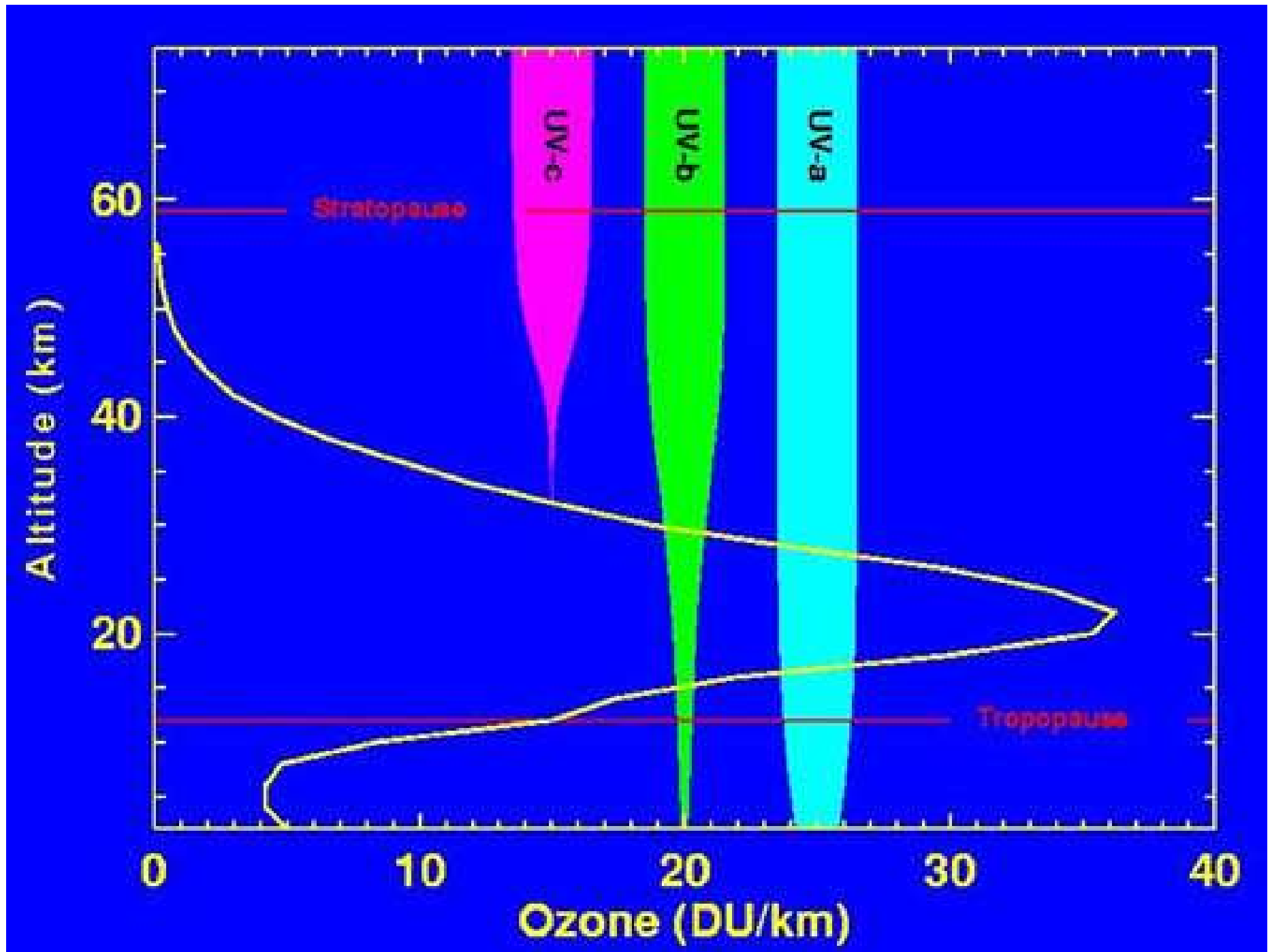


Ozone Depletion and the Ozone Hole

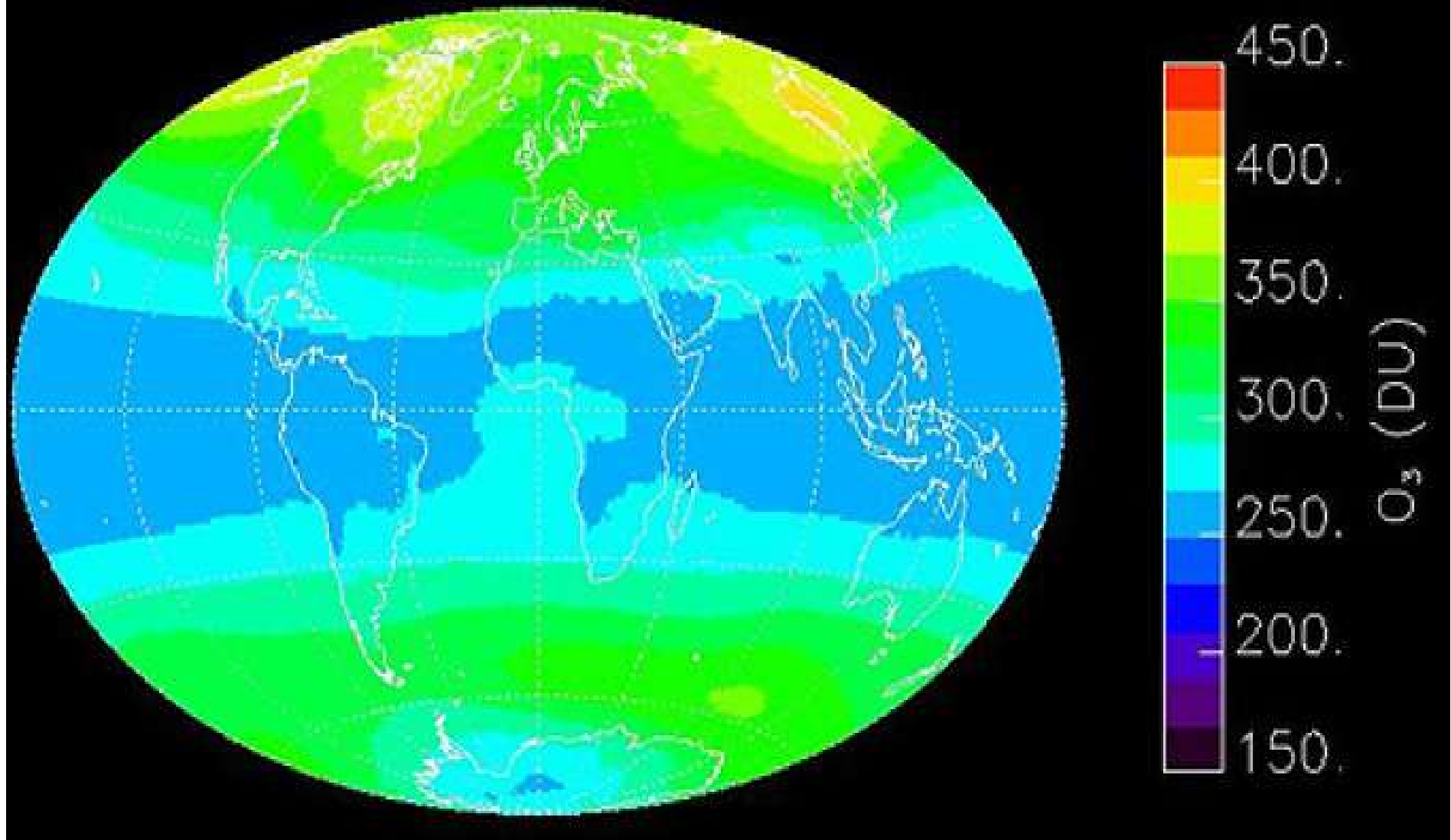
Preview:

