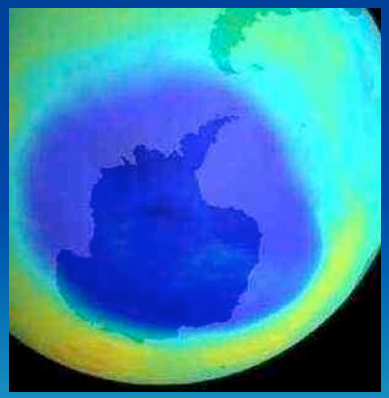
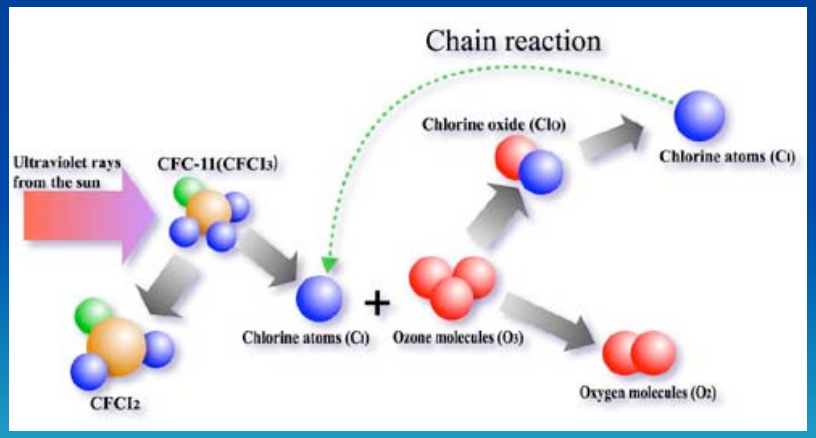
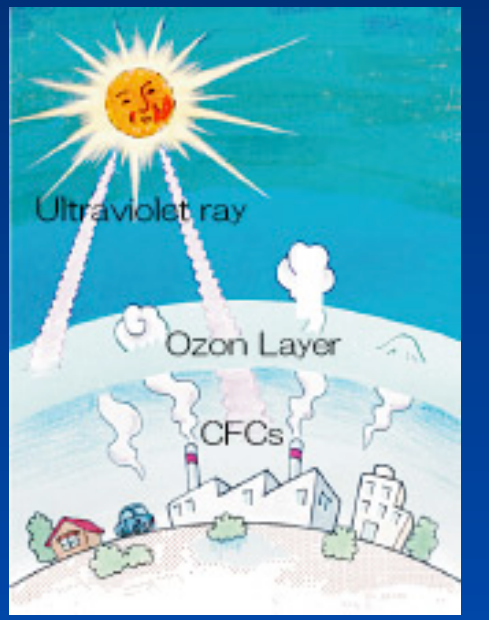
CLIM-111/PHYS-111
Introduction to the Fundamentals of Atmospheric Science
Lecture Notes #5 Part 2: **Atmospheric Chemistry**

1. **Composition of Tropospheric Air**
2. **Sources, Transport, and Sinks of Trace Gases**
3. **Some Important Tropospheric Trace Gases**
4. **Tropospheric Aerosols**
5. **Air Pollution**
6. **Tropospheric Chemical Cycles**
7. **Stratospheric Chemistry**







Surface Bubbles





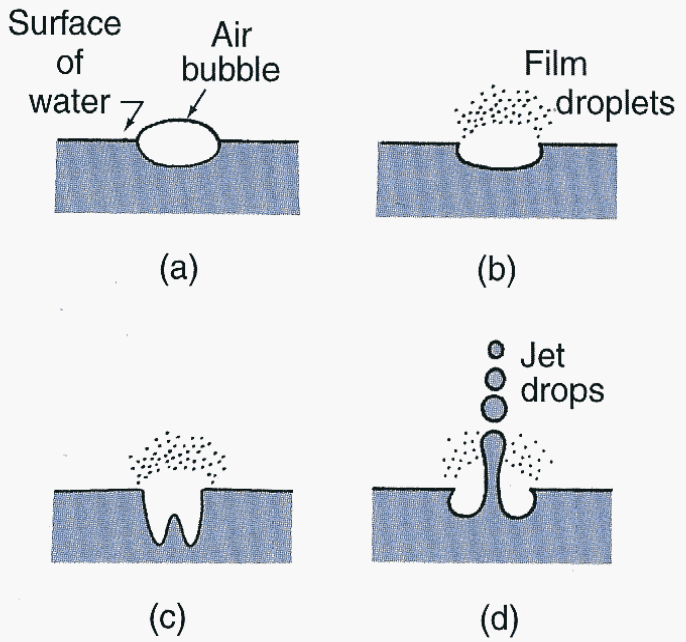


Fig. 5.8 Schematics to illustrate the manner in which film droplets and jet drops are produced when an air bubble bursts at the surface of water. Over the oceans some of the droplets and drops evaporate to leave sea-salt particles and other materials in the air. The time between (a) and (d) is ~2 ms. The film droplets are ~5–30 μm diameter before evaporation. The size of the jet drops are ~15% of the diameter of the air bubble.

Sources of Atmospheric Particulates

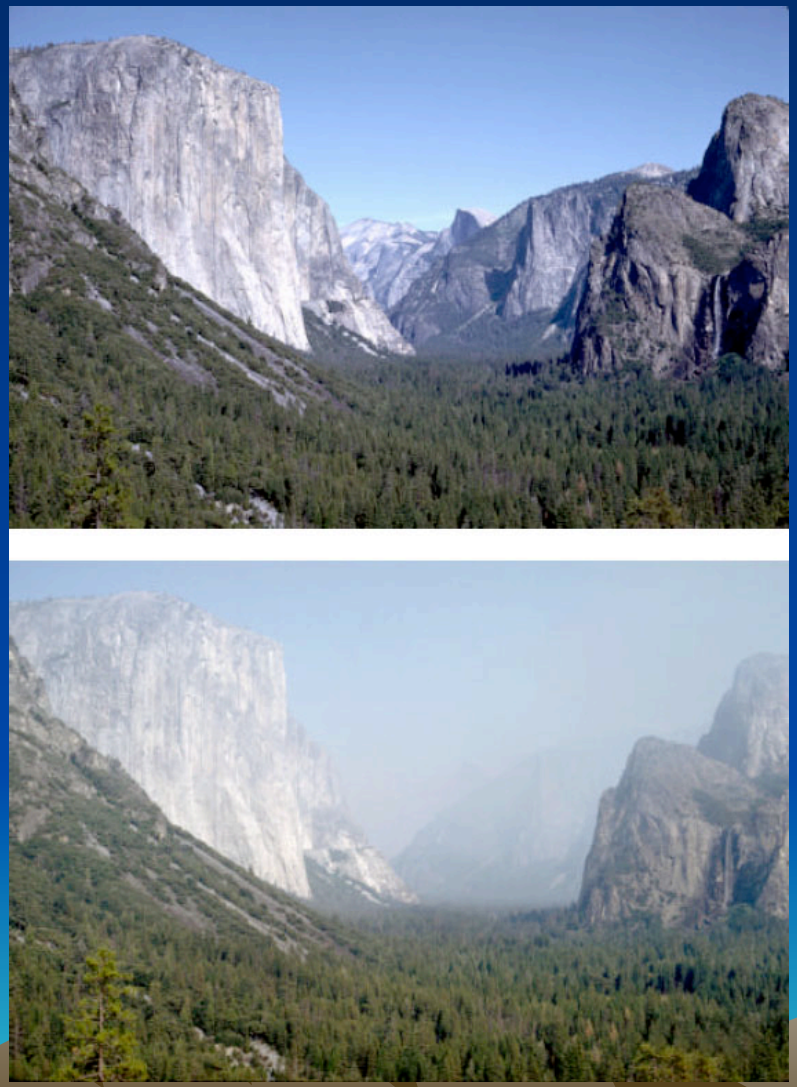


Table 5.3 Estimates (in Tg per year) for the year 2000 of (a) direct particle emissions into the atmosphere and (b) *in situ* production

(a) Direct emissions

	Northern hemisphere	Southern hemisphere
Carbonaceous aerosols		
Organic matter (0–2 μm)[a]		
Biomass burning	28	26
Fossil fuel	28	0.4
Biogenic (>1 μm)	—	—
Black carbon (0–2 μm)		
Biomass burning	2.9	2.7
Fossil fuel	6.5	0.1
Aircraft	0.005	0.0004
Industrial dust, etc. (>1 μm)		
Sea salt		
<1 μm	23	31
1–16 μm	1,420	1,870
Total	1,440	1,900
Mineral (soil) dust		
<1 μm	90	17
1–2 μm	240	50
2–20 μm	1,470	282
Total	1,800	349

In Situ Sources of Atmospheric Particulates (in Tg/year)

(b) *In situ*

	Northern hemisphere	Southern hemisphere
Sulfates (as NH_4HSO_4)	145	55
Anthropogenic	106	15
Biogenic	25	32
Volcanic	14	7
Nitrate (as NO_3^-)		
Anthropogenic	12.4	1.8
Natural	2.2	1.7
Organic compounds		
Anthropogenic	0.15	0.45
Biogenic	8.2	7.4

[a] Sizes refer to diameters. [Adapted from Intergovernmental Panel on Climate Change, *Climate Change 2001*, Cambridge University Press, pp. 297 and 301, 2001.]

Number Distribution of Tropospheric Aerosols



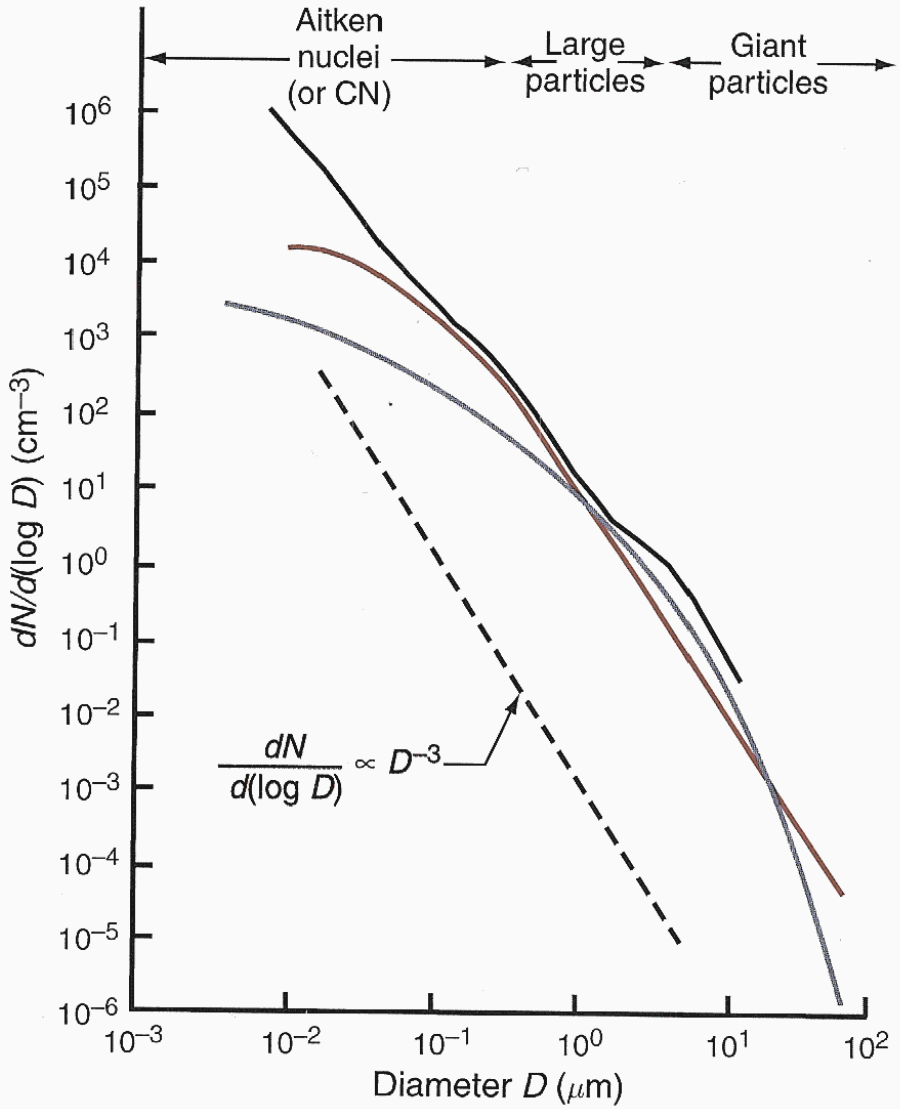
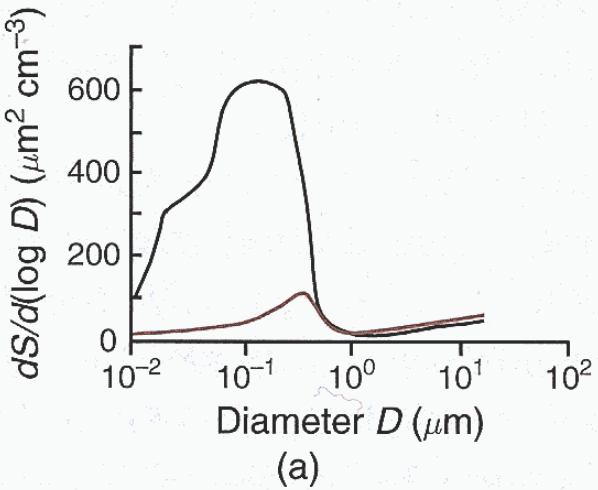


Fig. 5.9 Number distributions of tropospheric particles obtained from averaging many measurements in continental (red), marine (blue), and urban polluted (black) air. Also plotted is Eq. (5.31) with $\beta = 3$, with the line (dashed) displaced from the other curves for the sake of clarity.


