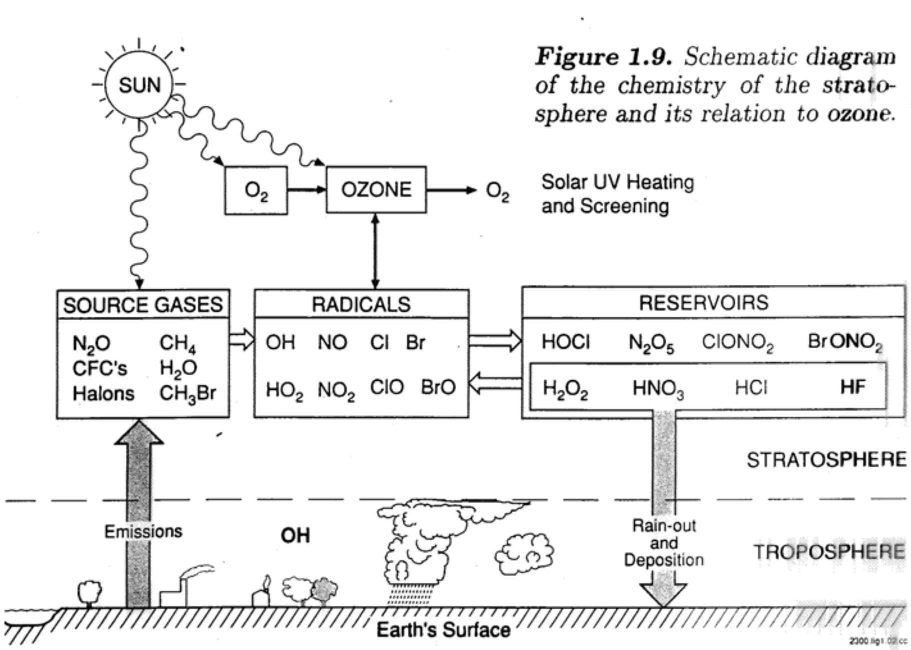


Figure 1.9. *Schematic diagram of the chemistry of the stratosphere and its relation to ozone.*

Brasseur, Orland, and Tyndall

Discovery of the Antarctic ozone hole: 1985

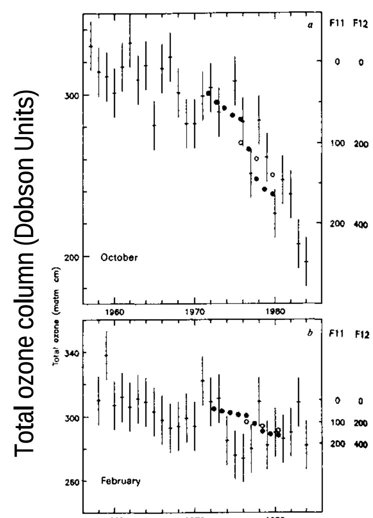


Fig. 2 Monthly means of total O_3 at Halley Bay, and Southern Hemisphere measurements of F-11 (●, p.p.t.v. (parts per thousand by volume) $CFCl_3$) and F-12 (○, p.p.t.v. CF_2Cl_2). *a*, October, 1957–84. *b*, February, 1958–84. Note that F-11 and F-12 amounts increase down the figure.

