Pollution of Earth's Stratosphere: Ozone Recovery and Chemistry/Climate Coupling

AOSC 433/633 & CHEM 433

Ross Salawitch

Class Web Site: http://www.atmos.umd.edu/~rjs/class/spr2015

Motivating questions:

a) Levels of CFCs have peaked and are slowly declining: are we seeing a response in total ozone column?

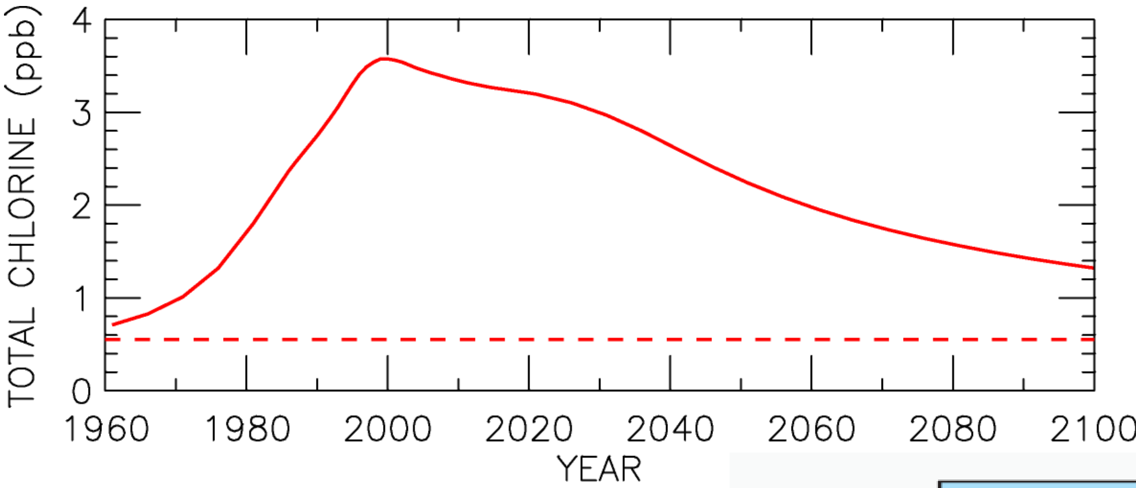
b) How might climate change (future variations in temperature *and / or* circulation) driven by rising GHGs affect stratospheric ozone?

c) Might climate at the surface be affected by stratospheric ozone?

Lecture 16

7 April 2015

Recovery of the Ozone Layer



Time series of chlorine content of organic halocarbons that reach the stratosphere. Past values based on direct atmospheric observation. Future values based on projections that include the lifetime for removal of each halocarbon.

Table 5A−3, WMO/UNEP 2010

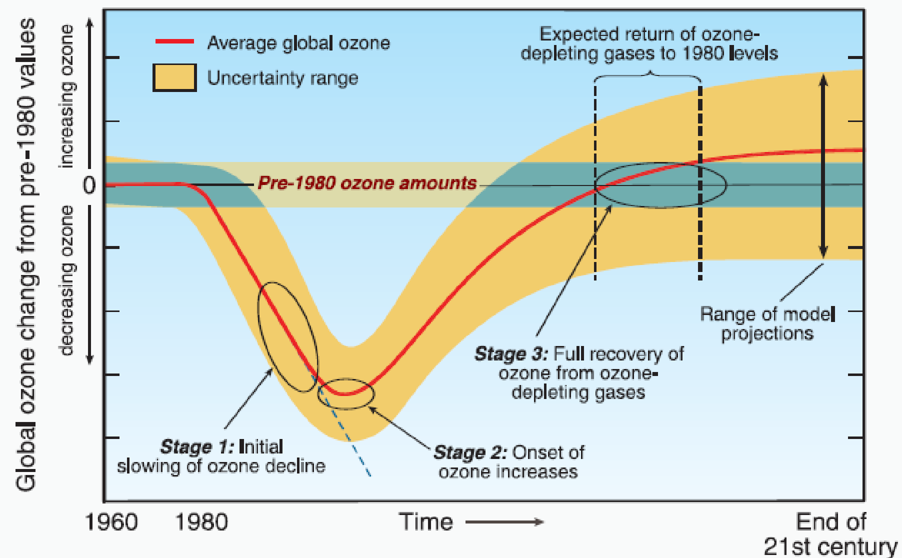
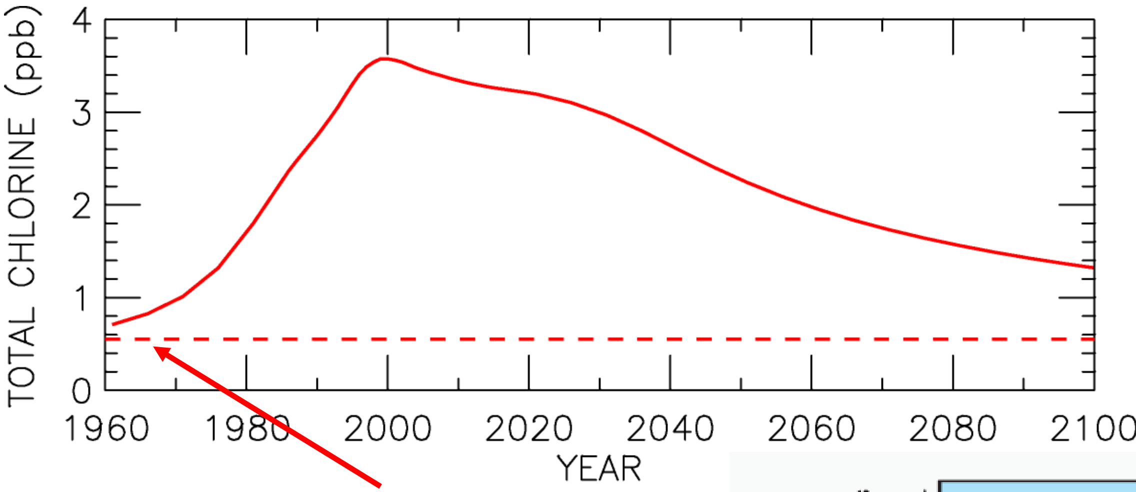


Figure Q19-1. Recovery stages of global ozone. Significant ozone depletion from the release of ozone-depleting gases in human activities first became recognized in the 1980s. The Montreal Protocol provisions are expected to further reduce and eliminate these gases in the atmosphere in the coming decades, thereby leading to the return of ozone amounts to near pre-1980 values. The timeline of the recovery process is schematically illustrated with three stages identified. The large uncertainty range illustrates natural ozone variability in the past and potential uncertainties in global model projections of future ozone amounts. When ozone reaches the full recovery stage, global ozone values may be above or below pre-1980 values, depending on other changes in the atmosphere (see Q20).

Recovery of the Ozone Layer



Why was total chlorine ~0.6 ppb in 1960?

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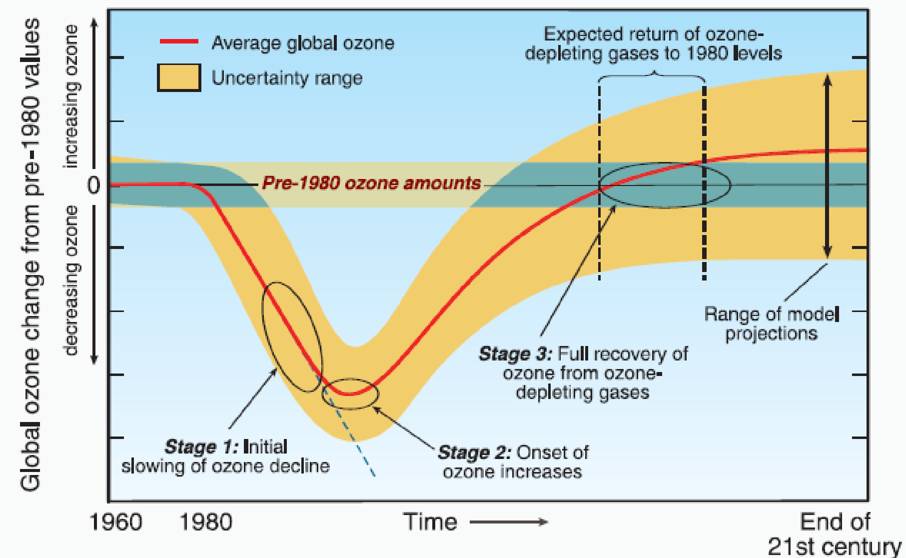

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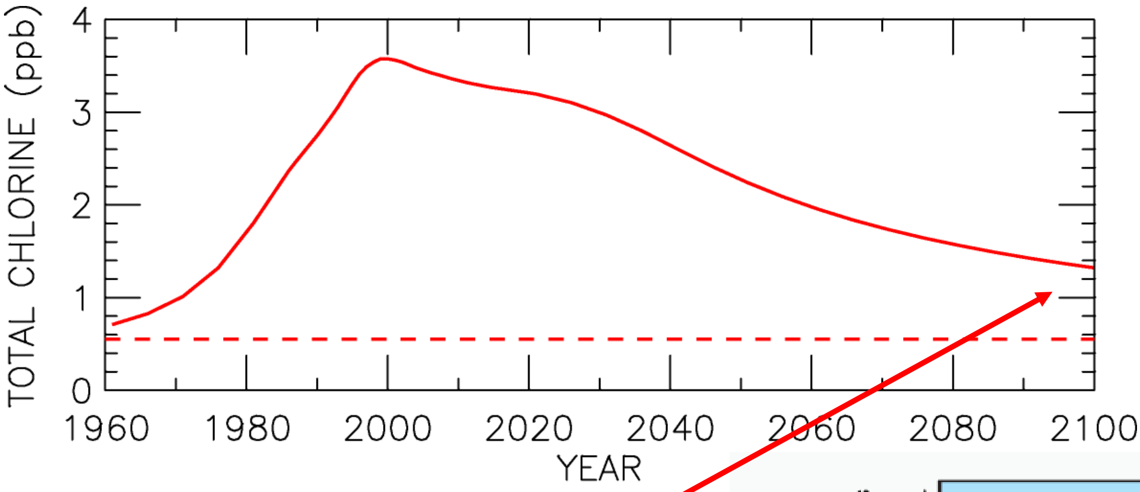

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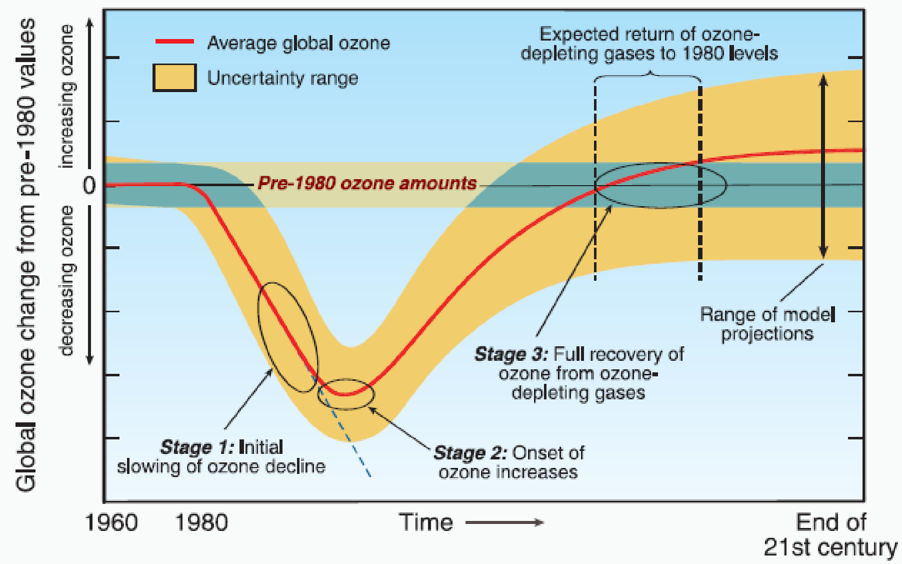
What very long lived halocarbon is responsible for CCl_y in year 2100 exceeding CCl_y in year 1960 ?



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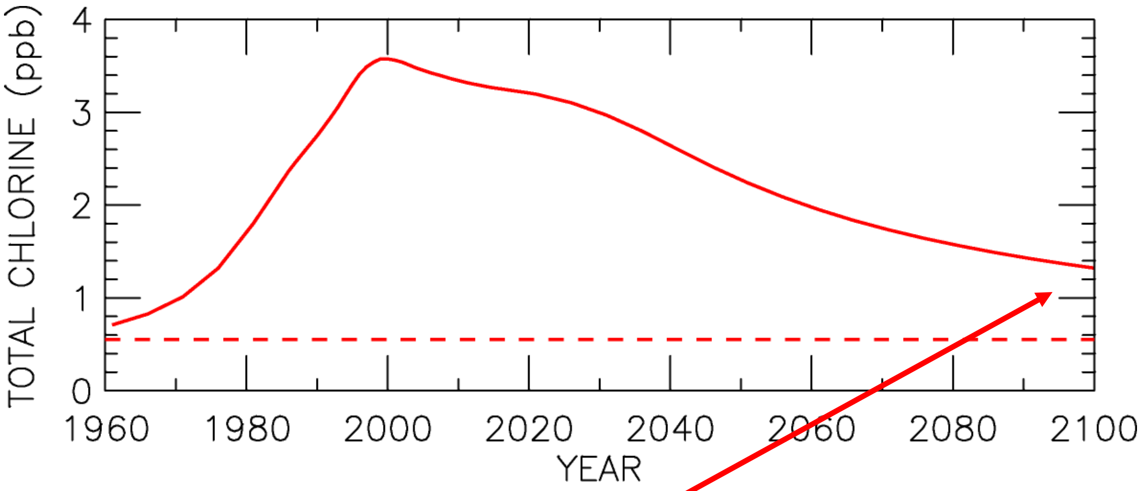

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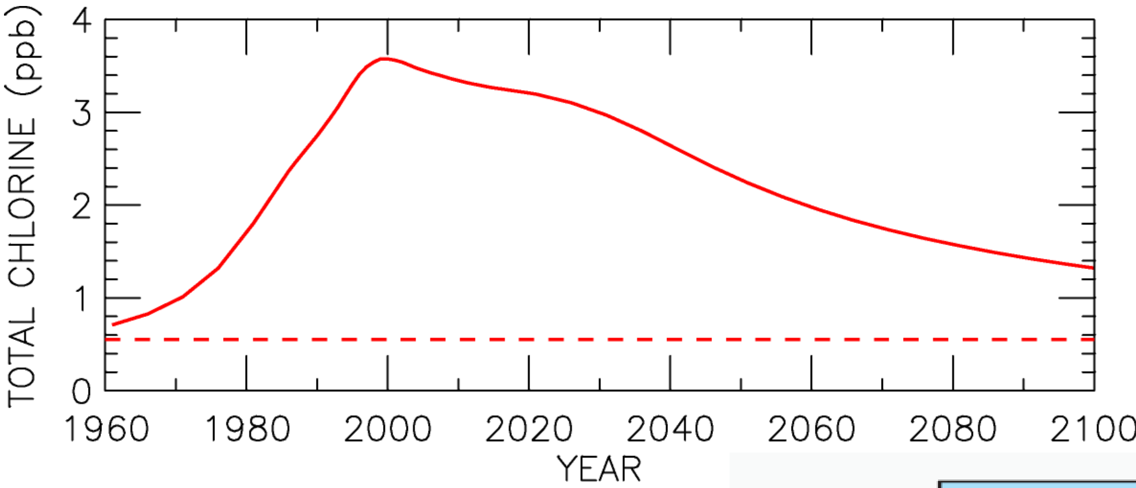
Table Q7-1. Atmospheric Lifetimes and Ozone Depletion Potentials of some halogen source & HFC substitute gases.

Gas	Atmospheric Lifetime (years)	Ozone Depletion Potential (ODP) [c]
Halogen source gases		
Chlorine gases		
CFC-11	45	1
CFC-12	100	0.82
CFC-113	85	0.85
Carbon tetrachloride (CCl_4)	26	0.82
HCFCs	1–17	0.01–0.12
Methyl chloroform (CH_3CCl_3)	5	0.16
Methyl chloride (CH_3Cl)	1	0.02
Bromine gases		
Halon-1301	65	15.9
Halon-1211	16	7.9
Methyl bromide (CH_3Br)	0.8	0.66
Very short-lived gases (e.g., $CHBr_3$)	Less than 0.5	[b] very low
Hydrofluorocarbons (HFCs)		
HFC-134a	13.4	0
HFC-23	222	0

Lecture 2, Slide 22

Recovery of the Ozone Layer



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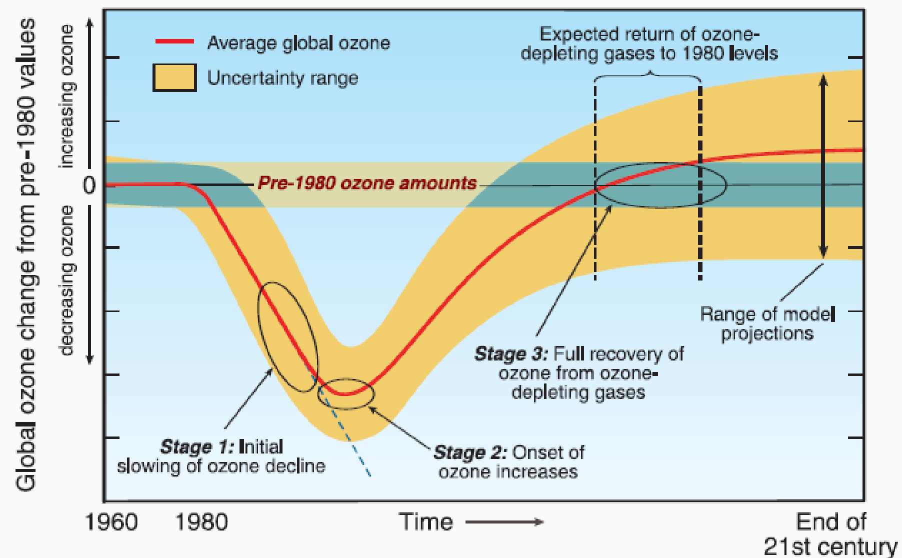
What is especially "odd" about these graphs when scrutinized in tandem ?



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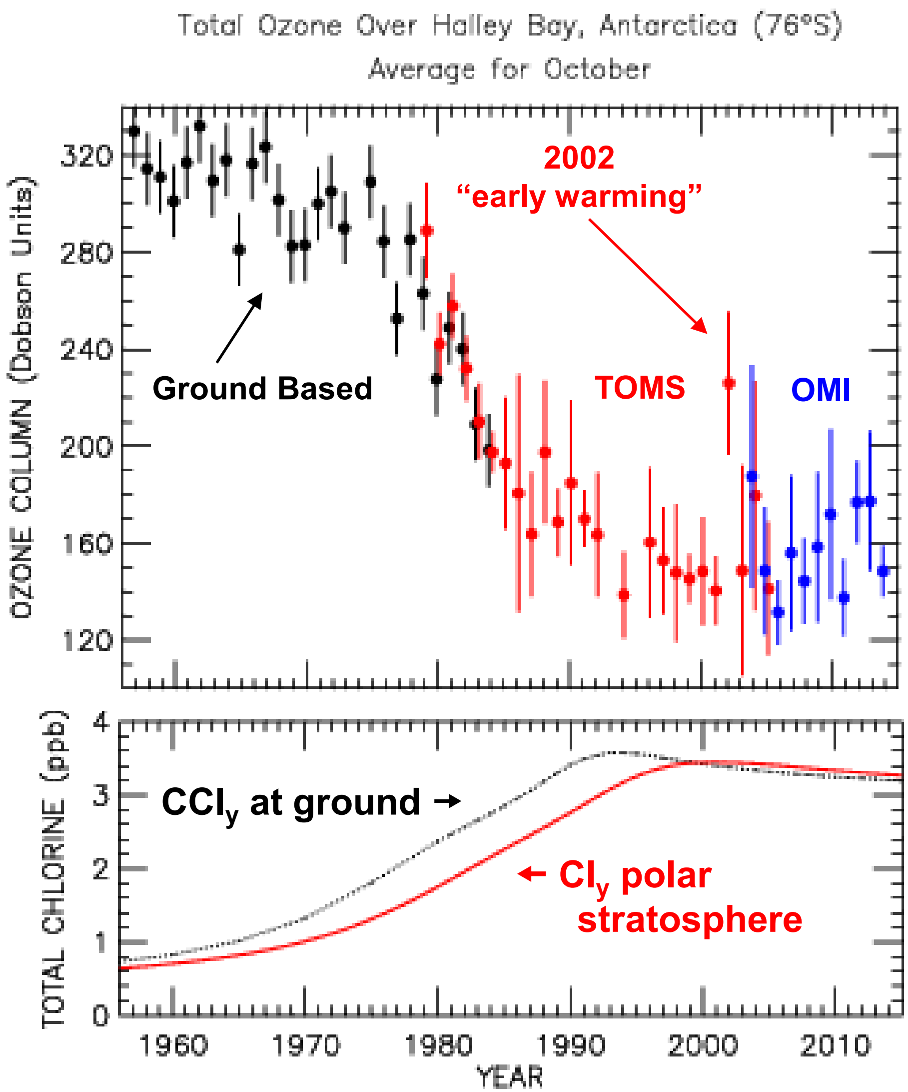
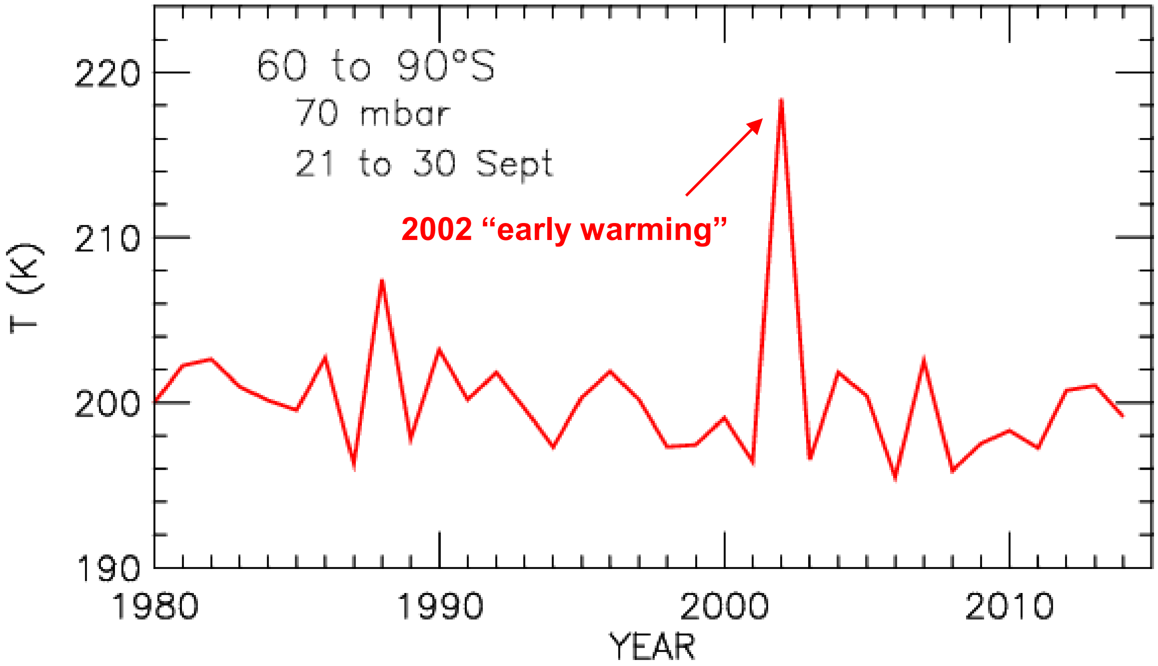
Polar Ozone Loss: Update



How much of this "leveling off" is due to the "leveling off" of halogens ?

