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Re-analysis of ground-based microwave ClO measurements from Mauna Kea, 1992 to early 2012

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Abstract

We present a re-analysis of upper stratospheric ClO measurements from the ground-based millimeter-wave instrument from January 1992 to February 2012. These measurements are made as part of the Network for the Detection of Atmospheric Composition Change (NDACC) from Mauna Kea, Hawaii, (19.8° N, 204.5° E). Here, we use daytime and nighttime measurements together to form a day-night spectrum, from which the difference in the day and night profiles is retrieved. These results are then compared to the day-night difference profiles from the UARS and Aura Microwave Limb Sounder (MLS) instruments. We also compare them to our previous analyses of the same data, in which we retrieved the daytime ClO profile. The major focus will be on comparing the year-to-year and long-term changes in ClO derived by the two analysis methods. We conclude that the re-analyzed data set has less short-term variability and exhibits a more constant long-term trend. Data from 1995–2012 indicate a linear decline of mid-stratospheric ClO of $0.64 \pm 0.08\,\%\,\mathrm{yr}^{-1}$.

1 Introduction

Chlorine monoxide (ClO) in the stratosphere is the product of catalytic destruction of ozone by chlorine released from anthropogenic compounds, especially CFCs. Remote measurements of ClO were begun from Mauna Kea, Hawaii in 1982, and have been made near-continuously since 1992, barring interruptions for instrument repair (Solomon et al., 1984, 2006). The measurements are made by ground-based observation of thermally-excited spectral emission lines at 278.6 GHz, by a small telescope and radiometer designed for the purpose. This instrument, and its sibling at Scott Base, Antarctica (Solomon et al., 2000, Connor et al., 2007), have made the longest continuous records of stratospheric ClO in existence.

The calibrated spectra are prepared for analysis by subtraction of nighttime spectra from daytime ones, to remove interfering spectral lines and instrument artifacts. This

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technique was justified by Solomon et al. (1984) with a detailed discussion of ClO diurnal variation. More recently, Ricaud et al. (2000) has shown that mid-stratospheric ClO rises rapidly after sunrise from low nighttime values, while upper stratospheric ClO shows little diurnal variation. Thus, (except in polar spring), the ClO emission line is narrow and very weak during night. Previously published data from Mauna Kea (but not from Scott Base) were processed after interpolation of the nighttime spectra over a narrow region around the ClO frequency, which effectively removed the nighttime signal and produced a background spectrum. This was subtracted from the full daytime spectrum, to produce an estimate of the ClO daytime signal, which was then used to retrieve the full daytime ClO amount.

We show here that interpolation of the nighttime spectra introduces small, variable errors, which result in increased uncertainty in the long-term trend of stratospheric ClO. Consequently, we now simply subtract night spectra from day. We have re-analyzed the entire data set from January 1992 to February 2012, and present those results here.

2 Atmospheric spectra

In June 2009, the millimeter-wavelength receiver failed. It was repaired and rebuilt at the University of Massachusetts, and returned to service in December 2009. Fig. 1 shows the average daytime spectrum measured in January-June 2009 compared to that measured in the same period of 2010. In 2010, a broad spectral artifact, of apparent amplitude roughly half the ClO signal, is visible at higher frequencies, with a small but broad peak near ~278.72 GHz. Such an artifact can easily be rationalized as the product of millimeter-wavelength standing waves internal to the receiver, and is part of what is called the instrument's spectral "baseline". The subtraction of nighttime spectra from daytime ones is intended to remove the baseline, as well as the ozone emission lines which dominate the spectral window observed.

