

20 Years of ClO Measurements in the Antarctic Lower Stratosphere

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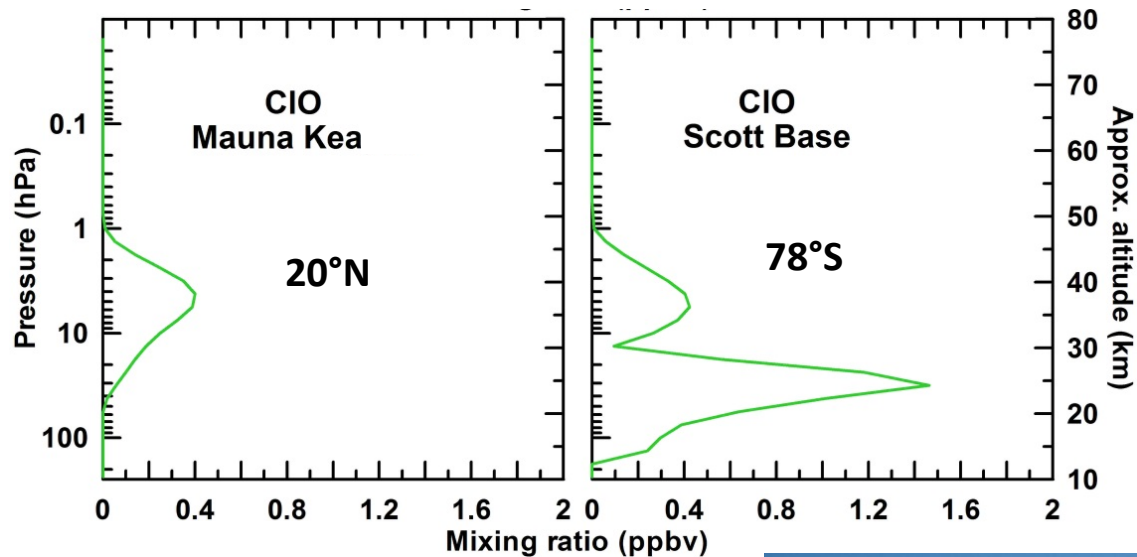
Ground-based Antarctic ClO Measurements

- Ground-based measurements of ClO, by microwave emission at 278.6 GHz, first made in the Antarctic during NOZE campaign in 1986.*
- NOZE was mounted by NASA in response to discovery of the Antarctic ozone hole.
- Radiometer was a first-generation device requiring 24 hr/day of expert attention.
- Second generation instruments operate remotely, at Mauna Kea, Hawaii 1992-2015 and Scott Base Antarctica, 1996-present
- Third generation instrument under testing and development at Mauna Loa, Hawaii

*deZafra et al, 1987, Solomon et al, 1987

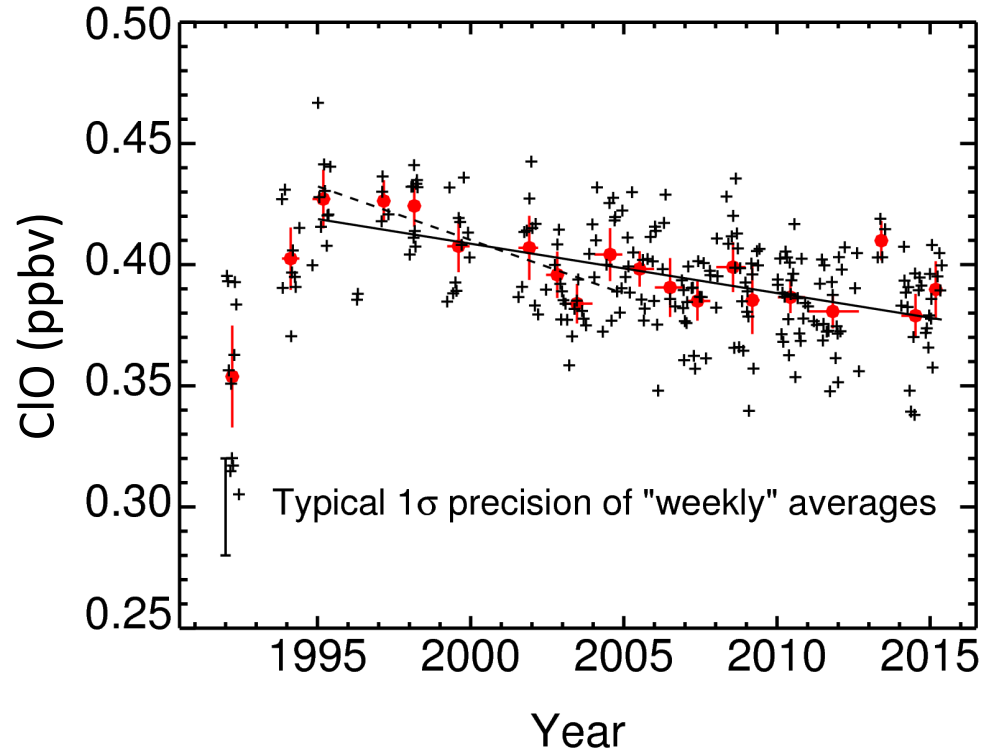
**We have measurements of ClO from two sites:
Mauna Kea, Hawaii and Scott Base, Antarctica.**

- The Mauna Kea site is at 4.3km, so the low tropospheric optical depth allows us to make ~weekly measurements of the smaller upper stratospheric ClO peak. (brief update)
- The Scott Base site is at sea level. When ClO mixing ratios in the polar vortex are high it is possible to make daily ClO measurements from this site. (focus of this talk)



Measurements from Mauna Kea since 1992

Day – Night ClO at 6 hPa



Seasonal variation is removed.

Red dots are annual averages

ChLOE1 measurements show that ClO over Mauna Kea began to decrease in ~1995.

1995 - 2005 Decline = 0.82 ± 0.16 %/yr

2005 - 2015 Decline = 0.32 ± 0.13 %/yr

1995 - 2015 Decline = 0.49 ± 0.06 %/yr

Lower stratospheric, polar ClO is highly variable, both day-to-day and year-to-year. Can we come up with a ClO trend estimate for Antarctica?

