Chemical Loss of Polar Ozone: Present Understanding and Remaining Uncertainties

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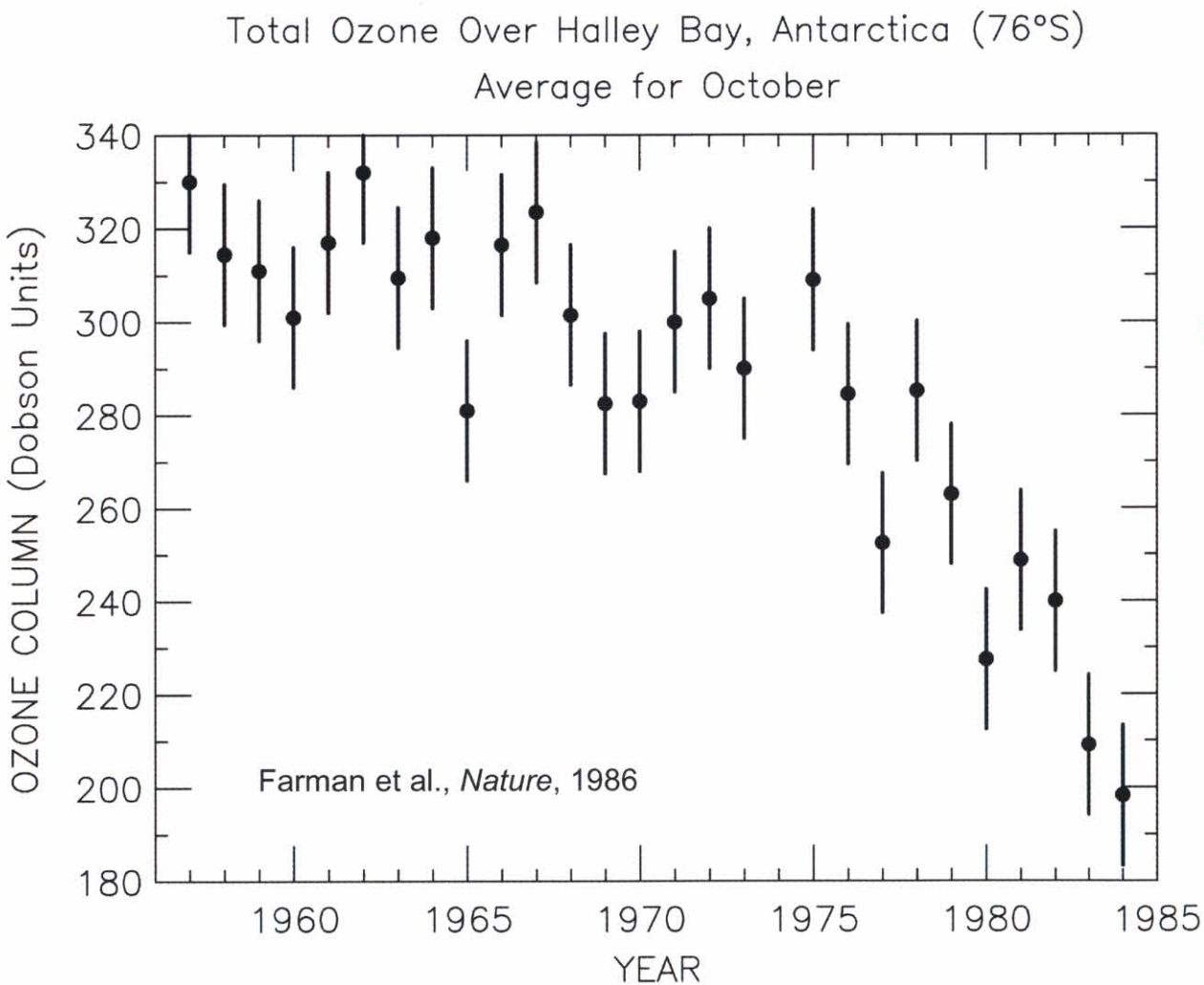
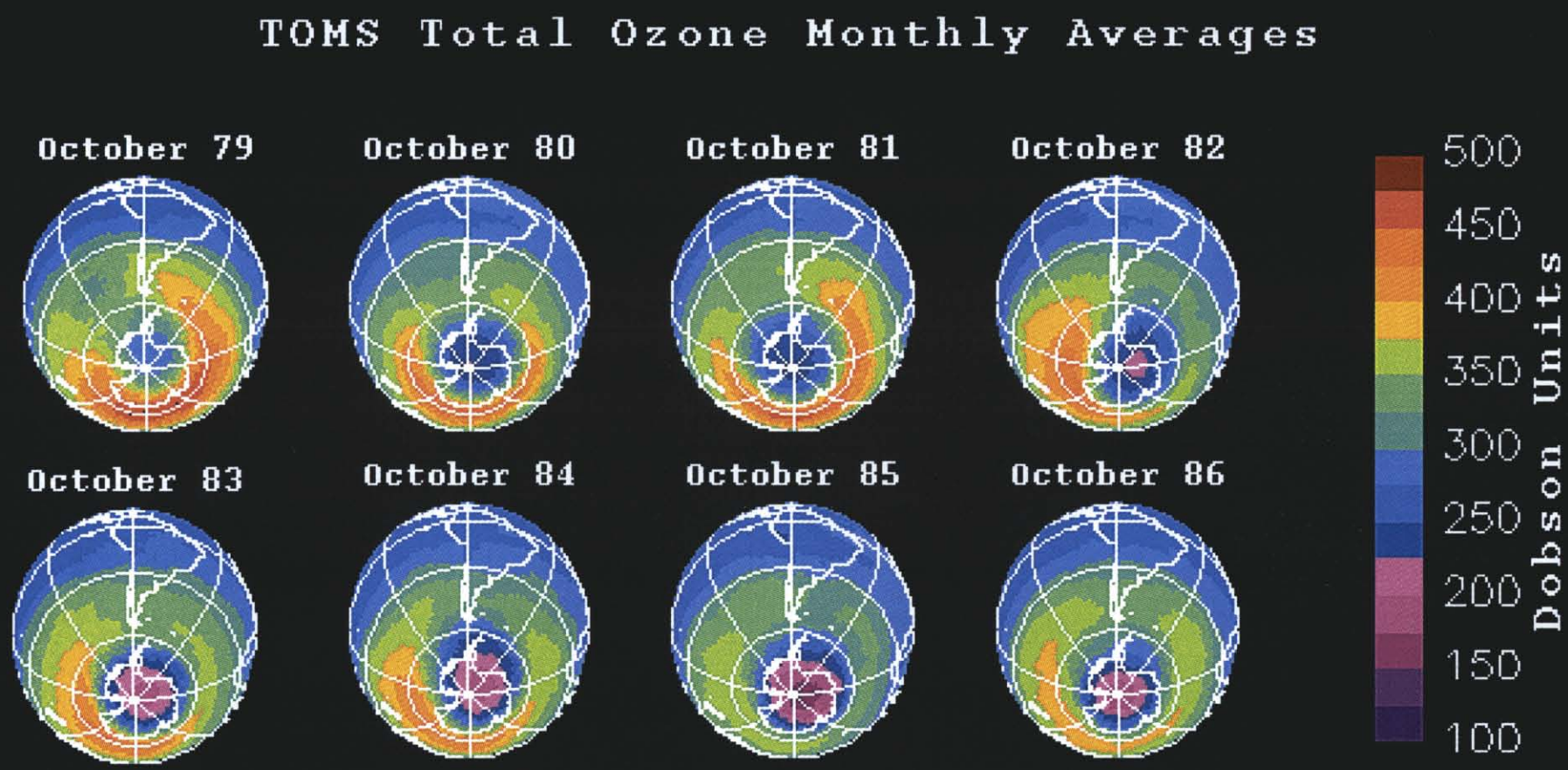
1. Introduction and Overview
2. Is Antarctic Ozone Recovering ?
3. Do We Understand Chemical Ozone Loss Rates ?
4. Arctic Ozone Loss and Climate Change ?