Lecture 15, Slide 2
Lecture 15, Slide 21

Complication #1



Considerable year to year variability in temperature

Data from http://acdb-ext.gsfc.nasa.gov/Data_services/met/ann_data.html

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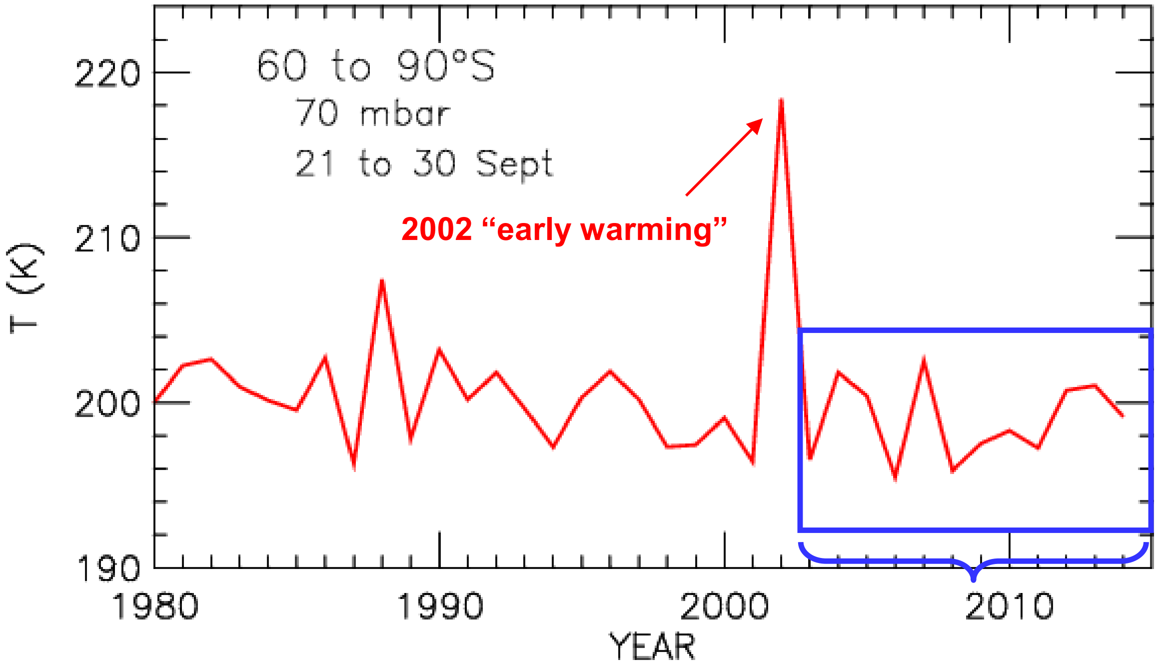

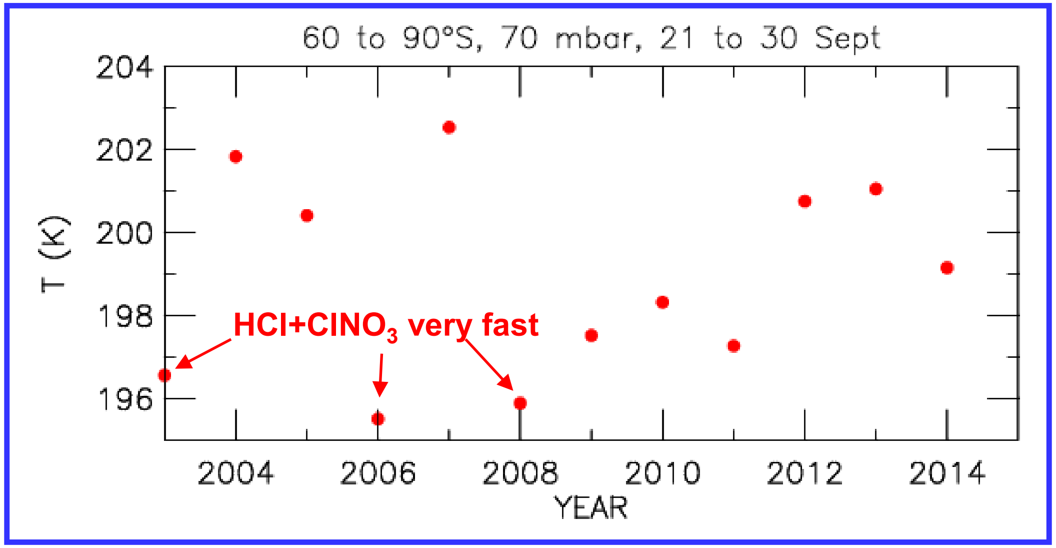

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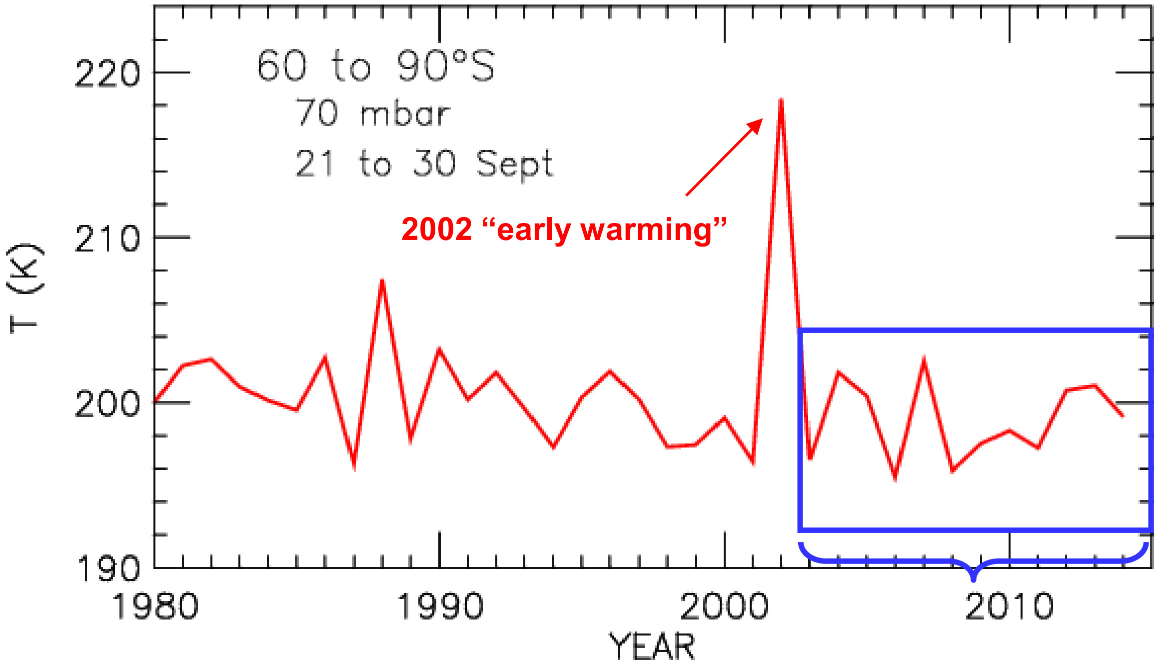

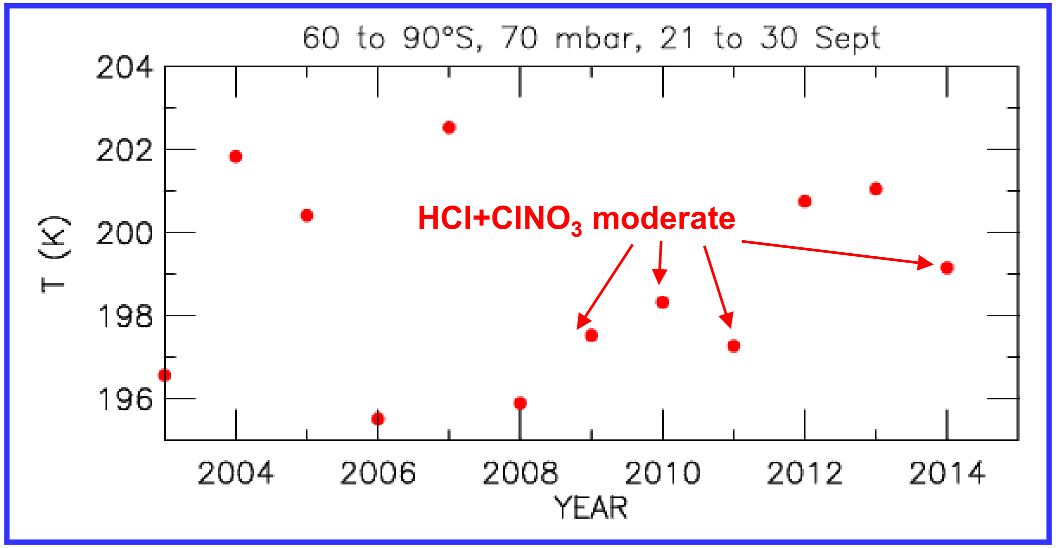

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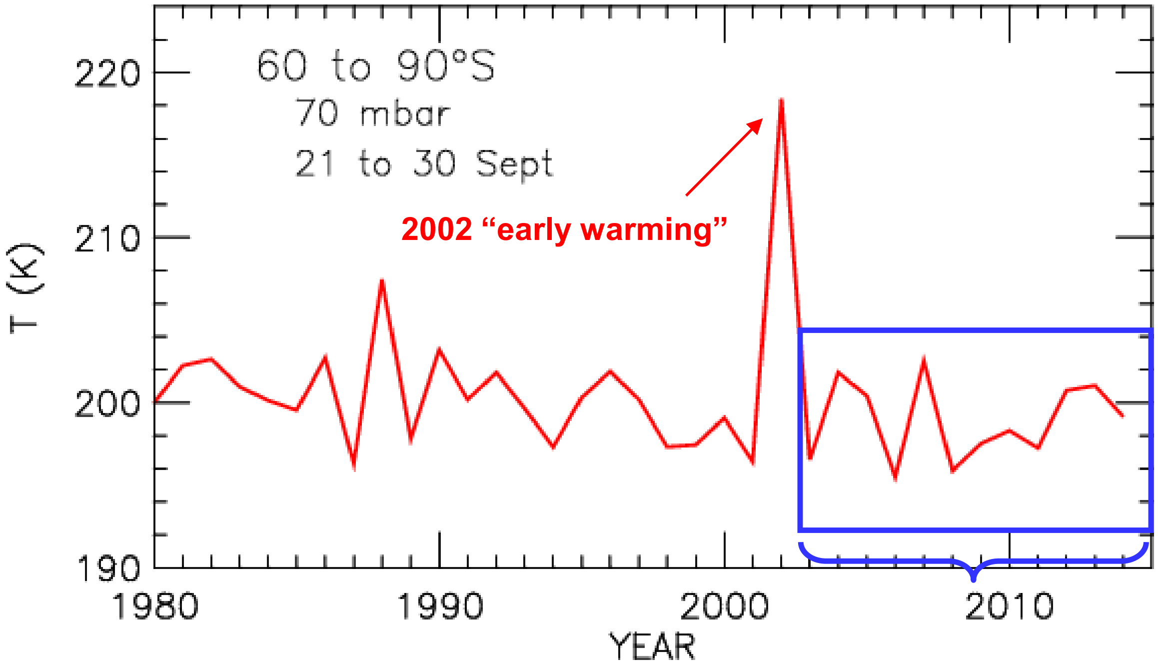
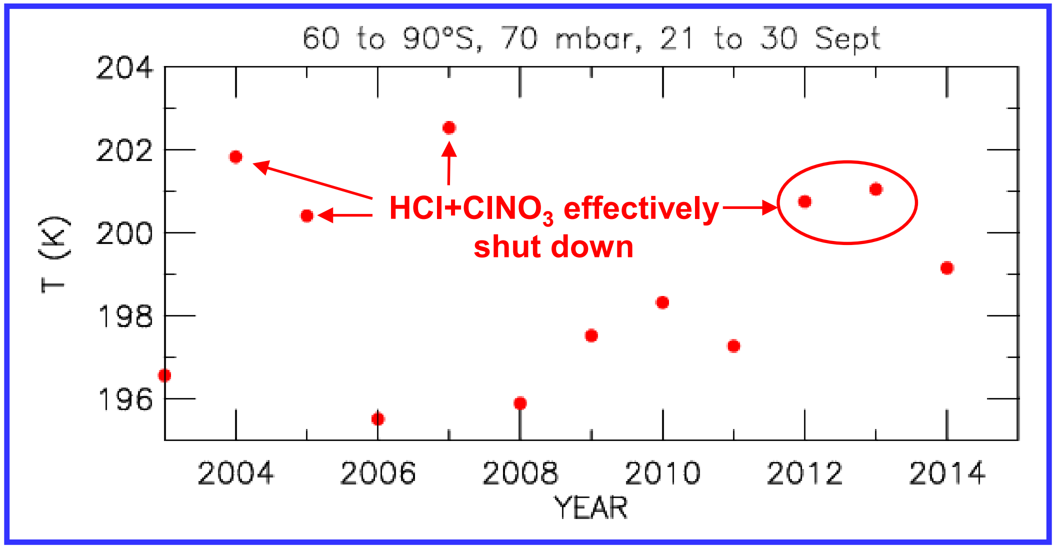
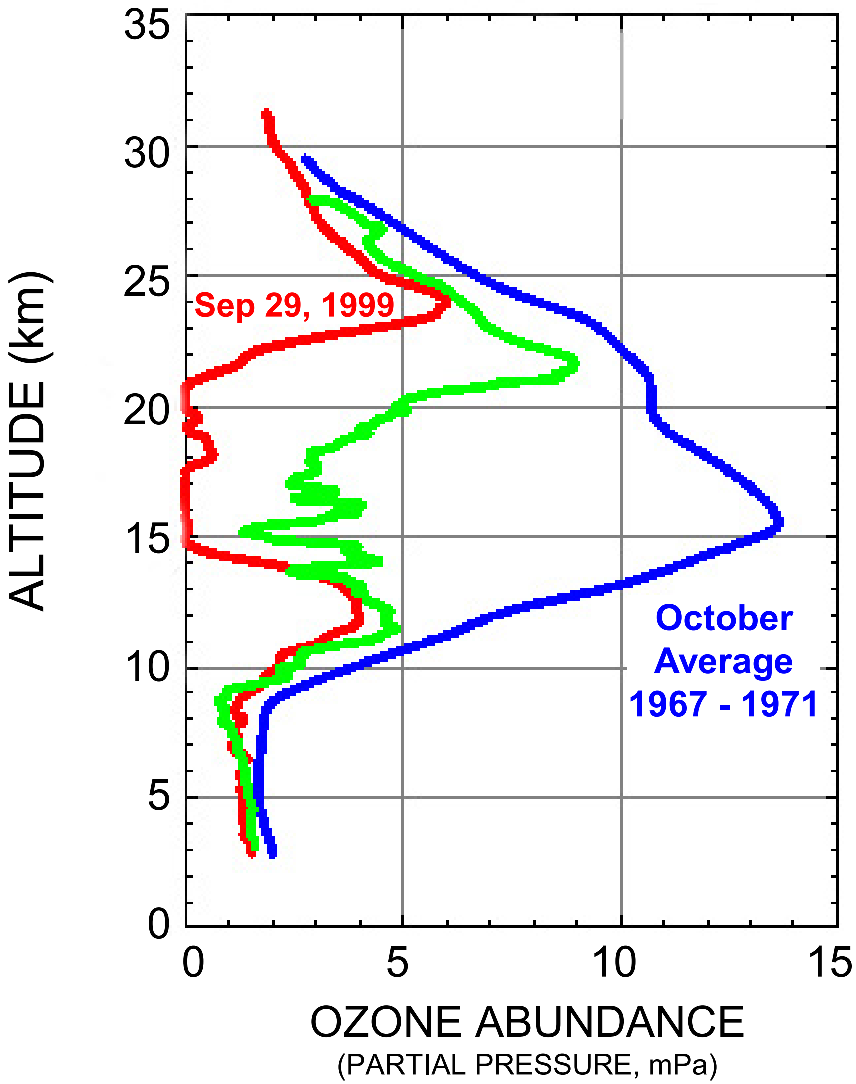




Complication #2

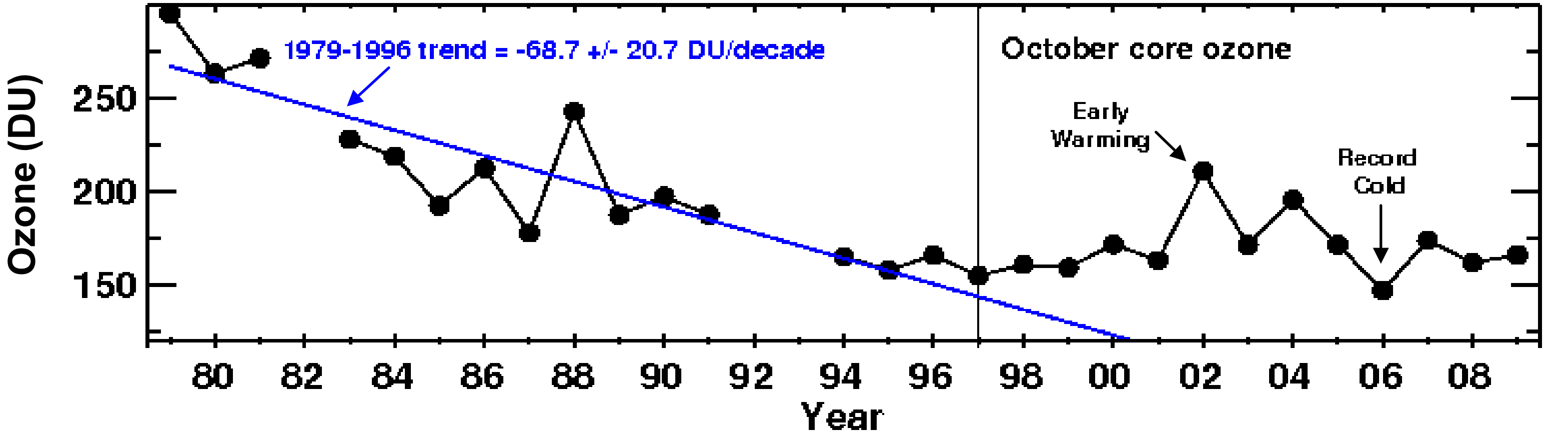


D. Hofmann, NOAA CMDL

Ozone reaches "zero" over considerable height range.

