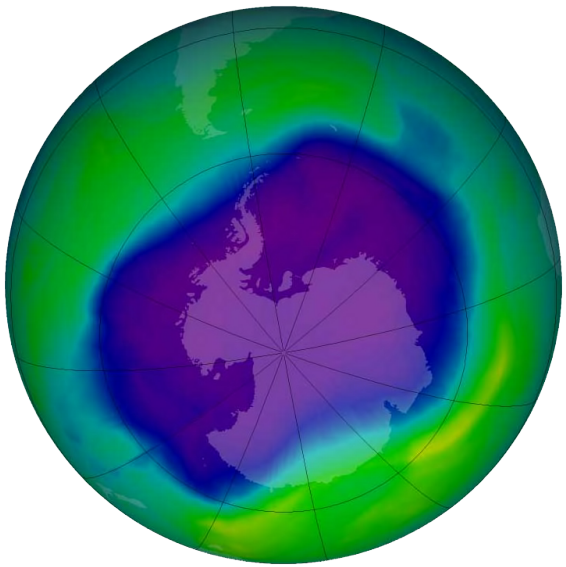
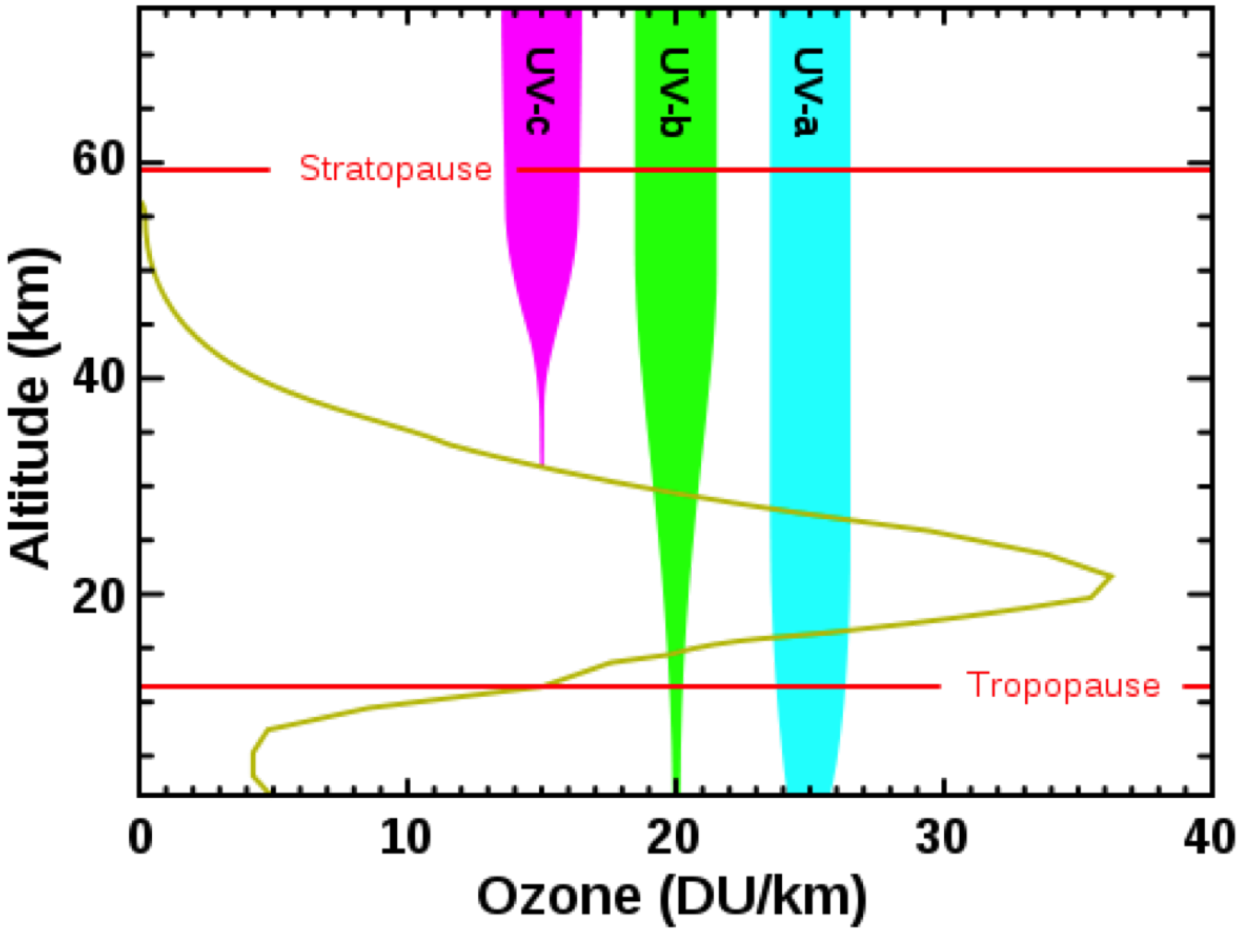
The Ozone Layer

Formation, Depletion and Recovery



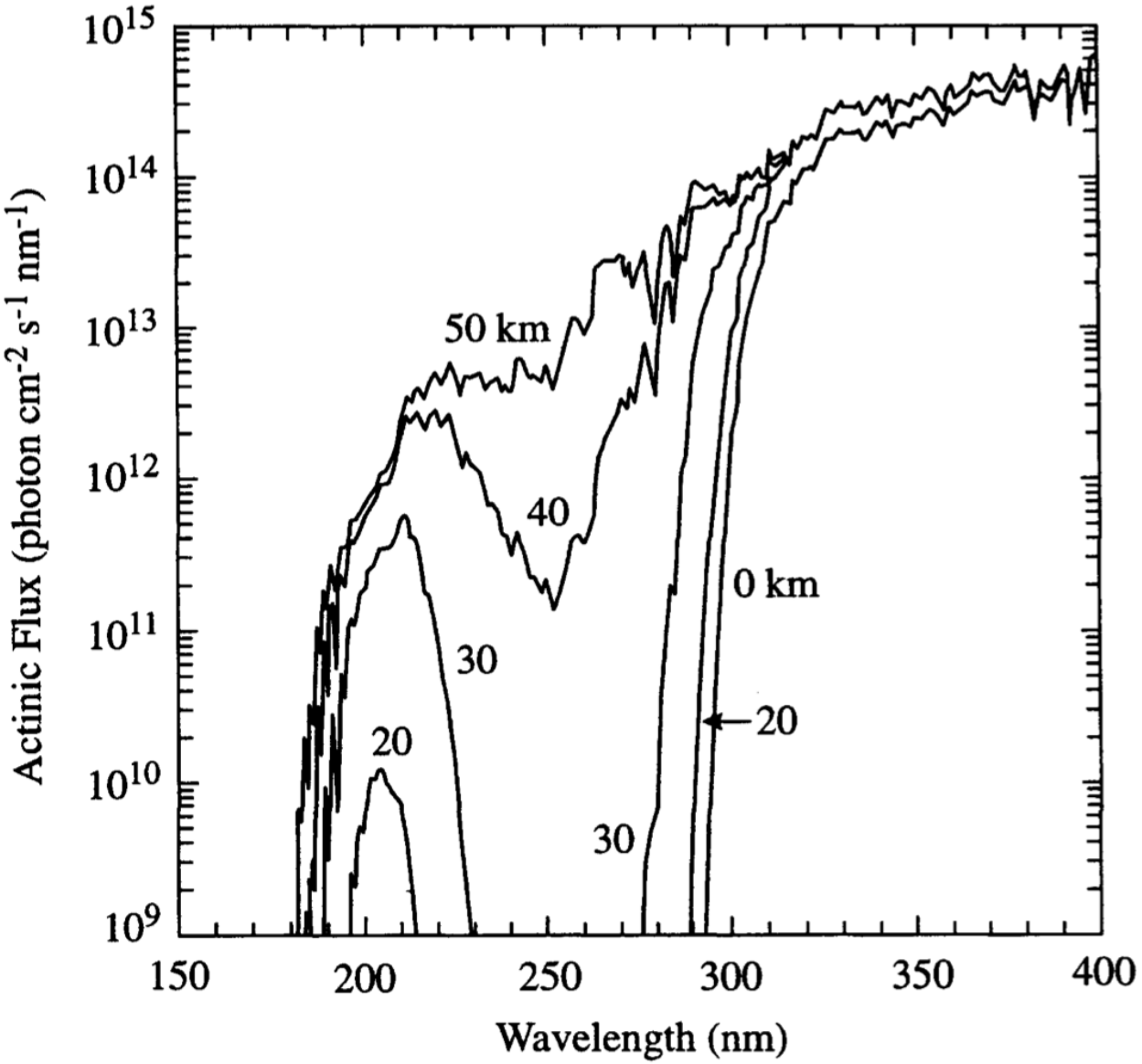
Outline of Topics

What does the ozone layer do for us?