DISCOVERY OF ANTARCTIC OZONE HOLE

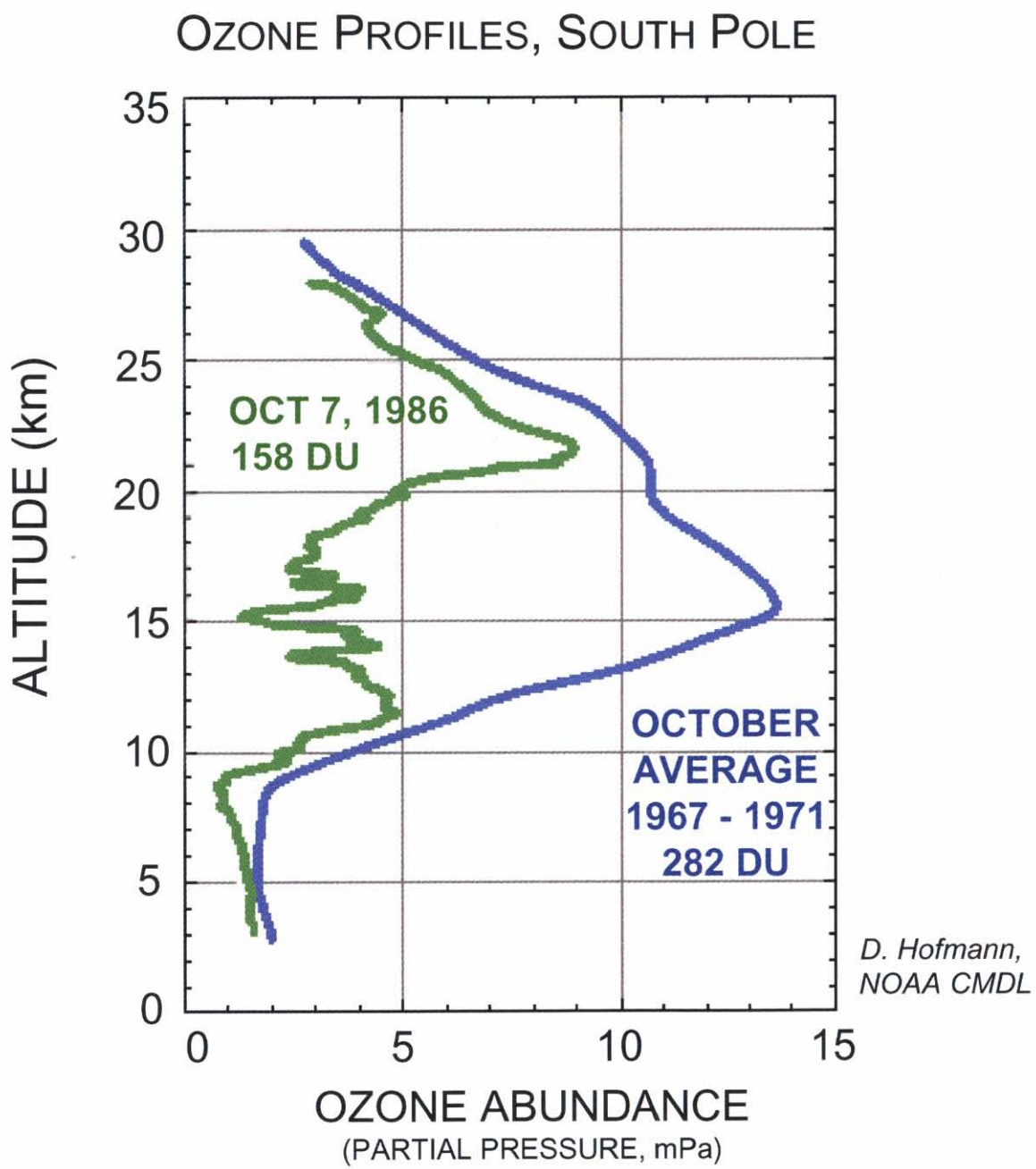


Southern Hemisphere

Antarctic Ozone Hole From Space



Stolarski et al., *Nature*, 1986


OZONE PROFILES, SOUTH POLE
ALTITUDE (km)
35
30
25
20
15
10
5
0
OCT 7, 1986
158 DU
OCTOBER
AVERAGE
1967 - 1971
282 DU
0
5
10
15
OZONE ABUNDANCE
(PARTIAL PRESSURE, mPa)
D. Hofmann,
NOAA CMDL

Chemical Hypothesis

- Cold Temperatures → Polar Stratospheric Clouds (**PSCs**)
- Reactions on PSC surfaces lead to elevated **ClO** :

$$HCl + ClNO_3 \rightarrow Cl_2\,(gas) + HNO_3\,(solid)$$
$$Cl_2 + \text{SUNLIGHT} + O_3 \rightarrow ClO$$
$$HNO_3 \text{ SEDIMENTS on PSCs}$$

- Elevated **ClO** + Sunlight destroys O_3
- BrO : Reaction Partner For ClO ⇒ Additional O_3 Loss

Ozone Loss Details

$$ClO + ClO \rightarrow ClOOCl$$

$$ClOOCl + \text{Sunlight} \rightarrow Cl + Cl + O_2$$

$$2\,[\,Cl + O_3 \rightarrow ClO + O_2\,]$$

Ozone Loss Details

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$$\text{Net: } 2\,O_3 + \text{Sunlight} \rightarrow 3\,O_2$$

Kinetics Studies:

~1 part per billion needed to match observed loss rates

Ozone Loss Details

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$$2\,[\,Cl + O_3 \rightarrow ClO + O_2\,]$$

$$\text{Net: } 2\,O_3 + \text{Sunlight} \rightarrow 3\,O_2$$

$$\boxed{BrO} + ClO \rightarrow Br + ClOO$$

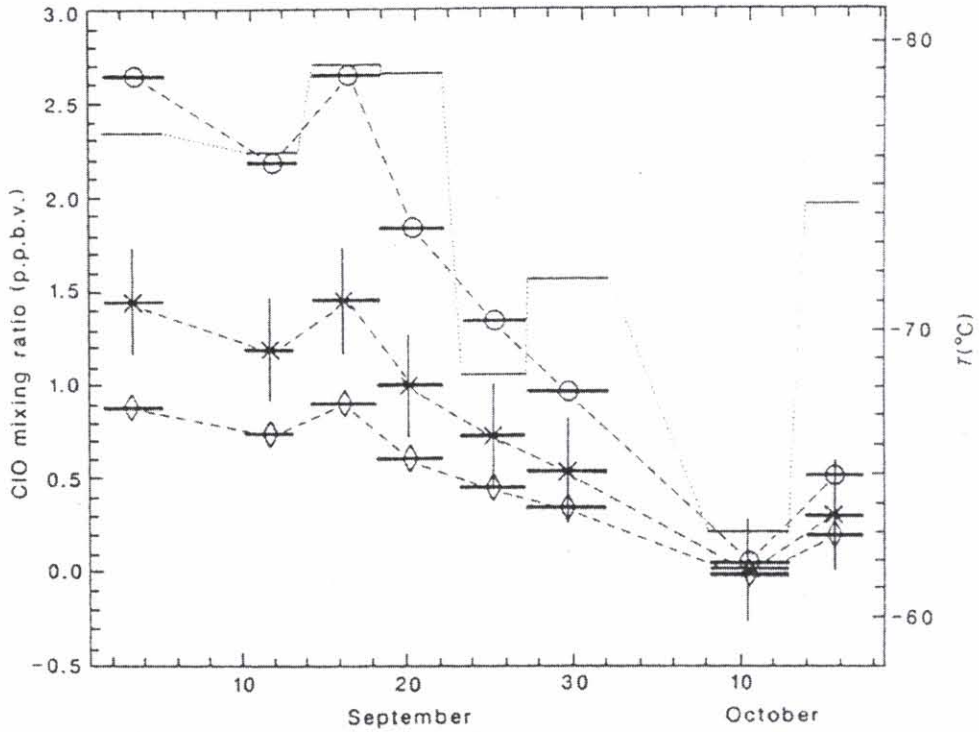
$$ClOO + \text{Heat} \rightarrow Cl + O_2$$