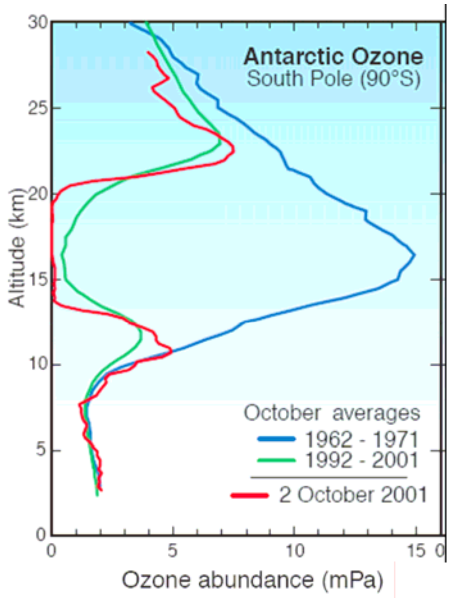
| Ozone column
• CFC-11
○ CFC-12

Total ozone observations at Halley Bay (76°S, 27°W), Antarctica: 1956-1985

Farman et al., Nature, 315, May 1985

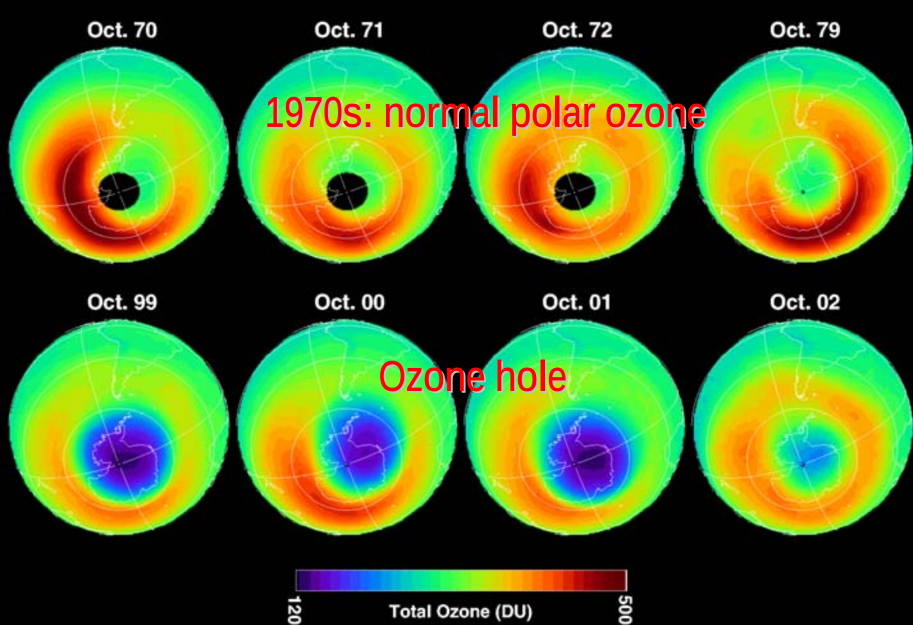
"Large losses of ozone in Antarctic reveal seasonal ClO_x/NO_x interactions"

Vertical distribution of ozone at the South Pole

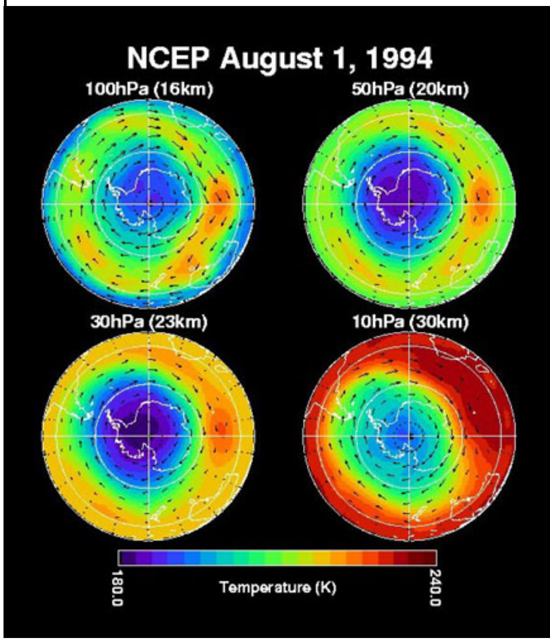


→ Depletion of Antarctic ozone column confined to 12-25 km

The Antarctic ozone hole viewed from space



The Antarctic Polar Vortex: Wind and temperature



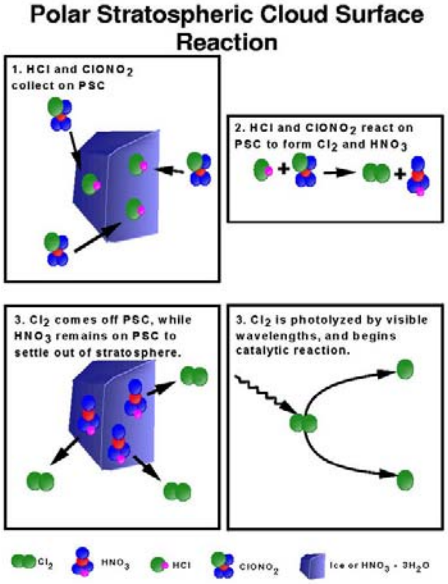
- Lack of sunlight between June and September → **cooling** of Antarctic stratosphere and adiabatic **downwelling**
- Large latitudinal temperature gradient (sunlight/polar night) →strong zonal winds = Polar night jet (150 km/h at 20 km)
- Antarctic polar vortex: region poleward of polar night jet
- **Isolation** of polar vortex: little mixing of warmer air from lower latitudes occurs
- **Sustained cold temperatures** over Antarctica during winter (~183K at 20km in early August).