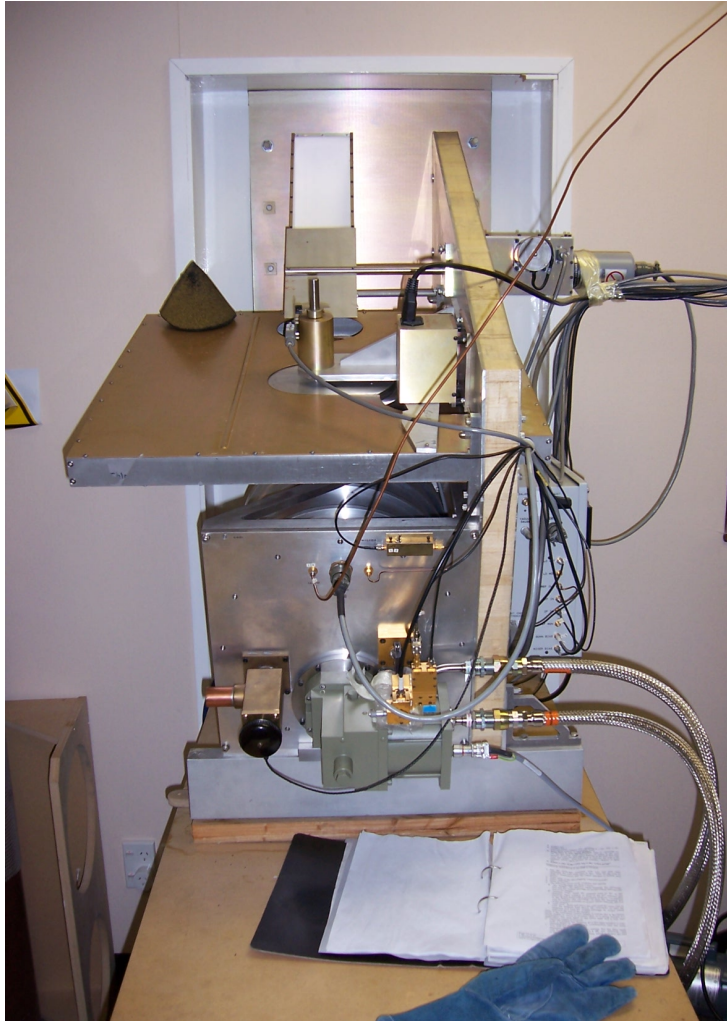
Background

- 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
- Stony Brook (to 2013), NRL (2013-), and NIWA jointly operated an automated ground-based millimeter wave spectrometer measuring ClO at Scott Base, Antarctica



It has made the only routine, near continuous ClO measurements in Antarctica since 1996

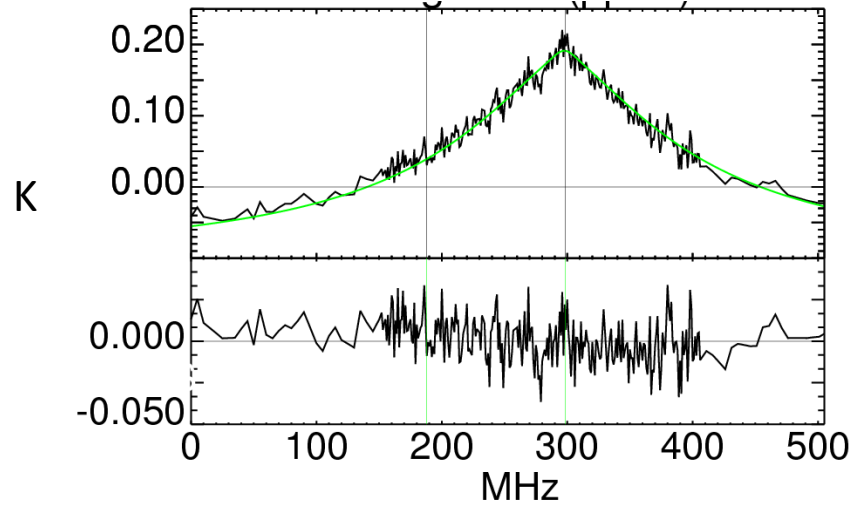
Background - 2



- We observe an emission line of ClO at 278.631 GHz. This line is thermally excited, and allows observation around the clock and throughout the year.
- 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, allowing us to remove the instrumental baseline by subtracting the nighttime spectrum from the daytime on

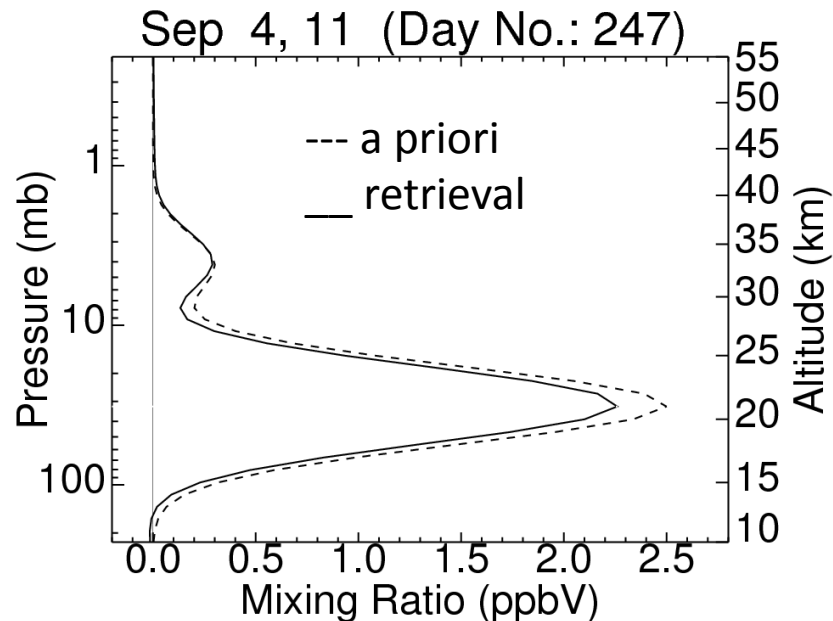
ChIOE Spectrum and Retrieval

CIO spectrum centered at 278.6 GHz



Measurement
& fit

Residual



The CIO retrieval is based on a **day minus night** spectrum.

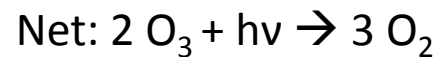
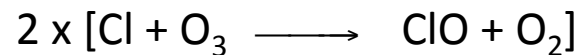
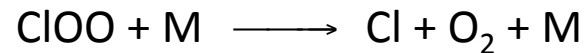
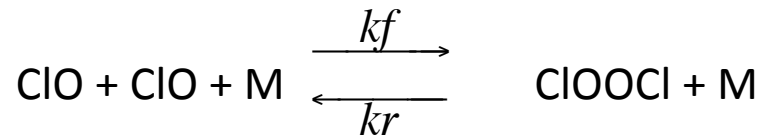
This helps to reduce the effect of spectral baselines in the instrument.

CIO Profile Retrieval

- An application of 'Optimal Estimation' as formulated in Rodgers, 2000
- 3 stage Process:
 1. Determine the altitude of the lower stratospheric peak:
 - Altitude is assigned based on day of year
 - Relationship derived from retrievals using a constant a priori profile
 - Assumed to apply to every year
 2. Estimate the peak mixing ratio
 - Single parameter fit of scale factor for lower stratospheric peak to the day-night measured spectrum
 3. Retrieve the full profile, 10-55 km, using Rodgers' algorithm
 - #1 and #2 determine the a priori profile for #3
- In the remainder of this talk, we will use the column CIO integrated from the retrieved profile