$$Cl + O_3 \rightarrow ClO + O_2$$

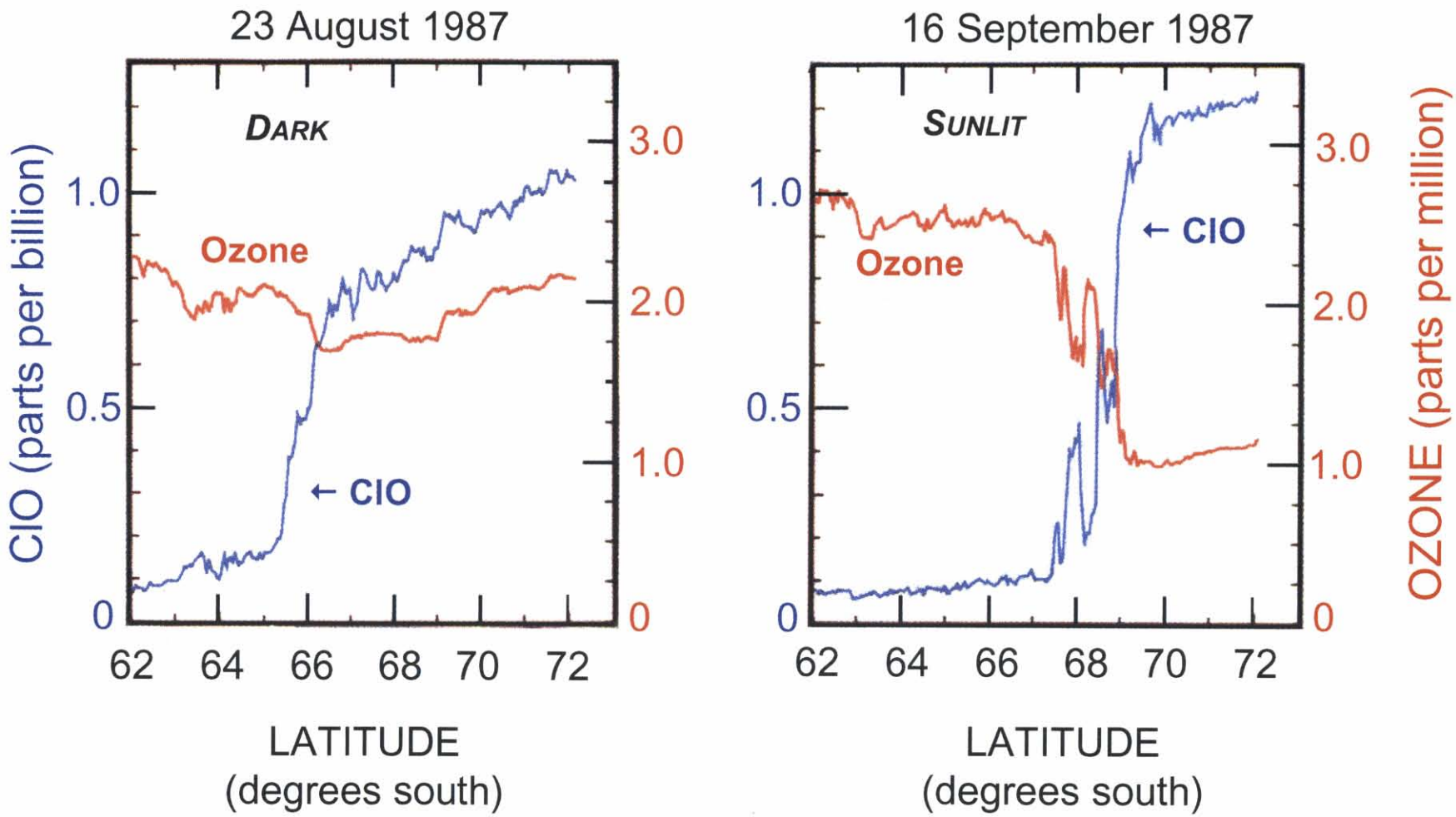
$$Br + O_3 \rightarrow BrO + O_2$$

$$\text{Net: } 2\,O_3 + \text{Sunlight} \rightarrow 3\,O_2$$

McMurdo Station, Antarctic, 1986

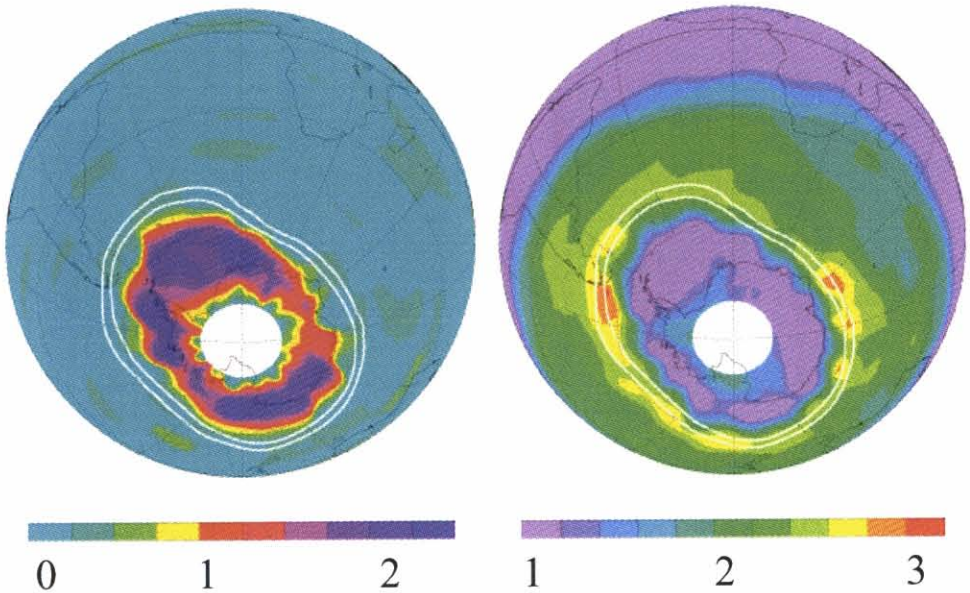


P. Solomon et al., *Nature*, 1987



Anderson et al., *Science*, 1991

Microwave Limb Sounder (MLS) Satellite Measurements of the Antarctic Ozone Hole



ClO
(parts per billion)

Ozone
(parts per million)

Waters et al., *Nature,* 1993
Santee et al., *Science*, 1995

MONTREAL PROTOCOL and AMENDMENTS ESSENTIALLY BANNED CFCs

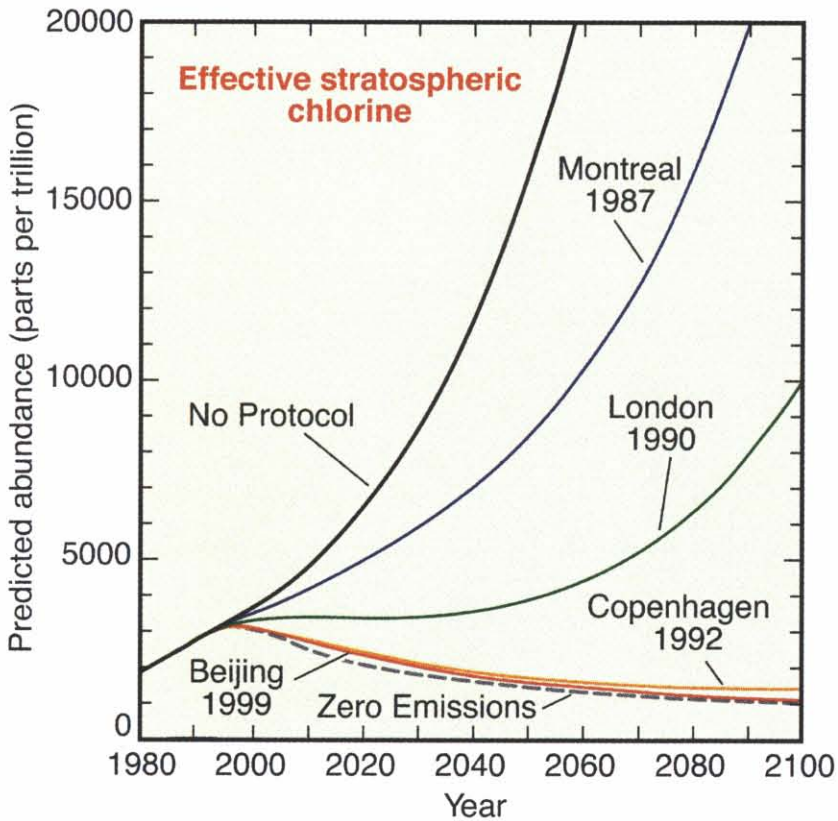
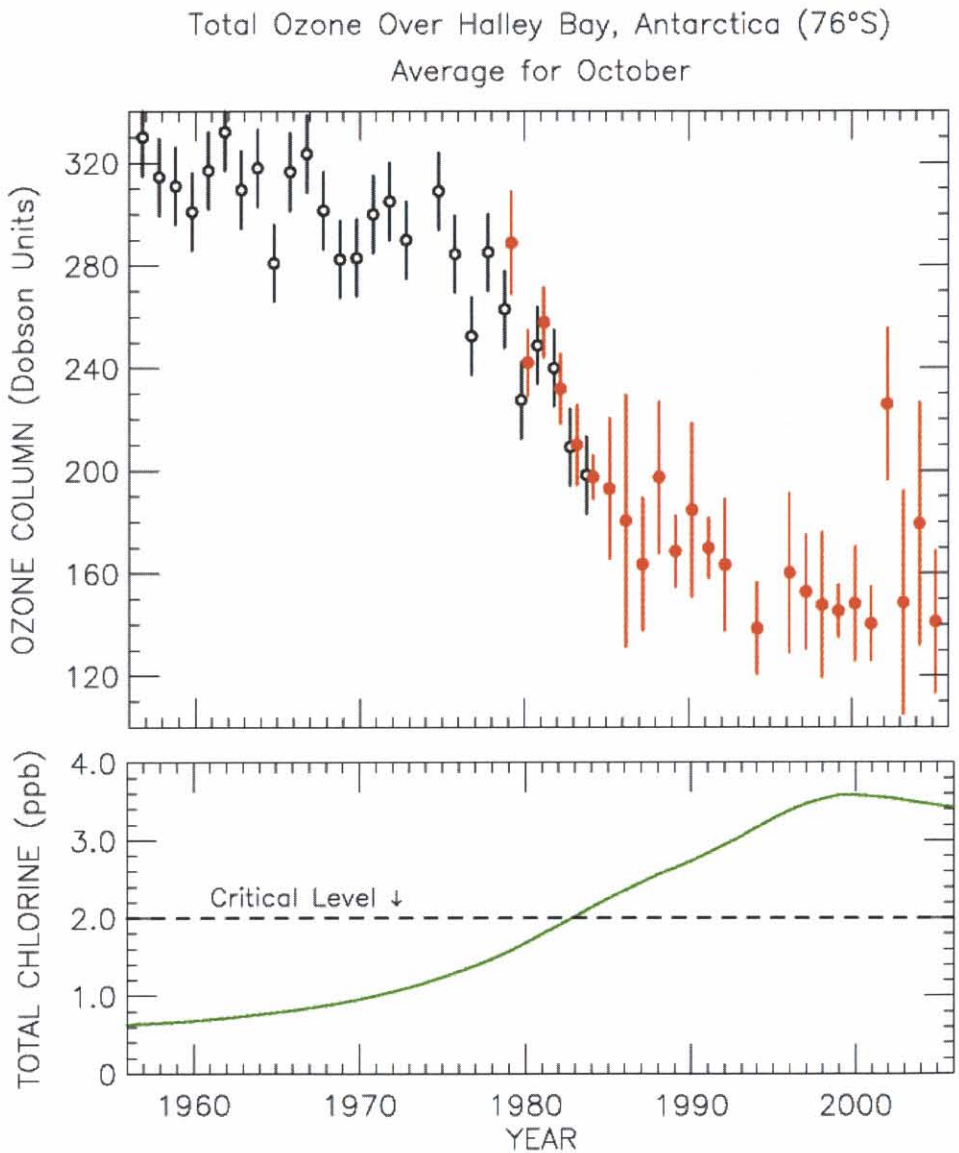
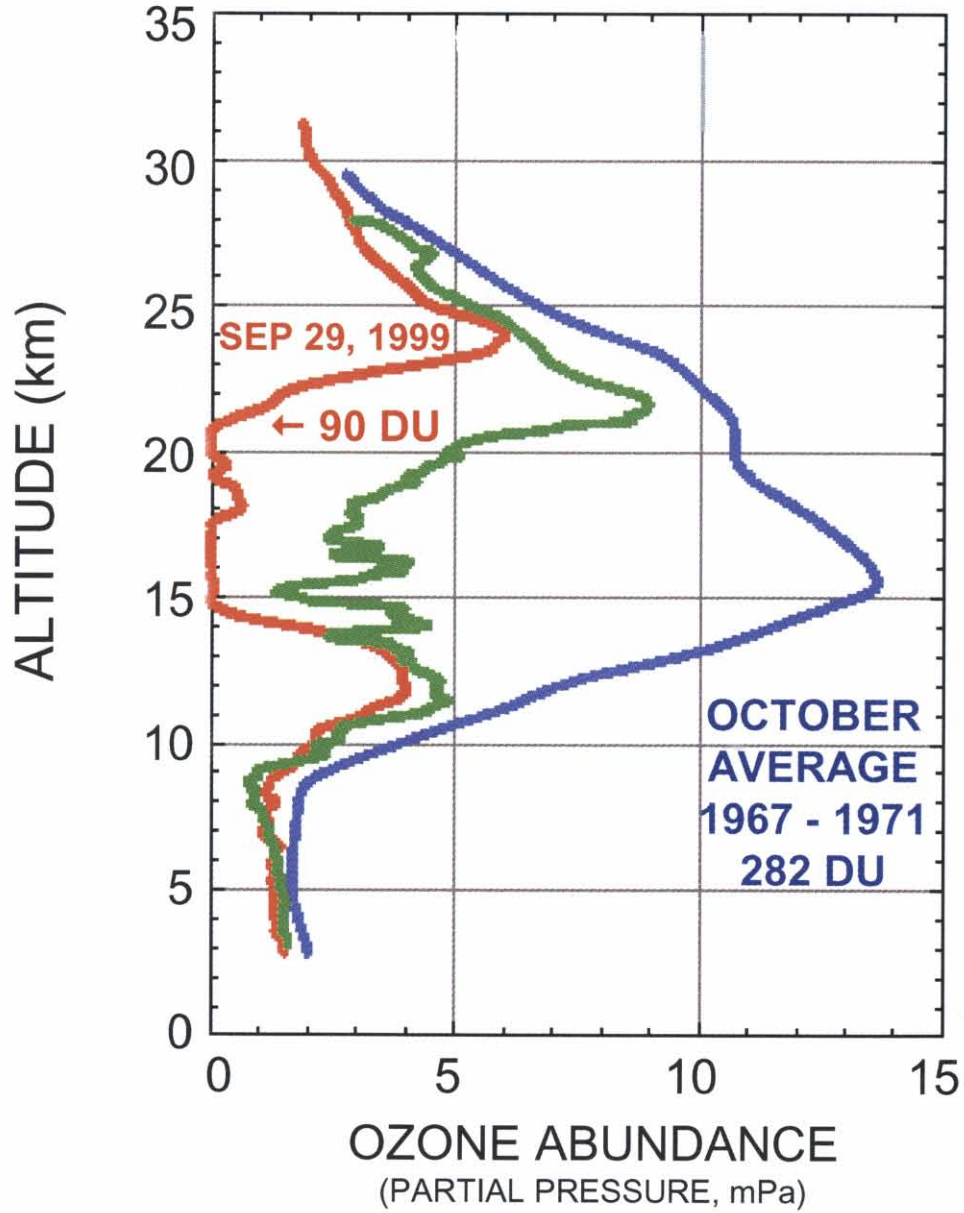


