A Supplement to "Re-analysis of ground-based microwave ClO measurements from Mauna Kea, 1992 to early 2012" by B. J. Connor et al., ACPD 12, 1-18, 2012

Altitude sensitivity and the effect of nighttime ClO on determination of trends

2 March 2013

Because the comments of the three referees had much in common, we have prepared the following document, which addresses many of their comments. Its material will be incorporated in a revised manuscript should we be asked to submit one.

Altitude sensitivity

The averaging kernels for the Mauna Kea ClO retrieval are shown in Fig. 1. These are effectively the same as shown in Nedoluha et al, 2011. They indicate that the sensitivity of the retrieval to the ClO profile is reasonably good from 15-45 km; at higher altitudes it decreases rapidly. This occurs because the observed ClO signal is in fact a group of hyperfine transitions, concentrated in a ~10 MHz wide spectral band. The pressure broadened linewidth is 10 MHz at ~4 hPa pressure, which is effectively the highest level where the retrieval has any sensitivity to altitude.

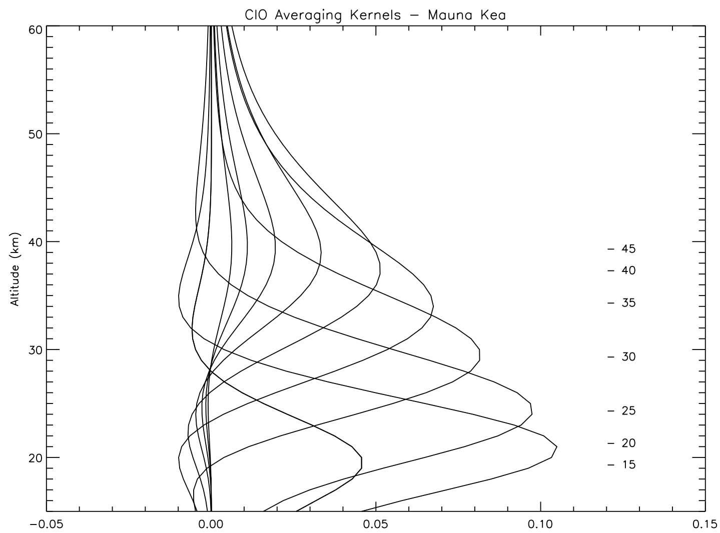

Figure 1. The averaging kernels of the Mauna Kea ClO retrieval for selected altitudes from 15 to 60 km. The labels to the right indicate the actual peak altitude of the function for the specified altitude. The functions for 50, 55, and 60 km are also shown; their amplitudes progressively decline, while the maximum value of all 3 is at about 40 km. They are not labeled to avoid clutter.

The averaging kernels are identically the same for both analysis methods, because the absolute spectral sensitivity is the same, to both the daytime and day-night mixing ratios. But of course, the daytime and day-night difference profiles are not the same things, and to assess the effect of switching analysis methods, there are two key questions. First, how different are the measured quantities, in particular the peak mixing ratios on which we base our trend determination? Second, does using the day-night value improve or detract from our ability for scientific interpretation of the data record? We will address the first question in the next few paragraphs, and the second question in the discussion of Trend Comparisons, below.

The effect of the nighttime profile on the day-night measurement was assessed as follows. First, a subset of the Aura data was created, including all the ClO profiles measured within ± 5° latitude and ± 30° longitude of Mauna Kea, between 2004 and early 2013. These are unambiguously day (local time near 1330) or night (local time near 0155). Daytime, nighttime, and day-night mean profiles were calculated from these data. The mean daytime and day-night profiles were convolved with the microwave averaging kernels and a priori profiles, and the mean value between 33-37 km was calculated from each convolved profile. This mean is defined as the 'peak mixing ratio' of the day-night MKO measurements. We use it for both daytime and day-night profiles here so we can isolate the effect of subtracting the nighttime profile. The daytime and day-night mean values differ by 16%, and we conclude that is the extent of the effect of nighttime ClO, in the upper stratosphere and mesosphere, on the retrieved day-night values.

