Observations of chlorine monoxide over Scott Base, Antarctica, during the ozone hole, 1996-2005

Brian Connor,[1] Philip Solomon,[2] James Barrett,[2] Thomas Mooney,[2] and Alan Parrish[3]

[1]National Institute of Water and Atmospheric Research, Lauder, New Zealand (b.connor@niwa.co.nz)
[2]Department of Physics and Astronomy, Stony Brook University, Stony Brook, NY 11794, USA (Philip.Solomon@stonybrook.edu)
[3]Department of Astronomy, University of Massachusetts, Amherst, MA 01003 USA (aparrish@astro.umass.edu)

Abstract We report observations of chlorine monoxide, ClO, in the lower stratosphere, made from Scott Base (77.85º S, 166.77º E) in springtime during each year, 1996-2005. The ClO amounts in the atmosphere are retrieved from remote measurements of microwave emission spectra. ClO column densities of up to about 2.5×10^{15} cm^{-2} are recorded during September, when chlorine is present in chemically active forms due to reactions on the surface of Polar Stratospheric Cloud (PSC) particles. Maximum mixing ratios of ClO are approximately 2 ppbv. The annual average of ClO column density during the activation period is anticorrelated with similar averages of ozone column measured at nearby Arrival Heights, with correlation coefficient of –0.81, and with averages of ozone mass integrated over the entire polar region, with similar correlation coefficients. There was a substantial decrease in ClO amounts during 2002-2004. There has been no systematic change in the timing of chlorine deactivation attributable to secular change in the Antarctic vortex.

Citation: Connor, Brian, Philip Solomon, James Barrett, Thomas Mooney, and Alan Parrish (2007), Observations of chlorine monoxide over Scott Base, Antarctica, during the ozone hole, 1996-2005, in Antarctica: A Keystone in a Changing World – Online Proceedings of the 10th ISAES, edited by A. K. Cooper and C. R. Raymond et al., USGS Open-File Report 2007-1047, 4 p.; doi:10.3133/of2007-1047.srp077

Introduction

Chlorine monoxide, ClO, is central to the formation of the Antarctic ozone hole. It is both the direct product of the reaction between Cl and ozone and the catalytic agent in the most important ozone-depleting chemical cycle (Waters et al., 1993, Salawitch et al., 1993). Stony Brook and NIWA have jointly operated an automated ground-based millimeter wave spectrometer measuring ClO at Scott Base, Antarctica, since February 1996. It has made the only routine, near continuous ClO measurements in Antarctica since then. A predecessor instrument made the first observation of enhanced lower stratospheric ClO in the ozone hole, in 1986 (Solomon et al., 1987).

In this paper, we first give a brief overview of the measurement technique, and then present results of the ten-year time series, 1996-2005, in some detail. We examine the variation of ClO from day-to-day and year-to-year. We compare annual average ClO to measures of ozone depletion, both locally and continent-wide. Finally we ask whether the evolution of ClO with day number has changed significantly over the 10 years of observation.

ClO Measurements

We observe an emission line of ClO at wavelength ~ 1 mm. This line is thermally excited, and allows observation around the clock and throughout the year. The spectrometer bandwidth permits measurement of the pressure-broadened lineshape from which ClO altitude profiles between 15 and 40 km are retrieved using 'optimal estimation' (Rodgers, 2000).

The measured spectra, their calibration, the retrieval of ClO from them, and their error analysis, are described in detail in Solomon et al. (2000, 2002). In brief, the instrument is a cryogenically cooled (~ 20 K) heterodyne receiver, tuned to observe the ClO transition at 278.631 GHz by adjustment of a phase-locked local oscillator. It is coupled to a spectrometer with 506 MHz total bandwidth, which is approximately the width of the ClO line at 15 km altitude.

The ClO line is pressure broadened throughout the lower and middle stratosphere. Its width is then approximately an exponential function of altitude, and the shape of the observed emission (integrated over altitude) is a sensitive function of the ClO altitude distribution. This sensitivity allows the ClO altitude distribution to be retrieved from the spectra.