This "saturation effect" may be the cause of the "leveling off" of the column ozone time series

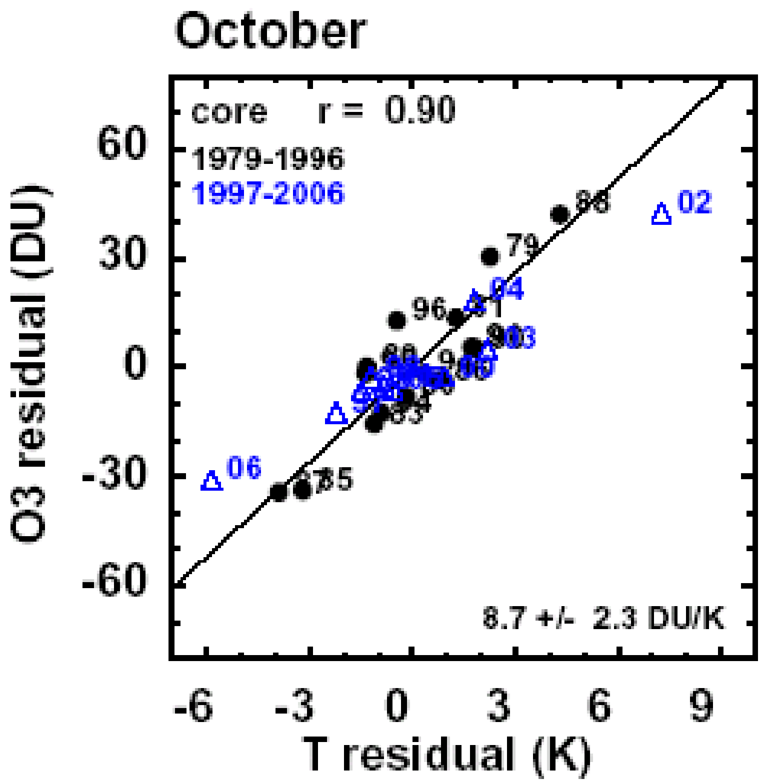
Total Ozone Over Antarctica, October



Yang *et al*., *JGR*, 2008, updated

Figure 2-28, WMO/UNEP 2011

Scatter plot, O_3' (ozone residual) versus T' (temperature residual)



Cold winters associated with larger vortices and less O_3 due mainly to "chemical effects" related to abundance of PSCs

Slopes of this curve combined with yearly temperature residual (T') used to remove influence of yearly variation of temperature on ozone

Yang *et al*., *JGR*, 2008

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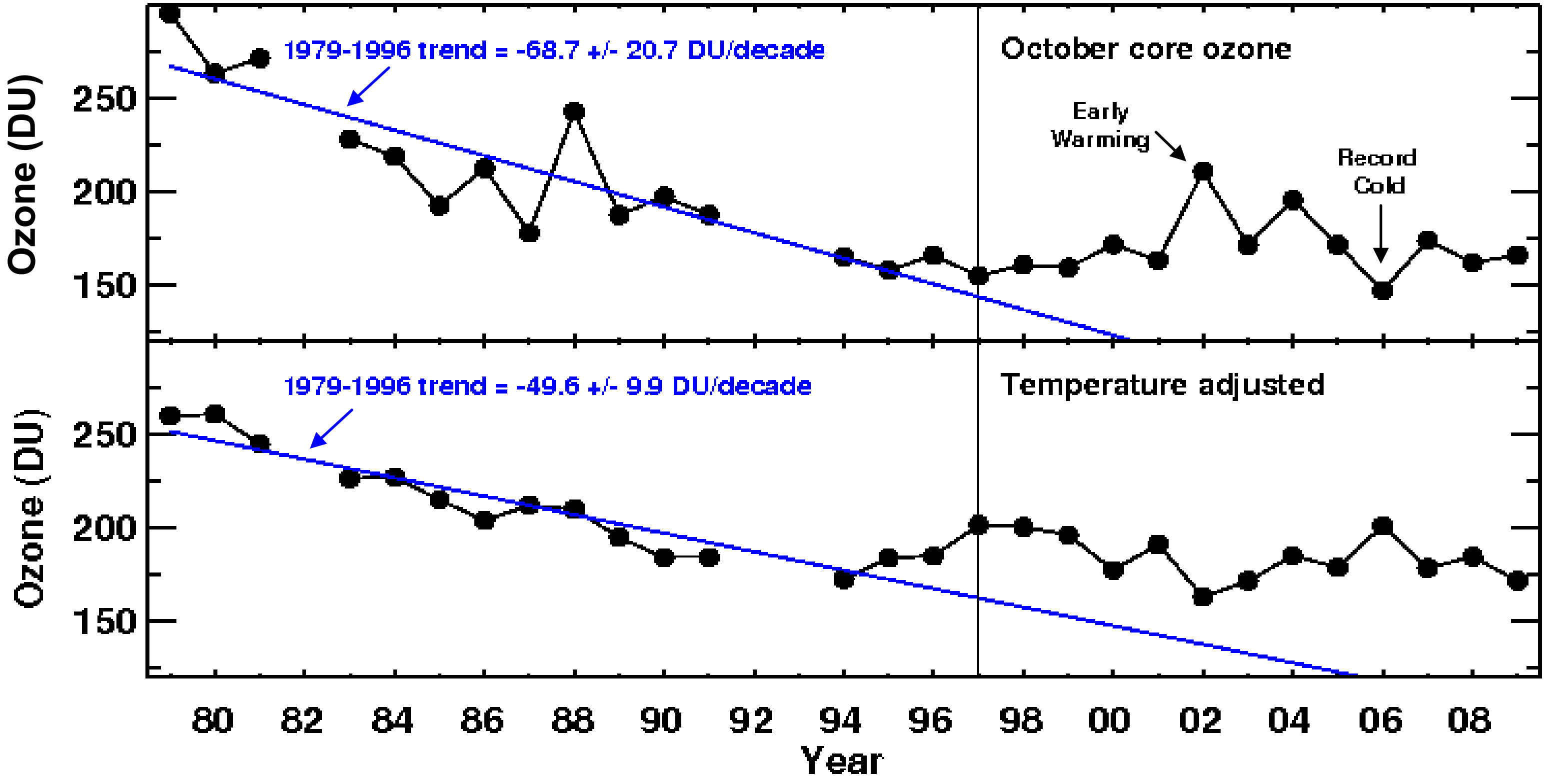

- **Have dealt with Complication #1 (Year to year variability in T)**
- **Now, must deal with Complication #2 (Loss Saturation)**

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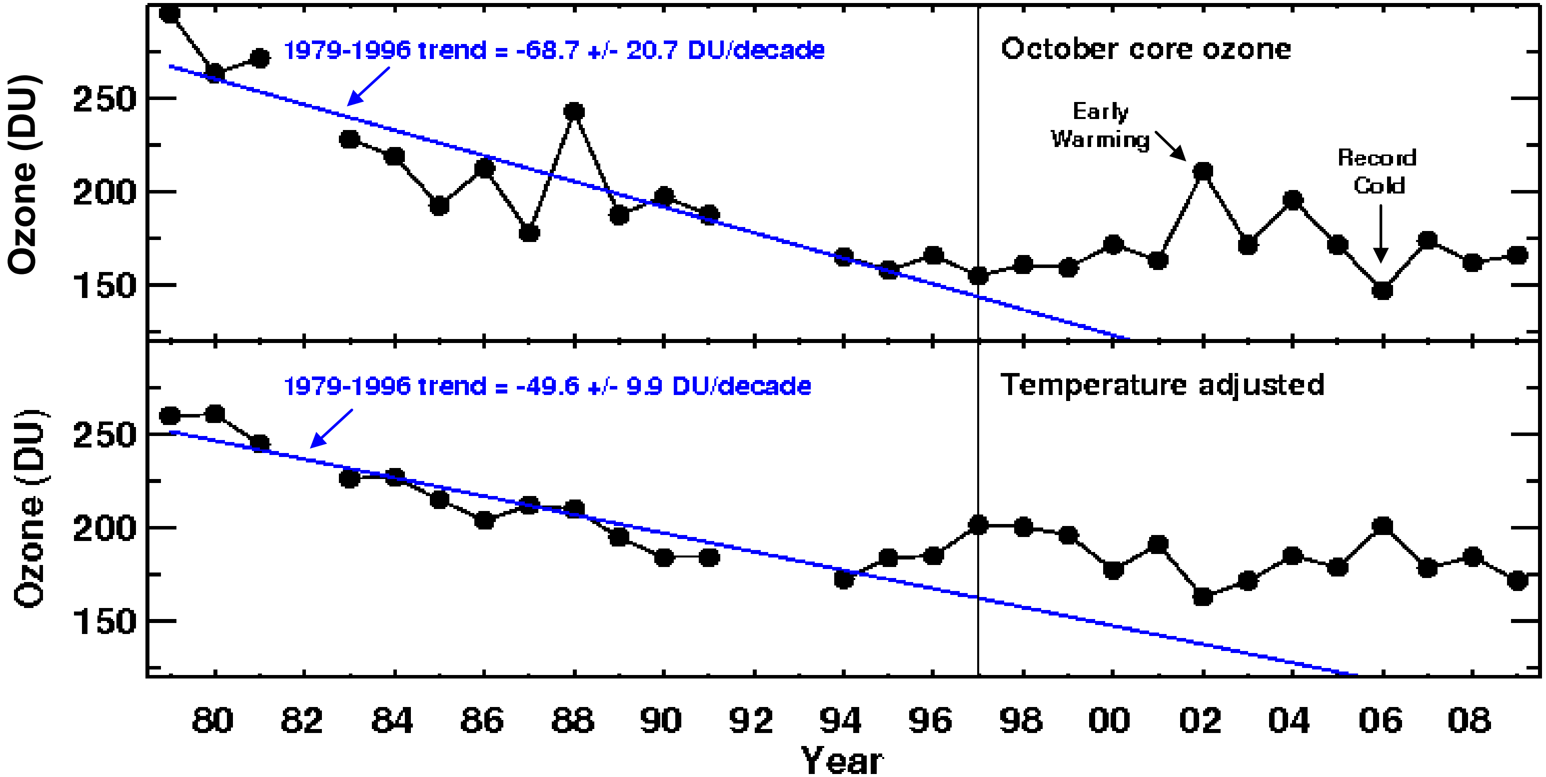
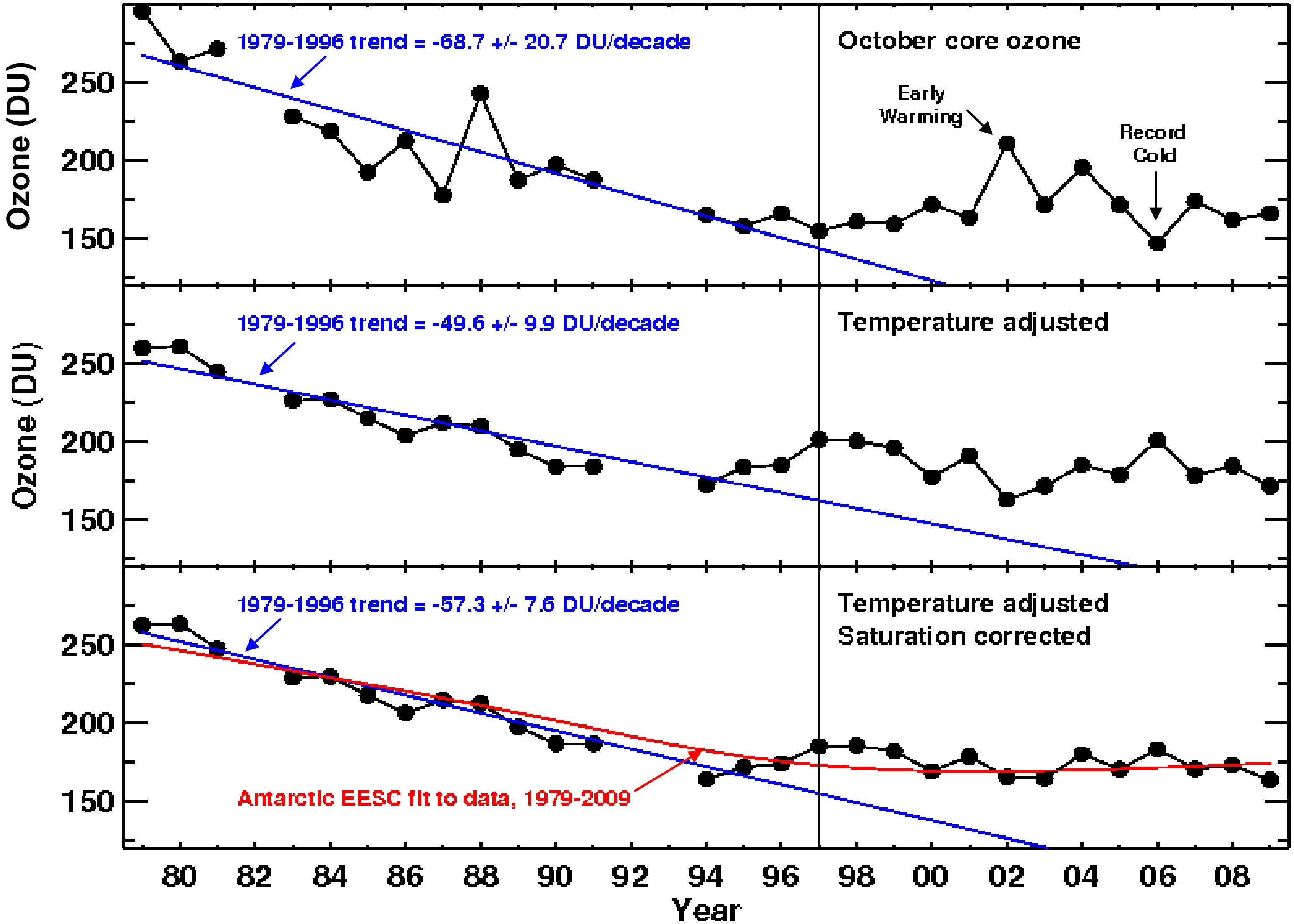


- **Have dealt with Complication #1 (Year to year variability in T)**
- **Now, must deal with Complication #2 (Loss Saturation)**
- **In our computer model, we allow ozone in the heart of the ozone depletion region to "go negative", to assess how much lower column ozone "would have been" without loss saturation**

Yang *et al.*, *JGR*, 2008, updated

Figure 2-28, WMO/UNEP 2011

Total Ozone Over Antarctica, October



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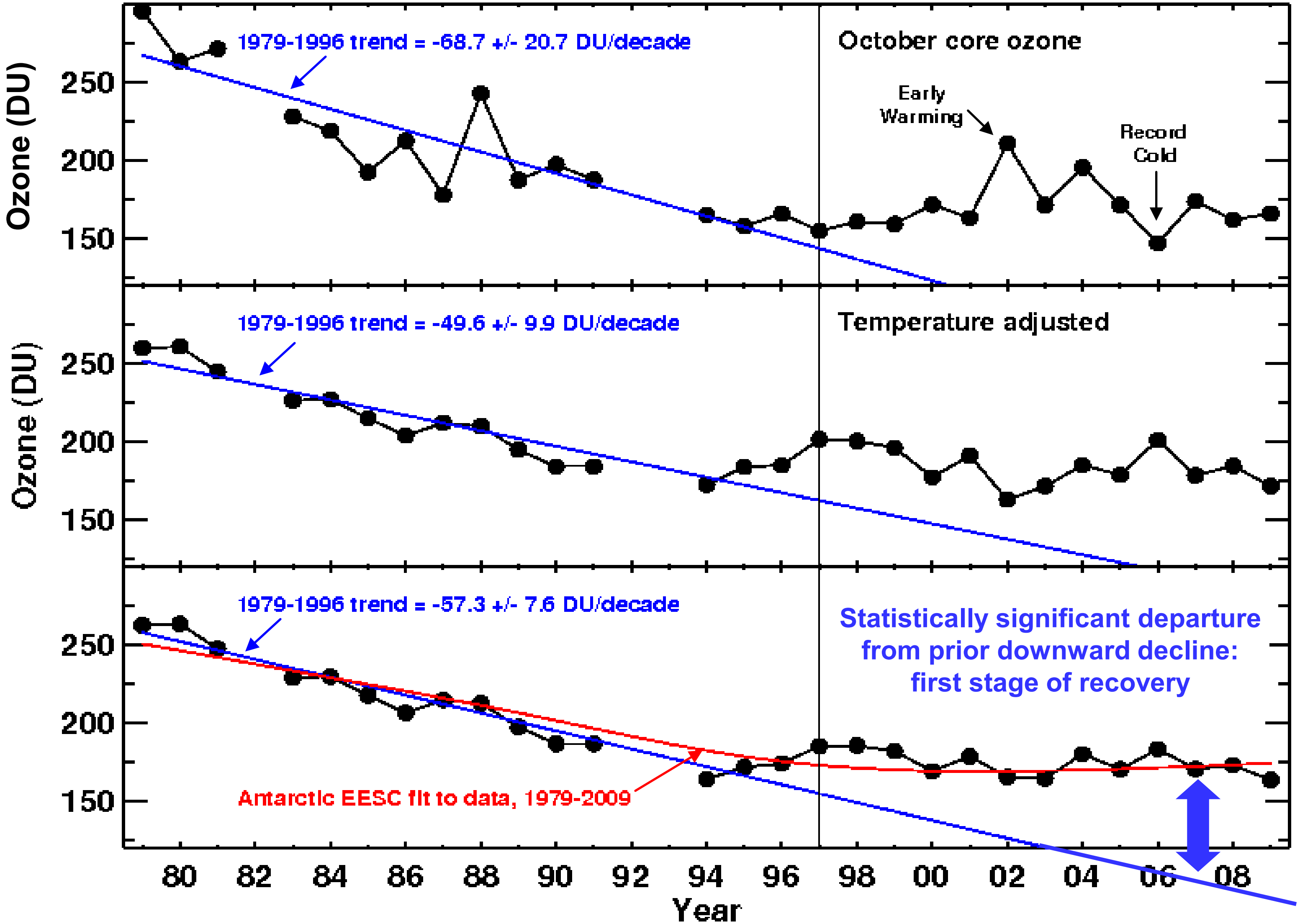


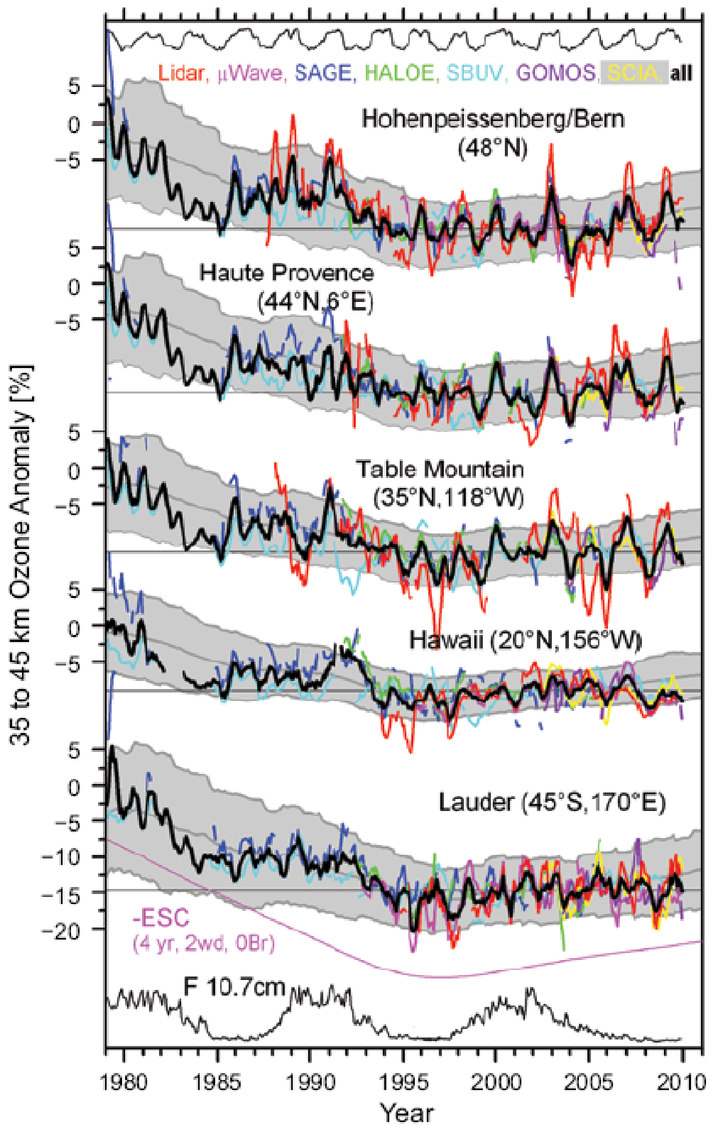
Update to Yang *et al*., *JGR*, 2008

Figure 2-28, WMO/UNEP 2011

Yang et al. (2008) concluded:

- **Antarctic Ozone is in the first stage of recovery due to the leveling off of ozone depleting substances**
- **In plain English: *chemical loss is not getting any worse***
  (use of word "recovery" seems strange, but the community has chosen this word to describe this situation!)
- **Yearly variations in Antarctic ozone now driven by meteorology**
- **Cold winters ⇒ low ozone**

Past Trends, Upper Stratospheric Ozone



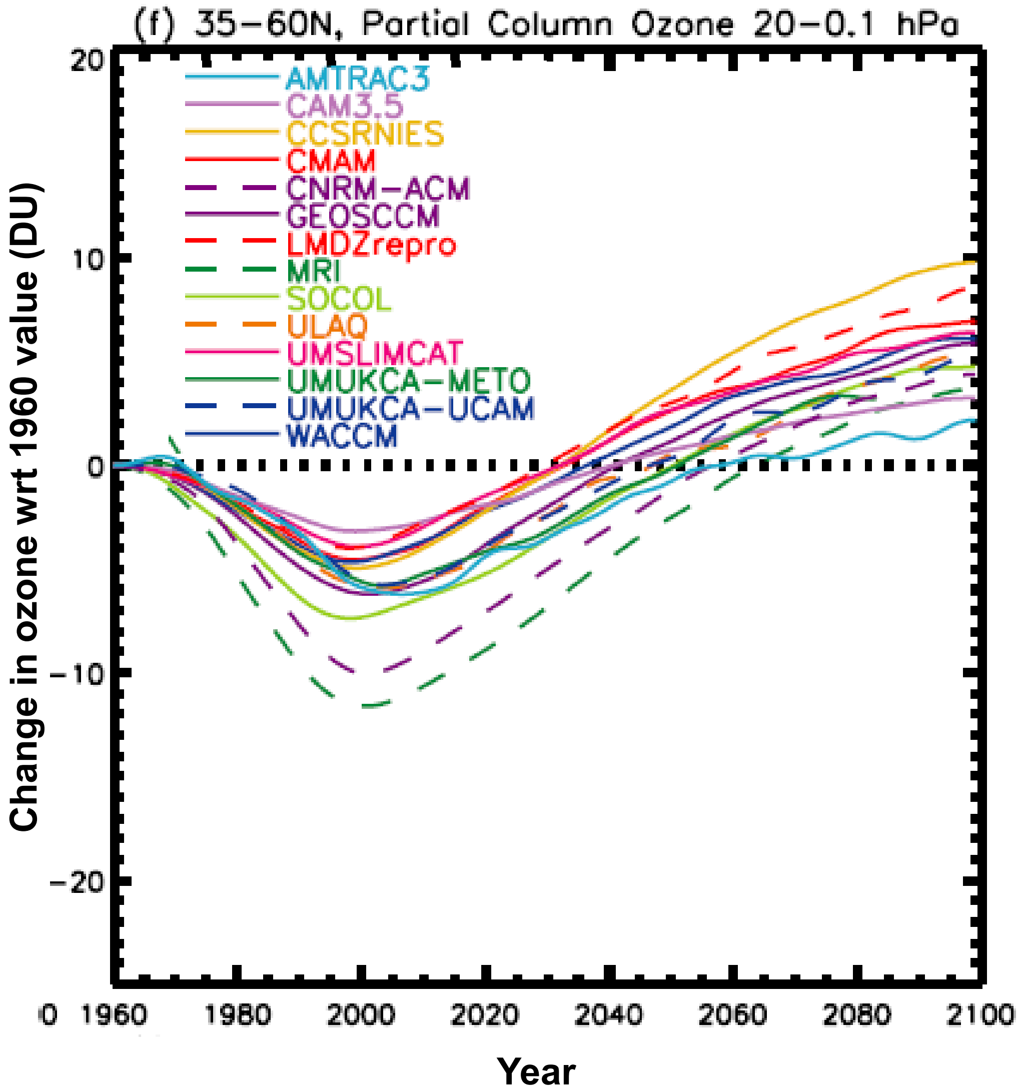
Grey: range of model calculations, where models are forced by rising levels of stratospheric halogens