- Stratospheric sunscreen, tropospheric pollutant
- 60's & 70's theories suggested depletion mechanisms
- 1985 discovery of ozone was a big surprise
- lead to increased research effort
- Chlorine and PSC hypothesized as cause
- lead to international restrictions and bans
- 80's & 90's ozone hole continued to expand and mid-latitude loss continues
- Present: growth slowed although 2003 was big
- Chlorine concentrations stabilizing, CFC's eliminated

Ozone as natural sunscreen



Average TOMS Ozone 1978 – 1993



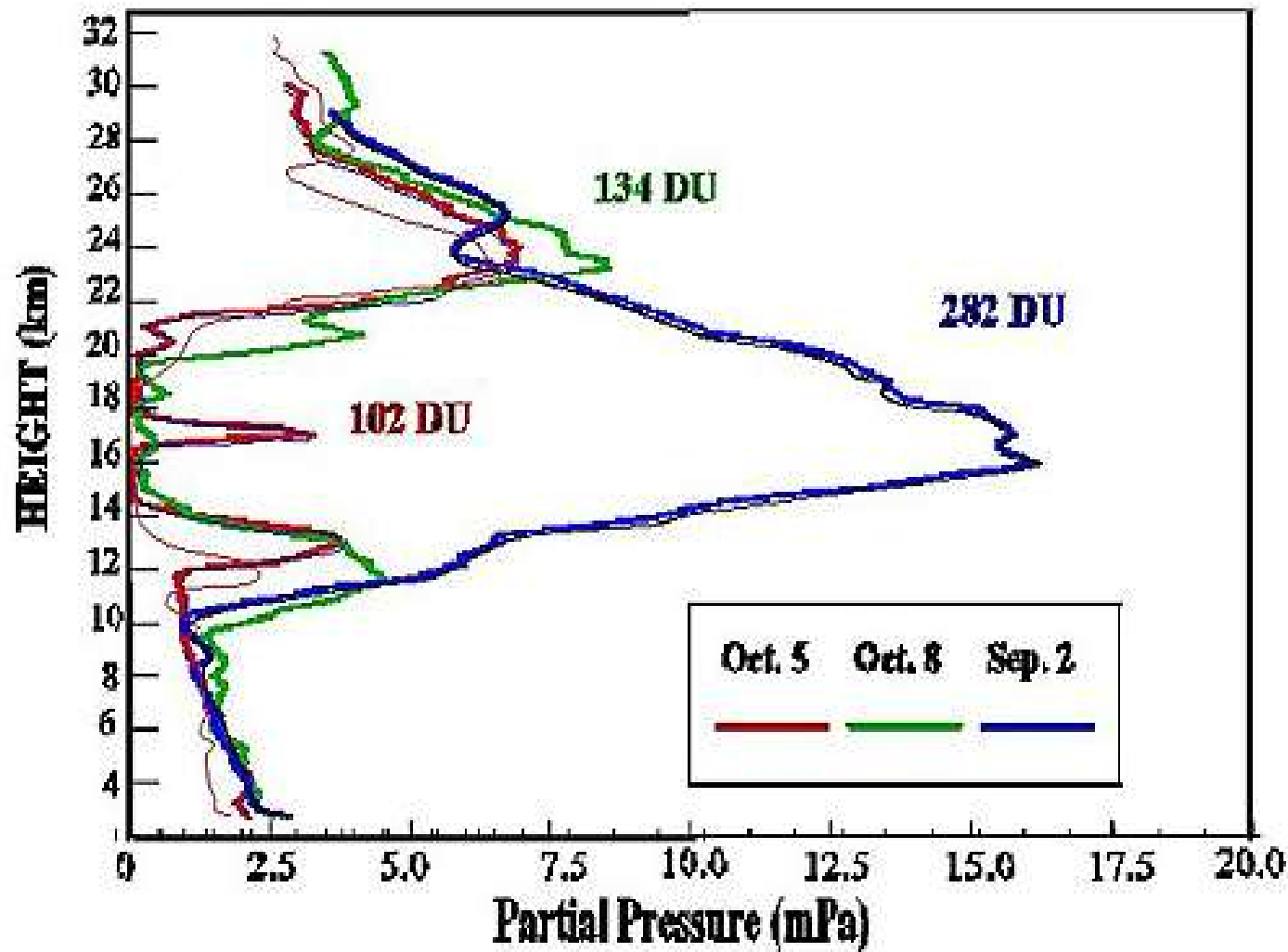
Average Ozone Column 1978-1993

Stratospheric Ozone: Brief Historical Perspective

- 1881: Hartley first hypothesized the presence of ozone (lab)
- 1924: Dobson invented spectrophotometer of measure ozone
- 1929: Gotz using Dobson s instrument found that ozone was in the stratosphere (~25 km)
- 1930: Chapman developed theory of stratospheric ozone origin
- 1949: Brewer, role of circulation in controlling ozone layer
Catalytic cycles: Hydrogen (Hunt, 1966); NO_x from tropospheric N₂O (Crutzen, 1970); NO_x from aircraft (Johnston, 1971); CFCs (Molina & Rowland, 1974)
- 1985: Farman discovers the ozone hole over Antarctica
- 1986: Solomon/McElroy unravel the role of polar stratospheric clouds and halogen catalysis
- Regulation of CFC production: Montreal Protocol (1987); London Agreement (1990); Copenhagen amendment (1992)

