98*(D6), 10,751–10,762, doi:10.1029/93JD00798.

Connor, B. J., T. Mooney, J. Barrett, P. Solomon, A. Parrish, and M. Santee (2007), Comparison of ClO measurements from the Aura Microwave Limb Sounder to ground-based microwave measurements at Scott Base, Antarctica, in spring 2005, *J. Geophys. Res.*, *112*, D24S42, doi:10.1029/2007JD008792.

De Mazie're, M., et al. (2008), Validation of ACE-FTS v2.2 methane profiles from the upper troposphere to the lower mesosphere, *Atmos. Chem. Phys.*, *8*, 2421–2435.

Egorova, T., et al. (2005), Influence of solar 11 year variability on chemical composition of the stratosphere and mesosphere simulated with a chemistry-climate model, *Adv. Space Res.*, *35*, 451–457.

Froidevaux, L., et al. (2000), Variations in the free chlorine content of the stratosphere (1991–1997): Anthropogenic, volcanic and methane influences, *J. Geophys. Res.*, *105*(D4), 4471–4481, doi:10.1029/1999JD901039.

Froidevaux, L., et al. (2006), Temporal decrease in upper atmospheric chlorine, *Geophys. Res. Lett.*, *33*, L23812, doi:10.1029/2006GL027600.

Livesey, N. J., W. G. Read, L. Froidevaux, J. W. Waters, M. L. Santee, H. C. Pumphrey, D. L. Wu, Z. Shippony, and R. F. Jarnot (2003), The UARS Microwave Limb Sounder version 5 data set: Theory, characterization, and validation, *J. Geophys. Res.*, *108*(D13), 4378, doi:10.1029/2002JD002273.

Molina, M., and F. S. Rowland (1974), Stratospheric sink for chlorofluoromethanes: Chlorine atomic catalysed destruction of ozone, *Nature*, *249*, 810–814.

Nedoluha, G. E., et al. (1998), Changes in upper stratospheric CH_4 and NO_2 as measured by HALOE and implications for changes in transport, *Geophys. Res. Lett.*, *25*(7), 987–990, doi:10.1029/98GL00489.

Nedoluha, G. E., et al. (2007), A comparison of middle atmospheric water vapor as measured by WVMS, EOS-MLS, and HALOE, *J. Geophys. Res.*, *112*, D24S39, doi:10.1029/2007JD008757.

Park, J. H., et al. (1996), Validation of halogen occultation experiment CH_4 measurements from the UARS, *J. Geophys. Res.*, *101*(D6), 10,183–10,203, doi:10.1029/95JD02736.

Parrish, A. (1994), Millimeter-wave remote sensing of ozone and trace constituents in the stratosphere, *IEEE Proc.*, *82*(12), 1915–1929.

Santee, M. L., et al. (2008), Validation of the Aura Microwave Limb Sounder ClO measurements, *J. Geophys. Res.*, *113*, D15S22, doi:10.1029/2007JD008762.

Siskind, D. E., L. Froidevaux, J. M. Russell, and J. Lean (1998), Implications of upper stratospheric trace constituent changes observed by HALOE for O_3 and ClO from 1992 to 1995, *Geophys. Res. Lett.*, *25*(18), 3513–3516, doi:10.1029/98GL02664.

Solomon, P. M., R. de Zafra, A. Parrish, and J. W. Barrett (1984), Diurnal variation of stratospheric chlorine monoxide: A critical test of chlorine chemistry in the ozone layer, *Science*, *224*, 1210–1214.
Solomon, P., et al. (2000), Seasonal observations of chlorine monoxide in the stratosphere over Antarctica during the 1996–1998 ozone holes and comparison with the SLIMCAT three-dimensional model, *J. Geophys. Res.*, *105*(D23), 28,979–29,001, doi:10.1029/2000JD900457.
Solomon, P., et al. (2002), Measurements of stratospheric ClO over Antarctica in 1996–2000 and implications for ClO dimer chemistry, *Geophys. Res. Lett.*, *29*(15), 1708, doi:10.1029/2002GL015232.
Solomon, P., et al. (2006), Rise and decline of active chlorine in the stratosphere, *Geophys. Res. Lett.*, *33*, L18807, doi:10.1029/2006GL027029.
Waters, J. W., et al. (2006), The Earth Observing System Microwave Limb Sounder (EOS MLS) on the Aura satellite, *IEEE Trans. Geosci. Remote Sens.*, *44*, 1075–1092.
Woods, T. N., W. K. Tobiska, G. J. Rottman, and J. R. Worden (2000), Improved solar Lyman α irradiance modeling from 1947 through 1999 based on UARS observations, *J. Geophys. Res.*, *105*(A12), 27,195–27,215, doi:10.1029/2000JA000051.
Wrotny, J. E., G. E. Nedoluha, C. Boone, G. P. Stiller, and J. P. McCormack (2010), Total hydrogen budget of the equatorial upper stratosphere, *J. Geophys. Res.*, *115*, D04302, doi:10.1029/2009JD012135.

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