Figure 15
20 Questions and Answers About the Ozone Layer
WMO/UNEP 2003 (Fahey et al.)
http://www.al.noaa.gov/assessments/2002/qandas.html

OZONE HOLE UPDATE



OZONE PROFILES, SOUTH POLE: UPDATE



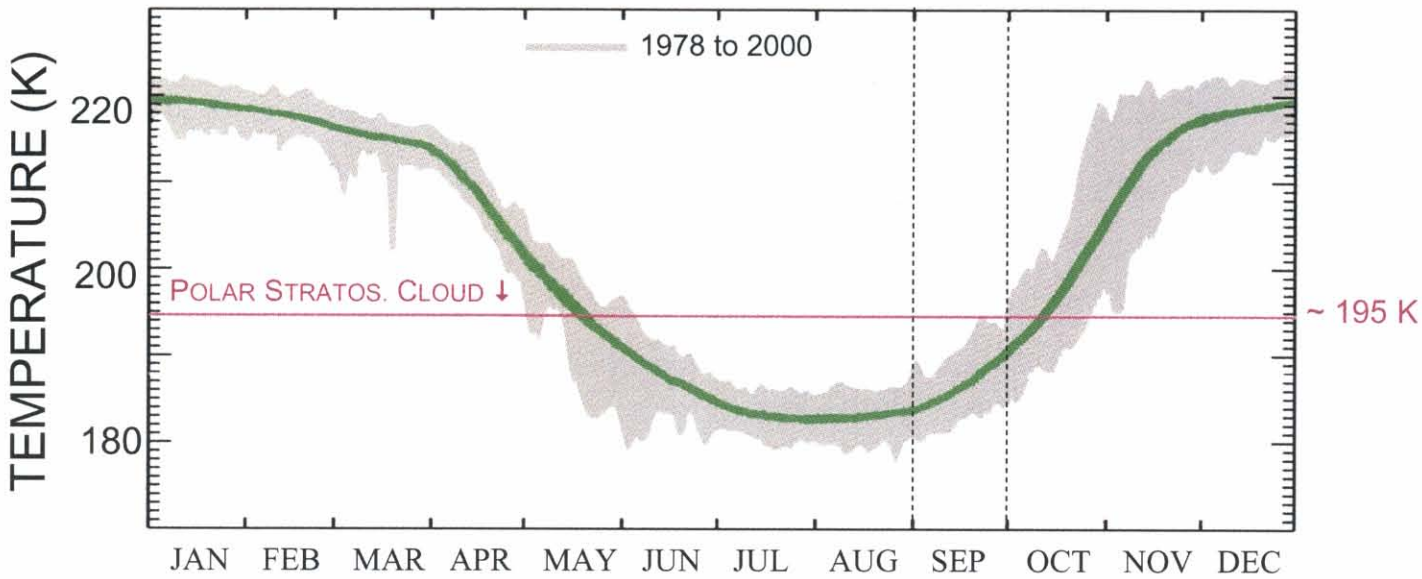
D. Hofmann, NOAA CMDL

"Recipe" for an Ozone Hole:

- Total Chlorine (> ~2 parts per billion)
- Cold Temperatures (→ PSCs)
- Sunlight

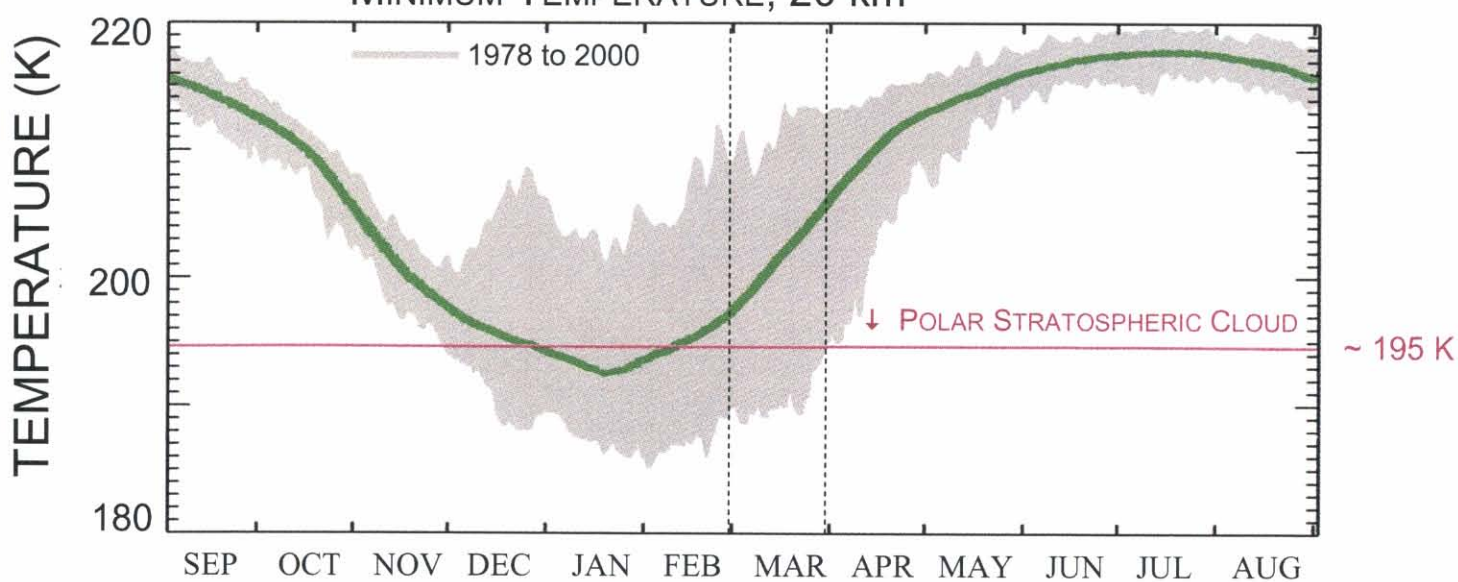
What about the Arctic ?

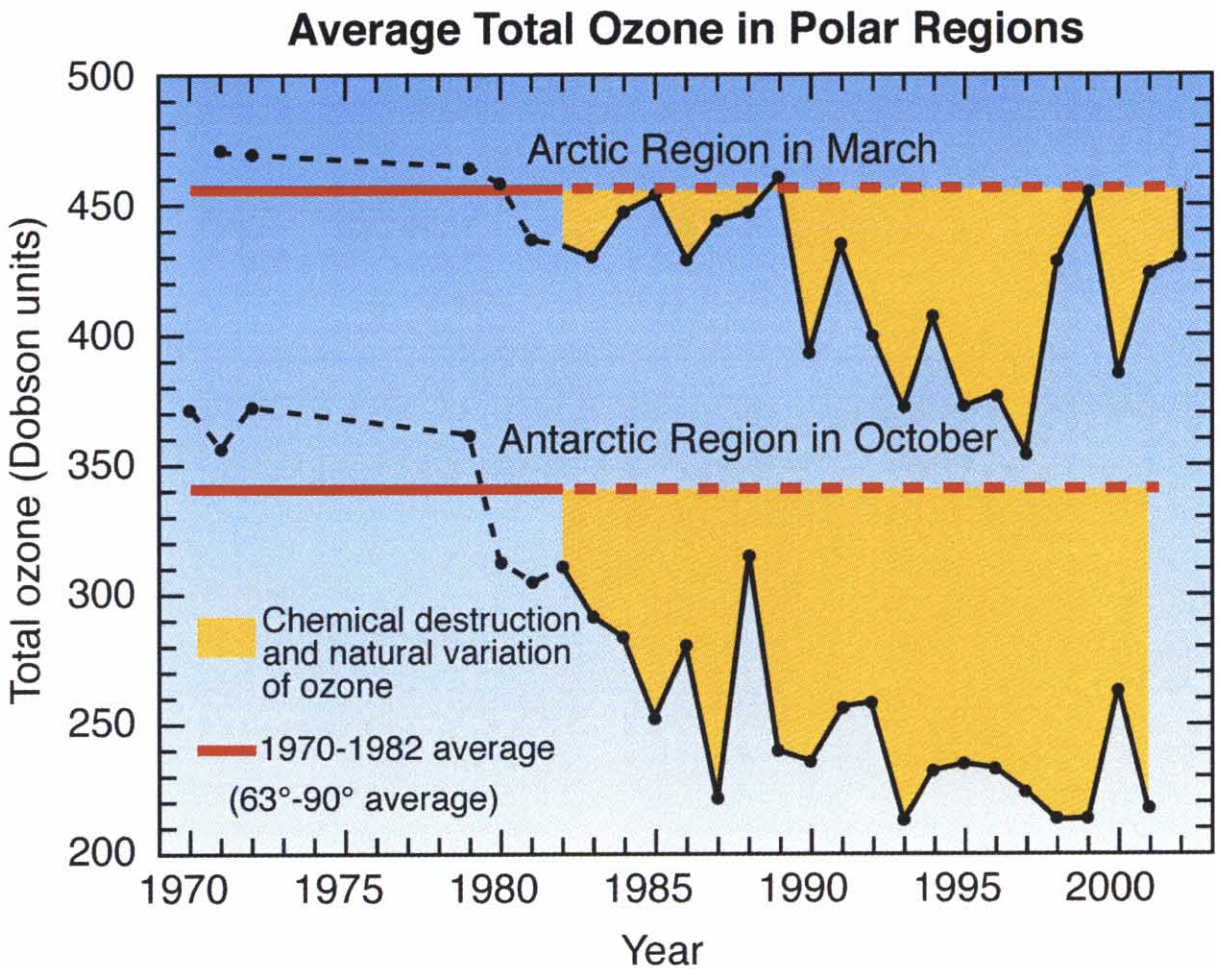
ANTARCTIC (S.H.) POLAR VORTEX
MINIMUM TEMPERATURE, 20 km