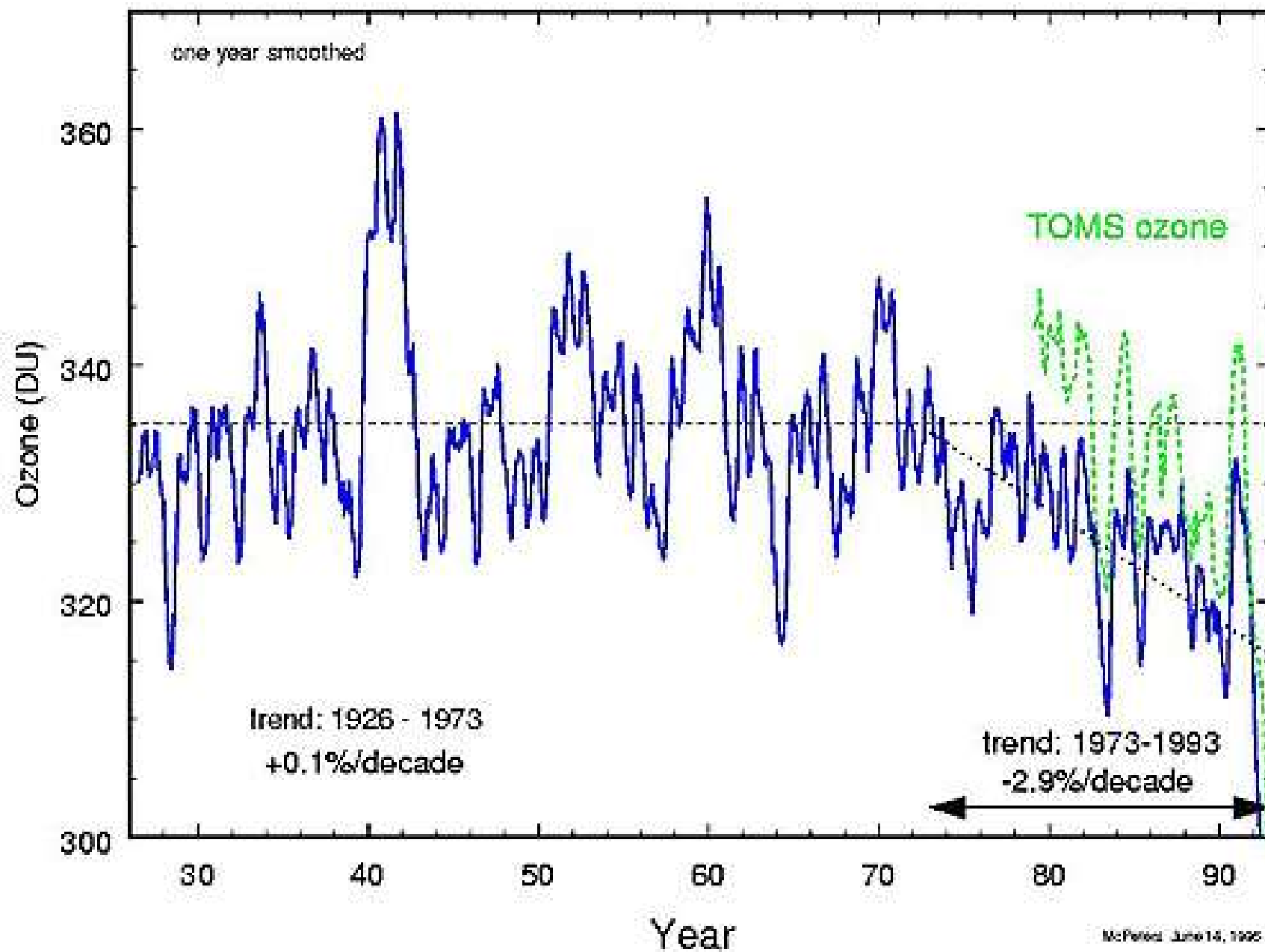
Antarctic Ozone Measurements vs Altitude