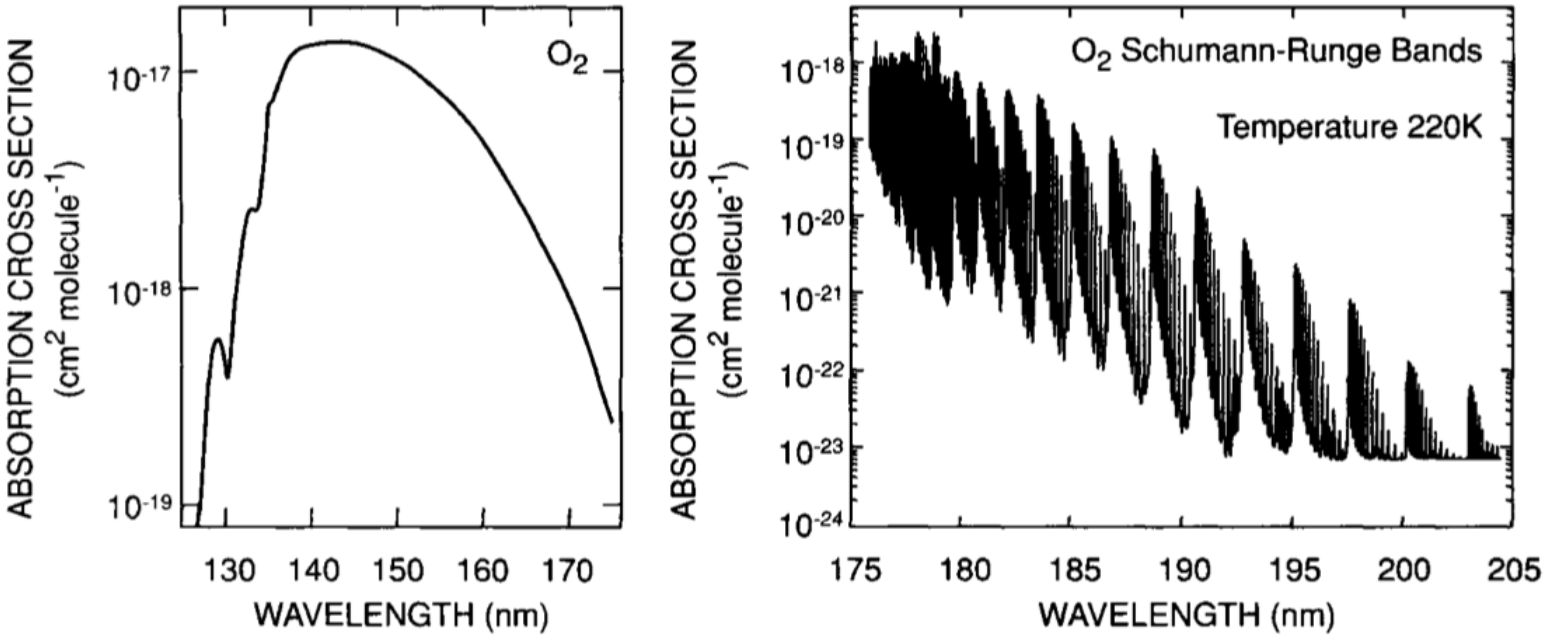
- 200-280 nm: UV-C (unaffected by O_3 depletion)
- 280-320 nm: UV-B (O_3 depletion affects this)
- 320-380 nm: UV-C (barely affected by O_3 depletion)

Give more detail on uv attenuation in the stratosphere.



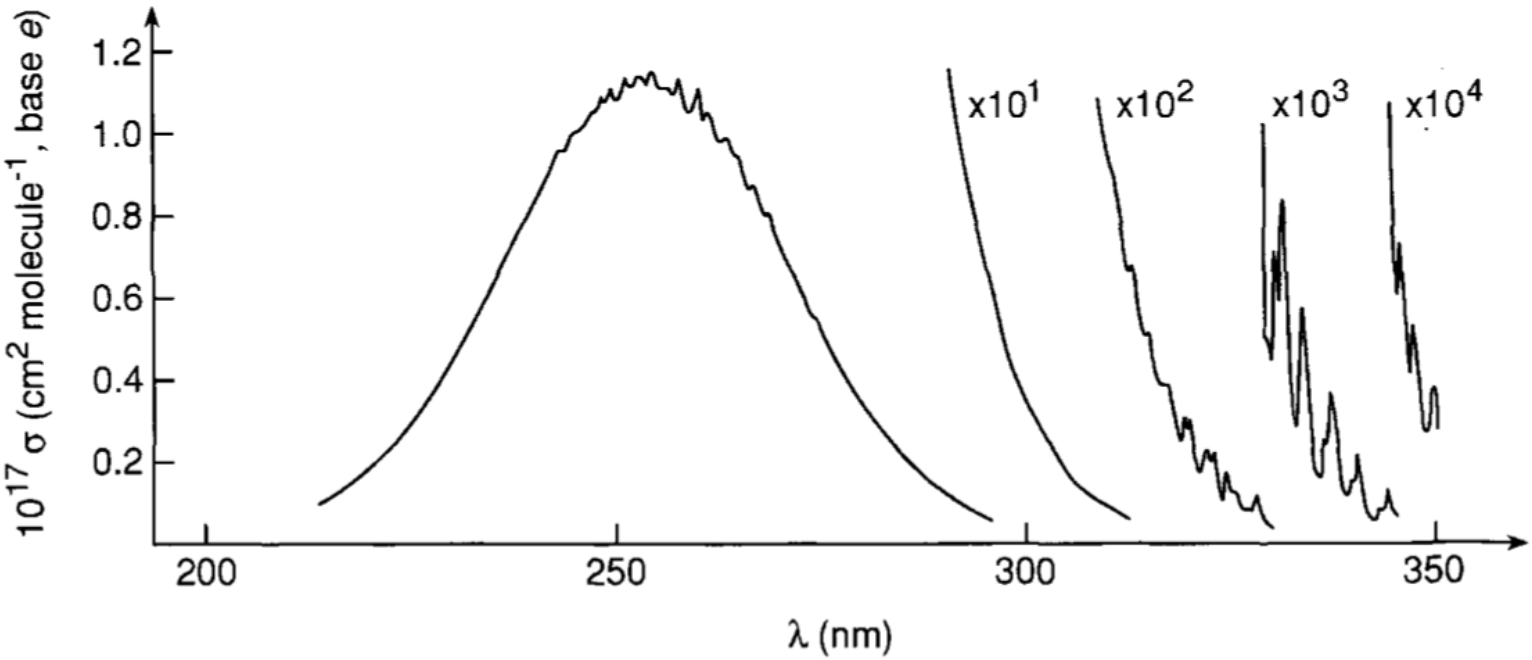
- 50 km: $\lambda > 185$ nm
- Strongly absorbed near 250 nm
- 200–210 nm penetrates more deeply
- 0 km: $\lambda > 295$ nm

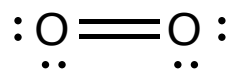
At what wavelengths does dioxygen, O_2, attenuate light in the atmosphere?

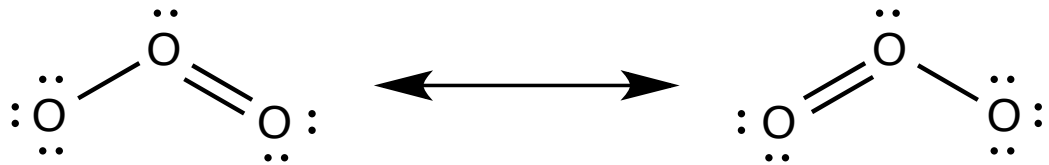


- note that y-axis is logarithmic in both plots
- absorbs strongly 130–170 nm
- absorbs weekly out to 205 nm
- absorption in Schumann-Runge bands is important in stratosphere

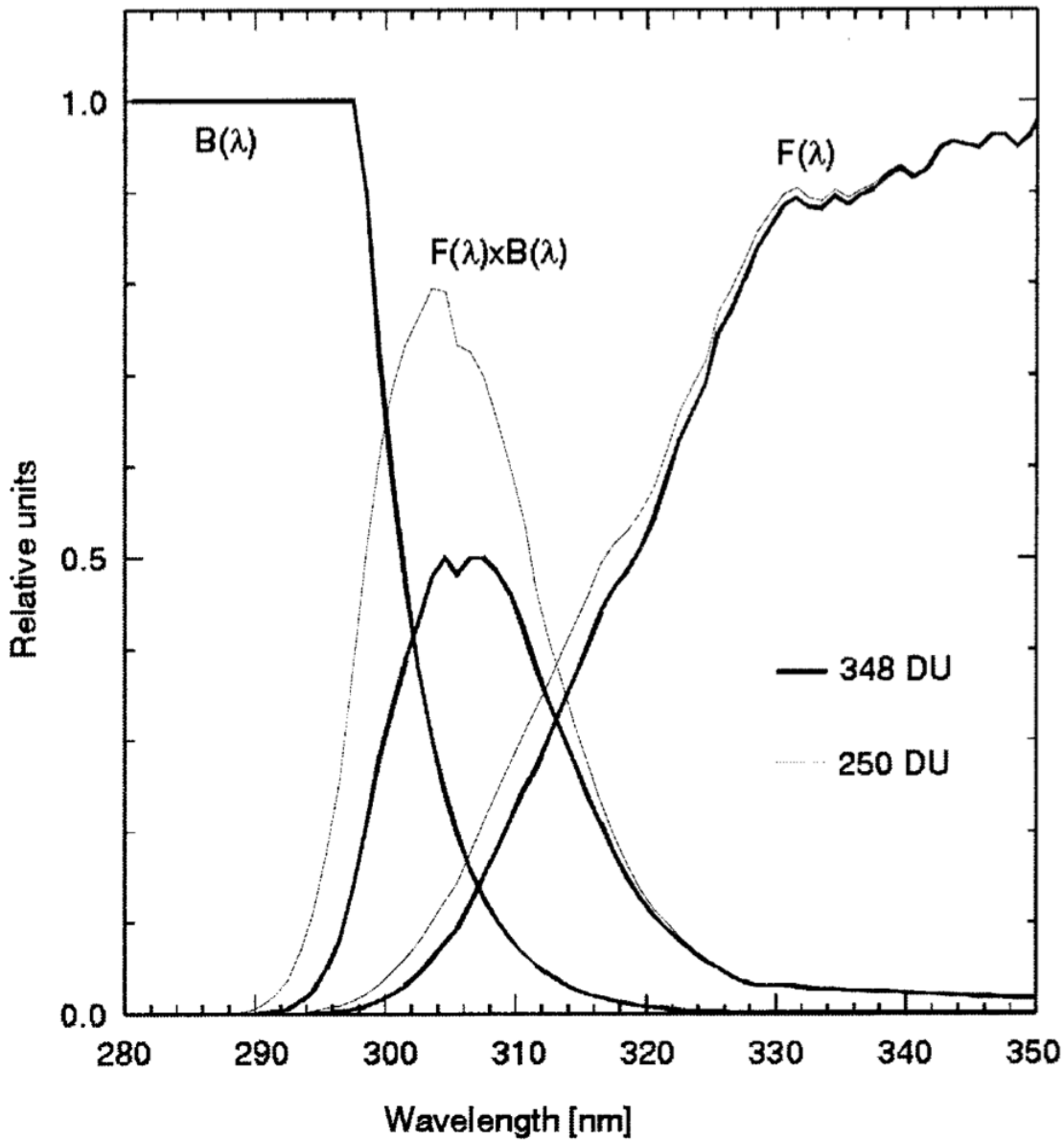
How about absorption by ozone, O_3? Why is it different than absorption by O_2? What causes the stratospheric 'spectral window?'