Data Courtesy
P. Newman,
E. Nash, &
R. Nagatani

ARCTIC (N.H.) POLAR VORTEX
MINIMUM TEMPERATURE, 20 km





After Newman et al., *GRL*, 1997

Figure 12
20 Questions and Answers About the Ozone Layer
WMO/UNEP 2003 (Fahey et al.)
http://www.al.noaa.gov/assessments/2002/qandas.html

Is Antarctic Ozone Recovering?

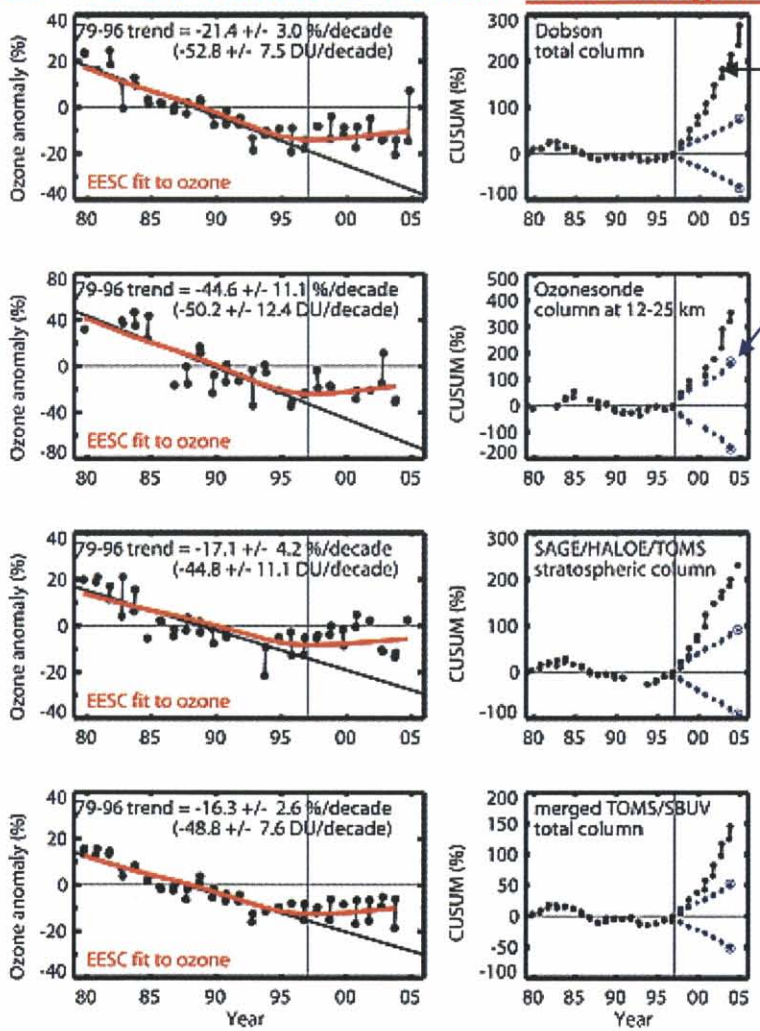
International Ozone Commission Definition, 1st of 3 Stages of Recovery:
"A statistically significant slowing of the downward trend"
http://ioc.atmos.uiuc.edu/documents/Statement-QOS2004.pdf

60 – 70°S : Antarctic Vortex "Collar Region"

BLACK Points:
Ozone data adjusted to account for dynamic variability

RED Curve:
Fits of Equiv Eff. Strat Cl to ozone data

BLACK Line:
Trend to data, 1979 – 1996, forecast linearly thereafter



BLACK:
Cumulative sun of ozone residuals from linear trend

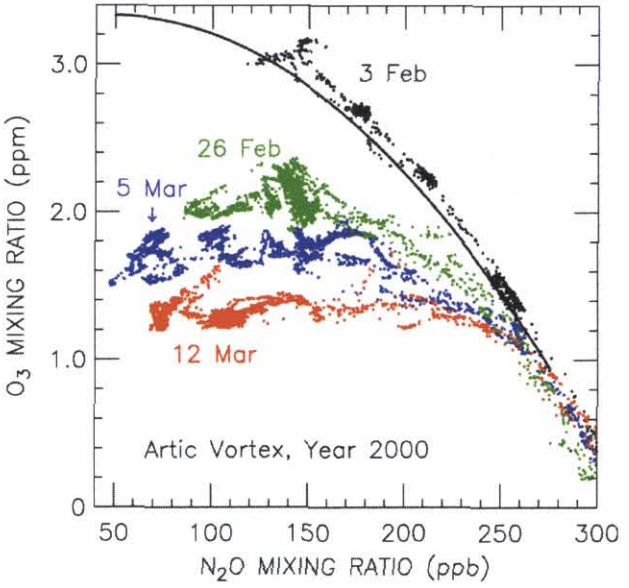
BLUE:
95% confidence envelope of departure from natural variability (including trend model uncertainty)

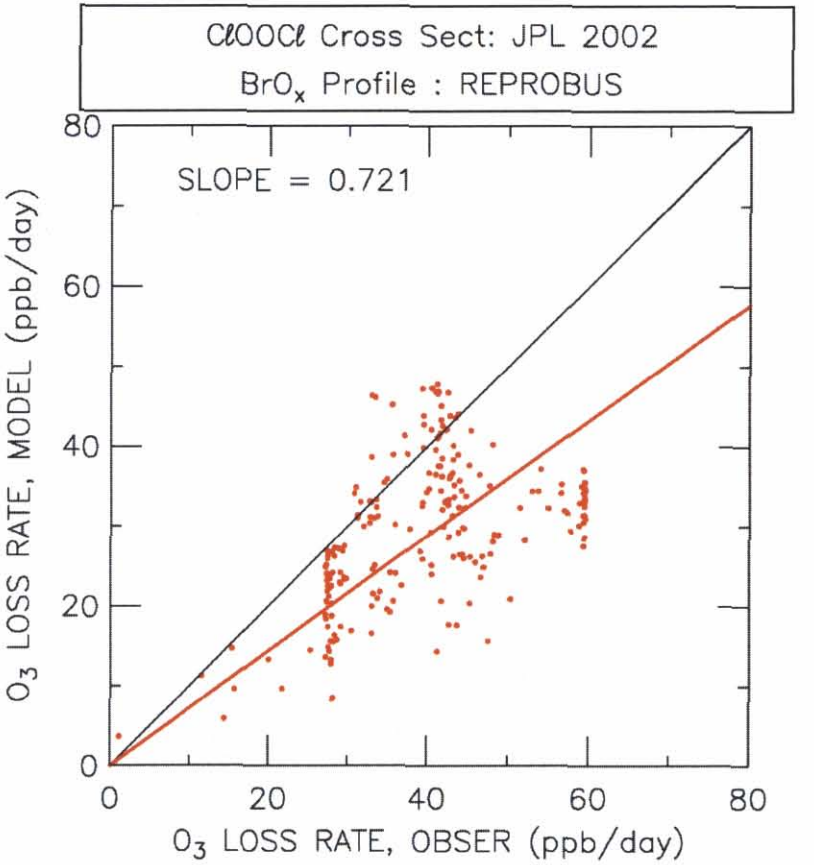
E-S. Yang et al., *GRL*, 2005

Note:
Yang et al. show this result not driven by "saturation" of chemical ozone loss

Do We Understand the Rate of Chemical Ozone Loss ?

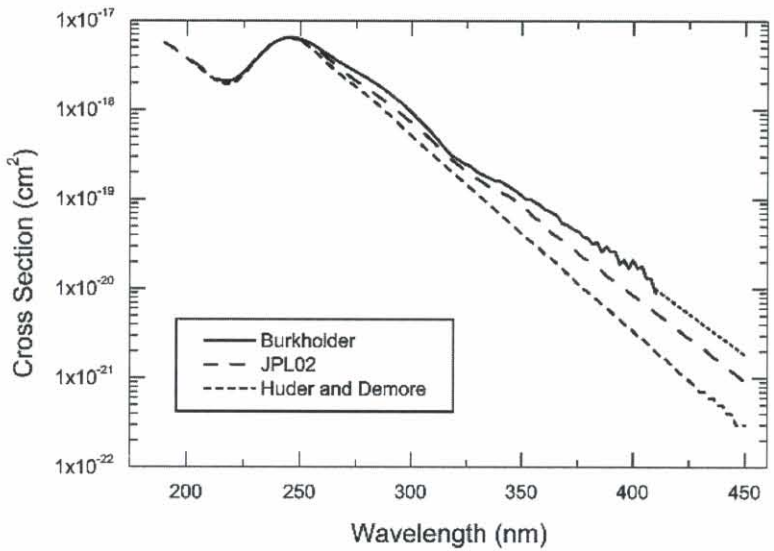
- Photochemical model run along 10-day back trajectories
- Observations of ClO+ClOOCl used to initialize model
- Observed ozone loss rate based on temporal evolution of the O_3 vs N_2O relation :