1994 SOUTH POLE OZONESONDES

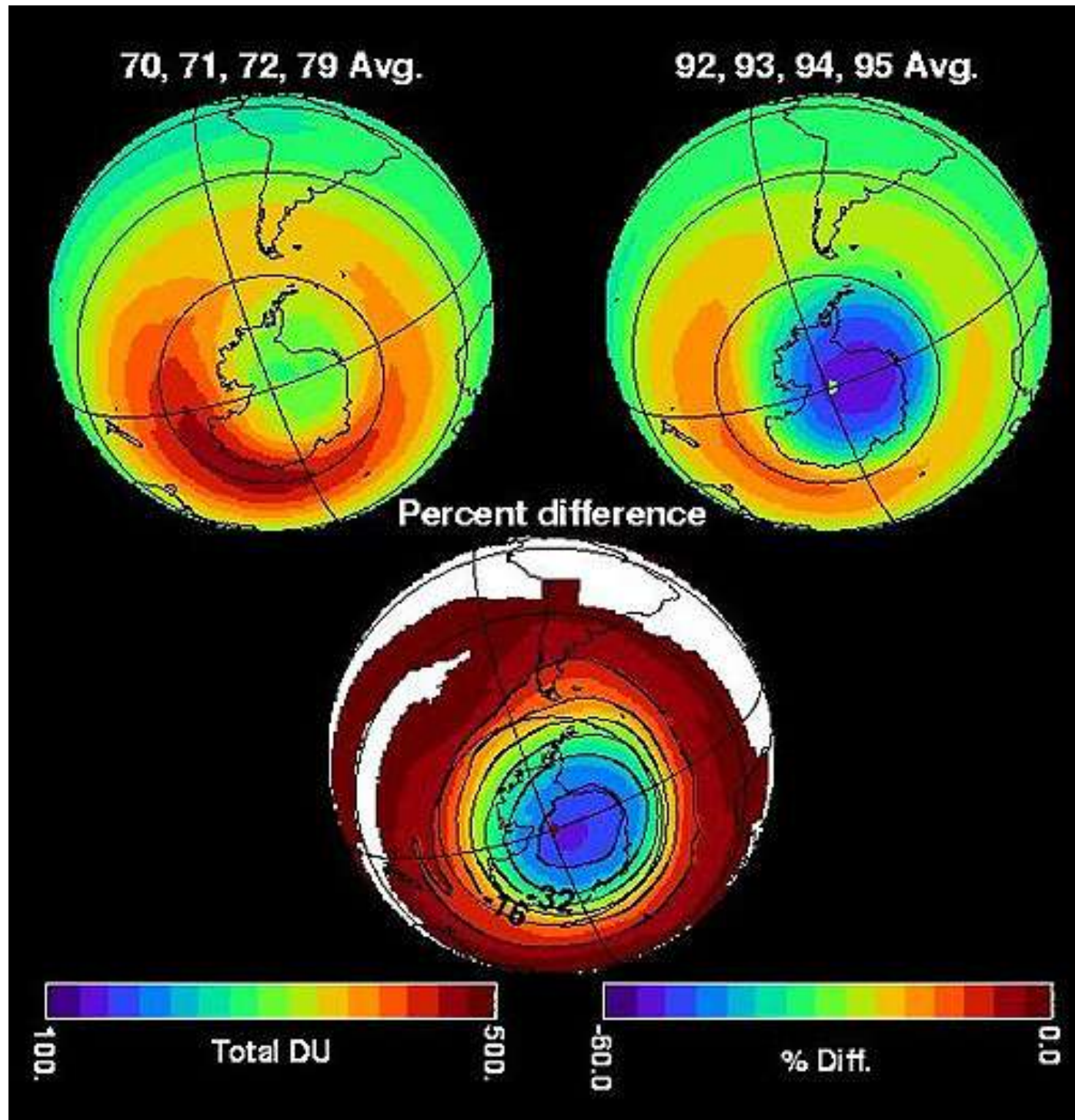


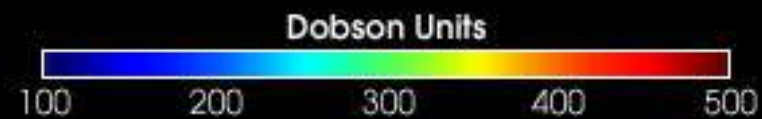
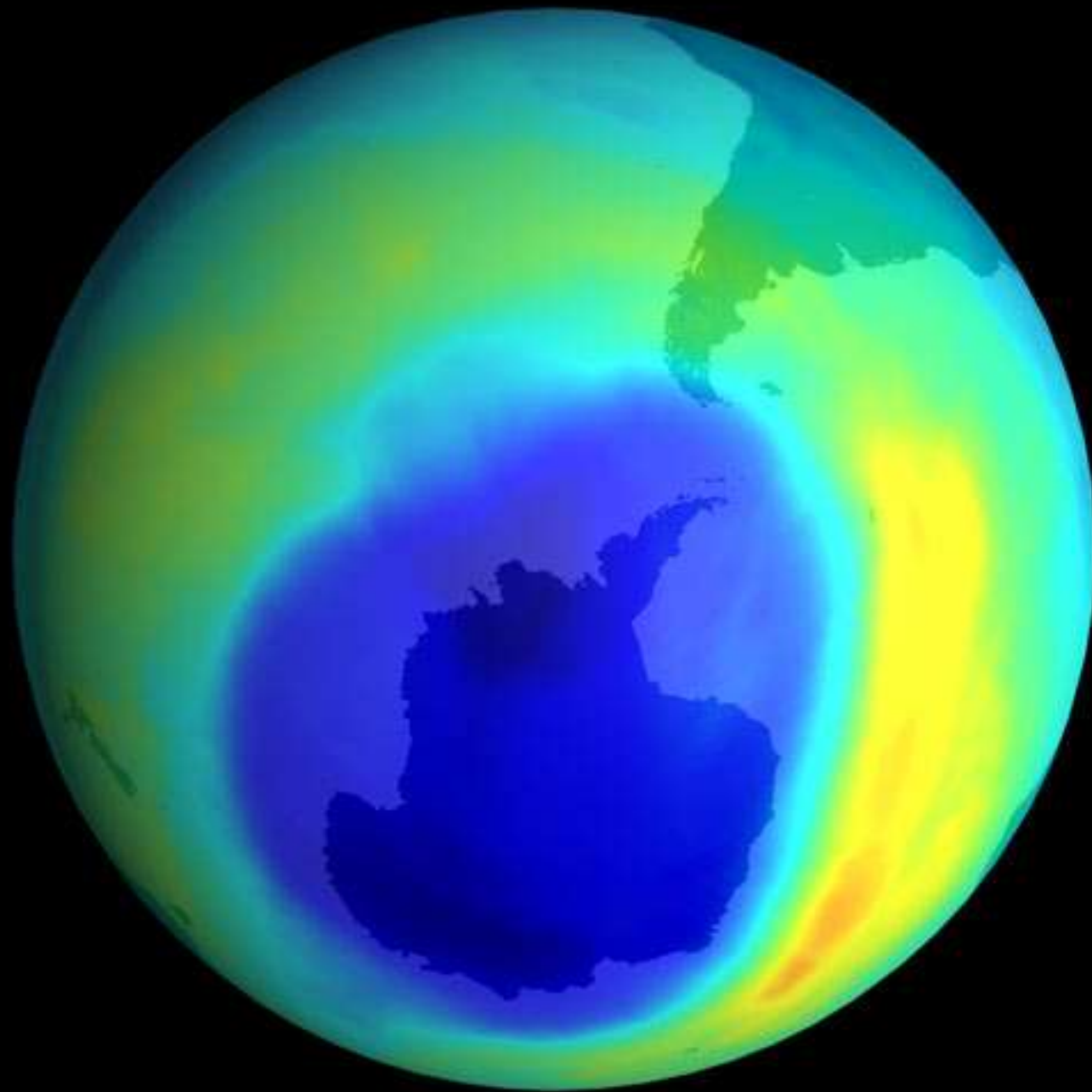
Measurements made by balloon ozonesondes
before and after intense depletion.