At night, the ClO emission is much weaker and narrower, because nearly all chemically active chlorine ('ClO_x') rapidly converts to Cl_2O_2 after sunset in the lower stratosphere (Solomon et al., 2002). This allows us to remove the instrumental baseline and a small number of interfering atmospheric spectral lines in the instrument bandpass (primarily the ozone line at 278.521 GHz), by subtracting the nighttime spectrum from the daytime one.

Discussion

ClO column density and peak mixing ratio

Figure 1 shows the ClO column density and peak mixing ratio as a function of time, with day of year on the x-axis and year on the y-axis. It may be seen that maximum values of ClO occur during the period of days 240-260, and that timing of the onset of ClO varies less than the timing of its annual decline. The multi-year record shows that the highest values of ClO occurred in 1999-2000, that values were consistently low in 2002-2004, but rebounded significantly in 2005. In addition, there is a hint of the annual decline occurring earlier over the course of the 10 years.

The peak mixing ratio plot shows essentially the same features as the column density. Since column density is more related to the large-scale features of the polar vortex, we will use it exclusively from here on.

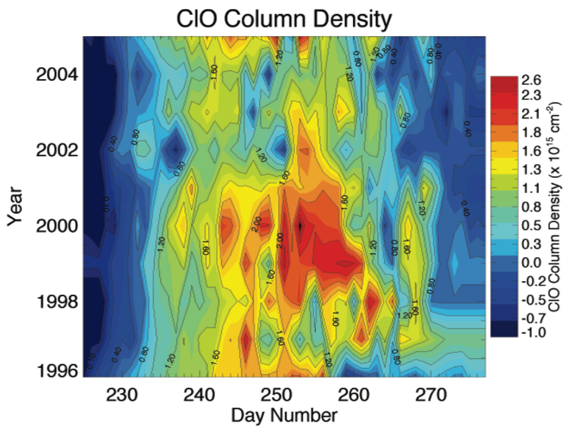

Figure 1a. ClO column density (10^{15} cm^{-2}) vs. day number and year.

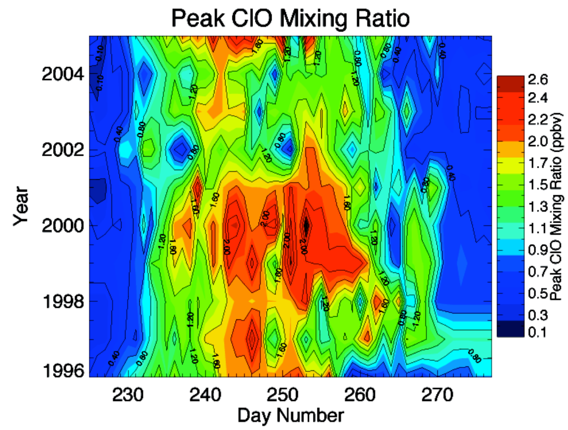

Figure 1b. The peak value of the ClO mixing ratio (ppbv) at 18-21 km altitude vs. day number and year.

Annual averages of column density

We have computed the average ClO column density for each year, over selected ranges of day number. The results are shown in Fig. 2. The day number ranges have included the entire period of springtime day-night observation (days 225-277), and subsets of that range. Shown in the Figure are September only (244-273) and days 240-270, chosen as the 30-day period when ClO was highest on average. Whichever period is chosen, there are relatively large values in 1997-2001, significantly smaller values in 2002-2004, and intermediate values in 1996 and 2005. Inspection of ozone maps observed by the TOMS satellite (not shown, but available on-line at http://jwocky.gsfc.nasa.gov/) shows 1996 was lower than 1997-2001 primarily because the vortex moved away from the Scott Base region by day 260 of 1996, though it remained intact. Thus Scott Base was not well placed to sample vortex air for part of the year.

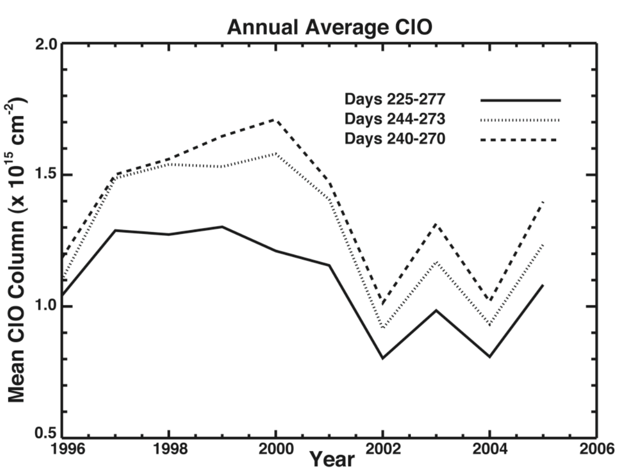

Figure 2. Average column density of ClO for different periods during each year.