Polar Stratospheric Clouds (PSC)

http://earthobservatory.nasa.gov/

	Type I PSC	Type II PSC
Composition:	Nitric Acid Trihydrate (HNO_3-3 H_2O) Ternary solution (H_2O, H_2SO_4, HNO_3)	Water Ice
Formation Temp.:	195 K	188 K
Particle diameter:	1 μm	>10 μm
Altitudes:	10-24 km	10-24 km
Settling rates:	1 km/30 days	> 1.5 km/day

Chlorine activation on polar stratospheric clouds



$$HCl + ClONO_2 \xrightarrow{PSCs} Cl_2 + HNO_3$$

Conversion of chlorine reservoirs HCl and $ClONO_2$ to Cl_2 and HNO_3 on PSCs
→Cl_2 photolyzes in sunlight (spring) releasing Cl and catalytic ozone loss begins
→HNO_3 remains on PSCs and settles out of stratosphere suppressing NO_x levels: $ClO+NO_2+ M \rightarrow ClONO_2 + M$ cannot deactivate ClO radicals.

Chlorine activation on PSCs

Reactions taking place on polar stratospheric clouds:

$HCl + ClONO_2 \rightarrow Cl_2 + HNO_3$

$ClONO_2 + H_2O \rightarrow HOCl + HNO_3$

$HOCl + HCl \rightarrow Cl_2 + H_2O$

$BrONO_2 + H_2O \rightarrow HNO_3 + HOBr$

$HCl + BrONO_2 \rightarrow HNO_3 + BrCl$

$HCl + HOBr \rightarrow H_2O + BrCl$

Chlorine/Bromine activation + sequestration of HNO_3 in PSCs

Rapid ozone destruction mechanisms

Polar sunrise: $Cl_2 + h\nu \rightarrow Cl + Cl$, $BrCl + h\nu \rightarrow Br + Cl$

Molina and Molina (1987): ClO dimer catalytic cycle

$$
\begin{aligned}
&2(Cl + O_3 \rightarrow ClO + O_2)\\
&ClO + ClO \rightarrow Cl_2O_2\\
&Cl_2O_2 + h\nu \rightarrow ClOO + Cl\\
&ClOO + M \rightarrow Cl + O_2 + M\\
\hline
&\text{Net:} O_3 + O_3 \rightarrow 3O_2
\end{aligned}
$$

~75 % of ozone removal in ozone hole

McElroy et al. (1986) and Tung et al. (1986): Bromine/chlorine coupling

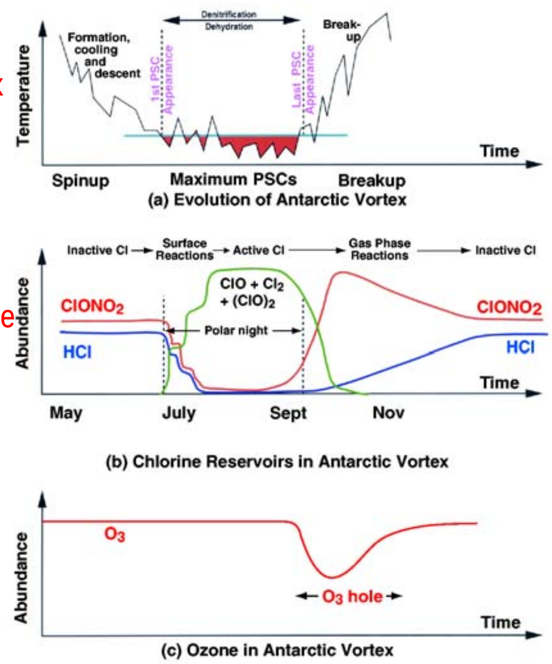
$$
\begin{aligned}
&Cl + O_3 \rightarrow ClO + O_2\\
&Br + O_3 \rightarrow BrO + O_2\\
&BrO + ClO \rightarrow Br + ClOO\\
&ClOO + M \rightarrow ClO + O_2\\
\hline
&\text{Net:} O_3 + O_3 \rightarrow O_2 + O_2
\end{aligned}
$$

~20% of ozone removal in ozone hole

Evolution of Antarctic Vortex

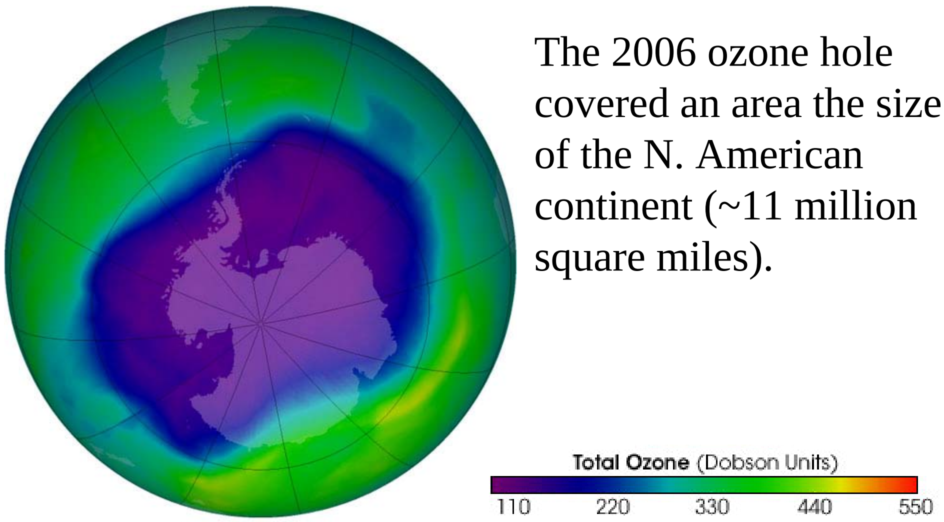
Reactive chlorine and chlorine reservoirs