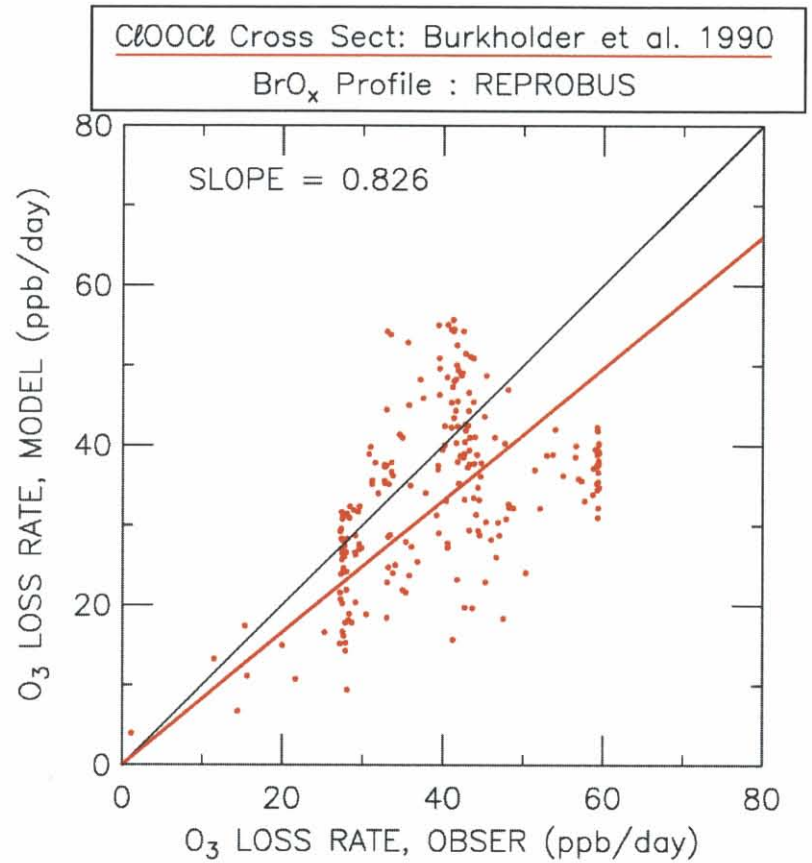




Model accounts for 72% of observed ozone loss

Do We Understand the Rate of Chemical Ozone Loss ?



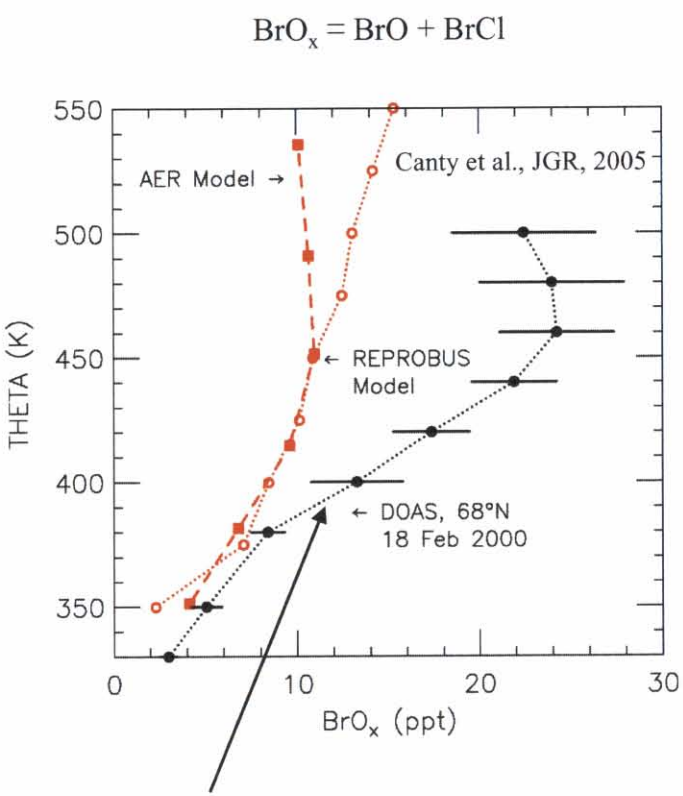


Stimpfle et al., JGR, 2004 show:

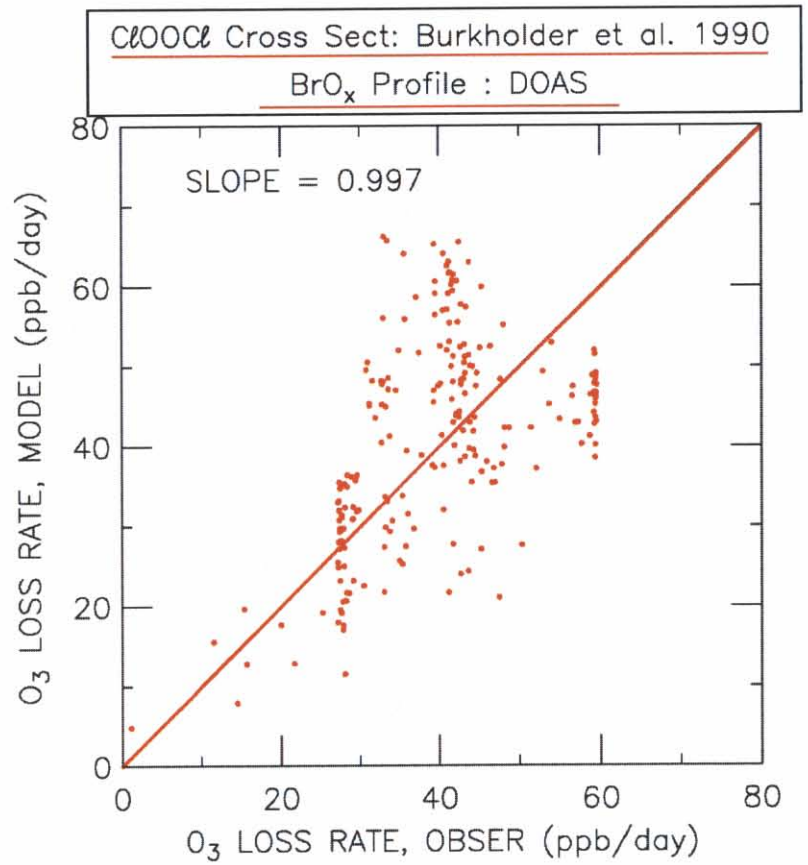
- Measured ClO/ClOOCl ratio agrees best with Burkholder cross section, given present understanding of ClO+ClO rate constant

Model accounts for 83% of observed ozone loss

Do We Understand the Rate of Chemical Ozone Loss ?



BLACK Line: BrO_x based on measured BrO



Model accounts for all of observed ozone loss

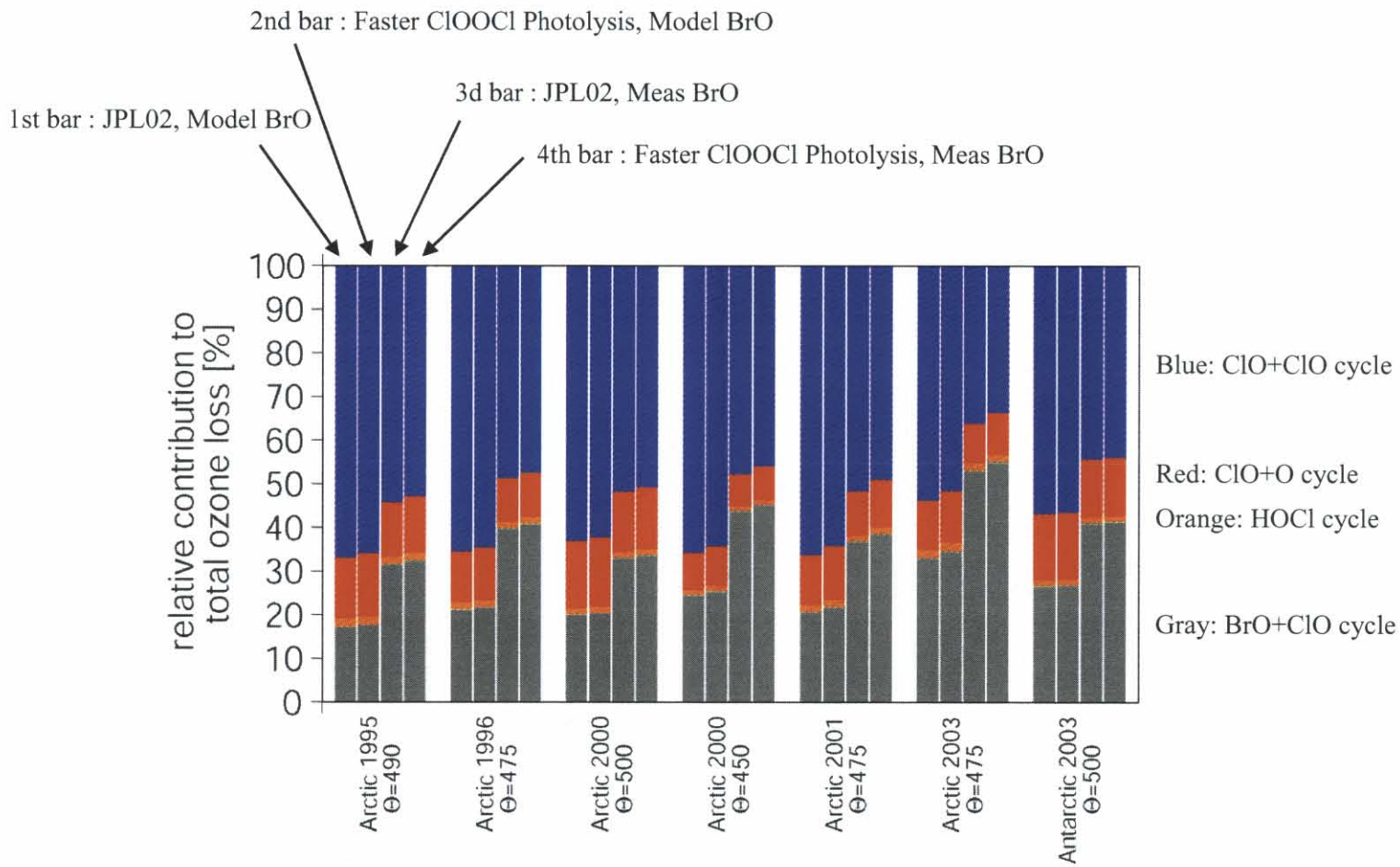
Why is empirical BrO_x ~factor of 2 > Model BrO_x ?