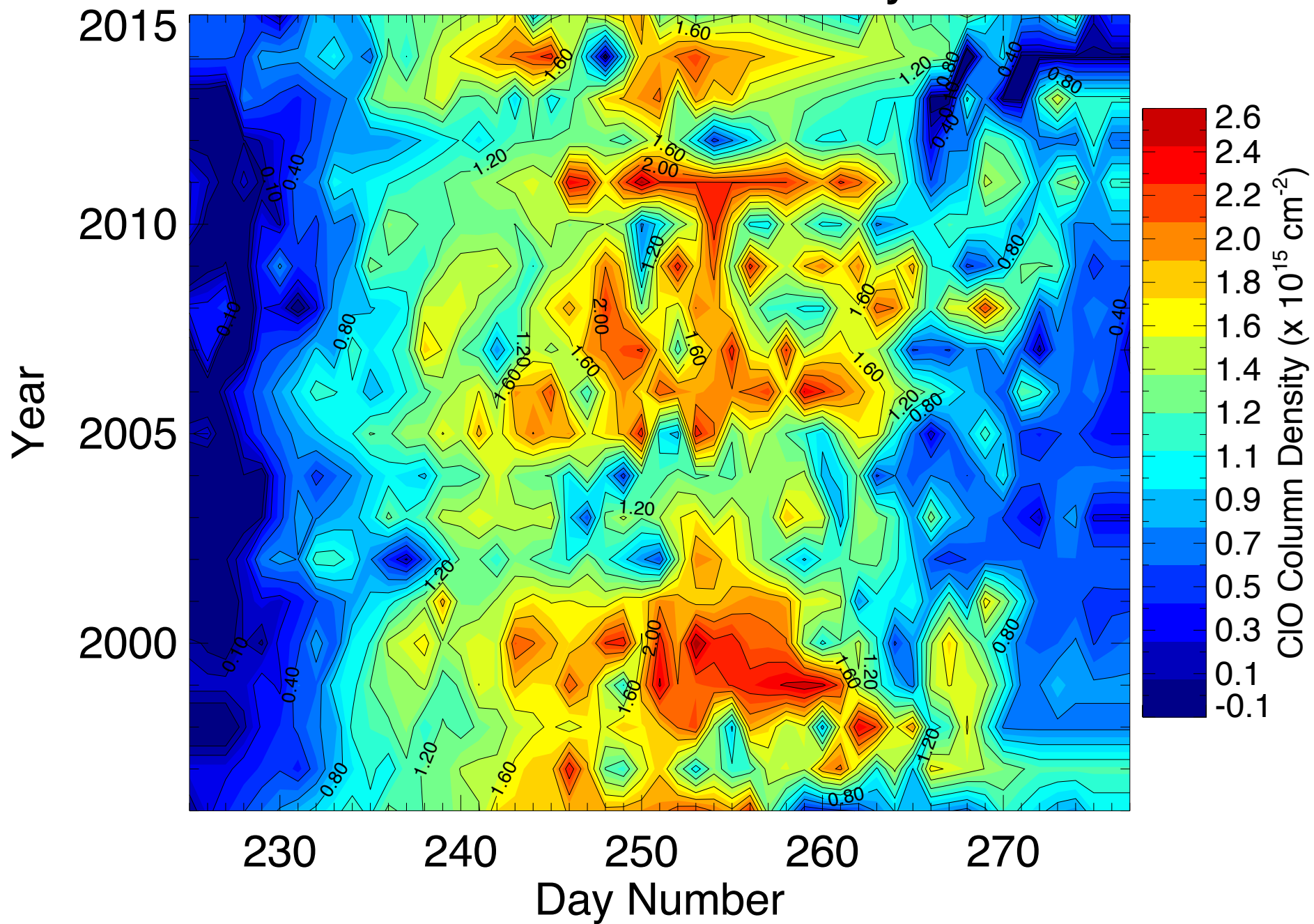
Background – 3 - Chemistry

- ClO-dimer cycle is responsible for the majority of spring-time ozone depletion in the Antarctic stratosphere:



- The heterogeneous chemistry which releases Cl from its reservoirs HCl and ClONO₂ commonly occurs on PSC particles in the lower stratosphere in the Antarctic spring.
- It also occurs in the Arctic, but only intermittently (Dufour et al, 2006)

CIO Column Density



Current Results

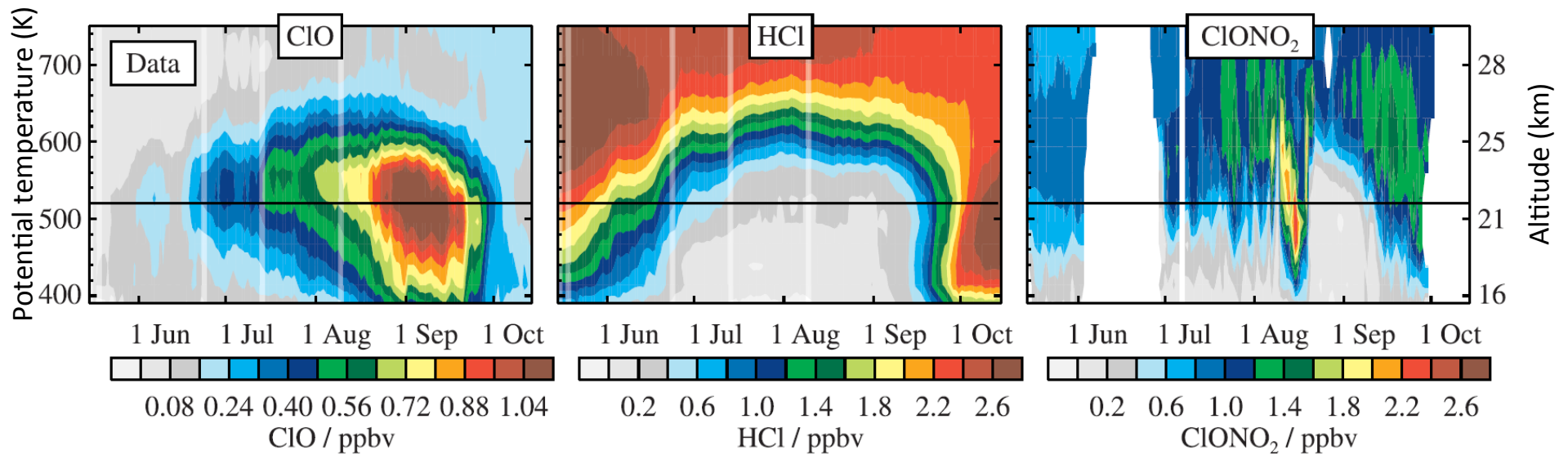
- The remainder of this talk summarizes the paper “20 Years of ClO Measurements in the Antarctic Lower Stratosphere” by Nedoluha, Connor, et al, currently in review in ACP (acp-2016-188 – discussions)
- In that paper, we analyze 20 years of (1996-2015) of austral springtime measurements of ClO over Antarctica from the ChLOE1 ground-based millimeter wave spectrometer at Scott Base, Antarctica and 12 years (2004-2015) of ClO measurements from MLS, to estimate the trend in total chlorine ($\text{Cly} = \text{HCl} + \text{ClONO}_2 + \text{HOCl} + 2 \times \text{Cl}_2 + 2 \times \text{Cl}_2\text{O}_2 + \text{ClO} + \text{Cl}$) in the Antarctic stratosphere