Ozone levels



Wallace & Hobbs

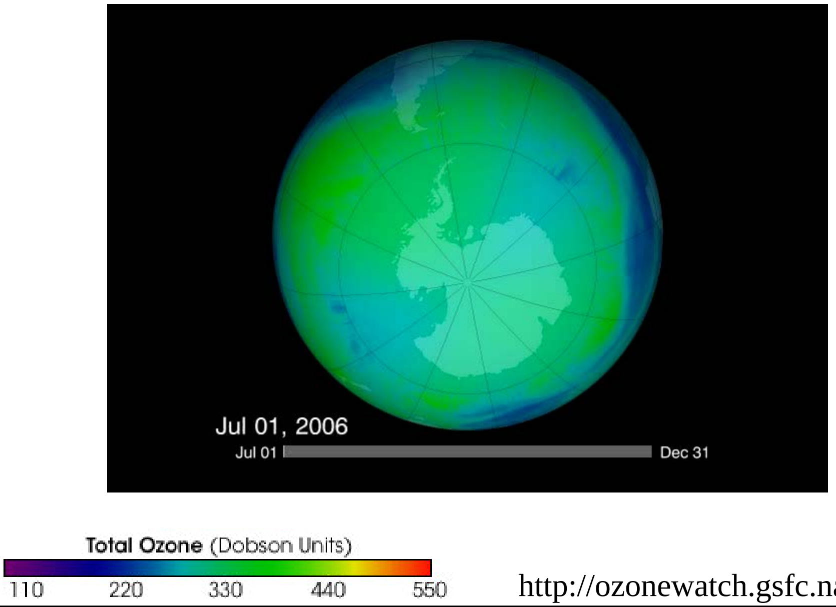
2006 Ozone hole – largest ever



The 2006 ozone hole covered an area the size of the N. American continent (~11 million square miles).

