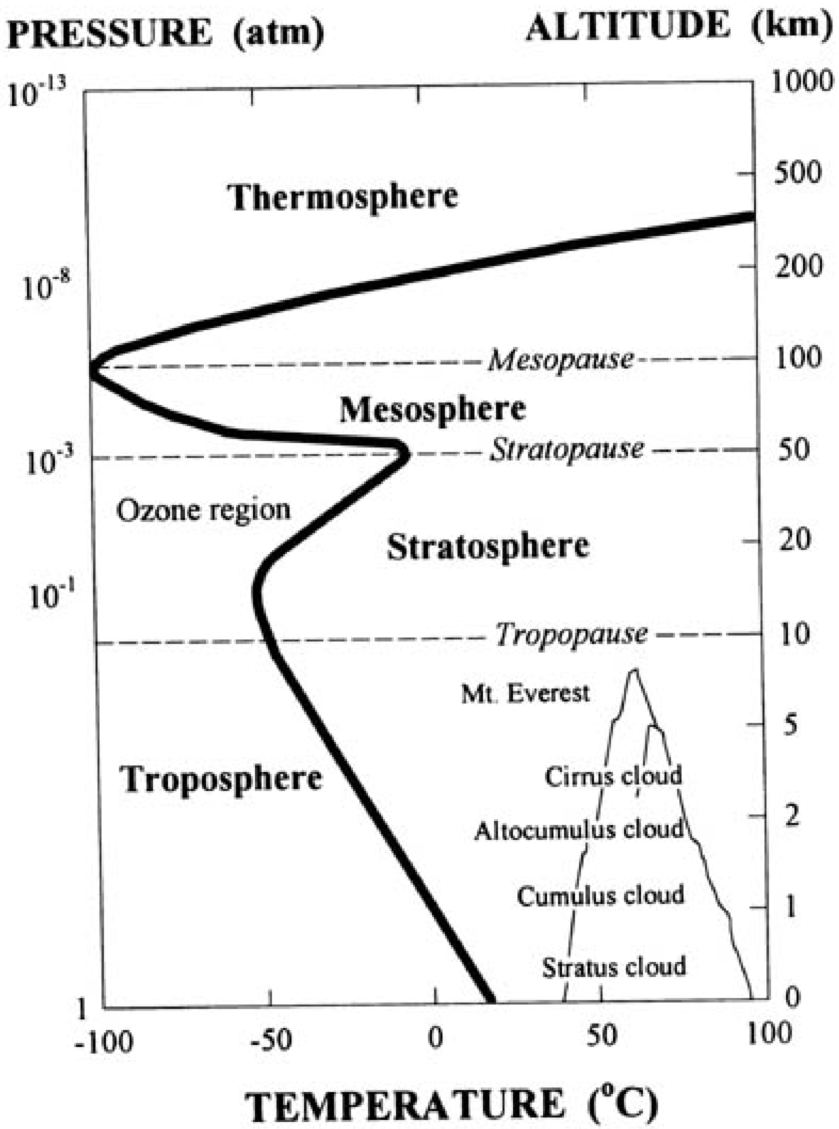
Atmospheric Chemistry

- Structure and Circulation
- Gas Composition
- Photochemistry
- Case Study: Ozone