Models consider supply of stratospheric bromine from only "long-lived" CH_3Br + halons

A suite of VSL (very short lived) bromocarbons may supply significant levels of stratospheric bromine

⇒ e.g., Salawitch et al., GRL, 2005; **Poster A23A-0914** (Tues Afternoon)

Do We Understand the Rate of Chemical Ozone Loss ?



Frieler et al., GRL, submitted:

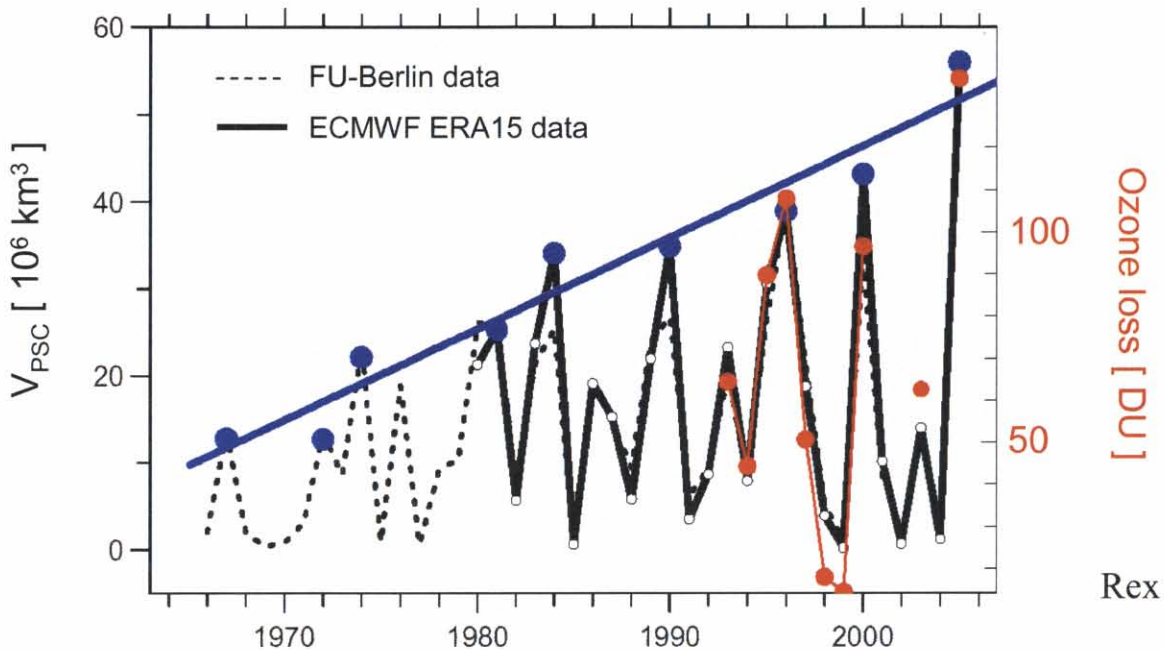
- Consistency between observed Arctic loss rates (Match method) & meas. ClO, ClOOCl, and BrO assuming Burkholder et al. cross section for ClOOCl
- Bromine catalysed O_3 loss may be more important, relative to chlorine catalysed loss, than previously thought:

  Reference Run (1st bar): bromine 17 to 33 % of total

  Final Run (4 th bar) : 32 to 55% of total

Poster A13D–0985

Arctic Ozone Loss and Climate Change

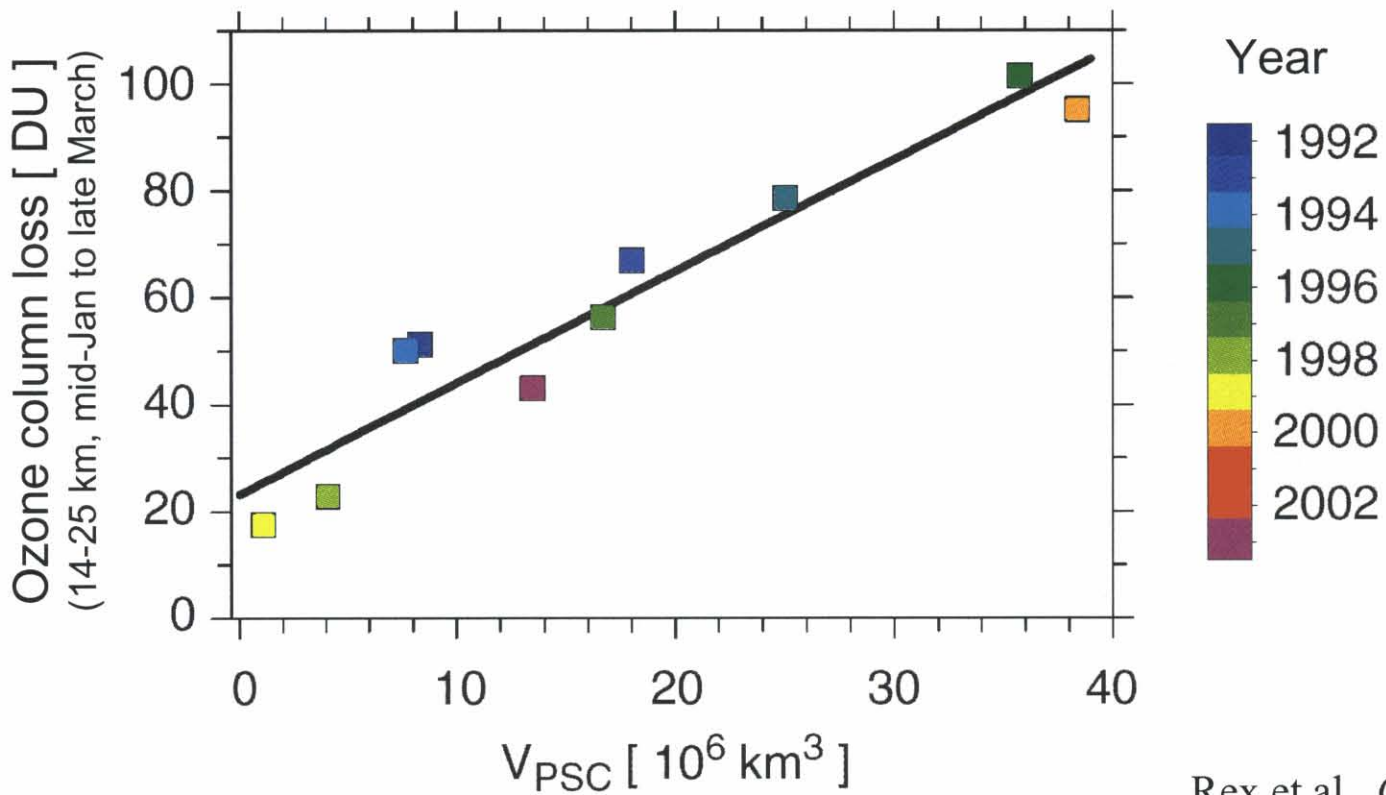


Rex et al., GRL, 2004 (updated)

- V_{PSC} : Volume of air in Arctic vortex exposed to Polar Stratospheric Clouds (PSCs)
- Factor of three increase in the maximum of V_{PSC} over the past four decades
- The coldest Arctic winters are getting colder !!!
- Cause uncertain : may be due to climate change
- Arctic winter of 2004-2005 : new record for maximum V_{PSC}

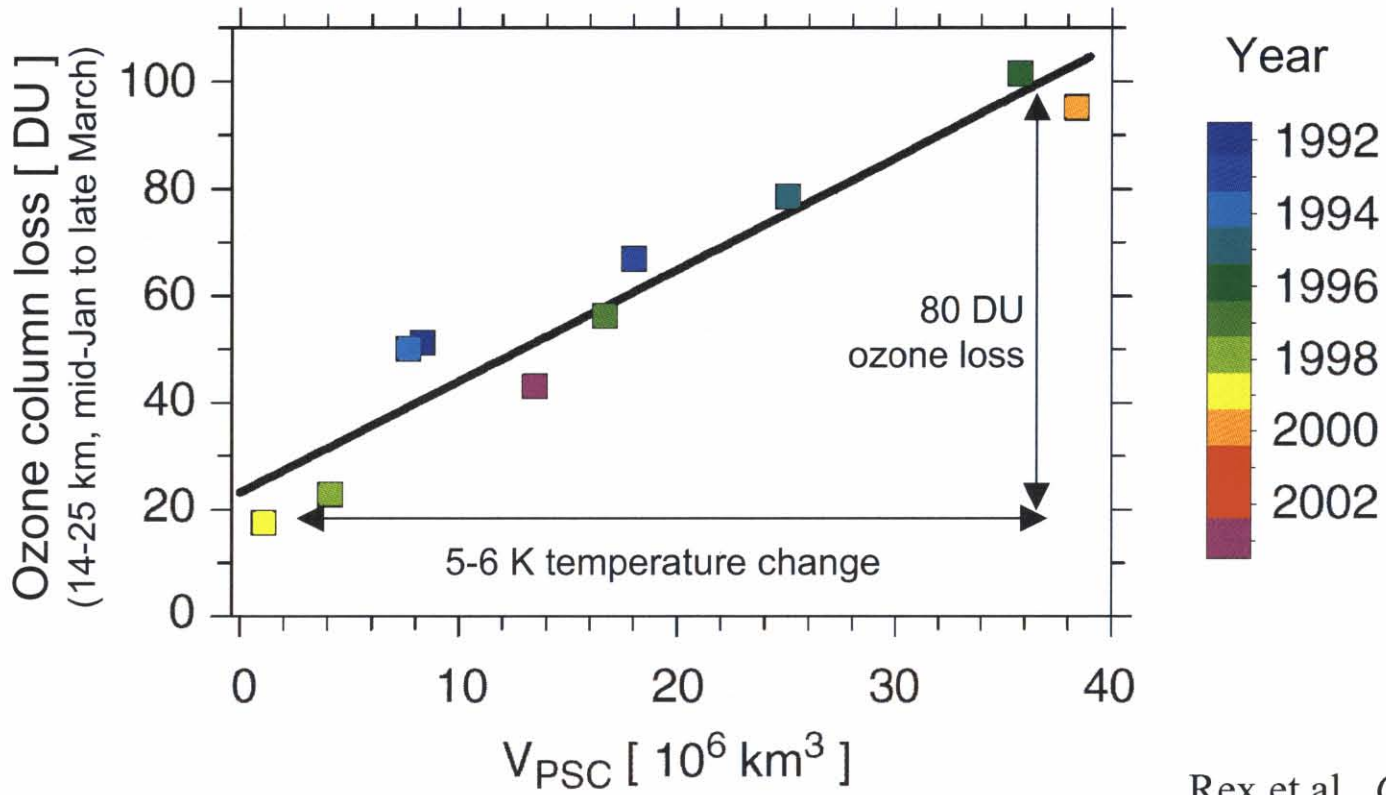
Several talks Wed morning, this session, about Arctic ozone loss 2004-2005 winter