http://www.nasa.gov/vision/earth/lookingatearth/ozone_record.html

Antarctic Ozone Hole: July 1-Dec 31 2006

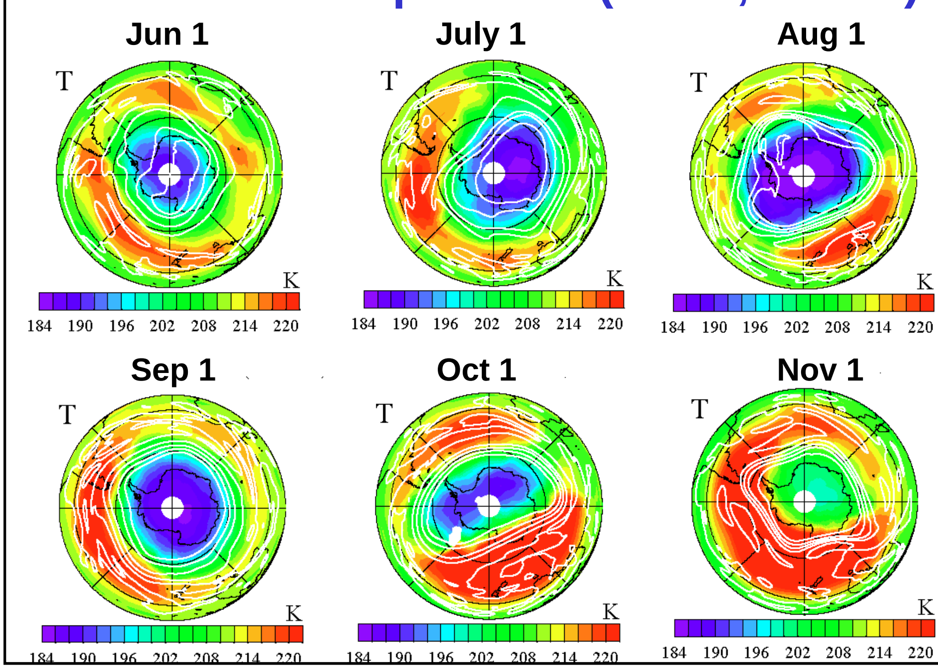


http://ozonewatch.gsfc.nasa.gov/

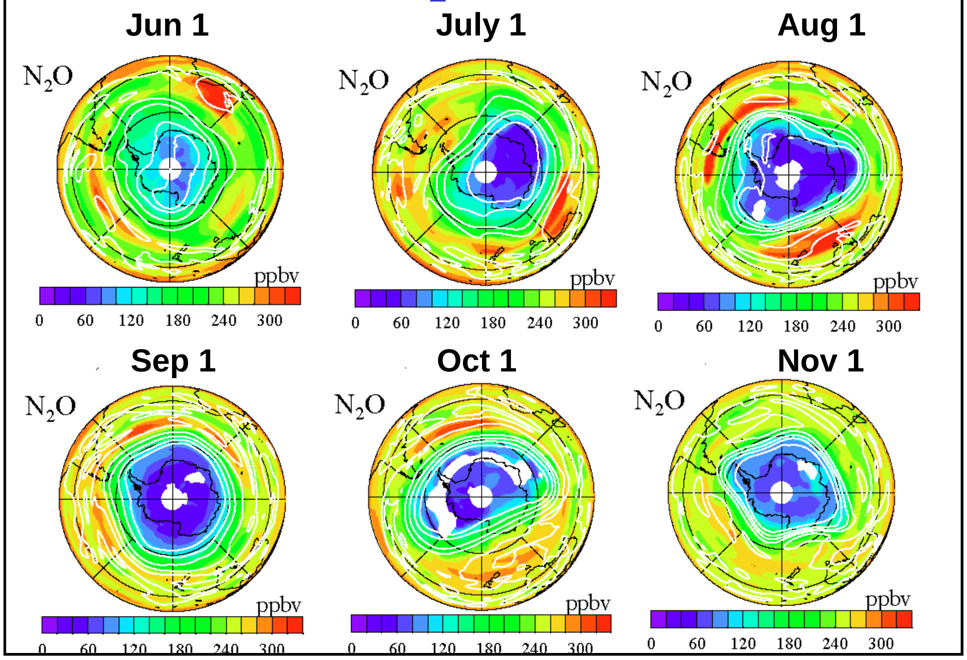
Satellite observations of the 2006 ozone hole

- Microwave Limb Sounder
- Onboard NASA's AURA satellite
- http://mls.jpl.nasa.gov/plots/mls/mls_plot_locator.php
- Temperature, O_3, N_2O, ClO, HCl, HNO_3

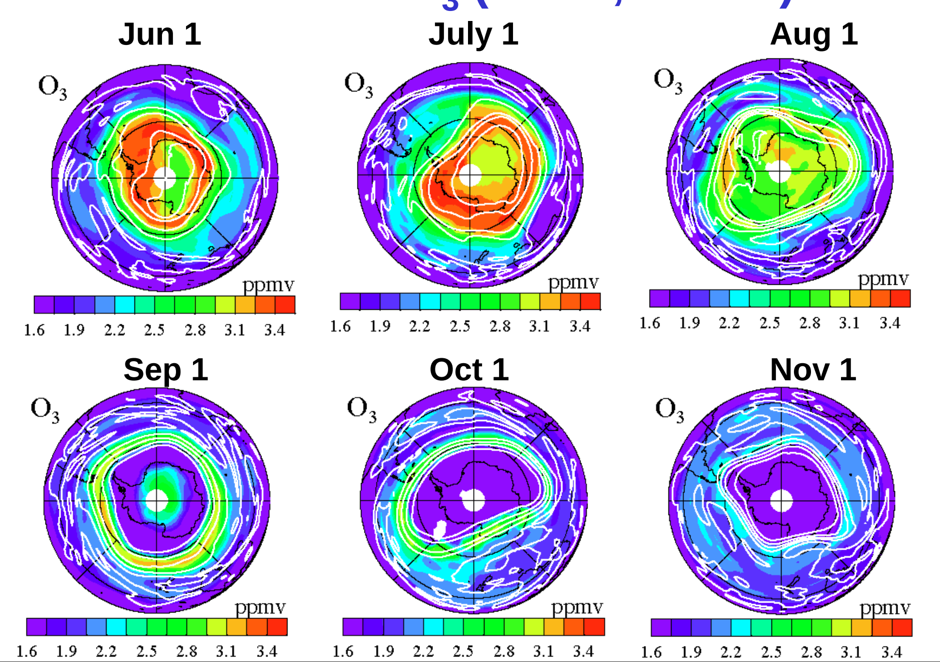
SH 2006: Temperature (18km, 56hPa)