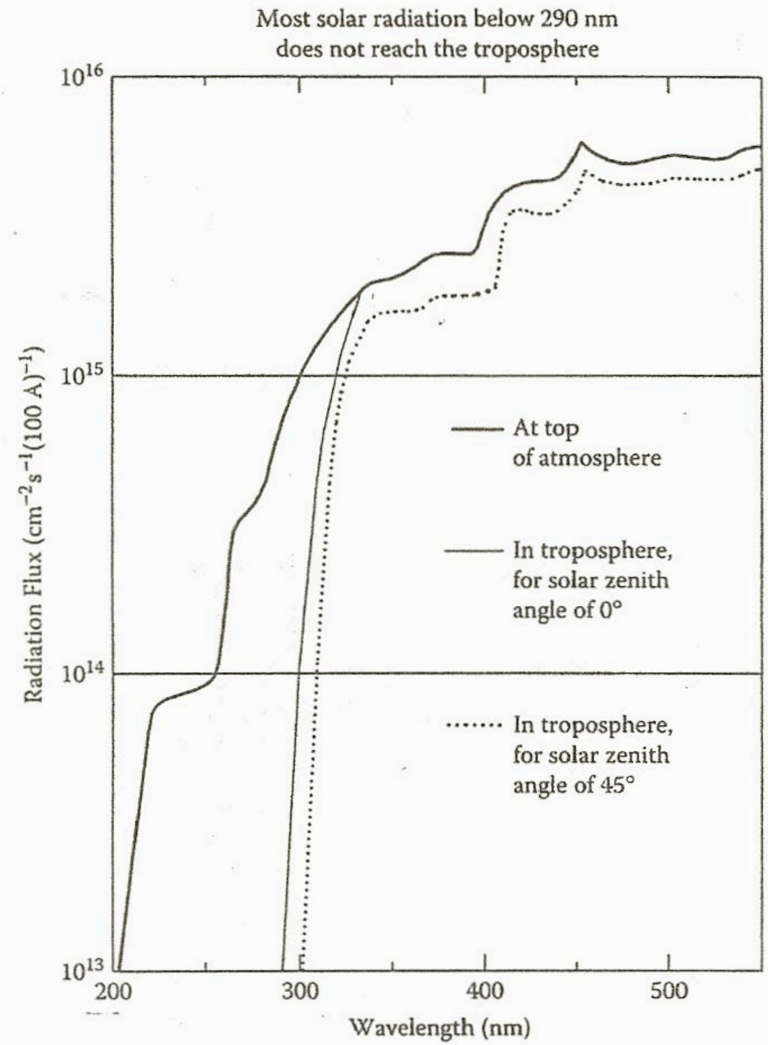


FIGURE 5.1. Changes in temperature in the layers of the atmosphere.

