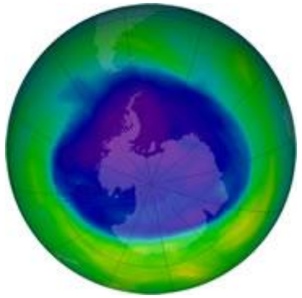
Stratospheric Chemistry - Ozone

1. Ozone layer and Solar Spectrum

2. O_3 formation/destruction
   → Chapman Reactions

3. Catalytic O_3 destruction

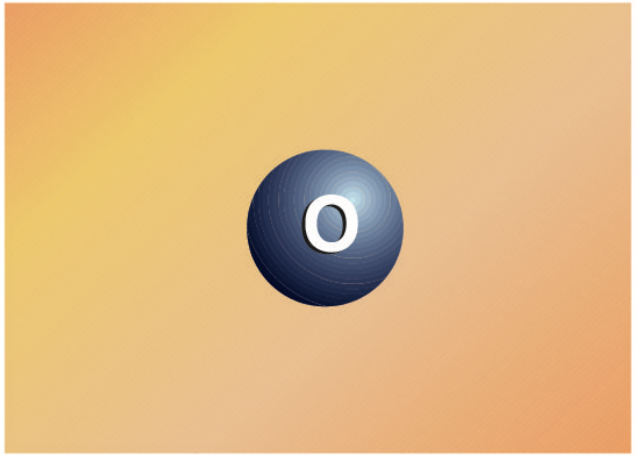


4. Null, 'holding' cycles & CFCs

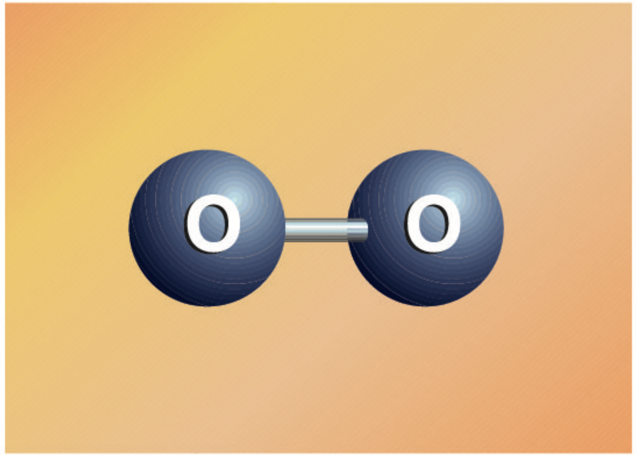
5. Antarctic and Arctic 'ozone hole' formation
   → Polar Stratospheric Clouds

Allotropes of Oxygen

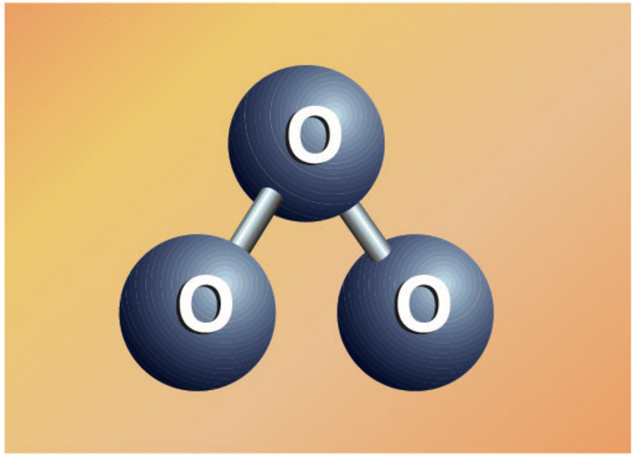
Oxygen atom (O)

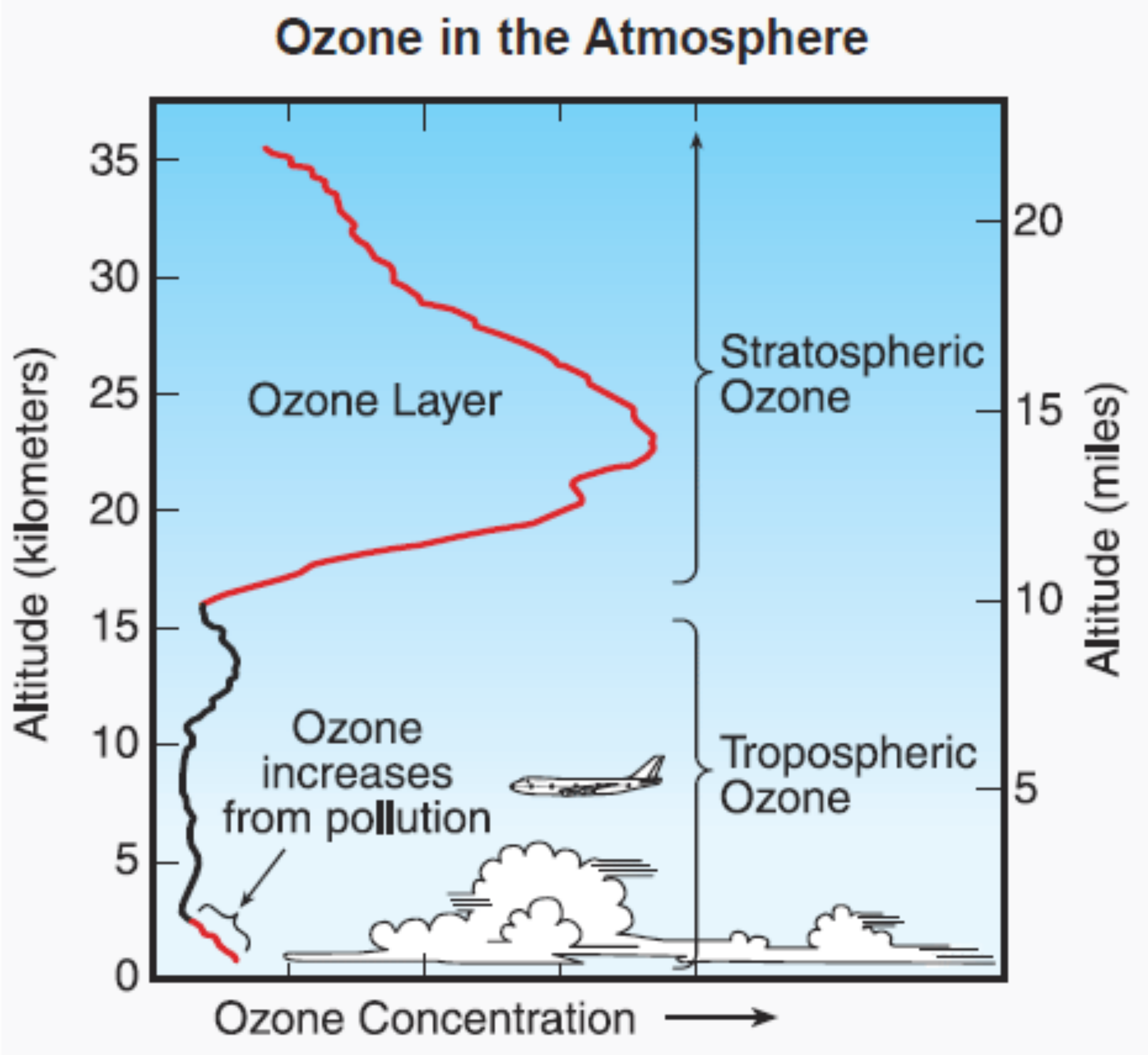


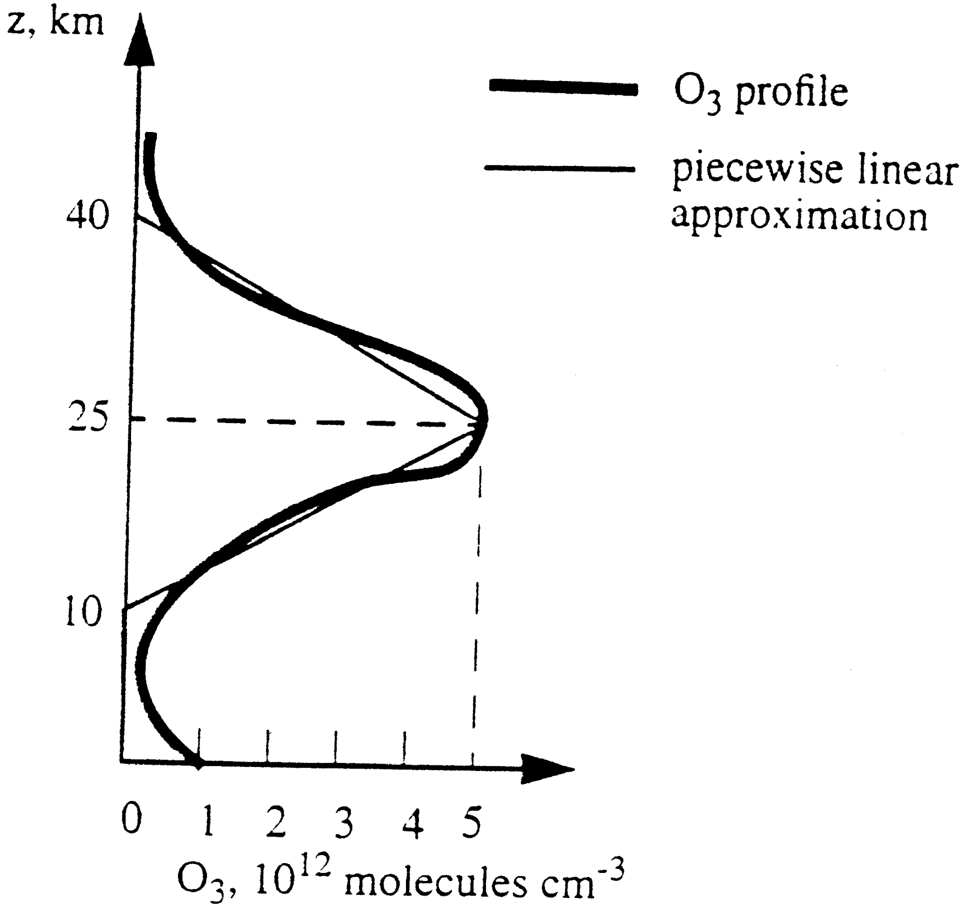
Oxygen molecule (O_2)

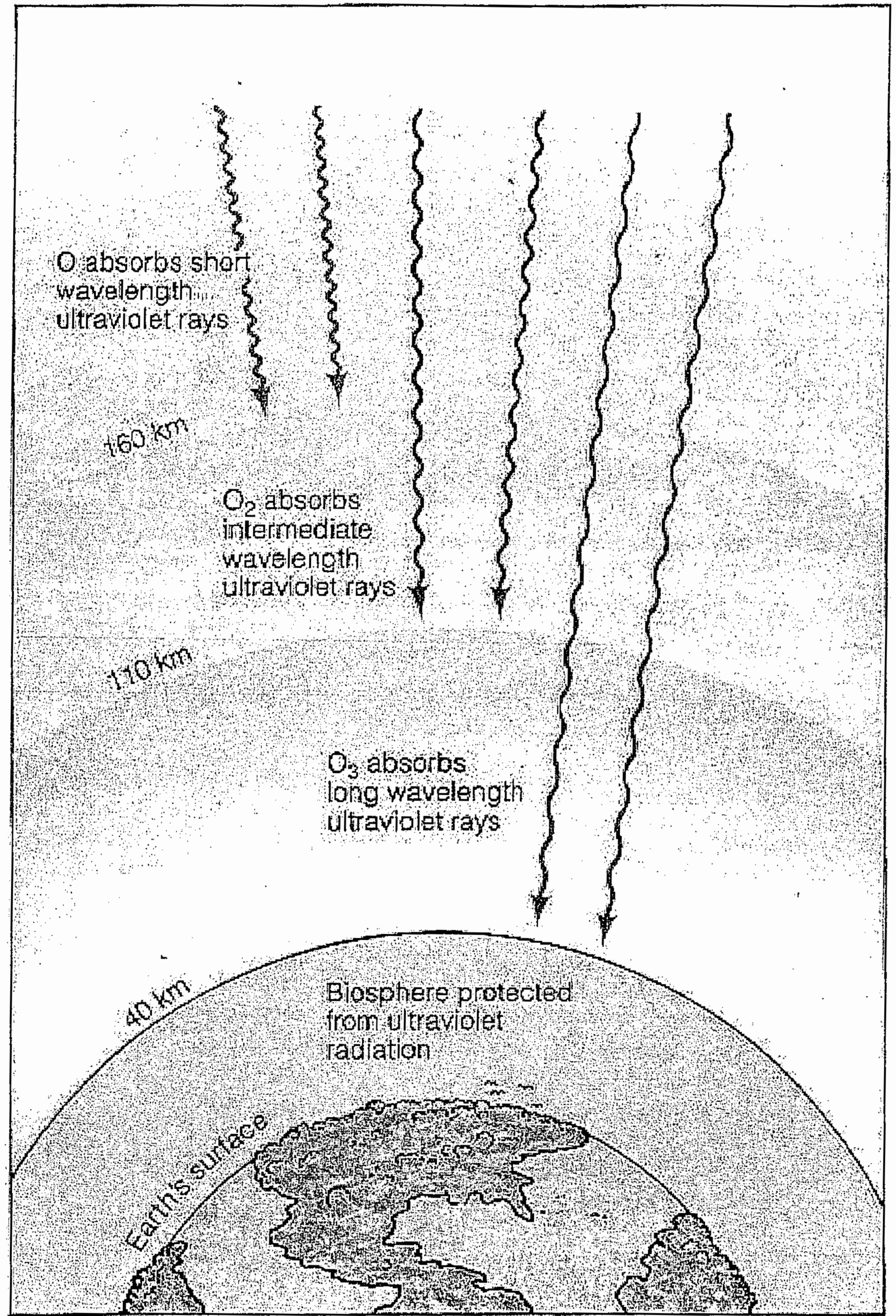


Ozone molecule (O_3)




Ozone in the Atmosphere
Altitude (kilometers)
35
30
25
20
15
10
5
0
Ozone Layer
Ozone increases from pollution
Stratospheric Ozone
Tropospheric Ozone
20
15
10
5
Altitude (miles)
Ozone Concentration


z, km
40
25
10
O3 profile
piecewise linear approximation
0
1
2
3
4
5
O3, 10^12 molecules cm^-3

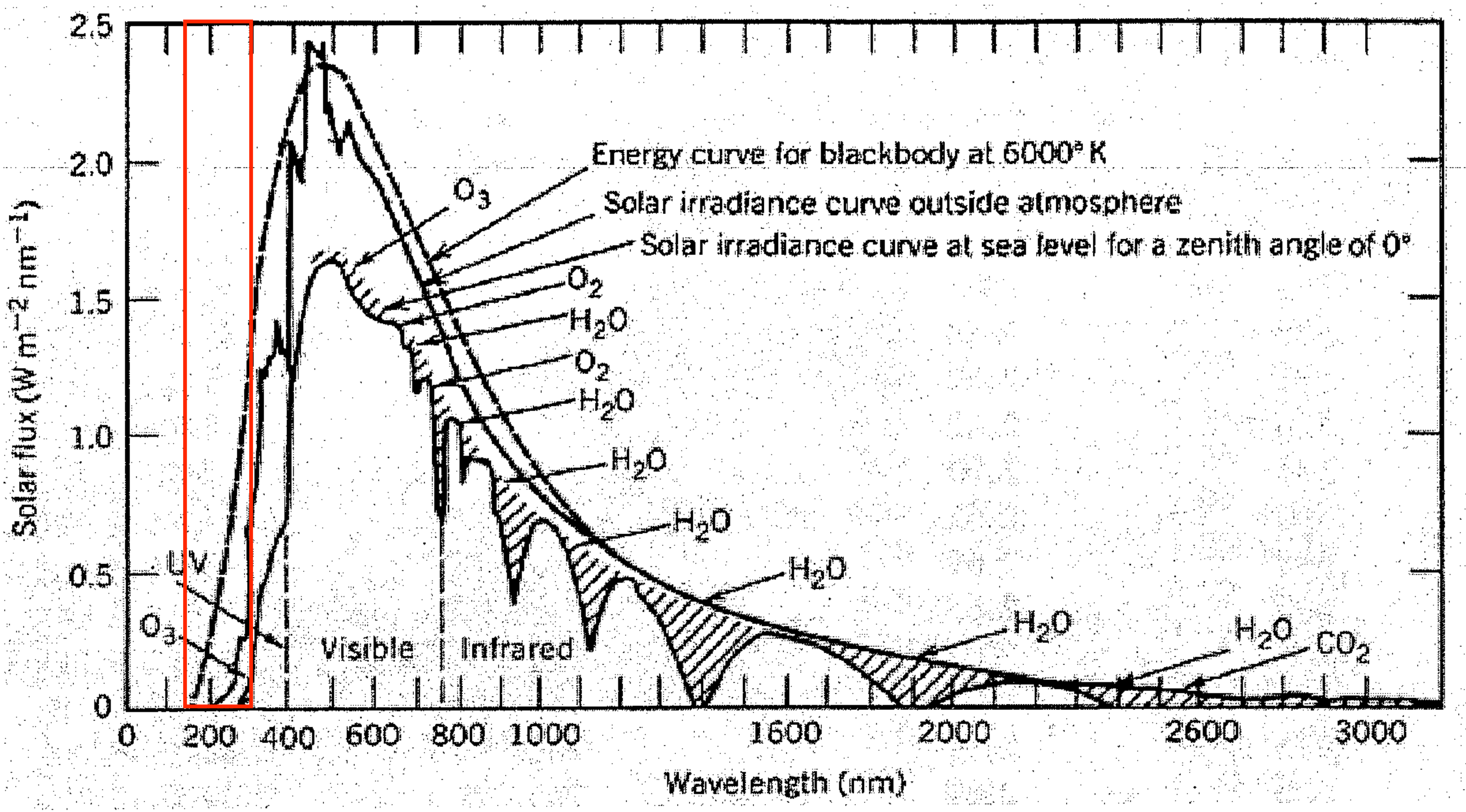


UV Absorption in Atmosphere

O absorbs $\lambda < 100$ nm

O_2 absorbs $\lambda < 200$ nm

O_3 absorbs $\lambda < 320$ nm



Energy curve for blackbody at 6000° K
Solar irradiance curve outside atmosphere
Solar irradiance curve at sea level for a zenith angle of 0°
O_3
O_2
H_2O
O_2
H_2O
H_2O
H_2O
H_2O
H_2O
H_2O
CO_2
UV
O_3
Visible
Infrared
Solar flux ($W\ m^{-2}\ nm^{-1}$)
2.5
2.0
1.5
1.0
0.5
0
0
200
400
600
800
1000
1600
2000
2600
3000
Wavelength (nm)

