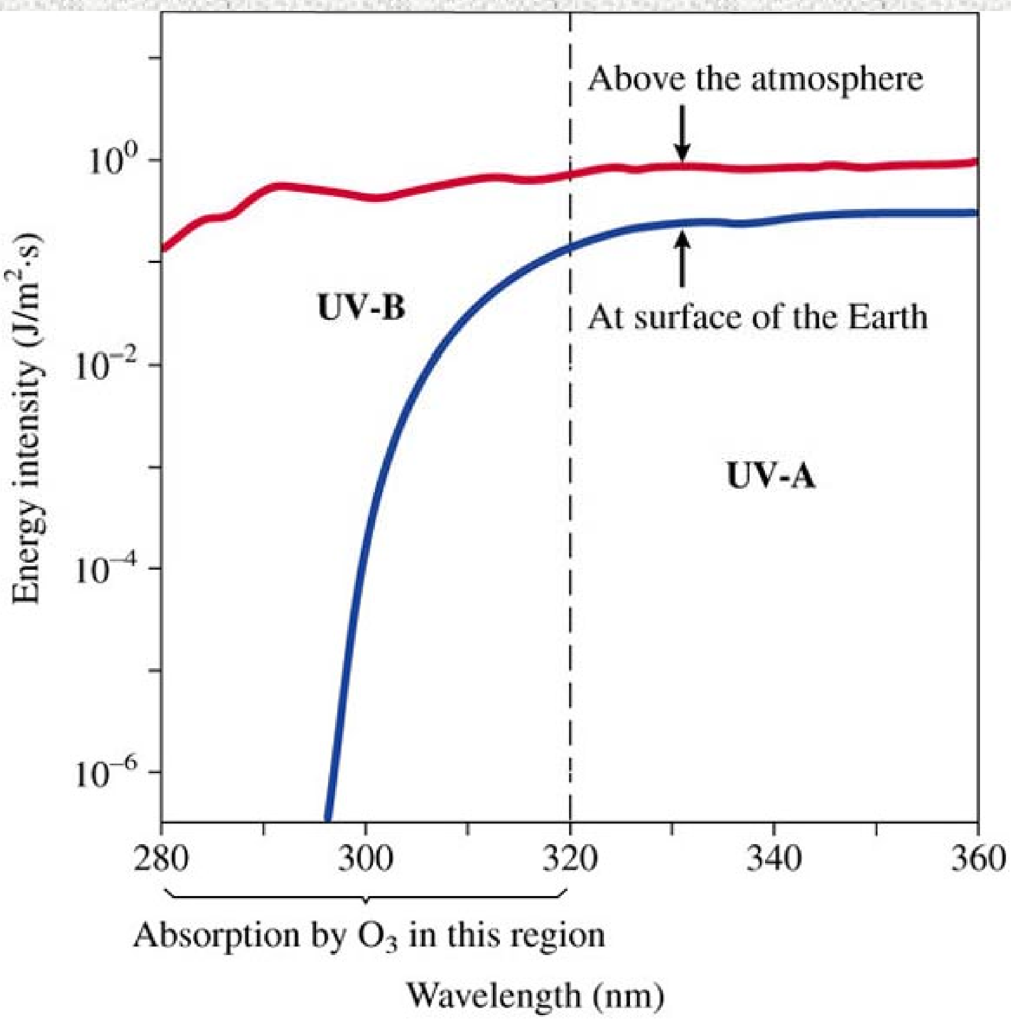
The Ozone Layer:
Formation and Depletion

Outline of Lectures

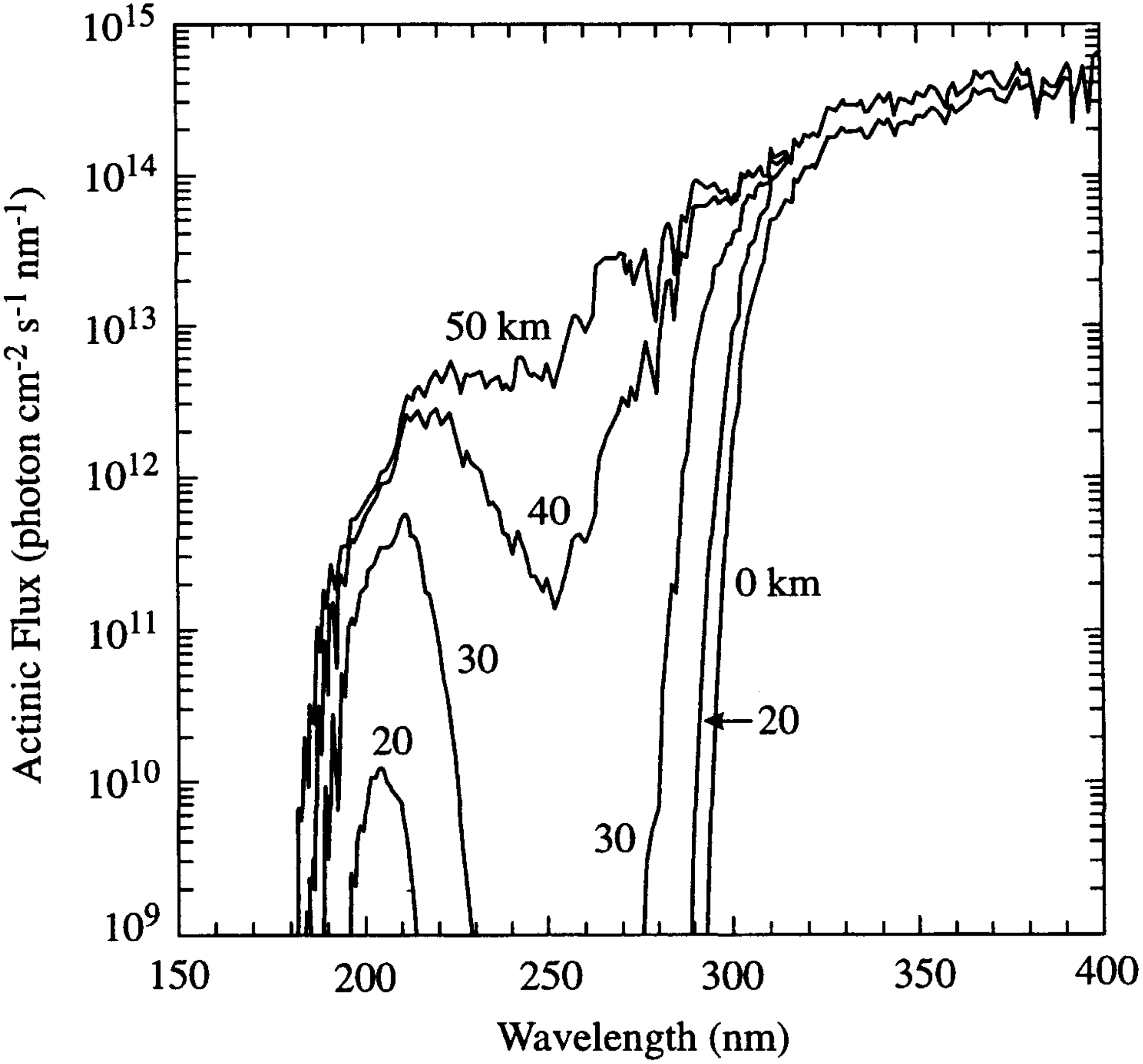
- Introduction
  - Structure and function of the ozone layer
  - Briefly: health effects of ozone depletion
- Formation of the Ozone Layer
  - The Chapman cycle
  - Problems with the Chapman cycle
- Catalytic Destruction of the Ozone Layer
  - General mechanism
  - Sources of catalysts, including CFCs
  - CFC-induced ozone destruction
  - Relative contributions of different catalysts
  - The ozone hole
- Phasing Out CFCs and other ODSs
  - Global trends in stratospheric ozone and ground-level UV light
  - The Montreal Protocol

Ozone Layer: Function

- Question
  - What does the ozone layer do for us?
  - Ozone is the only major atmospheric constituent that absorbs significantly between 210 and 290 nm.
  - Without it life would have remained underwater
  - The ozone layer is a consequence of *oxygen-only chemistry*. It formed once photosynthetic marine organisms (cyanobacteria) began “polluting” the atmosphere with oxygen.

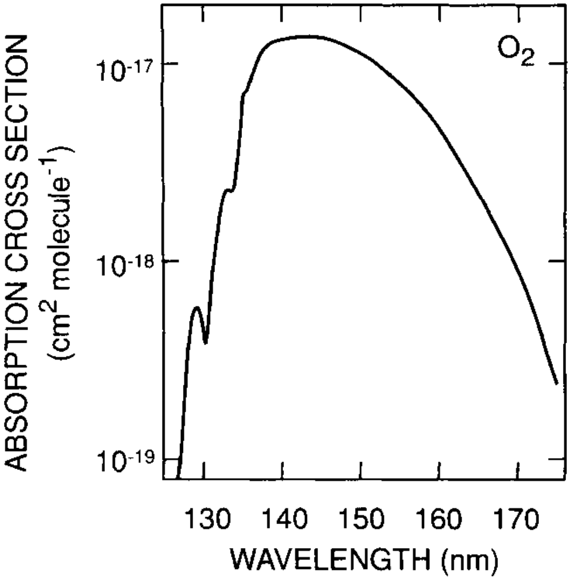


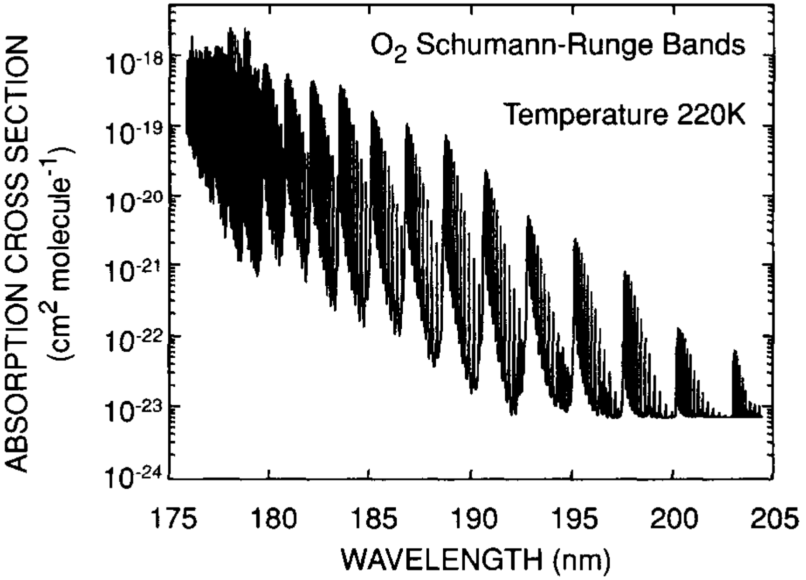
Attenuation of Solar Flux in the Stratosphere