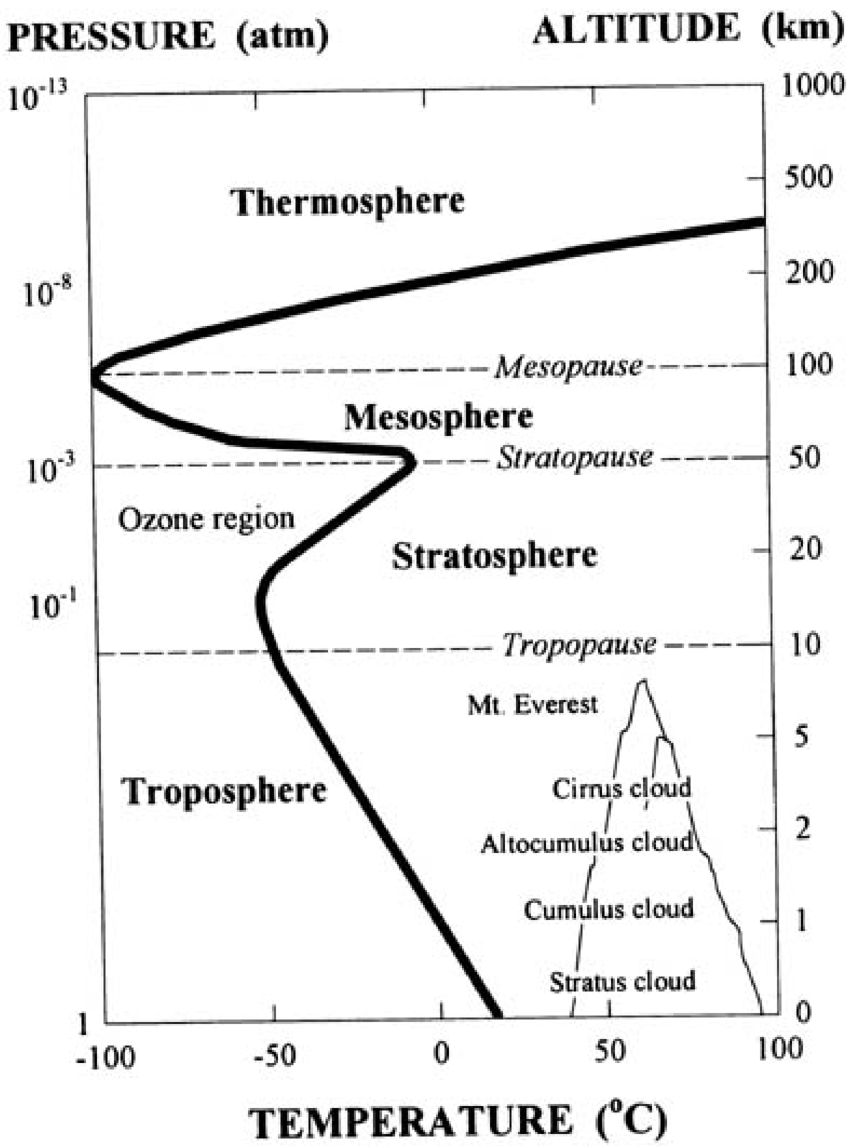


FIGURE 5.1. Changes in temperature in the layers of the atmosphere.

Thermosphere (Above 100 km)

N_2 and O_2 absorb light below 240 nm

Stratosphere (10 to 50 km)

O_3 absorbs light between 240 and 300 nm

$$O_2 + h\nu \rightarrow 2\,O^{\cdot}$$
$$O_2 + O^{\cdot} + M \rightarrow O_3 + M$$

$$O_3 + h\nu \rightarrow O_2 + O(^1D)$$

Troposphere (below 10 km)

no light available to break O-O bonds
(> 300 nm, photons not energetic enough to break 120 kcal bonds)