9° 10° 11° 12° 13° 14° 15° 16° 17° 18° 19° 20° 21° 22° 23° 24° 25° 26° 27° 28° 29° 30° 31° 32° 33° 34° 35° 36° 37° 38° 39°
50° 49° 48° 47° 46° 45° 44° 43° 42° 41° 40° 39° 38° 37° 36° 35° 34° 33° 32° 31° 30° 29° 28° 27°

Number Distributions of Tropospheric Aerosols



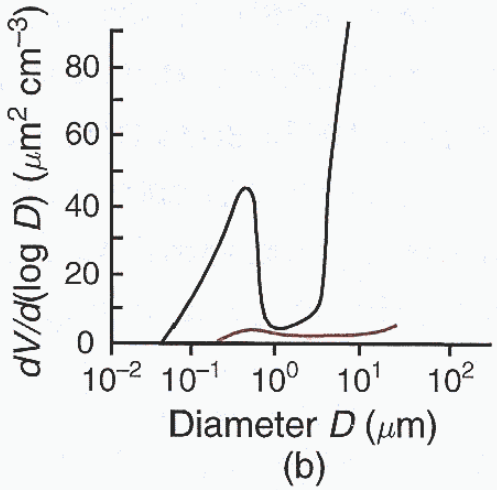


Fig. 5.10 (a) Typical particle surface area and (b) particle volume distribution plots in urban-polluted air (black line) and cleaner continental air (solid red line).

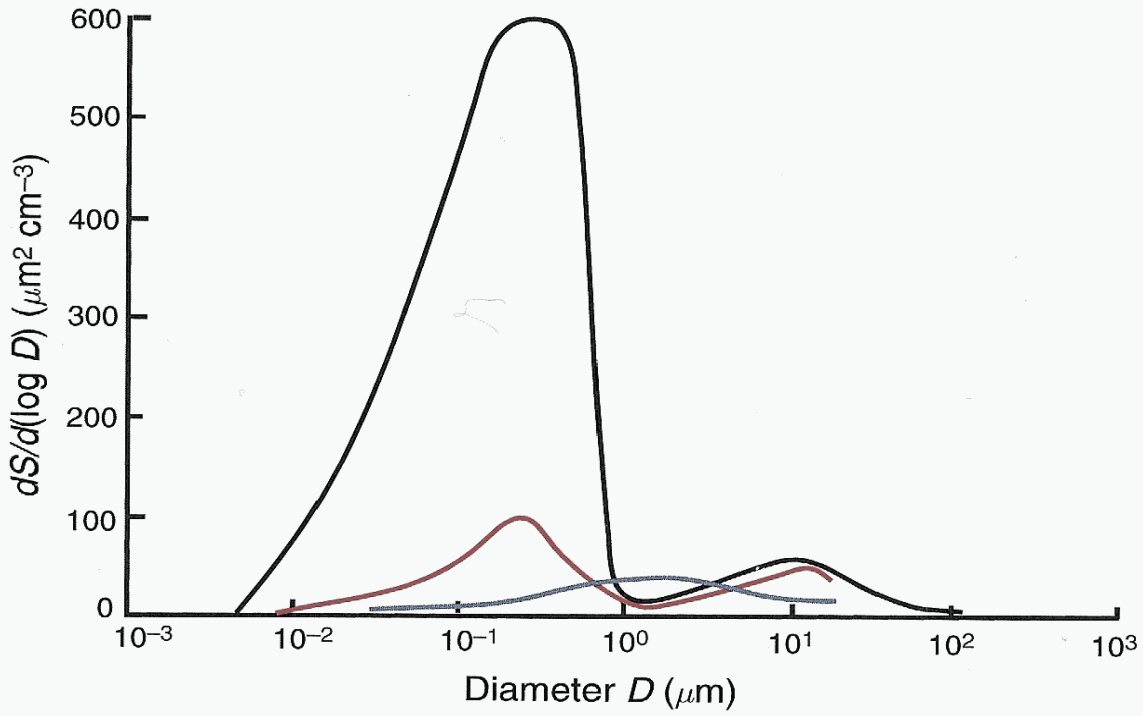
5. Air Pollution

- In Urban and industrialized locations, anthropogenic emissions lead to large concentrations of undesirable chemical species which can adversely affect air quality, visibility, and pose threats to human health.

- Severe air pollution episodes occur when the rates of emissions or formation of pollutants greatly exceed the rates at which the pollutants are dispersed by winds, chemical reactions, or deposition.

- Severe air pollution episodes tend to occur in association with extended periods of light winds and strong static stability.

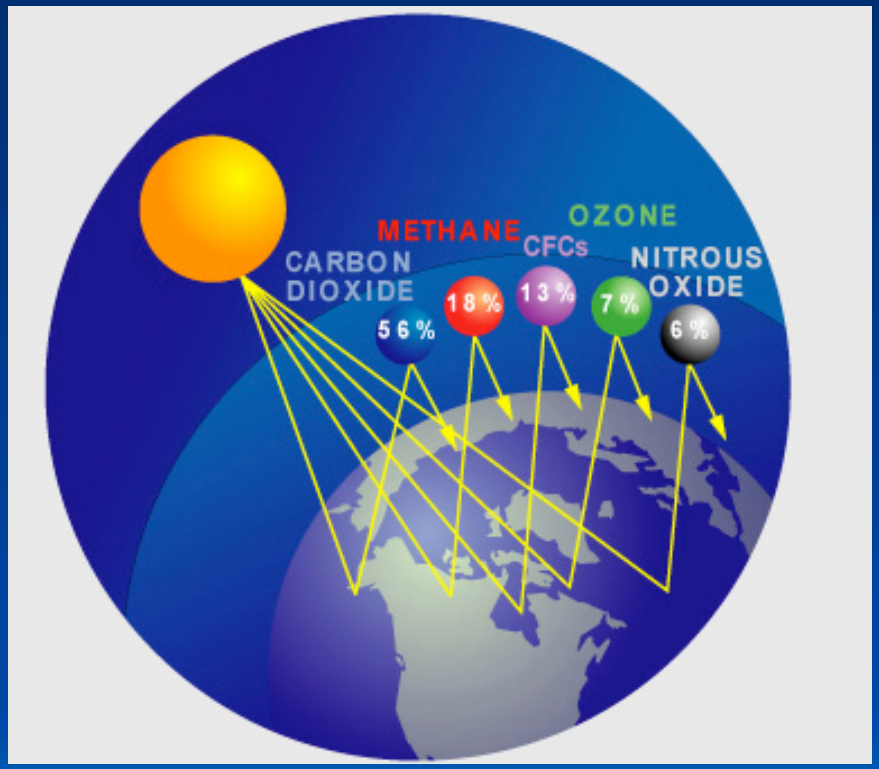
Emissions from Fossil Fuel Combustion:
CO, CO_2, NOx (radicals of N), SO_2, hydrocarbons, etc.



Desig-nation	Aitken nuclei	Large particles	Giant particles
Sources	← Combustion →		← Windblown dusts →
	← Gas-to-particle conversions →	← Fly ash, sea-salt, pollens →	
	← Coagulation of Aitken nuclei →		← Giant particles from industries →
	← Cloud droplet evaporation →		
Sinks	← Coagulation →	← Precipitation scavenging →	
	← Capture by cloud particles →	← Dry fallout →	
Resi-dence time	Less than an hour in polluted air or in clouds	Days to weeks	Hours to days / Minutes to hours

Fig. 5.11 Schematic curves of particle surface area distributions for urban polluted air (black line), continental air (red line), and marine air (blue line). Shown below the curves are the principal sources and sinks of atmospheric particles and estimates of their mean residence times in the troposphere. [Adapted from *Atmos. Environ.* **9**, W. G. N. Slinn, Atmospheric aerosol particles in surface-level air, 763, copyright (1975), with permission from Elsevier.]

Anthropogenic Greenhouse Gases



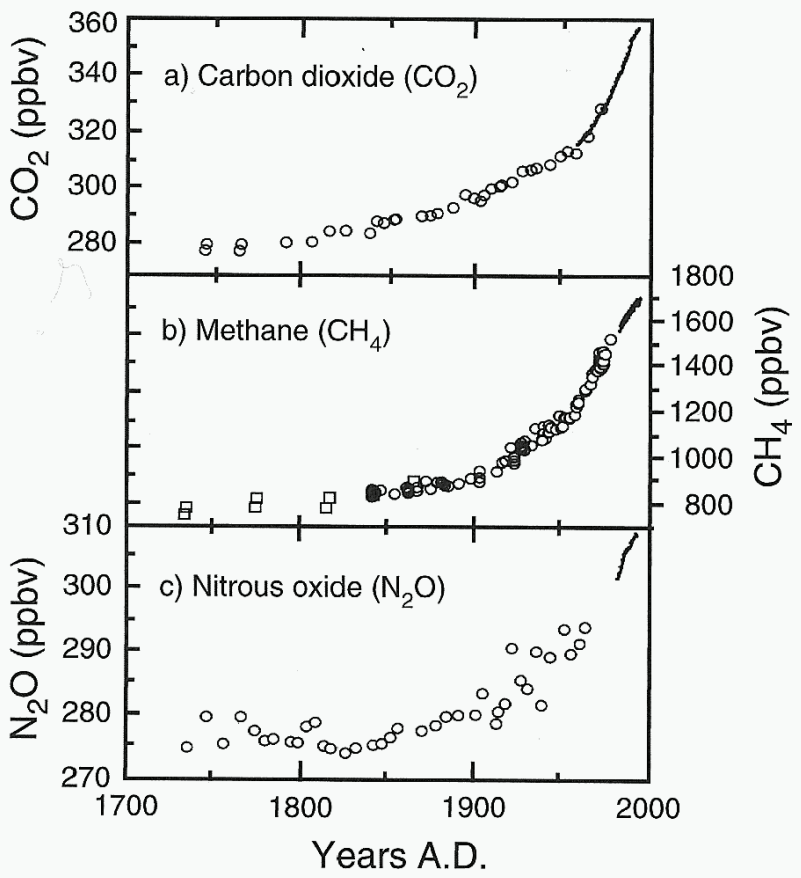


Fig. 5.13 Changes in the concentrations of (a) CO_2, (b) CH_4, and (c) N_2O over 300 years deduced from analysis of Greenland and Antarctic ice cores. [Adapted from D. J. Wuebbles et al., "Changes in the chemical composition of the atmosphere and potential impacts," in Brasseur, Prinn and Pszenny, eds, *Atmospheric Chemistry in a Changing World*, Springer, 2003, p. 12, Copyright 2003 Springer-Verlag.]