In Fig. 2 we enlarge the spectral region near the ClO signal, for 2009 (panel a) and 2010 (panel b). In each is shown the daytime and nighttime average, and the nighttime

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spectrum after interpolation over the 50 MHz wide region around the ClO line frequency (which we call "interpolated night" for brevity). This "interpolated night" spectrum provides a good estimate of all spectral components besides those contributed by the ClO emission. Thus, as described in the last section, subtracting "interpolated night" from the daytime spectrum produces an approximation to the daytime ClO emission independent of other atmospheric and all instrumental signals. This technique has served its purpose well, and has been applied in numerous publications over nearly 30 yr, most recently by Nedoluha et al. (2011). However, the interpolation function does not match the instrument baseline exactly, and so when the baseline character changes, a differential error is introduced. From Fig. 2 it is clear that the background curvature in the vicinity of the ClO line is very different in 2009 and 2010, due to the spectral artifact (change in instrument baseline) seen in Fig. 1. Thus one would expect somewhat different errors in the retrieved ClO in the 2 yr.

In Fig. 3 we show the spectra for 2009 and 2010 after subtraction of the nighttime spectra. In 3a we show the spectra of day minus "interpolated night", while in Fig. 3b is seen the spectrum of day minus night, without interpolation over the nighttime signal. Examination of Fig. 3a reveals an apparent difference of approximately 5 mK, or 7 %, in the amplitude of the 'day-interpolated night' ClO signal observed in 2009 and 2010. Figure 3b on the other hand shows that there is no difference in the 'day-night' ClO signal between the 2 yr large enough to be visible relative to the spectral noise.

Comparison of Fig. 3a and b illustrates that the procedure of simply subtracting night spectra from day is less sensitive to instrumental baseline artifacts than the more sophisticated interpolation procedure heretofore used in analysis of the Mauna Kea ClO data. Therefore we have adopted the simpler procedure, and now analyze the day-night difference spectrum, rather than attempting to estimate the daytime spectrum by subtracting 'interpolated night'. It is worth noting that this change to the algorithm makes it effectively identical to that used for the Scott Base ClO data. In Antarctic spring, the nighttime ClO line is highly variable and very broad in frequency; therefore we have

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never attempted to remove it by interpolation, and have always analyzed day-night spectra.

Further, since "day – interpolated night" spectra and altitude profiles are approximations to the daytime values, we will hereafter refer to them simply as "daytime".

3 ClO mixing ratio

3.1 Profiles

Retrievals from the daytime spectra of Fig. 3a suggest a significant decrease in ClO in 2010. On the other hand, retrievals from the day-night spectra in Fig. 3b show almost no change between 2009 and 2010. The difference between years is illustrated for both methods in Fig. 4. The significance of the change in daytime retrievals in 2010 is shown by the error bar in Fig. 5a, discussed below.

It would seem clear that the baseline artifact illustrated in Fig. 1 introduced a distortion of the nighttime spectrum seen in Fig. 2, resulting in a spurious difference between spectra for 2009 and 2010, as seen in Fig. 3a. That difference, and thus the spectral artifact, is the cause of the significant difference in ClO profiles in the 2 yr (Fig. 4).

3.2 Secular trend

In Fig. 5, we show time series of ClO mixing ratios from 1992 to 2012. Values shown are averages over a 5 km wide range near the peak of their altitude profile, for daytime (a) and day-night (b). Seasonal variations, of 3 to 12 month periods, have been separately derived and subtracted from each data set. Measurements averaged over periods of about one week are shown as "+" symbols, while large red dots are averages over periods of about one year. For convenience these are called 'weekly' and "annual" averages, respectively.

Both Fig. 5a and b show the values near the peak of the relevant ClO mixing ratio profile; however the pressure level of this peak is different for the two data sets because

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the nighttime ClO peak is at higher altitudes than the daytime ClO peak. Hence, the daytime ClO peak is at higher altitudes than the daytime ClO minus nighttime ClO peak. It is clear by inspection that the day-night time series is less scattered and more self-consistent, on both short and longer time scales, and appears consistent with a steady linear decrease in annual-average ClO mixing ratio over the period 1995-2012.