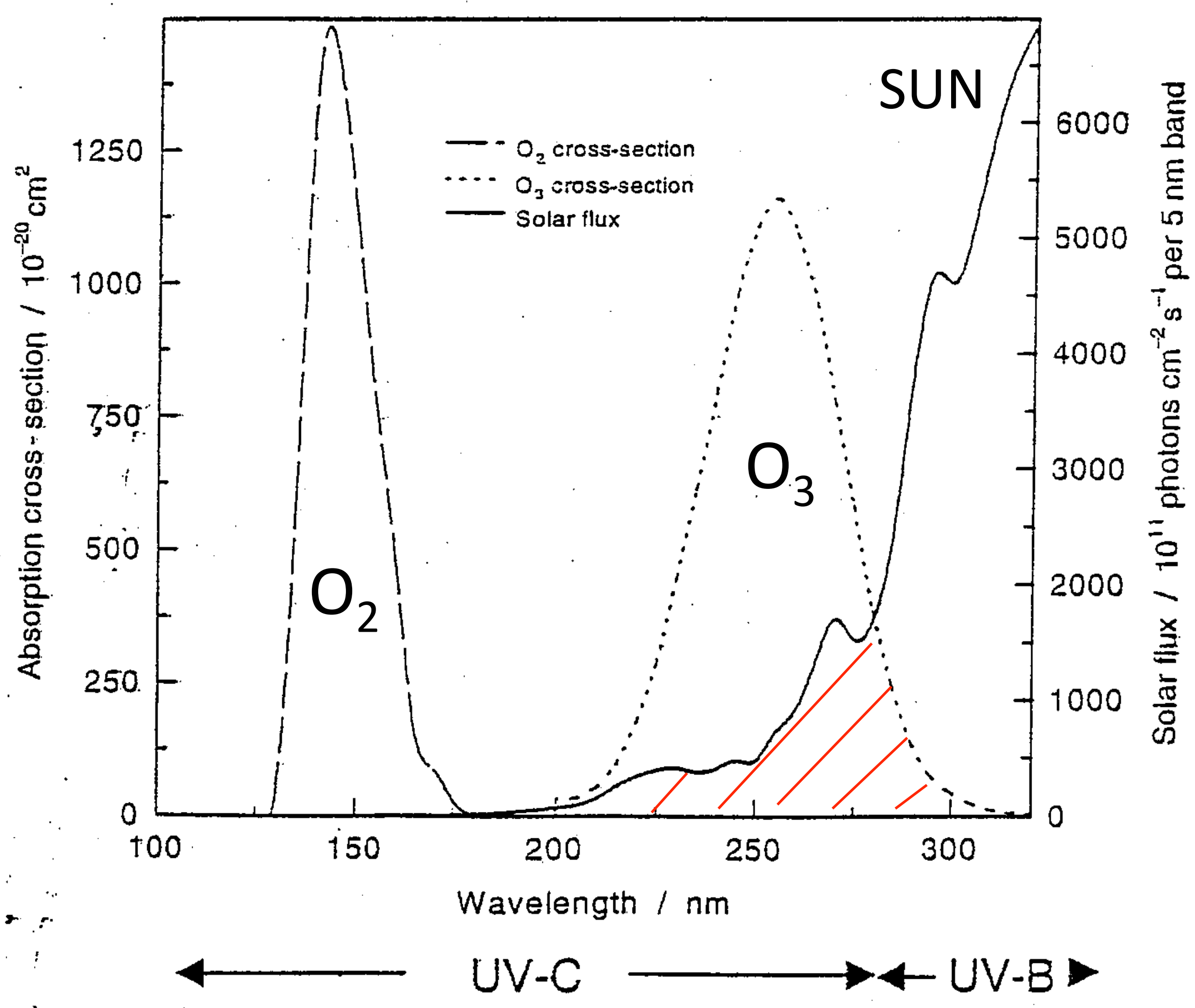
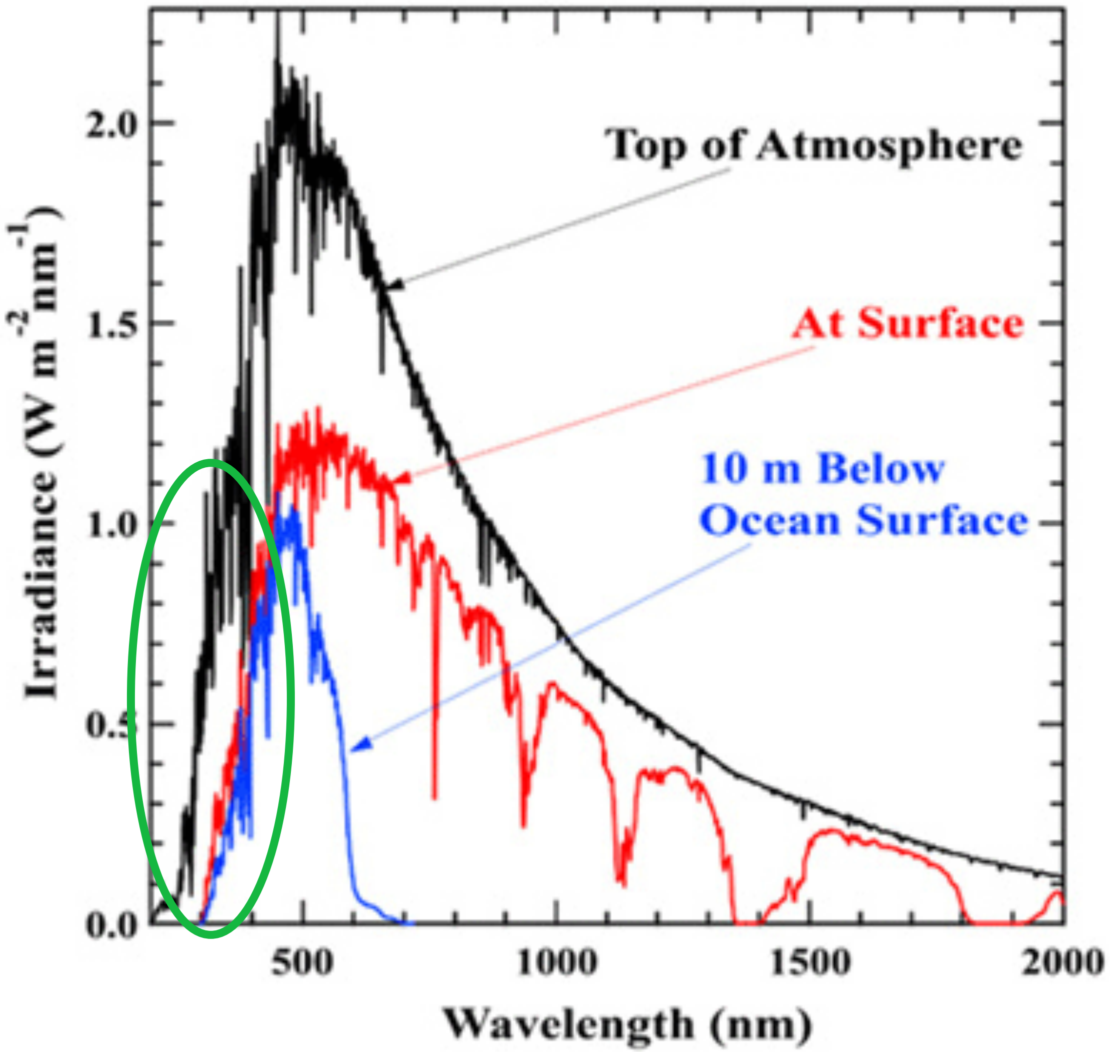
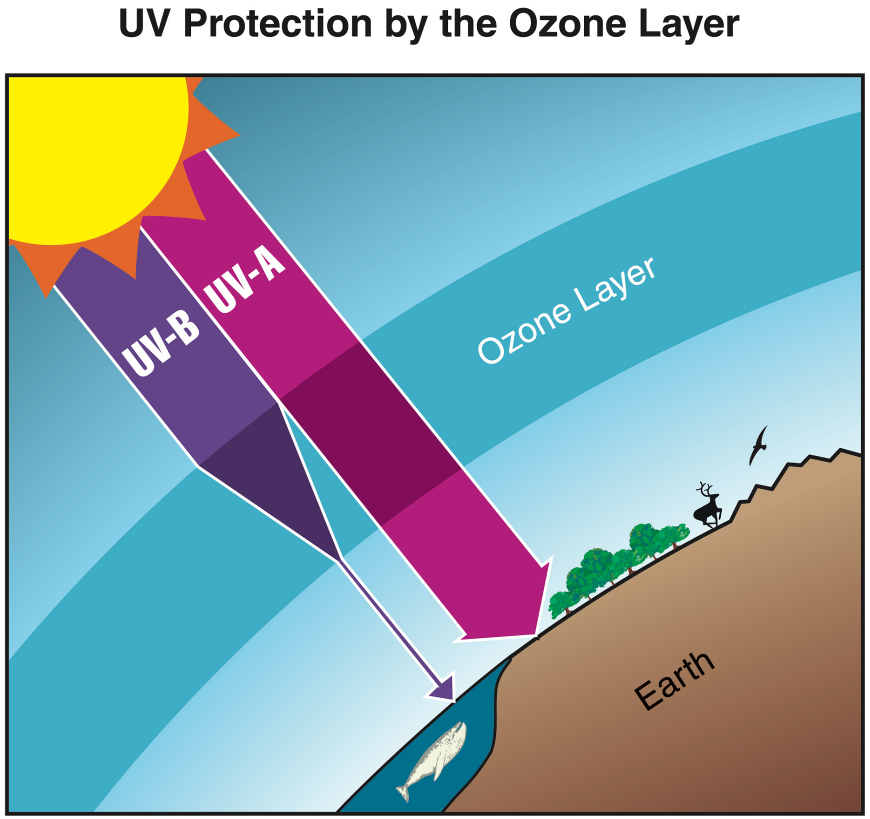


Fig. 3.2 Absorption cross-section of oxygen (broken line) and ozone (dotted line) compared to the solar flux density (solid line) over the region of biologically harmful ultraviolet radiation (Data from Chamberlain, J. W. and D. M. Hunten, *Theory of Planetary Atmospheres*, Academic Press; 1987. Reprinted with permission.)

Ozone: UV-b (280-320 nm) 'sunscreen'





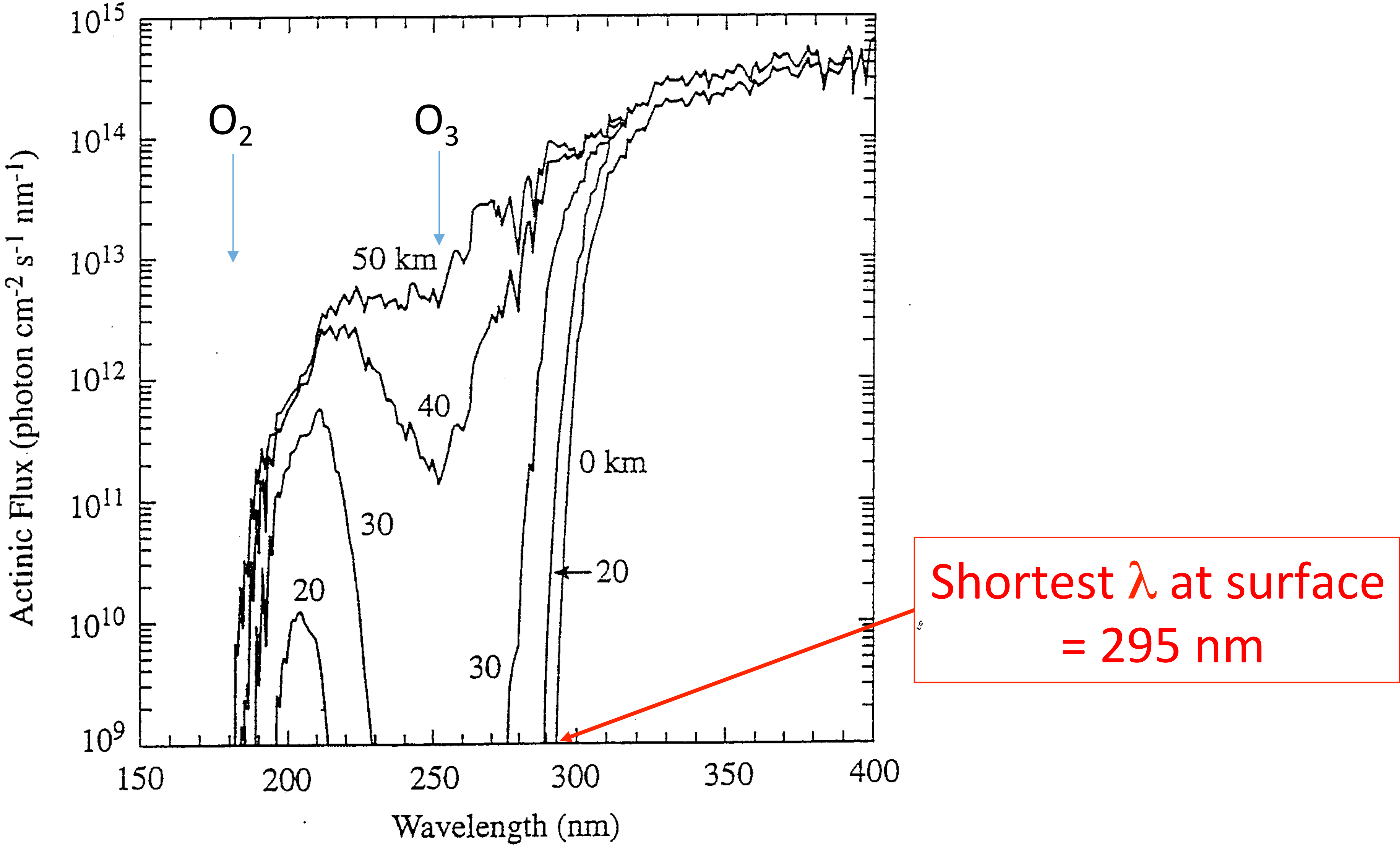


Fig. 10-2 Solar actinic flux at different altitudes, for typical atmospheric conditions and a 30° solar zenith angle. From DeMore, W. B., et al. *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling*. JPL Publication 97-4. Pasadena, Calif.: Jet Propulsion Lab, 1997.

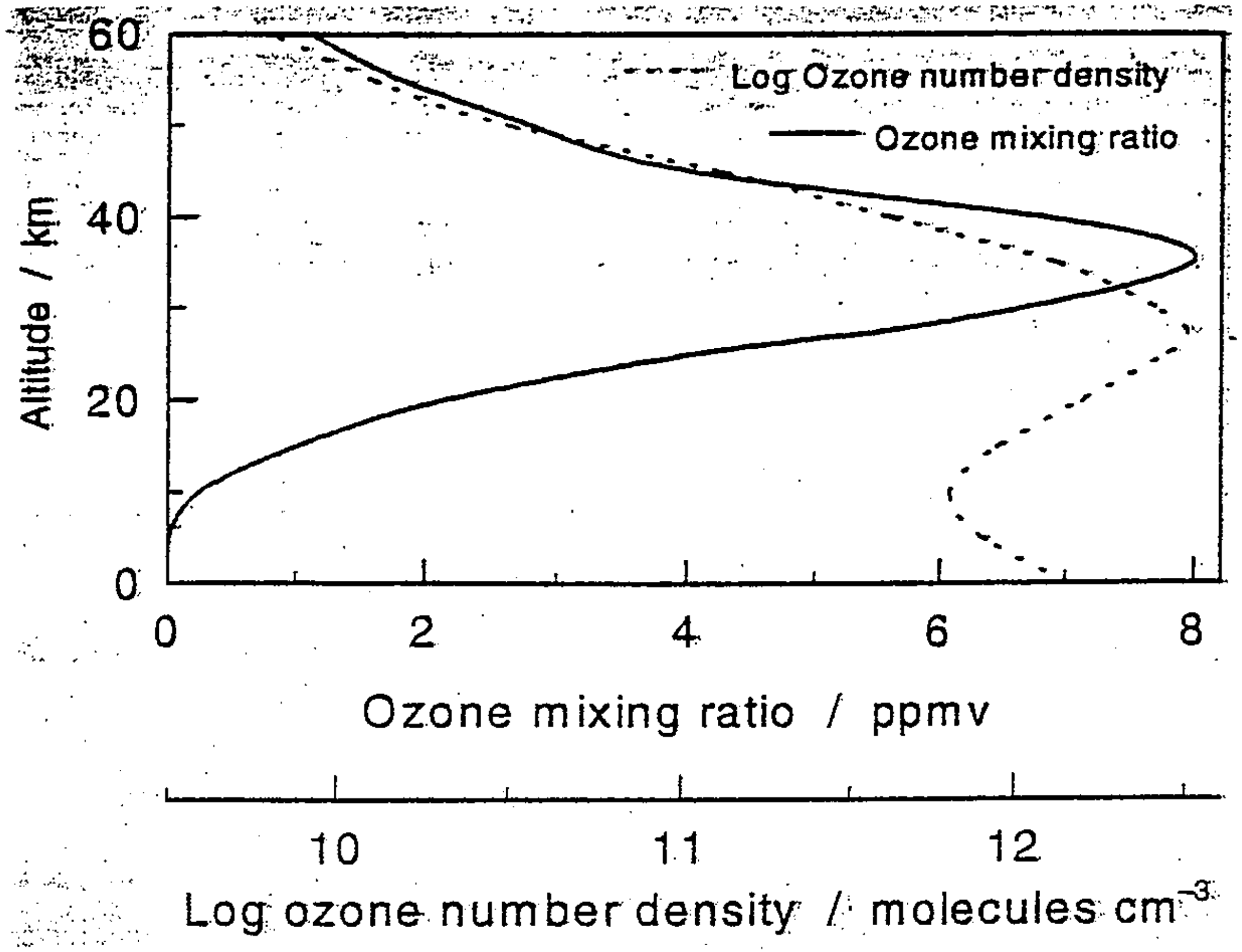


Fig. 3.1 Concentration profile of ozone in the lower atmosphere, shown both as the mixing ratio (solid line) and as the log of number density (broken line). (Data from Wayne, R. P., *Chemistry of Atmospheres*, Clarenden Press; Oxford; 1991. Reprinted with permission.)