Oxidizer is the $OH^{\cdot}$ radical not O_3 or H_2O_2

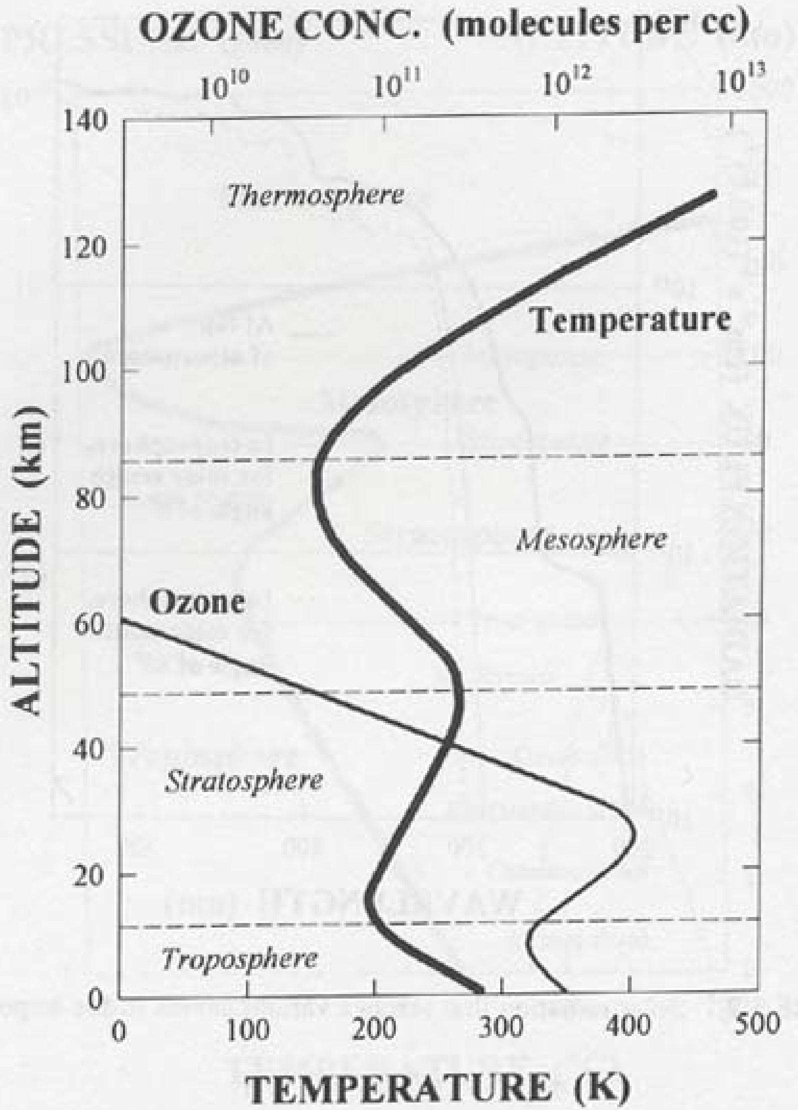
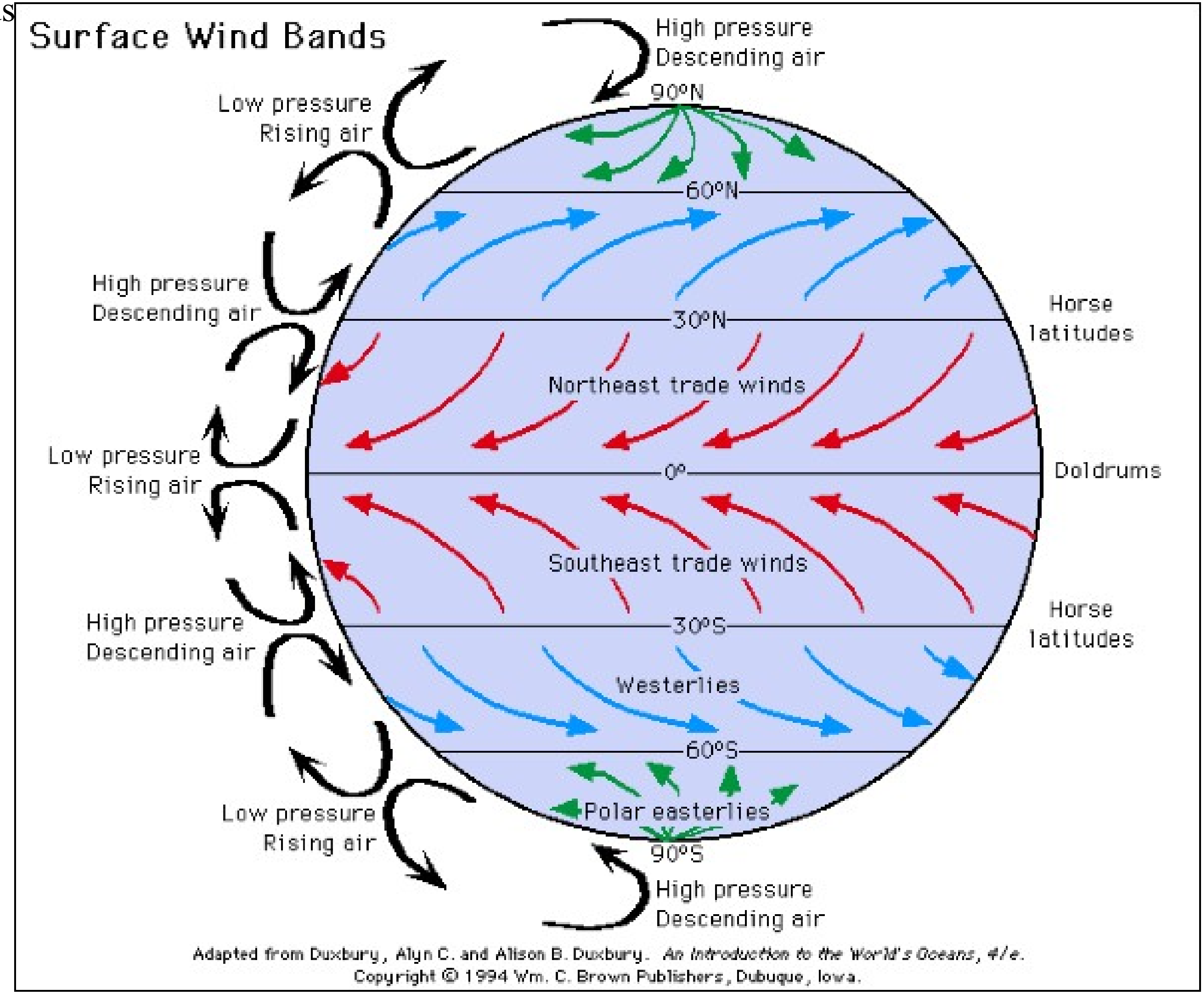


FIGURE 5.3. Concentration of ozone in various layers of the atmosphere.