Ozone at Arosa, Switzerland since 1926



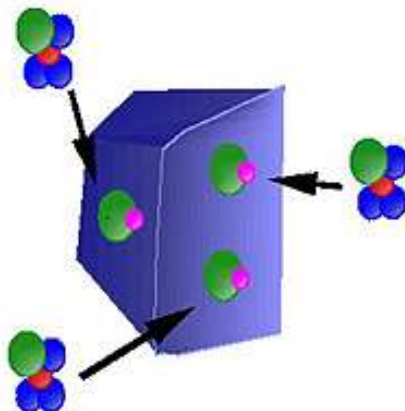
October average ozone concentrations



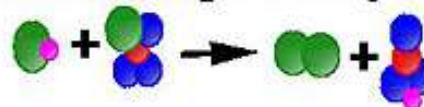


Polar Stratospheric Cloud Surface Reaction

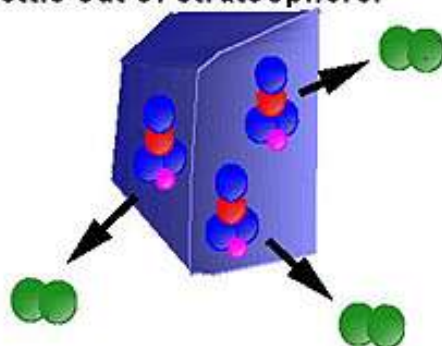
1. HCl and ClONO₂ collect on PSC



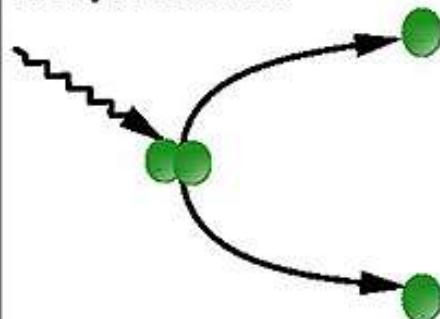
2. HCl and ClONO₂ react on PSC to form Cl₂ and HNO₃



3. Cl₂ comes off PSC, while HNO₃ remains on PSC to settle out of stratosphere.



3. Cl₂ is photolyzed by visible wavelengths, and begins catalytic reaction.



Polar Stratospheric Clouds

Type I PSC:

Nitric acid trihydrate ($\text{HNO}_3 \cdot 3\text{H}_2\text{O}$)
Ternary solution (H_2O , H_2SO_4 , HNO_3)

Formation Temp:

195 K

Particle diameter:

$1\mu\text{m}$

Altitudes:

10- 24 km

Settling rates:

1km/30 days

Type II PSC:

Water Ice

Formation Temp:

188 K

Particle diameter:

$> 10\mu\text{m}$

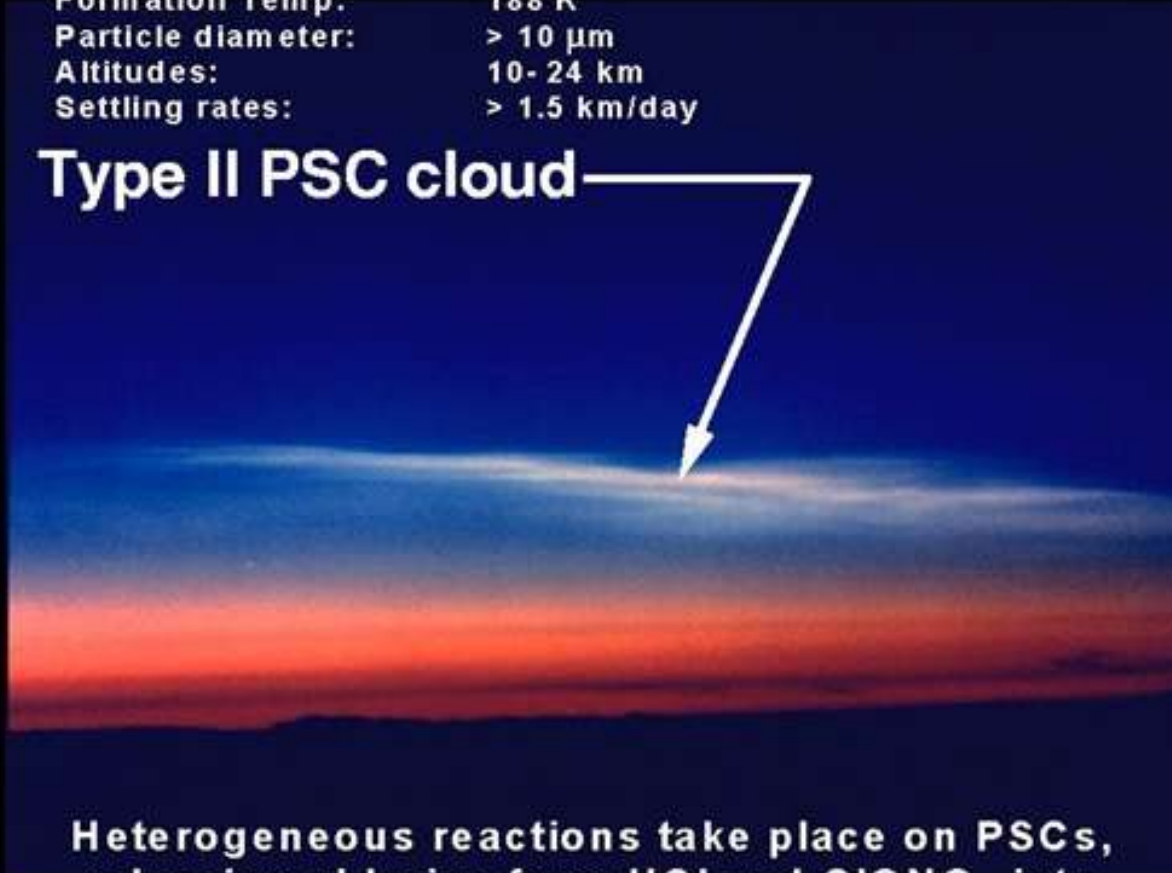
Altitudes:

10- 24 km

Settling rates:

$> 1.5\text{ km/day}$

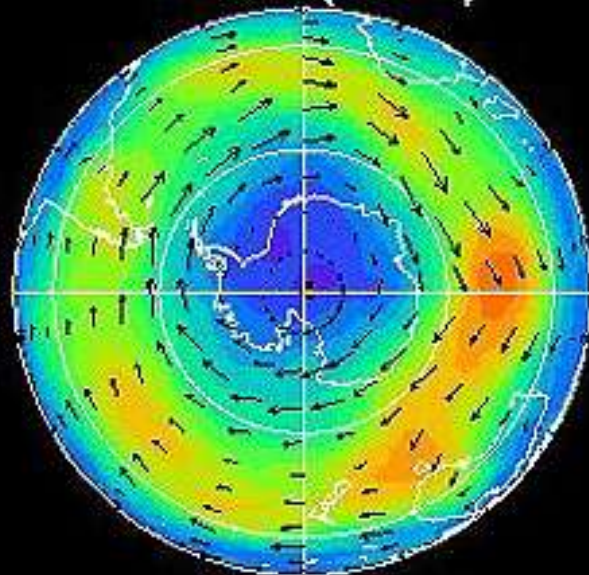
Type II PSC cloud



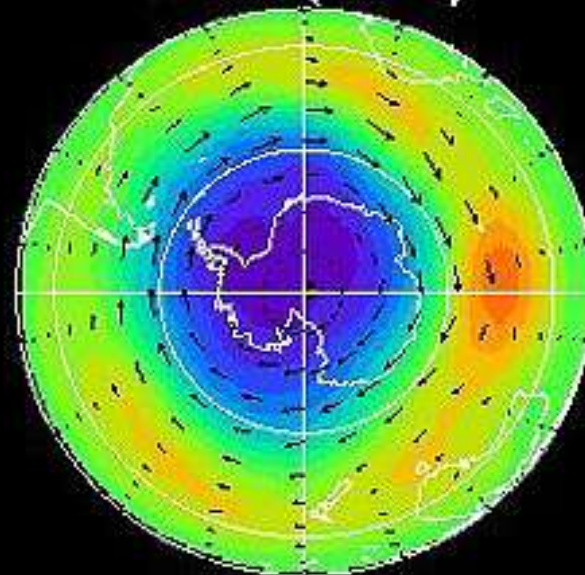
Heterogeneous reactions take place on PSCs, releasing chlorine from HCl and ClONO_2 into reactive forms (ClO) that can rapidly destroy ozone.

NCEP August 1, 1994

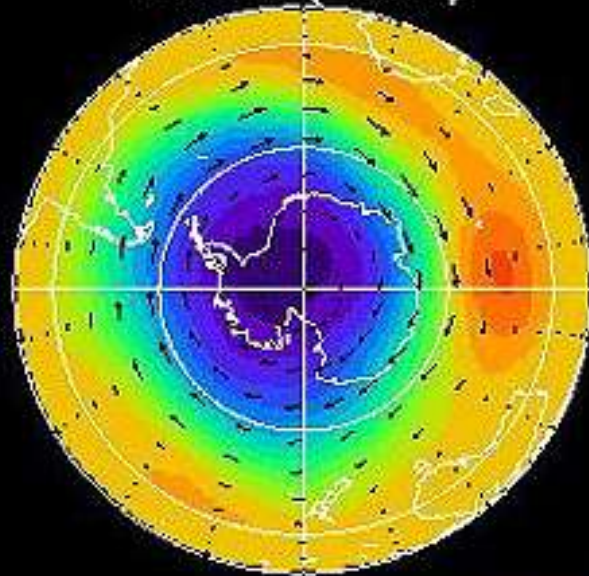
100hPa (16km)



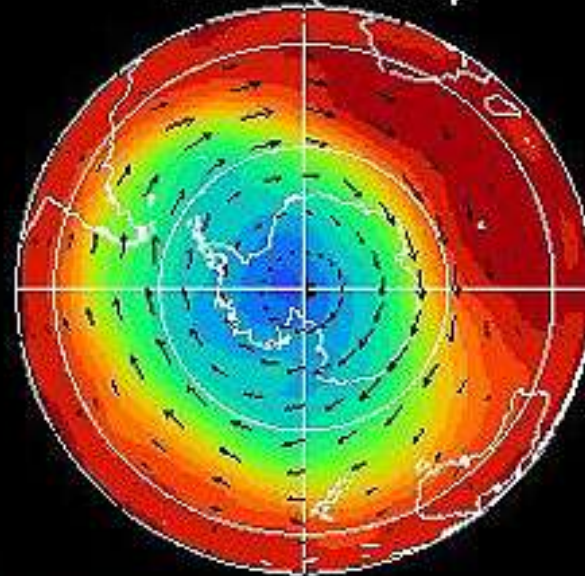
50hPa (20km)



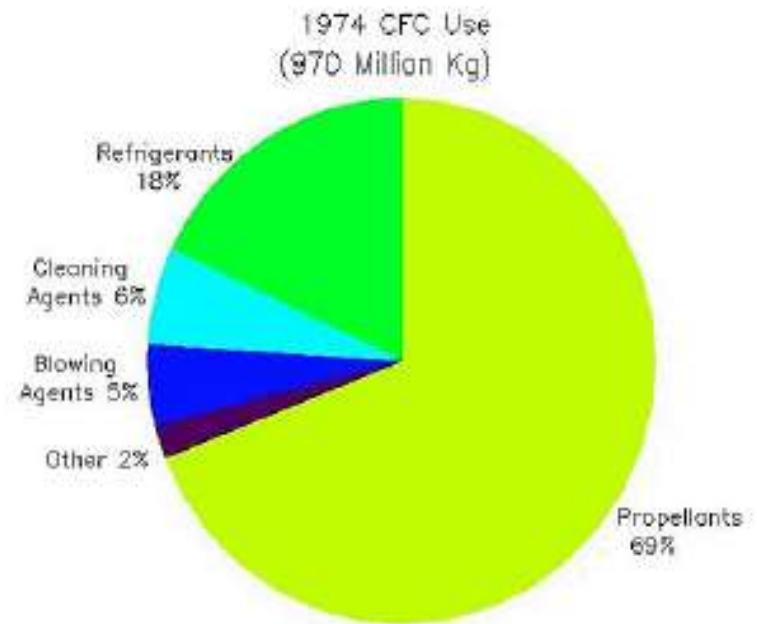
30hPa (23km)