It is interesting to compare estimates of the long-term decrease in ClO, both between the two time series, and between two time periods. Solomon et al. (2006) reported the trend from 1995–2004, using an earlier version of the daytime data in Fig. 5a, so we compare 1995–2004 to 1995–2012, and show the results in Table 1. Uncertainties shown are one standard deviation in the slope from a simple linear regression of the deseasonalized weekly averages.

The linear trend inferred from the day-night analysis is less than that inferred from the daytime analysis, though the difference is insignificant for the full 17 yr period. Daytime annual averages would suggest that there have been significant variations (as shown by the error bars) in ClO on time scales of a few years, for example the higher values in 2008–2009. The day-night annual averages, on the other hand, have both smaller errors bars, reflecting less short-term variability, and show no significant departure from a linear decrease over the full period. Values slightly lower than average in 2003–2004 cause trends derived from the 1995–2004 period to be larger (more negative) than trends from the full period, for both data sets. The values in Table 1, from both time series, are consistent with the value of $-0.9 \pm 0.2\,\%\,\mathrm{yr}^{-1}$ for 1995–2007, which was based on the daytime data, and reported in WMO (2011).

We note in passing that the 'annual' point in mid-2003 is the only one from the day-night series that is more than 1σ from the linear trend line. It is slightly more than 2σ from the line and may indicate a real, relatively short-lived variation in mid-stratospheric ClO.

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4 Comparison to MLS Instruments

The revised Mauna Kea ClO profiles (MKO) agree reasonably well with measurements in a similar geographic region by UARS and Aura MLS instruments. In Fig. 6 (upper panel) is shown the mean of 118 coincident Aura and Mauna Kea ClO profiles. For Aura, the original and "convolved" profiles (combined with the ground-based averaging kernels and a priori profiles, e.g. Connor et al., 2007) are shown. In Fig. 6 (lower panel), the MLS-MKO mean difference is shown, for the 118 Aura profiles and for 24 UARS profiles. The smaller number of UARS coincidences is the result of both sparser UARS data and sparser ground-based data during the UARS years (see Fig. 4 of Nedoluha et al., 2011).

The error bars reflect the observed scatter in the actual comparisons; the estimated typical accuracy for MKO (Solomon et al., 2006) is shown separately; the MLS-MKO difference is everywhere less than the MKO accuracy. These comparisons of MLS to the revised MKO data are slightly improved relative to the previous version of the MKO data, which made use of daytime MKO profiles (Nedoluha et al., 2011). The scatter is very similar, while the mean difference is marginally smaller and also less oscillatory. The uncertainty in the UARS-MKO vs Aura-MKO comparison is essentially unchanged from that discussed in Nedoluha et al; thus their conclusion stands that UARS and Aura ClO can be used as a single data set without correction.

We have also compared calculations of the rate of decline of ClO between Mauna Kea and the Aura MLS instrument, August 2004 (Aura's start of operation) to 2012. The inferred linear decline is shown in Table 2 for both MKO and MLS. The two data sets agree well. Although the difference between them is formally a bit more than 1 standard deviation, it is equivalent to only ~2 % over the 7.5 yr period, which is well within the uncertainties of both instruments (Solomon et al., 2006; Santee et al., 2008; Livesey et al., 2011).

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5 Summary and conclusions

The failure and repair, in 2009, of the ClO millimeter-wave receiver at Mauna Kea, Hawaii, has led to a refined understanding of the long-term ClO record at that site. After repair, we observed what seemed to be an unexpected decrease in mid-stratospheric ClO. We have shown that this apparent change was due to a change in the instrument's spectral baseline, which was not fully corrected by the analysis procedure heretofore used routinely. The procedure in question attempted to retrieve the daytime ClO mixing ratio profile by subtracting a spectral baseline from which the nighttime ClO signal had been removed. The removal process caused small errors whose character changed as the system baseline itself changed. We have further shown that direct subtraction of the nighttime spectrum from the daytime one is largely free of this error.