Dioxygen bonding 

Ozone bonding 

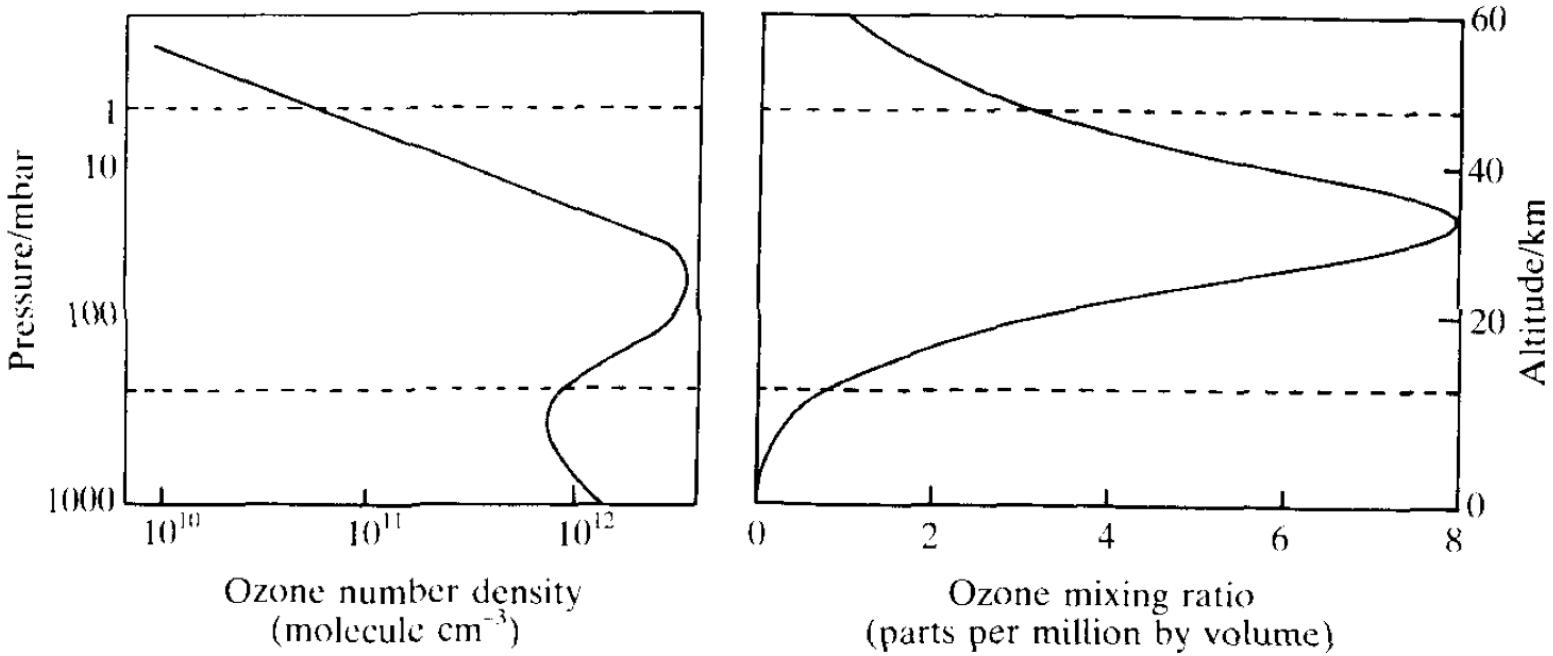
So it filters out some uv light. Is that a big deal?



- $B(\lambda)$ is the 'biological damage function' of light on DNA
- $F(\lambda)$ is the predicted light intensity at two O_3 levels
- Product $B(\lambda)F(\lambda)$ shows effect of depletion

Lecture Question

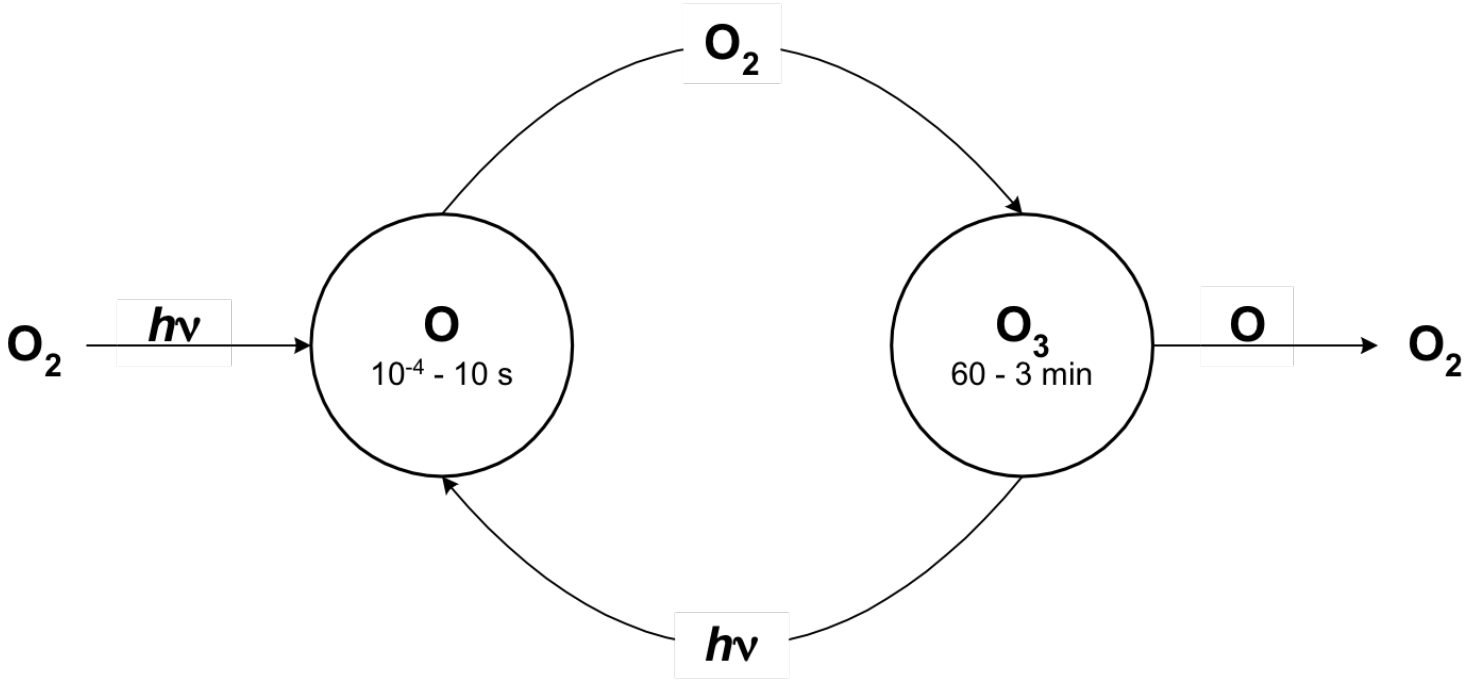
Where is the ozone layer and how concentrated is it?



- left plot is (log) absolute conc, right is relative conc
- absolute more important for most purposes, max 25–30 km
- relative: O_3 is 1–8 ppm, max at 35 km

Lecture Question

How is the stratospheric ozone layer formed?



Initiation: $O_2 \xrightarrow{h\nu} 2\,O$ $(\lambda \leq 242\,\text{nm})$

Cycling: $O + O_2 \longrightarrow O_3 + \text{heat}$

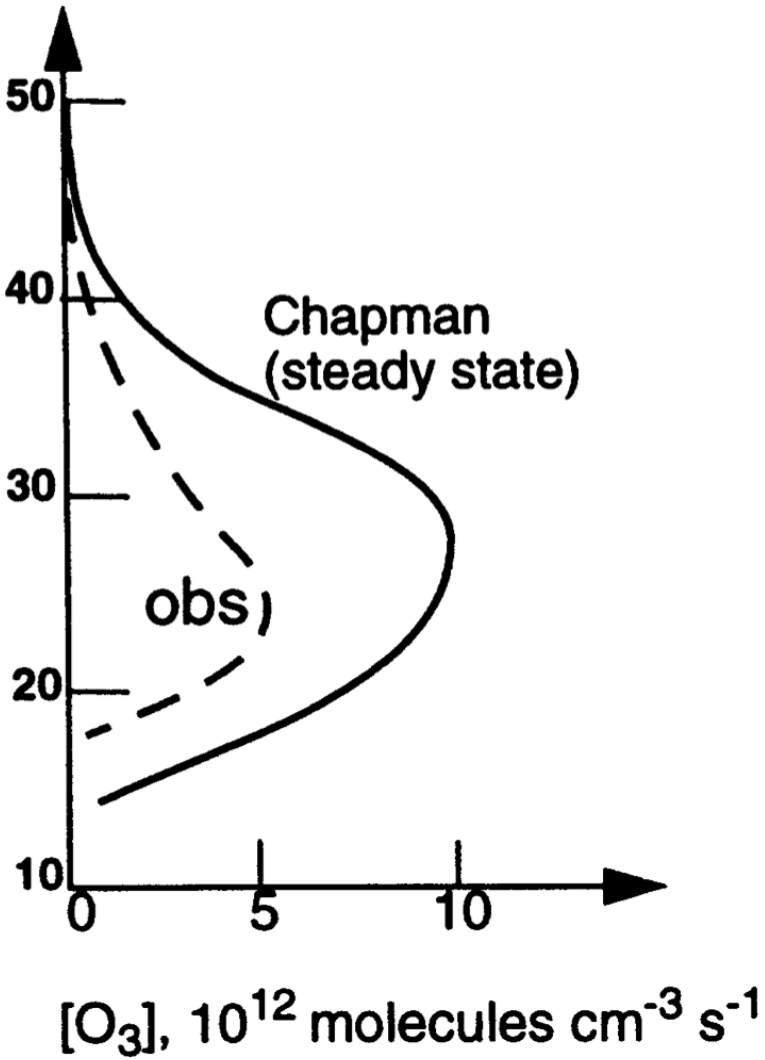
Cycling: $O_3 \xrightarrow{h\nu} O_2 + O$ $(\lambda \leq 340\,\text{nm})$

Termination: $O_3 + O \longrightarrow 2\,O_2$

How does the Chapman cycle predict a stratospheric ozone layer as well as the stratospheric thermal inversion?

- Rate of heating is det'd by rate of O_x cycling
  - Heat is supplied by O_3 photodissociation followed by $O + O_3$
  - Light is converted to heat
  - Controlled by rate of O_3 photodissociation. Upper stratosphere: 20 cycles/hr, lower stratosphere 1 cycle/hr.
- Conc of ozone (O_x) det'd largely by the source: rate of O_2 photodissociation
  - Depends on intensity of light 130–205 nm and absolute conc of O_2
  - Mesosphere: lots of light but air is v thin
  - Troposphere: lots of O_2 but no UV light below 295 nm

Is the Chapman cycle correct? How could we evaluate it 'quantitatively' (and what does that mean)?