10hPa (30km)

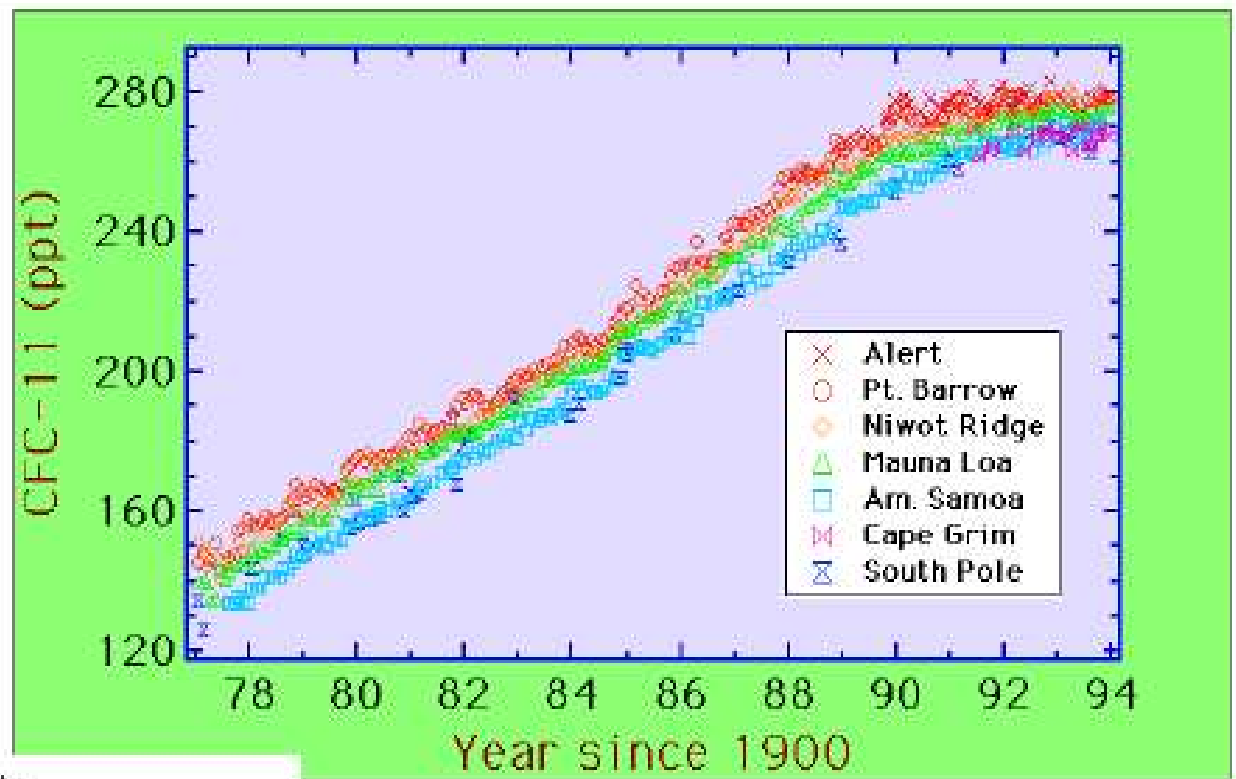


“wonder gas” CFCs were invented in 1928



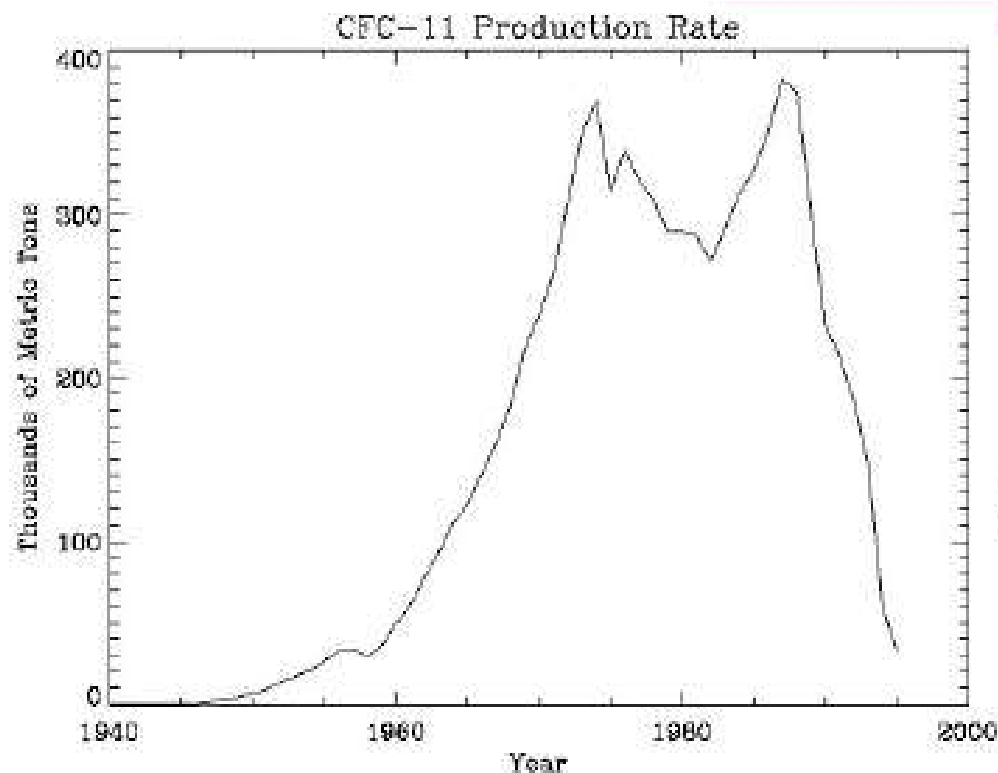
Use of CFCs increases rapidly

1970-1994: rapid
increase in CFC-11
atmospheric levels

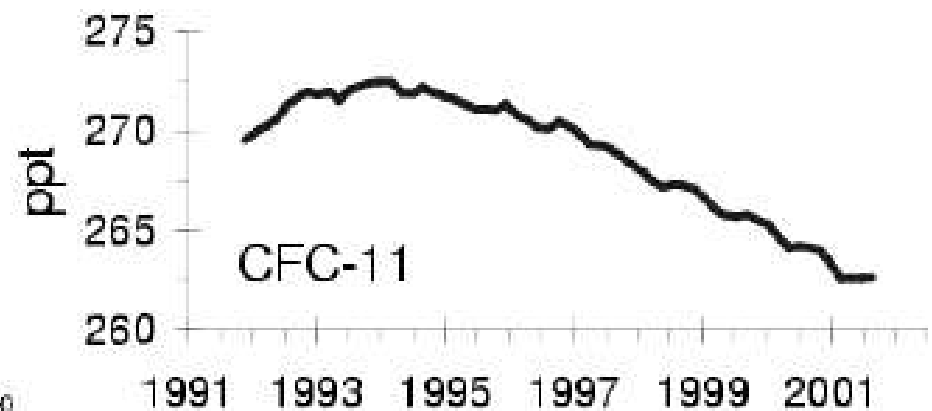


Elkins et al., Nature, 1993.