Which range of day numbers is used makes relatively little difference in the year-to-year variation in ClO. Averaging over the full period essentially integrates over the total amount of ClO available for ozone depletion in that year. For both these reasons, we have chosen to use the full period, days 225-277, for further analysis in the next section.

Correlations of annual averages with measures of ozone

Not surprisingly, the annual average ClO column is strongly anti-correlated with measures of ozone in the polar vortex. We have assessed ClO correlations with 4 different ozone time series. Three of the ozone series are derived from the total ozone mass at 60º-90º S, taken from the NIWA global ozone mass data set (Bodeker et al. 2005), namely the ozone mass averages over September, October, and the 3 month period September through November ('SON'), less the corresponding averages for the period 1979-1981. The fourth ozone measure is the ozone column measured by Dobson spectrophotometer at Arrival Heights (3 km from Scott Base), averaged over days 258-300. The correlation coefficients and their statistical significance are shown in the following table:

O_3 Data Set	r	p
O_3 Mass, Sept	-0.68	0.016
O_3 Mass, Oct	-0.82	0.005
O_3 Mass, SON	-0.76	0.008
Arrival Heights	-0.81	0.005

The correlations of annual ClO to the October O_3 mass and to Arrival Heights O_3 are stronger than to the SON mass, or the September mass alone, although the differences are too small to be significant. Figures 3a and 3b show comparison of ClO column averaged over days 225-277 to the October O_3 mass and to the Arrival Heights column. Fig. 3a shows the 3 time series as a function of year, and Fig. 3b plots annual ozone vs. ClO directly, and regression lines fit to the ozone and ClO data sets.

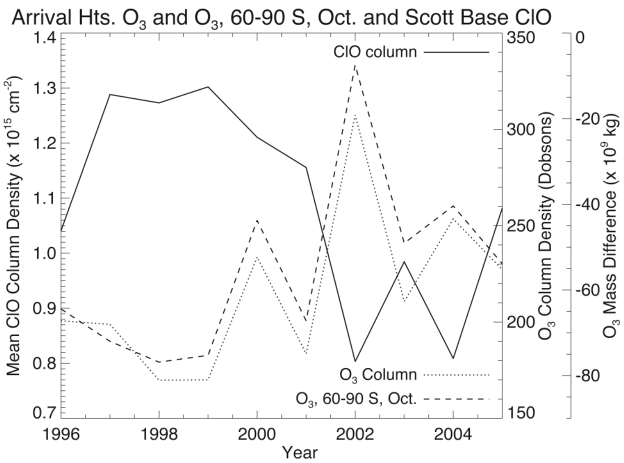

Figure 3a. Time series of annual mean ClO column and ozone at Arrival heights, averaged over 60° - 90° S in October.

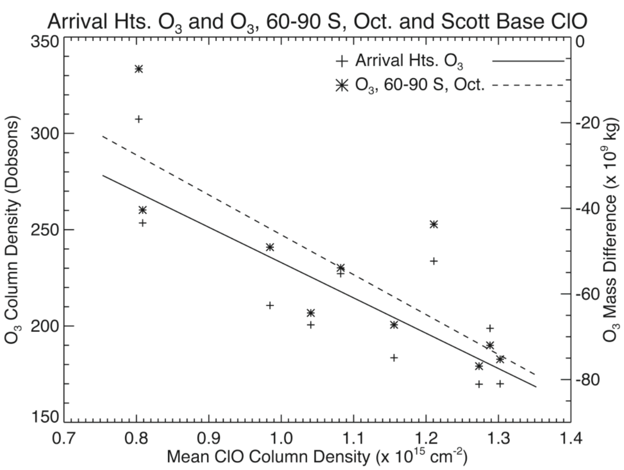

Figure 3b. The same ozone series vs. ClO column and linear regression fits to the data sets.