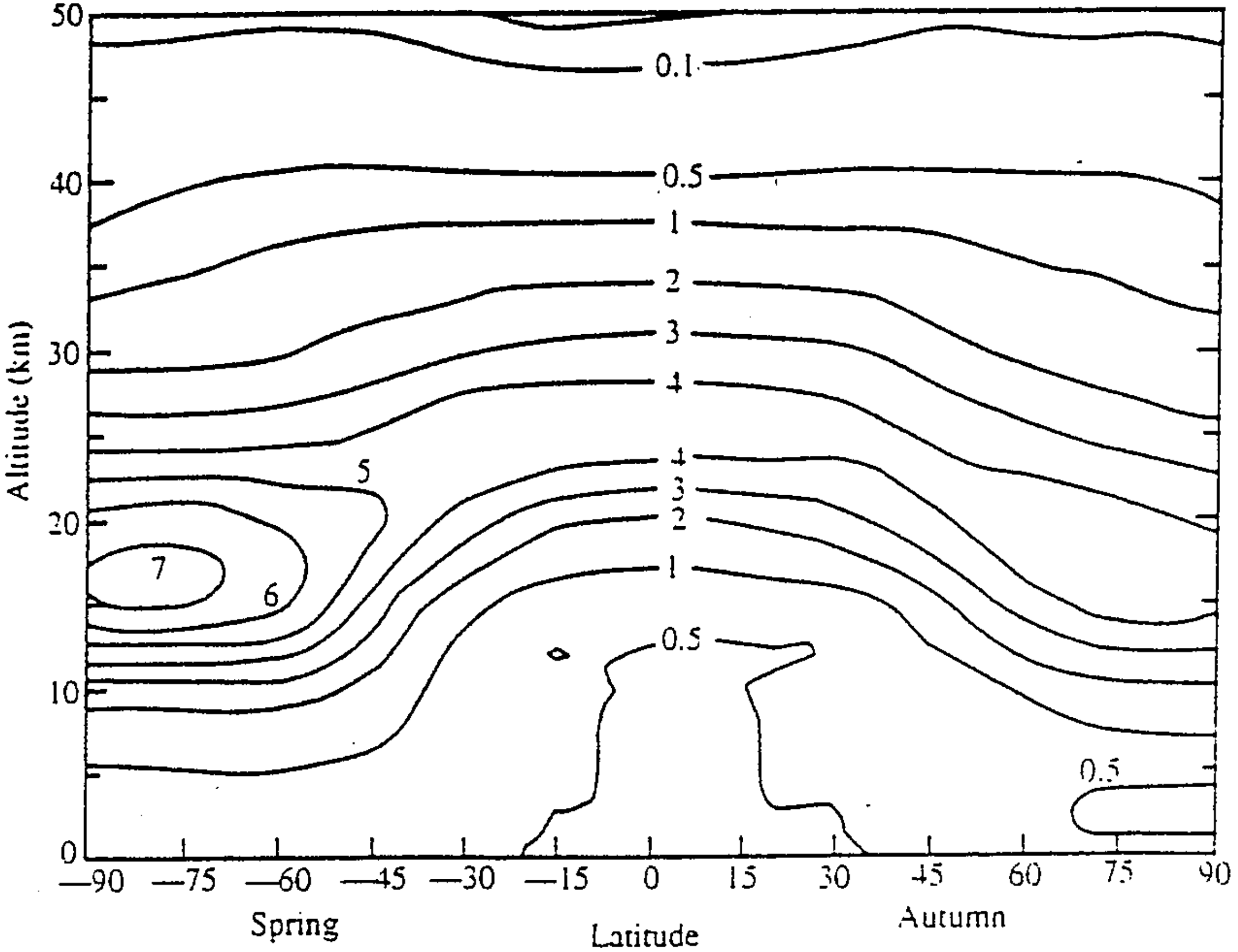


Fig. 10-1 The natural ozone layer: vertical and latitudinal distribution of the ozone number density (10^{12} molecules cm^{-3}) at the equinox, based on measurements taken in the 1960s. From Wayne, R. P. *Chemistry of Atmospheres*. Oxford: Oxford University Press, 1991.

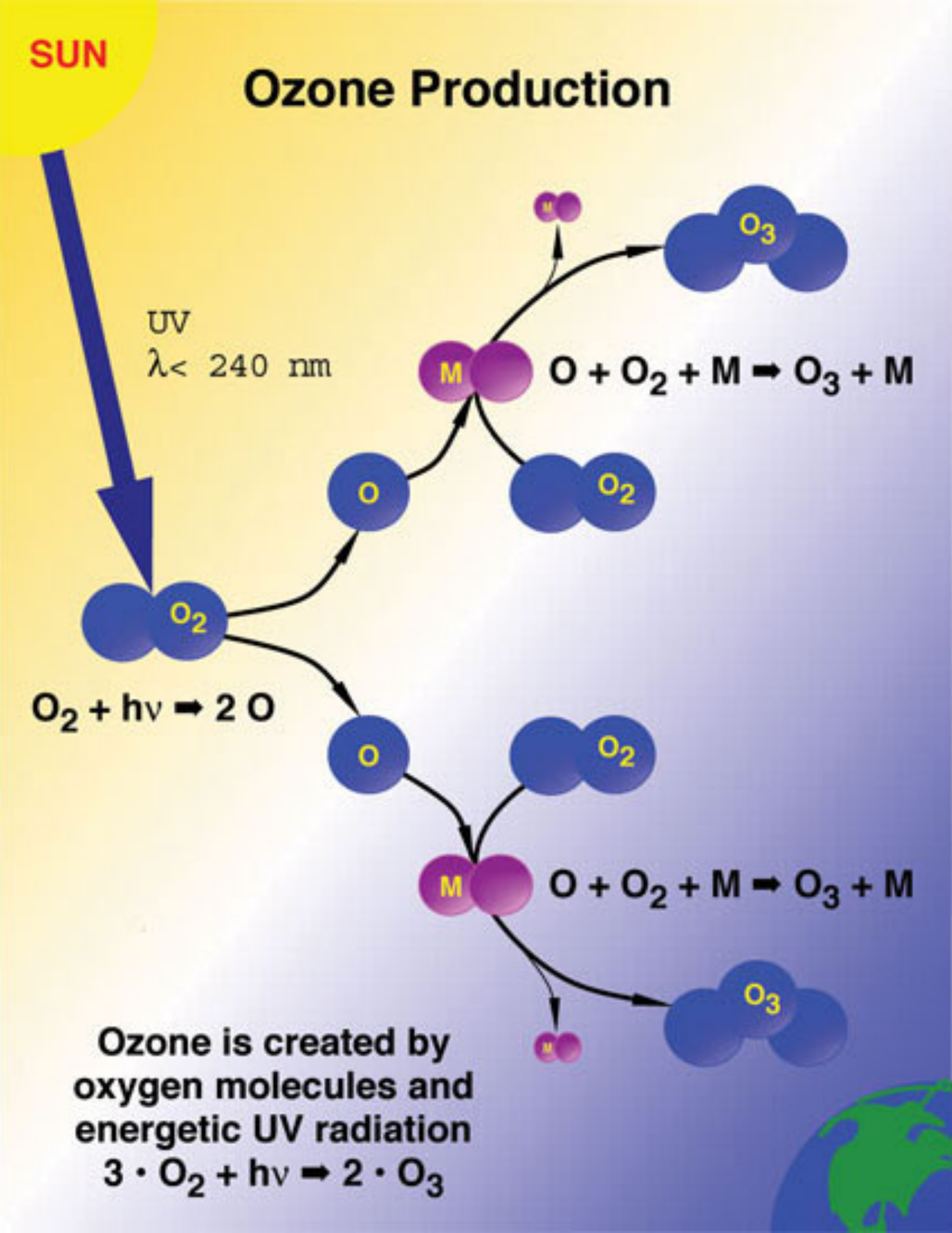
2. Ozone Formation/Destruction

O_3 Formation Chemistry

O_2 + $h\nu$ (λ << 240 nm) → 2 O

O + O_2 + M → O_3 + M

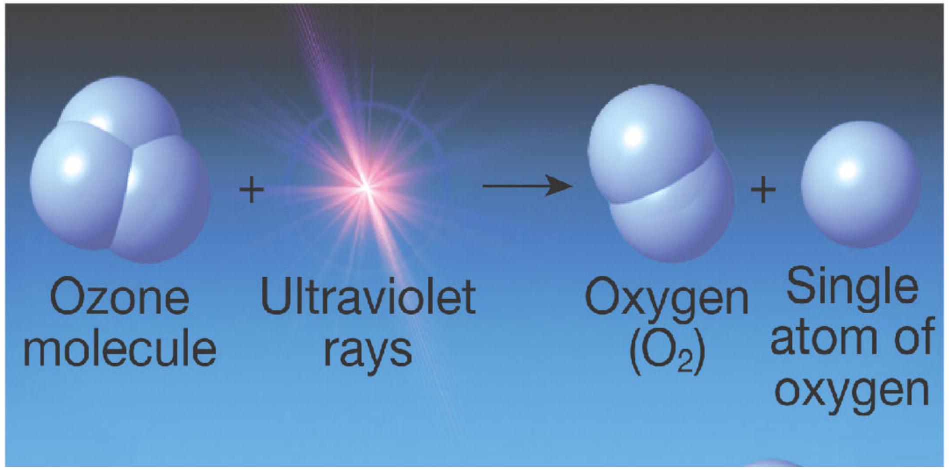
Overall : 3 O_2 $\rightleftharpoons$ 2 O_3



Ozone Destruction Chemistry (oxygen only)

$O_3 + h\nu\ (\lambda \sim 240\text{-}320\ \text{nm}) \rightarrow O_2^* + O^*$

$O + O_3 + M \rightarrow 2\ O_2 + M$



Overall : $2\ O_3 \rightleftharpoons 3\ O_2$

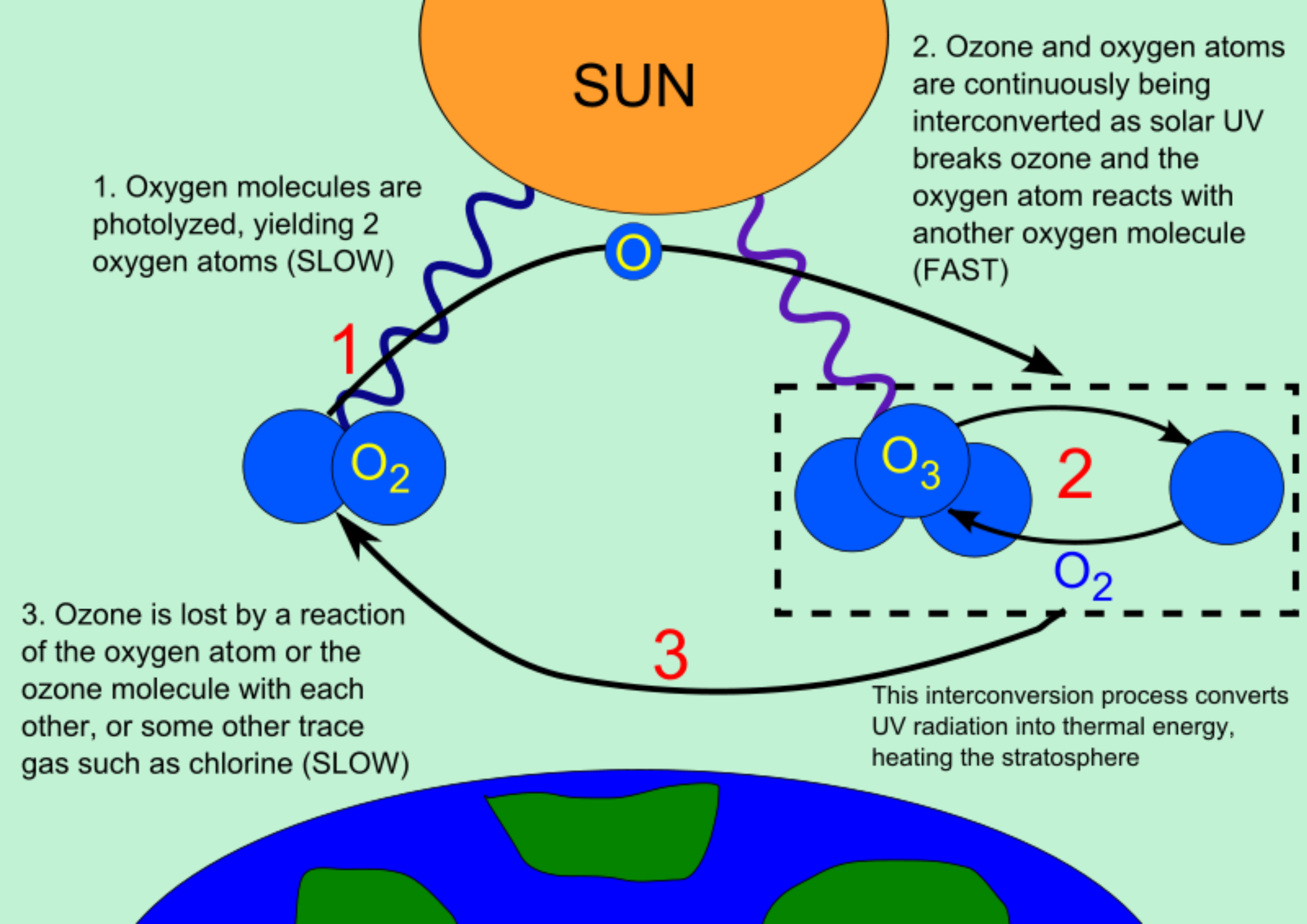
The Chapman Reactions

Synthesis

$O_2 + h\nu$ (λ << 240 nm)	$\Rightarrow$	$O + O$	(1)	SLOW
$O + O_2 + M$	$\Rightarrow$	$O_3 + M$	(2)	FAST

Decomposition

$O_3 + h\nu$ (λ ~ 240-320 nm)	$\Rightarrow$	$O_2^* + O^*$	(3)	FAST
$O + O_3$	$\Rightarrow$	$O_2 + O_2$	(4)	SLOW


SUN
1. Oxygen molecules are photolyzed, yielding 2 oxygen atoms (SLOW)
2. Ozone and oxygen atoms are continuously being interconverted as solar UV breaks ozone and the oxygen atom reacts with another oxygen molecule (FAST)
O
1
O_2
O_3
2
O_2
3
3. Ozone is lost by a reaction of the oxygen atom or the ozone molecule with each other, or some other trace gas such as chlorine (SLOW)
This interconversion process converts UV radiation into thermal energy, heating the stratosphere

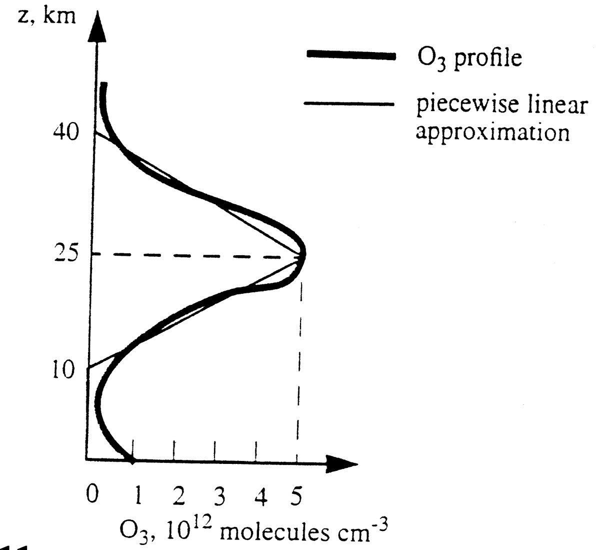
Why does O_3 Concentration peak ~ 20-30 km altitude?

Recall the Chapman Reactions…

$$O_2 + h\nu\ (\lambda < 240\ \text{nm}) \rightarrow O + O$$

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

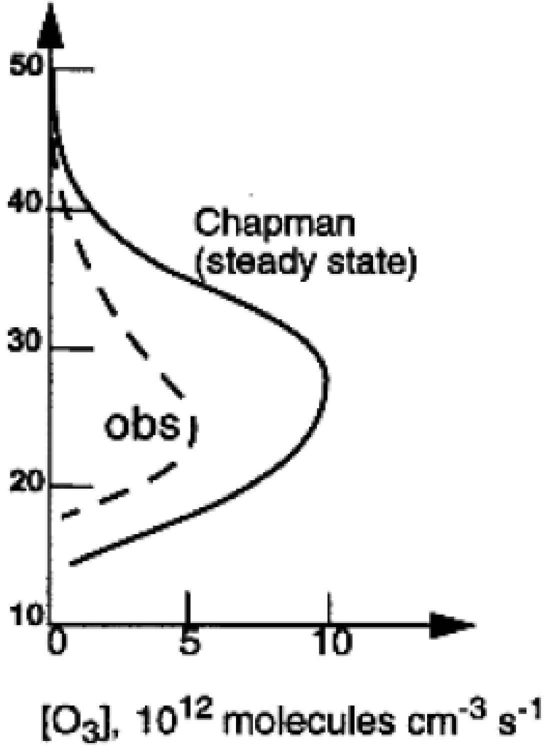
The upper stratosphere has plenty of high-energy photons which create enough O, but at higher altitudes, the concentration of O_2 is limited.



The lower stratosphere has plenty O_2, but has limited high-energy photons (to split O_2) and therefore, is limited in O.

At 20~30 km, there is enough high-energy photons to produce O and still plenty O_2

$$3\ O_2 \rightleftharpoons 2\ O_3$$



When,

O_3 formation rate = O_3 destruction rate

Then $[O_3]$ is at *steady-state*

Oxygen-only chemistry explains the appearance of the ozone layer, but over-estimates the peak ozone concentration by 2x.