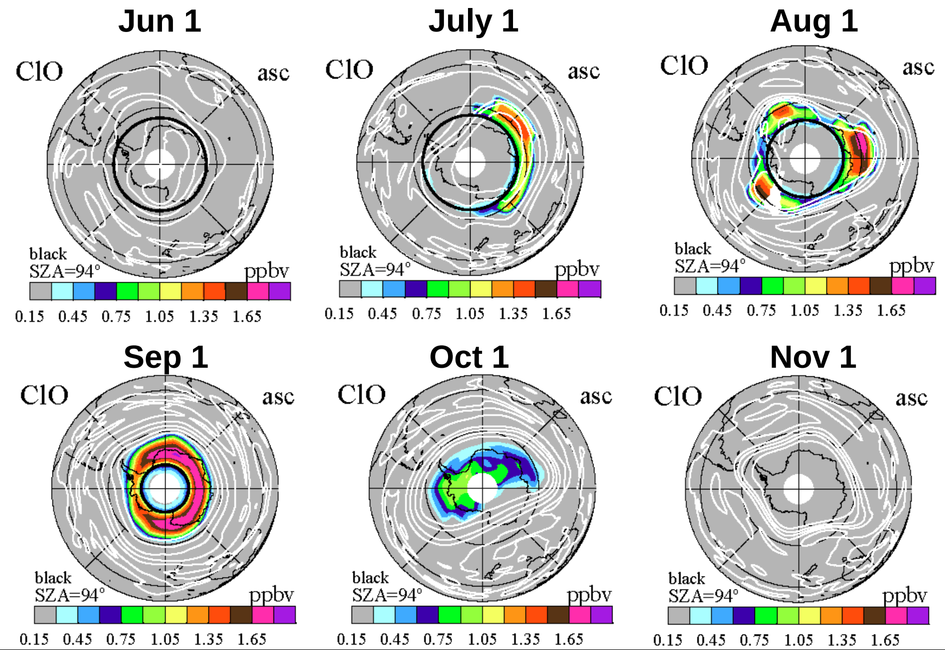
SH 2006: N_2O (18km, 56hPa)



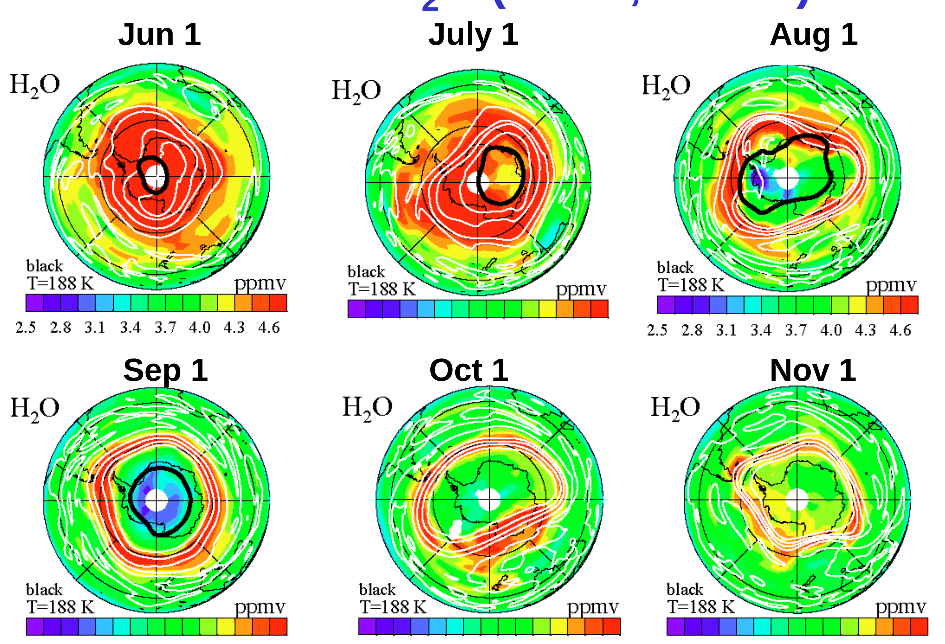
SH 2006: O_3 (18km, 56hPa)