Antarctic Chlorine Partitioning

2005 inside-the-vortex average measurements

MLS: ClO and HCl

ACE-FTS: ClONO₂



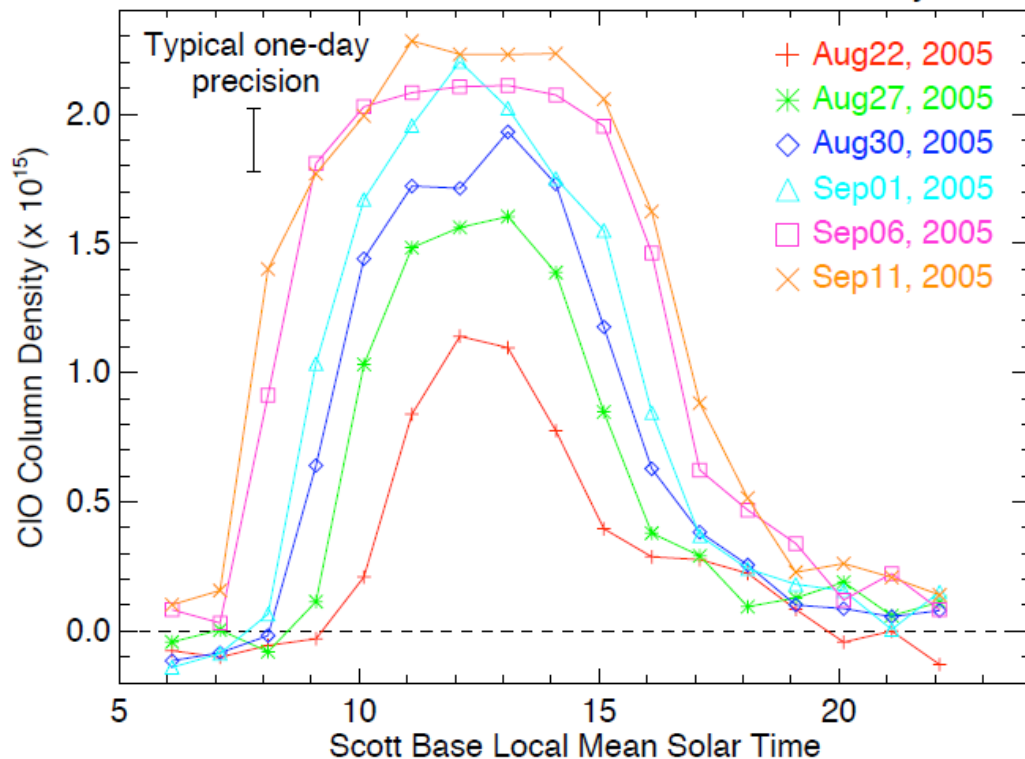
Santee et al., JGR, 2008

Antarctic CIO

Day minus Night at Scott Base (78°S) more complicated than at Mauna Kea



Diurnal Variation of CIO Column Density



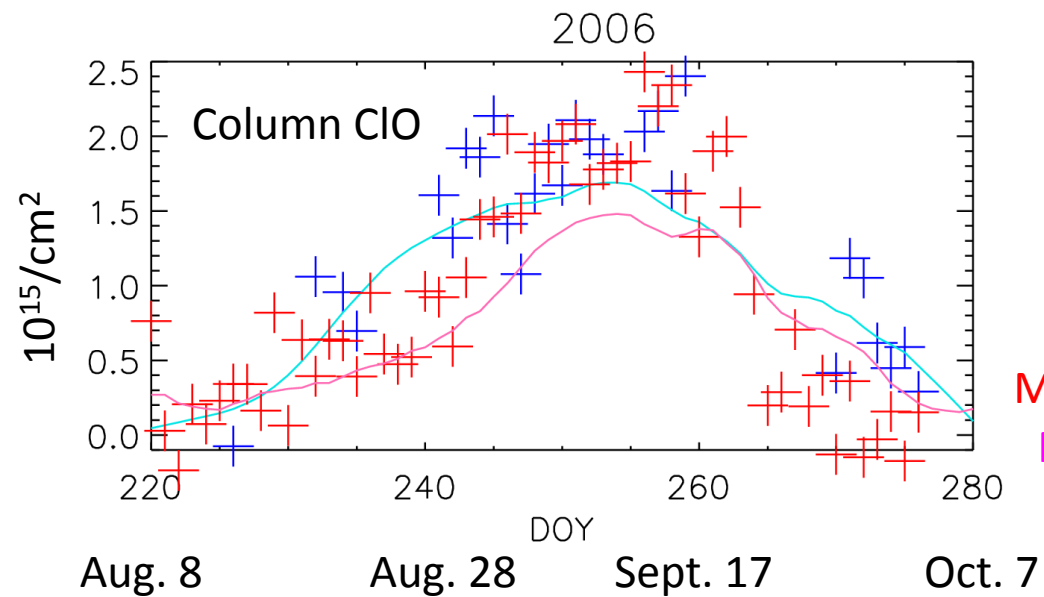
ChOE2 measurements:
 "Day" => sunrise + 3hr to sunset - 1hr
 "Night" => sunset + 4hr to sunrise - 1hr

Aura MLS measurements:
 "Day" ~1630
 "Night" ~2300

"Day minus Night" Aura MLS CIO will have a different seasonal variation than "Day minus Night" ChOE2 CIO.

UARS MLS and Aura MLS measure at different local times.

2006 Daily ClO Column Measurements



Column ClO (day-night):