Therefore, additional O_3 destruction processes are occurring.

3. Catalytic Ozone Destruction

General Mechanism:

$$X + O_3 \rightarrow XO + O_2$$

$$XO + O \rightarrow X + O_2$$

Net Reaction **$O + O_3 \rightarrow 2\,O_2$**

Where X can be;

1. HO_x ($H\cdot$, $HO\cdot$, $HO_2\cdot$)
2. NO_x ($\cdot NO$, $\cdot NO_2$)
3. ClO_x ($Cl\cdot$, $ClO\cdot$)

Hydroxyl Radical (HOx) Cycle

Photochemical production;

$$O\,(^1D) + H_2O \rightarrow 2\,HO\cdot$$

$$H_2O + h\nu \rightarrow H\cdot + HO\cdot$$

Note: $O\,(^1D)$ = singlet excited state oxygen aka $^1O^*$ (generated photochemically from O_3)

$$HO\cdot + O_3 \rightarrow HO_2\cdot + O_2$$

$$HO_2\cdot + O \rightarrow HO\cdot + O_2$$

Net Reaction $\mathbf{O + O_3 \rightarrow 2\,O_2}$

Natural contribution to O_3 destruction. Increasing importance with altitude.

Nitric Oxide (NOx) cycle

$N_2O \quad + \quad O\,(^1D) \quad \rightarrow \quad 2\,\cdot NO$

Nitrous oxide tropospheric lifetime ~160 yr, reaction occurs in stratosphere. Increasing tropospheric concentrations due to fertilization.

Nitric oxide removal via reaction with hydroxyl

$\cdot NO \; + \; HO\cdot \; \rightarrow \; HNO_2$

$$\cdot NO \; + \; O_3 \; \rightarrow \; \cdot NO_2 \; + \; O_2$$

$$\cdot NO_2 \; + \; O \; \rightarrow \; \cdot NO \; + \; O_2$$

Net Reaction $\mathbf{O \; + \; O_3 \; \rightarrow \; 2\,O_2}$

'Natural' contribution to O_3 destruction. Increasing importance at lower altitude.

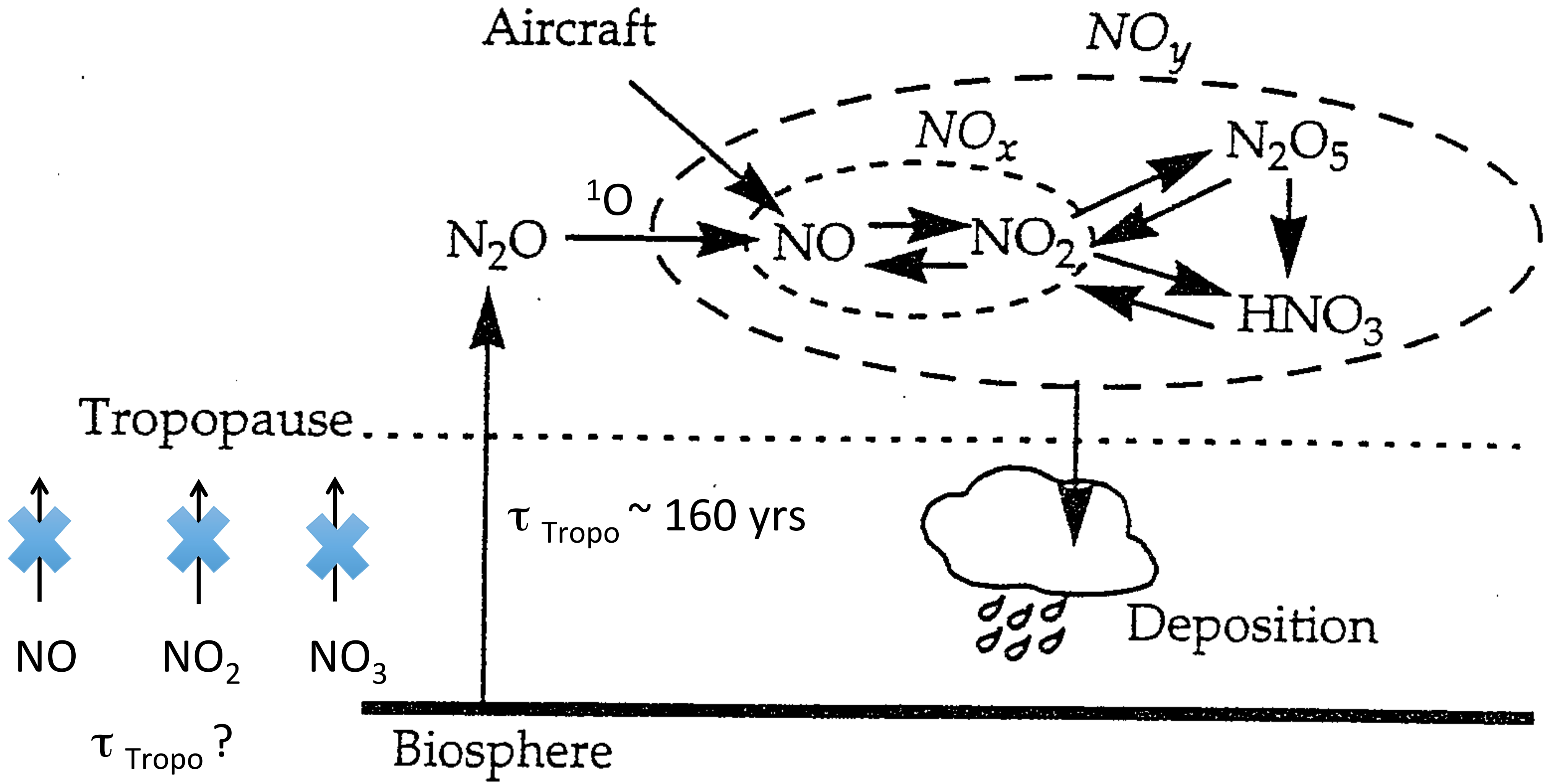


Fig. 10-6 Sources and sinks of stratospheric NO_x and NO_y. The direct conversion of N_2O_5 to HNO_3 takes place in aerosols and will be discussed in section 10.4.

Chlorine radical (ClOx) cycle

$$\cdot Cl + O_3 \rightarrow ClO\cdot + O_2$$
$$ClO\cdot + O \rightarrow \cdot Cl + O_2$$

Net Reaction $\mathbf{O + O_3 \rightarrow 2\ O_2}$

Most ·Cl and ClO· radicals in stratosphere are from anthropogenic sources

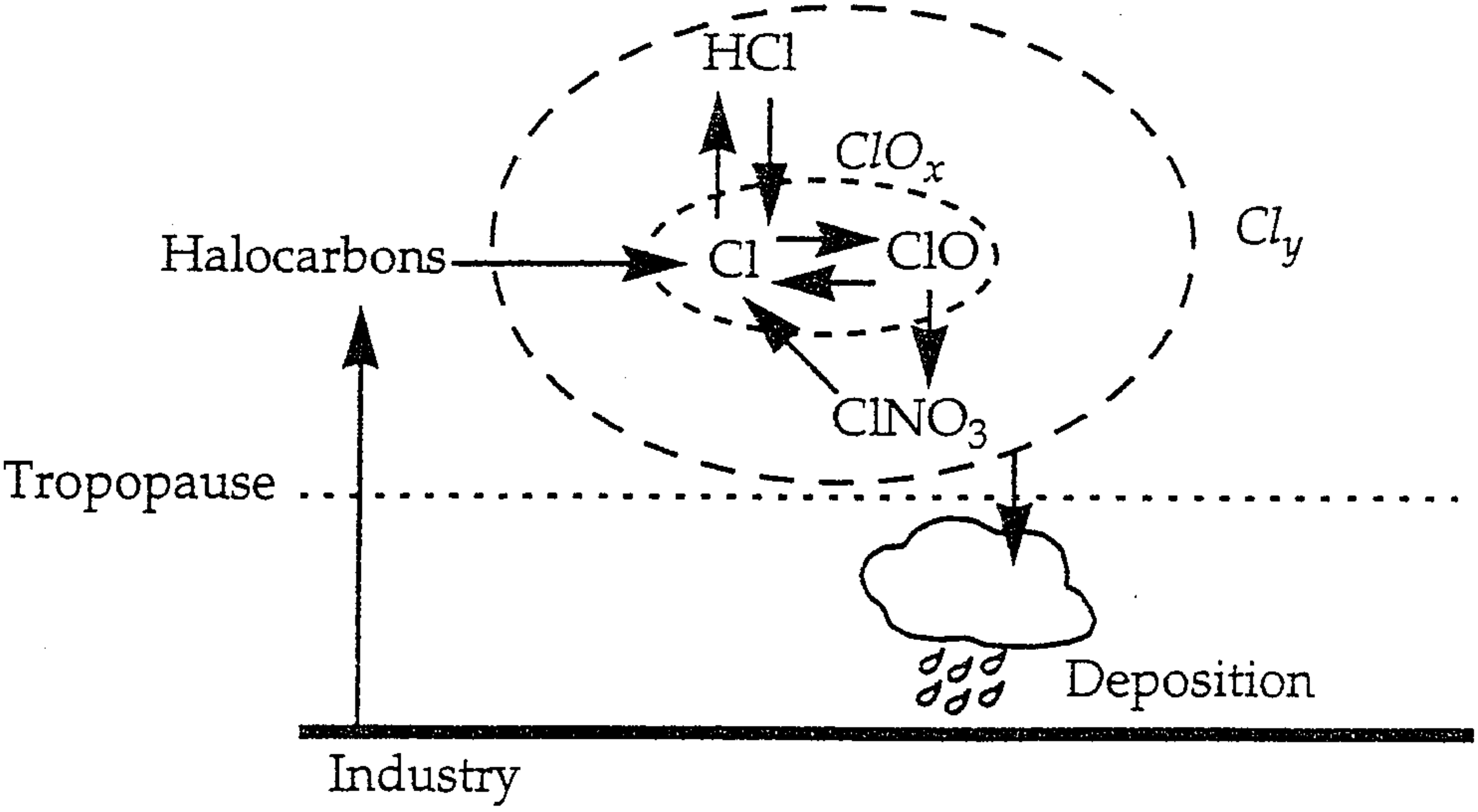


Fig. 10-8 Sources and sinks of stratospheric ClO_x and Cl_y.

Sources of ClOx species

CH_3Cl (biogenic)

CH_2Cl_2, $CHCl_3$, CCl_4 – solvents

CFC's – refrigerants, foaming agents and propellants (freons)

CFC-*xyz* (*x* = # C-1; *y*=#H+1; *z*=#F)

Long tropospheric lifetimes (λ > 300 nm)

Photo-dissociate in stratosphere (λ < 300 nm)

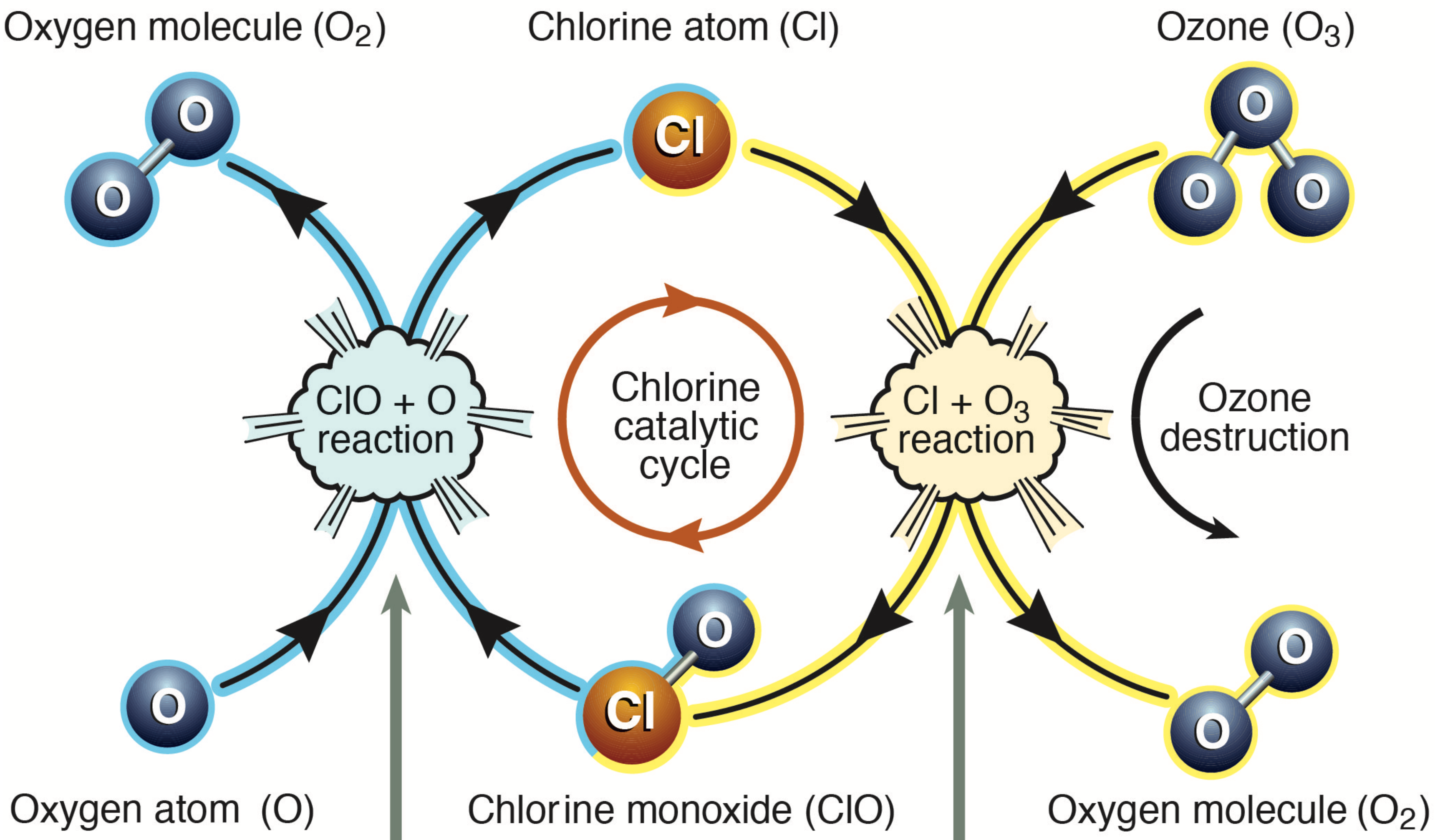
e.g., CFC-11

$CFCl_3 + h\nu \rightarrow CFCl_2 + Cl$ (initiation step)

$Cl + O_3 \rightarrow ClO + O_2$ (ozone destruction)

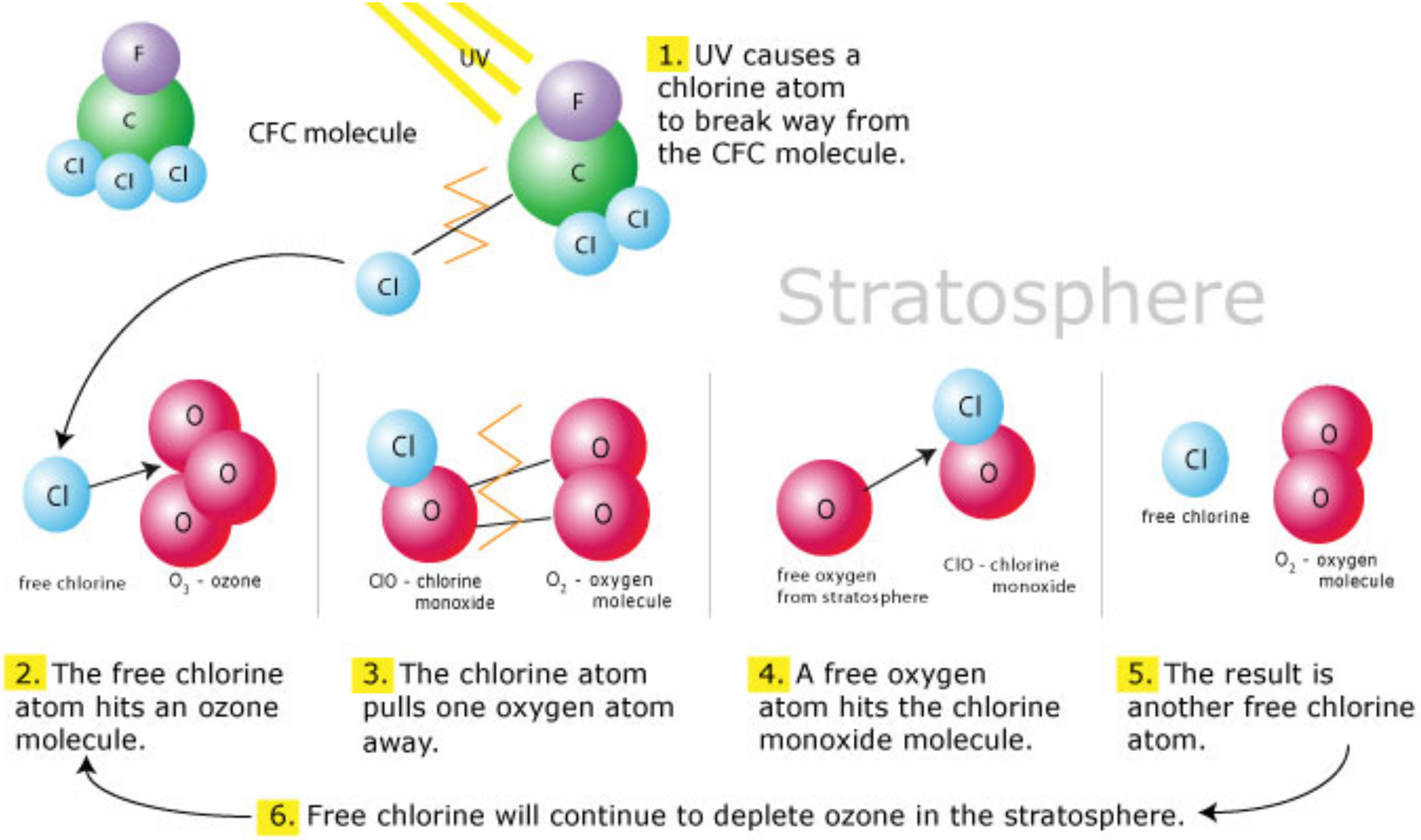
$ClO + O \rightarrow Cl + O_2$ (propogation step)

Ozone Destruction Cycle 1



$$Cl + O_3 \rightarrow ClO + O_2$$
$$ClO + O \rightarrow Cl + O_2$$

$$\text{Net: } O + O_3 \rightarrow 2O_2$$


F
C
Cl
CFC molecule
UV
1. UV causes a chlorine atom to break way from the CFC molecule.
Stratosphere
O
free chlorine
O3 - ozone
ClO - chlorine monoxide
O2 - oxygen molecule
free oxygen from stratosphere
ClO - chlorine monoxide
free chlorine
O2 - oxygen molecule
2. The free chlorine atom hits an ozone molecule.
3. The chlorine atom pulls one oxygen atom away.
4. A free oxygen atom hits the chlorine monoxide molecule.
5. The result is another free chlorine atom.
6. Free chlorine will continue to deplete ozone in the stratosphere.