- Qualitative agreement is not enough
- Quantitative: must measure/predict reaction rates
- Off by factor of 2–4, depending on altitude

What's wrong with the Chapman model and how can it be fixed?

- Related: what does the term **steady-state ozone** mean (in the previous figure)?
- O_x source too strong or sink too weak?

What are the mechanisms that Chapman missed to destroy ozone?

- **Missing sink(s): catalytic destruction of O_x**
- Why is it important that the destruction process be catalytic?

What are the catalytic species that deplete the ozone layer?

- Stratospheric NO_x
- Stratospheric HO_x
- Stratospheric ClO_x and BrO_x

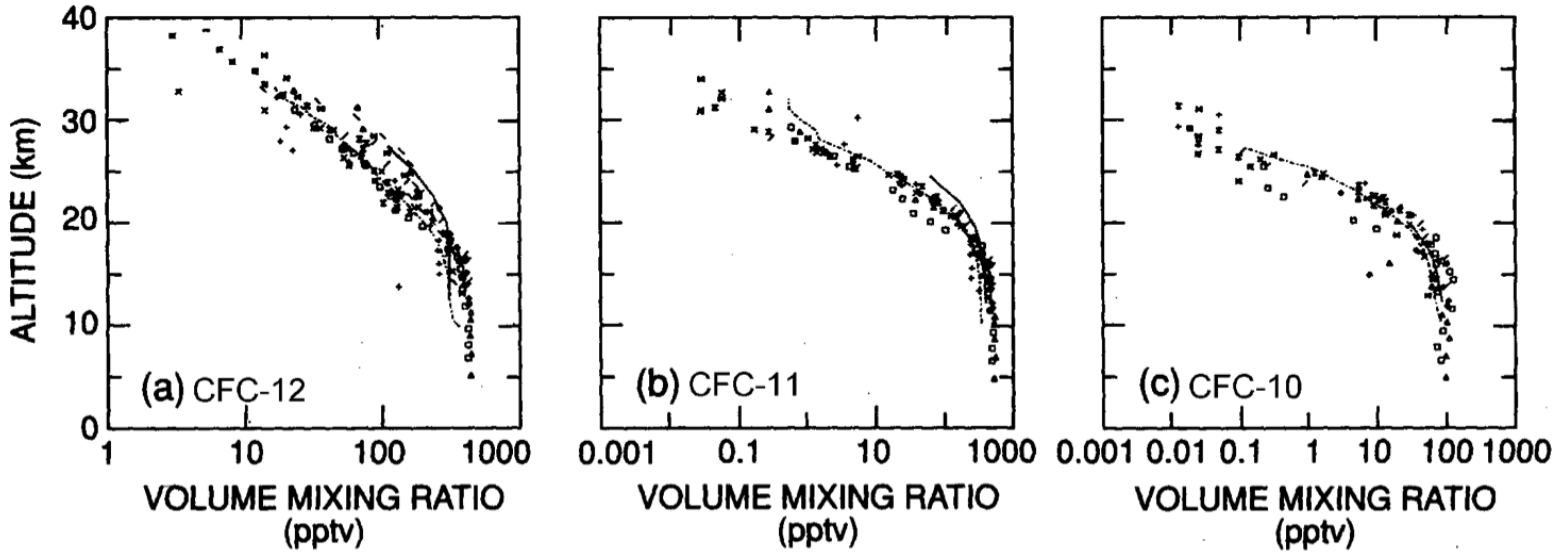
Lecture Question

What are CFCs, and what are they used for?

- CFCs are chlorofluorocarbons: small molecules that contain Cl, F and C atoms.
- Usually are only 1–2 carbon atoms
- Sometimes called Freons (trade name for DuPont)
- CFCs referred to by a number, most common are: CFC-11, CFC-12, CFC-113
- HCFCs are CFCs that contain hydrogen.

  This makes them more reactive to the OH radical, decreasing their tropospheric lifetime. That means that, on a pound-per-pound basis, HCFCs ('soft CFCs') destroy less stratospheric ozone than CFCs ('hard CFCs') because a smaller fraction of HCFCs reach the stratosphere.

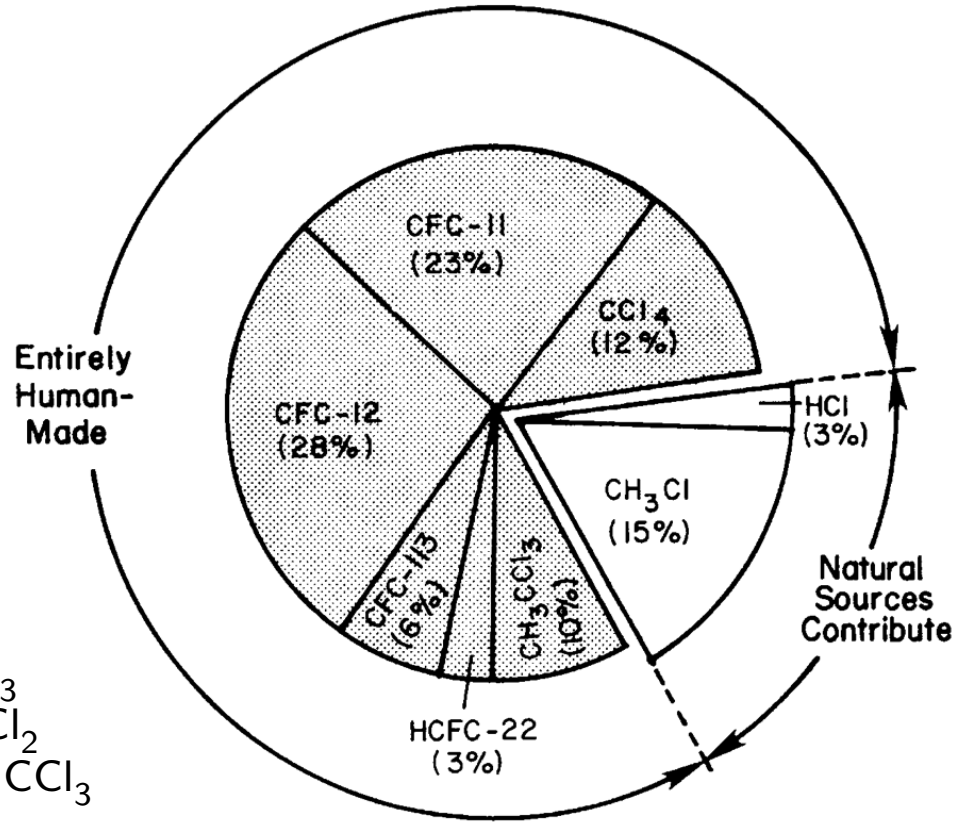
What do the vertical concentration profiles of CFCs suggest about their fate in the atmosphere?



- VMR is constant for the first 15 km or so (ie, the troposphere). What does this mean?
- Rate of removal of CFCs from the troposphere is slow:
  - No photodissociation *in troposphere*
  - These CFCs do not react with OH
  - CFCs not water soluble
- Once in the stratosphere, rate of removal is faster than rate of vertical mixing. Why?

What are the *tropospheric* sources of *stratospheric* chlorine?

Primary Sources of Chlorine Entering the Stratosphere in the Early 1990s



CFC-11: $CFCl_3$
CFC-12: CF_2Cl_2
CFC-113: CF_3CCl_3

HCFC-22: CHF_2Cl

- More than 80% of stratospheric Cl is anthropogenic
- HCl is very water soluble

Lecture Question

Let's put it all together: how do CFCs deplete the stratospheric ozone layer? Explain in detail.

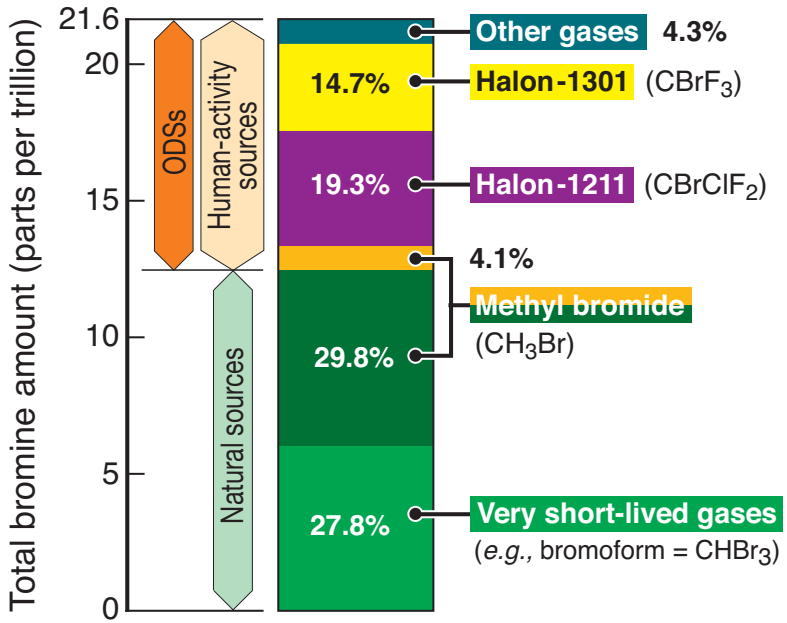
1. CFC discharged to the troposphere
2. After 5–10 yr, CFCs enter the stratosphere
3. Soon after entering the stratosphere they photodissociate.

$$\mathrm{CFCl_3} \xrightarrow{h\nu} \mathrm{CFCl_2} + \mathrm{Cl} \qquad (\lambda \leq 225\,\mathrm{nm})$$

4. Cl atoms destroy O_x catalytically

$$\begin{aligned} \mathrm{Cl} + \mathrm{O_3} &\longrightarrow \mathrm{ClO} + \mathrm{O_2} \\ \mathrm{ClO} + \mathrm{O} &\longrightarrow \mathrm{Cl} + \mathrm{O_2} \\ \text{net: } \mathrm{O_3} + \mathrm{O} &\longrightarrow 2\,\mathrm{O_2} \end{aligned}$$