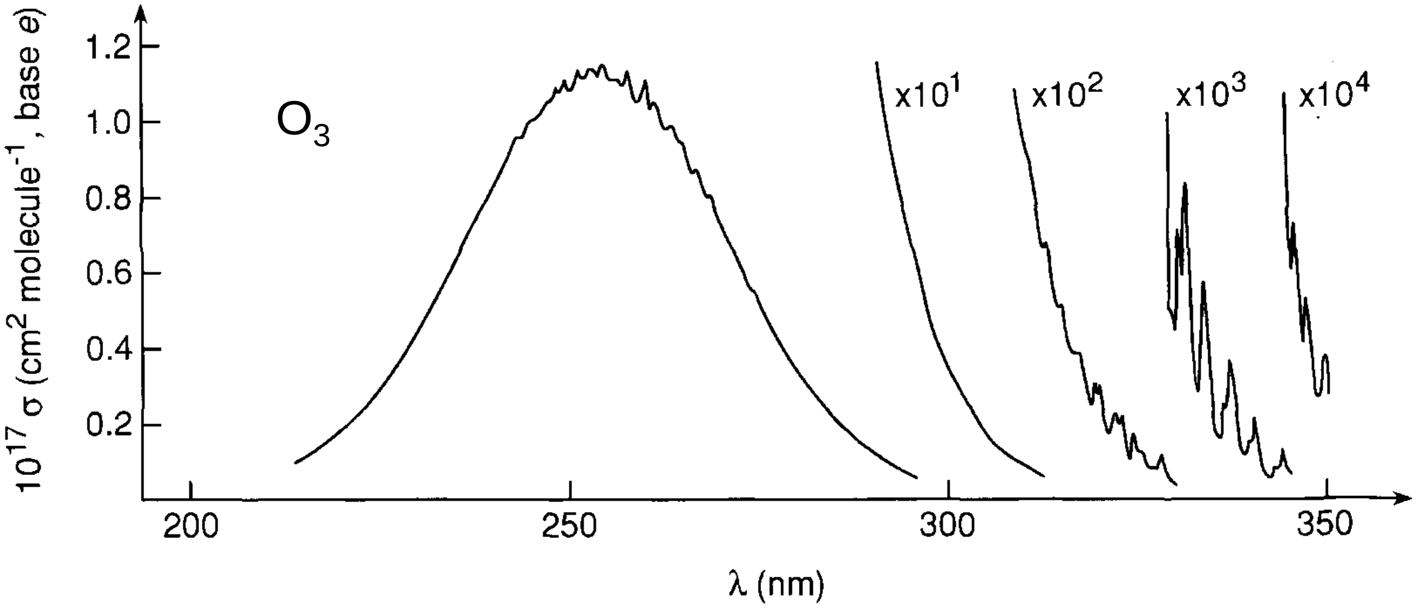


- Ground-level sunlight is limited to λ < 290nm
- Stratosphere filters out light between 180 and 290 nm
- There is a “spectral window” centered at 205nm where uv light penetrates more deeply into the stratosphere.

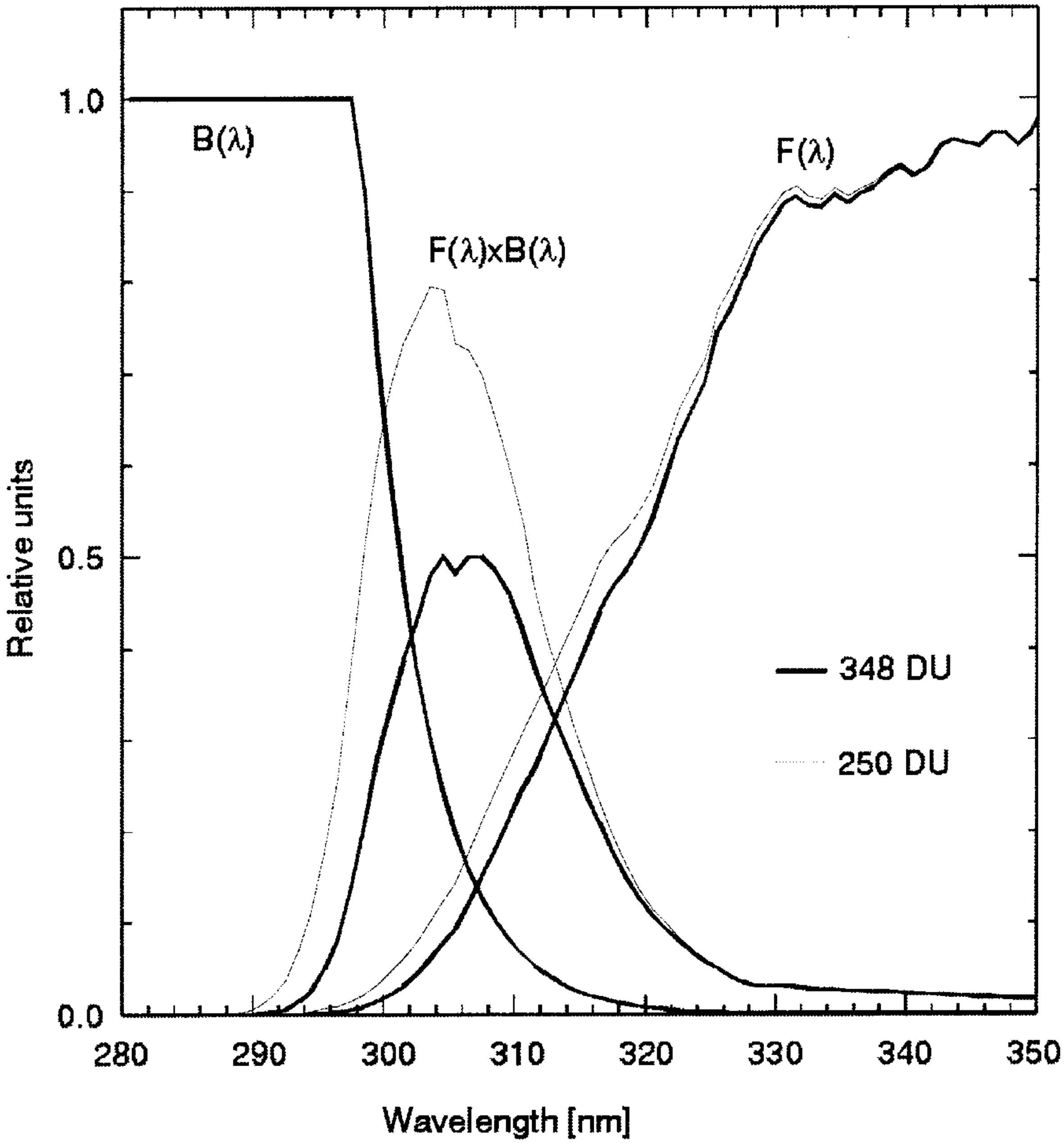
UV Absorption by Dioxygen and Ozone







Health Effects of Ozone Depletion



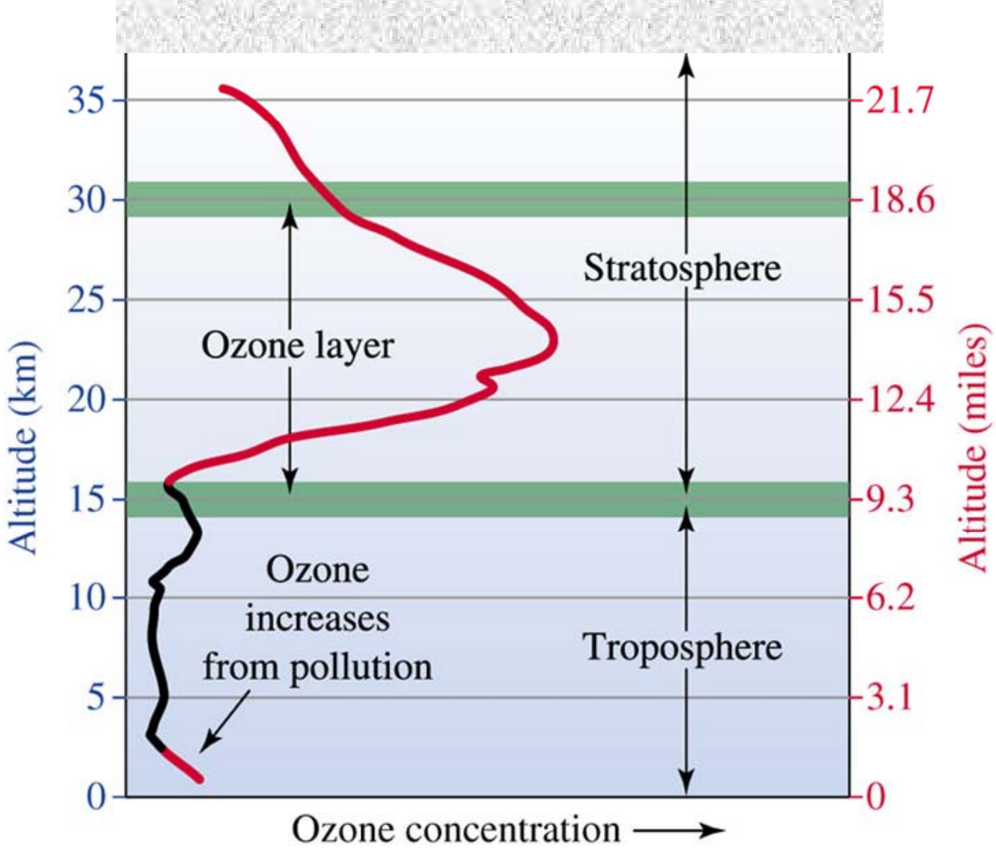
- B(λ) is the biological "damage" function as a function of wavelength

- F(λ) is the light that penetrates to ground level for two different column ozone levels: "normal" and "depleted."

- The product B(λ)F(λ) gives an indication of the additional biological damage potentially caused by ozone depletion

The Ozone Layer

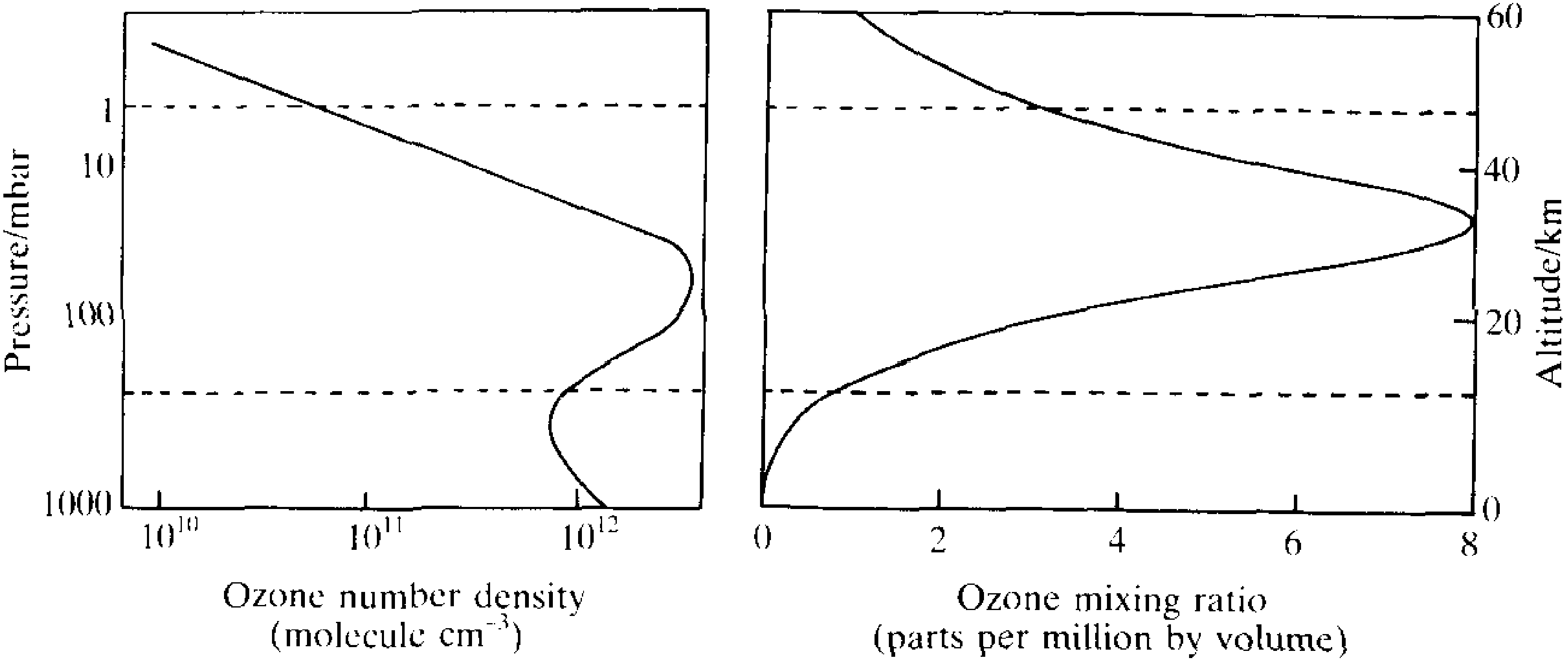
- *Lecture Questions*
  - At what altitudes is the ozone layer located?