Trends in ozone at 40 km are "well understood" and **generally follow track time history of stratospheric chlorine loading.**

Lecture 14, Slide 22

Figure 2-5, WMO/UNEP 2011

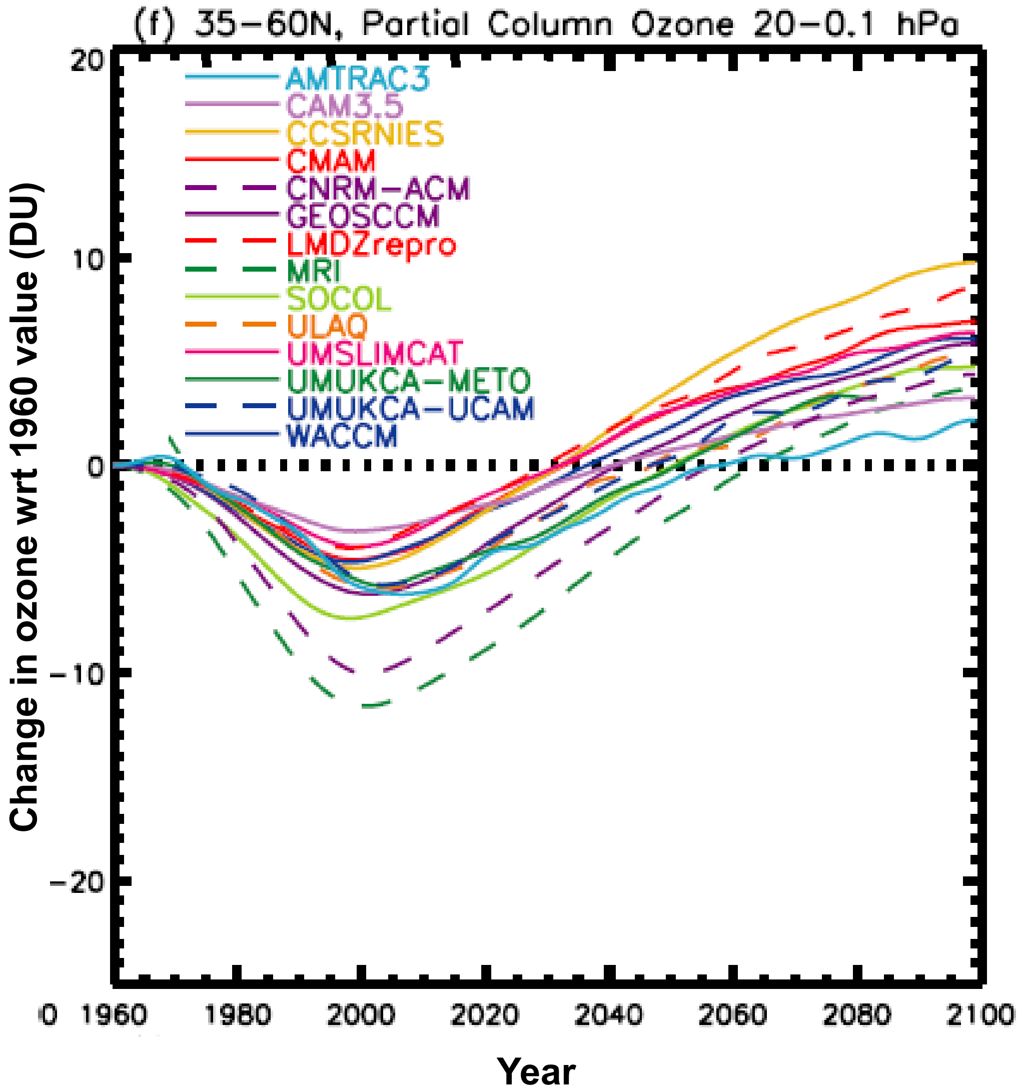
Future Trends, Upper Stratospheric Ozone



Oman et al., *JGR*, 2010

14 coupled chemistry climate models (CCMs) predict upper stratospheric ozone in 2100 will exceed upper stratospheric ozone in 1960

Future Trends, Upper Stratospheric Ozone



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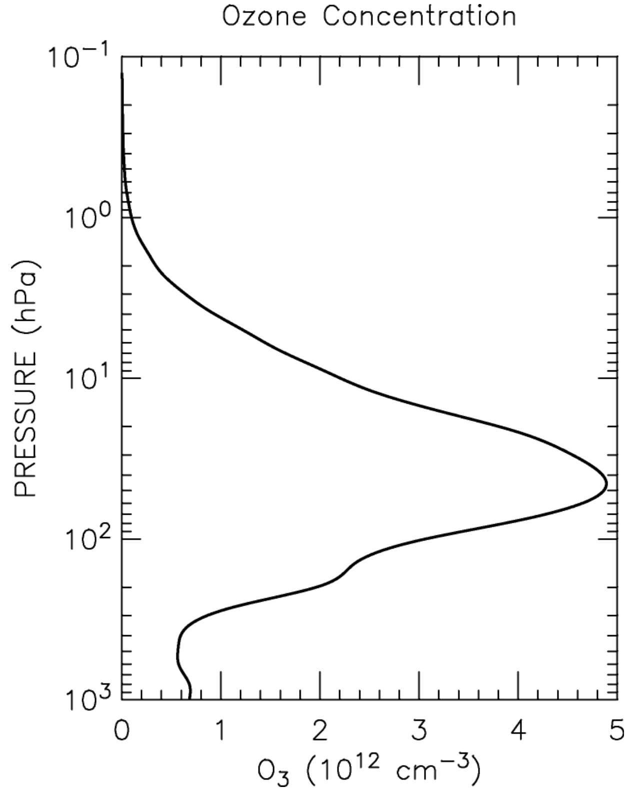
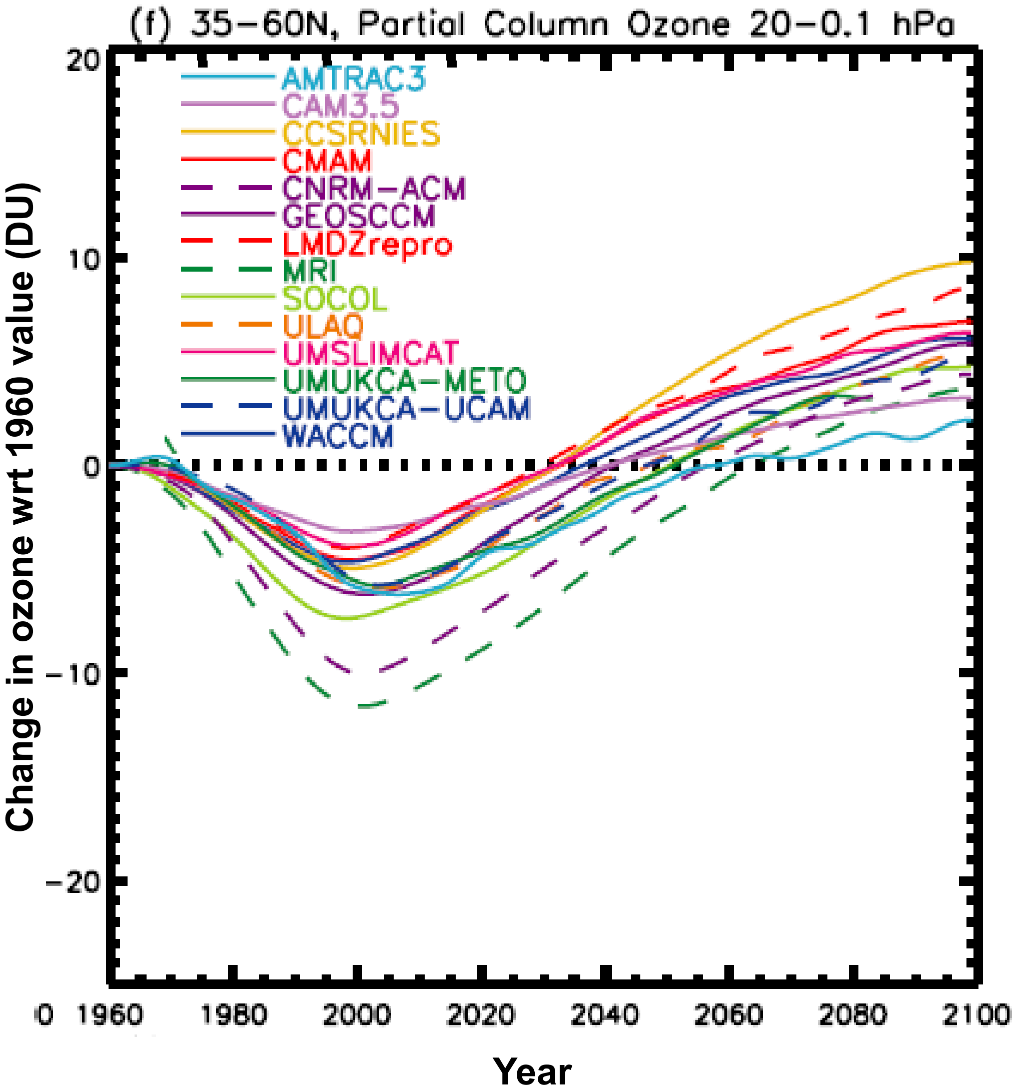


Future Trends, Upper Stratospheric Ozone



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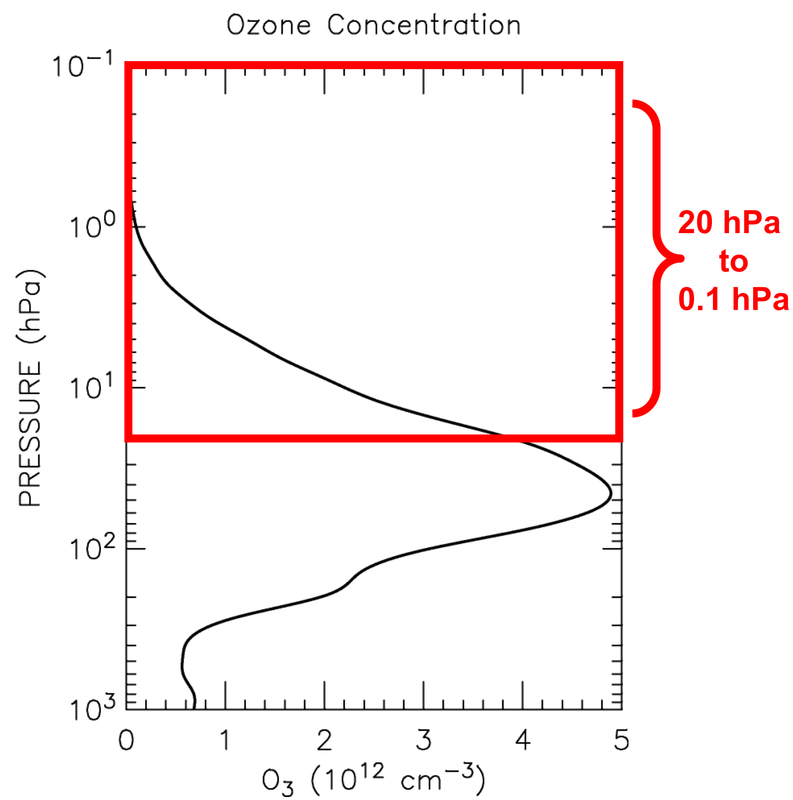
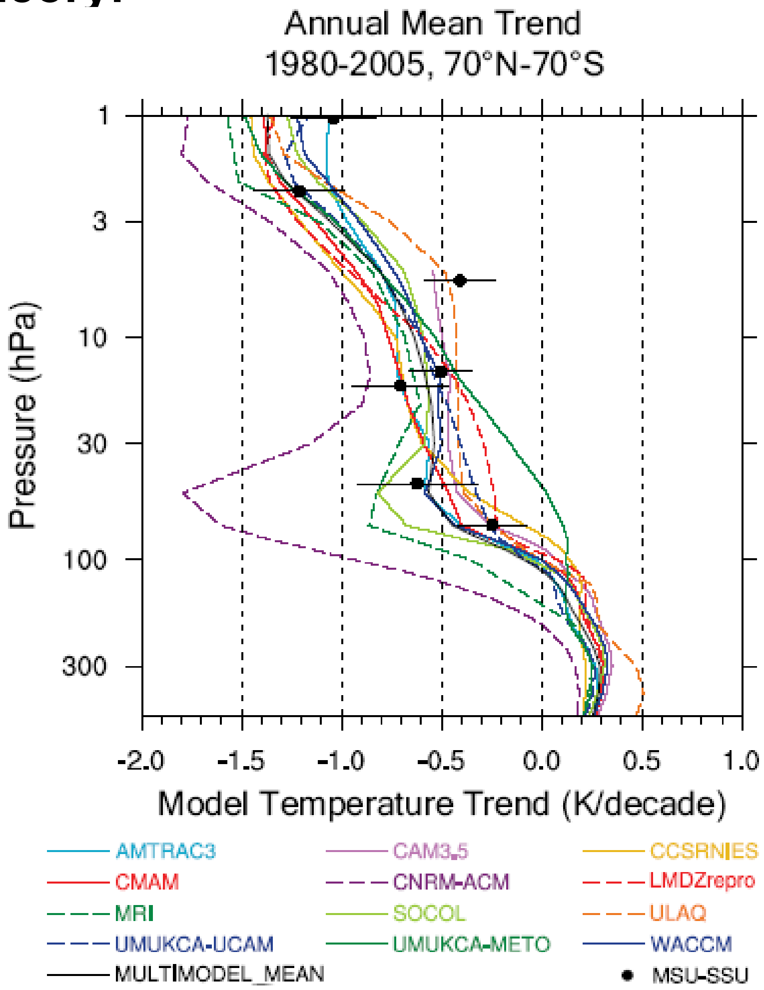


Climate and Chemistry Coupling

Scientists have long known that rising GHGs leads to cooling of the stratosphere, due to direct radiative effects

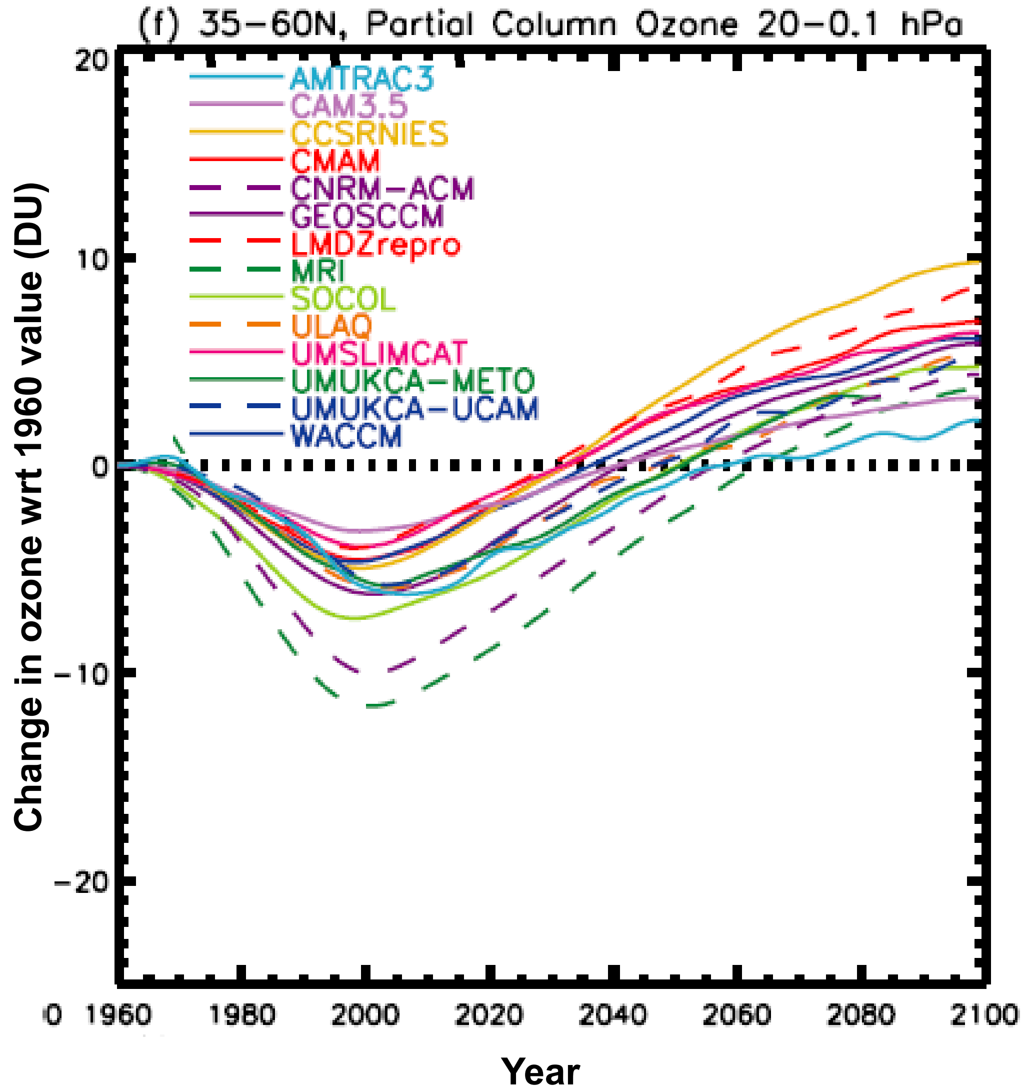
The stratosphere has been cooling past several decades in a manner broadly consistent with theory:



Lecture 15, Slide 30

Figure 4−11, WMO/UNEP (2011)

Future Trends, Upper Stratospheric Ozone



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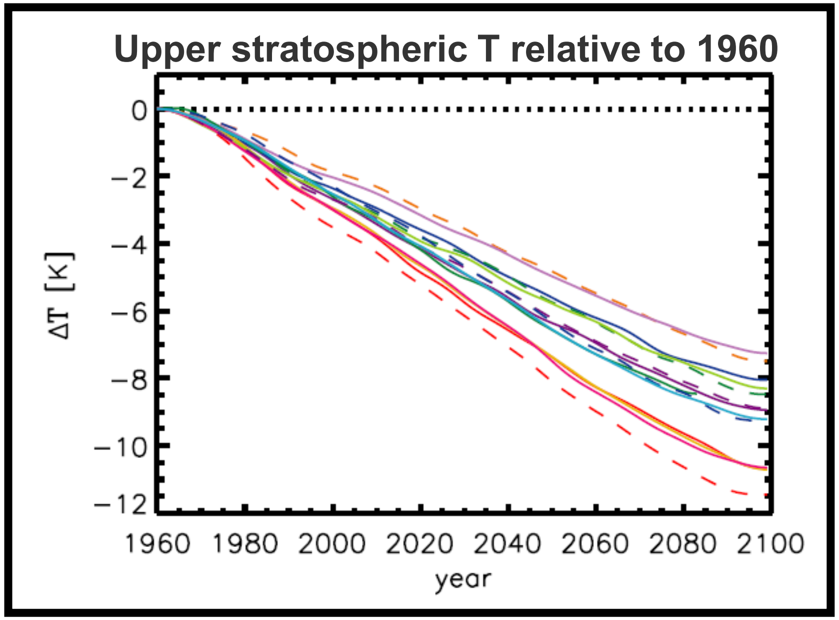
Due to stratospheric cooling !