Concern has been expressed in particular about the influence of mesospheric ClO on the day-night measurement, since the chemical processes operating in the mesosphere are rather different from those in the stratosphere. To quantify that effect, we tested how the day-night measurement would change if the mixing ratio of nighttime ClO was equal to zero at all altitudes in the mesosphere. In that case, the derived day-night value would increase by ~5%.

It is also worth considering the implications for trend determination. Mesospheric ClO could well have a different trend from stratospheric ClO. It is influenced by CH4 and total chlorine, while nighttime upper stratospheric ClO depends on NO2 as well. (Sato et al, 2012). However the fact that mesospheric ClO only affects our day-night 'peak mixing ratio' by ~5% indicates that any differential trend in the mesosphere would have a similarly small impact on our trend computation.

We note in passing that for comparison of our results to models and to other available measurements, in particular MLS and SMILES, it is a simple matter to compute the convolved day-night profile from the other data set, and said convolved profile is directly equivalent to the ground-based measurement. In the following section we make such a comparison to Aura MLS, expanding on the more limited results in the discussion paper.

Trend comparisons

The reported trends in the MKO time series were calculated as follows. Measurements are averaged over periods of about one week, as described in section 3.2. The mixing ratio profiles retrieved from these measurements are then averaged between 33-37 km for day-night, and 35-39 km for daytime. These two ranges were chosen to represent the typical altitude of the peak mixing ratio of the day-night and daytime profiles, ± 2 km. The resulting values are the 'peak mixing ratios' plotted with symbol + in Fig 5. The time series of weekly peak mixing ratios is then fit, by simple linear regression, over a selected time period, with a function including a constant, linear slope, and sine and cosine functions with periods of 3, 4, 6, and 12 months. The linear slope and its uncertainty are then quoted as the 'trend' ± 1σ. In the discussion paper, we followed our past standard practice of reporting the 1σ uncertainty. However, for ease of comparison to other published estimates, we have quoted a 2σ uncertainty in the following tables, and will adopt that practice uniformly in a revised manuscript.

Questions have been raised as to whether the transition from estimated daytime retrievals to day-night does in fact improve the trend determination. To address them, we will first compare trends over several time periods from the two analysis methods, then compare those to Aura measurements in the vicinity of Hawaii, and finally to other, selected published values.

Table 1: Mauna Kea ClO Observations

Day-night (33-37km)	
1995 - 2004	-1.08 ± 0.40 %/yr
2001[1] - 2008	-0.32 ± 0.48
2004[2] - 2012	-0.79 ± 0.40
1995 - 2012[3]	-0.64 ± 0.15
Daytime (35-39km)	
1995 - 2004	-1.45 ± 0.38 %/yr
2001[1] - 2008	+0.22 ± 0.44
2004[2]- 2012	-1.45 ± 0.48
1995 - 2012[3]	-0.86[4] ± 0.17

[1]July 2001 following extended instrument repair
[2]Aug 2004 to coincide with Aura operations
[3]last date is 18 February 2012
[4]a value for 1995-2010 (-0.73) was incorrectly reported in the discussion paper

Three of the time periods selected were chosen for comparison to other results. 1995-2004 was the period reported in Solomon et al, 2006. 2001-2008 is used by Jones et al, 2011, and Aug. 2004 – Feb 2012 is for comparison to Aura data. In addition to the observations made in the discussion paper, two notable features are worthy of comment. First, the daytime retrievals produce trend estimates which vary much more than the corresponding day-night retrievals. Secondly, while the error bars of the two analyses overlap for the full period (1995-2012), the uncertainty of the fit to the day-night data is somewhat smaller. Both of these factors suggest the day-night analysis is more stable than using the estimated daytime values.