- 16 – 35 km (above bkgd level)
- Stratosphere contains about 90% of all atmospheric ozone
- Total column ozone: ~300 DU (1 DU = 0.3 cm thick layer at 1 atm)

  - What is the maximum concentration of ozone in the ozone layer?
    - Maximum of absolute conc about 23 km (up to 10^{13} molecules/mL)
    - Maximum of relative conc about 35 km (up to 10 ppm)

Structure of the Ozone Layer



Observations: (i) O_3 is ***NOT*** the most concentrated gas in the ozone layer (not even close!) (ii) maximum concentration is in the middle stratosphere.

Big question: why does the ozone layer exist in the stratosphere? What processes are responsible for its formation and maintenance?

The Chapman Cycle

- 1930
  - Sydney Chapman proposed a series of reactions to account for the ozone layer: t*he Chapman Cycle*
- *Lecture Question*
  - The *Chapman Cycle* explains how the ozone layer is formed and maintained. Describe this process in some detail.
  - Four chemical reactions
    - *Initiation* O_2 + light → 2O (120 – 210 nm)

    - *Propagation* (cycling)

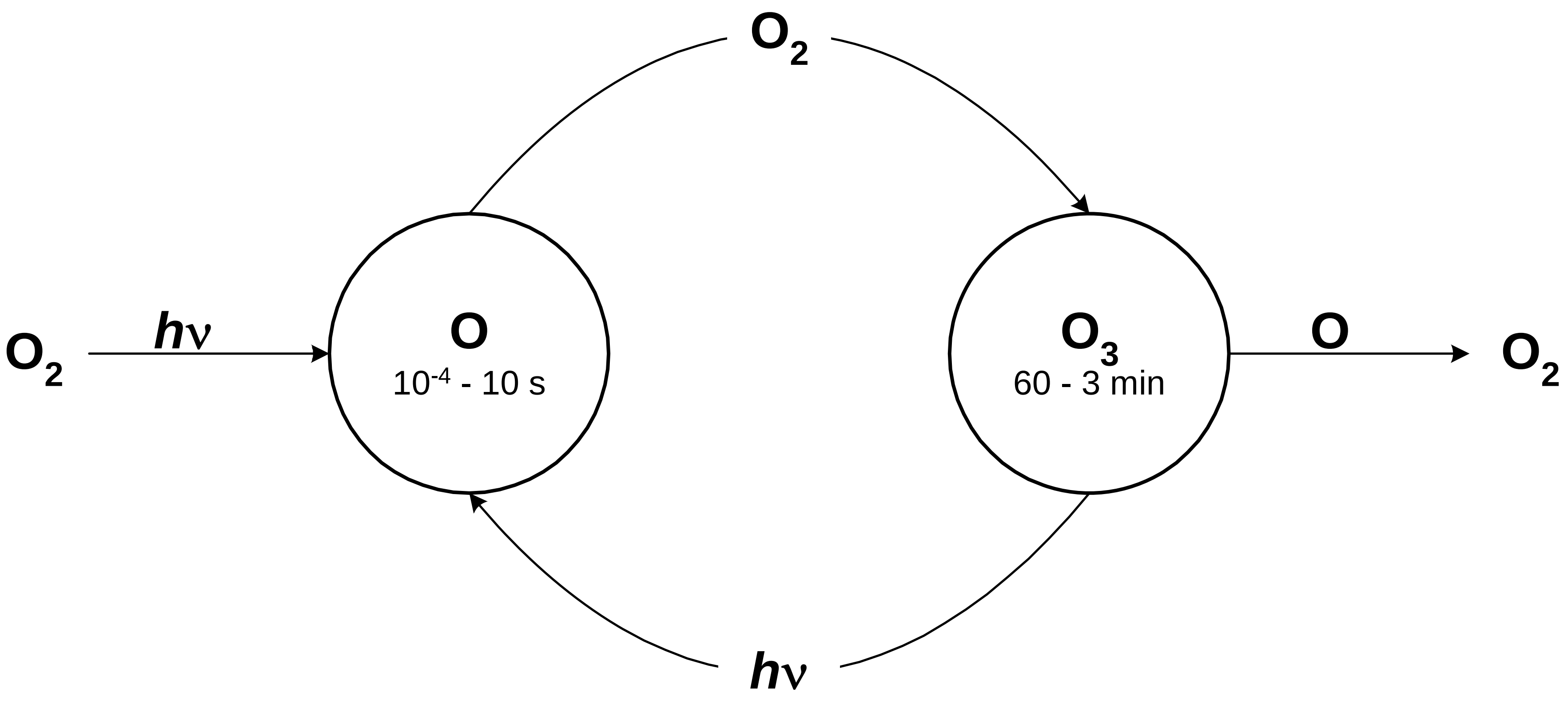
      $O + O_2 + M \rightarrow O_3 + M^*$ (generates heat)

      O_3 + light → O_2 + O (220 – 320 nm)

    - *Termination* $O_3 + O \rightarrow 2O_2$

The Chapman Cycle

Oxygen-only Chemistry



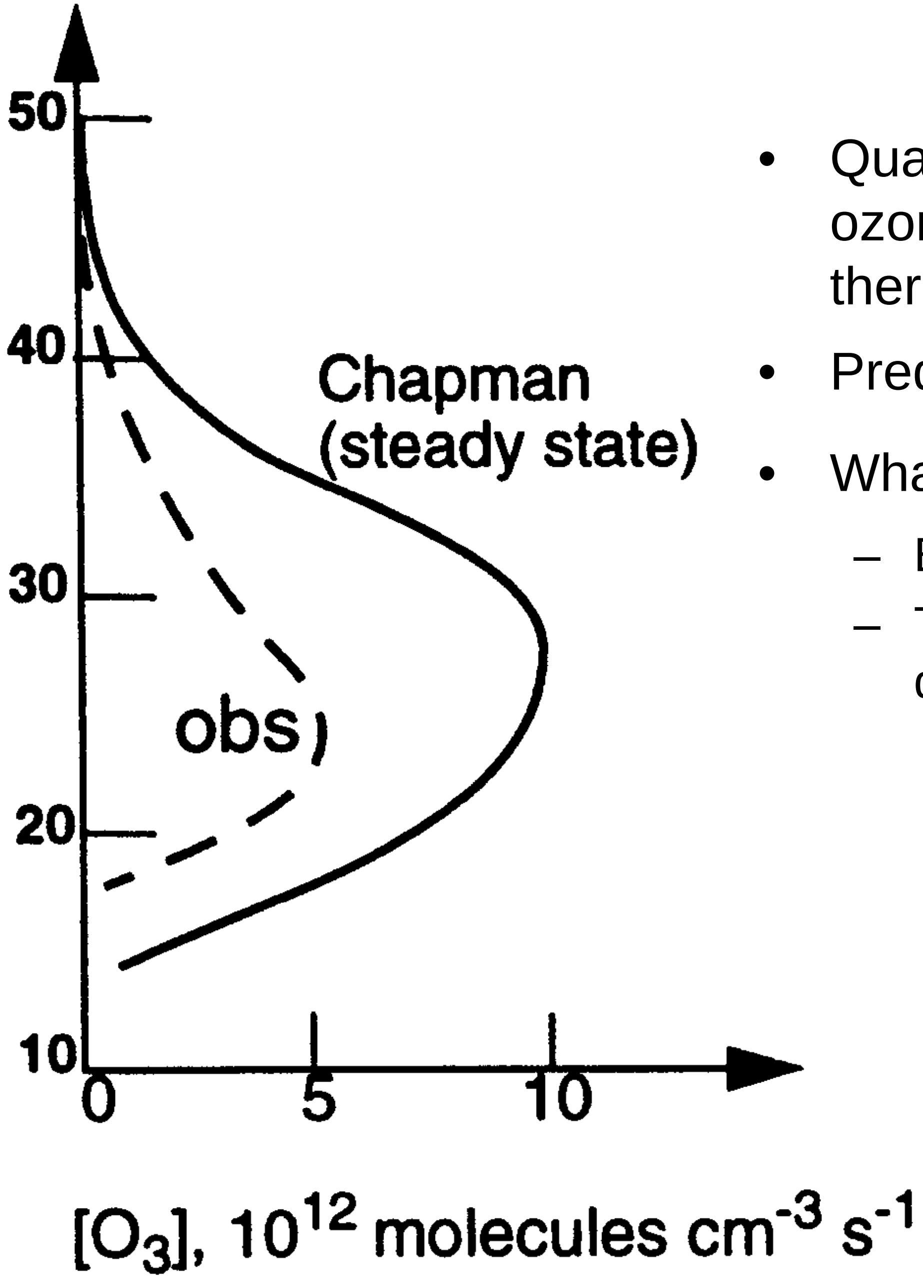
"odd-oxygen" species (O_x) are rapidly interconverted

$O_x = O + O_3$

Evaluation of Chapman’s Model

- How to evaluate Chapman’s Theory?
- Qualitative agreement:
  - Predicts stratosphere as a source of ozone
  - Predicts thermal inversion in the stratosphere
- Quantitative agreement?
  - Check by comparing measured ozone levels with those predicted by Chapman’s model

Problem with Chapman’s Model



- Qualitative agreement: presence of an ozone layer at the right height; predicts thermal inversion. But…
- Predicts too much ozone
- What is wrong?
  - Either there is an extra ***source*** of O_x OR
  - There are other ***sinks***: pathways that destroy ozone

Missing Element –
Catalytic Destruction of Ozone

- Four main "families" of chemicals responsible for catalyzing ozone destruction:

1. Nitrogen oxides: NO_x
   - $NO + NO_2$
2. Hydrogen oxides: HO_x
   - $OH + HO_2$
3. Chlorine: ClO_x
   - $Cl + ClO$
4. Bromine: BrO_x
   - $Br + BrO$

A common type of catalytic destruction cycle (there are others)