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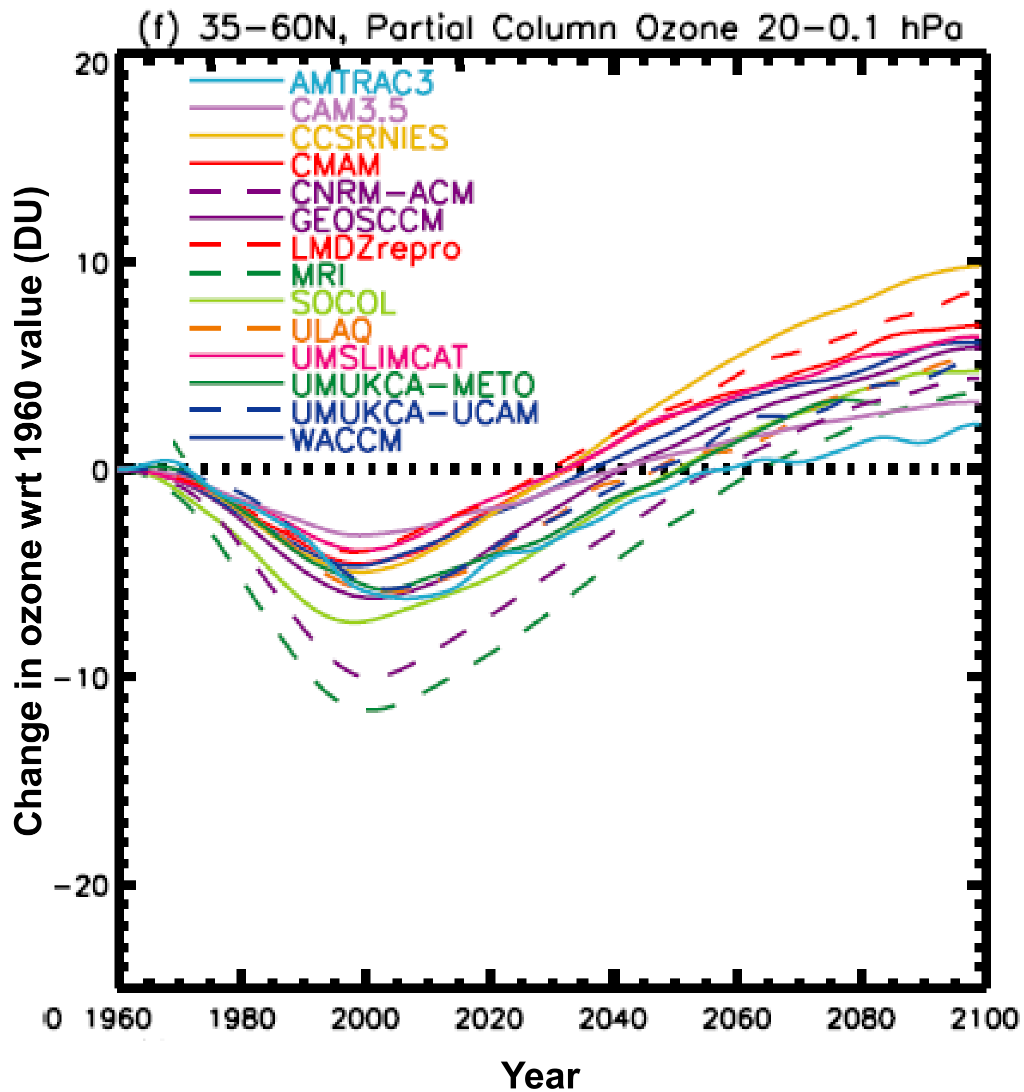
Future Trends, Upper Stratospheric Ozone



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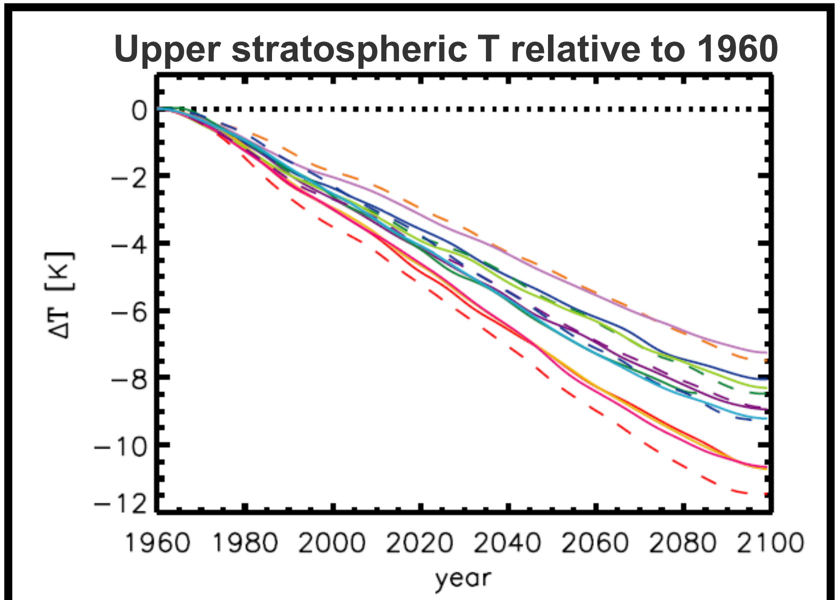
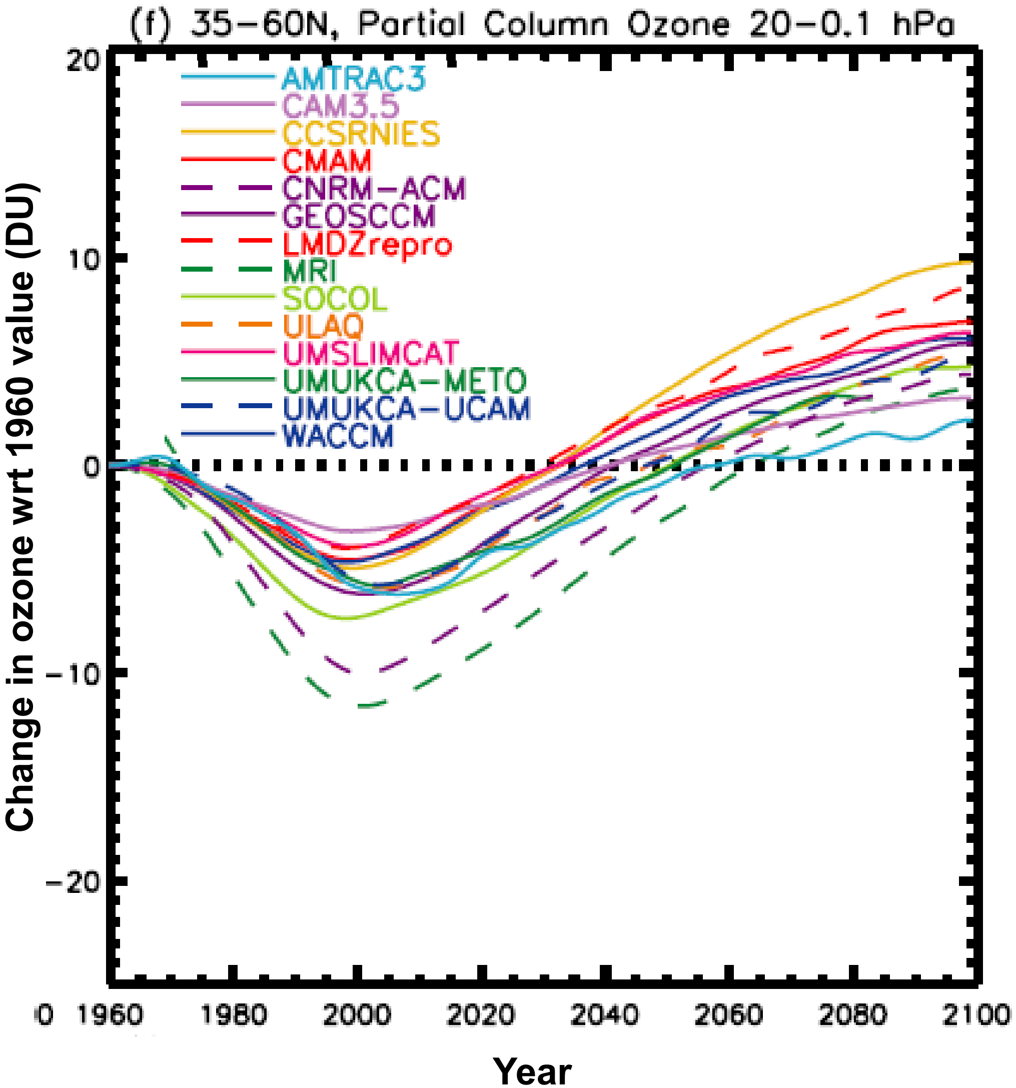
Why this response of ozone to lower T ?



Future Trends, Upper Stratospheric Ozone



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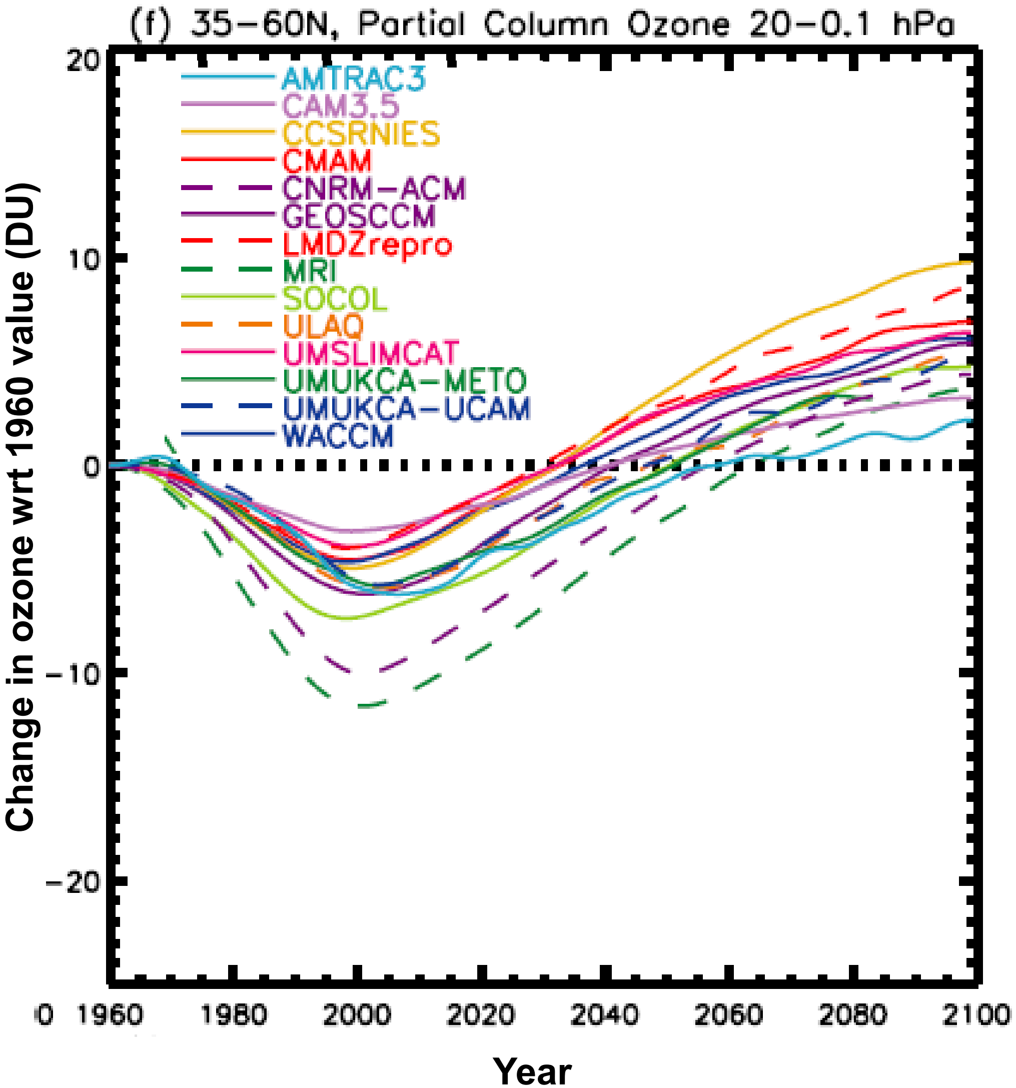

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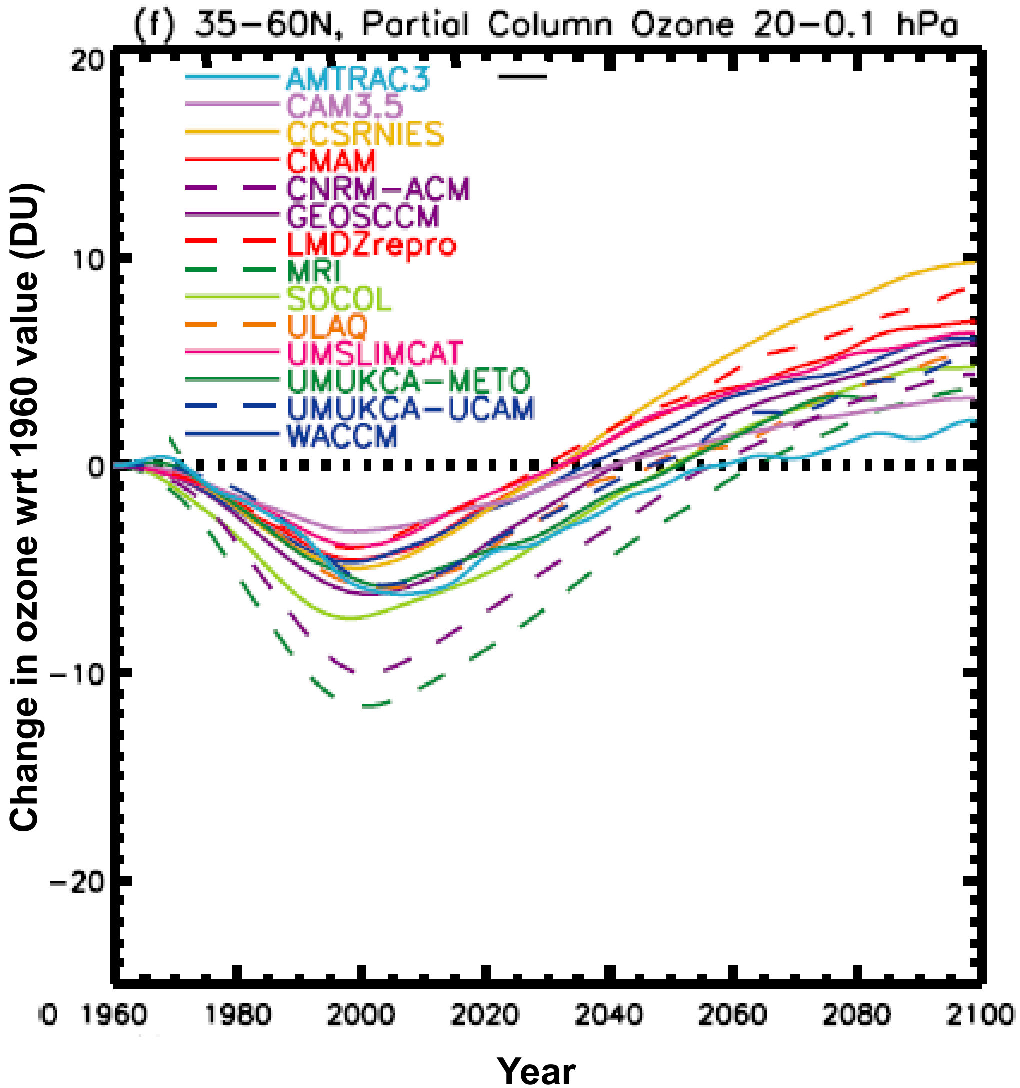
Future Trends, Upper Stratospheric Ozone



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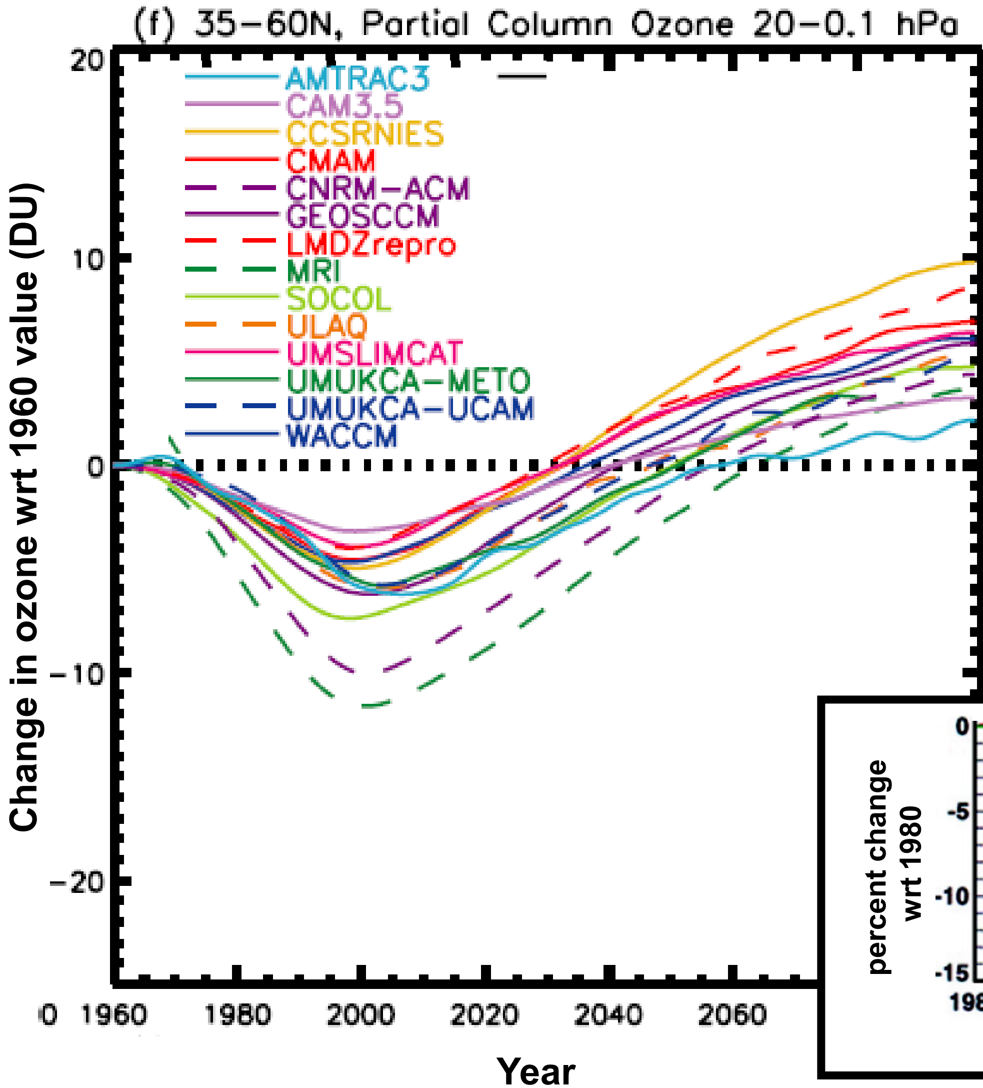
Future Trends, Upper Stratospheric Ozone



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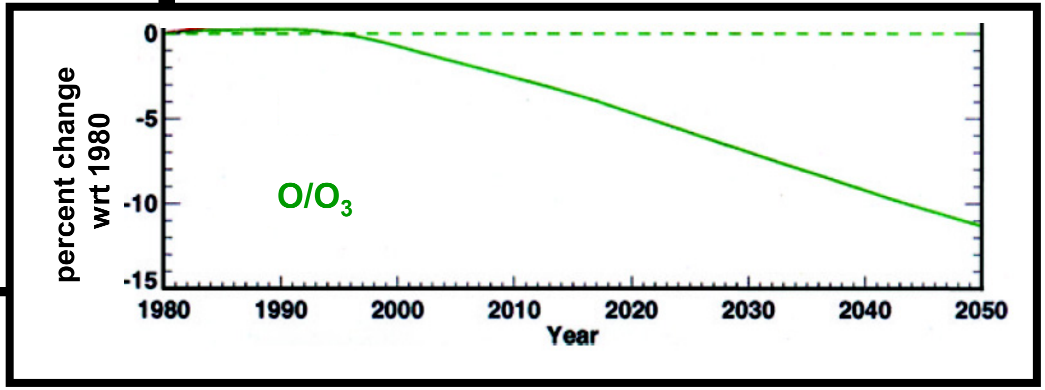
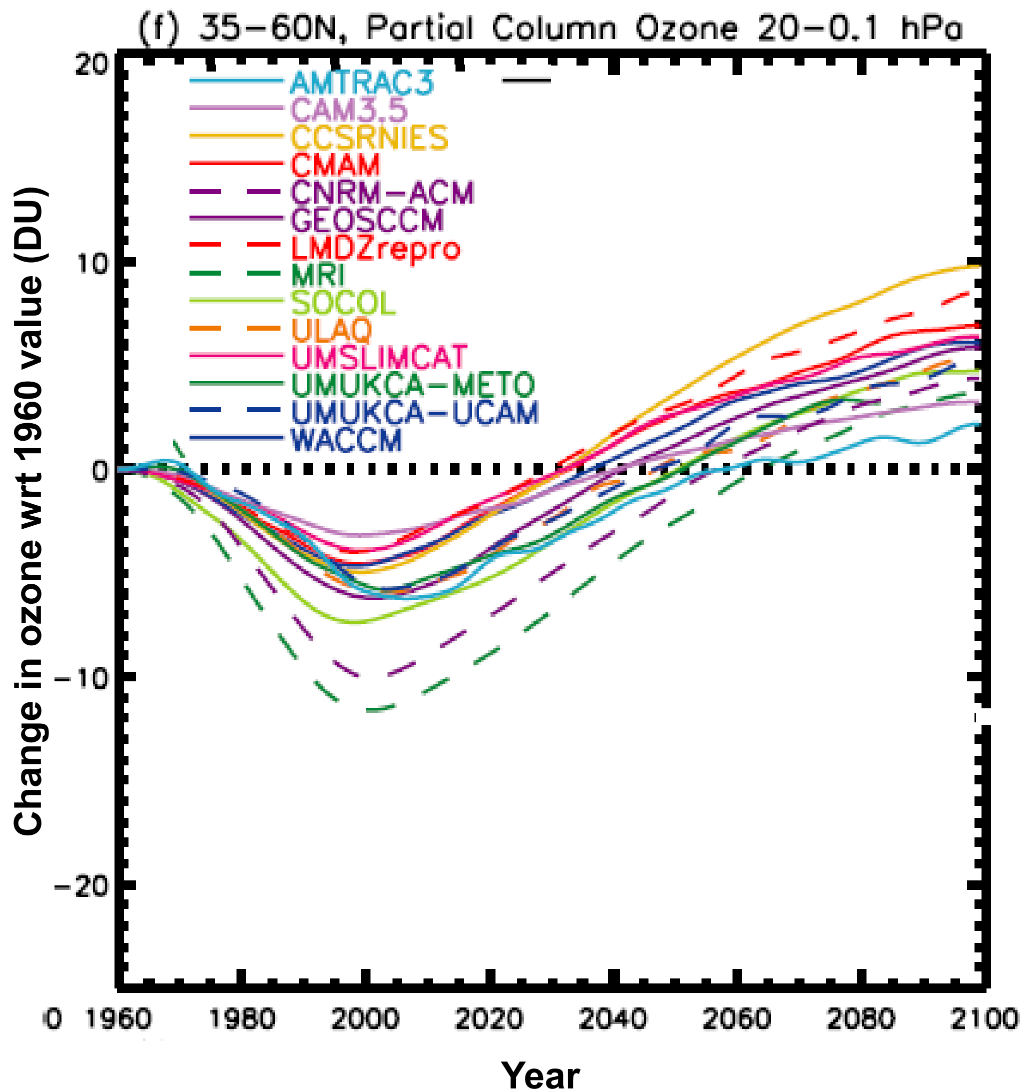