Nitrogen-containing Gases

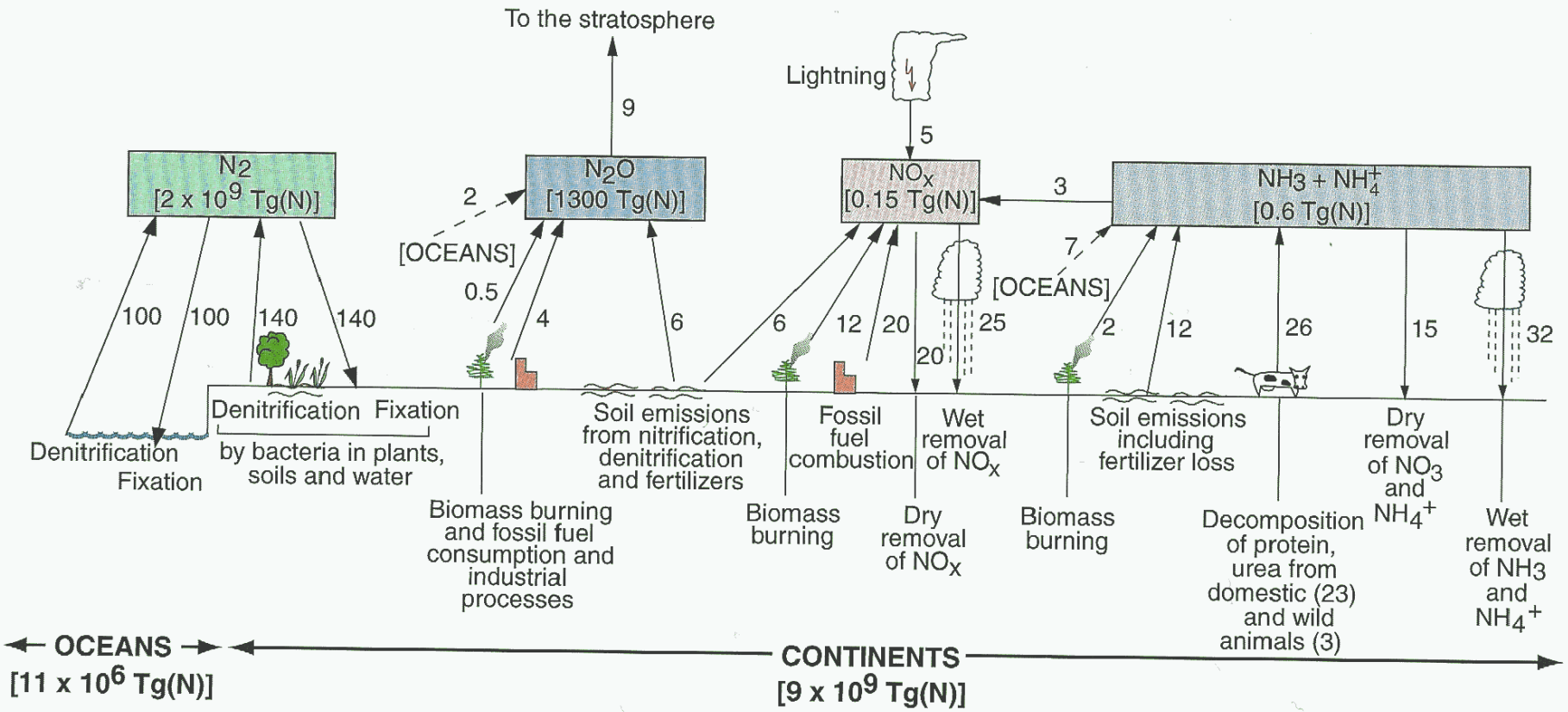


Fig. 5.14 Principal sources and sinks of nitrogen-containing gases in the atmosphere. Numbers alongside the arrows are estimates of average annual fluxes in Tg(N) per year; various degrees of uncertainty, some quite large, are associated with all of the fluxes. Numbers in square brackets are total amounts of the species in the atmosphere. [Adapted from P. V. Hobbs, *Introduction to Atmospheric Chemistry*, Camb. Univ. Press, 2000, p. 148. Reprinted with the permission of Cambridge University Press.]

Sulfur-containing gases

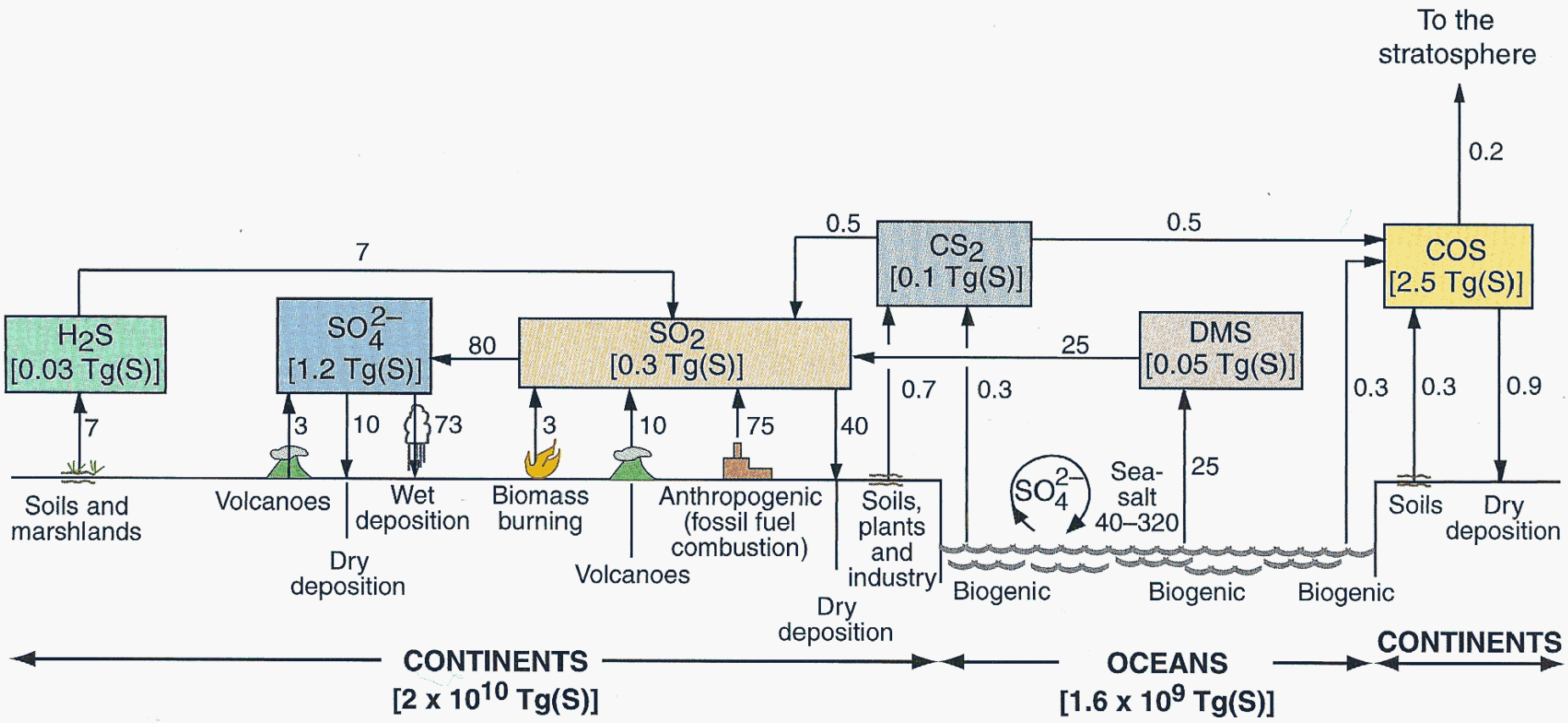


Fig. 5.15 As for Fig. 5.14 but for sulfur-containing species in the troposphere. Fluxes are in Tg(S) per year. For clarity, wet and dry removal are shown only over the continents, although they also occur over the oceans. [Adapted from P. V. Hobbs, *Introduction to Atmospheric Chemistry*, Camb. Univ. Press, 2000, p. 150. Reprinted with the permission of Cambridge University Press.]

7. Stratospheric Chemistry

Ozone Vertical Distribution

- It forms a protective shield that reduces the intensity of UV radiation (with wavelengths between 0.23 and 0.32 μm) from the sun that reaches the earth's surface.
- Because of the absorption of UV radiation by O_3, it determines the vertical profile of temperature in the stratosphere.
- It is involved in many stratospheric chemical reactions.

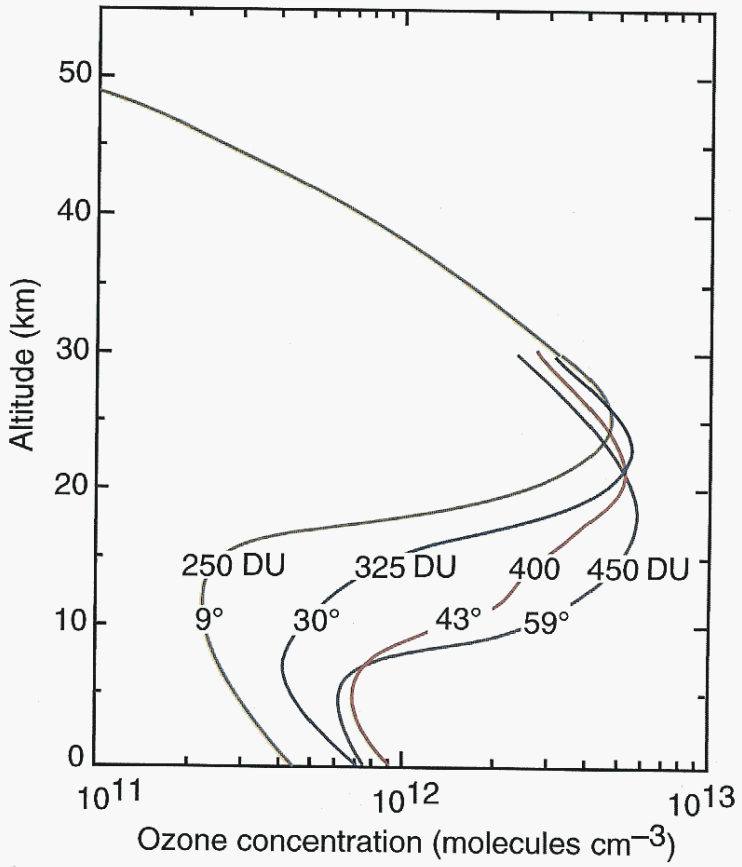


Fig. 5.16 Mean vertical distributions of ozone concentrations based on measurements at different latitudes (given in degrees). Note the increase in the total ozone column abundance (given in DU) with increasing latitude. [Adapted from G. Brasseur and S. Solomon, *Aeronomy of the Middle Atmosphere*, D. Reidel Pub. Co., 1984, Fig. 5.7, p. 215. Copyright 1984 D. Reidel Pub. Co., with kind permission of Springer Science and Business Media.]