Total ozone will lag the presence of ClO by a time period of order a few weeks in the Antarctic spring, based on various observations and on model calculations (Ko et al., 1989). That is, in the presence of a constant amount of ClO_x, O_3 will be gradually depleted over several weeks. So it is reasonable to correlate ClO averaged over mid-August to September with O_3 several weeks later. This may even explain the improved correlation to the October O_3 mass data. Second, because of the selection of time periods, the Arrival Heights and Scott Base data are not 'coincident'. However, they are of course at essentially the same latitude.

Finally, the observed anti-correlation suggests that sampling ozone and ClO at the Arrival Heights/Scott Base location, and integrating over the season, is, on average, representative of the Antarctic vortex as a whole. There are exceptions, such as 1996, discussed above, and perhaps 2000.

Evolution of ClO with Day of Year

As we can see in Figure 1, there is considerable year-to-year variation in the evolution of ClO with time of year. This is shown more clearly in Fig. 4a, which displays the daily time series for all 10 years, as well as the 10-year average. Through August (days ~ 225 – 245), ClO increases steadily, with relatively little year-to-year variation. This reflects the fact that the Antarctic vortex is cold and stable during this time, and daytime ClO increases as the sun reappears, in direct proportion to noontime insolation. An exception is 2002, when an anomalous, major stratospheric warming occurred in late August (Newman & Nash, 2005). During September, there is much more year-to-year variability. This reflects increasing temperature as the sun rises. At a precise

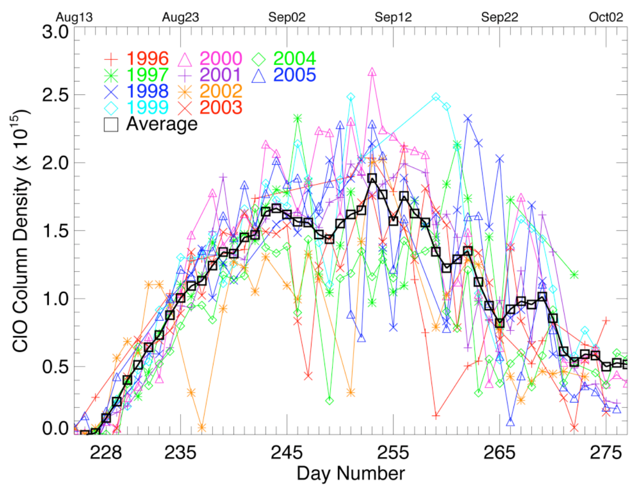

Figure 4a. ClO for each of the years 1996-2005 and the average of the ten years vs. day number.

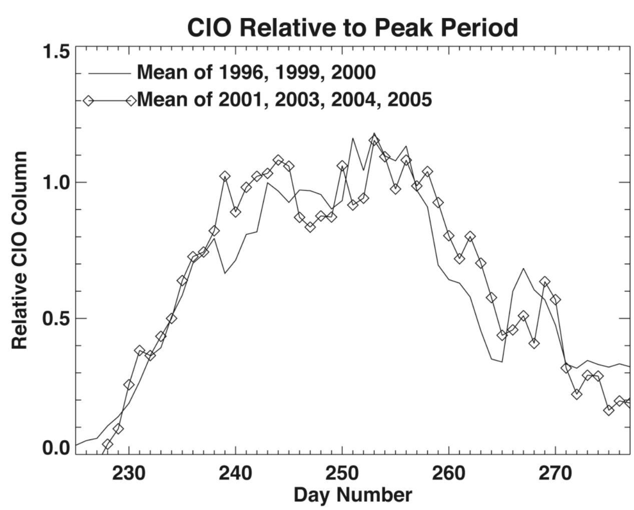

Figure 4b. Average ClO for selected subsets of years relative to the average value in the period of days 243-258.

threshold of temperature (varying slightly with pressure), evaporation of PSC particles will occur, after which chlorine is deactivated into its reservoir species over a period of several days, primarily by reaction with CH_4 (Douglass et al., 1995). Once this threshold is neared, chlorine activation varies widely with time and location, responding to small variations in temperature. The question arises, whether the timing of chlorine deactivation has changed on average during the ten years under study. As just described, this timing could be a sensitive indicator of change in stratospheric temperature in Antarctic spring. To investigate this question, we divided the ten years into two five-year periods, and compared the ClO seasonal variation in the two periods. We paid particular attention to data taken in the last week during which there is sufficient nighttime in the stratosphere for our day-night processing, namely days 271-277. That week was well sampled in 7 of the 10 years of observation. Excluding the three poorly sampled years, we examine an average of 1996, 1999, and 2000, compared to 2001 and 2003 - 2005. We further adjusted for changes in the annual amounts of ClO (Figs. 2 and 3) by averaging days 243-258 in each year, and dividing the daily values by this average. The decrease in this ratio in the latter part of September represents Cl deactivation.