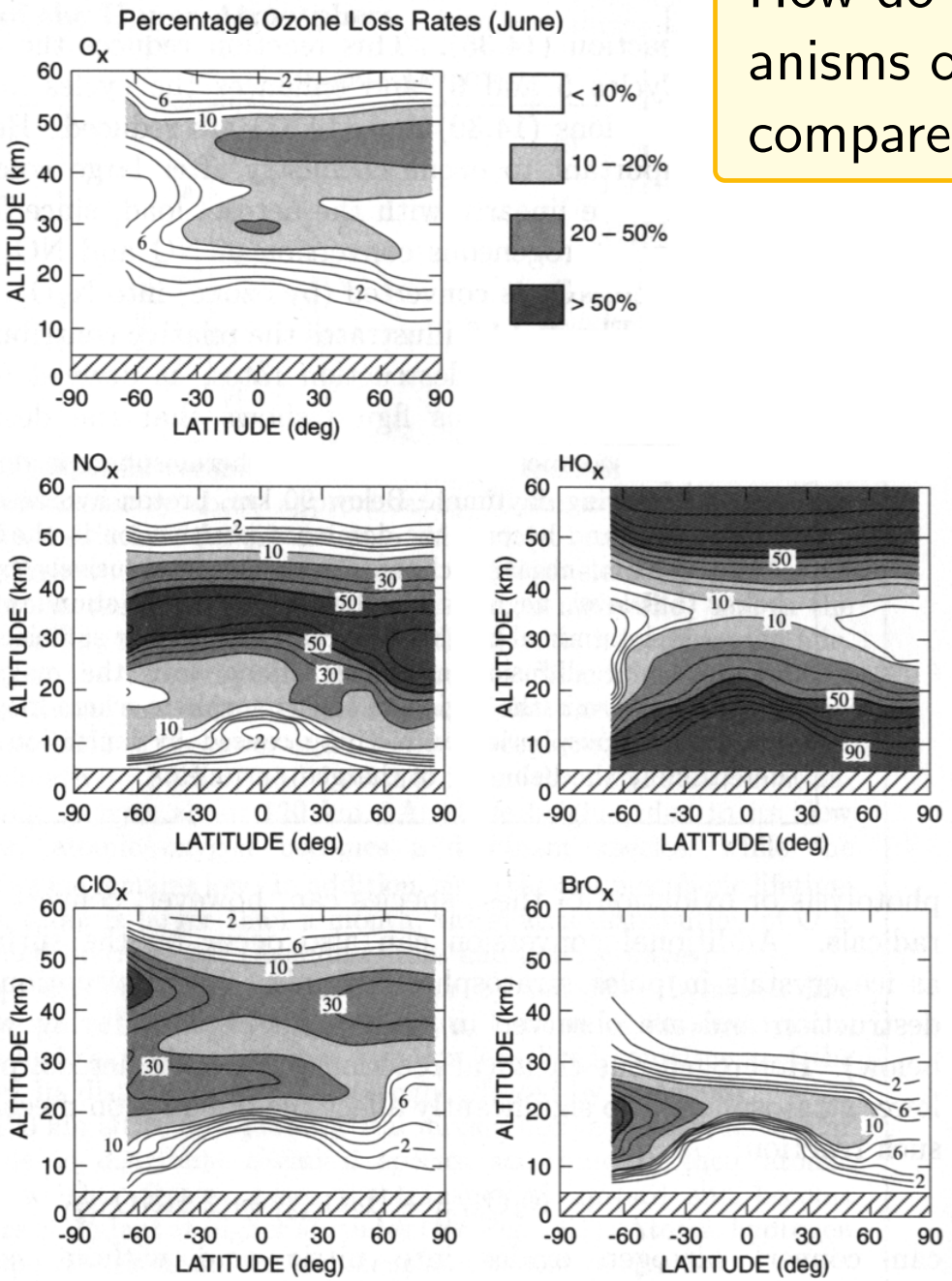
What are the sources of stratospheric NO_x , HO_x , and BrO_x? How much is due to human activity?



- Stratospheric BrO_x shown in figure; 40–45% increase in BrO_x due to human activities.
- Stratospheric NO_x

  Source is tropospheric N_2O. 15–20% increase due to human activities. Use of nitrogenous fertilizers and fossil fuel combustion are the main causes.
- Stratospheric HO_x

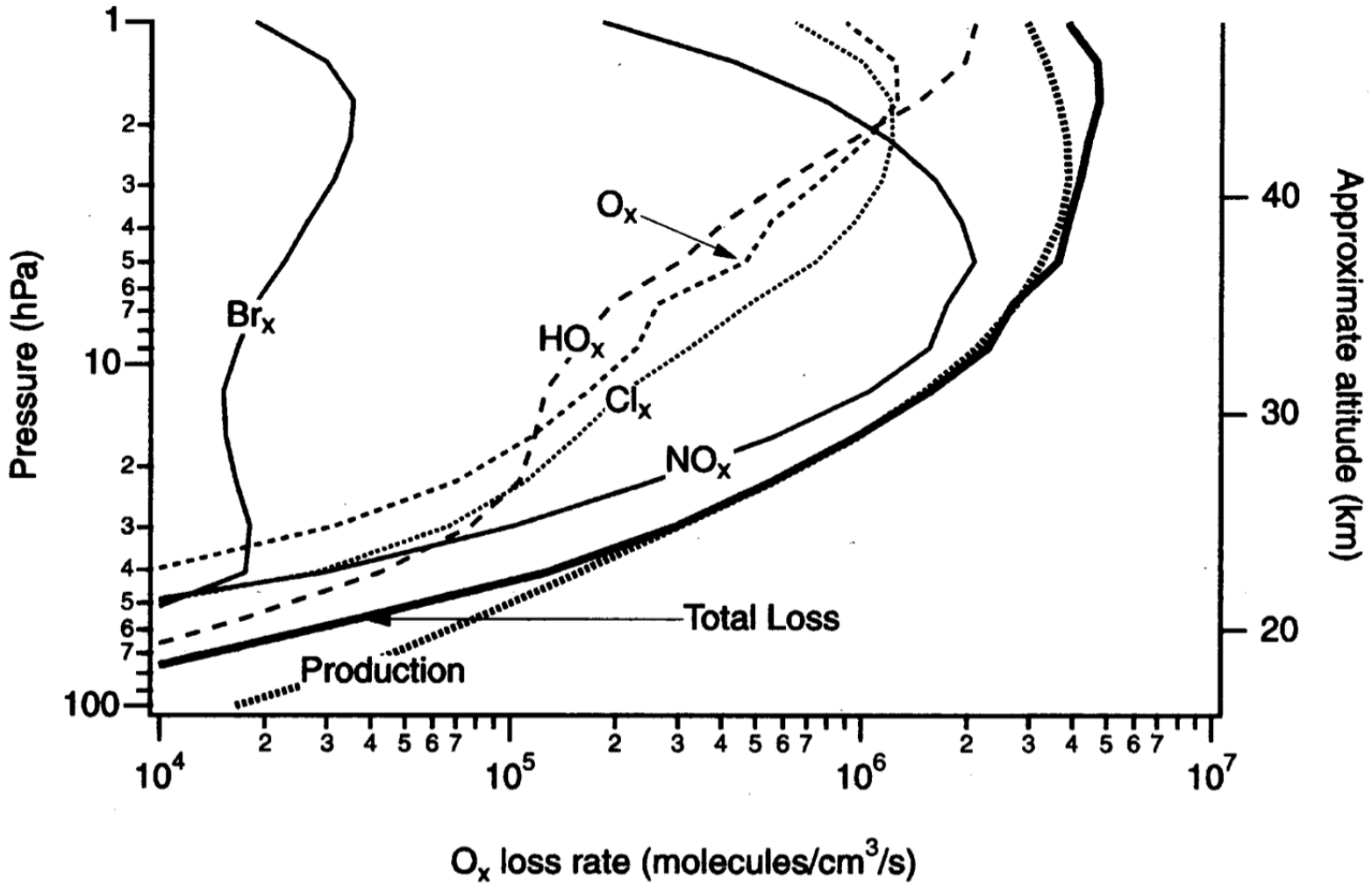
  Sources: tropospheric CH_4, H_2, H_2O. 150% increase in CH_4 due to a variety of human activities.



How do the different mechanisms of ozone depletion compare?

- O_x is Chapman: $O_3 + O \longrightarrow 2\,O_2$. Never the dominant mechanism.
- NO_x is dominant in middle stratosphere, HO_x in lower and upper.
- ClO_x is significant but never dominant, BrO_x is even less.

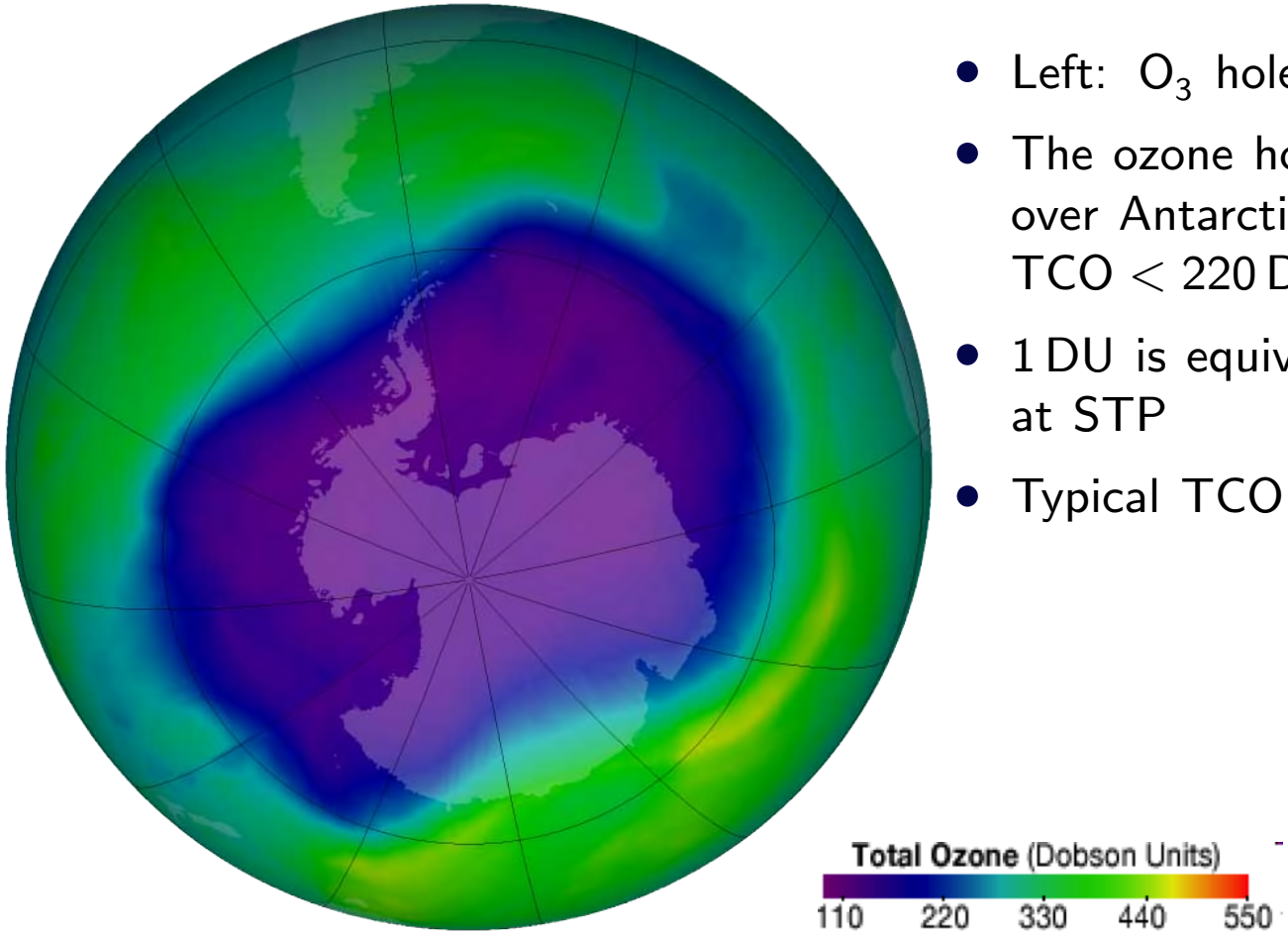
How do the different mechanisms of ozone depletion compare?