The Ozone Layer

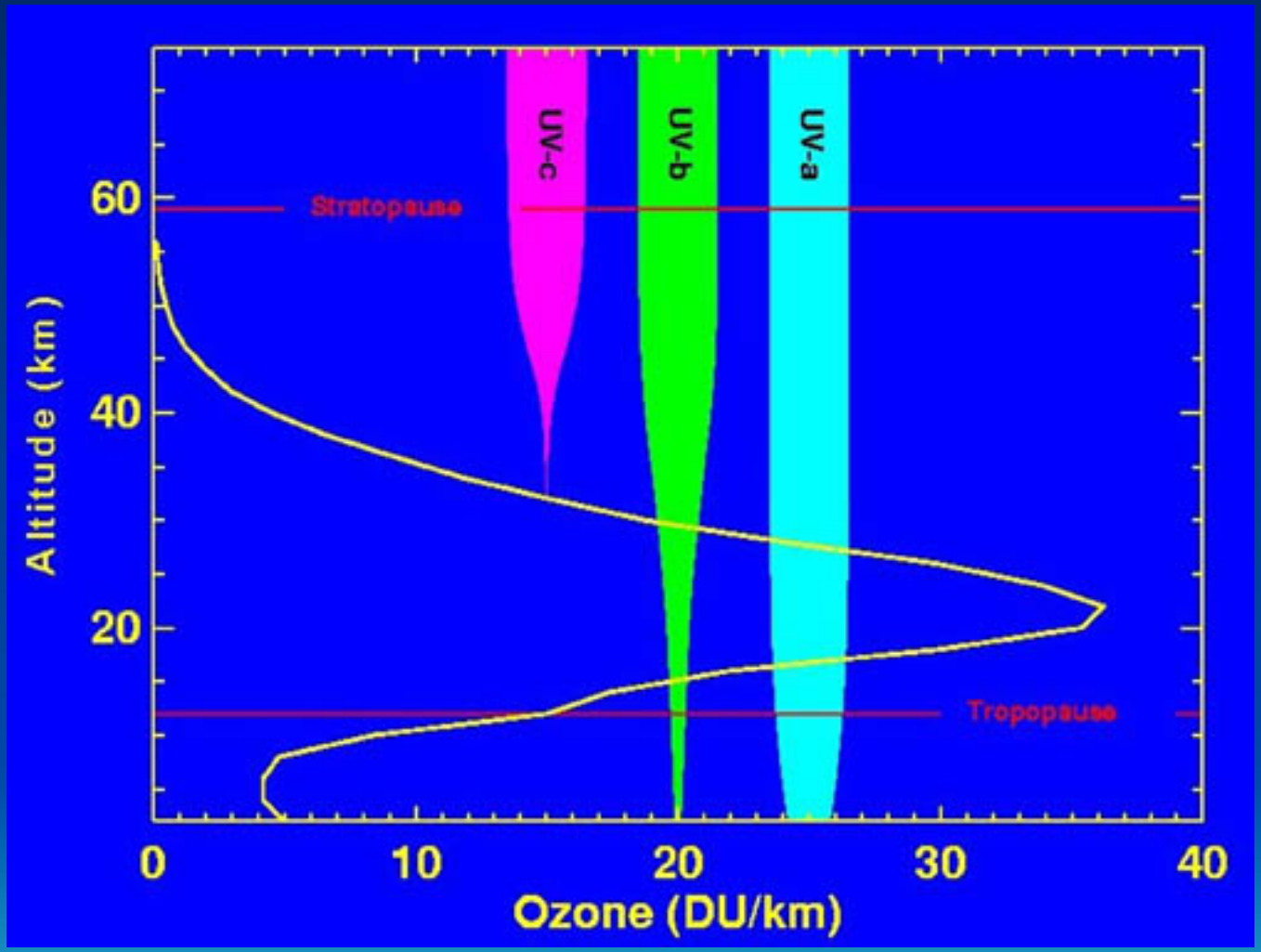
The **ozone layer**, or **ozonosphere layer** (rarely used term), is that part of the Earth's atmosphere which contains relatively high concentrations of ozone (O_3). "Relatively high" means a few parts per million - much higher than the concentrations in the lower atmosphere but still small compared to the main components of the atmosphere.

The ozone layer was discovered in 1913 by the French physicists Charles Fabry and Henri Buisson. Its properties were explored in detail by the British meteorologist G. M. B. Dobson, who developed a simple spectrophotometer that could be used to measure stratospheric ozone from the ground. Between 1928 and 1958 Dobson established a worldwide network of ozone monitoring stations which continues to operate today.

The "Dobson unit", a convenient measure of the total amount of ozone in a column overhead, is named in his honor.

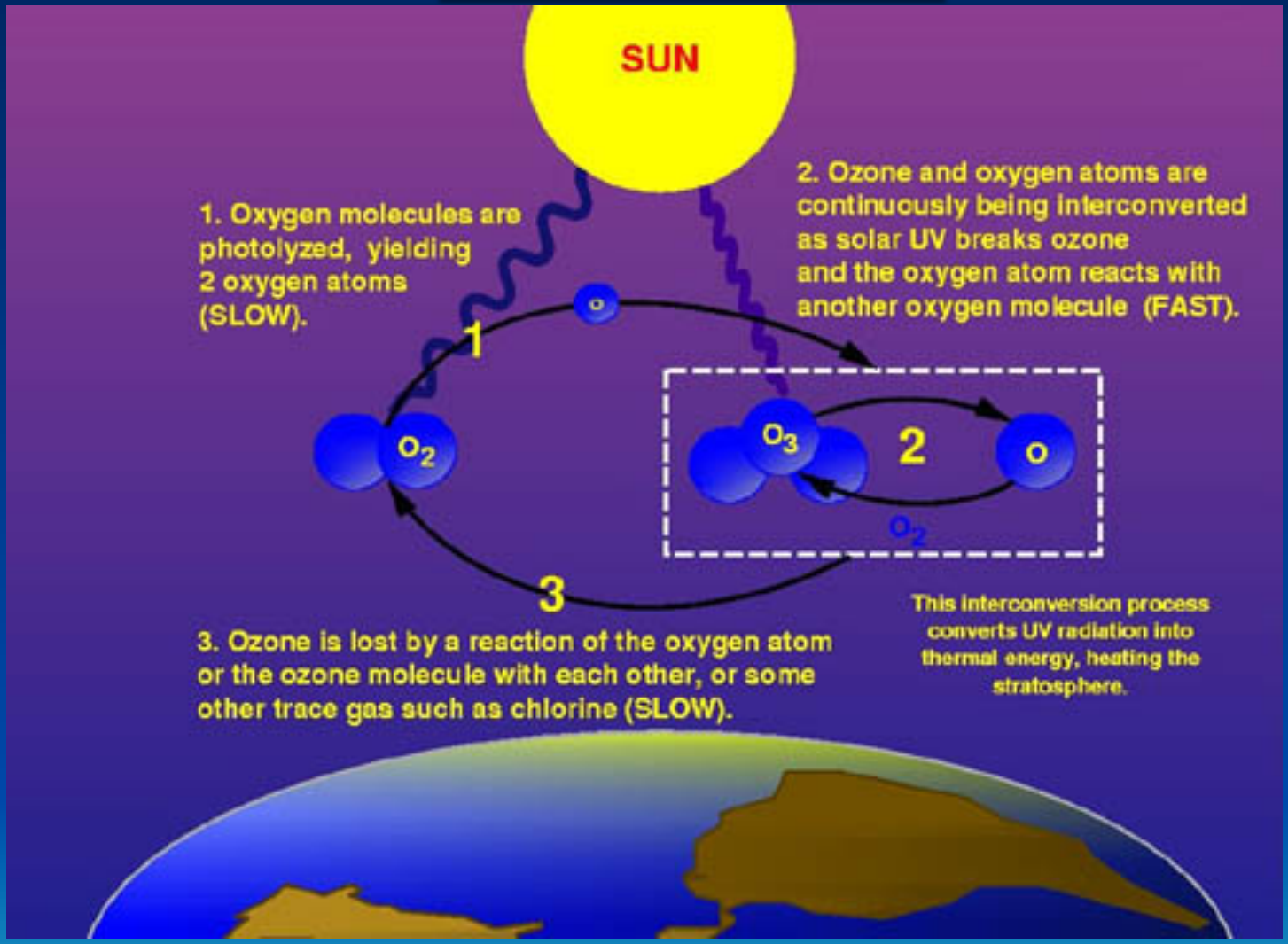
http://www.search.com/reference/Ozone_layer

Solar UV Radiation and Ozone



http://en.wikipedia.org/wiki/Image:Ozone_altitude_UV_graph.jpg

The Sun and Ozone



http://en.wikipedia.org/wiki/Image:Ozone_cycle.jpg

Techniques for Measuring Ozone

5.5 Continued

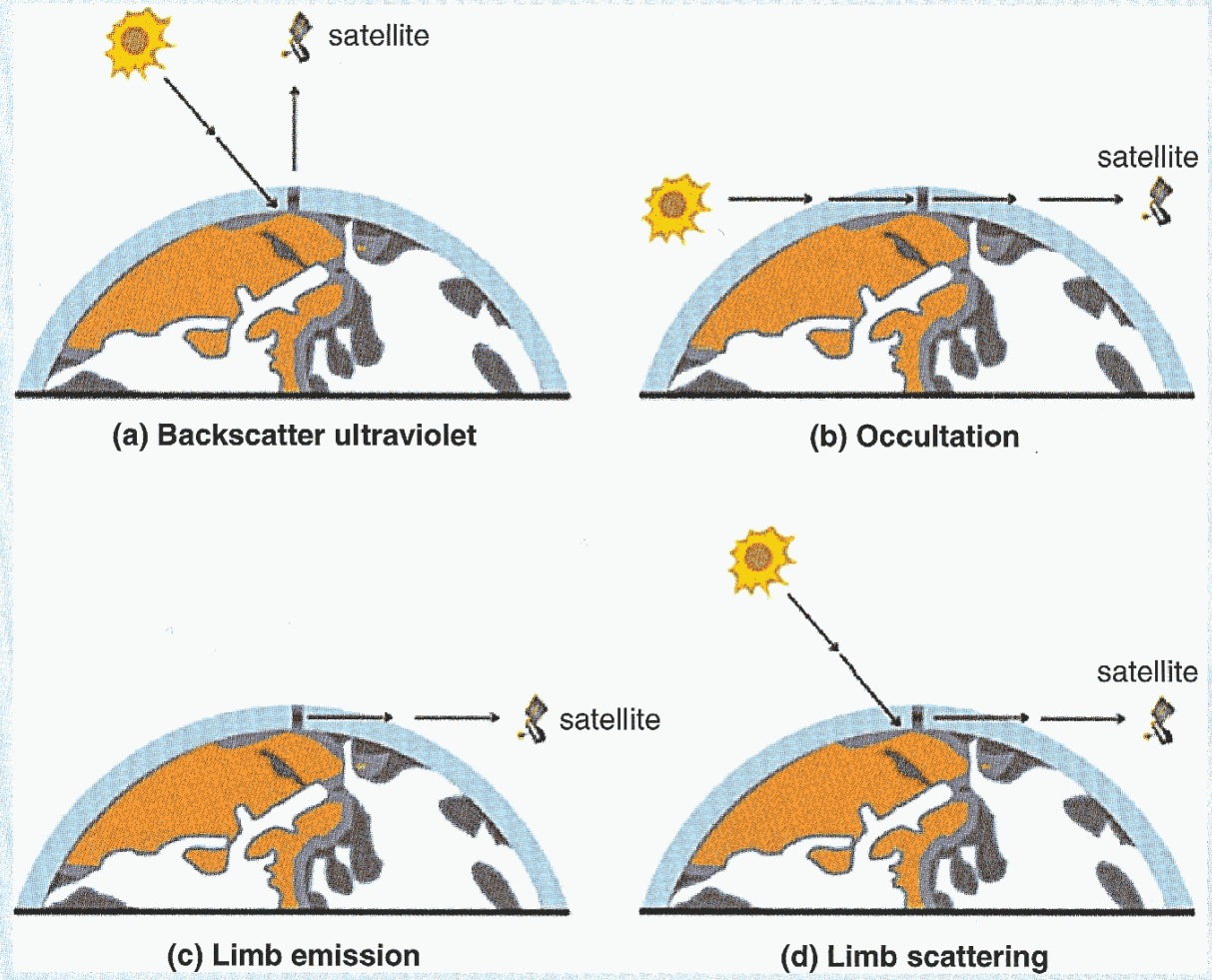
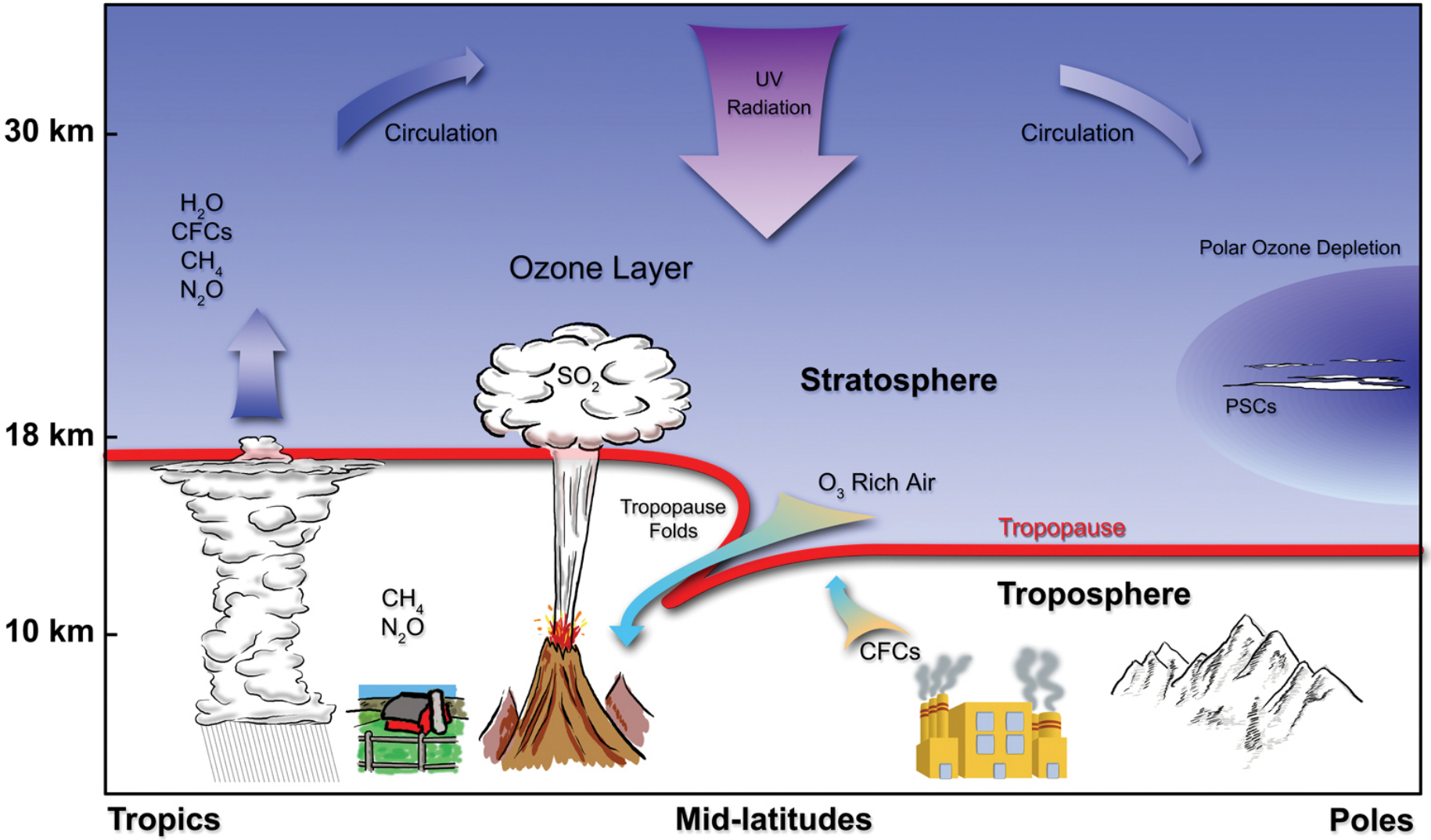