$$\mathrm{Y+O_3 \rightarrow YO+O_2}$$

$$\mathrm{YO+O \rightarrow Y+O_2}$$

where Y = NO, OH, Cl or Br

Sources of Catalysts

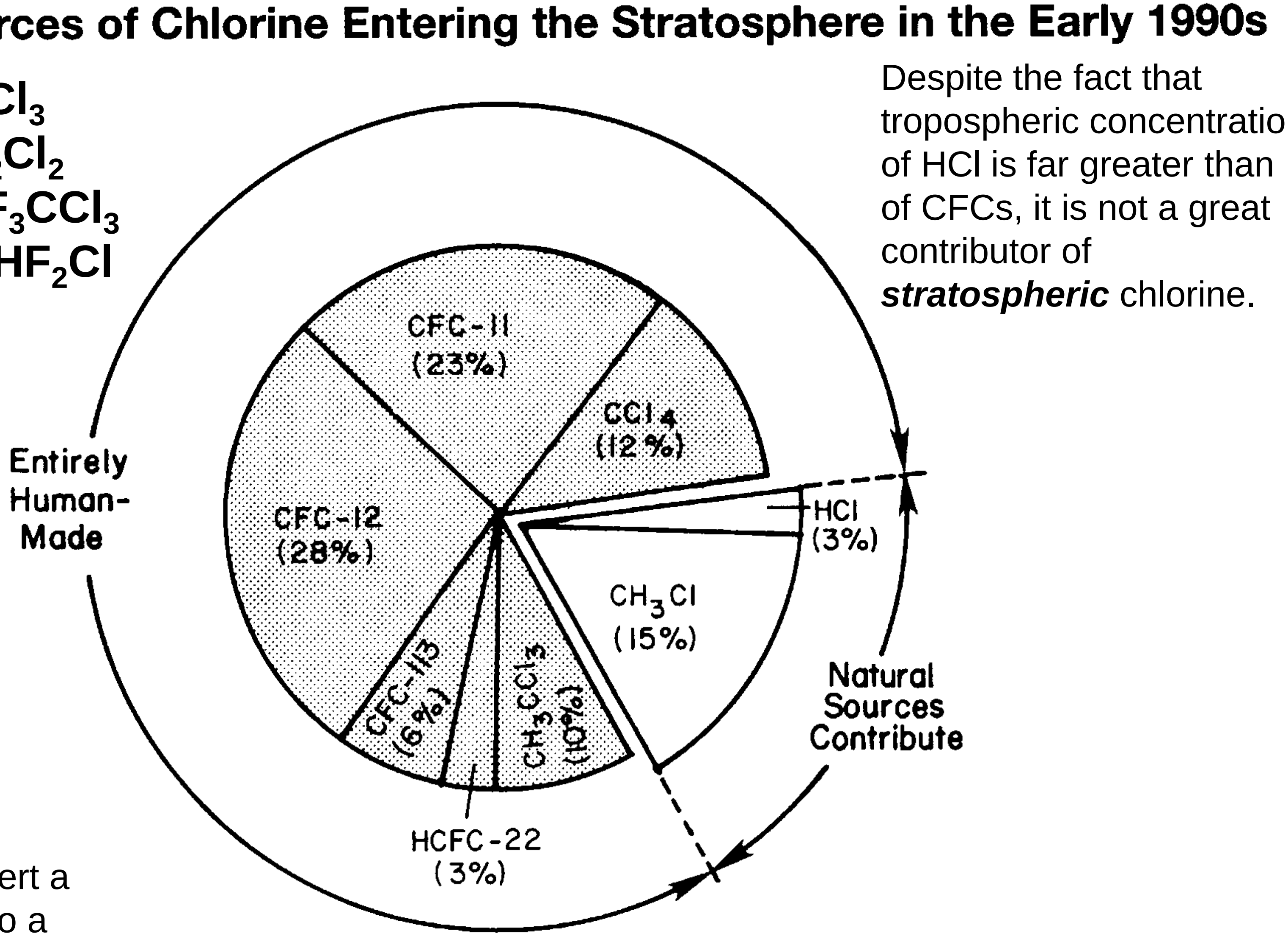
- Stratospheric NO_x
  - Source: tropospheric N_2O
  - Natural sources (mostly)
  - 10% increase since 1850 (ie, due to anthropogenic activities...mostly fertilizer application)
- Stratospheric HO_x
  - Source: tropospheric CH_4, H_2, H_2O
  - Much is natural, however...
  - 150% increase in tropospheric CH_4 since 1850 (agricultural activities; landfills; other sources)
- Stratospheric Cl and Br
  - Almost entirely due to human activity
  - Sources: tropospheric CFCs, HCFCs, halons

CFCs

- *Lecture Question*
  - What are CFCs? What are they used for?

  - CFCs are ***chlorofluorocarbons***; they are small molecules that contain chlorine, fluorine and carbon atoms. Usually there are only 1-2 carbon atoms.
  - CFCs are sometimes called ***Freons*** (that was their trade name for DuPont)
  - CFCs are referred to by a number. The most common CFCs are: CFC-11, CFC-12, CFC-113 (formulas on the next page)
  - 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 “survive” to reach the stratosphere

Most Stratospheric Chlorine is Anthropogenic



CFC-11: $CFCl_3$
CFC-12: CF_2Cl_2
CFC-113: CF_3CCl_3
HCFC-22: CHF_2Cl

Despite the fact that tropospheric concentration of HCl is far greater than of CFCs, it is not a great contributor of ***stratospheric*** chlorine.

Aside: to convert a CFC number to a chemical formula, use the "rule of 90."

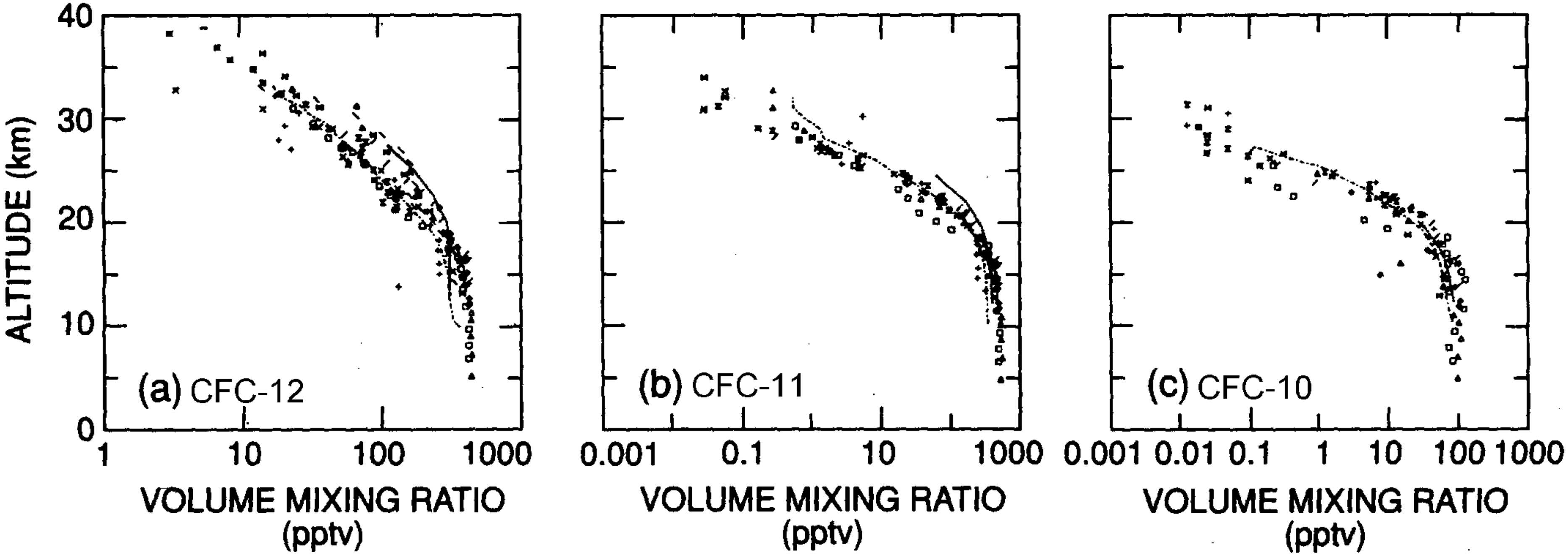
Destruction of Ozone Layer by CFCs

- How do CFCs destroy ozone? Answer in some detail.

- “Hard” CFCs are unreactive to OH and other reactive radicals in the troposphere. They are also pretty insoluble in water. That means their tropospheric lifetimes are easily long enough that the majority of tropospheric CFCs pass through the tropopause into the stratosphere.
- Once there, they are subject to light of shorter wavelengths (ie, more energetic photons). In particular, many CFCs absorb in the “uv window” (centered at 205 nm) between strong O_2 and O_3 absorption. That means most can photodissociate in the bottom half of the stratosphere.
- Photodissociation releases chlorine atoms:
  - For example: $CFCl_3 + \text{light} \rightarrow CFCl_2 + Cl$ ($\lambda < 225$ nm)
- Chlorine atoms deplete odd oxygen (O_x) largely by the following cycle
  - $Cl + O_3 \rightarrow ClO + O_2$
  - $ClO + O \rightarrow Cl + O_2$

Atmospheric Fate of CFCs

Vertical concentration profiles of "hard CFCs" consistent with long tropospheric lifetimes followed by destruction in the stratosphere.

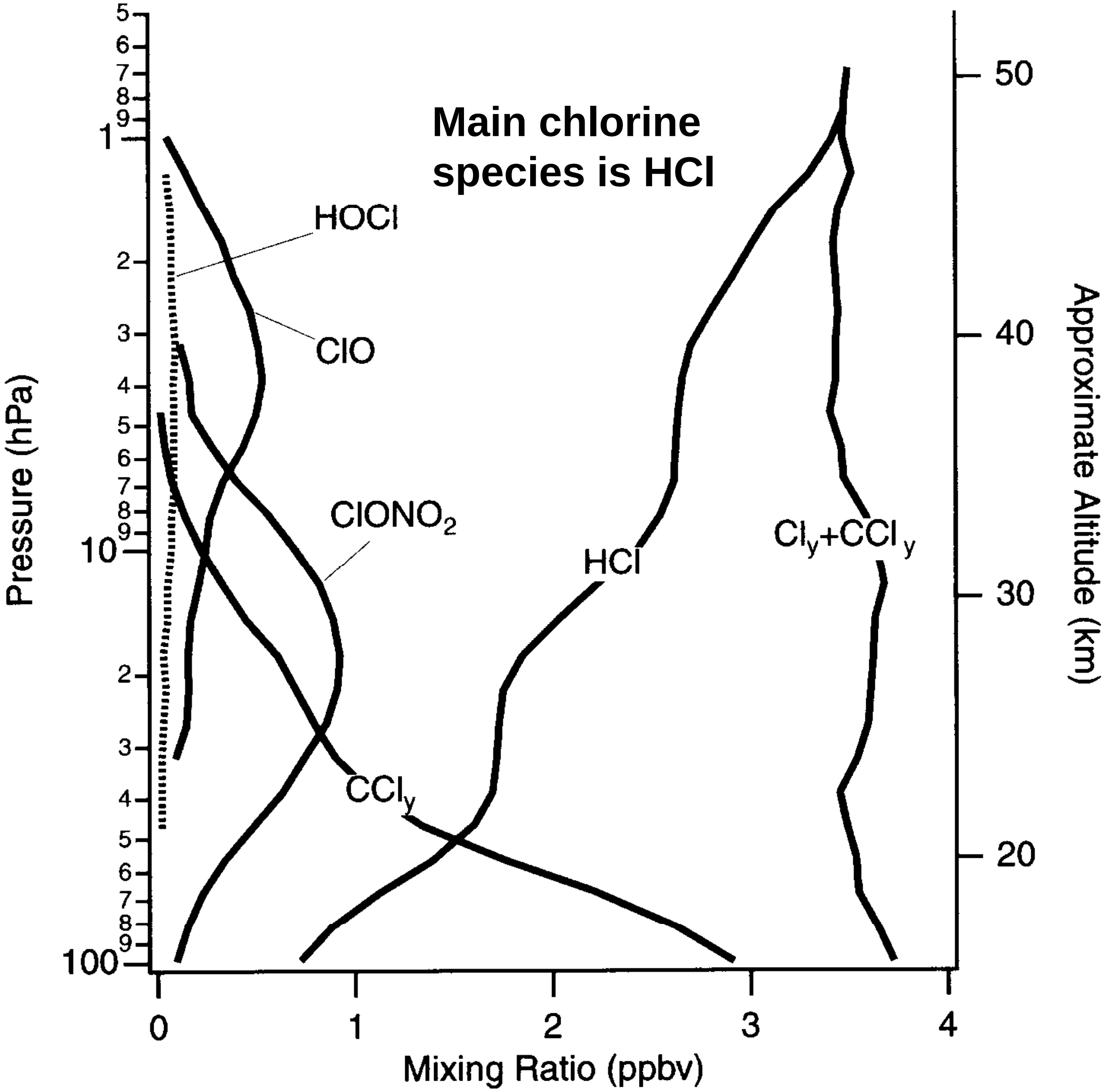


Chlorine in the Stratosphere

- Once released from CFCs, what happens to chlorine in the stratosphere? How does it leave the stratosphere?