In response to our new understanding of the effects of the analysis procedures, we reprocessed the entire Mauna Kea ClO data set, extending from 1991–2012. The new data set has less scatter than the earlier one, and the ClO exhibits a more constant and linear decrease over the entire period. Consequently we have adopted the "day-night" subtraction as the new standard procedure, and have replaced the Mauna Kea ClO in the NDACC database with the reprocessed version.

Using the reprocessed data set and the full 17 yr of measurements from early 1995 to early 2012, we report a long-term trend in stratospheric ClO of $-0.64\,\% \pm 0.08\,\%\,\mathrm{yr}^{-1}$, as shown in Fig. 1 and discussed further in the relevant text.

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Table 1. Long-term ClO decrease.

Day-night	
1995–2004	$-1.08 \pm 0.20\,\%\,yr^{-1}$
1995–2012*	$-0.64 \pm 0.08\,\%\,yr^{-1}$
Daytime	
1995–2004	$-1.45 \pm 0.19\,\%\,yr^{-1}$
1995–2012*	$-0.73 \pm 0.09\,\%\,yr^{-1}$

* last date is 18 February 2012

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Table 2. The linear decline in ClO (% yr^{-1} ± 1σ) near the peak of the day-night distribution (35 km), 2004–2012, from Aura MLS and Mauna Kea.

MLS	−0.48 ± 0.04
MKO	−0.78 ± 0.18

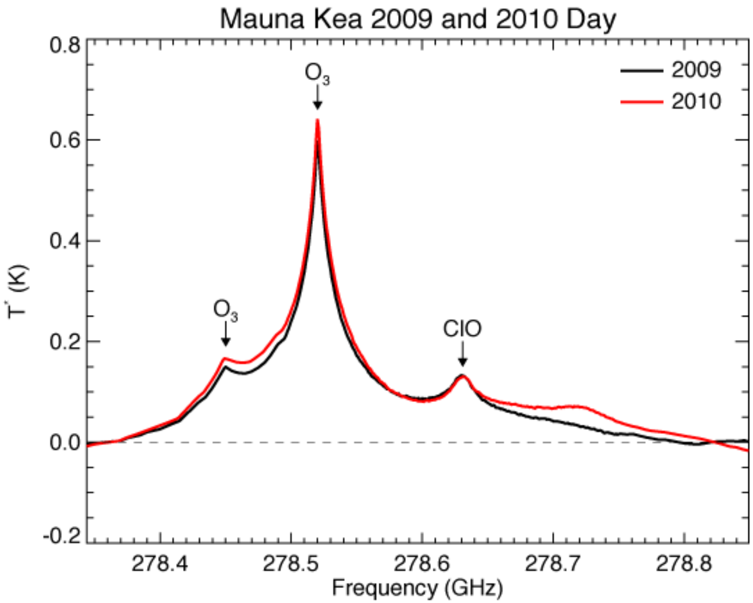

Fig. 1. Average daytime spectra in 2009 and 2010.

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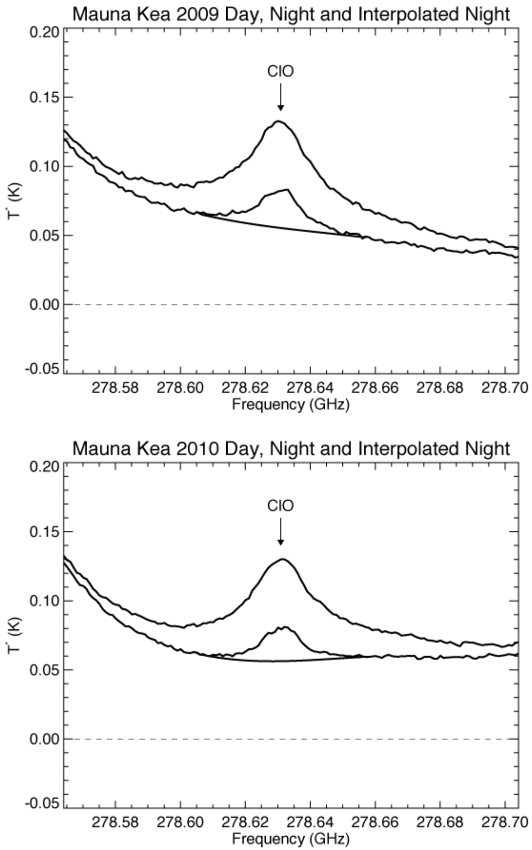