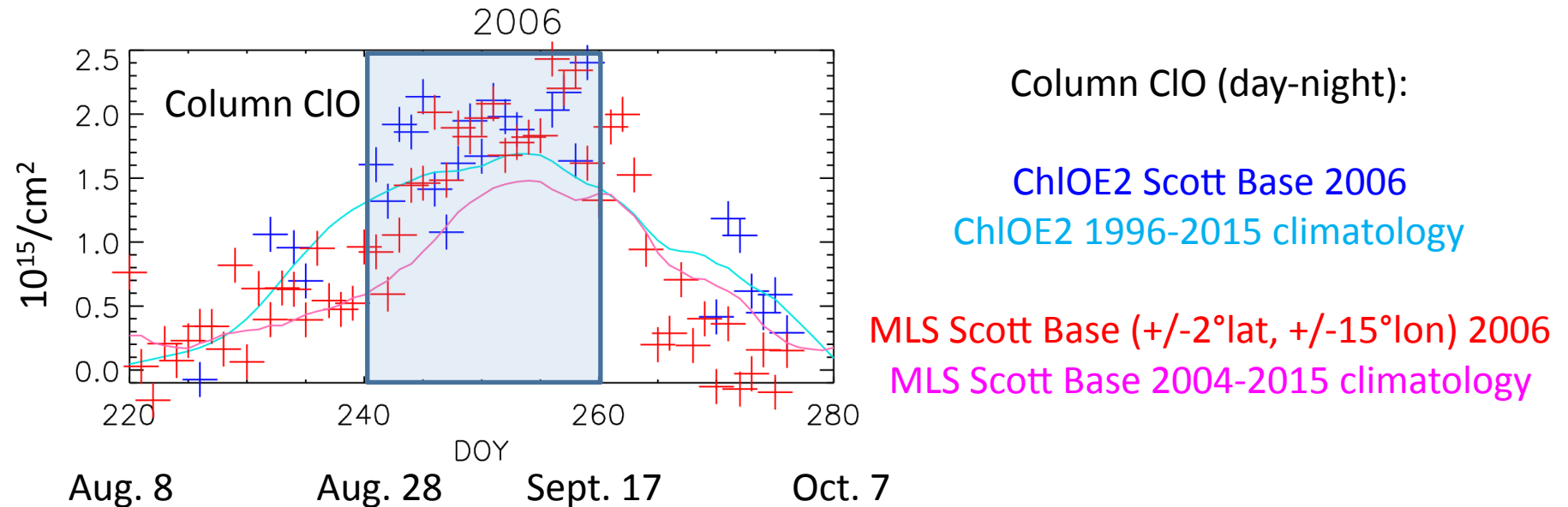
ChIOE2 Scott Base 2006

ChIOE2 1996-2015 climatology

MLS Scott Base ($\pm 2^\circ$ lat, $\pm 15^\circ$ lon) 2006

MLS Scott Base 2004-2015 climatology

Calculate a CIO anomaly for each year



- Measurements are not always available on every day.
- Calculate, for each year, the average difference from each instrument/site specific climatology for CIO variations on days 240-260 (Aug. 28-Sept. 17).
- Annual uncertainties calculated from standard error of the mean for the anomalies for each year ($\sigma/n^{1/2}$).

There is a correlation between ozone mass deficit and average ClO over Scott Base for day-of-year 240-260

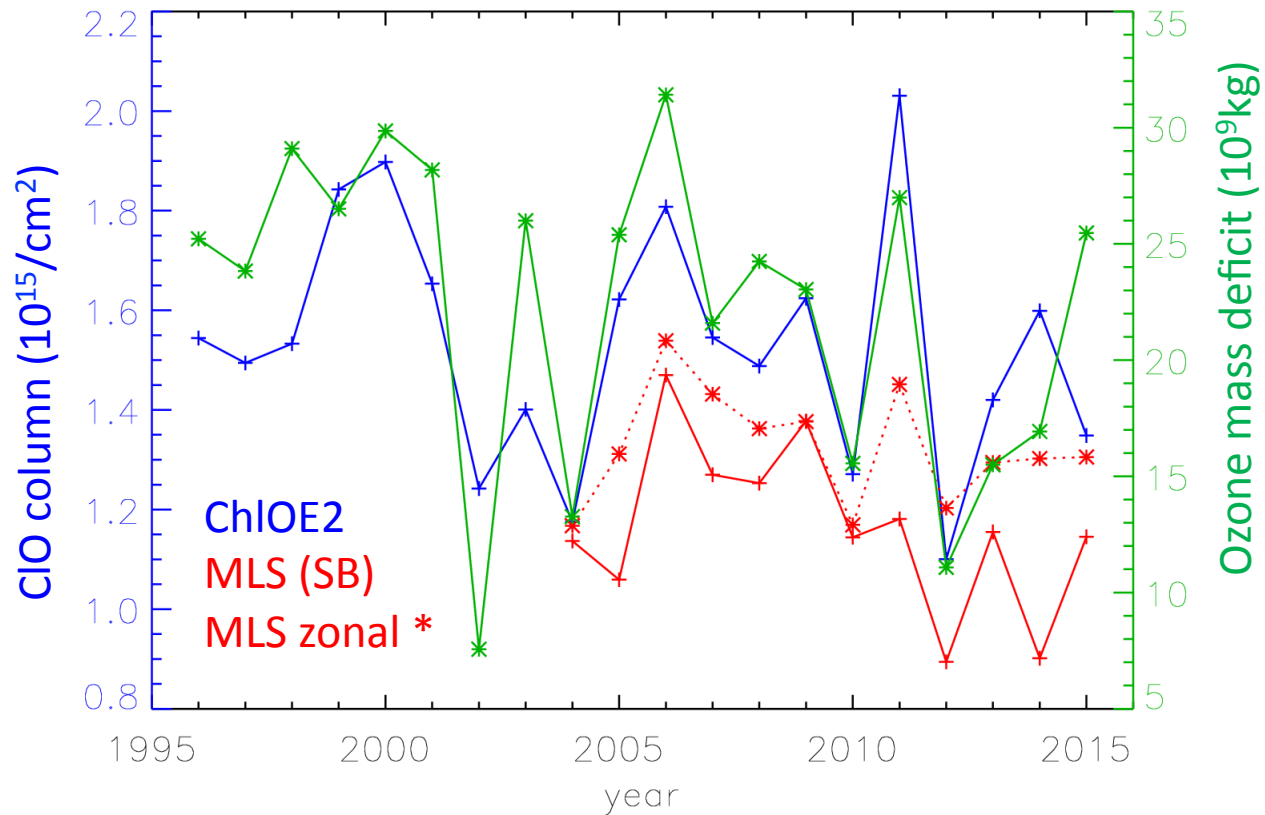
ChIOE2 $r=0.78$

MLS (near Scott Base) $r=0.66$

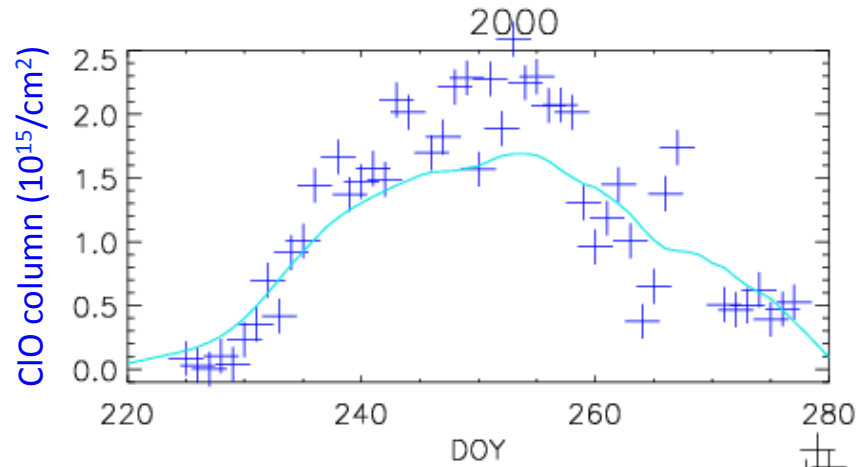
MLS (78°S +/- 2°) (dotted) $r=0.85$

and

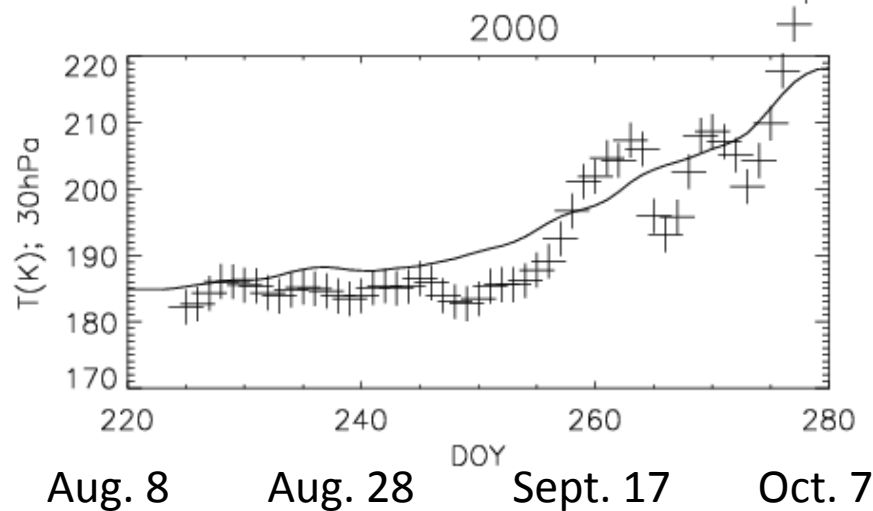
Sept.-Oct. O₃ mass deficit (ozonewatch.gsfc.nasa.gov)