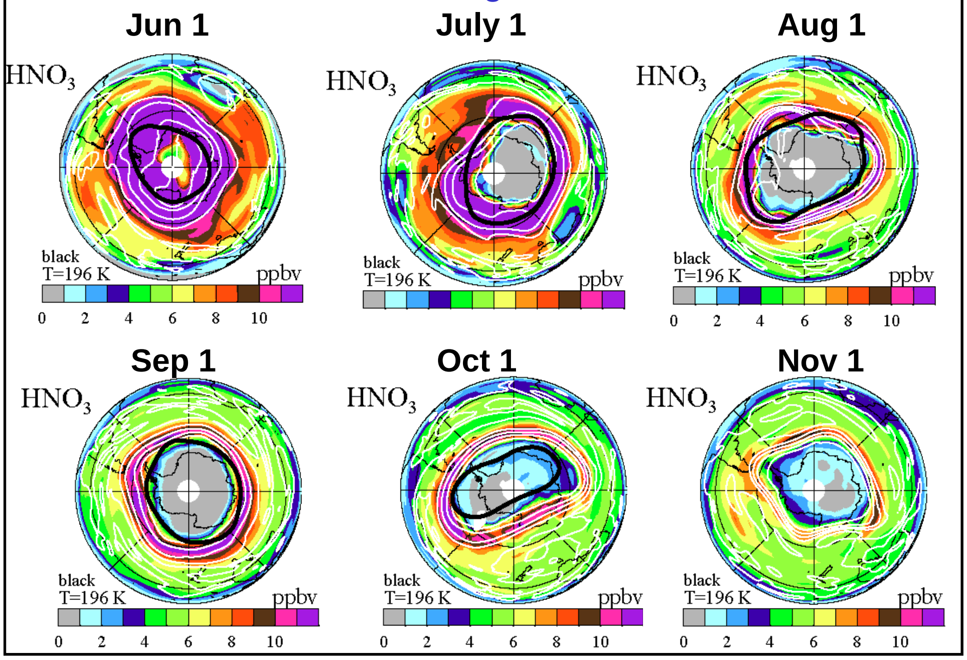
SH 2006: ClO (18km, 56hPa)



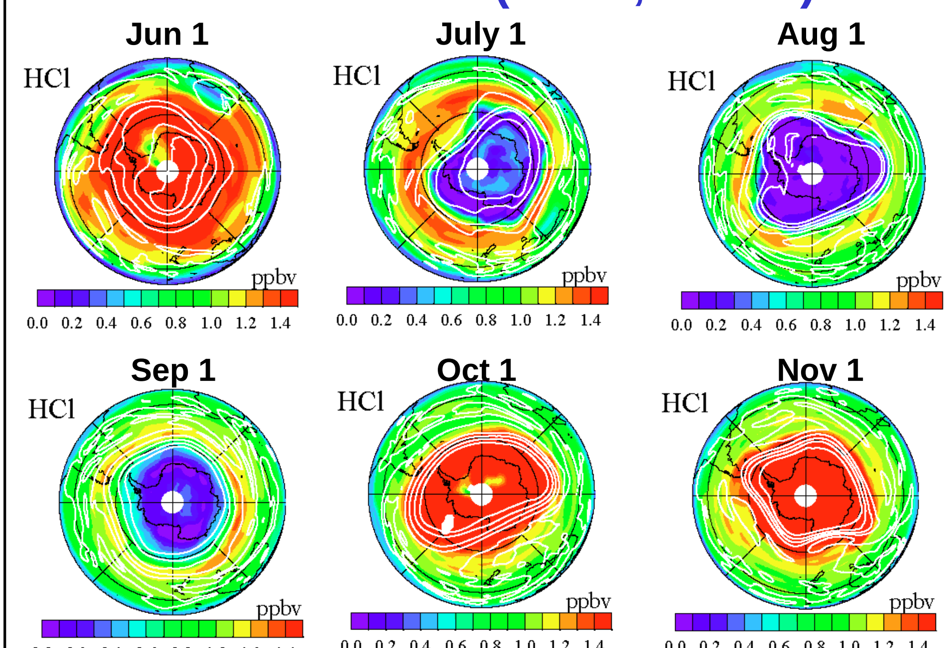
SH 2006: H_2O (18km, 56hPa)



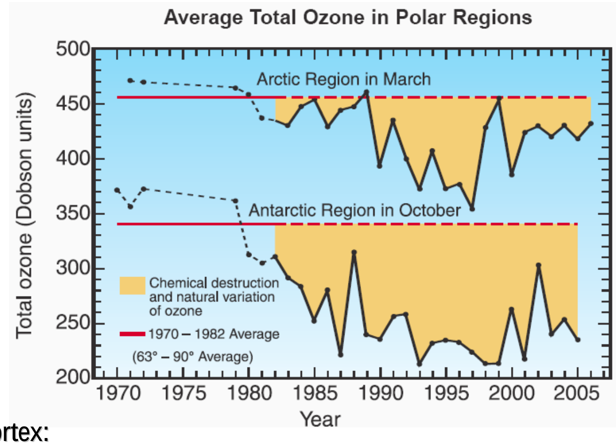
SH 2006: HNO_3 (18km, 56hPa)



SH 2006: HCl (18km, 56hPa)



An Arctic ozone hole?