Fig. 5.17 Four passive techniques for measuring ozone from satellites. [Courtesy of P. Newman, NASA Goddard Space Flight Center.]

Processes Influencing Ozone



http://earthobservatory.nasa.gov/Library/Aura/Images/StratosphericChemical_HiRes.jpg

Chapman Chemistry and Ozone

$O_2 + hv \rightarrow 2O$	j_a	Slow
$O + O_2 + M \rightarrow O_3 + M$	k_b	Fast
$O_3 + hv \rightarrow O_2 + O$	j_c	Fast
$O + O_3 \rightarrow 2\ O_2$	k_d	Slow

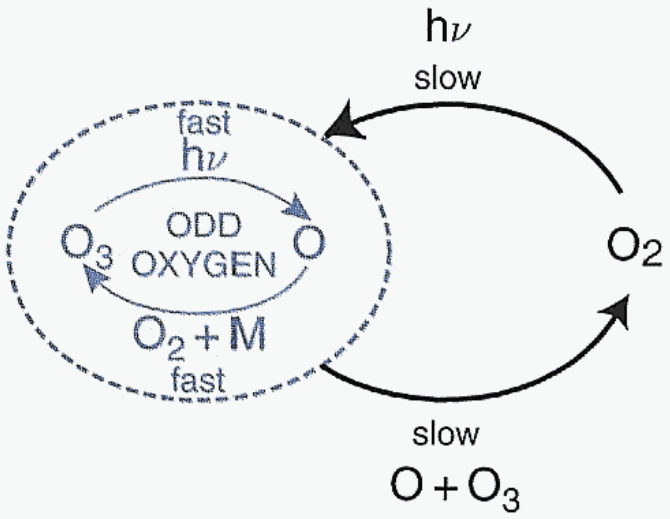


Fig. 5.18 Schematic of the Chapman reactions. [Adapted from *The Chemistry and Physics of Stratospheric Ozone*, A. Dessler, Academic Press, p. 44, copyright (2000), with permission from Elsevier.]

Solution of Chemical Equations (Chapman Chemistry)

$O_2 + hv \rightarrow 2O$	j_a	Slow	Let:
$O + O_2 + M \rightarrow O_3 + M$	k_b	Fast	$n_1 = [O]$ Atomic Oxygen
$O_3 + hv \rightarrow O_2 + O$	j_c	Fast	$n_2 = [O_2]$ Molecular Oxygen
$O + O_3 \rightarrow 2\,O_2$	k_d	Slow	$n_3 = [O_3]$ Ozone

Atomic Oxygen

$$\frac{dn_1}{dt} = 2j_a n_2 - k_b n_1 n_2 n_M + j_c n_3 - k_d n_1 n_3$$

In steady state:

$$2j_a n_2 + j_c n_3 = k_b n_1 n_2 n_M + k_d n_1 n_3$$

Ozone

$$\frac{dn_3}{dt} = k_b n_1 n_2 n_M - j_c n_3 - k_d n_1 n_3$$

These last two equations imply:

$$\frac{dn_3}{dt} = 2j_a n_2 - 2k_d n_1 n_3$$

Solution of Chemical Equations (Chapman Chemistry)

$O_2 + hv \rightarrow 2O$	j_a	Slow
$O + O_2 + M \rightarrow O_3 + M$	k_b	Fast
$O_3 + hv \rightarrow O_2 + O$	j_c	Fast
$O + O_3 \rightarrow 2\,O_2$	k_d	Slow

Let:
$n_1 = [O]$ Atomic Oxygen
$n_2 = [O_2]$ Molecular Oxygen
$n_3 = [O_3]$ Ozone

Atomic Oxygen

$$\frac{dn_1}{dt} = 2j_a n_2 - k_b n_1 n_2 n_M + j_c n_3 - k_d n_1 n_3$$

In steady state:

$$2j_a n_2 + j_c n_3 = k_b n_1 n_2 n_M + k_d n_1 n_3$$

Using only the Fastest Two Reactions

$$j_c n_3 = k_b n_1 n_2 n_M$$

The last relation implies:

$$n_1 = \frac{j_c n_3}{k_b n_2 n_M}$$

Solution of Chemical Equations (Chapman Chemistry)

$O_2 + hv \rightarrow 2O$	j_a	Slow
$O + O_2 + M \rightarrow O_3 + M$	k_b	Fast
$O_3 + hv \rightarrow O_2 + O$	j_c	Fast
$O + O_3 \rightarrow 2\,O_2$	k_d	Slow

Let:
$n_1 = [O]$ Atomic Oxygen
$n_2 = [O_2]$ Molecular Oxygen
$n_3 = [O_3]$ Ozone

Ozone Abundance

$$\frac{dn_3}{dt} = 2j_a n_2 - 2k_d n_1 n_3$$

$$n_1 = \frac{j_c n_3}{k_b n_2 n_M}$$

Finally:

$$\frac{dn_3}{dt} = 2j_a n_2 - \frac{2k_d j_c n_3^2}{k_b n_2 n_M}$$

In Steady State, we can solve algebraically for n_3 in terms of background atmospheric properties and known rate coefficients.

Ozone and Catalytic Cycles

$O + O_2 + M \rightarrow O_3 + M$

$O_3 + h\nu \rightarrow O_2 + O$

Net: Nothing (no net change)

$OH + O_3 \rightarrow HO_2 + O_2$

$HO_2 + O \rightarrow OH + O_2$

Net: $O + O_3 \rightarrow 2\ O_2$

$NO + O_3 \rightarrow NO_2 + O_2$

$NO_2 + O \rightarrow NO + O_2$

Net: $O + O_3 \rightarrow 2\ O_2$

$Cl + O_3 \rightarrow ClO + O_2$

$ClO + O \rightarrow Cl + O_2$

Net: $O + O_3 \rightarrow 2\ O_2$

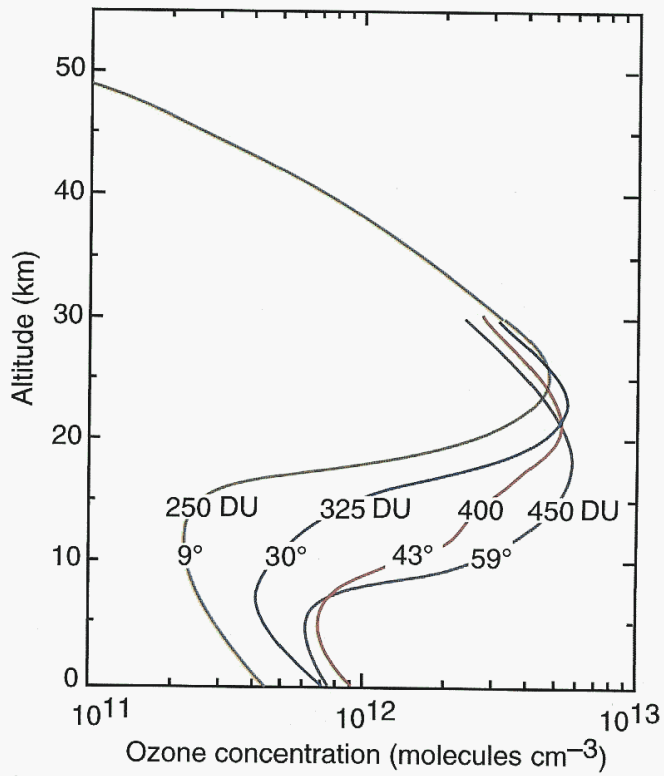


Fig. 5.16 Mean vertical distributions of ozone concentrations based on measurements at different latitudes (given in degrees). Note the increase in the total ozone column abundance (given in DU) with increasing latitude. [Adapted from G. Brasseur and S. Solomon, *Aeronomy of the Middle Atmosphere*, D. Reidel Pub. Co., 1984, Fig. 5.7, p. 215. Copyright 1984 D. Reidel Pub. Co., with kind permission of Springer Science and Business Media.]

Anthropogenic Effects on Ozone

Industrially manufactured chlorofluorocarbons (CFCs): compounds containing Cl, F, and C. They were produced for non-toxic, non-flammable refrigerants.

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

In the troposphere CFCs have residence times of hundreds of years. But in once they are transported into the stratosphere, UV radiation photo-dissociates them, releasing highly reactive Cl.

By 1990, ~85% of the chlorine in the stratosphere was anthropogenic.