The result is shown in Fig 4b. The two periods agree very well through day 238. After that, they depart from each other by ~10% for periods of several days; however neither remains systematically higher than the other. In particular during the deactivation phase (after day ~ 258) the two curves cross each other four times. In the day 271-277 period, the years through 2000 are significantly higher than the later years, relative to the observed day-to-day variability, by 6.6 ± 3.1%. However, the fact that there is no consistent relationship between the early and late years over the whole time of deactivation precludes attributing this result to a secular evolution of the vortex.

Summary

Annual mean ClO column density measured at Scott Base is strongly anti-correlated to ozone values, both locally measured and integrated over the Antarctic vortex, with significance of 99%. Average ClO values were consistently lower in 2002-2004 than through 2001 or during 2005, corresponding to relatively high ozone values during those years.

The amount of lower stratospheric ClO is very similar in August of each year, very variable both day-to-day and year-to-year during September, and largely gone, through conversion to reservoir chlorine species, by October. There is no conclusive evidence that the timing of this deactivation has systematically changed since 1996.

Acknowledgements. We thank the Foundation for Research, Science, and Technology (New Zealand) and NASA for financial support, and Antarctica New Zealand for logistical support. We are particularly grateful to Stephen Wood, Michael Kotkamp, and the Scott Base staff for essential technical and logistical contributions to the measurements.

References

Bodeker, G., Shiona H. and H. Eskes, Indicators of Antarctic ozone depletion (2005), Atmos. Chem. Phys., 5, 2603-2615.

Douglass, A.R., M.R. Schoeberl, R.S. Stolarski, J.W. Waters, J.M. Russell, A.E. Roche, and S.T. Massie (1995), Interhemispheric differences in springtime production of HCl and $ClONO_2$ in the polar vortices, J. Geophys. Res., 100 (D7), 13967-13978.

Ko, M., J. Rodriguez, N.D. Sze, M. Proffitt, W. Starr, A. Krueger, E. Browell, and M.P. McCormick (1989), Implications of Airborne Antarctic Ozone Experiment observations for proposed chemical explanations of the seasonal and interannual behavior of Antarctic ozone, J. Geophys. Res., 94, 16,704.

Newman, P., and E. Nash (2005), The Unusual Southern Hemisphere Stratosphere Winter of 2002, J. Atmos. Sci., 62, 614-628.

Rodgers, C. D. (2000), *Inverse Methods for Atmospheric Sounding*, World Scientific Publishing Co., Hackensack, NJ.

Salawitch, R. J., et al. (1993), Chemical loss of ozone in the Arctic polar vortex in the winter of 1991-1992, Science, 261, 1146-1149.

Solomon, P. M., B. Connor, R. L. de Zafra, A. Parrish, J. Barrett, and M. Jaramillo (1987), High concentrations of chlorine monoxide at low altitudes in the Antarctic spring stratosphere: Secular variation, Nature, 328, 411-413.

Solomon, P., J. Barrett, B.J. Connor, S. Zoonematkermani, A. Parrish, A.M. Lee, J.A. Pyle, and M.P. Chipperfield (2000), Seasonal observations of chlorine monoxide in the stratosphere over Antarctica during the 1996-1998 ozone holes and comparison with the SLIMCAT 3D model, J. Geophys. Res., 105 (D23), 28979-29001.

Solomon, P., B. Connor, J. Barrett, T. Mooney, A. Lee, and A. Parrish (2002), Measurements of stratospheric ClO over Antarctica in 1996-2000 and implications for ClO dimer chemistry, Geophys. Res. Lett., 29 (15), 10.1029/2002GL015232, 2002.

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