- Chlorine undergoes a series of reactions to form a variety of compounds
- Some of these are ***active*** in depleting ozone:
  - Cl, ClO
- Some of these do not directly deplete ozone; these are chlorine ***reservoirs***
  - **HCl**, $ClONO_2$, HOCl
- The most important (long-lived) stratospheric chlorine reservoir is HCl
- The reservoirs can become activated by various processes such as photodissociation or reaction with OH
- Loss of stratospheric chlorine occurs when they cross-back into the troposphere and are removed from the atmosphere
  - Most common route: HCl crosses back, dissolves in water, and is washed out

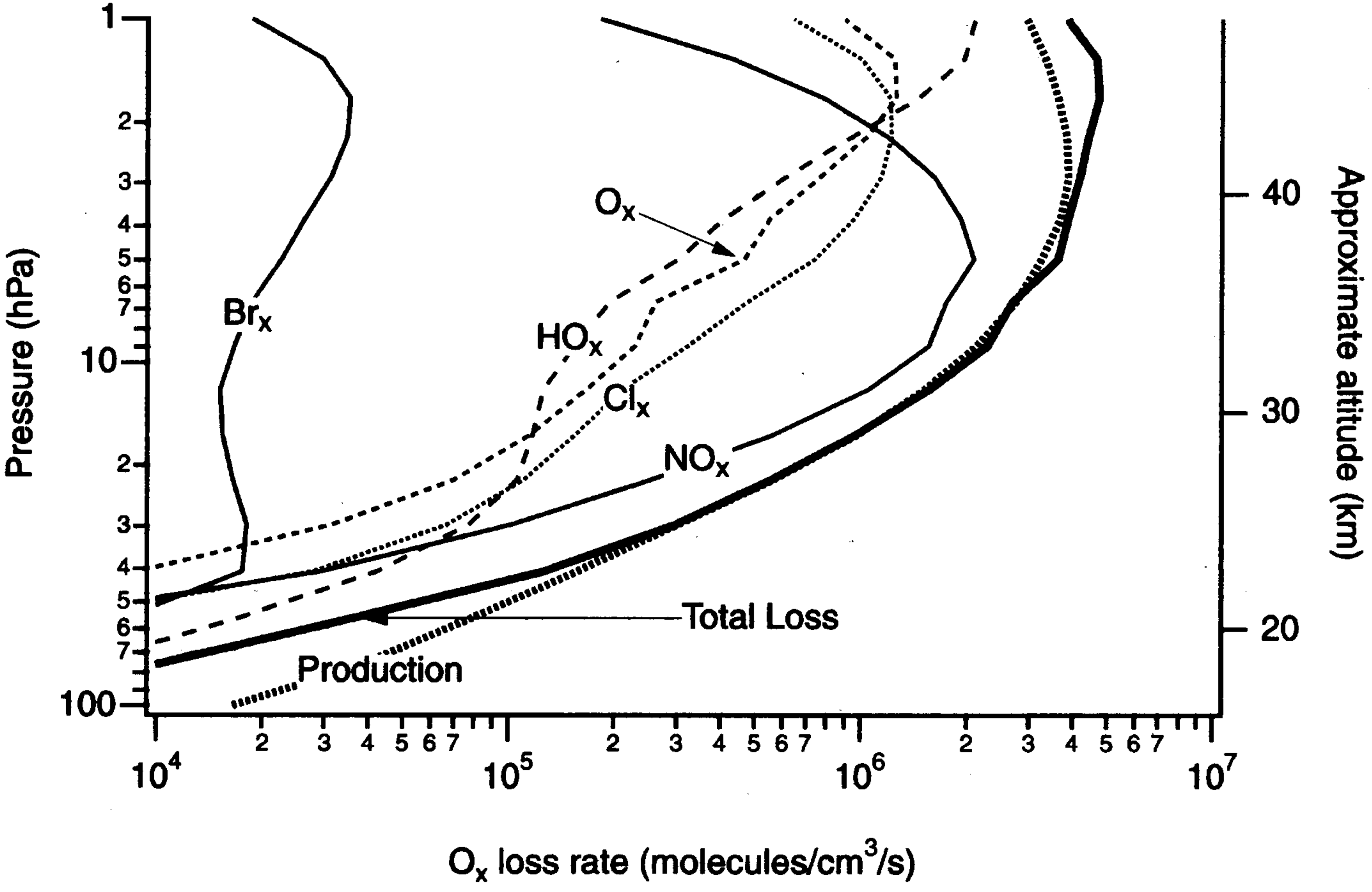
Chlorine in the Stratosphere

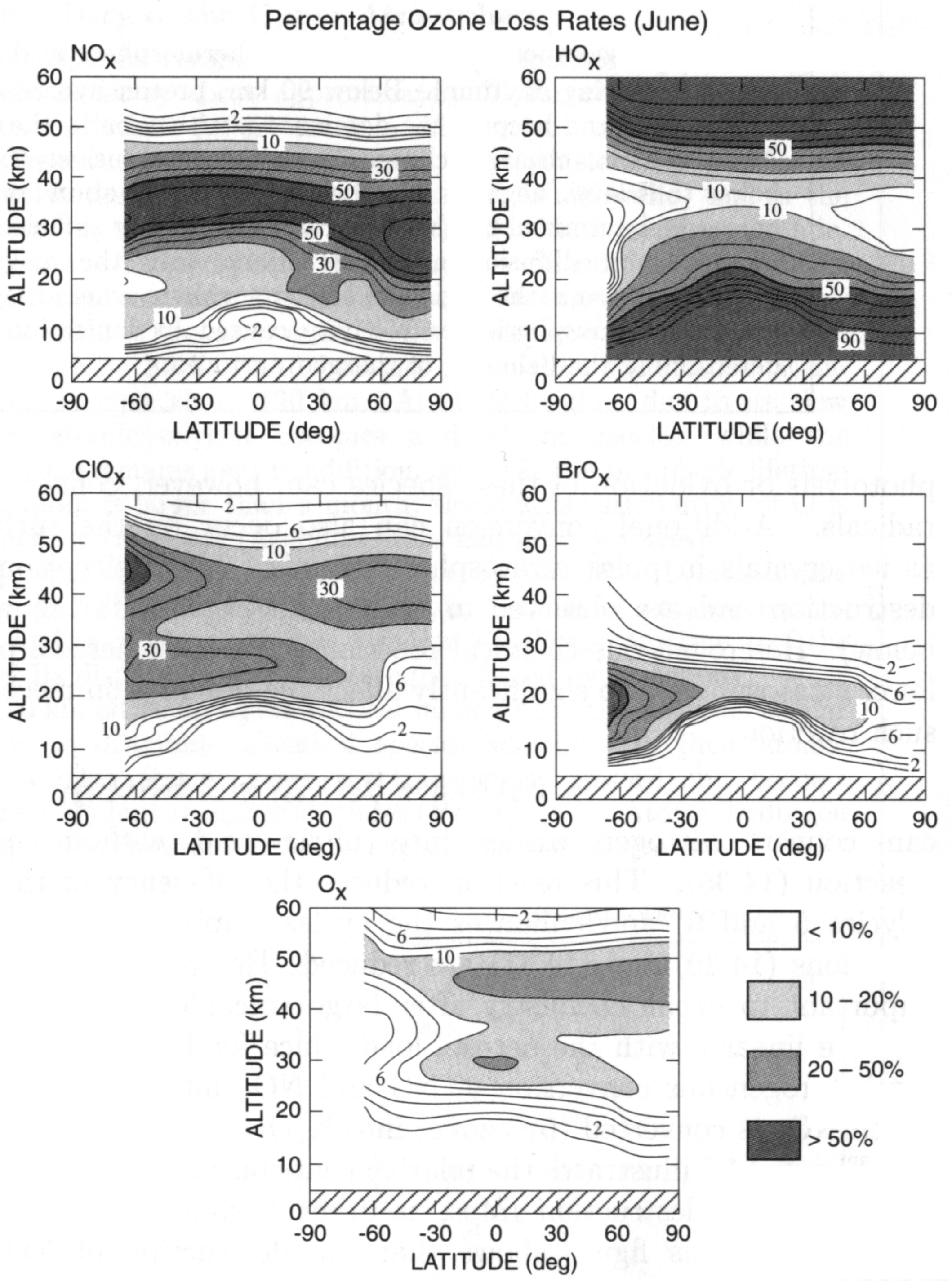


Main chlorine species is HCl

- "CCl_y" refers to CFCs and other tropospheric sources of Cl
- Cl_y refers to the statospheric chlorine "family" of active and reservoir species

Relative Contributions to Ozone Loss



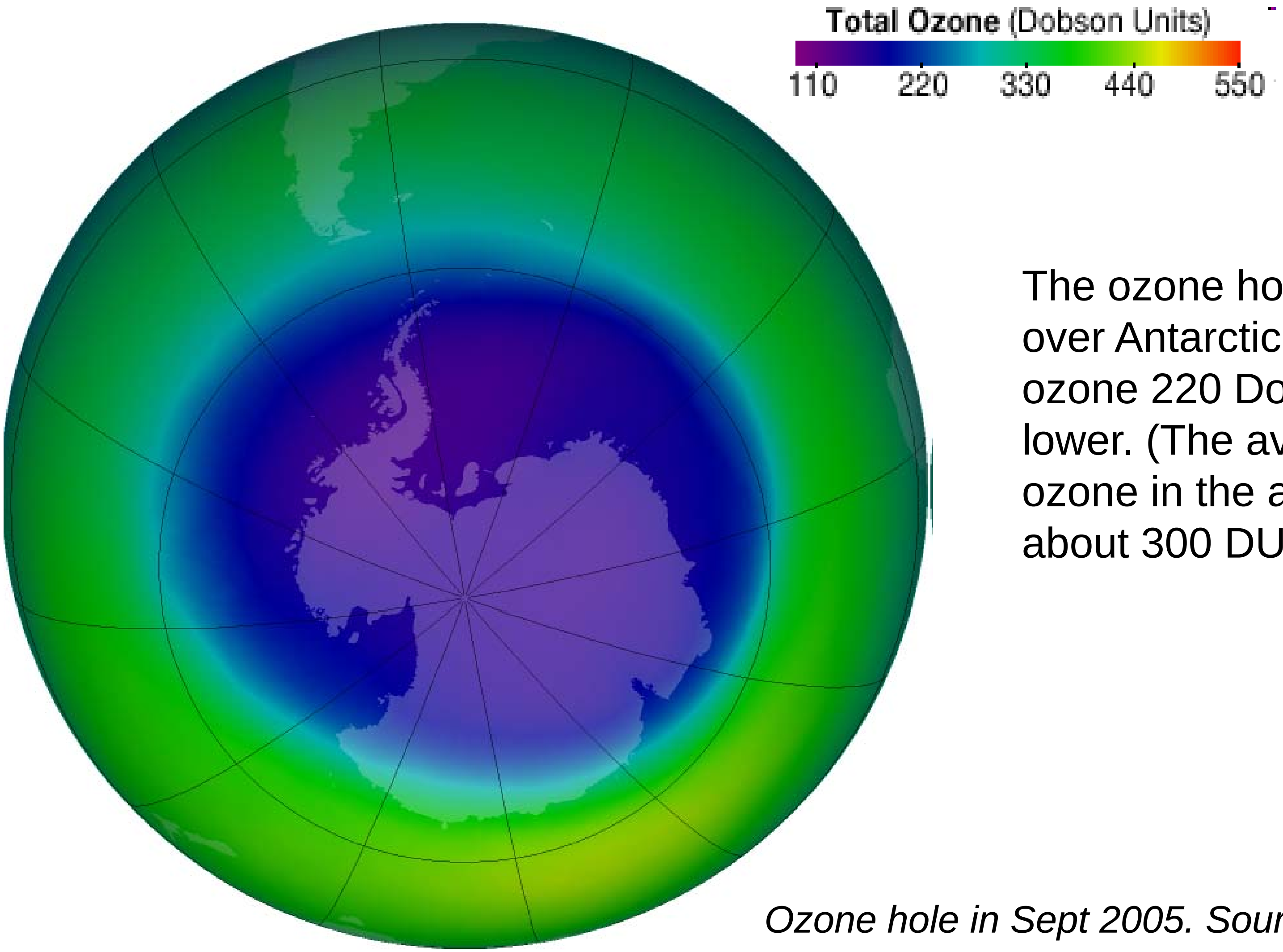


Relative contributions to ozone loss by family

- Predictions from computer models
- Note that plots show *relative* contributions, not absolute rate of Ox destruction
- Remember that max Ox concentration is at about 25km, and max production/loss peaks at about 40km
- NOx is the most important family, particularly in the middle stratosphere.
- HOx is most important at top and bottom of stratosphere
- ClOx contributes up to 30% of loss under typical circumstances (exception: polar ozone holes)