Above are absolute rates. Approx 60% of all loss due to NO_x , 20% due to Chapman, 20% due to all others.

Lecture Question

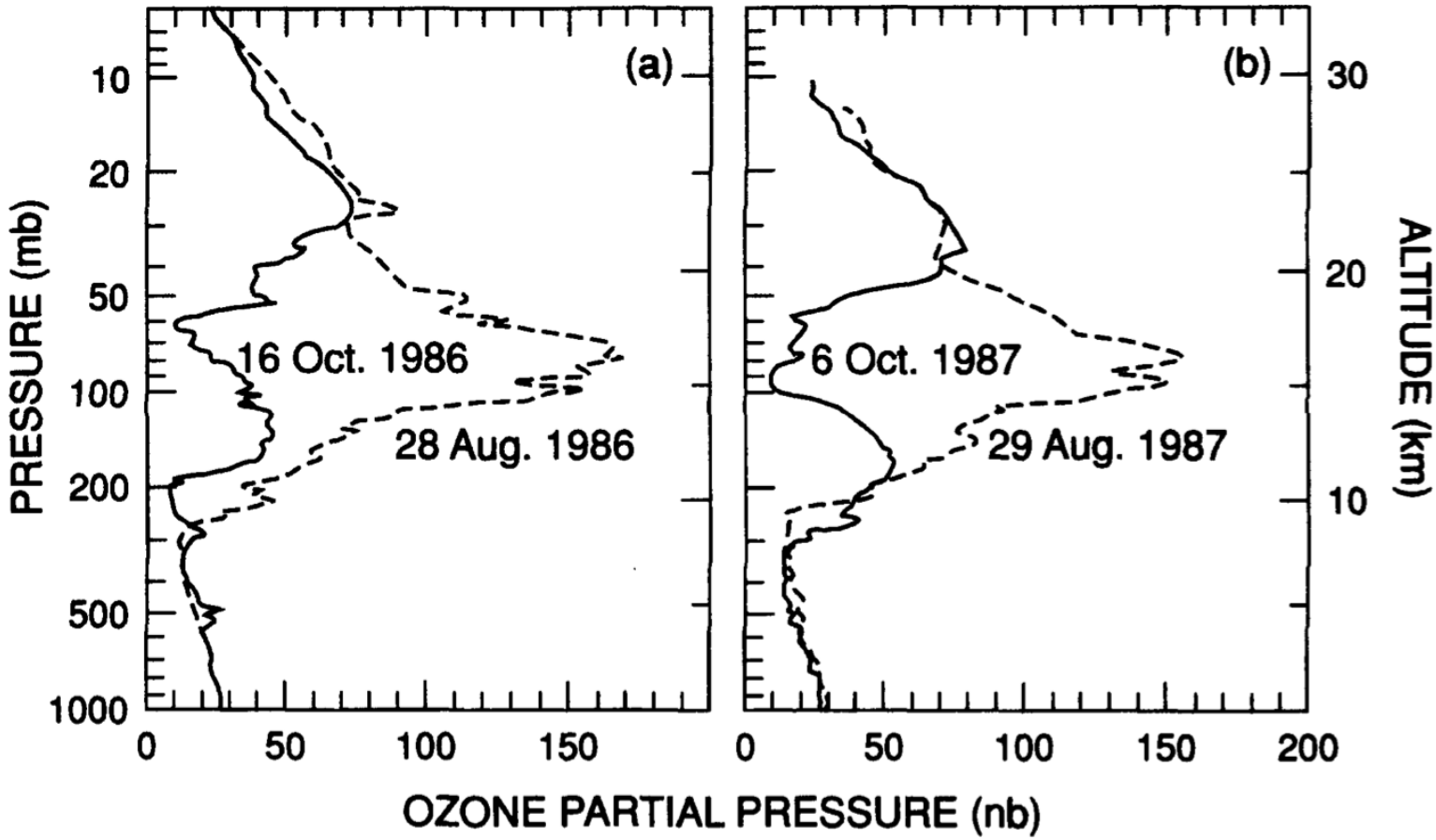
What is the ozone hole and where does it form?



- Left: O_3 hole for Sept 2006
- The ozone hole is the region over Antarctica with TCO < 220 DU.
- 1 DU is equivalent to 10 µm at STP
- Typical TCO is 300 DU

Lecture Question

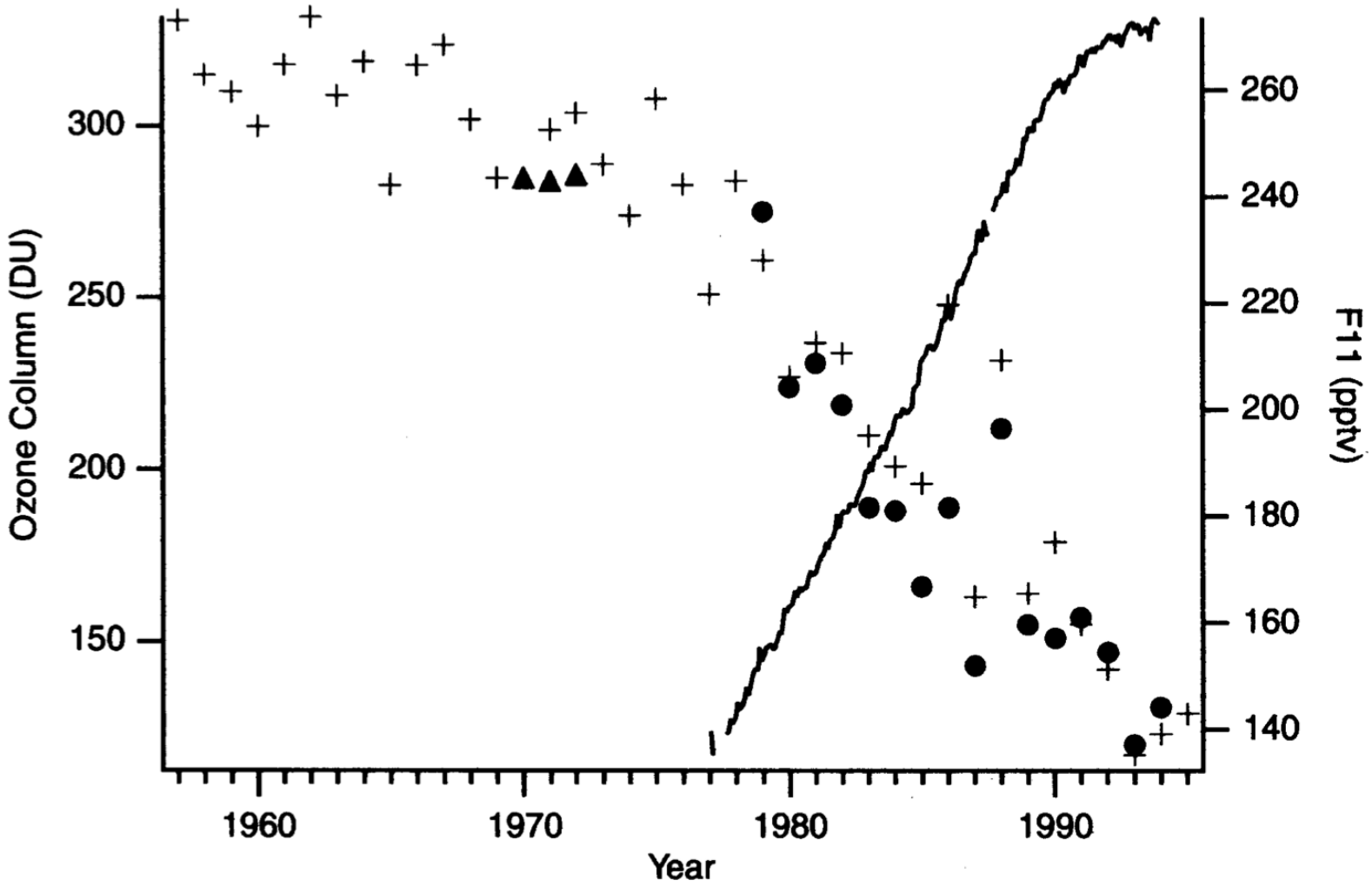
Is the ozone hole a permanent feature of the Antarctic? If not, when does it form?



The ozone hole appears soon after the sun rises in the spring (there is no sun in the polar winter).