Arctic Ozone Loss and Climate Change



Rex et al., *GRL*, 2004

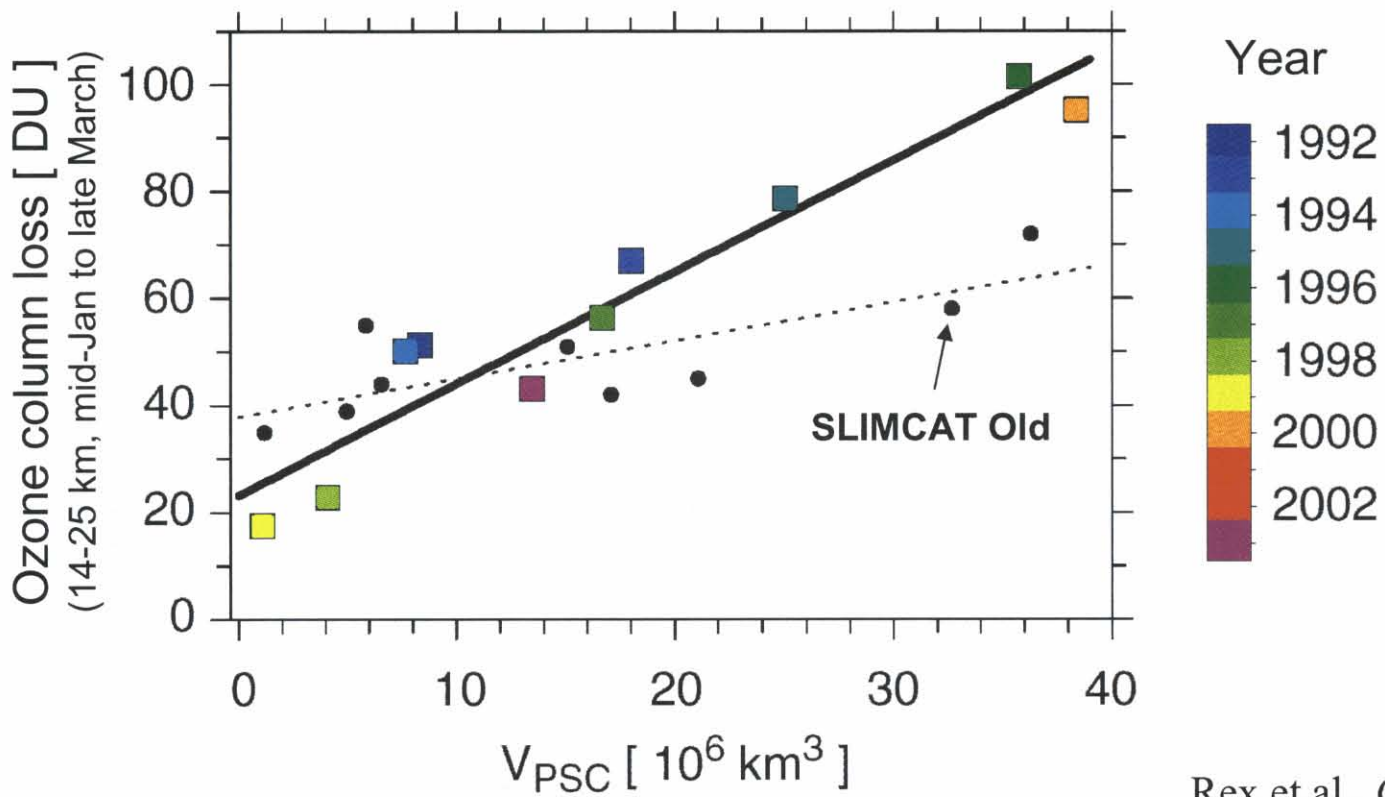
Arctic Ozone Loss and Climate Change



Rex et al., *GRL*, 2004

~ 15 DU additional ozone loss
per Kelvin cooling of the Arctic stratosphere

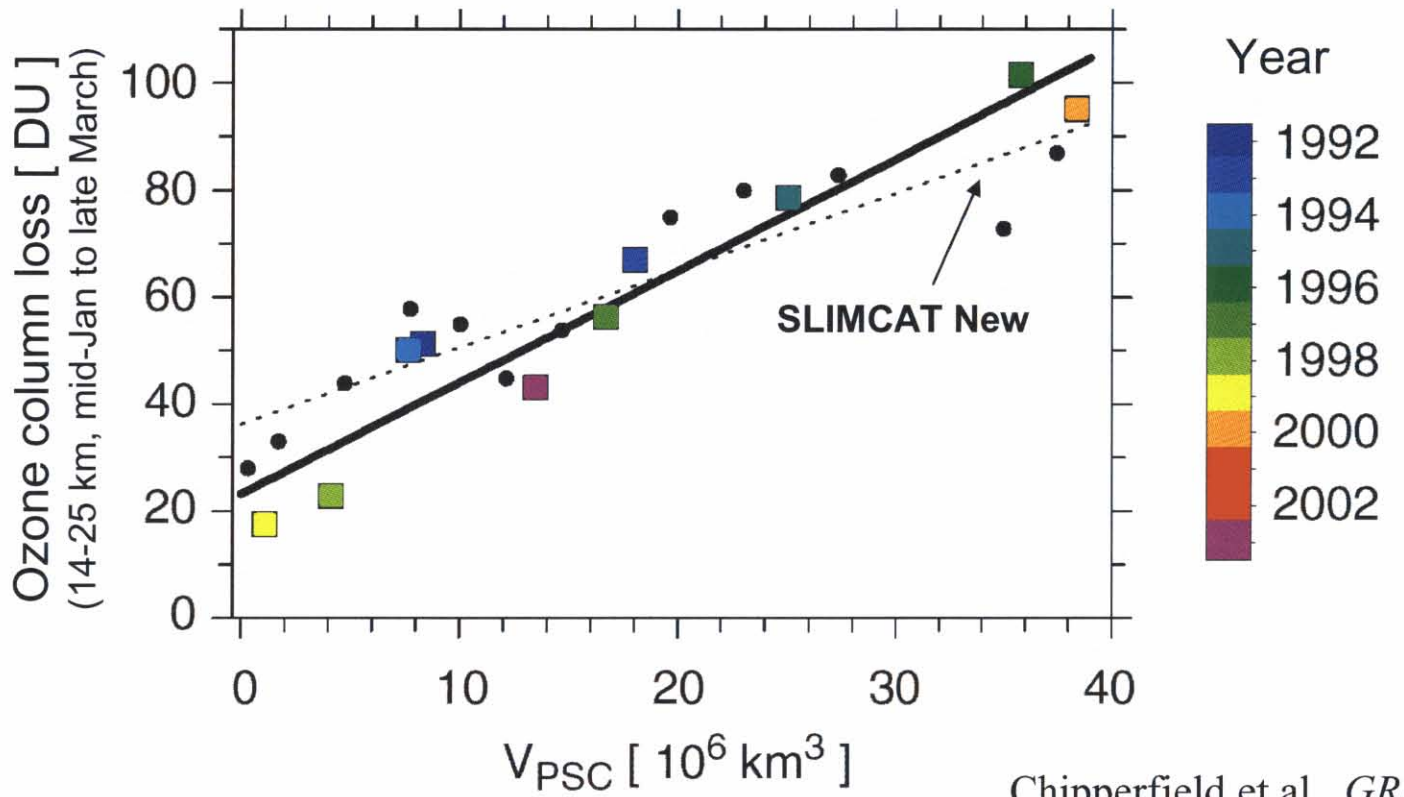
Arctic Ozone Loss and Climate Change



Rex et al., *GRL*, 2004

SLIMCAT "Old" underestimates sensitivity of Arctic ozone loss to climate change by nearly factor of three

Arctic Ozone Loss and Climate Change



Chipperfield et al., *GRL*, 2005

New SLIMCAT run reproduces observed data quite well.

New SLIMCAT : JPL 2002 + Burkholder Cross Section + NAT-based Denit. Scheme + Improved Radiation (More Realistic Polar Descent & Cl_y)

Summary

Is Antarctic Ozone Recovering ?

- Collar region (area near edge of vortex) showing "first signs" of recovery
- Lots of debate about meaning of "recovery"
- Considerable uncertainty regarding when "Pre Ozone Hole" levels will be attained

Do We Understand Chemical Ozone Loss Rates ?

- Perhaps!
- Long standing model underestimation of ozone loss rate may be resolved by:
  - a) Faster photolysis of ClOOCl ⇐ **requires better lab confirmation of cross section**
  - b) Factor of 2 more bromine ⇐ **subject of active research**

Arctic Ozone Loss and Climate Change ?

- Recent ozone loss proportional to volume of polar vortex exposed to PSC temperatures
- 15 DU (~4% of total column) additional ozone loss per Kelvin cooling ⇐ **reproduced by model**
- Coldest Arctic winters, in terms of V_{PSC}, are getting colder

Climate change ?

↓ PWD (planetary wave drag) due to stronger vertical shear of the zonal wind at **high latitudes** (Limpasuvan and Hartmann, J. Climate, 2000)
↓ PWD due to increased westerly winds in the **subtropics** (Shindell et al., Nature, 1998)
↓ PWD ⇒ ↑ Arctic Vortex Strength ⇒ lower T ⇒ Higher V_{PSC}

Natural Variability ?