The “Ozone Hole”

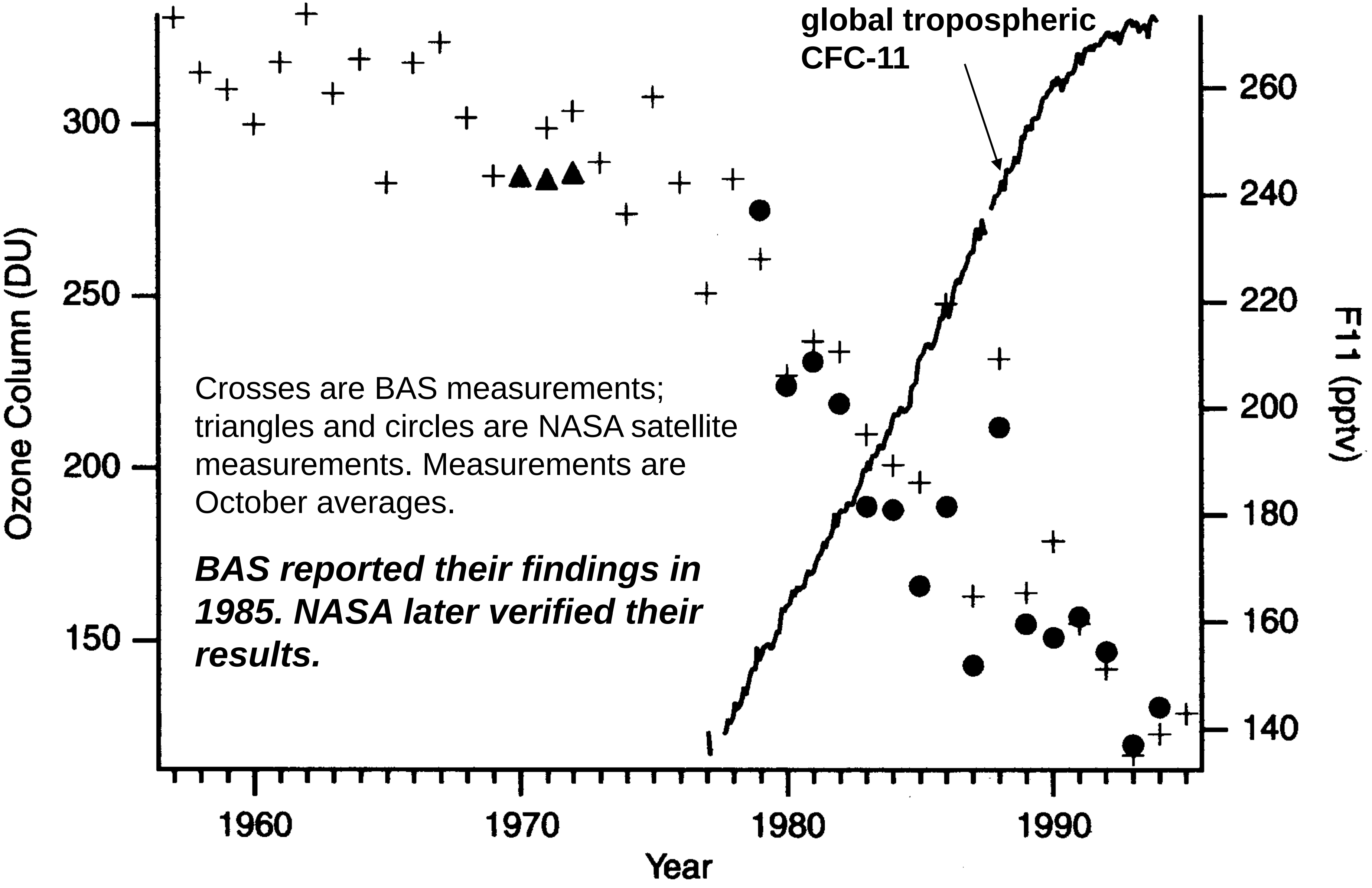
- What is the “ozone hole?” When did it first appear? How does it form?



The ozone hole is the region over Antarctica with total ozone 220 Dobson Units or lower. (The avg total column ozone in the atmosphere is about 300 DU.)

Ozone hole in Sept 2005. Source: NASA

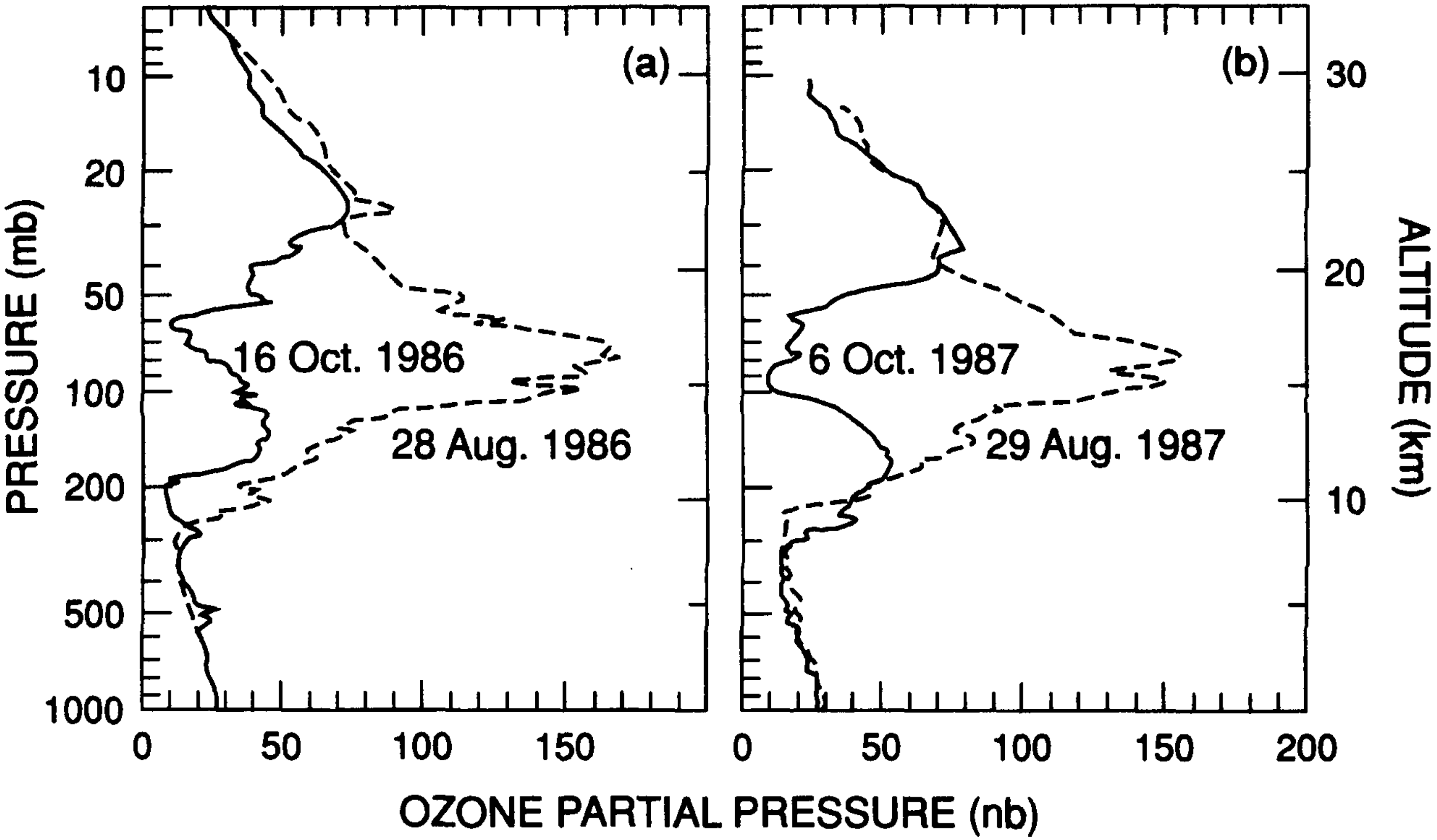
Detection of the Antarctic Ozone Hole



Crosses are BAS measurements; triangles and circles are NASA satellite measurements. Measurements are October averages.

BAS reported their findings in 1985. NASA later verified their results.

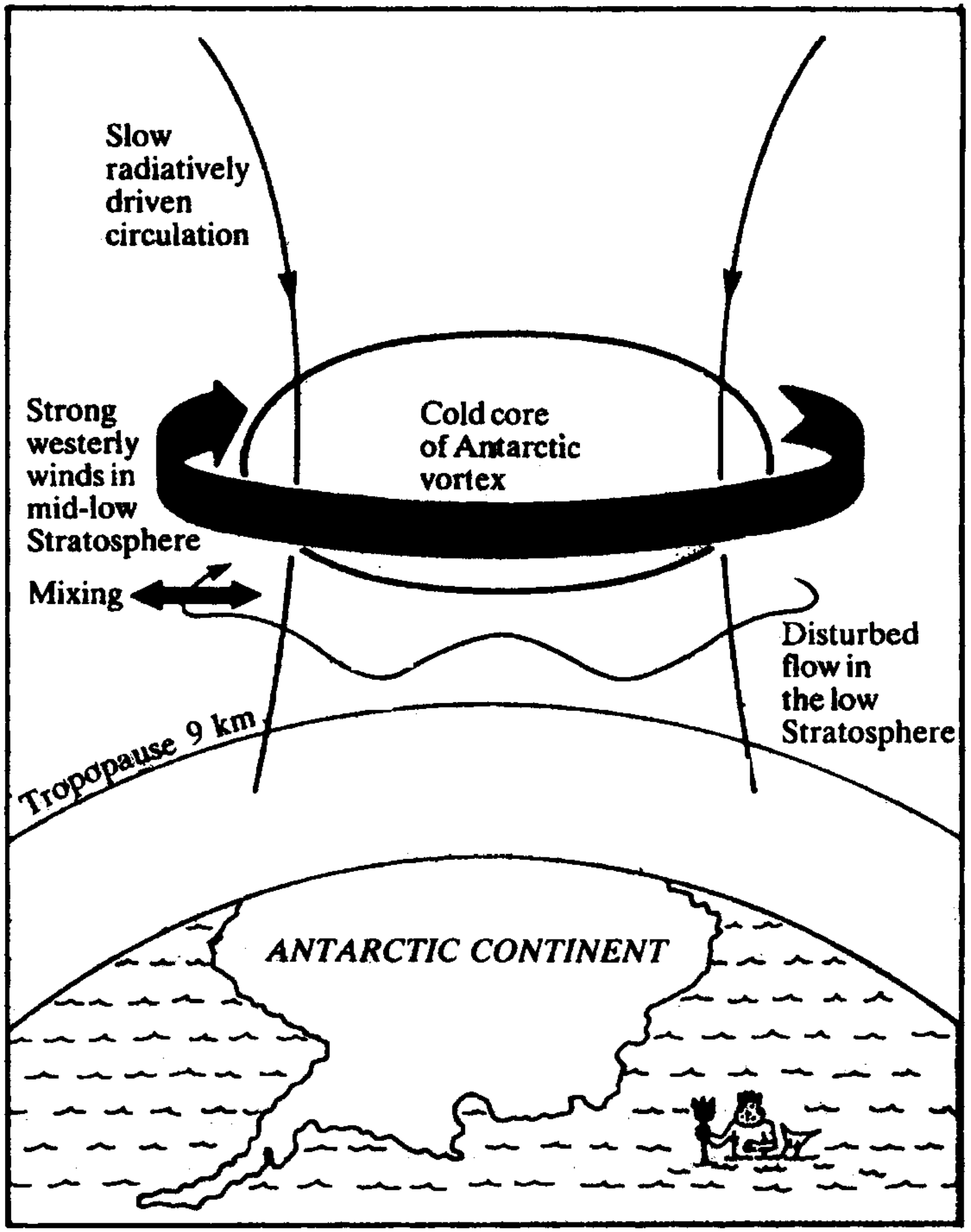
Concentration Profile during Ozone Hole



The “ozone hole” is a sudden, marked depletion of ozone – a loss of 50% or more of total column ozone – in the lower stratosphere of the Antarctic in the weeks after the Spring sunrise. In 1985 the area of the hole was 10 million sq. km (and growing yearly).