Rosenfield *et al.*, *JGR*, 2002

Future Trends, Upper Stratospheric Ozone



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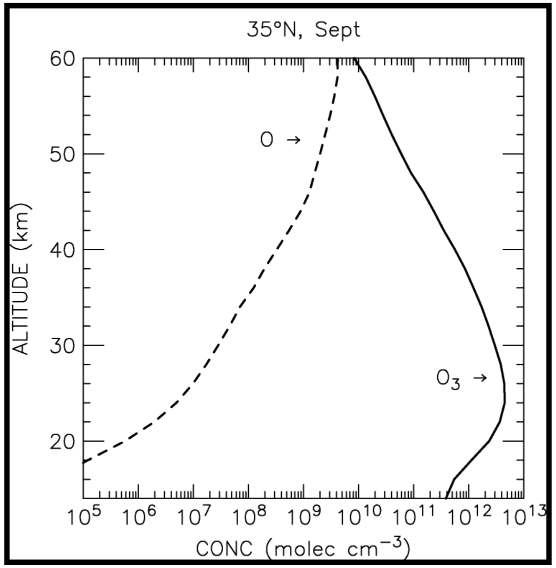


More Chemistry and Climate Coupling

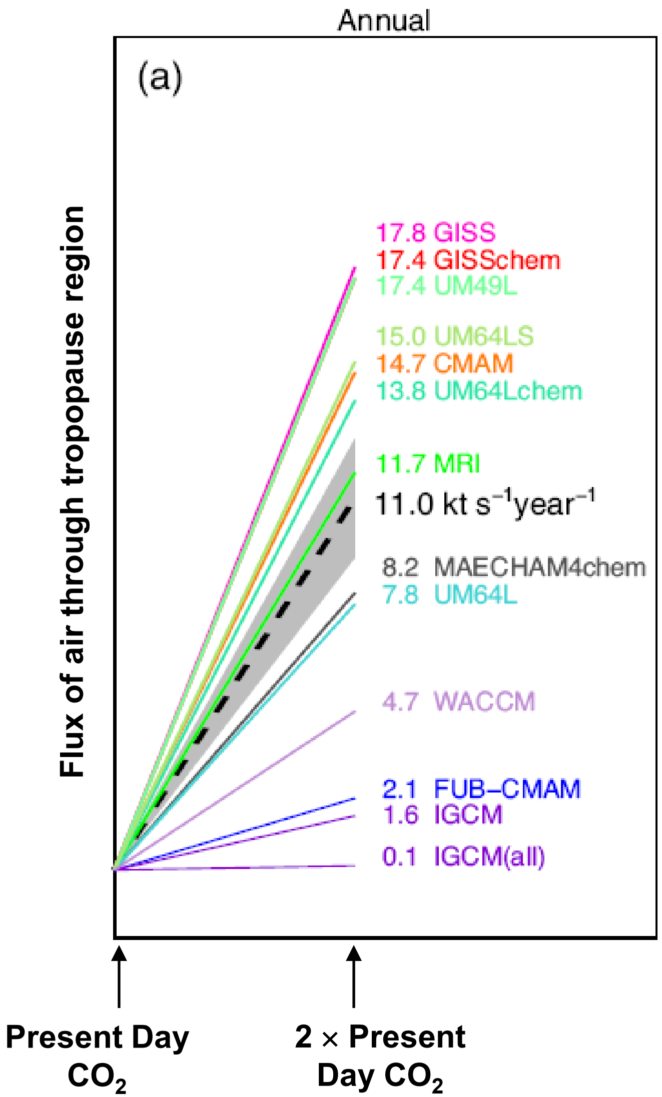


Figure 5-17. Trends in exchange of air from troposphere-to-stratosphere computed by 14 CCMs.

Trends (units of Gg s^{-1} $year^{-1}$) are represented by the slope of each line.

Dashed line is the multi-model mean.

After Butchart *et al*., *Clim. Dyn*., 2006.

WMO/UNEP Ozone Assessment Report 2007

Brewer-Dobson Circulation

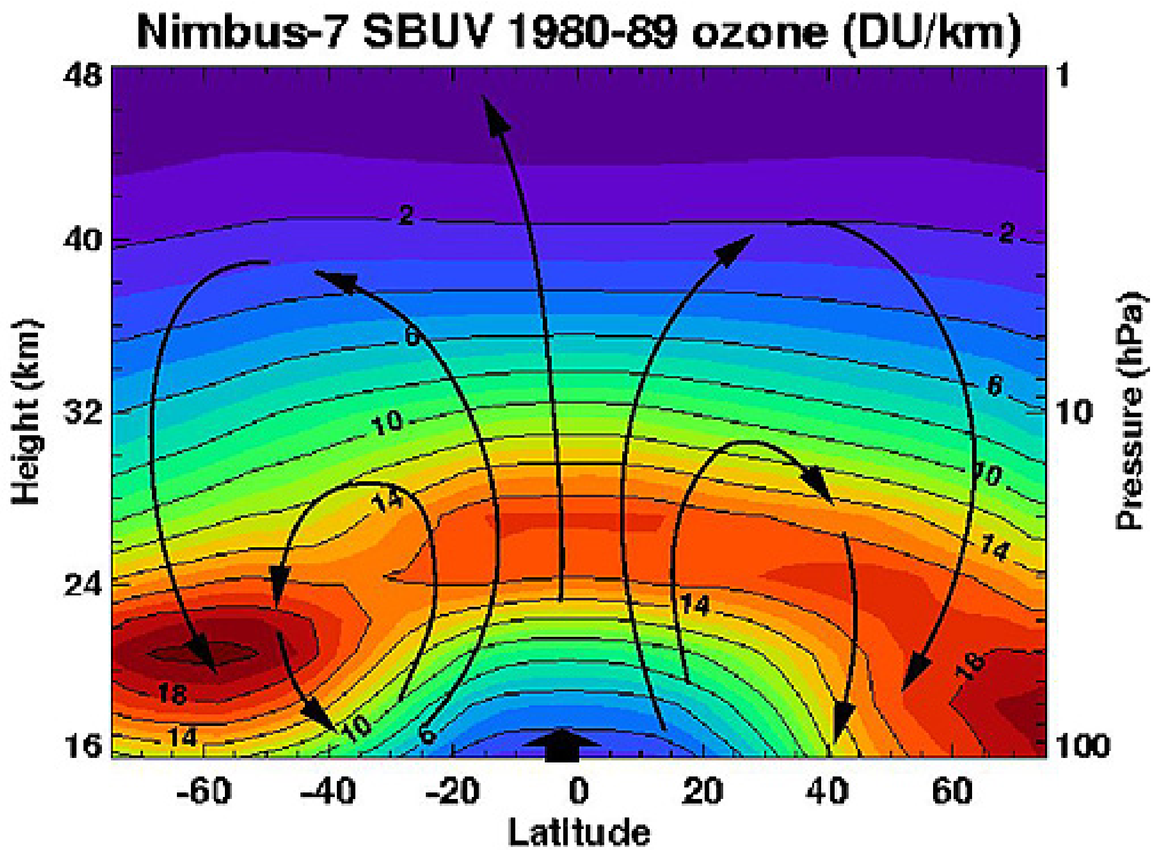
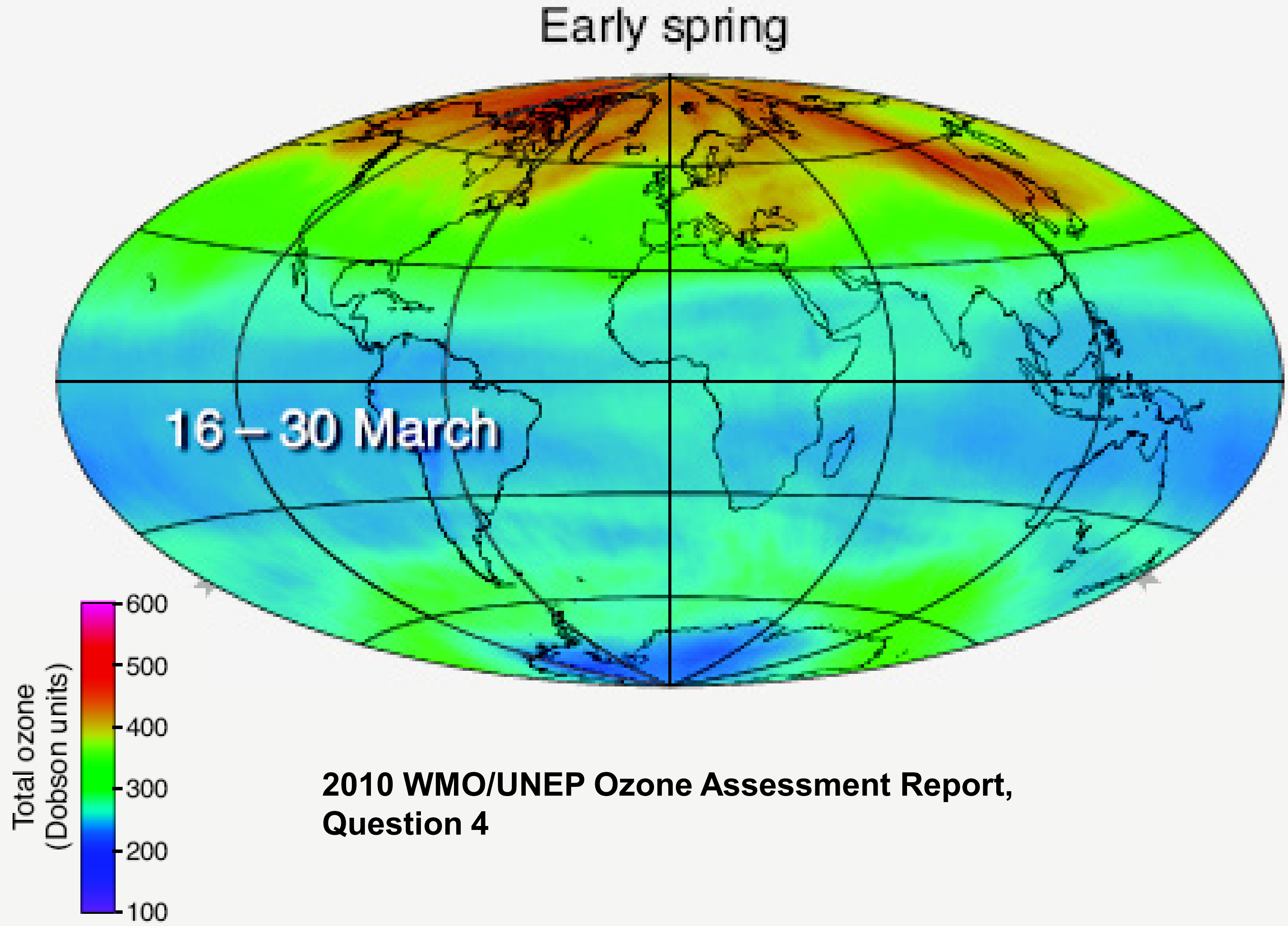


Figure 6.03 Schematic diagram of Brewer-Dobson circulation with seasonally averaged ozone concentration

http://www.ccpo.odu.edu/~lizsmith/SEES/ozone/class/Chap_1/1_Js/1-06.jpg

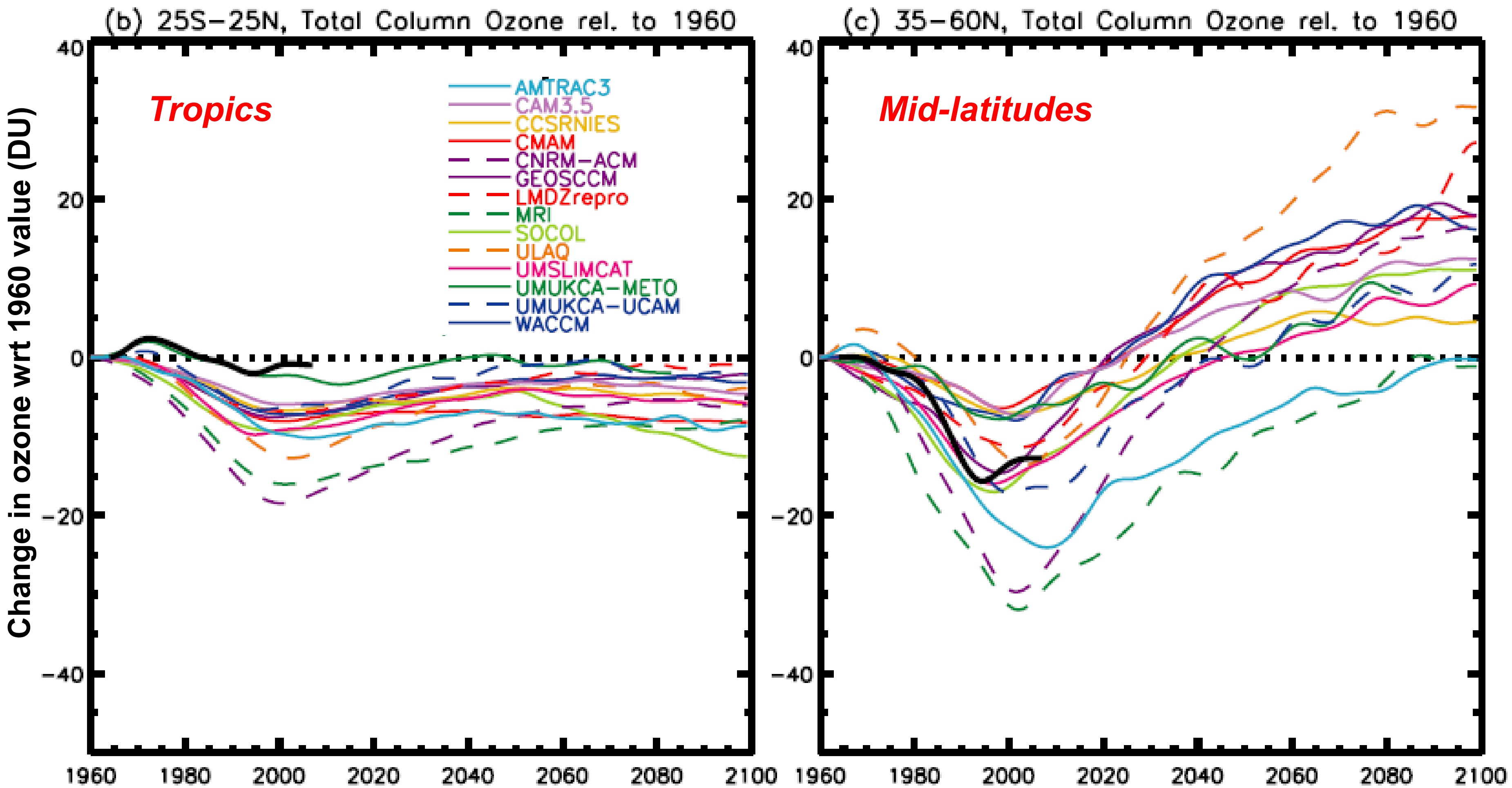
Brewer-Dobson Circulation is a model of atmospheric circulation, proposed by Alan Brewer in 1949 and Gordon Dobson in 1956, that attempts to explain why tropical air has less column ozone than polar air, even though the tropical stratosphere is where most atmospheric ozone is produced

Global Satellite Maps of Total Ozone in 2009



2010 WMO/UNEP Ozone Assessment Report, Question 4

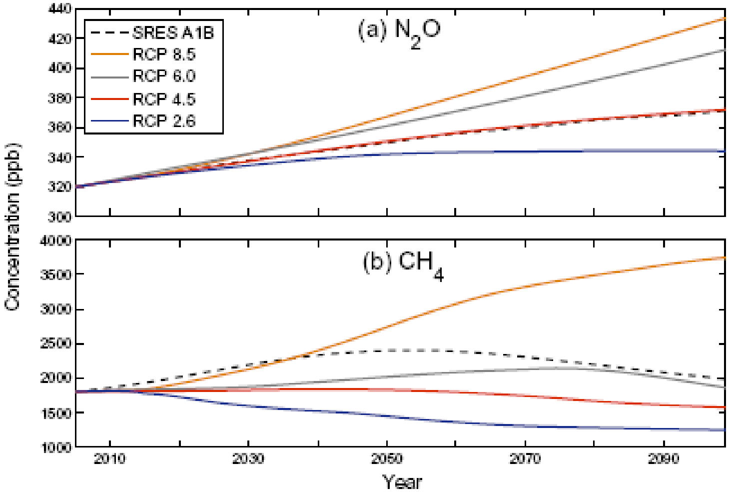
More Chemistry and Climate Coupling



Acceleration of the *Brewer-Dobson Circulation* causes modeled total ozone column in the tropics to exhibit a sustained, long term decline and modeled total ozone column in the NH to experience a "super recovery"

Oman et al., *JGR*, 2010

Future Mid-Latitude Ozone: CH_4



Rising CH_4 leads to ozone loss in the upper & lower stratos. by increasing the speed of HO_x mediated loss cycles (blue regions, Fig 6b).

However, there are other processes that result in more ozone (red regions, Fig 6b):

- Rising CH_4 leads to more stratospheric H_2O, cooling this region of the atmosphere, which slows the rate of all ozone loss cycles
- Rising CH_4 speeds up the rate of $Cl+CH_4$, shifting chlorine from ClO into HCl
- Rising CH_4 leads to more HO_2 in the lowermost stratosphere, where there is sufficient CO to result in production of O_3 by photochemical smog chemistry

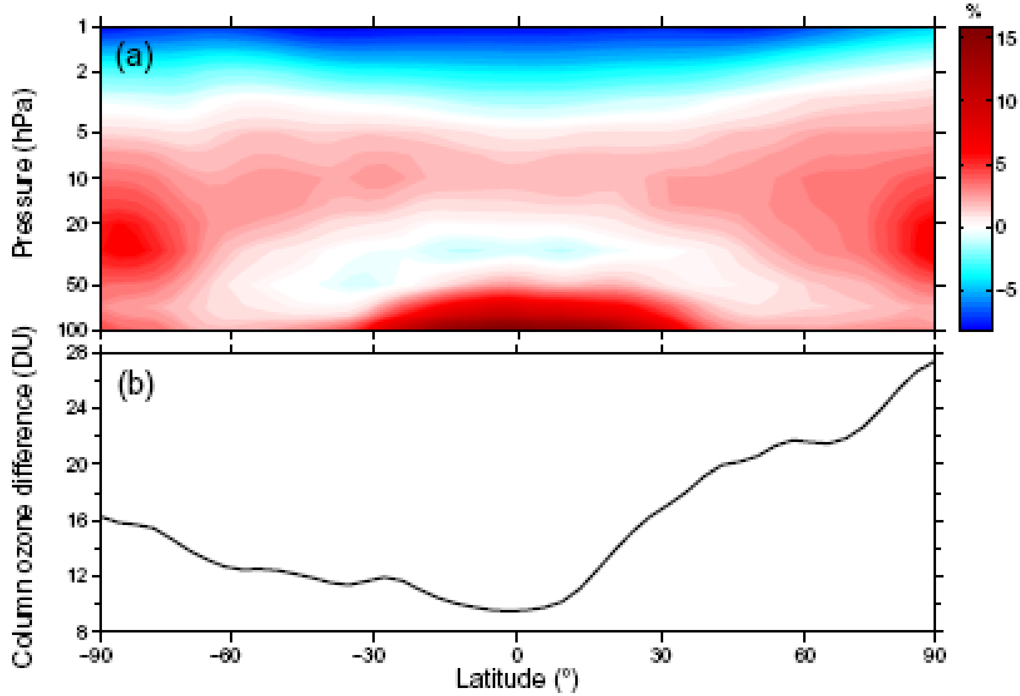
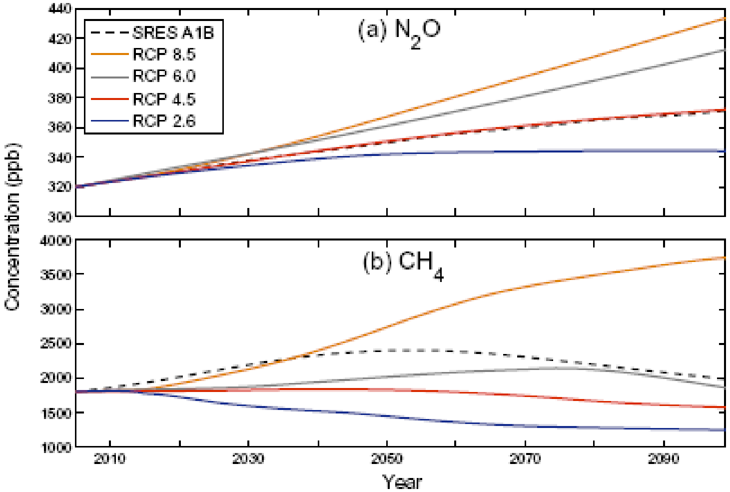


Fig. 6. (a) CH_4-8.5 ozone minus CH_4-2.6 ozone in the 2090s decade, calculated as a percentage of ozone in the CH_4-2.6 simulation. **(b)** 2090s-decade CH_4-8.5 total column ozone minus CH_4-2.6 total column ozone.