Lecture Question

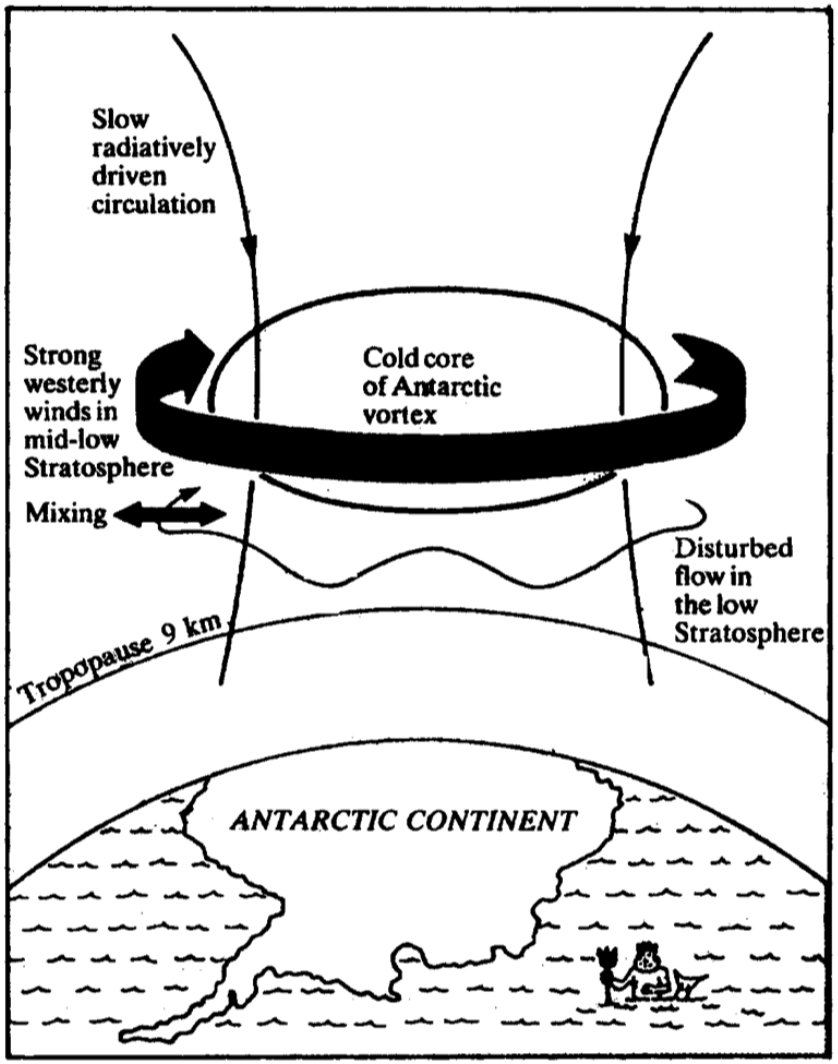
When was the ozone hole first detected? By whom?



Crosses are BAS measurements (Oct averages), triangles and circles are NASA. BAS reported findings in 1985, later verified by NASA.

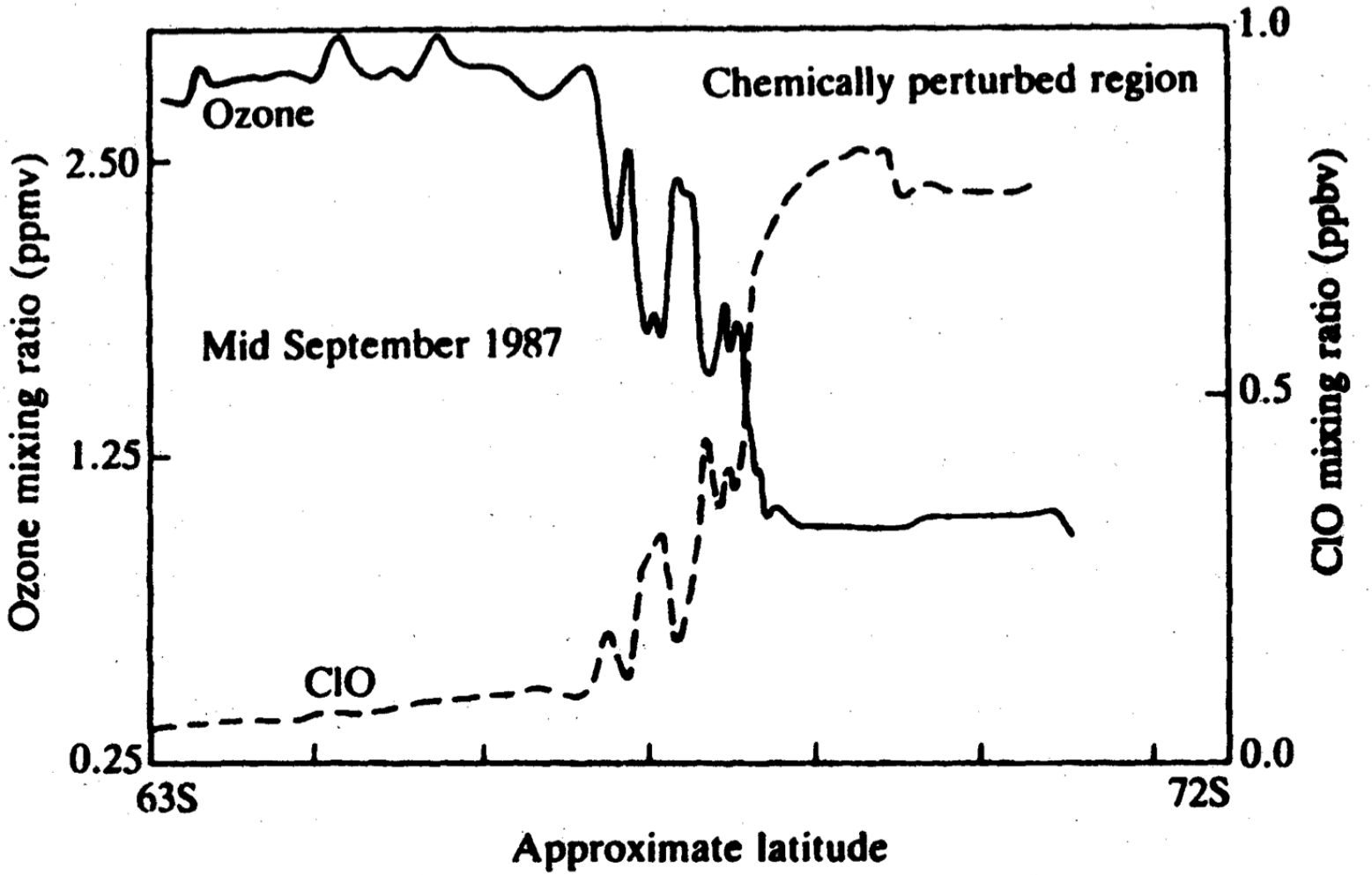
Lecture Question

Why doesn't the ozone hole form elsewhere? (What about arctic holes?)



- Polar vortex develops during the winter
- Atmosphere is effectively isolated from the rest of the southern hemisphere
- Interior temperatures plummet during long winter night: large area is below 200 K, and it can get as cold as 180 K
- Arctic vortex is not as strong or as cold as the one that forms in the Antarctic

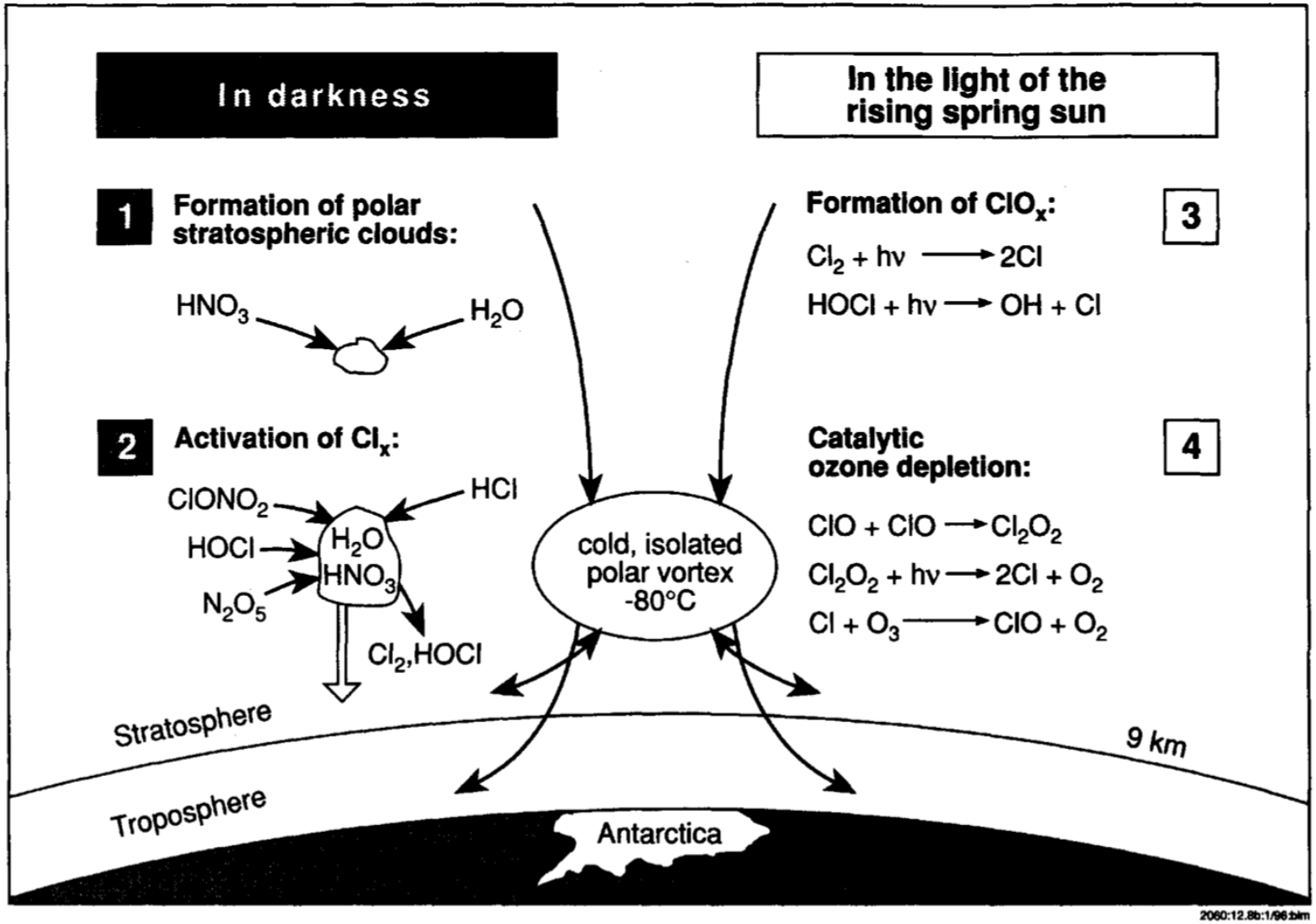
Do we know that stratospheric chlorine from CFCs is responsible for the ozone hole?



The above 'smoking gun' measurement was part of a conclusive body of research conducted in 1985–1989 showing ozone holes were due to stratospheric Cl and Br.