What causes it???

Unique Feature of Antarctic Meteorology: Winter Vortex

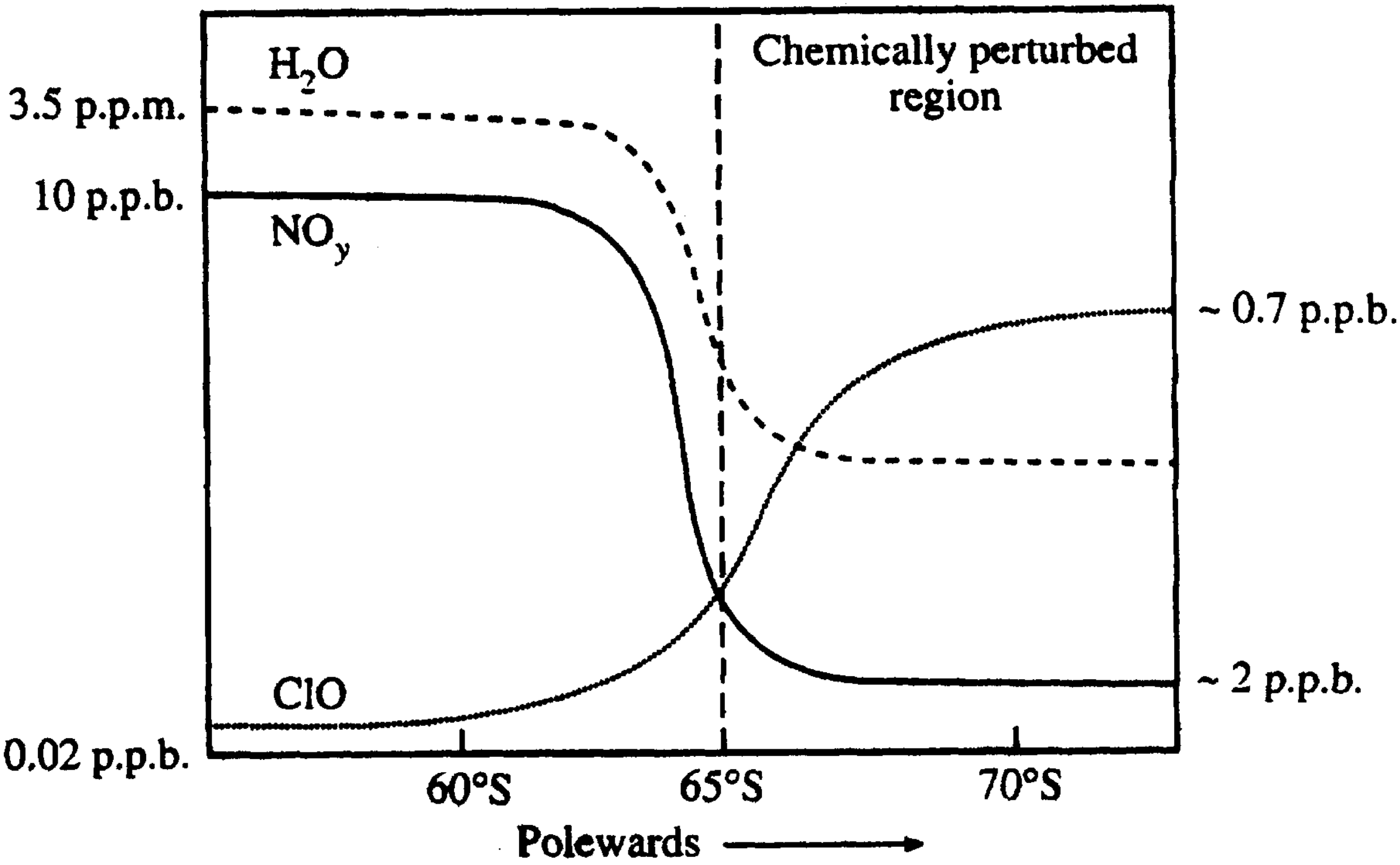


- •Polar vortex develops during the winter
- •Atmosphere is effectively isolated from the rest of the southern hemisphere
- •Interior temperatures plummet during long winter night – large area is below 200K, and it can get as cold as 180K

Three Competing Theories

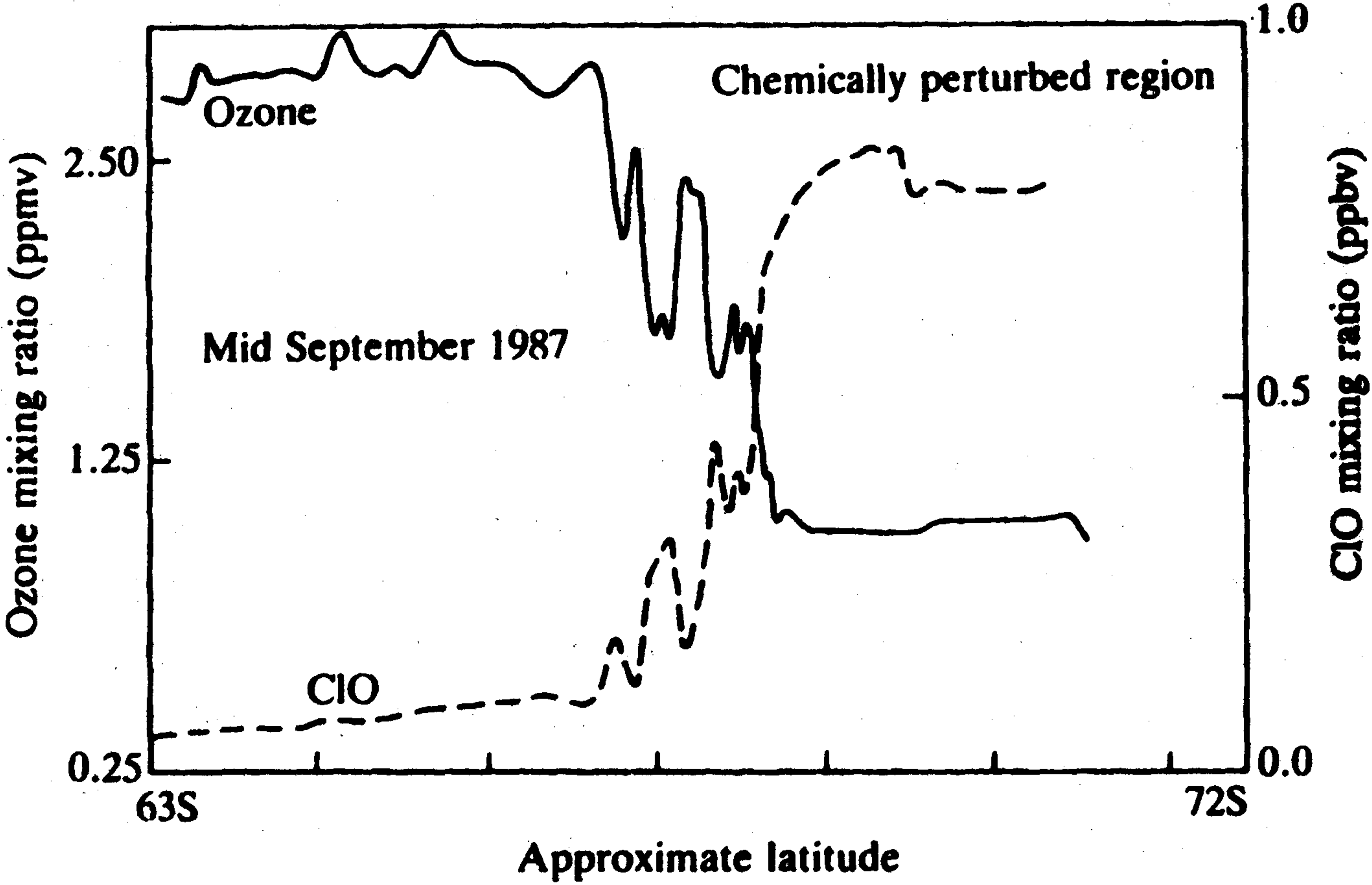
- Chlorine-induced
  - Supported by the timing (ozone hole began appearing in the 1970’s), BUT
  - Existing chemical models inadequate
- Circulation-driven
  - After sun rises, tropospheric upwelling “pushes” ozone out of the vortex (ozone displacement, not destruction)
- Solar storms
  - NO_x created in upper stratosphere during winter

Concentration Gradients Develop Across Vortex

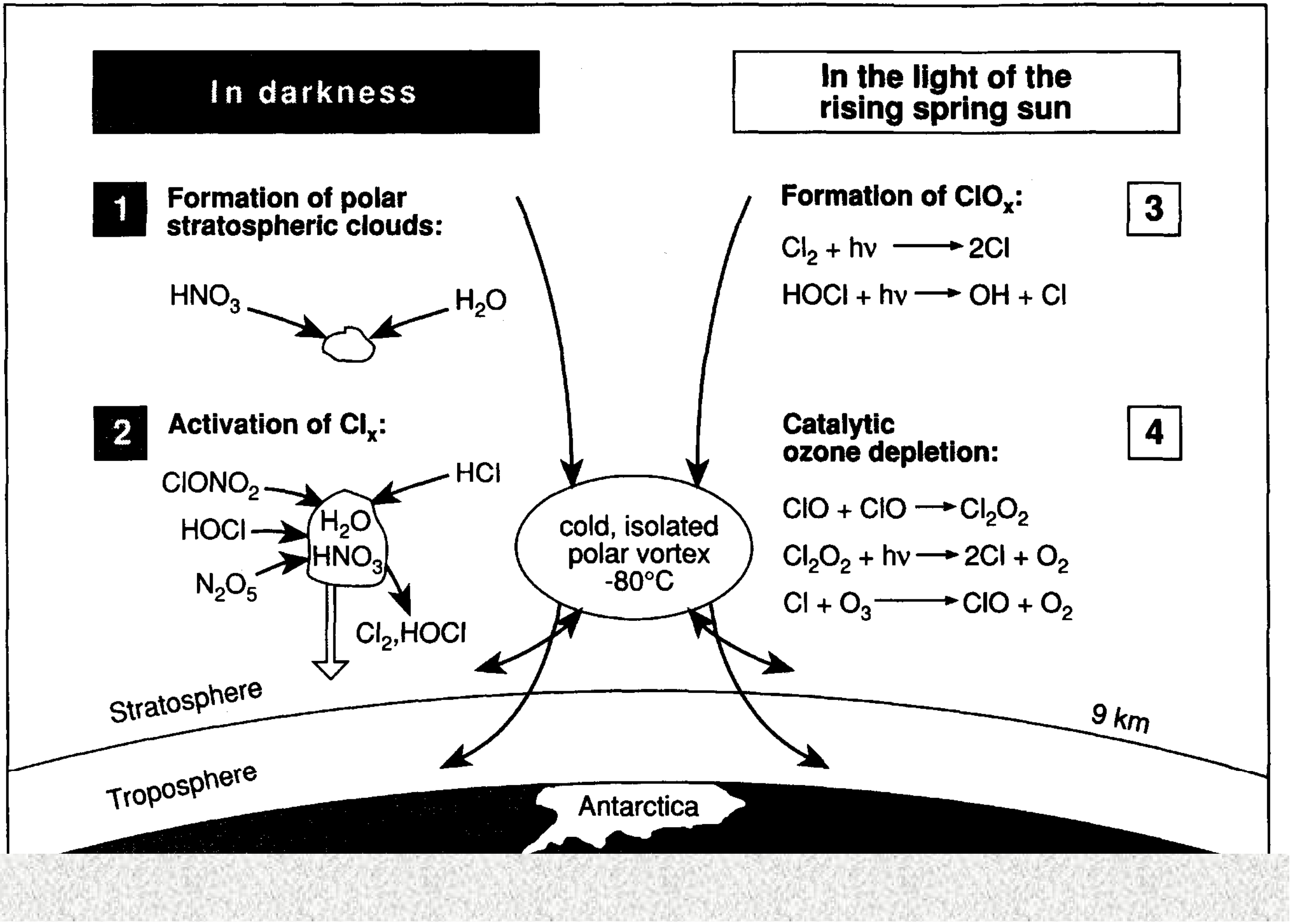


During ozone hole episode, polar region is very dry and denitrified (low NO_y). Concentrations of active chlorine (ClO_x) increases dramatically.