Revell *et al.*, *ACP*, 2012

Future Mid-Latitude Ozone: N_2O



Ozone depleting NO_x cycles speed up with increasing N_2O throughout the middle stratosphere, where these cycles make the largest relative contribution to odd oxygen loss (blue region, Fig 5a).

• As NO_2 increases due to rising N_2O, the abundance of ClO declines, particularly in the lower stratosphere, leading to reduced rates in the total speed of all ozone depleting cycles (red region, Fig 5a); small contrib. to the red region due to production of O_3 by photochemical smog chemistry.

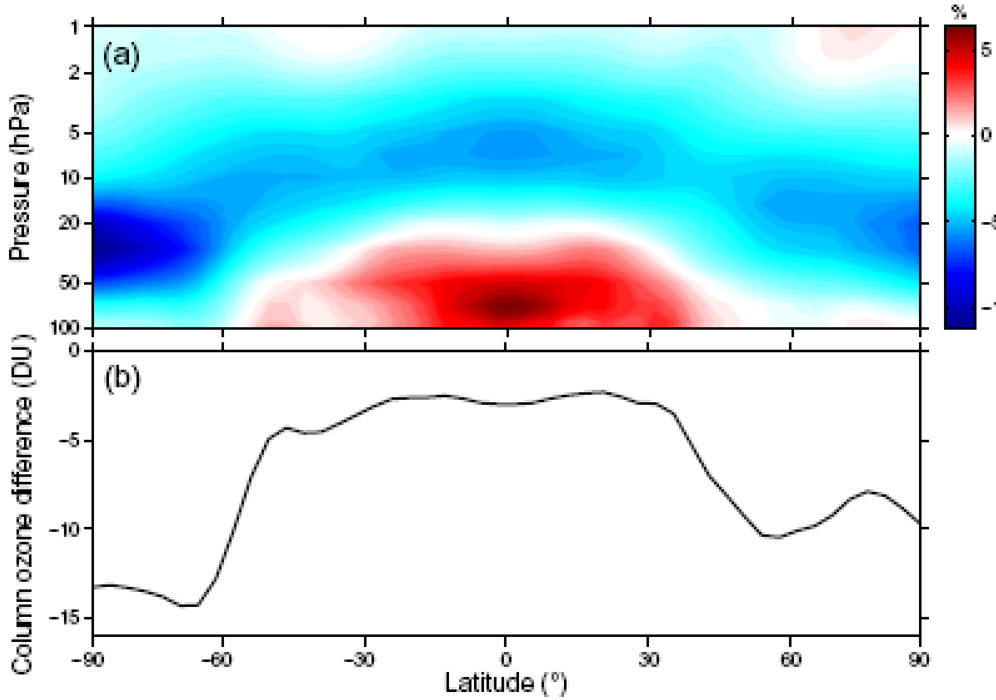
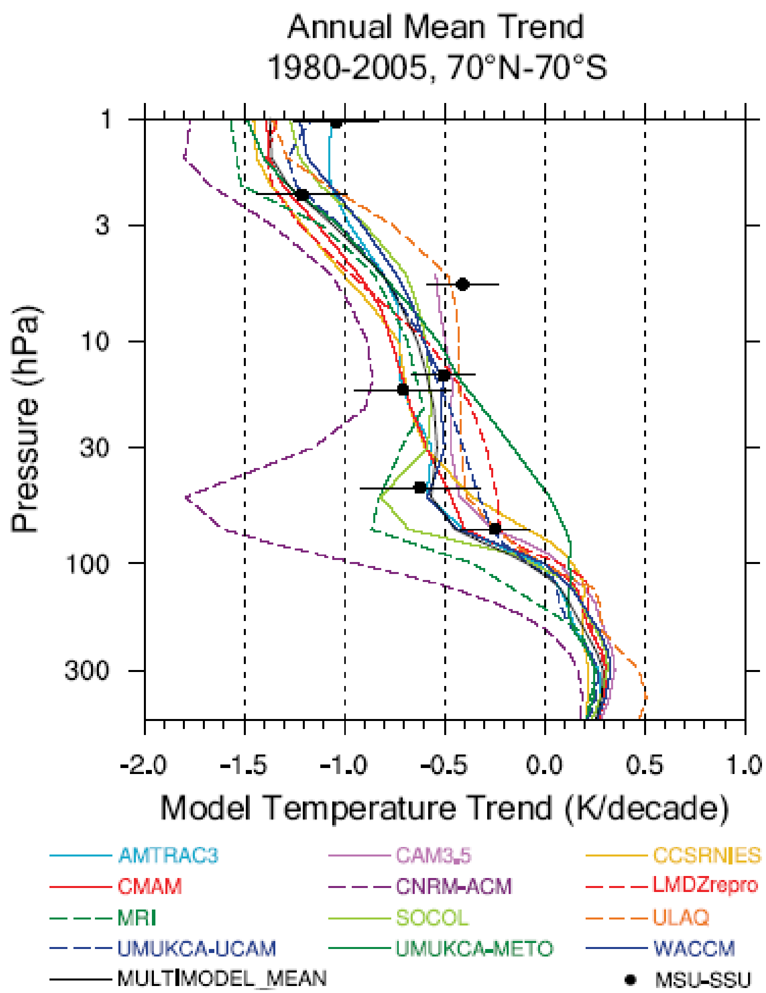


Fig. 5. (a) N_2O-8.5 ozone minus N_2O-2.6 ozone in the 2090s decade, calculated as a percentage of ozone in the N_2O-2.6 simulation. **(b)** 2090s-decade N_2O-8.5 total column ozone minus N_2O-2.6 total column ozone.

Revell *et al*., *ACP*, 2012

Future Trends, Stratospheric Ozone

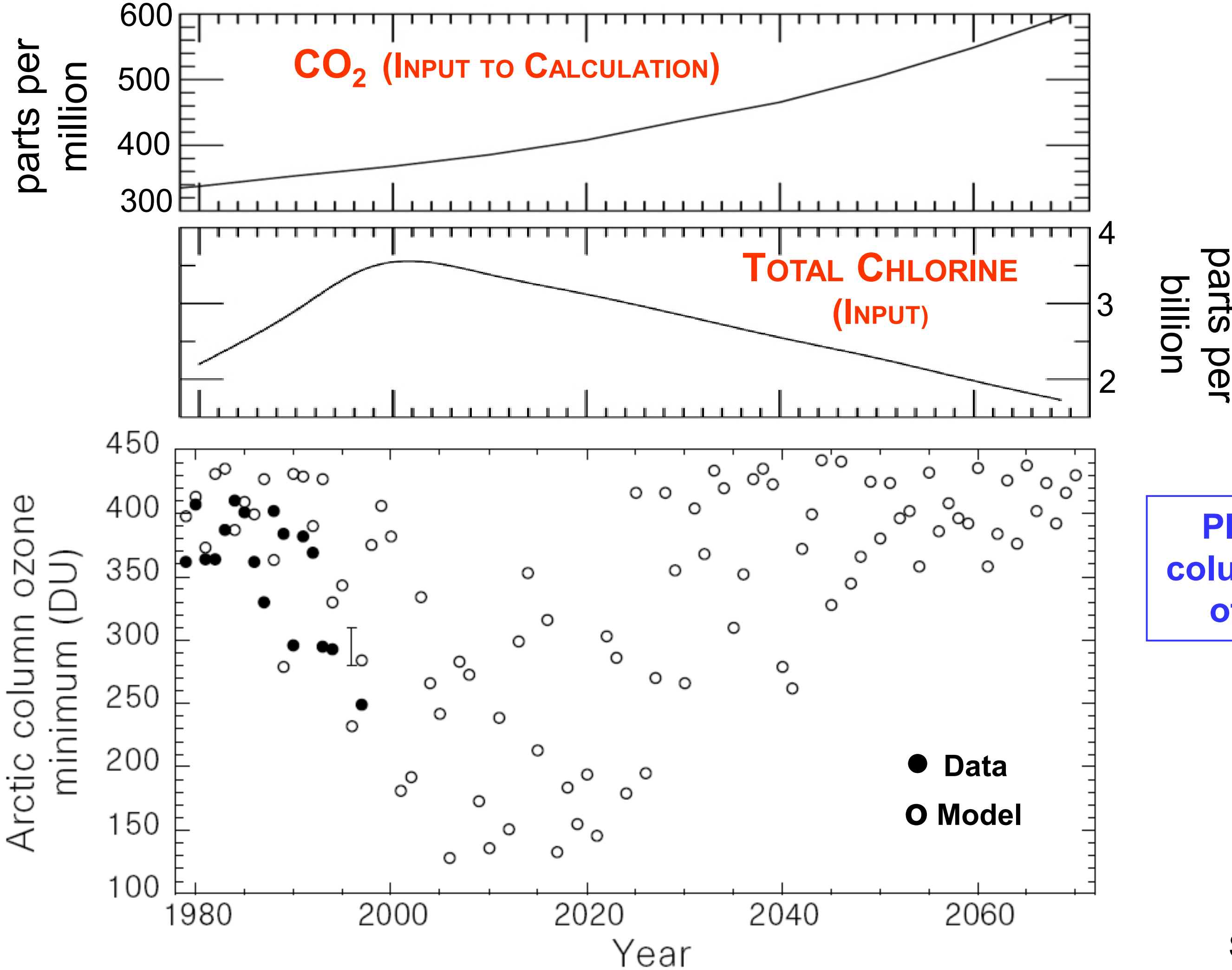


If the stratosphere *continues to cool*, for which region of the stratosphere is ozone "most vulnerable"?

Figure 4−11, WMO/UNEP (2011)

Lecture 15, Slide 30

Arctic Ozone Loss - Climate and Chemistry Coupling



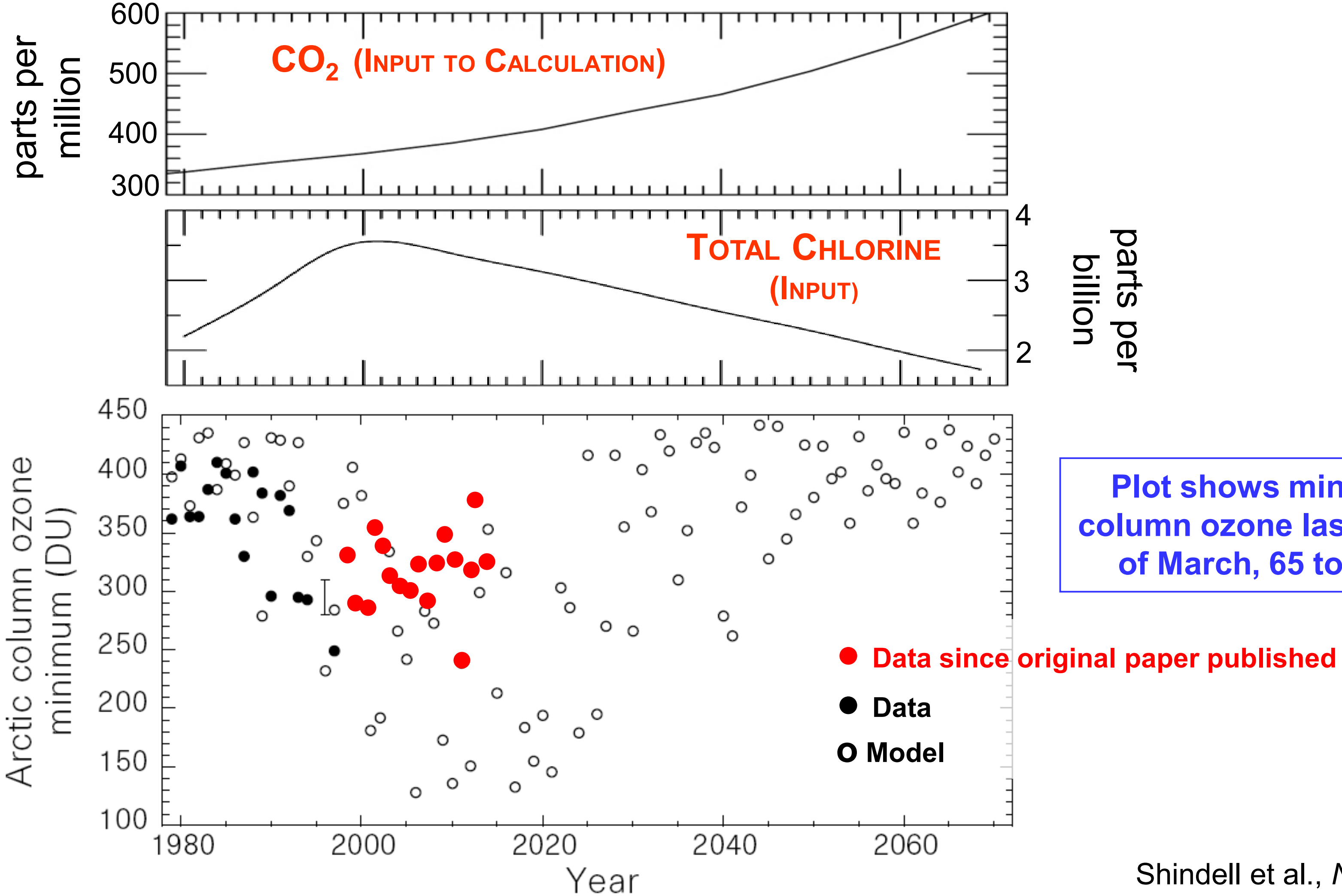
Plot shows minimum column ozone last 3 days of March, 65 to 90°N

Shindell et al., *Nature*, 1998

Shindell et al. (1998) postulated that rising GHGs would lead to more stable polar vortex circulations, resulting in **maximum loss of Arctic ozone in the decade 2010 to 2019**.

Driving factor is a decrease in the poleward propagation of planetary waves i.e., dynamics

Arctic Ozone Loss - Climate and Chemistry Coupling

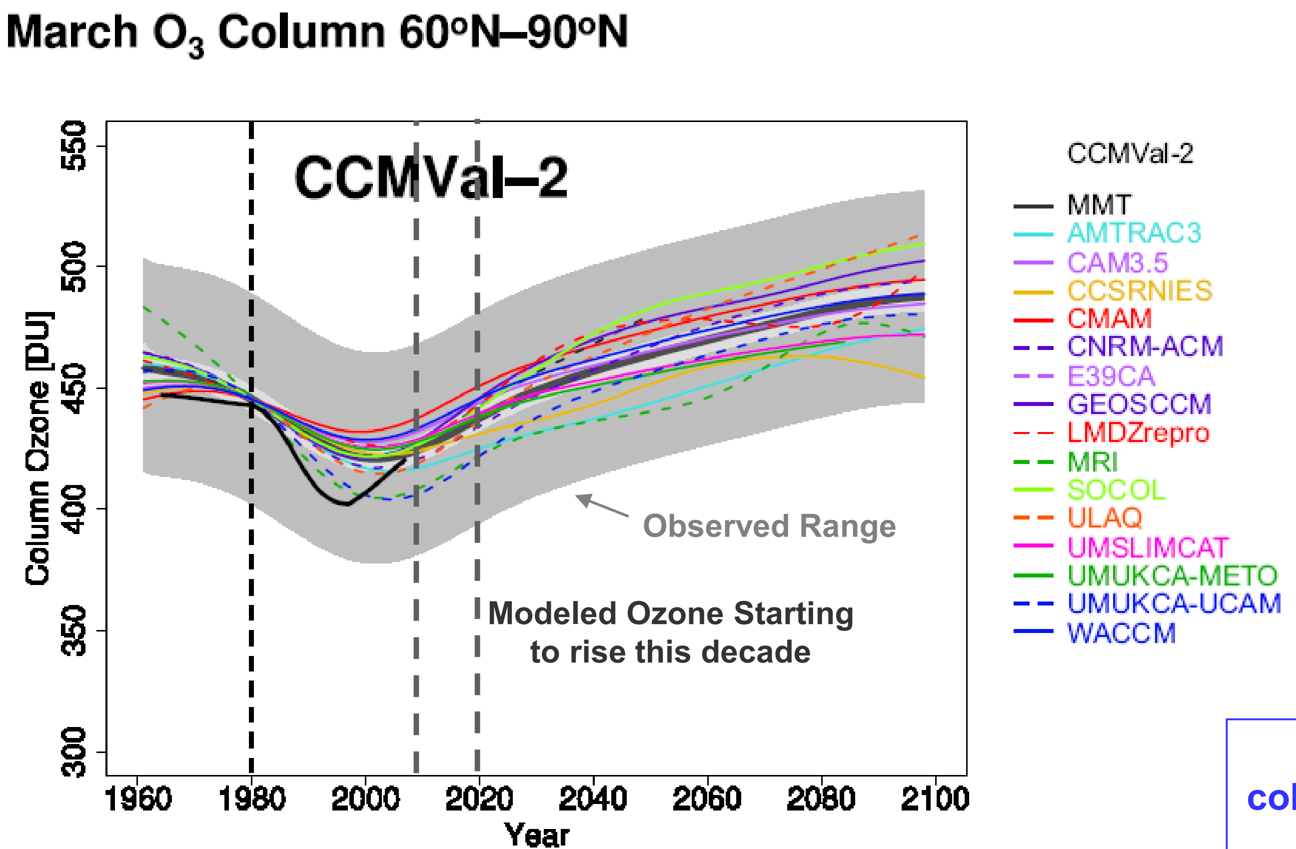


Plot shows minimum column ozone last 3 days of March, 65 to 90°N

Shindell et al., *Nature*, 1998

Arctic column ozone has not reached the very deep minima predicted by Shindell et al., even in 2011

Arctic Ozone Loss - Climate and Chemistry Coupling

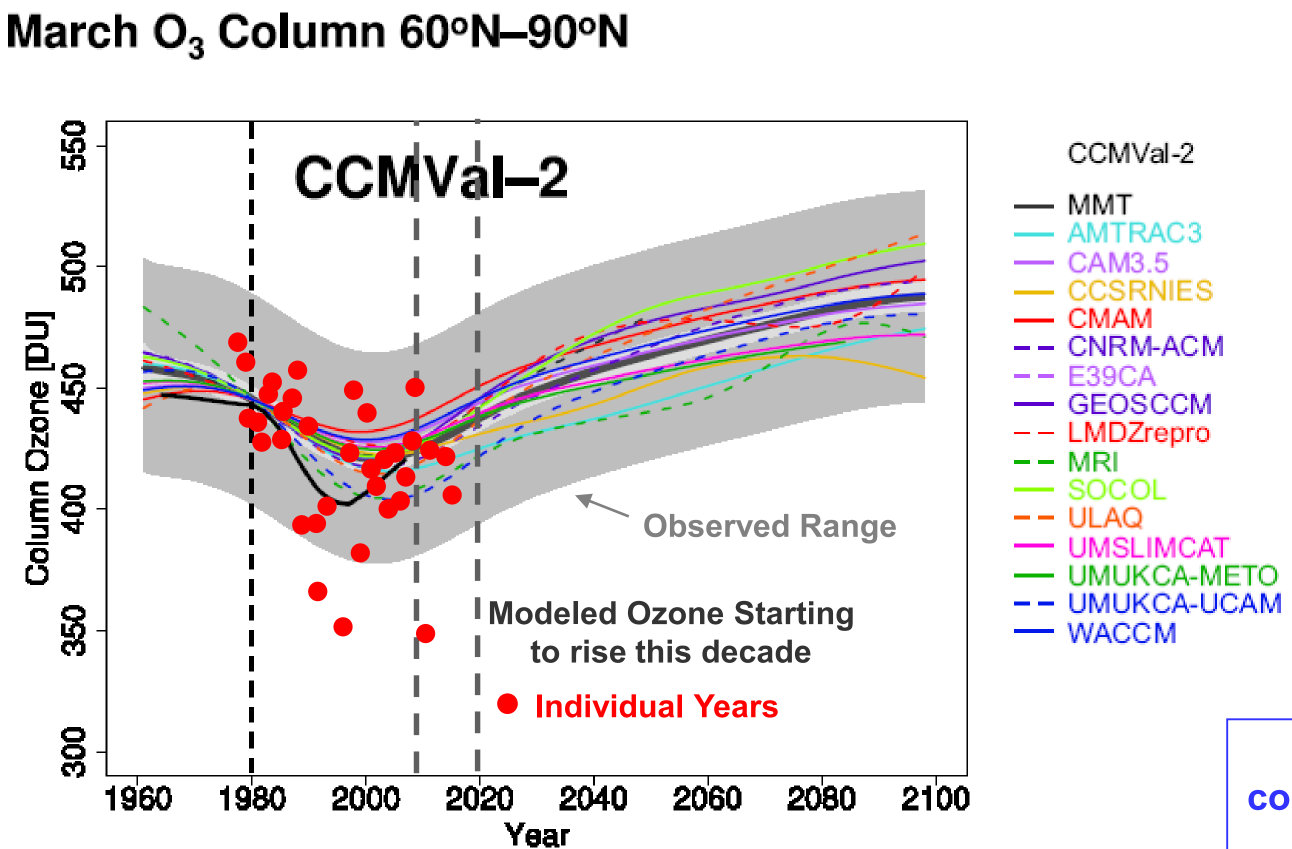


Plot shows mean column ozone for March, 60 to 90°N

Figure 9.11, CCMVal-2
http://www.atmosp.physics.utoronto.ca/SPARC/ccmval_final/index.php

Latest generation of chemistry climate models do not reproduce the results of Shindell et al. (1998)
No consensus on how Arctic ozone will be affected by climate change.