Anomalies in ClO column related to 30 hPa temperature anomaly

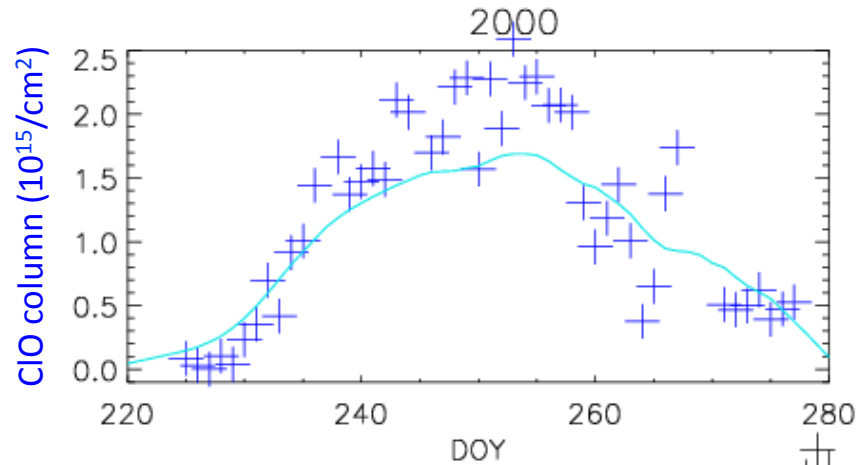


ChIOE2 column ClO for 2000
ChIOE2 climatology

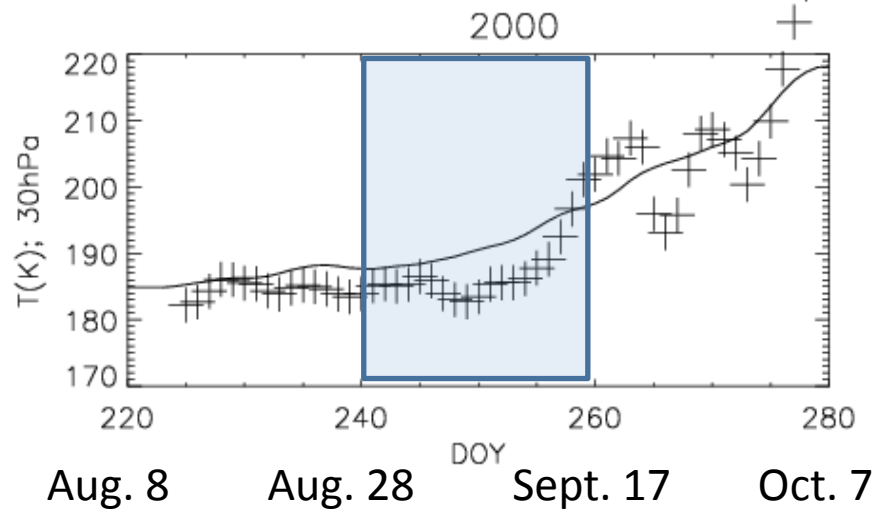


30 hPa MERRA temperature coincident with
Scott Base
2000 (crosses)
1996-2015 climatology (line)

Anomalies in ClO column related to 30 hPa temperature anomaly



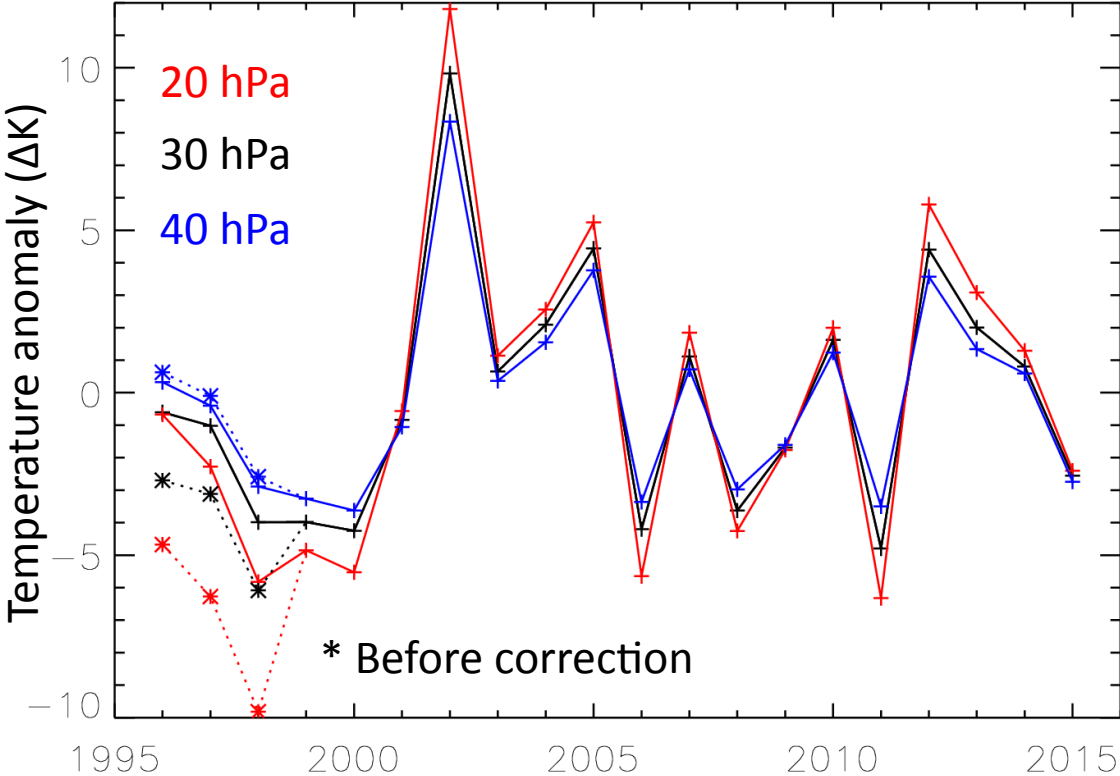
ChIOE2 column ClO for 2000
ChIOE2 climatology



30 hPa MERRA temperature coincident with
Scott Base
2000 (crosses)
1996-2015 climatology (line)

We want to compare interannual temperature and CIO column anomalies for day-of-year 240-260, but first we need to make a small correction to 1996-1998 temperatures