Ozone Depleting Potential (ODP)

Common CFCs			
Substance	Formula	τ (troposphere)	ODP
CFC-11	$CFCl_3$	60	1
CFC-12	CF_2Cl_2	195	1
CFC-113	$CF_2ClCFCl_2$	101	0.8
CFC-115	CF_2ClCF_3	522	0.6

CFC alternatives		
Substance	Formula	ODP
HCFC-22	$CHClF_2$	0.06
HCFC-123	$CHCl_2CF_3$	0.02
HCFC-124	$CHClFCF_3$	0.02
HFC-125	CHF_2CF_3	0.00

4. 'Null' and 'Holding' cycles

Null (do nothing) cycles interconvert odd oxygen species

$NO + O_3 \rightarrow NO_2 + O_2$

$NO_2 + hv \rightarrow NO + O$

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

Holding cycles store reactive species in stable forms that act as a temporary reservoir

$NO_3 + NO_2$ ===== $\mathbf{N_2O_5}$

Other important reservoir species (**bold**)

$NO_2 + HO \rightarrow \mathbf{HNO_3}$

$Cl + CH_4 \rightarrow \mathbf{HCl} + CH_3$

Other reservoir species

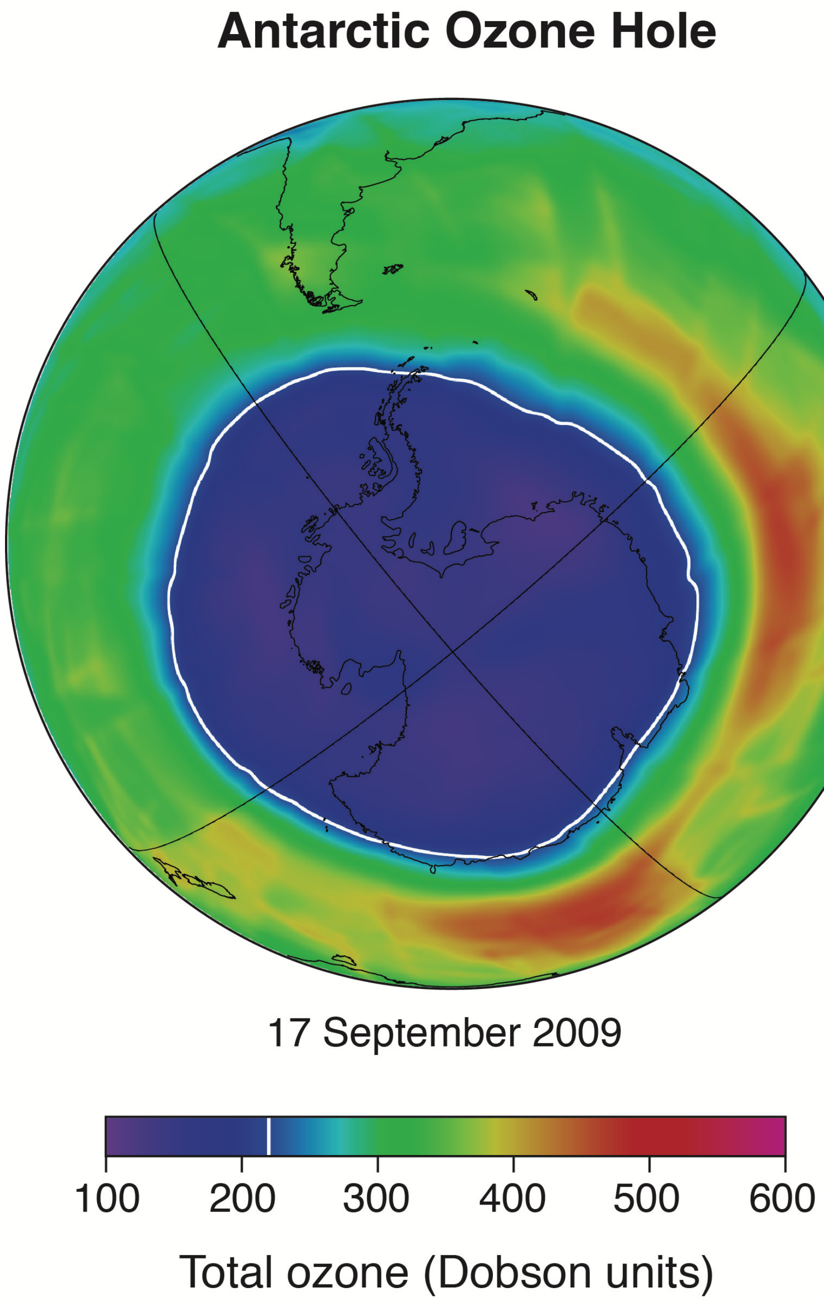
$$ClO\bullet + HO_2\bullet \longrightarrow \mathbf{HOCl} + O_2$$

$$ClO\bullet + \bullet NO_2 + M \longrightarrow \mathbf{ClONO_2} + M$$

Reservoir species are non-reactive and store the reactive radicals until they are later released and re-enter the catalytic cycle to destroy ozone

5. Antarctic and Arctic Ozone Hole

- Occurs during polar SPRING
- After very cold and dark conditions
- Polar stratospheric clouds
- Reservoir species release Cl



Why does the ozone hole form at the poles?

During the dark winter, it is very cold and due to the Earth's rotation, a polar vortex is created as air is drawn towards the South Pole.

Due to the low temperatures, you get polar stratospheric clouds (PSCs).

Type I: ~193 K, particles 1 μm of $HNO_3{\bullet}3H_2O_{(s)}$

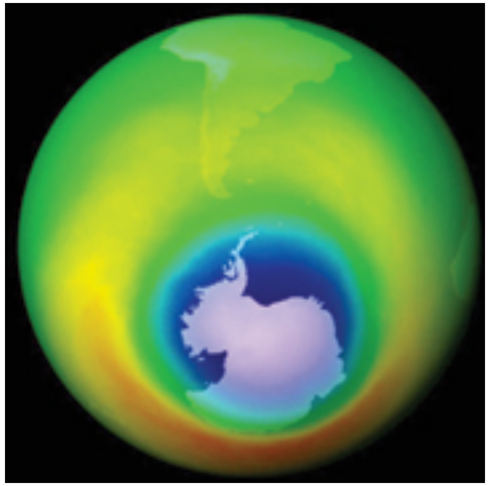
Type II: 187 K, particles 10 μm $H_2O_{(s)}$

Accumulated reservoir species are also present in the vortex. The reservoir species react on the PSCs, releasing Cl_2 and HOCl.

$$HCl + ClONO_2 \rightarrow Cl_2 + HNO_3$$

$$H_2O + ClONO_2 \rightarrow HOCl + HNO_3$$

Here comes the sun!



$$Cl_2 + h\nu \rightarrow 2\ \bullet\mathbf{Cl}$$

$$HOCl + h\nu \rightarrow \bullet\mathbf{Cl} + \bullet OH$$

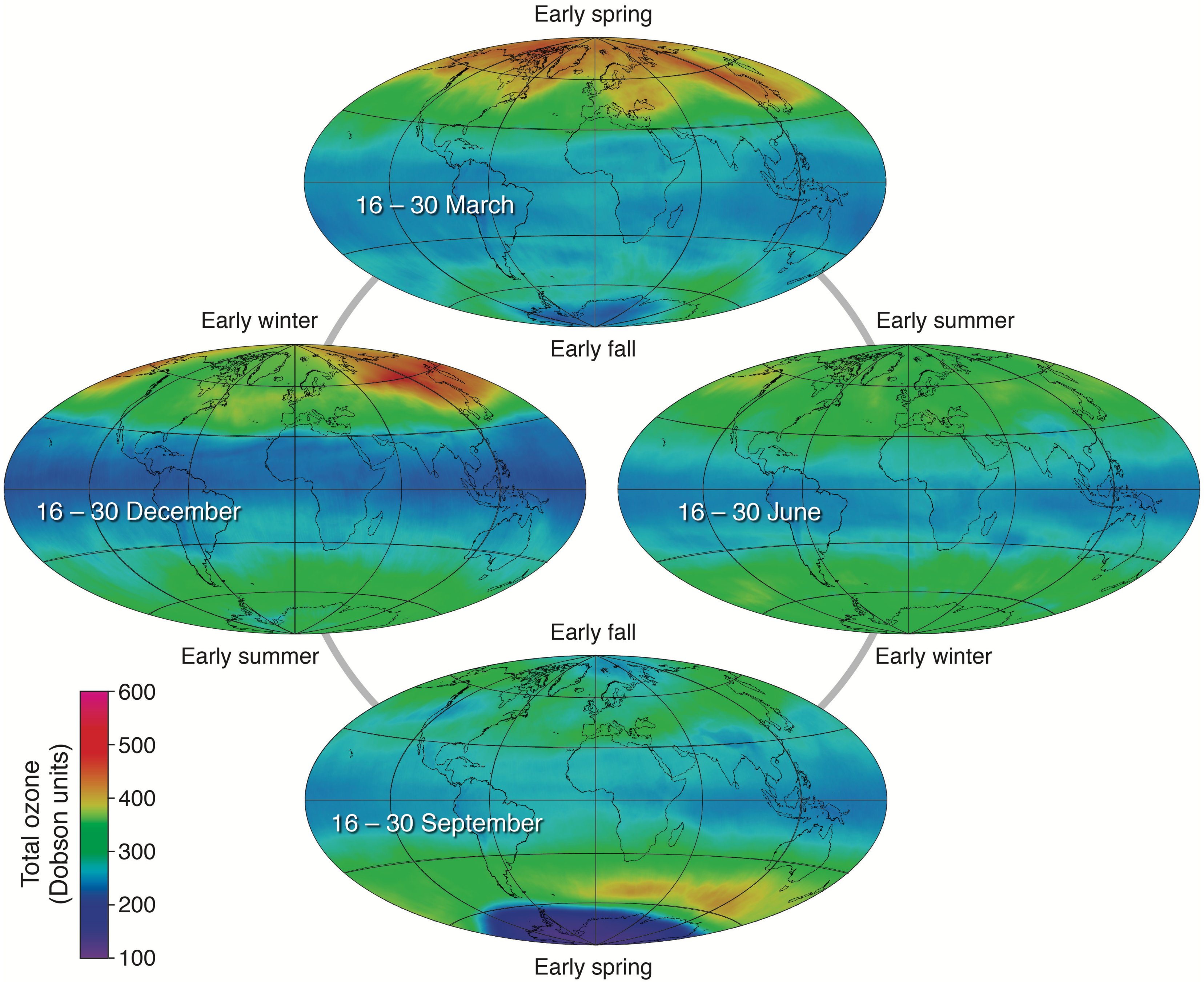
The chlorine radical can now enter the catalytic cycles and destroy ozone

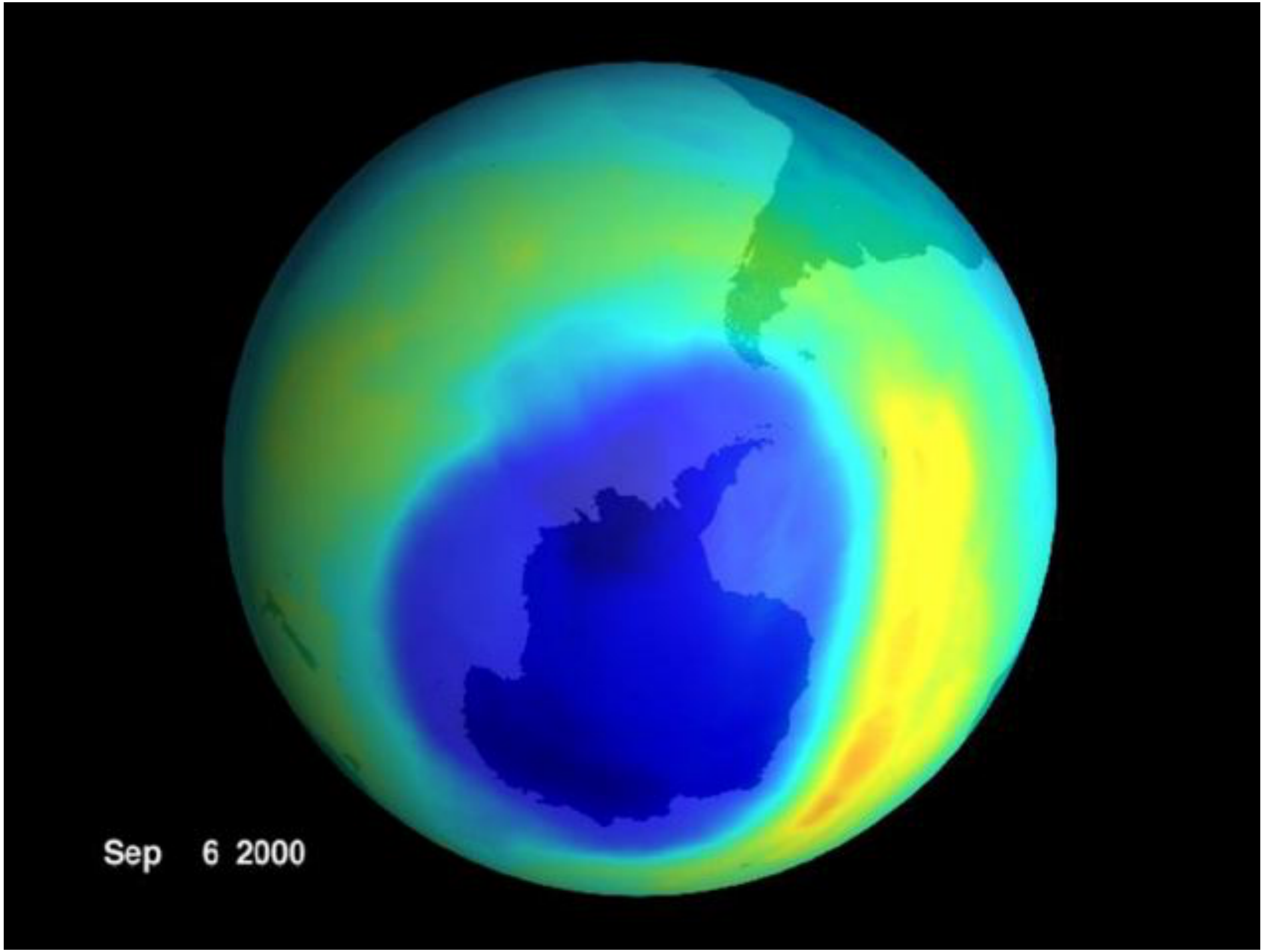
Occurs very quickly (within days), the ozone levels drop to less than half their winter value

As the temperature increases, the polar vortex breaks up and the PSCs begin to disappear

Chlorine radicals become reservoir species (HCl and $ClONO_2$) once again

Global Satellite Maps of Total Ozone in 2009




Sep 6 2000

Polar Vortex

- extreme cold (minus 80-90 °C)
- descending air
- PSCs

Reservoir species?

HCl & $ClONO_2$
react on PSCs to form Cl_2 & $HOCl$

$Cl_2 + h\nu \rightarrow$ BOOM

$HOCl + h\nu \rightarrow$ BOOM

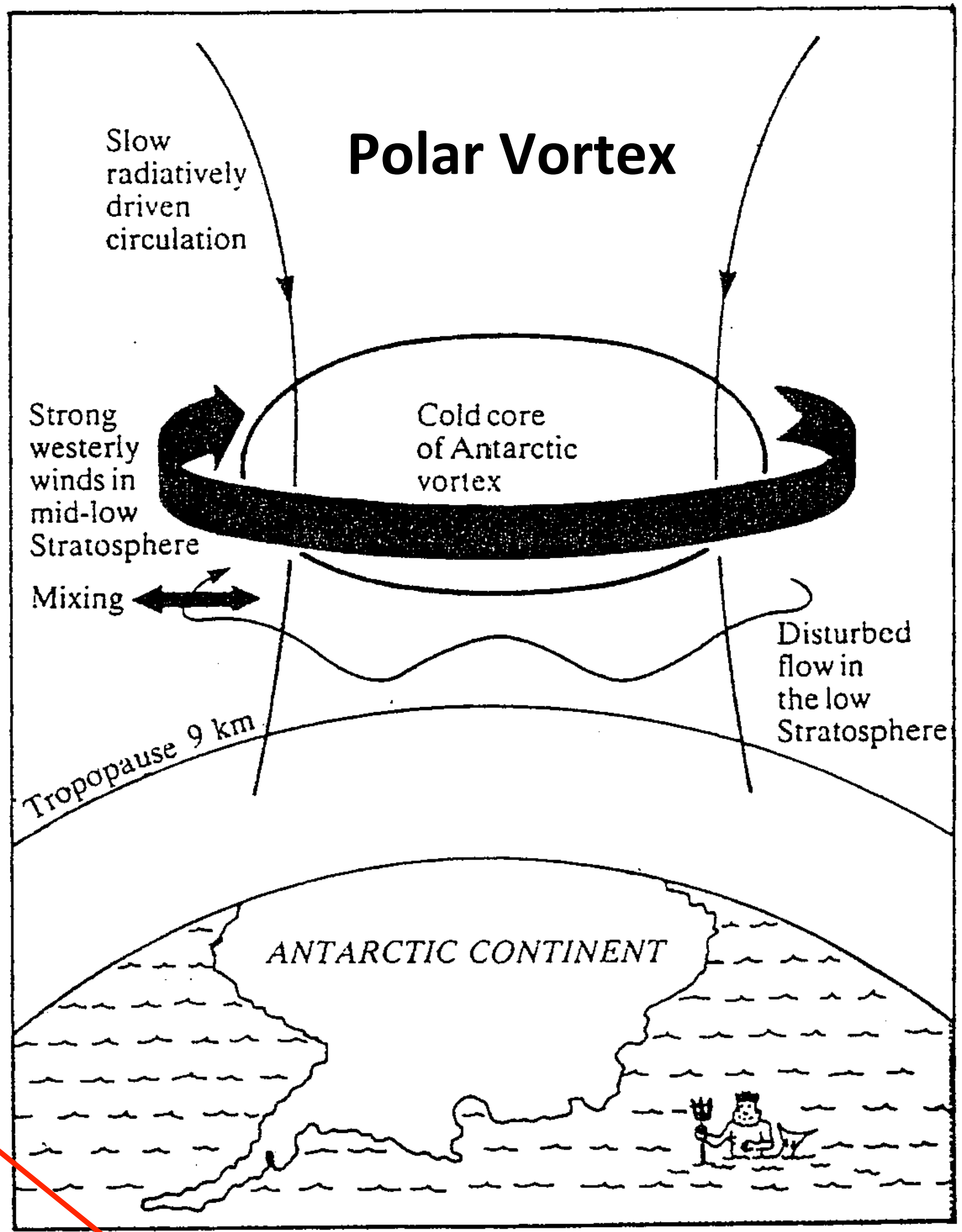


Fig. 4.29. The winter vortex over Antarctica. The cold core is almost isolated from the rest of the atmosphere, and acts as a reaction vessel in which the constituents may become chemically 'preconditioned' during the long polar night.