Arctic Ozone Loss - Climate and Chemistry Coupling



Plot shows mean column ozone for March, 60 to 90°N

Figure 9.11, CCMVal-2
http://www.atmosp.physics.utoronto.ca/SPARC/ccmval_final/index.php

Data for individual years suggest latest generation of models in need of major improvement

Arctic Ozone Loss and Climate Change

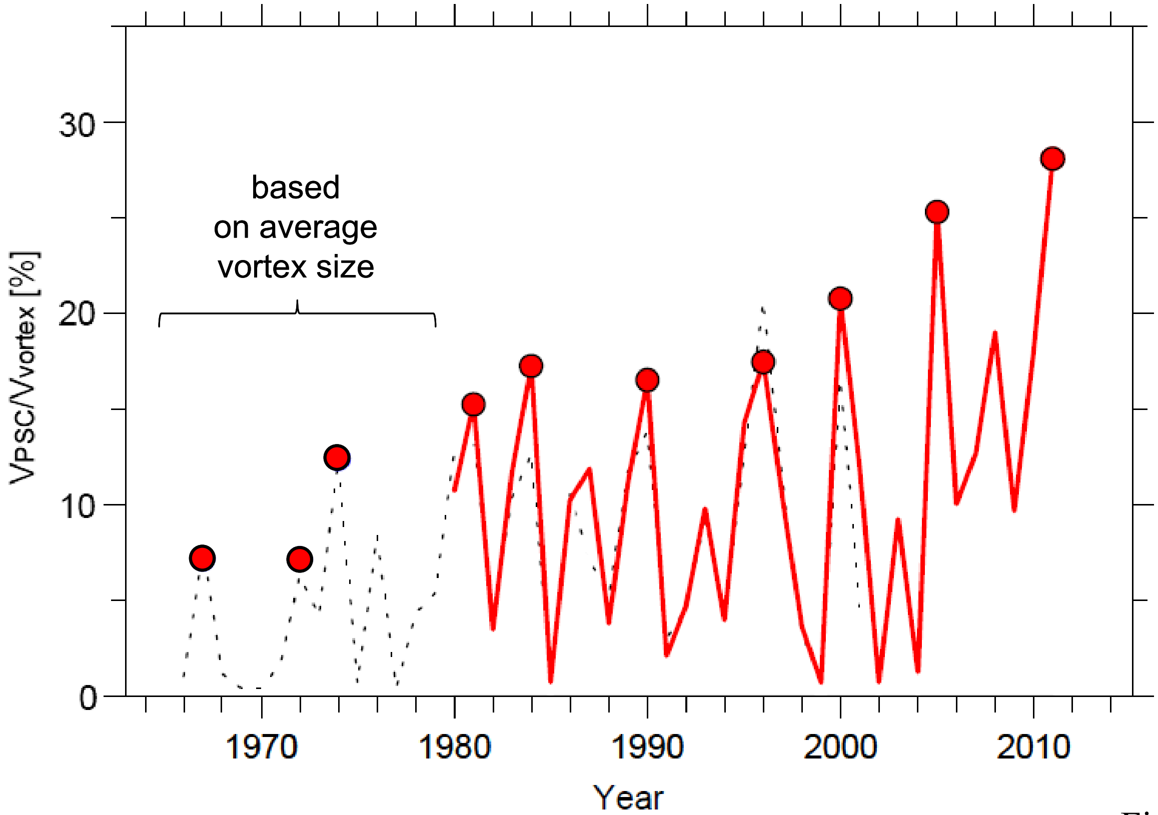
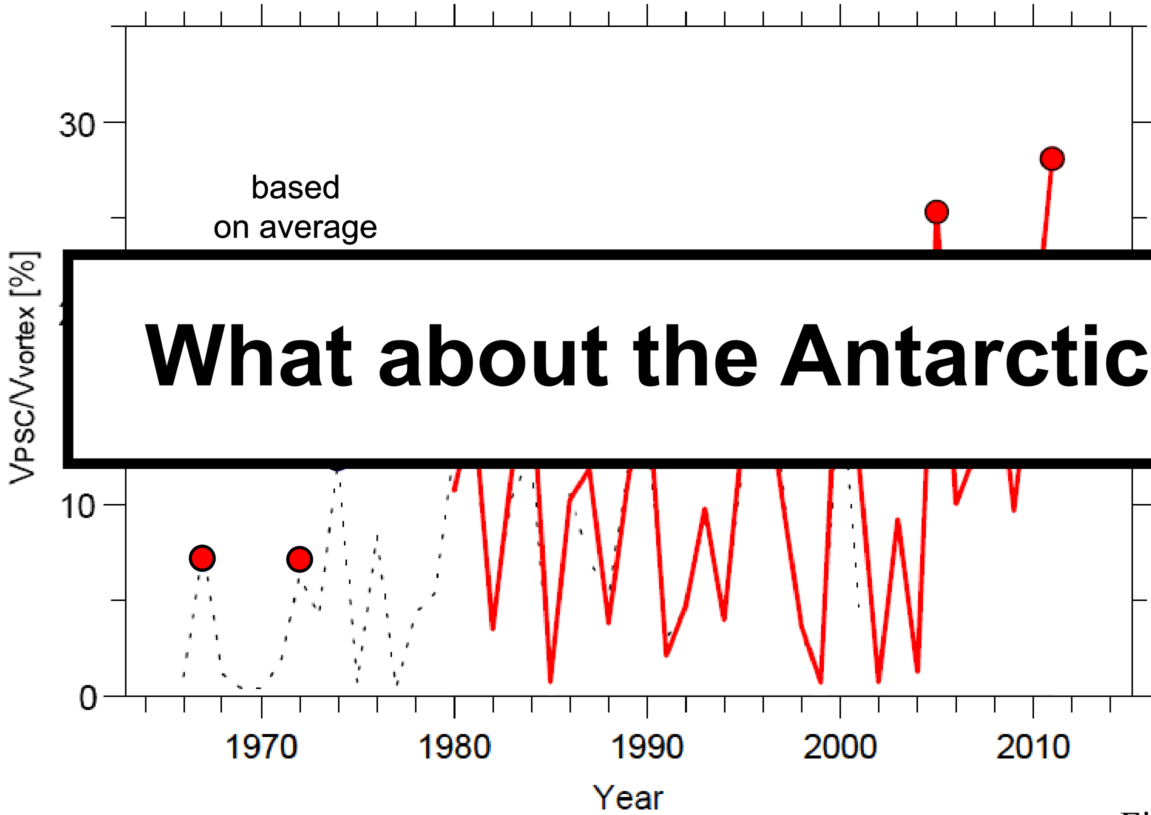


Figure 2-16, WMO/UNEP (2011)

Updated for Arctic winter 2011 and normalized for vortex area

- **Factor of three increase in the maximum of V_{PSC} over the past four decades**
- **Coldest Arctic winters may be getting colder !!!**
- **Cause uncertain: might be due to increased radiative efficiency of vortex during dynamically quiet years**

Arctic Ozone Loss and Climate Change



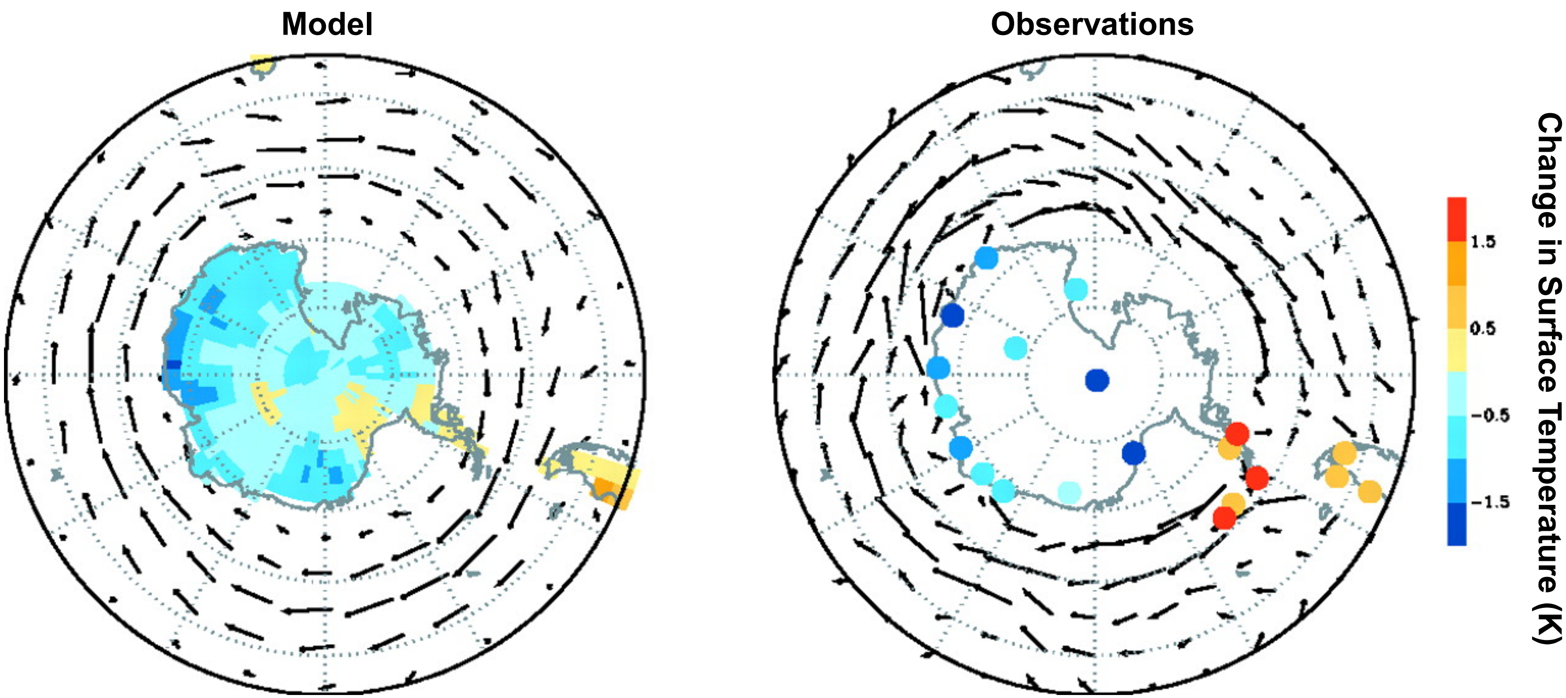
What about the Antarctic ?!?

Figure 2-16, WMO/UNEP (2011)

Updated for Arctic winter 2011 and normalized for vortex area

- **Factor of three increase in the maximum of V_{PSC} over the past four decades**
- **Coldest Arctic winters may be getting colder !!!**
- **Cause uncertain: might be due to increased radiative efficiency of vortex during dynamically quiet years**

The Ozone Hole may have shielded the Antarctic surface from warming!



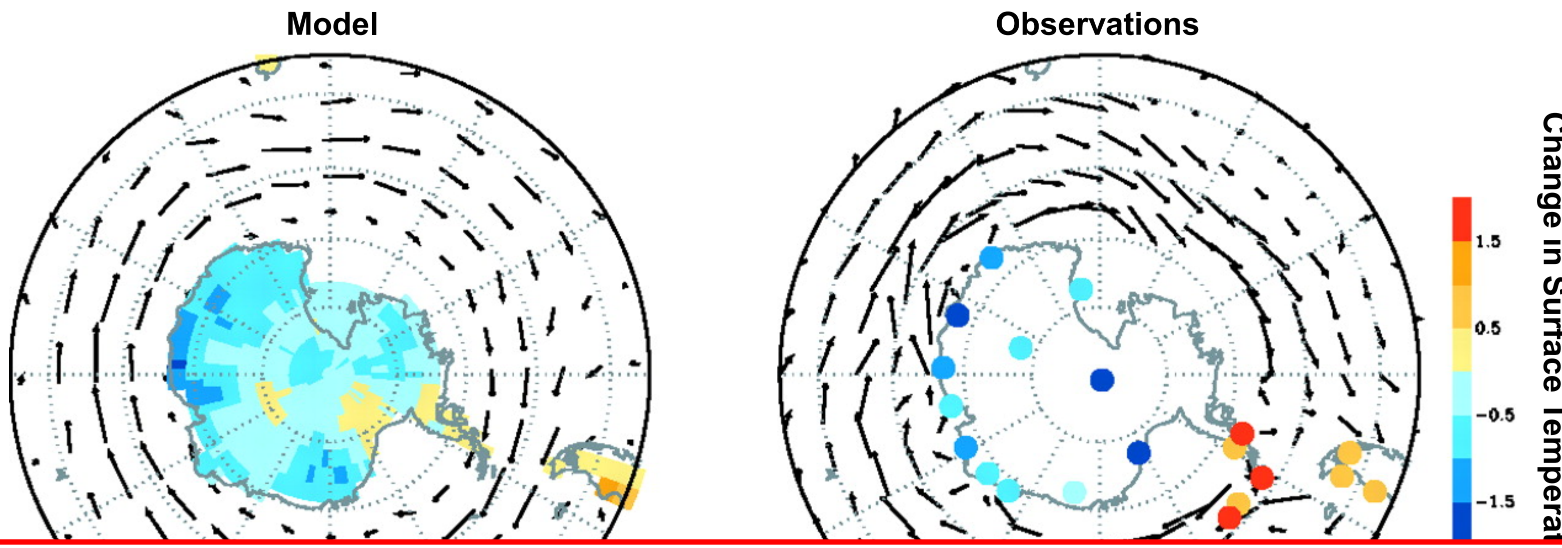
Simulated and observed changes in surface temperature (K) and wind speed,1969 to 2000, averaged over December to May. The longest wind vector corresponds to 4 m/s.

Gillett and Thompson, *Science*, 2003

As ozone depletion occurs:

The positive phase of the southern annular mode (SAM) increases, causing Antarctic surface westerlies to intensify, resulting in cooling of Antarctic continent

The Ozone Hole may have shielded the Antarctic surface from warming!



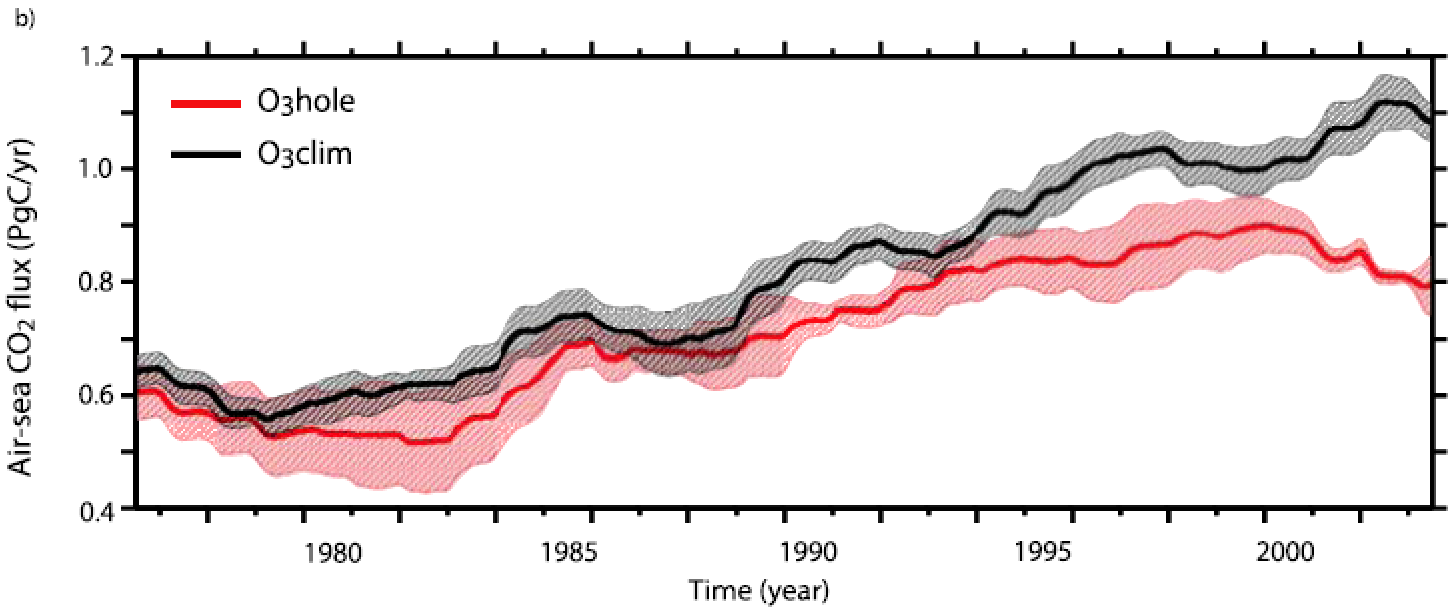
SAM: difference in zonal mean sea-level pressure between 40°S and 65°S. The pattern associated with SAM is a nearly annular pattern with a large low pressure anomaly centered on the South Pole and a ring of high pressure anomalies at mid-latitudes. The SAM effects storm tracks, precipitation patterns, etc.

http://www.climate.be/textbook/chapter5_node6.html

As ozone depletion occurs:

The positive phase of the southern annular mode (SAM) increases, causing Antarctic surface westerlies to intensify, resulting in cooling of Antarctic continent

The Ozone Hole may have lead to increased ventilation of CO_2 from southern ocean



(b) Integrated air to sea CO_2 flux (south of 40°S) showing stratospheric ozone depletion (O_3hole) significantly reduces CO_2 uptake (relative to O_3clim), and is strongly correlated with changes in ΔpCO_2.

Lenton *et al.*,*GRL*, 2009

As ozone depletion occurs:

The positive phase of the southern annular mode (SAM) increases, causing Antarctic surface westerlies to intensify, resulting in increased ventilation of CO_2 from southern ocean

Uptake of Atmospheric CO_2 by Oceans

– Solubility Pump:

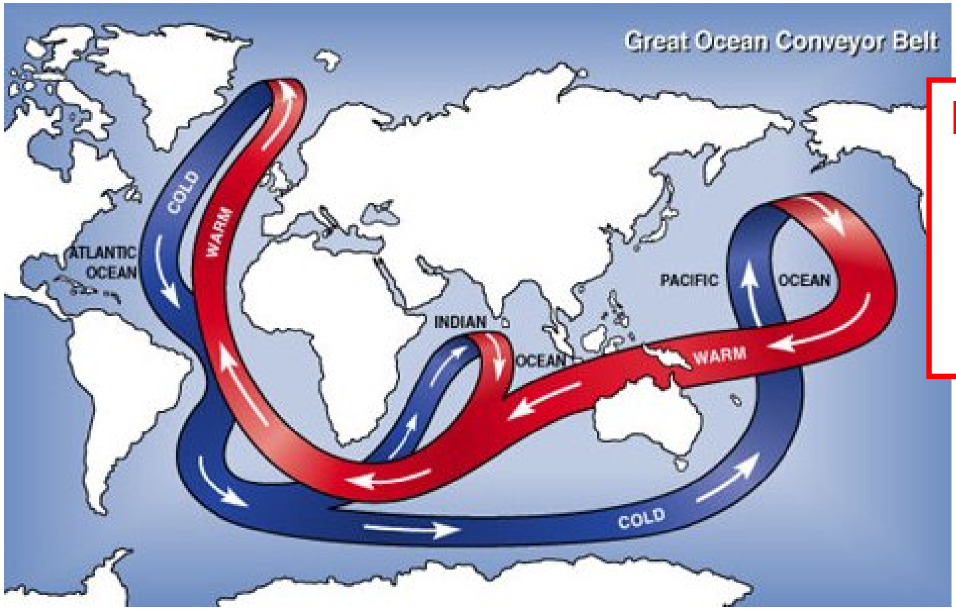
a) More CO_2 can dissolve in cold polar waters than in warm equatorial waters. As major ocean currents (e.g. the Gulf Stream) move waters from tropics to the poles, they are cooled and take up atmospheric CO_2

b) Deep water forms at high latitude. ***As deep water sinks, ocean carbon (ΣCO$_2$) accumulated at the surface is moved to the deep ocean interior***.

– Biological Pump:

a) Ocean biology limited by availability of nutrients such as NO_3^-, PO_4^-, and Fe^{2+} & Fe^{3+} . Ocean biology is never carbon limited.

b) Detrital material "rains" from surface to deep waters, ***contributing to higher CO_2 in intermediate and deep waters***



In the model, this elevated oceanic CO_2 is returned to the atmosphere due to stronger winds, which lead to more ocean turbulence … all due to the Antarctic ozone hole !

Lecture 5, Slide 25

http://science.nasa.gov/headlines/y2004/05mar_arctic.htm

Chemistry Climate Coupling

CCMs (chemistry climate models): developed to quantify impacts of climate change on stratospheric ozone *and* impacts of ozone depletion/recovery on climate:

As GHGs rise:

1. **Brewer-Dobson circulation predicted to accelerate leading to:**
   - **a) less ozone in tropical lower stratosphere ("permanent depletion")**
   - **b) more ozone in mid-latitude lower stratosphere ("super recovery")**
2. **Upper stratosphere cools, slowing down rate limiting steps for ozone loss and therefore leading to "super recovery"**
3. **Eventually, CH_4 and N_2O will drive future levels of ozone**

Data analysis suggests "coldest Arctic winters getting colder":

1. **Possibly due to rising GHGs**
2. **Not represented by CCMs**

As Antarctic ozone depletion occurs:

The positive phase of the southern annular mode (SAM) increases, causing Antarctic surface westerlies to intensify, resulting in:

1. **Cooling of Antarctic continent**
2. **Increased ventilation of CO_2 from southern ocean**