The first measurements indicating a global effect of anthropogenic Cl on ozone were in the Antarctic.

$$CFCl_3 + h\nu \rightarrow CFCl_2 + Cl$$

$$CF_2Cl_2 + h\nu \rightarrow CF_2Cl + Cl$$

$$Cl + O_3 \rightarrow ClO + O_2$$
$$ClO + O \rightarrow Cl + O_2$$
Net: $O + O_3 \rightarrow 2\,O_2$

Antarctic Ozone Hole

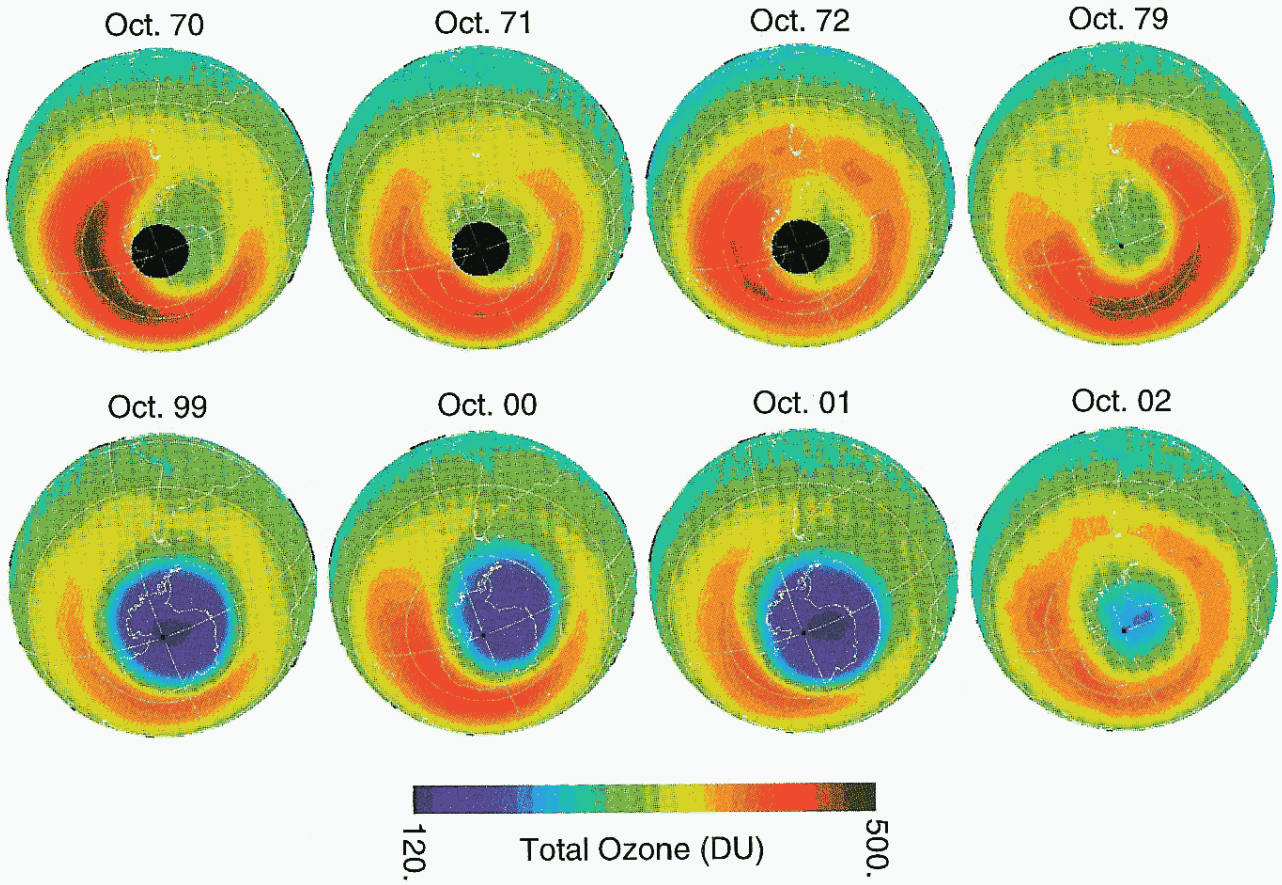
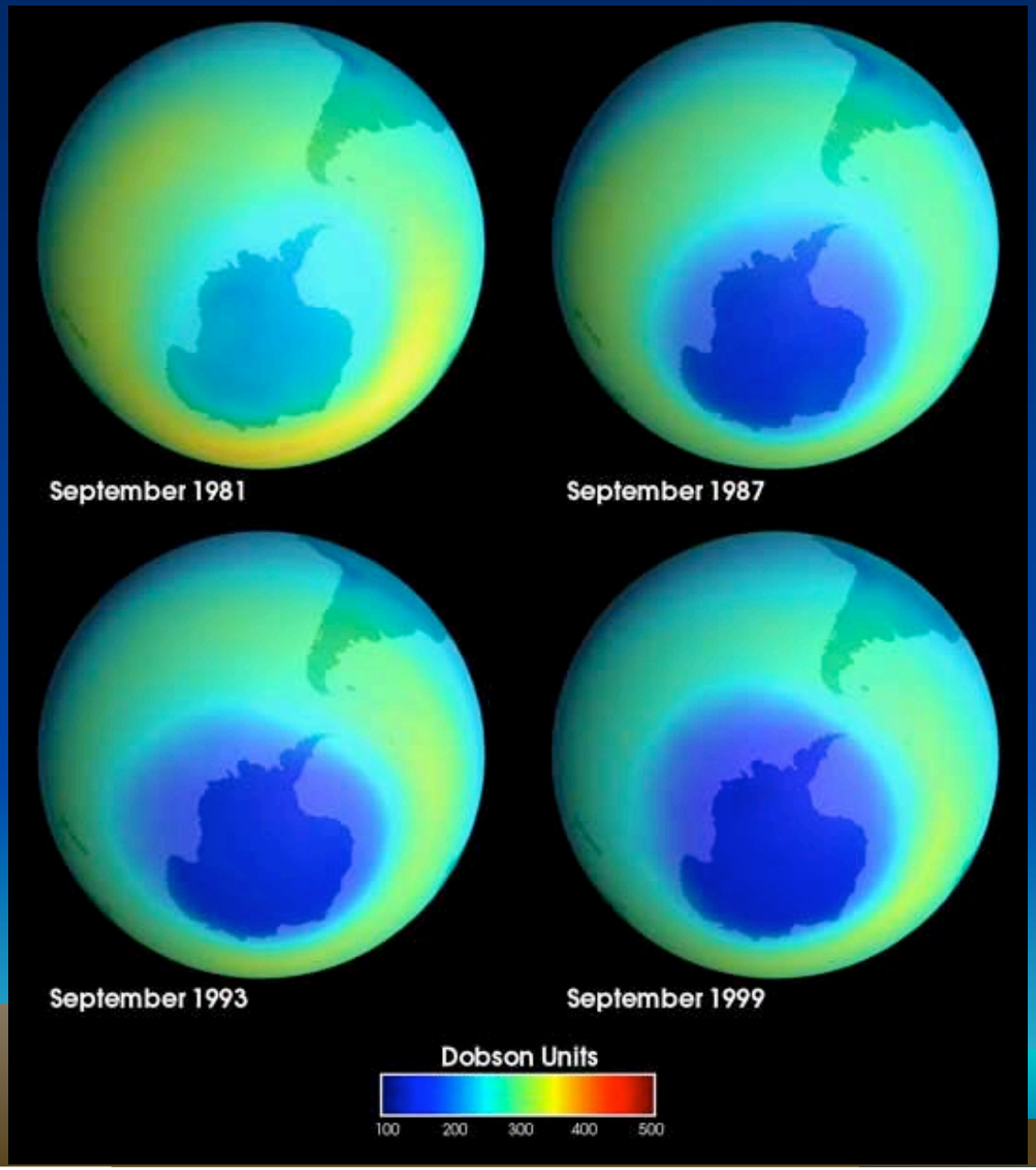
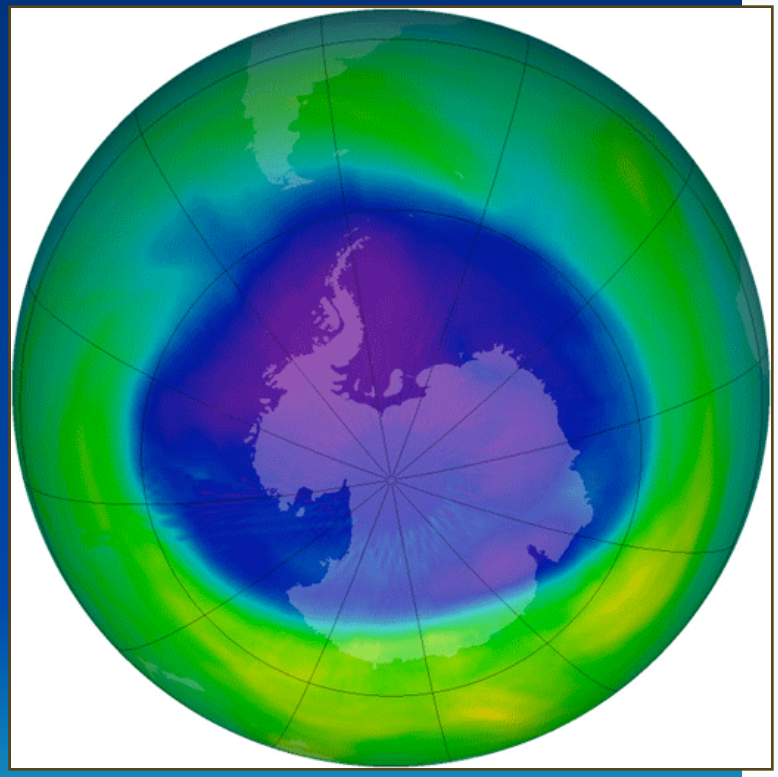


Fig. 5.19 Satellite observations of the total ozone column in the southern hemisphere during October for 8 years from 1970 to 2002. The color scale is in Dobson units (DU). The small black circles over the pole in 1970, 1971, and 1972 are a reflection of missing data. [Courtesy P. Newman, NASA Goddard Space Flight Center.]

The Ozone Hole



Aerial Extent of the Ozone Hole



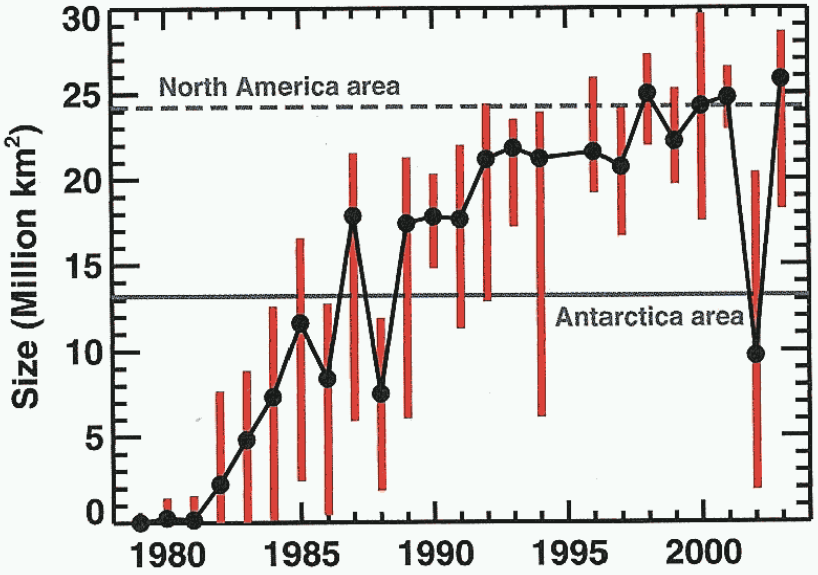


Fig. 5.20 Average areal extent of the ozone hole (defined as less than 220 Dobson units) averaged from September 7–October 13 of each year from 1979 to 2003. Vertical red bars are the range of values for each period. Year-to-year variations are caused by temperature fluctuations near the polar vortex edge. Warmer years have smaller holes (e.g., 2002), whereas colder years have larger ozone holes (e.g., 2003). The blue horizontal line highlights the total area of the Antarctic continent; for comparison, the area of North America (dashed blue line) is about twice the area of Antarctica. (Courtesy of P. Newman, NASA Goddard Space Flight Center.)