Fig. 2. Daytime, nighttime, and "interpolated nighttime'; average spectra in 2009 (top) and 2010 (bottom).

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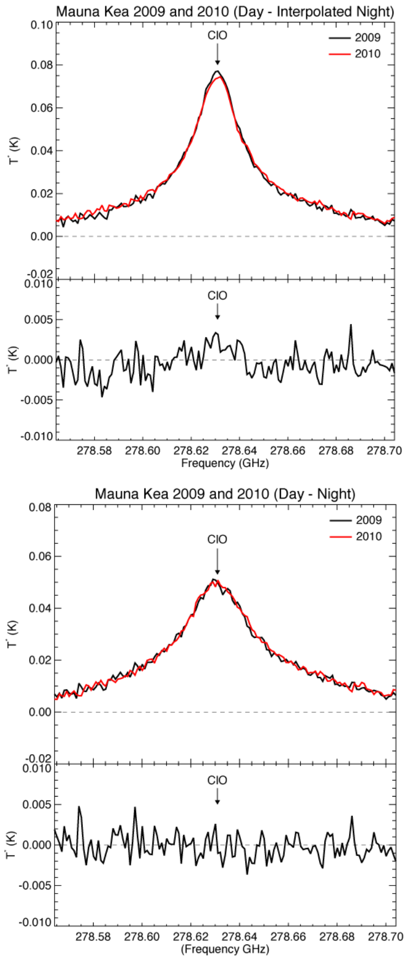

Fig. 3. Day-"interpolated night" and day-night average spectra for 2009 and 2010, and the difference of the 2 yr.

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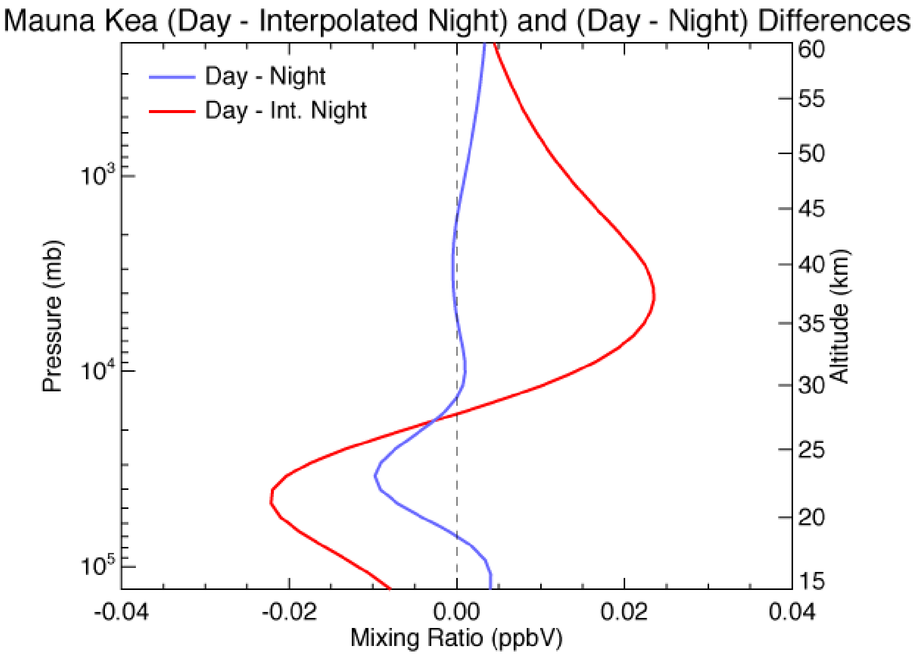

Fig. 4. Change in ClO between 2009 and 2010, with and without the revised analysis.