Average annual temperature anomaly at Scott
Base for Aug. 28-Sept. 17



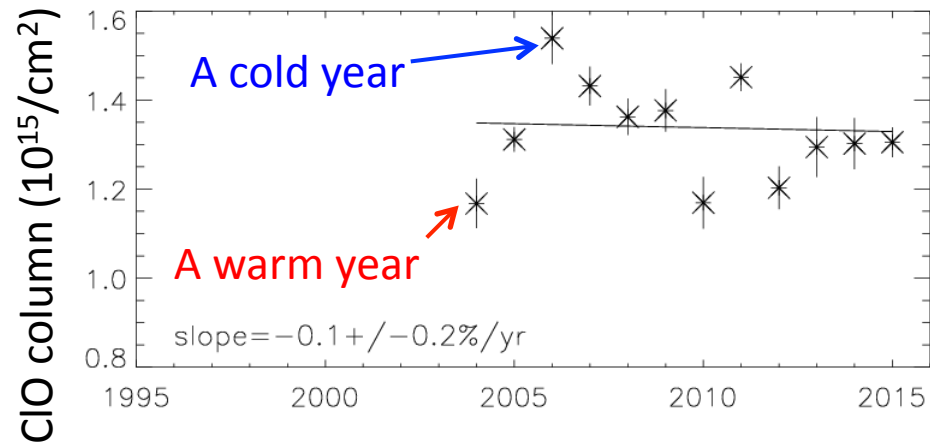
MERRA temperatures for 1996-1998 (before ATOVS) look different.

Using sonde measurements we bias-corrected the 1996-1998 MERRA temperatures.

30 hPa temperatures were 2.1K too cold.

Estimated CIO trend after accounting for the effect of interannual temperature variations

CIO column from zonal (78°S) MLS measurements

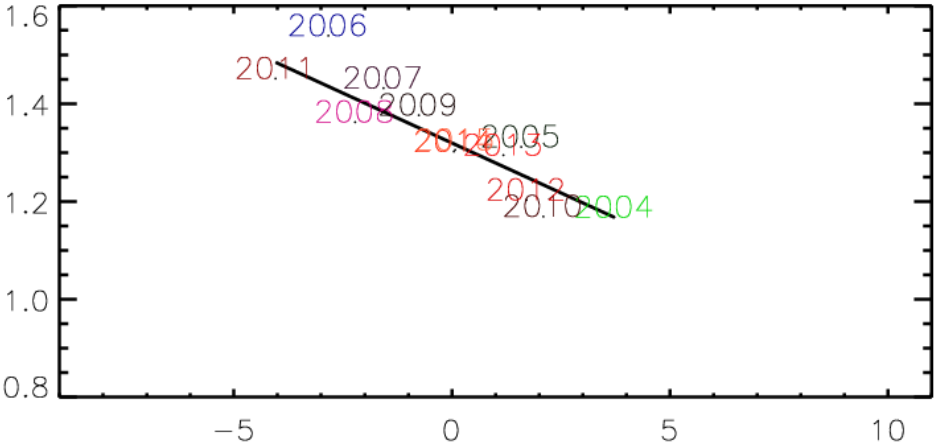


**Interannual changes in Column ClO and
30hPa Temperature**

Zonal MLS ClO Column
vs.

Zonal 30hPa Temperature

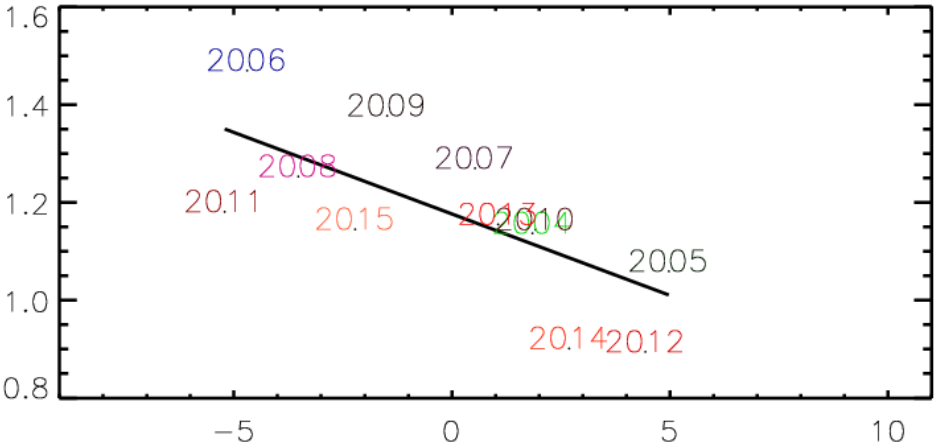
Slope=-0.040+/-0.006 $10^{15}\text{cm}^{-2}/\text{K}$



Scott Base MLS ClO Column
vs.

Scott Base 30hPa Temperature

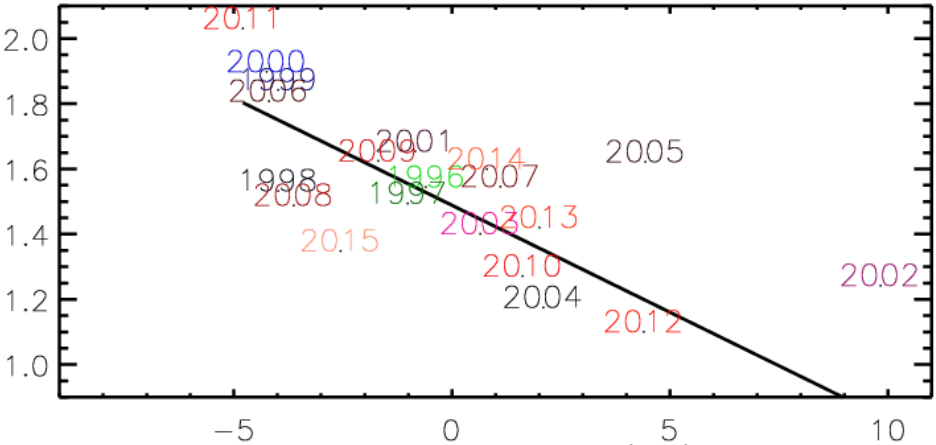
Slope=-0.033+/-0.012 $10^{15}\text{cm}^{-2}/\text{K}$



ChIOE2 ClO Column
vs.