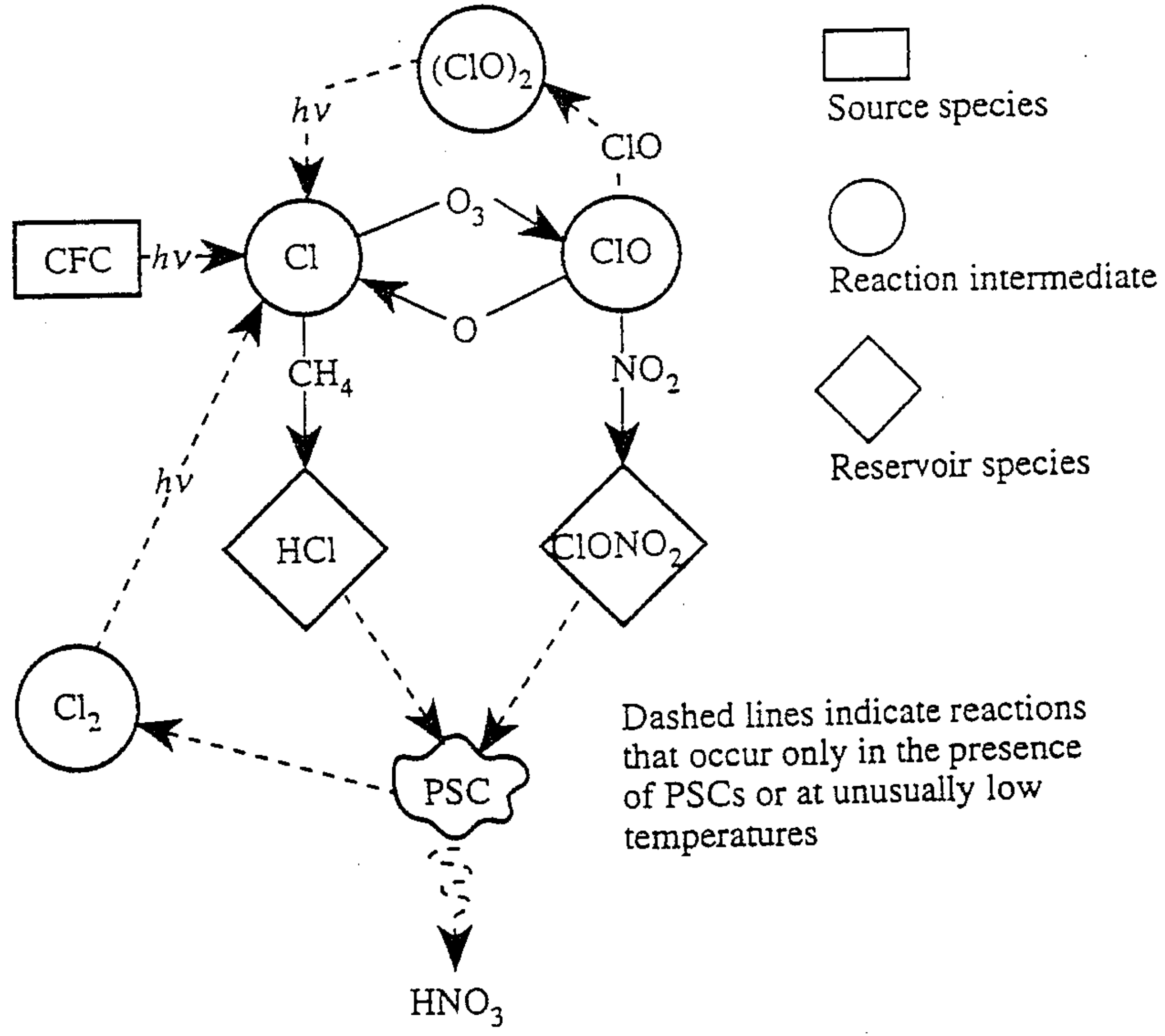
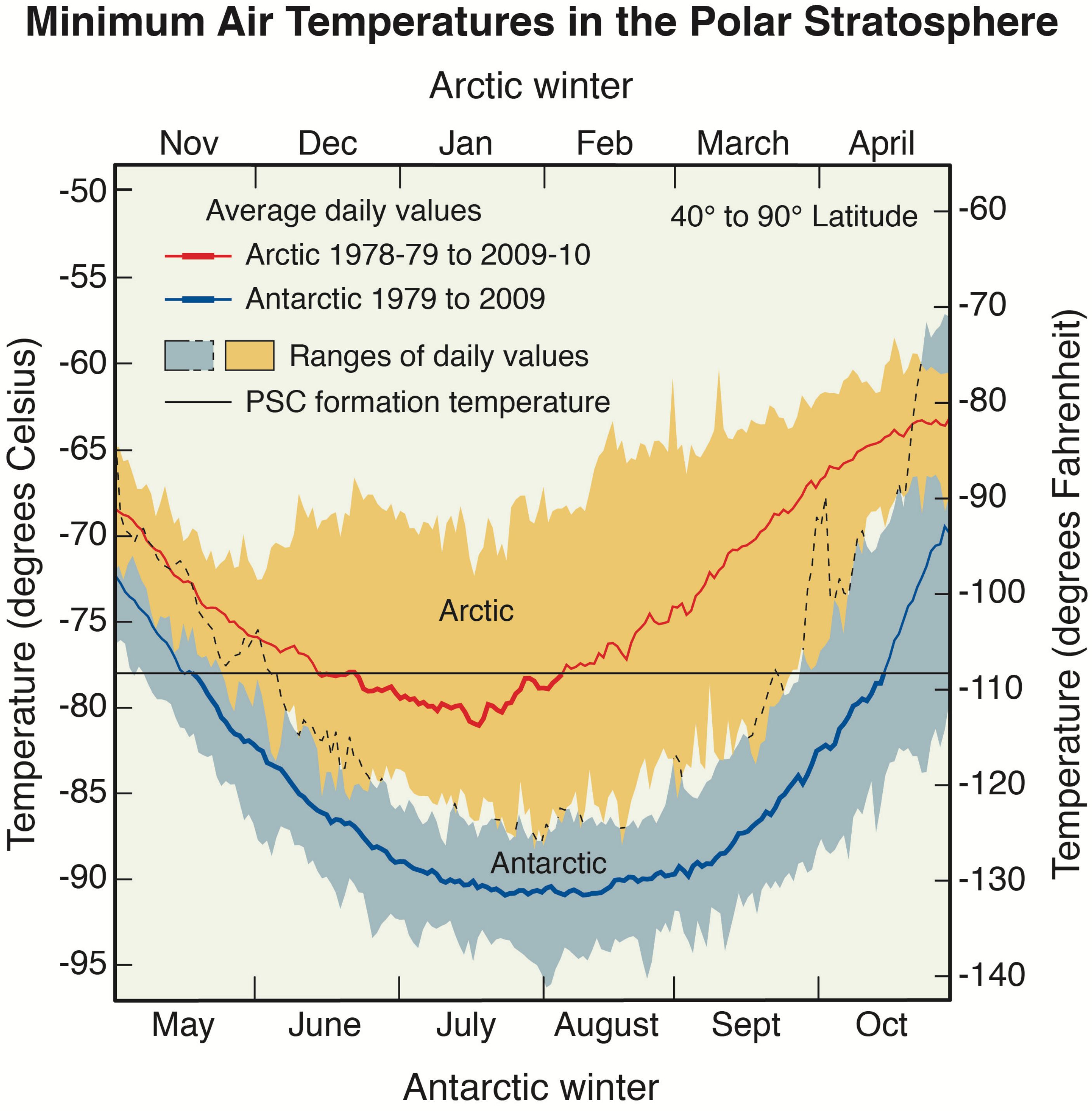
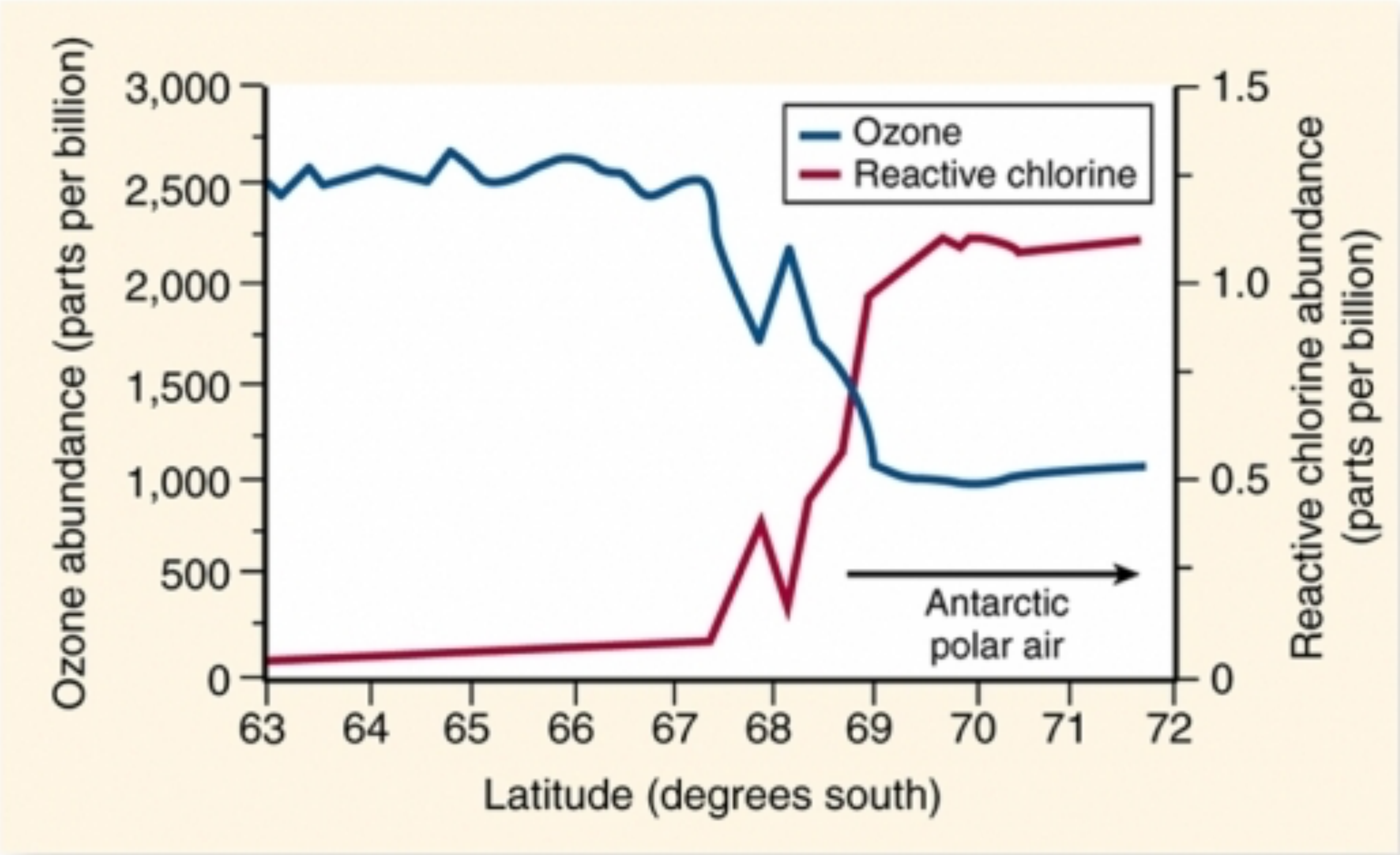


Fig. 4.34 Schematic diagram of chemical conversions in the ClO_x-catalysed decomposition of ozone in the presence of PSCs. Source: *European research in the stratosphere*, European Communities, Luxembourg, 1997.

Why South pole?

Colder temps → more PSCs




Ozone
Reactive chlorine
Ozone abundance (parts per billion)
3,000
2,500
2,000
1,500
1,000
500
0
Reactive chlorine abundance (parts per billion)
1.5
1.0
0.5
0
Antarctic polar air
63
64
65
66
67
68
69
70
71
72
Latitude (degrees south)

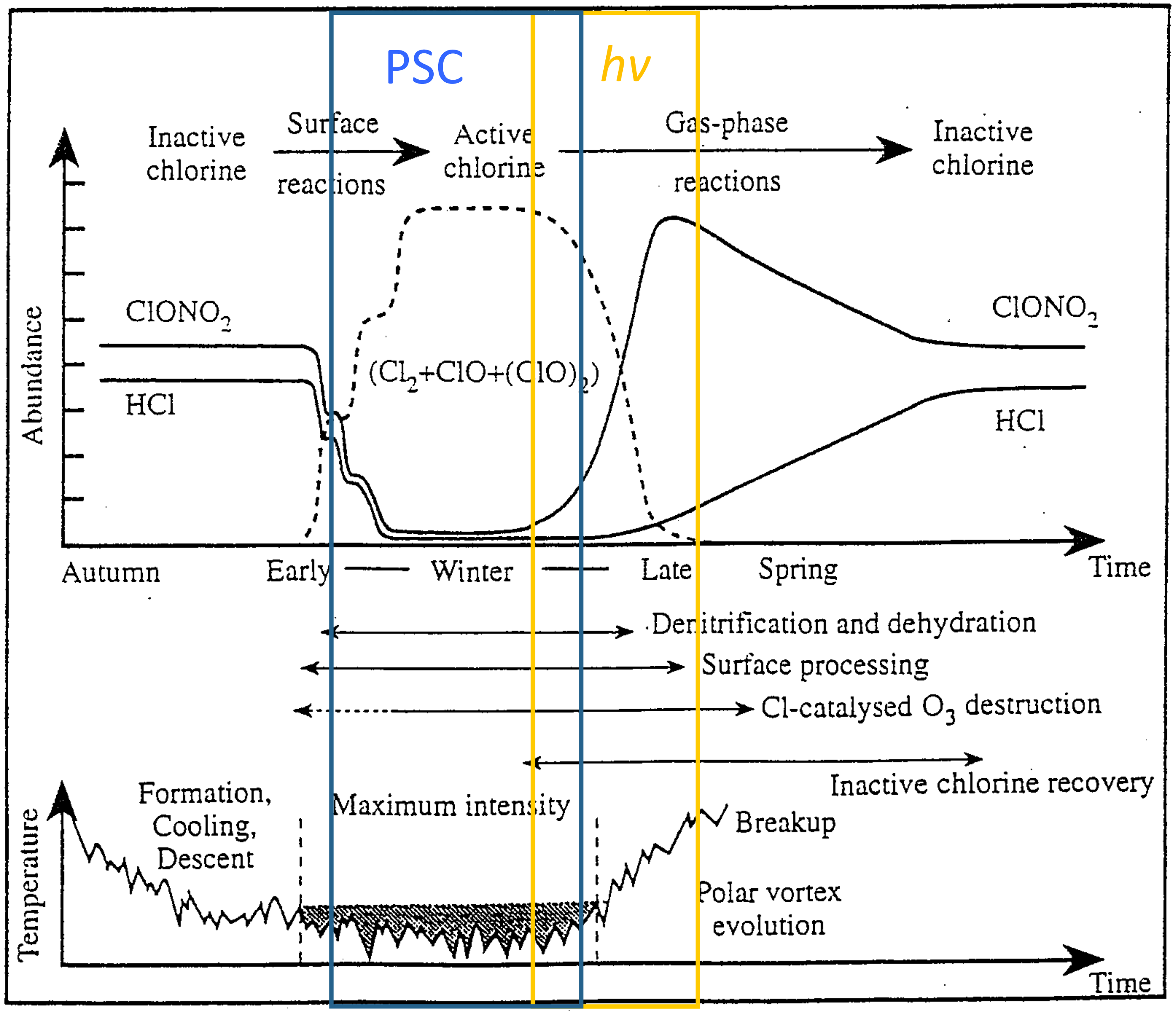
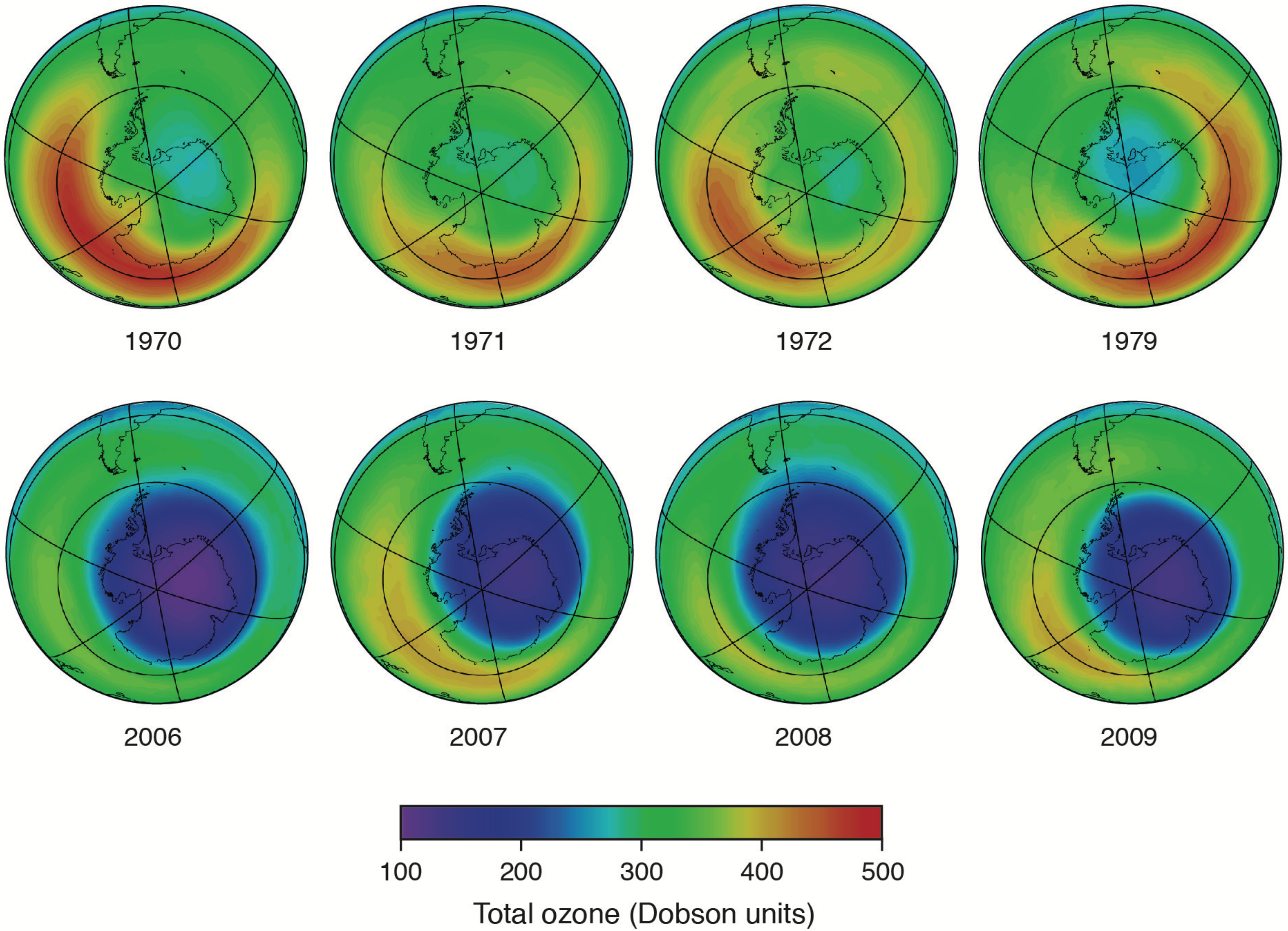