The Antarctic Polar Vortex

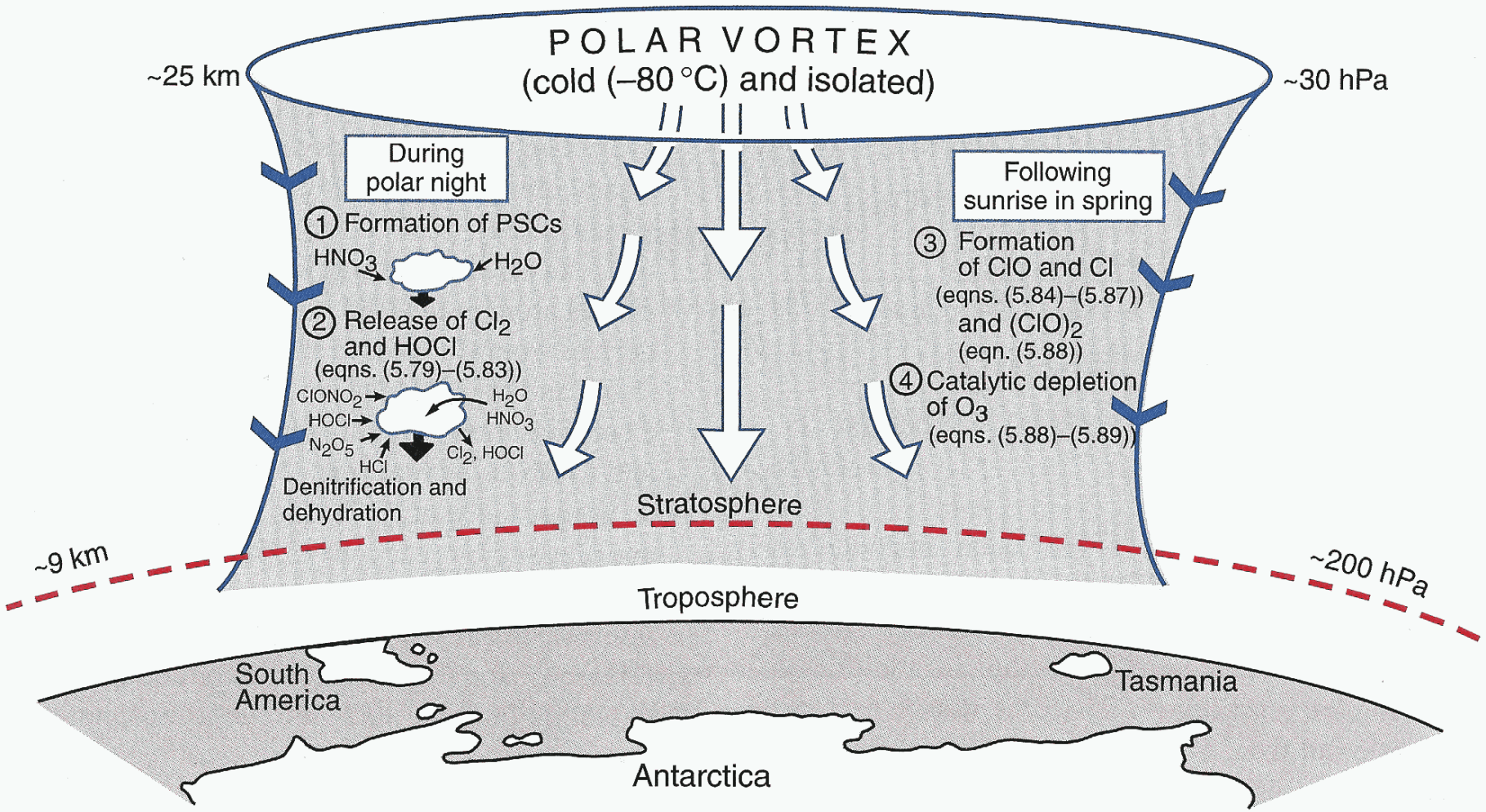


Fig. 5.21 Schematic of the polar vortex (blue) over Antarctica. Large arrows indicate cold descending air. The sequence of events (1 through 4) leading to the Antarctic ozone hole is summarized. For clarity, bromine reactions are not shown. See text for details.

Ozone Hole Formation

During Polar Night:

1) Cold, stagnant, isolated air leads to formation of polar stratospheric clouds (PSCs, ice particles of H_2O and HNO_3).
2) Heterogeneous chemistry inside the PSCs produce and release the molecules Cl_2 and HOCl.

During Polar Spring:

3) Immediately upon sunrise, photolysis of HOCl and Cl_2 produces free Cl atoms.
4) Free Cl atoms rapidly catalyzes the destruction of O_3, leading to extreme depletion of lower stratospheric ozone.

Formation and Evolution of the Ozone Hole

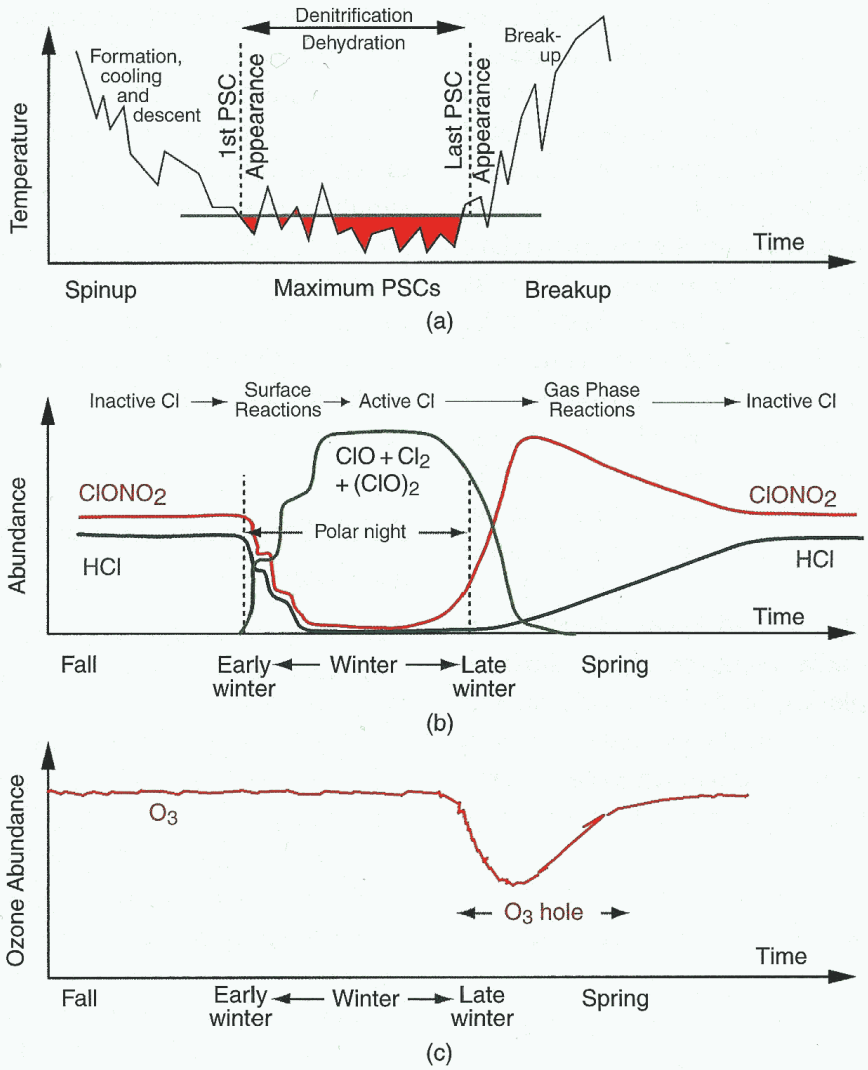


Fig. 5.22 Schematic illustrating time evolution of the main processes associated with the development of the Antarctic ozone hole. (a) The Antarctic vortex. Polar stratospheric clouds (PSCs) form, and reactions occur on the PSC particles when stratospheric temperatures fall into the region colored red. (b) Chlorine reservoirs in the Antarctic vortex. The inactive reservoir species $ClONO_2$ and HCl are converted into the active chlorine species Cl_2, ClO, and $(ClO)_2$ when the temperature falls below the value required for the formation of PSCs. The reservoir species return after the disappearance of the PSCs. (c) Ozone in the Antarctic vortex. Ozone is depleted rapidly by photolysis when the sun rises in September. As the active chlorine species are depleted, and the vortex breaks up, the concentration of O_3 rises. [Figures 5.22a and 5.22c adapted from World Meteorological Organization *Scientific Assessment of Ozone Depletion*, 1994. Figure 5.22b adapted with permission from Webster et al., *Science* **261**, 1131 (1993), Copyright 1993 AAAS.]

Northern Hemisphere Ozone Depletion

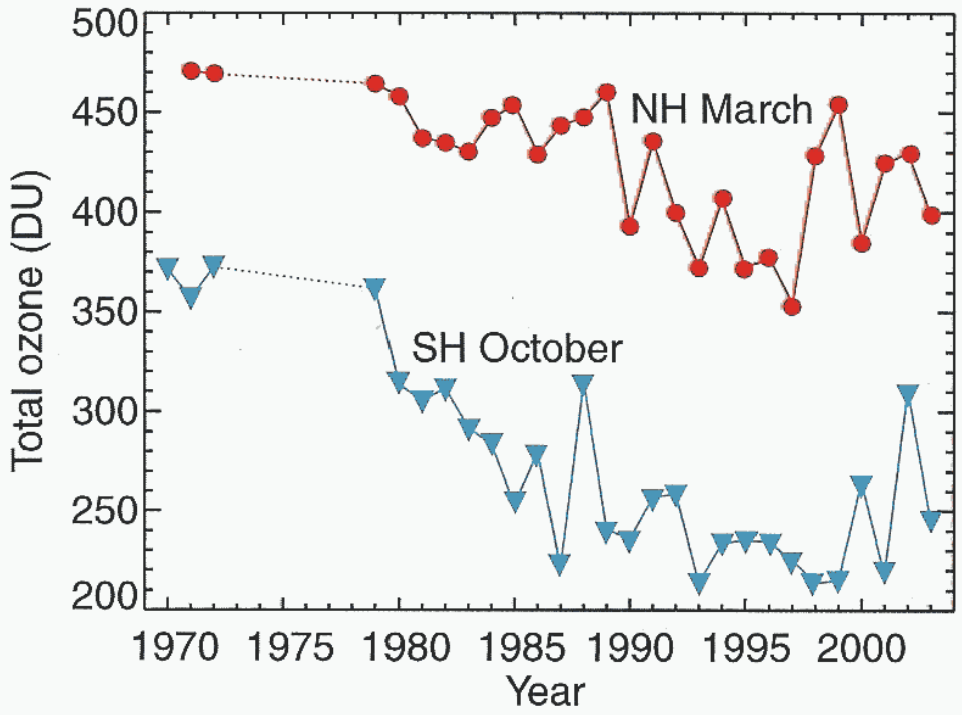


Fig. 5.23 Average ozone columns between latitudes 63°–90° for the northern hemisphere in March (red line and symbols) and the southern hemisphere in October (blue line and symbols). [Adapted with courtesy of P. Newman, NASA Goddard Space Flight Center.]

Montreal Protocol on Substances that Deplete the Ozone Layer

1987 – Montreal Protocol signed

1992 – Copenhagen amendment called for complete elimination of CFC by 1996.