Scott Base 30hPa Temperature

Slope=-0.065+/-0.014 $10^{15}\text{cm}^{-2}/\text{K}$

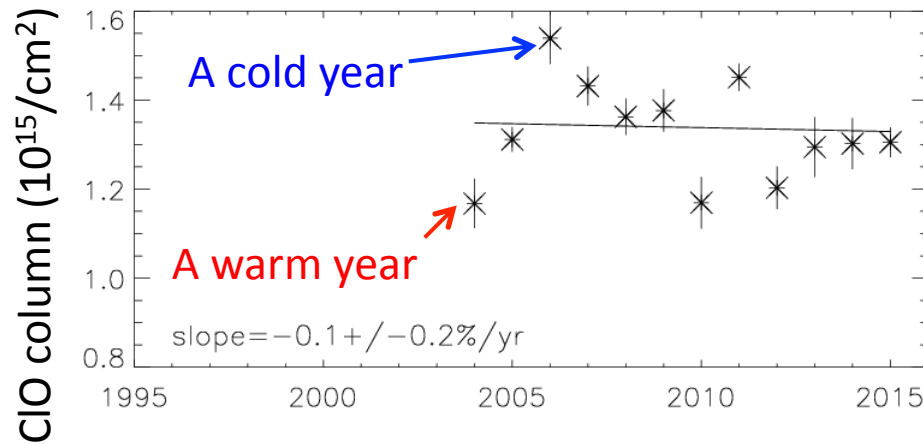


ClO column ($10^{15}/\text{cm}^2$)

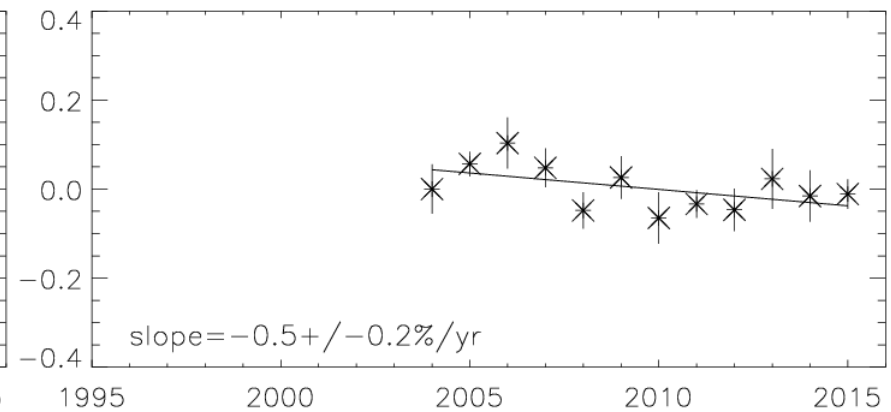
Temperature anomaly (ΔK)

Estimated ClO trend after accounting for the effect of interannual temperature variations

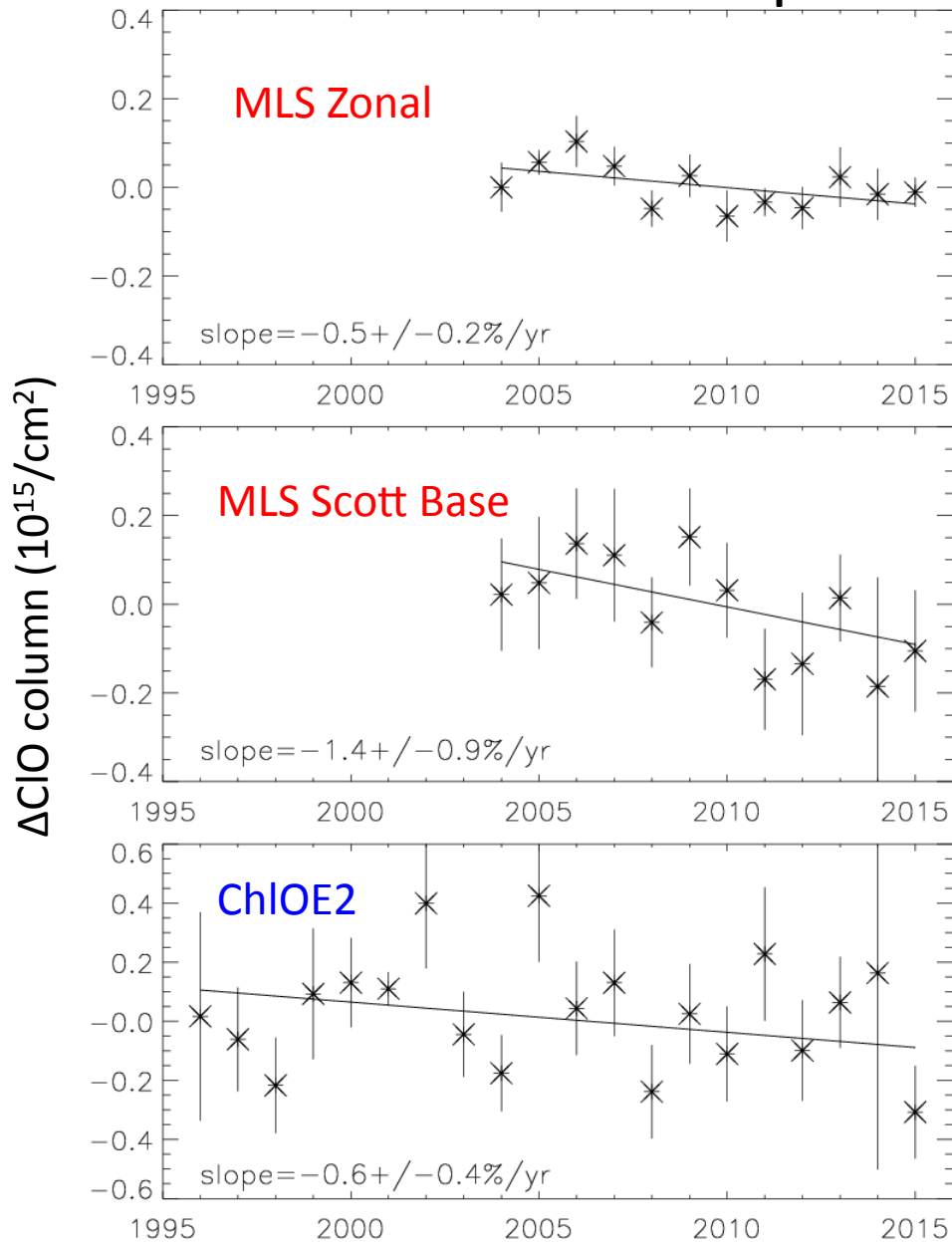
ClO column from zonal (78°S) MLS measurements



Estimated Δ ClO column from zonal MLS measurements after temperature correction



Estimated ClO trend after accounting for the effect of interannual temperature variations



Zonal MLS ClO column adjusted
for temperature anomalies
Slope= $-0.5 \pm 0.2 \text{ \%/yr}$

Scott Base MLS ClO column adjusted
for temperature anomalies
Slope= $-1.4 \pm 0.9 \text{ \%/yr}$

ChIOE2 ClO column adjusted
for temperature anomalies
Slope= $-0.6 \pm 0.4 \text{ \%/yr}$

Summary

- ChIOE1 measurements from Mauna Kea show a ClO trend
= $-0.49 \pm 0.06\%/yr$ from 1995-2015
- Annual measured Antarctic ClO anomalies from Aug.28-Sept. 17 are correlated with Sept.-Oct. O₃ mass deficit ($r=0.78$ for ChIOE2).
- We used the 30 hPa temperature as a proxy for interannual variations in meteorology and then calculated trends:
- Estimate of zonal MLS ClO trend for 78°S
= $-0.5 \pm 0.2\%/yr$ from 2004-2015
- Estimate of MLS ClO trend near Scott Base
= $-1.4 \pm 0.9\%/yr$ from 2004-2015
- Estimate of ChIOE2 ClO trend at Scott Base
= $-0.6 \pm 0.4\%/yr$ from 1996-2015
- We believe these adjusted ClO trends represent the underlying trend in Cl_y

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