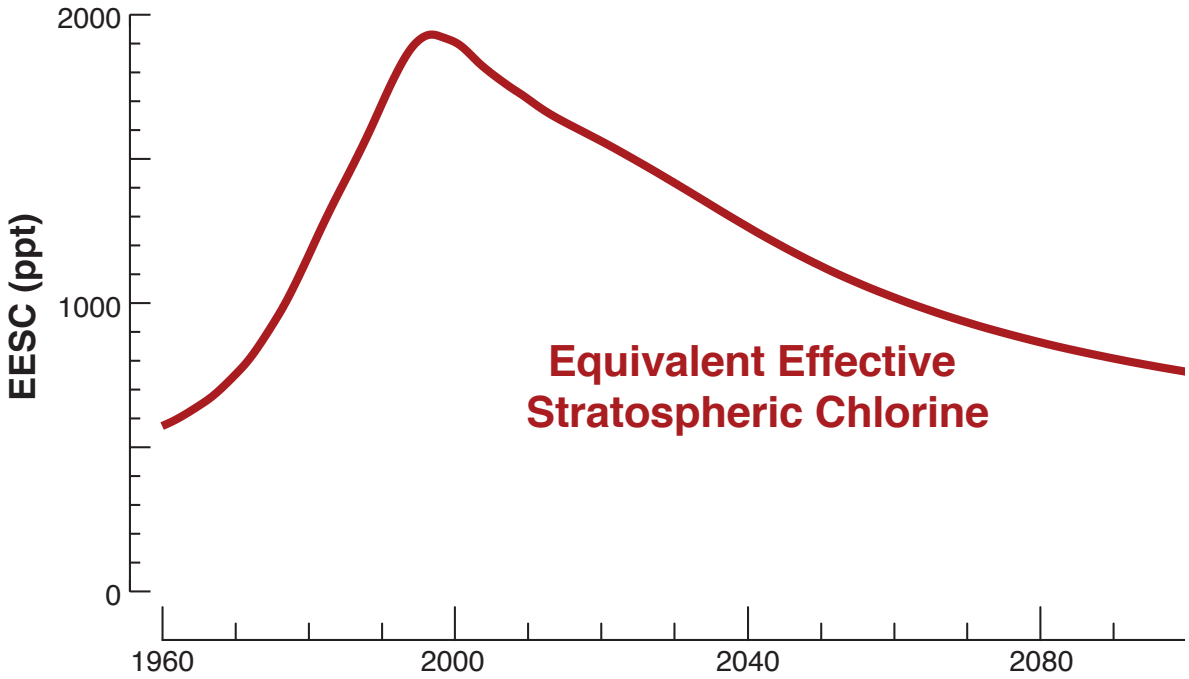
Lecture Question

So how does the ozone hole form?



Lecture Question

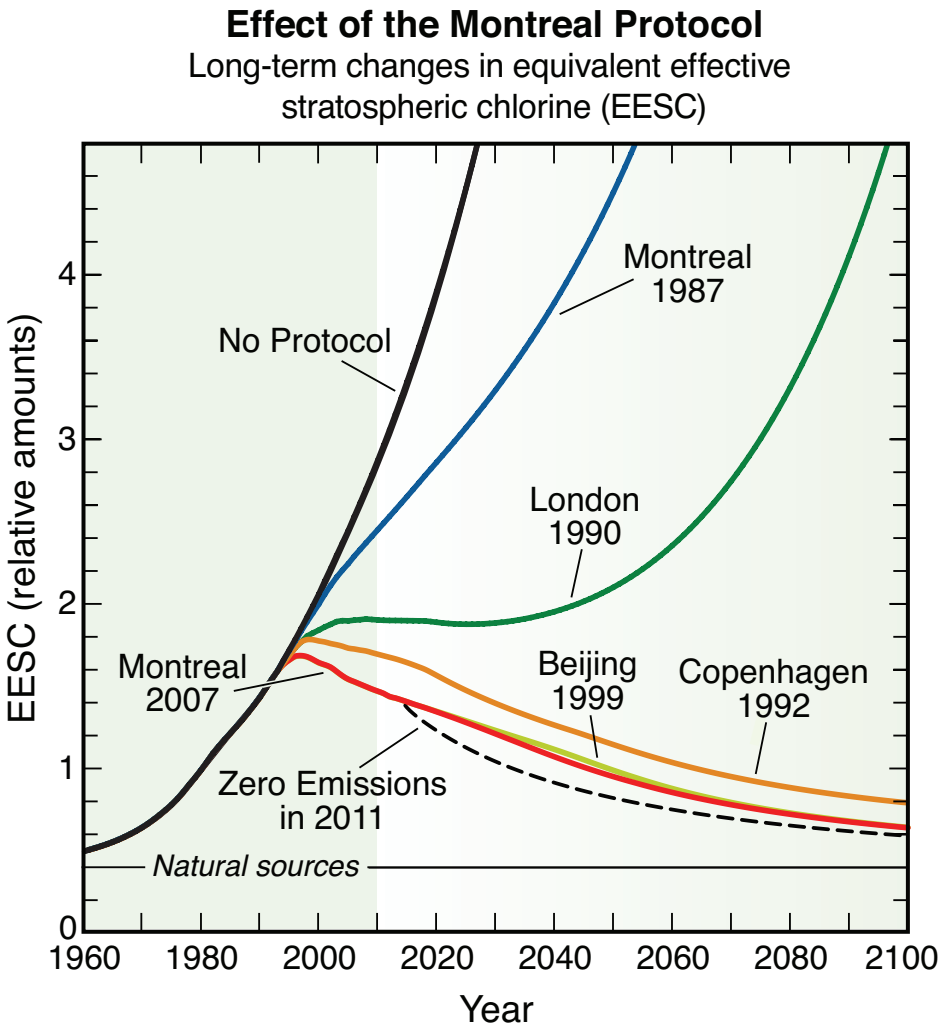
What treaty was signed to control ozone depletion, and when did it go into effect? How effective has it been in controlling stratospheric chlorine levels?



- The Montreal Protocol was signed in 1987 and went into effect in 1989
- Regulated CFCs and HCFCs separately
- Phase-out schedules relaxed for LDCs
- Stratospheric Cl levels have been decreasing since the late 1990s.

Lecture Question

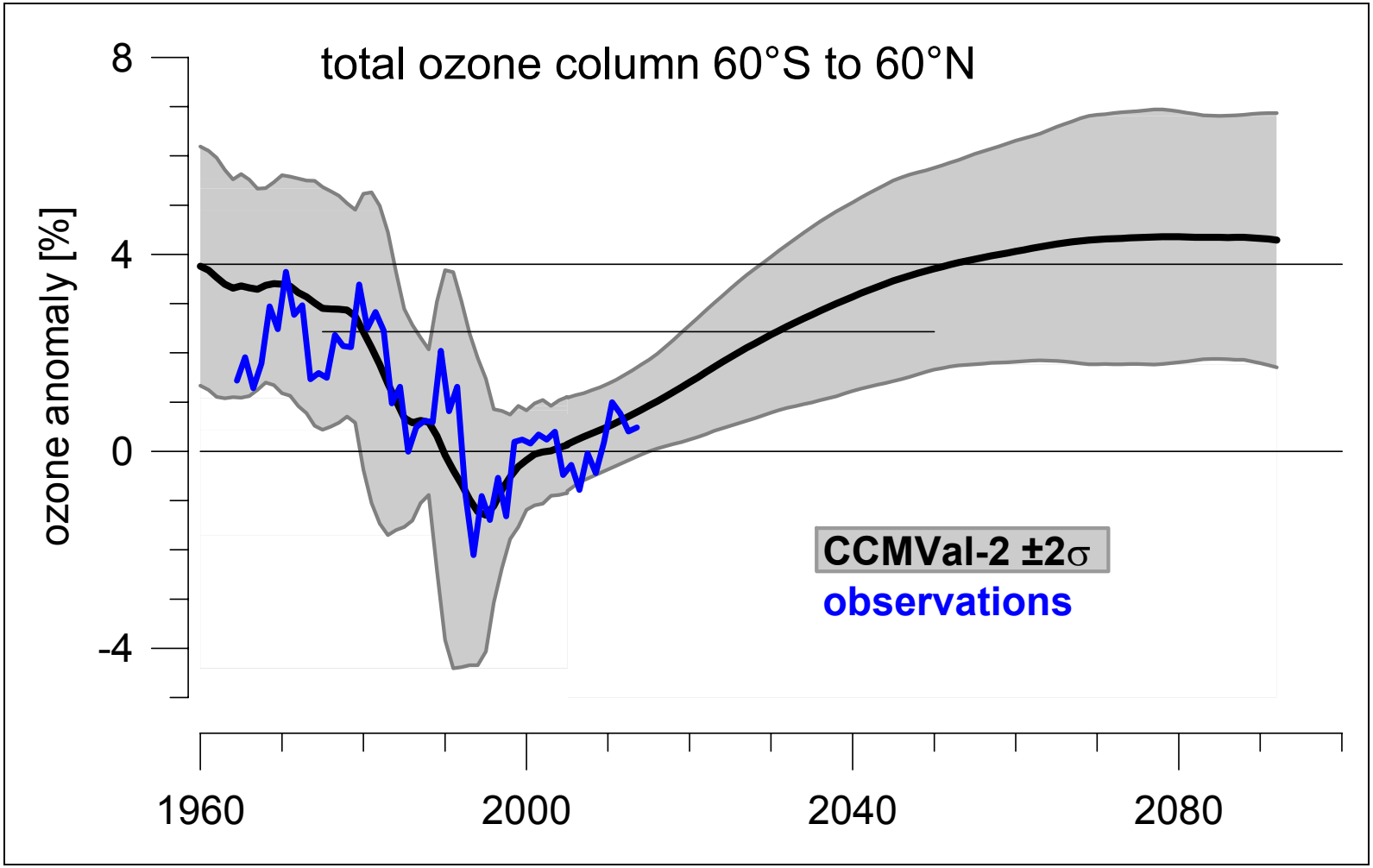
What treaty was signed to control ozone depletion, and when did it go into effect? How effective has it been in controlling stratospheric chlorine levels?



- Montreal Protocol could be revised as new scientific evidence was discovered
- Results/projections of original treaty and of revisions on stratospheric Cl shown in the figure

Lecture Question

How severe has stratospheric ozone depletion been in the mid-latitudes? When is it expected to recover?



Lecture Question

How severe has stratospheric ozone depletion been at the poles? When is it expected to recover?