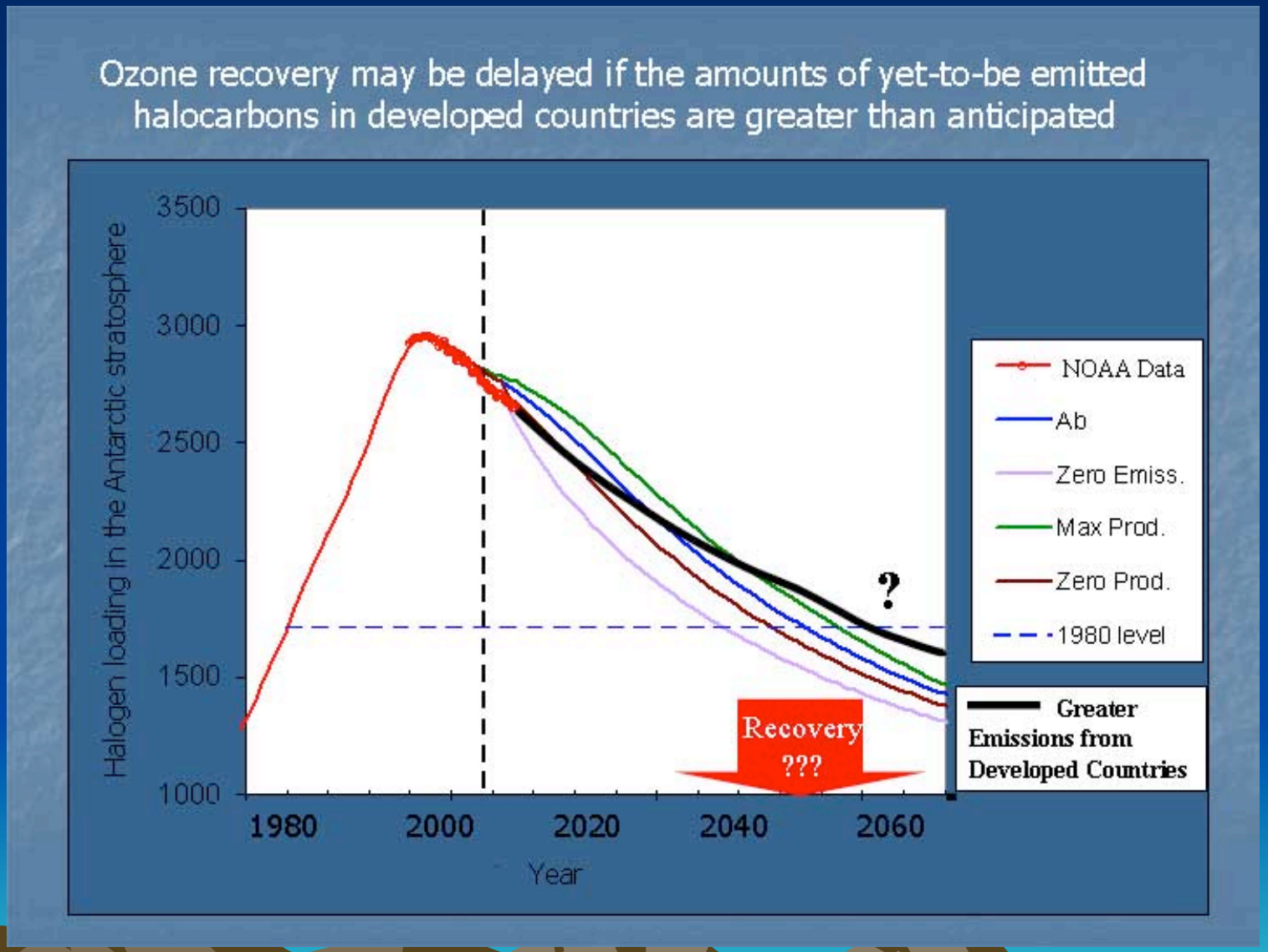
1995 – Vienna Amendment called for complete elimination of HCFCs by 2020

2001 – First evidence that stratospheric levels of anthropogenic Cl was leveling off.

2005 – First evidence that stratospheric levels of Cl were decreasing.

Several decades will be required for all stratospheric Cl of anthropogenic origin to disappear.

Recovery of the Ozone Layer



http://www.nasa.gov/centers/goddard/images/content/139177main_ozone_recover_hurst.jpg

Stratospheric Aerosols





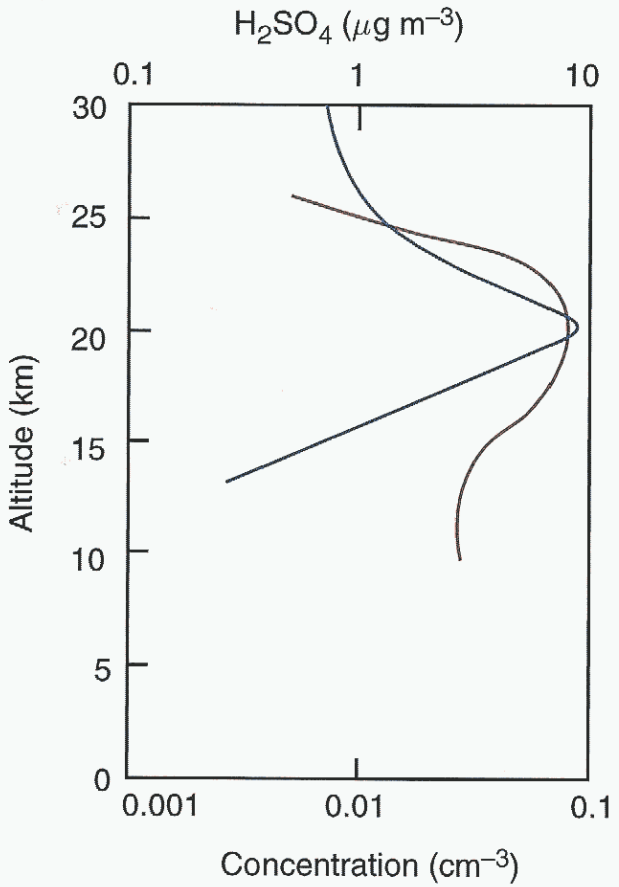


Fig. 5.24 Vertical profiles in the lower stratosphere of the number concentration of particles with radius ~0.1–2 μm (red line and bottom scale) and mass concentration of liquid sulfuric acid at standard temperature and pressure (blue line and upper scale). Measurements were obtained from balloons launched from midlatitudes. [Adapted from P. V. Hobbs, *Introduction to Atmospheric Chemistry*, Camb. Univ. Press, 2000, p. 179. Reprinted with permission of Cambridge University Press.]

Stratospheric Aerosols



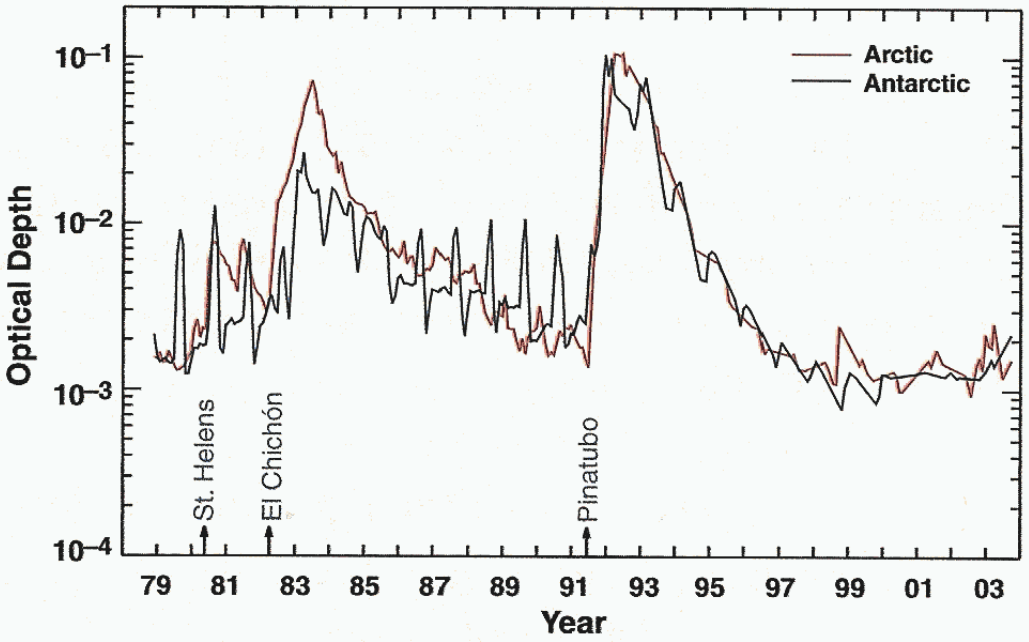


Fig. 5.25 Monthly averaged stratospheric vertical column aerosol optical depths at a wavelength of 1 μm, integrated from 40 km down through 2 km above the tropopause, from 1979 to 2003. "Arctic" data are for measurements north of 65 °N and "Antarctic" data are for measurements south of 65 °S. Some of the major volcanic eruptions during the past 25 years are indicated. The most conspicuous perturbations of optical depth occurred after the eruptions of El Chichón (4 April 1982) and Mt. Pinatubo (15 June 1991). Antarctic data prior to 1991, when measurements from a suitable satellite were available, indicate the presence of polar stratospheric clouds. [Courtesy of M. P. McCormick and NASA.]

Stratospheric Sulfur Layer: Volcanic Perturbations

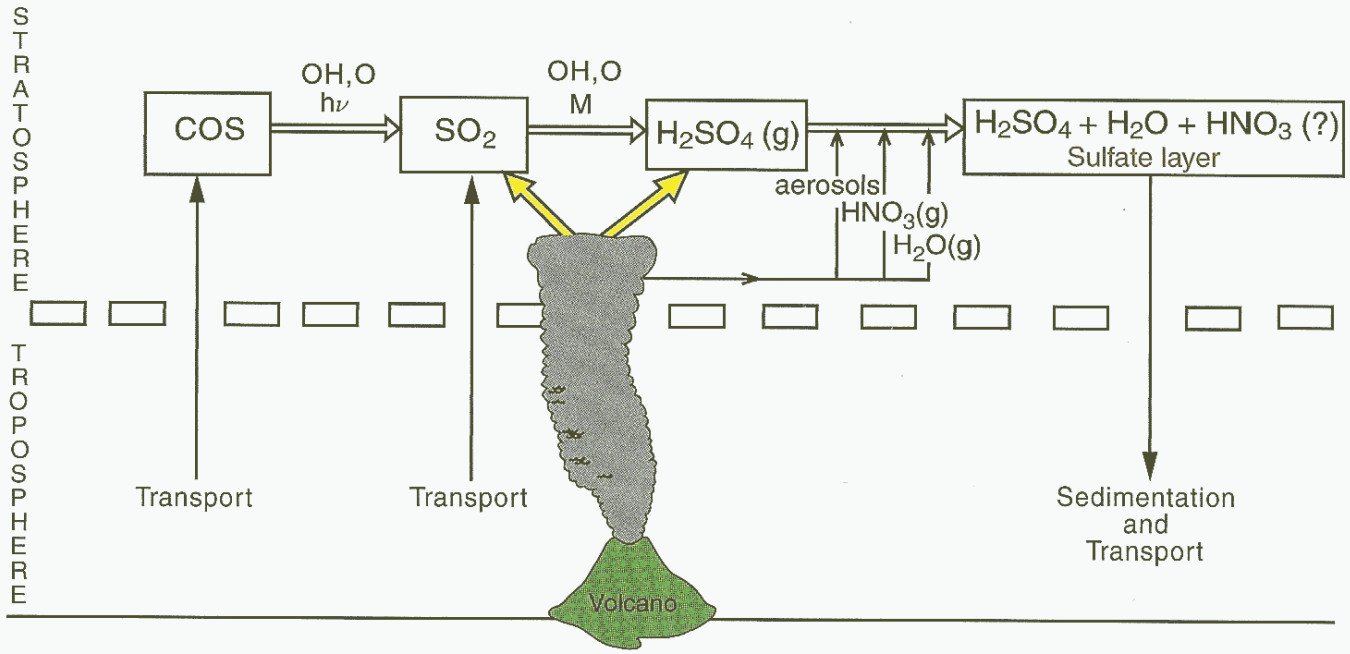


Fig. 5.26 Schematic of the processes responsible for the stratospheric sulfate layer. [Adapted from P. V. Hobbs, *Introduction to Atmospheric Chemistry*, Camb. Univ. Press, 2000, p. 182. Reprinted with the permission of Cambridge University Press.]

Stratospheric Aerosols; Sulfur in the Stratosphere

Stratospheric sulfate aerosols are produced primarily by oxidation of SO_2 to SO_3, followed by formation of H_2SO_4 that condenses with H_2O to form high altitude stratospheric haze.

$$OH + SO_2 + M \rightarrow HOSO_2 + M$$

$$HOSO_2 + O_2 \rightarrow HO_2 + SO_3$$

$$O + SO_2 + M \rightarrow SO_3 + M$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \text{ (condenses onto aerosols)}$$

Stratospheric Aerosols: The Junge Layer



Discussion Questions

1) What is it about the atmosphere that makes atmospheric chemistry so complex?
2) Does atmospheric chemistry drive climate or vice versa?
3) Would chemistry occur in the atmosphere without sunlight?
4) Could the ozone hole "grow" with time to eventually cover the entire globe?
5) If the Earth was completely cloud covered, would tropospheric chemistry cease?
6) In what situations do transport effects dominate over chemical effects?
7) If the Earth was in a global ice age (Snowball Earth episode) with complete ice cover and hence high surface albedo, would stratospheric chemistry be substantially different?