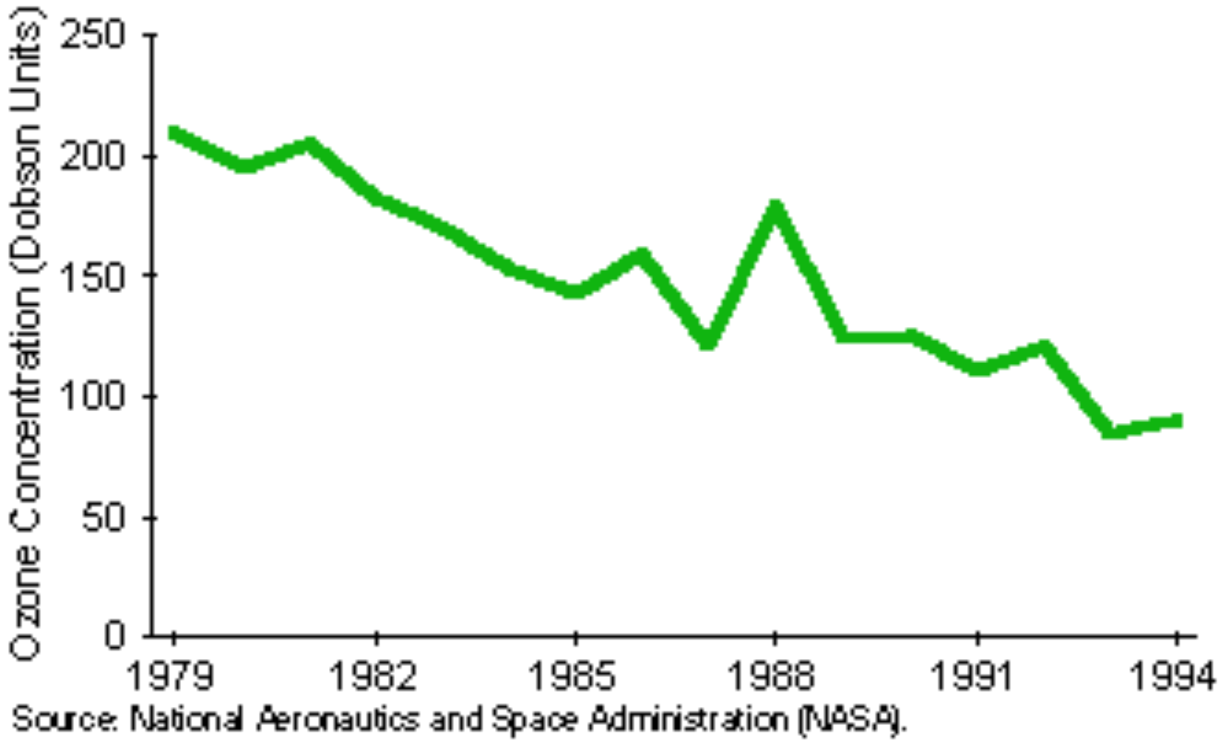
Fig 4.35. Photochemistry and dynamics in the polar stratosphere. From *Scientific assessment of ozone depletion: 1998*, World Meteorological Organization, Geneva, 1999.

Antarctic Total Ozone
(October monthly averages)

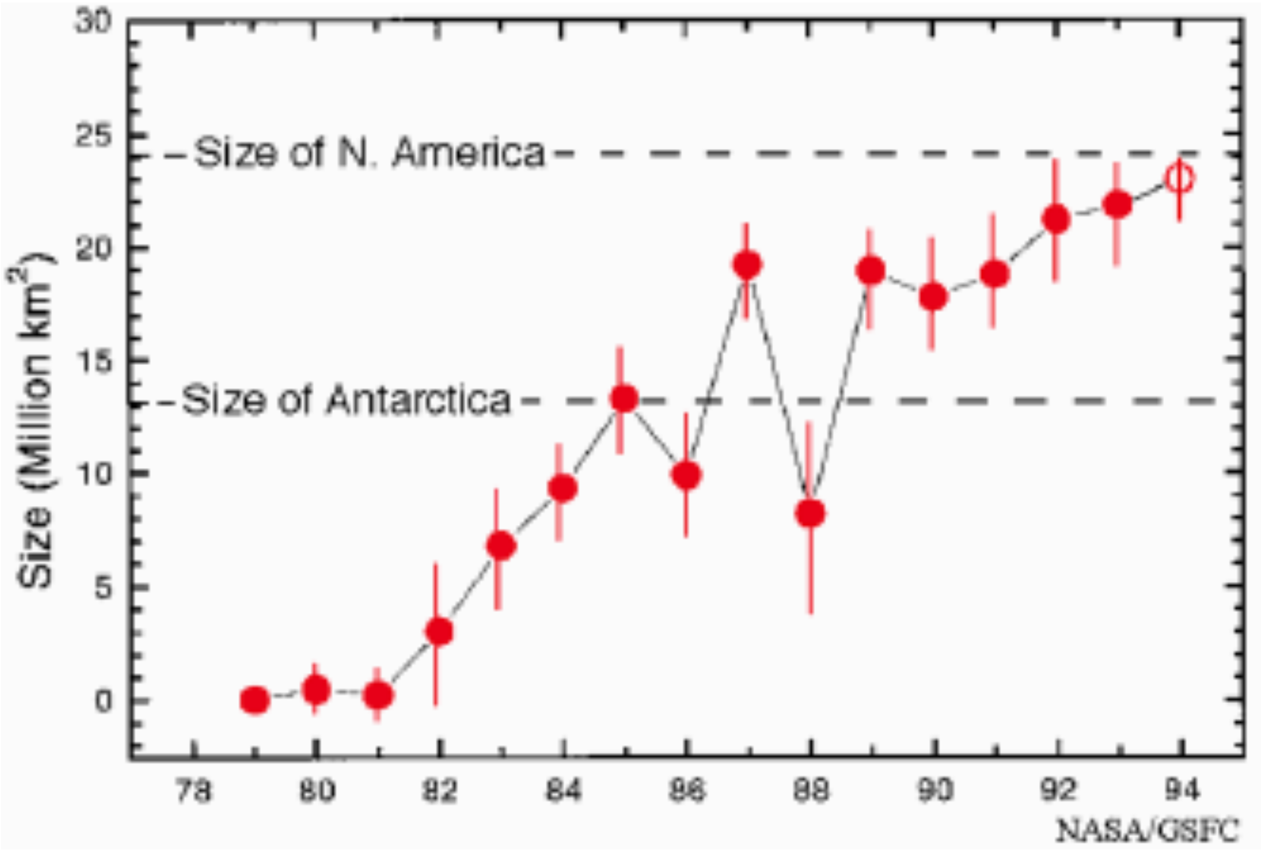


Antarctic Ozone 1979-94

O_3 Concentration



O_3 Hole Size



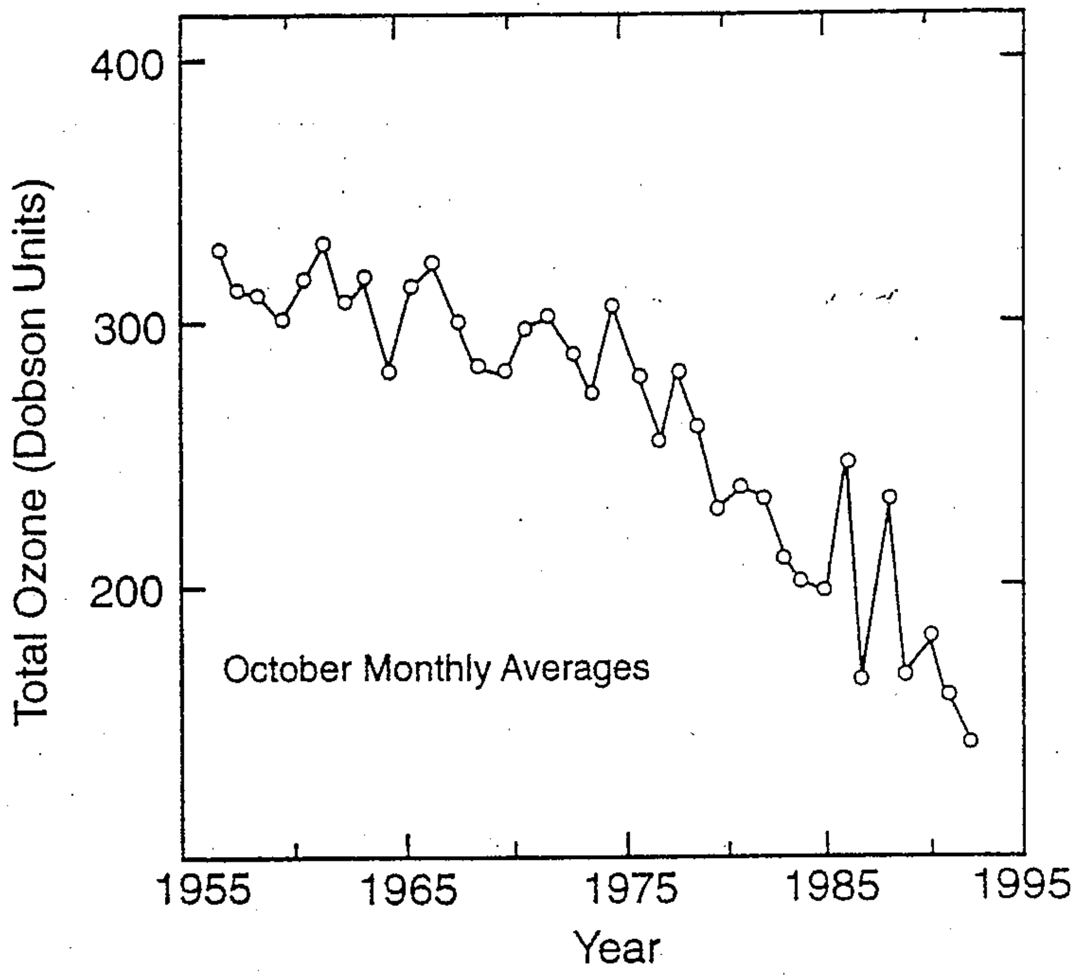
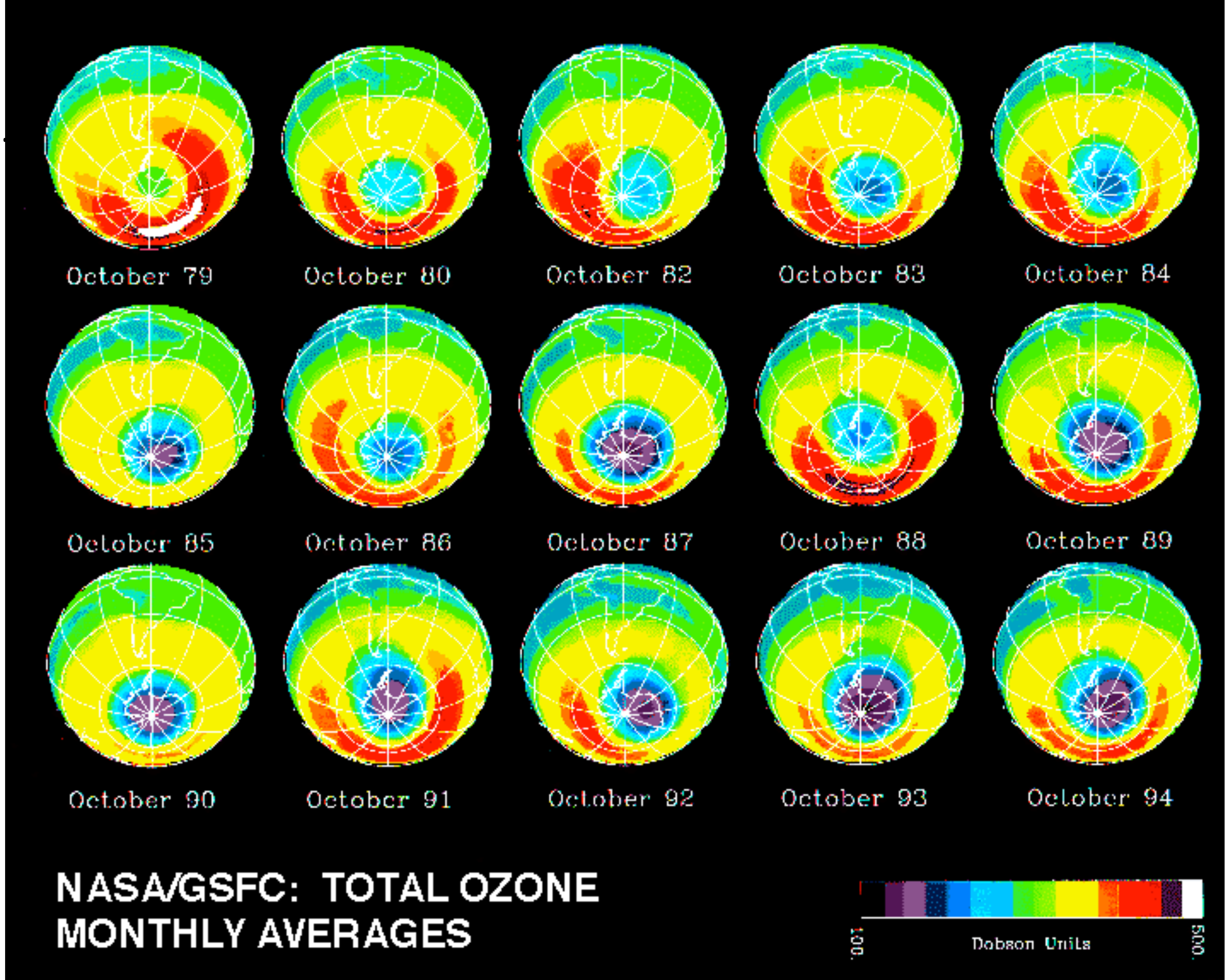


Fig. 10-9 Historical trend in the total ozone column measured spectroscopically over Halley Bay, Antarctica in October, 1957–1992. One Dobson unit (DU) represents a 0.01-mm-thick layer of ozone under standard conditions of temperature and pressure; 1 DU = 2.69×10^{16} molecules cm^{-2}. From *Scientific Assessment of Ozone Depletion: 1994*. Geneva: WMO, 1995.

Oc


October 79
October 80
October 82
October 83
October 84
October 85
October 86
October 87
October 88
October 89
October 90
October 91
October 92
October 93
October 94
NASA/GSFC: TOTAL OZONE
MONTHLY AVERAGES
100.
Dobson Units
500.