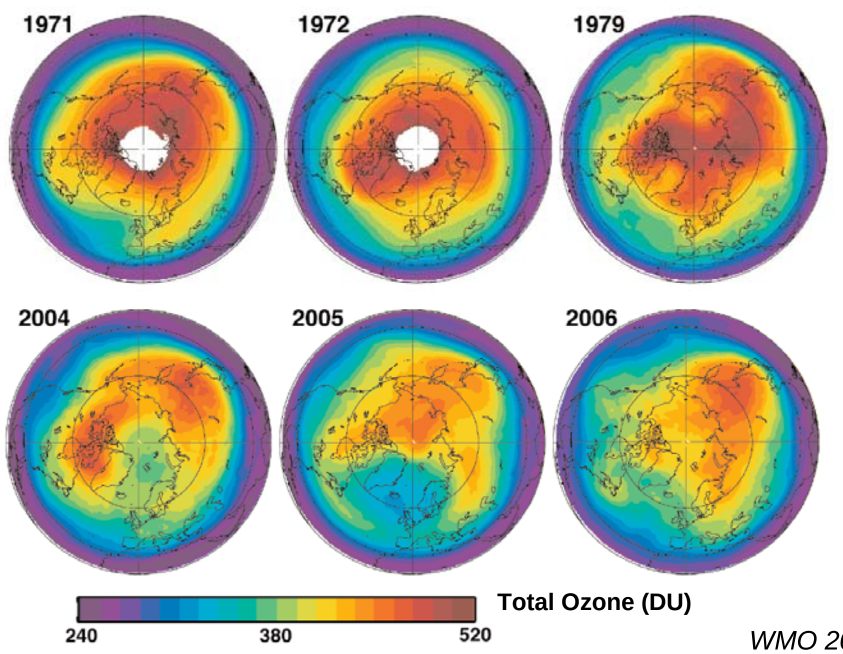


Arctic vortex:

- No land mass (warmer)
- Less symmetric
- Planetary wave activity (Tibet, North America…)

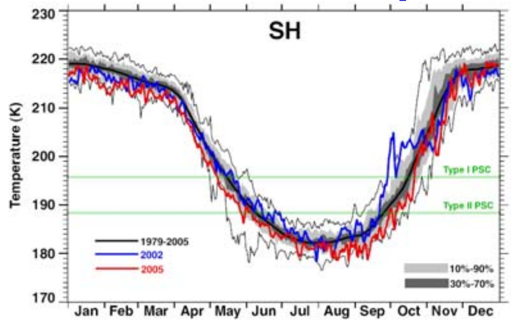
→ Overlap between cold temperatures and sunlight are limited in the Arctic and ozone depletion episodic and minor

Arctic Ozone depletion: March



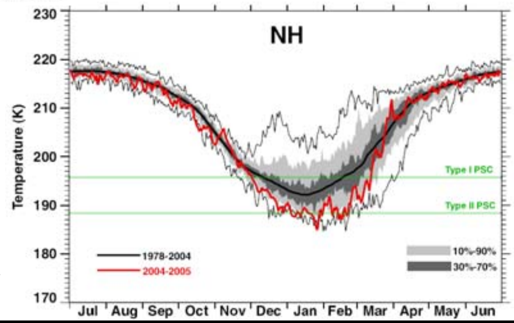
WMO 2006

Minimum temperatures at 50 hPa



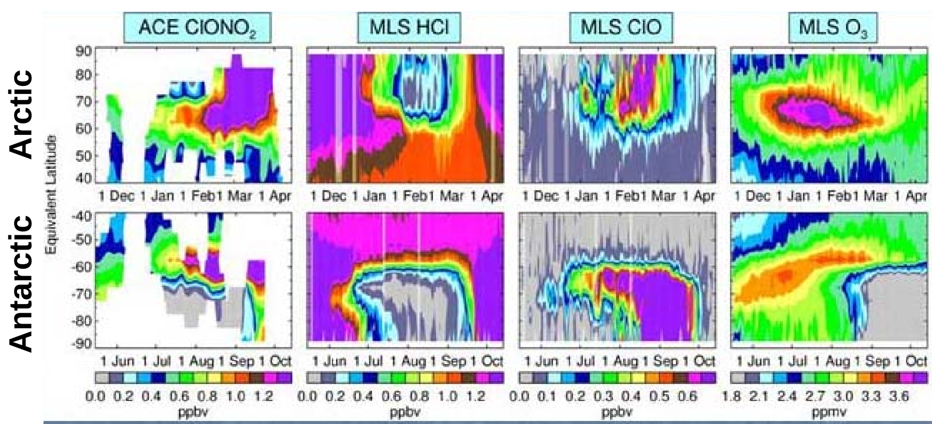
SH: 50-90°S

WMO, 2006



NH: 50-90°N

Comparison: Arctic, Antarctic lower stratosphere



NASA’s AURA satellite observations. MLS and ACE instruments
~20 km altitude

Santee et al.