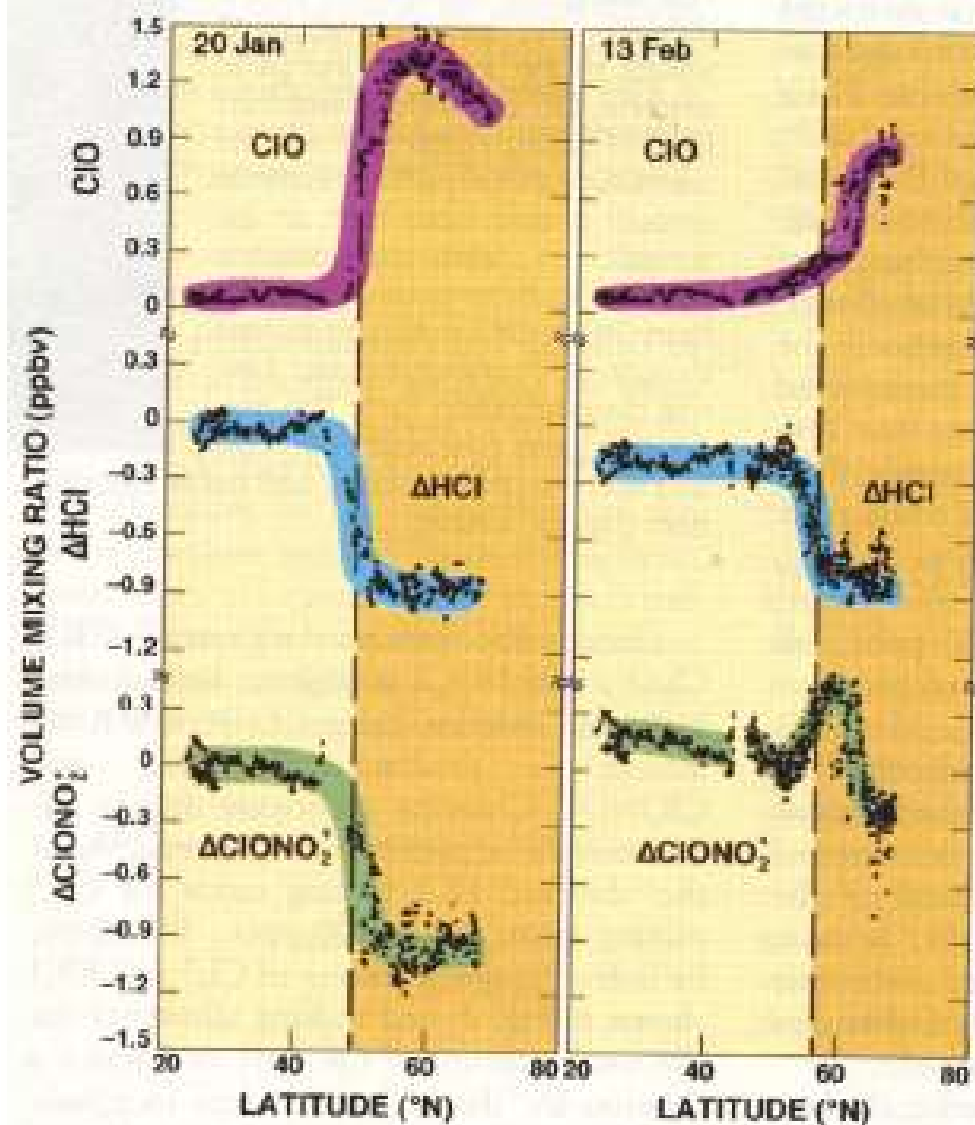
CFC-11 production rate



1994-today: CFC-11
is decreasing



Field observations confirming PSC theory



Simultaneous observations of CIO and HCl inside polar vortex (Arctic 1993)

→ CIO increases and HCl decrease inside the polar vortex

Webster et al., Science, 261, 1130, 1993.


Ozone Hole Observations


- Begins to develop in August, fully developed by early October, broken up in early December.
- First began to appear in the early 1980's.
- Compared to 1970's, 60% reduction of ozone over Antarctica in early October.
- 100% loss of ozone in the 12–20 km region over Antarctica, some ozone remains both above 20 and below 12 km.
- Ozone hole covers approximately 22 million km² (slightly less than the surface area of the N. American continent).
- Ozone hole associated with cold Antarctic stratospheric temperatures.

Regulations on the production of CFCs

- **Vienna convention (1985):** .Convention for the Protection of the ozone layer. signed by 20 nations (research, future protocols)
- **Montreal Protocol (1987):** .Protocol on substances that deplete the ozone layer. Ratified in 1989. Legally binding controls freezing production to 1985 levels.
- **London Amendment (1990):** Phaseout of production by 2000 for developed nations and by 2010 for developing nations
- **Copenhagen Agreement (1992):** Phaseout for developed nations by 1996.

The Montreal Protocol is Working!

 Without the Montreal Protocol, ozone depletion in 2050 would be at least 50% at midlatitudes in the Northern Hemisphere and 70% at midlatitudes in the Southern Hemisphere, about 10 times larger than today.

 Surface UV-B radiation in 2050 would at least double at midlatitudes in the Northern Hemisphere and quadruple at midlatitudes in the Southern Hemisphere compared with an unperturbed atmosphere. This compares to the current increases of 5% and 8% in the Northern and Southern Hemispheres, respectively, since 1980.

WMO 1998 Scientific Assessment of Ozone Depletion