Comparisons to Aura

Table 2 – Aura ClO* Convolved with Mauna Kea Averaging Kernels

Day-night	-0.48 ± 0.08%/yr
Daytime	-0.56 ± 0.08%/yr

*Aug 2004 – 18 Feb 2012

The values in Table 2 have been calculated from the original Aura profiles, selected in the region of Hawaii, by convolving them with the ground-based averaging kernels and a priori, and averaging them over altitude to derive the 'peak mixing ratio' as described above. They are directly comparable to the '2004-2012' figures of Table 1. The day-night values are in good agreement (-0.48 ± 0.08%/yr vs. -0.79 ± 0.40%/yr), while the daytime values suggest a significant discrepancy (-0.56 ± 0.08%/yr vs. -1.45 ± 0.48%/yr). It is our view that this apparent discrepancy is an artifact of the Mauna Kea 'daytime' estimate, and we take the agreement of the day-night values between Mauna Kea and Aura as validation of the analysis procedure introduced in this paper.

Comparisons to Published Results

There is a fairly limited selection of published results which are directly comparable to the Mauna Kea ClO measurements. To the best of our knowledge, the only published long-term ClO trend estimate is in Jones et al, 2011. The authors have performed a sophisticated analysis which allows them to combine different satellite data sets. In the case of ClO, they have published a trend in the 35-45 km altitude region using a data set which combines Aura MLS with the Odin Sub-millimeter Radiometer. We note that our 45km averaging kernel peaks near 40km, hence a direct comparison with the Jones et al. altitude ranges is not possible. For the period 2001-2008, they find a trend of -0.71 ± 0.78 %/yr. The comparable number for day-night at Mauna Kea, from Table 1, is -0.32 ± 0.48,
thus the two central values are consistent. The daytime estimate of +0.22 ± 0.44 from Table 1 differs from the Jones et al (2011) value by approximately 3σ. We believe this is another point validating our day-night analysis.

Comparison of the ClO trend to other chlorine species is certainly possible (e.g. WMO 2010, Table 1-13), and informative about the evolution of stratospheric chemistry, but complicated by dependencies on the concentration of CH4 and NO2 (Jones et al, 2011). Thus its value as validation for a given technique is debatable.
In the interests of rounding out the context of our results we will briefly look at trends in stratospheric HCl.

Table 3. HCl trends

Mauna Loa[1]	total column	2000-2009	-0.39 ± 0.19%/yr
Izana[1]	total column	2000-2009	-0.66 ± 0.15
Tropics[2]	35-45 km	1997-2008	-0.58 ± 0.17
Global[3]	upper stratosphere	2004-2010	-0.6 ± 0.1

[1] Kohlhepp, 2012
[2] Jones et al, 2011
[3] MLS, WMO 2010, Table 1-13

It is beyond the scope of this study to quantitatively compare these HCl trends to our measured ClO trends. We note that "measured ClO trends are not directly comparable to changes in total stratospheric chlorine" (WMO, 2011). It would be interesting in a future study to use observed changes in CH4, which have varied substantially since the mid 1990s (Kohlhepp, 2012), to compute the chlorine change implied by the observed ClO changes at Mauna Kea over selected time periods, and in turn compare that to total stratospheric chlorine, represented by the sum HCl + ClONO2.

Jones, A., J. Urban, D.P. Murtagh, c. Sanchez, K.A. Walker, N.J. Livesey, L. Froidevaux, and M.L. Santee, Analysis of HCl and ClO time series in the upper stratosphere using satellite data sets, ACP-11-5321-2011, 2011.

Kohlhepp, R.: Trends of stratospheric chlorine and fluorine reservoir species, PhD Thesis, Karlsruhe Institute of Technology, 2012.

Sato, T. O., H. Sagawa, D. Kreyling, T. Manabe, S. Ochiai, K. Kikuchi, P. Baron, J. Mendrok, J. Urban, D. Murtagh, M. Yasui, and Y. Kasai, Strato-mesospheric ClO observations by SMILES: error analysis and diurnal variation. Atmos. Meas. Tech., 5, 2809–2825, 2012.