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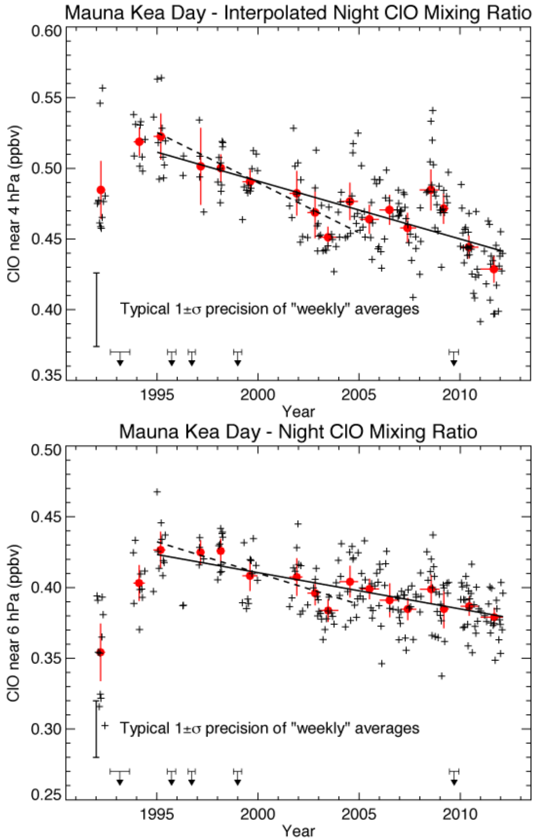

Fig. 5. Time series of peak ClO mixing ratios over Mauna Kea, 1992–2012. Data in **(a)** is derived from daytime spectra, while for data in **(b)** simple day-night spectra are used. The dashed lines show regression fits to data from 1995–2004, while solid lines are regression for 1995–2012.

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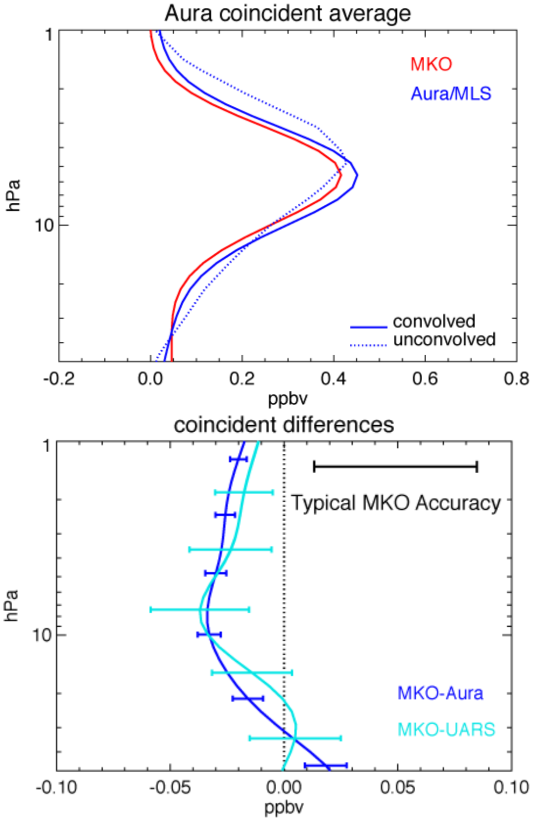

Fig. 6. Comparison of revised Mauna Kea ClO to that from Aura and UARS MLS.