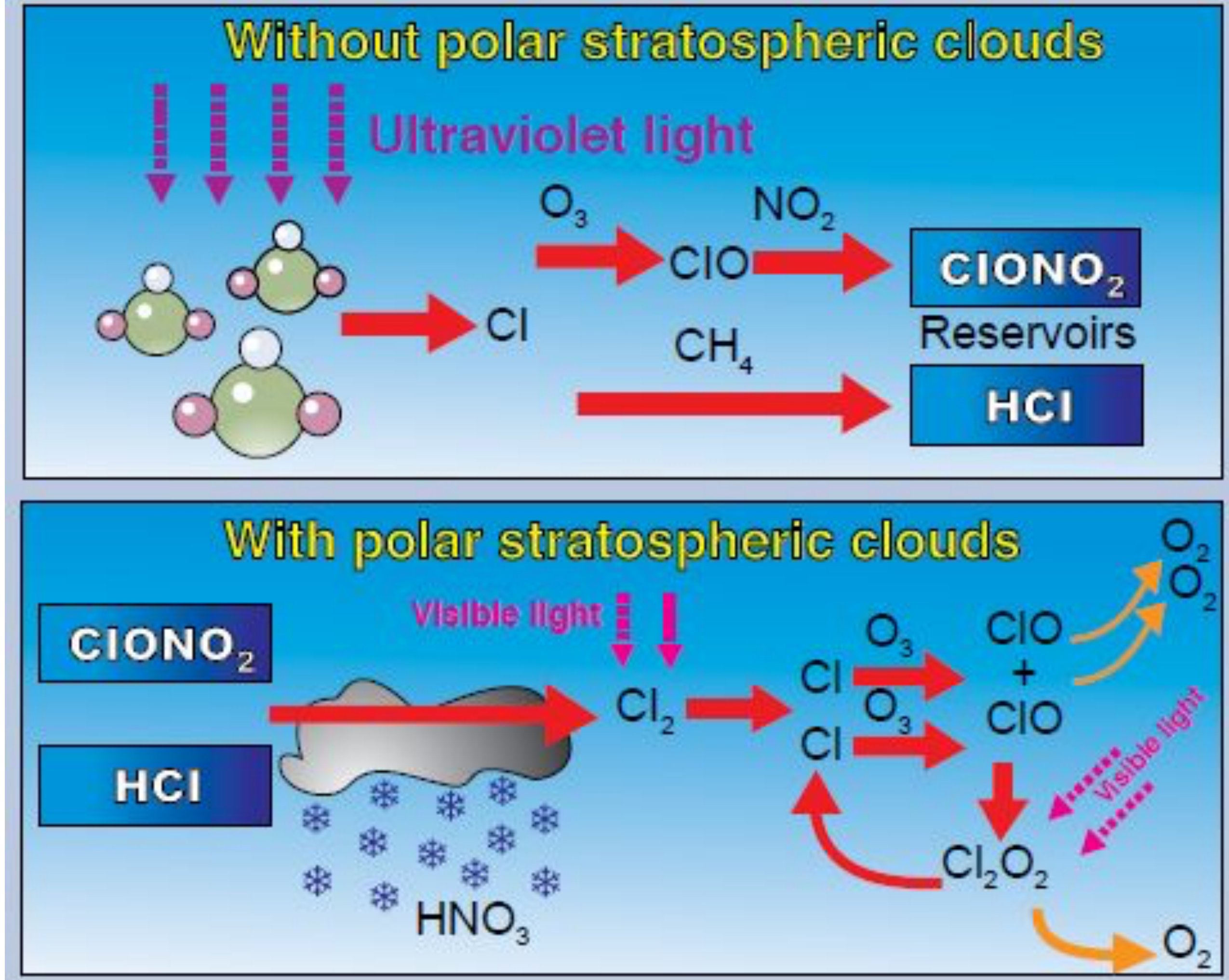
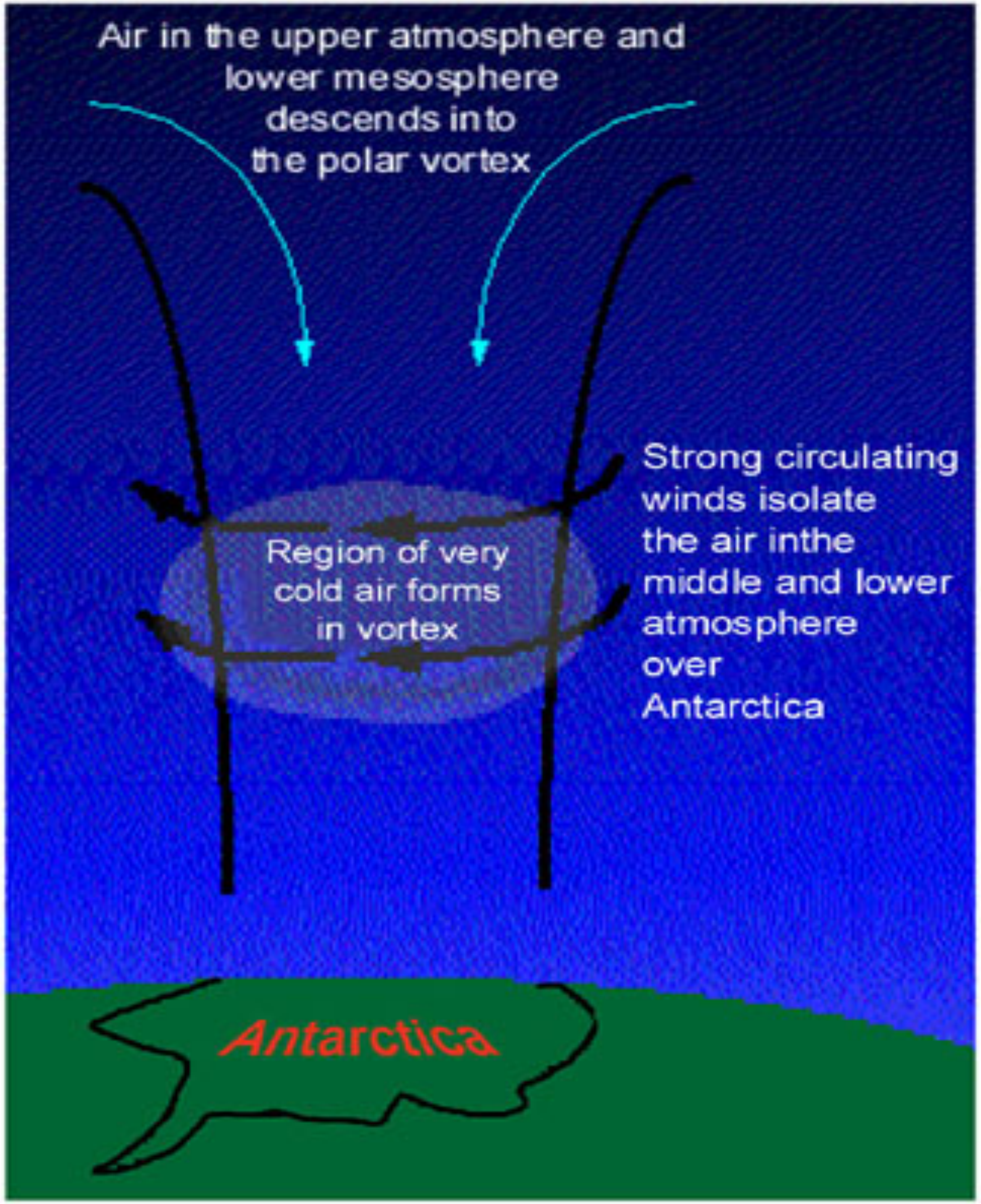
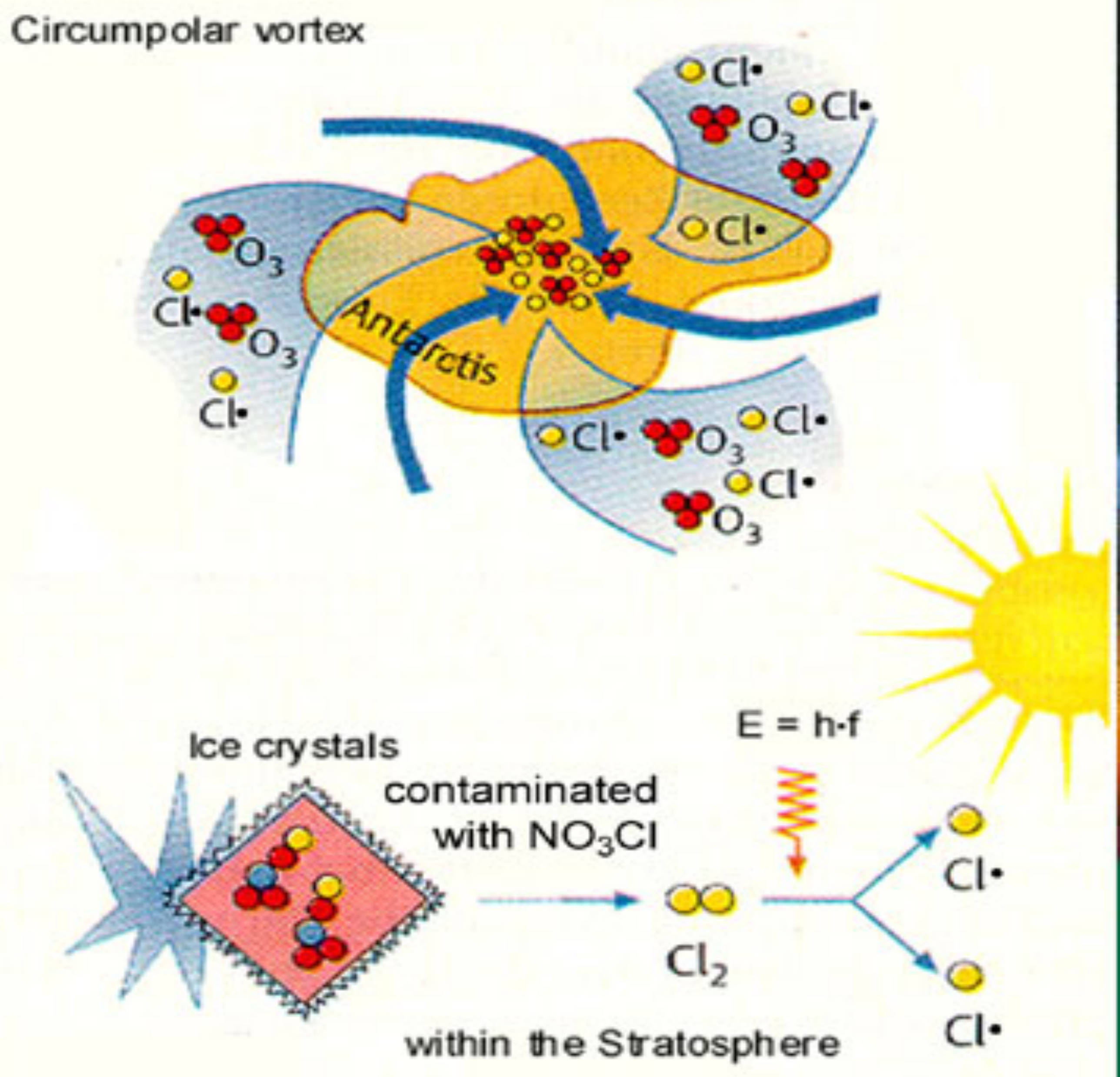
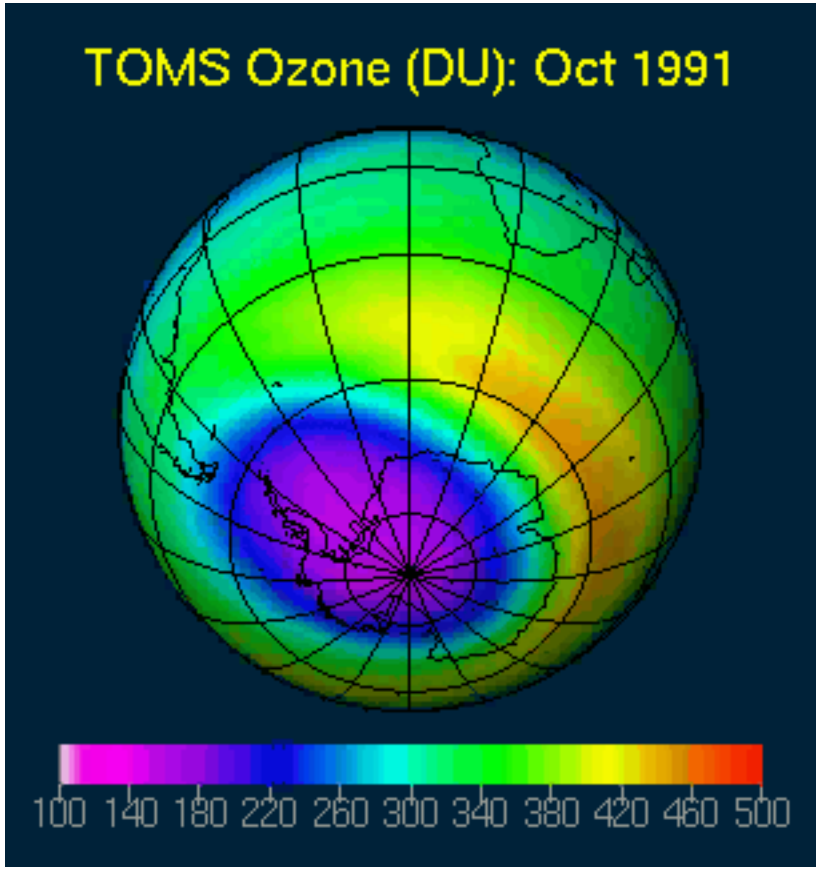


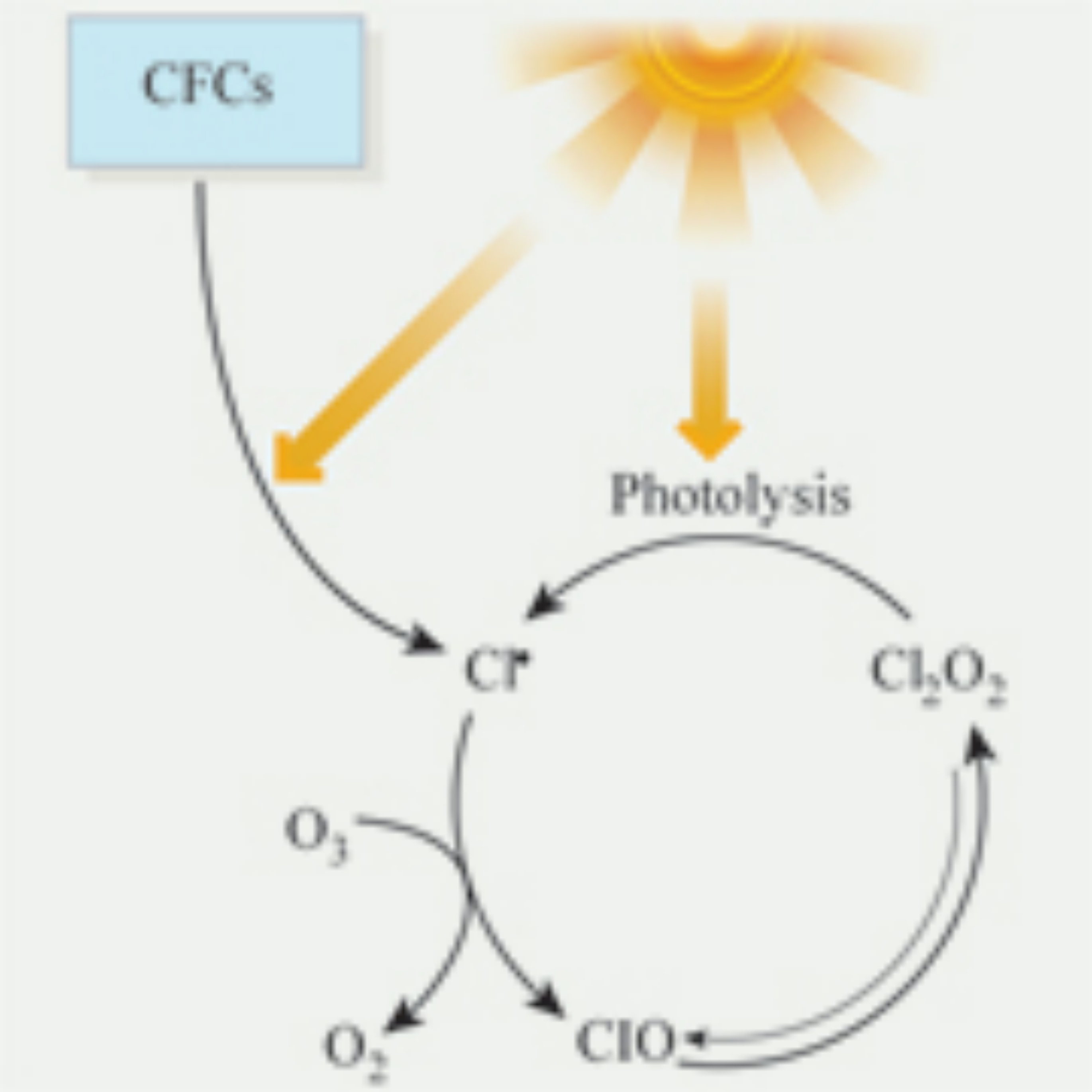
Figure 1. Diagram showing the effect of polar stratospheric clouds on ozone loss. The upper panel shows the situation when there are no polar stratospheric clouds. Ozone depletion takes place only in the gas phase (homogeneous chemistry). The lower panel shows the situation when there are polar stratospheric clouds present. The reservoir gases hydrochloric acid and chlorine nitrate react with each other on the surface of the PSC particles through a red-ox reaction and liberate elementary chlorine (Cl_2). Elementary chlorine is easily photolysed by sunlight and forms atomic chlorine, which reacts fast with ozone to form chlorine monoxide (ClO, active chlorine) and oxygen (O_2). ClO dimerises and forms Cl_2O_2, which is easily photolysed, liberating atomic chlorine again. Due to this catalytic cycle, one atom of Cl can destroy thousands of ozone molecules before it is passivated through reaction with NO_2, methane or other substances. This explains why a few ppb of chlorine can destroy several ppm of ozone. In addition, PSC particles can grow large enough to sediment, thereby removing HNO_3 from the stratosphere. This means that there will be limited amounts of NO_2 present to quench the active chlorine, and the ozone depleting process can continue for several weeks. The diagram has been made by Finn Bjørklid, Norwegian Institute for Air Research (NILU).





Ozone depletion facilitated by the polar vortex


TOMS Ozone (DU): Oct 1991
100 140 180 220 260 300 340 380 420 460 500


CFCs
Photolysis
Cl
Cl2O2
O3
O2
ClO