The “Smoking Gun” Points to Chlorine!



The Ozone Hole – Explained!

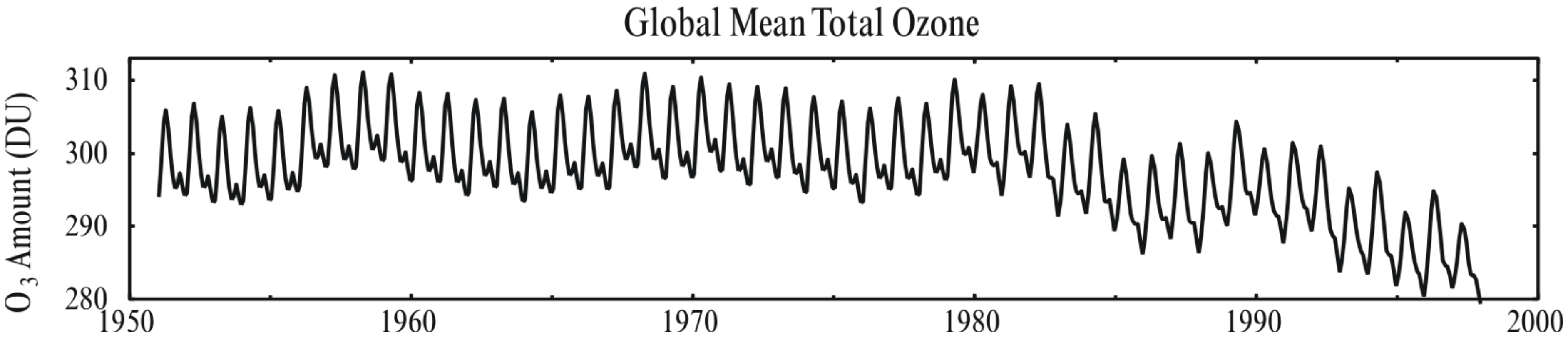


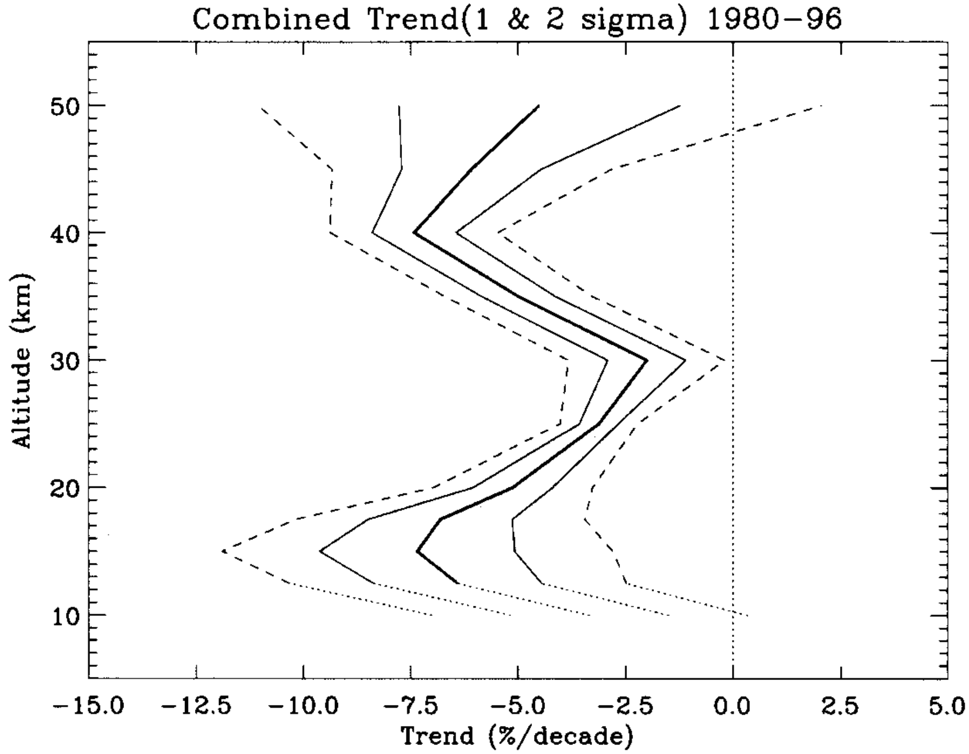
Global Ozone Depletion (and Effects)

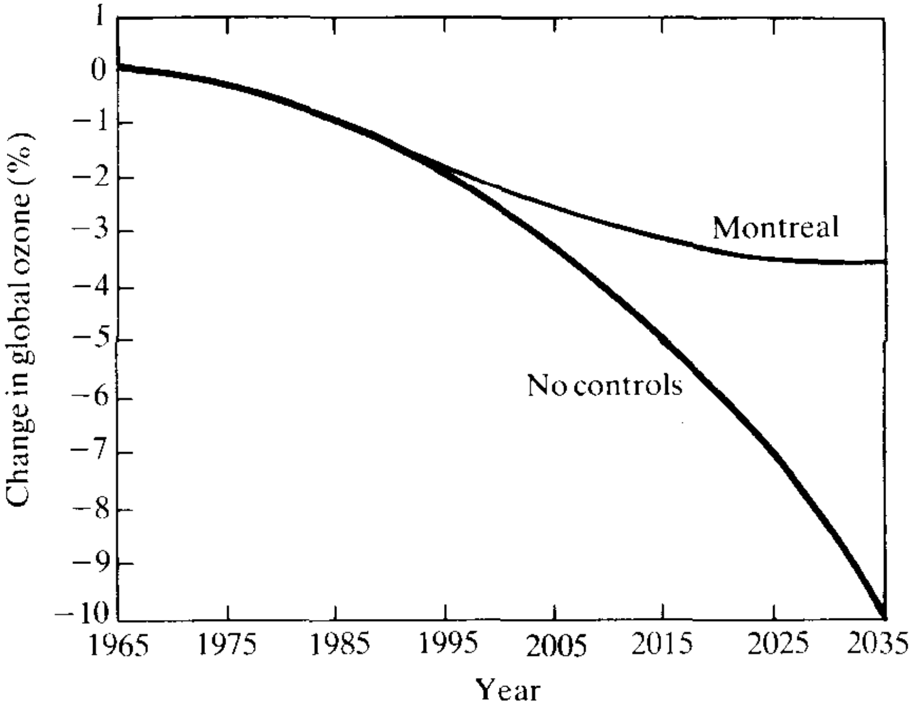
- How severe is ozone depletion now on a global scale?
- What was the name of the treaty signed to halt ozone depletion?

- Roughly 3% global stratospheric ozone has been depleted (averaged globally – excepting the ozone hole – and annually)
- The Montreal Protocol was signed in 1987 by 46 countries, including the US. It entered into force in 1989.
- By 1996, developed countries phased out use of CFCs, halons and CCl_4; developing countries have until 2010.
- Developed countries are scheduled to phase out production of HCFCs by 2030; developing countries have until 2040.

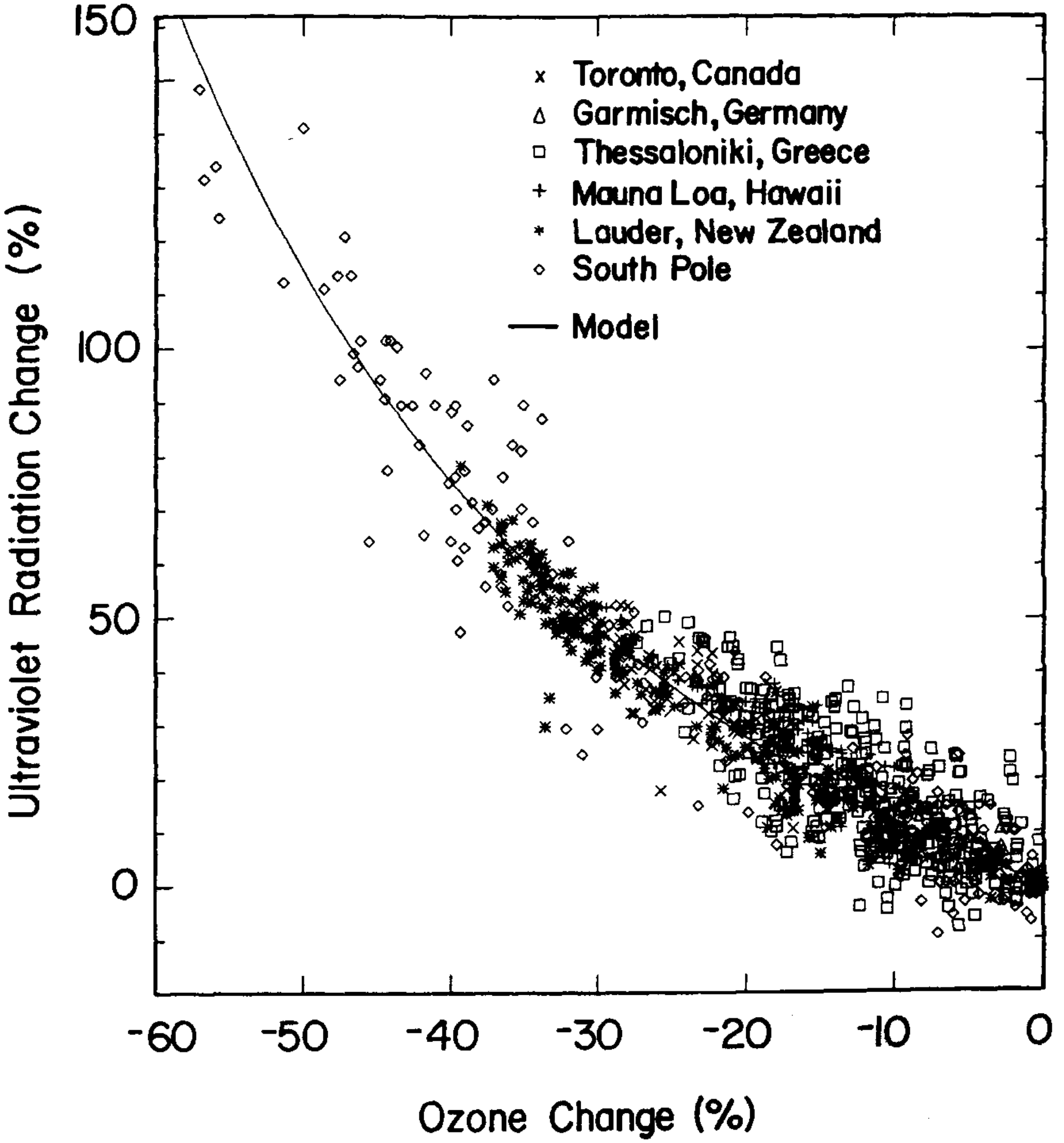
Global Ozone Depletion Trends







Ozone and UV Trends



Effect of the Montreal Protocol on Stratospheric Cl