Winds



Surface Wind Bands
High pressure
Descending air
90ºN
Low pressure
Rising air
60ºN
High pressure
Descending air
30ºN
Horse latitudes
Northeast trade winds
Low pressure
Rising air
0º
Doldrums
Southeast trade winds
High pressure
Descending air
30ºS
Horse latitudes
Westerlies
60ºS
Low pressure
Rising air
Polar easterlies
90ºS
High pressure
Descending air
Adapted from Duxbury, Alyn C. and Alison B. Duxbury. An Introduction to the World's Oceans, 4/e.
Copyright © 1994 Wm. C. Brown Publishers, Dubuque, Iowa.

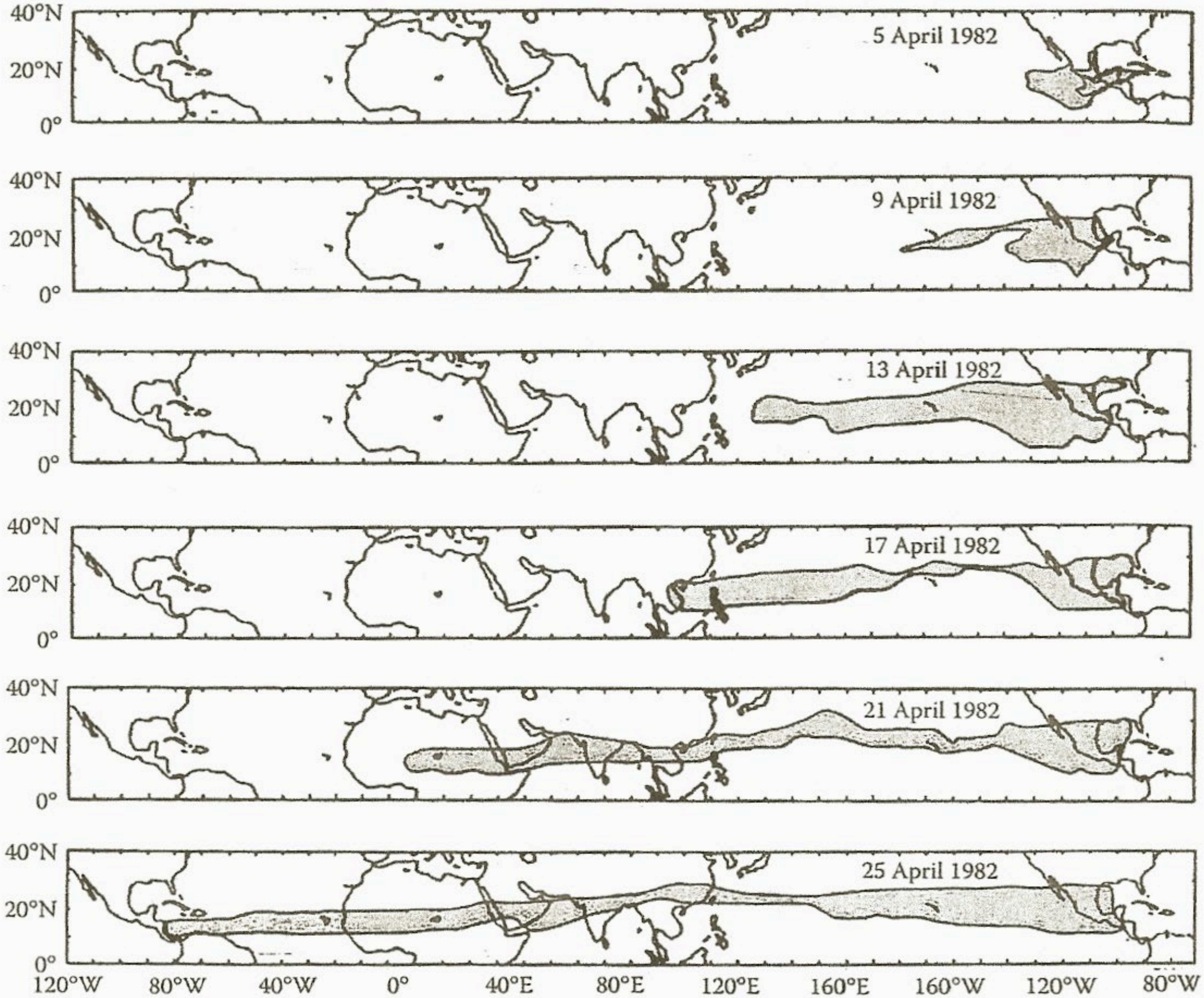


FIGURE 5.9
The movement of dust and particles in the northern hemisphere after the El Chichon Volcano eruption.

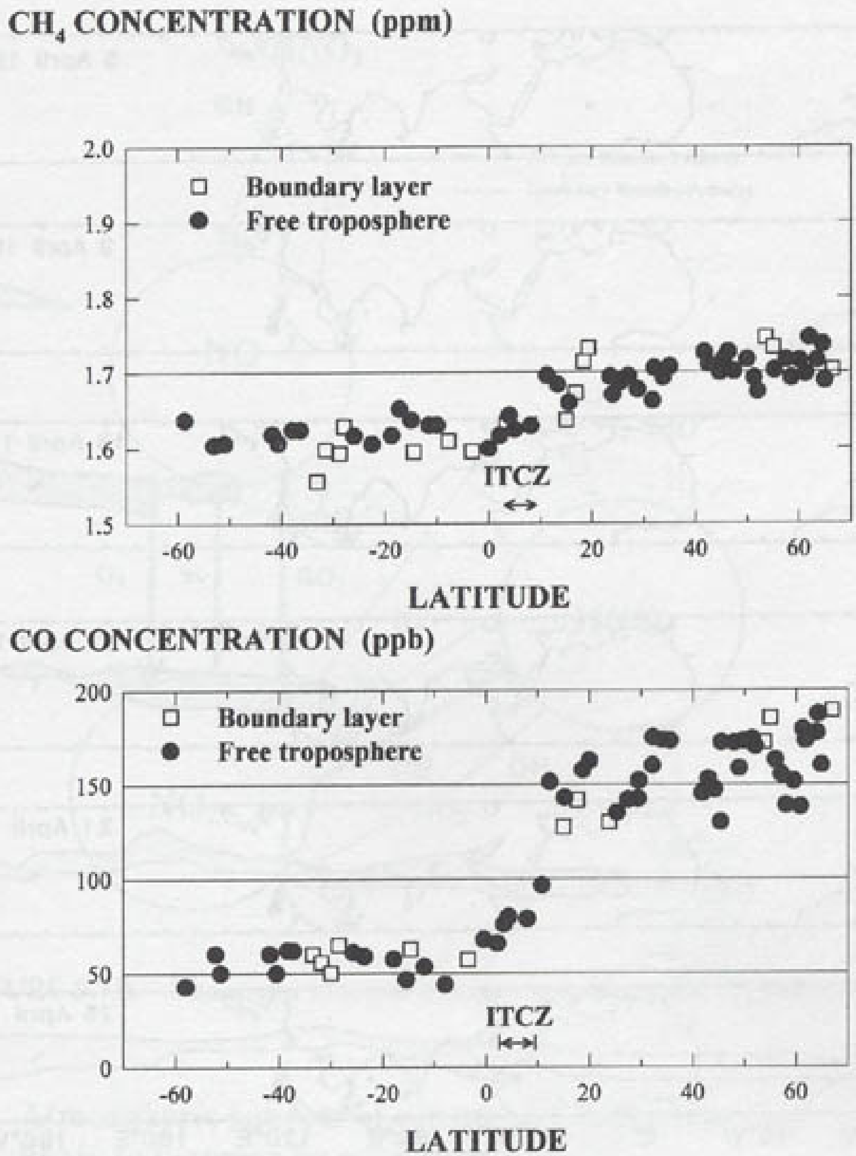


FIGURE 5.8. Distribution of methane (top) and carbon monoxide (bottom) between the hemispheres.

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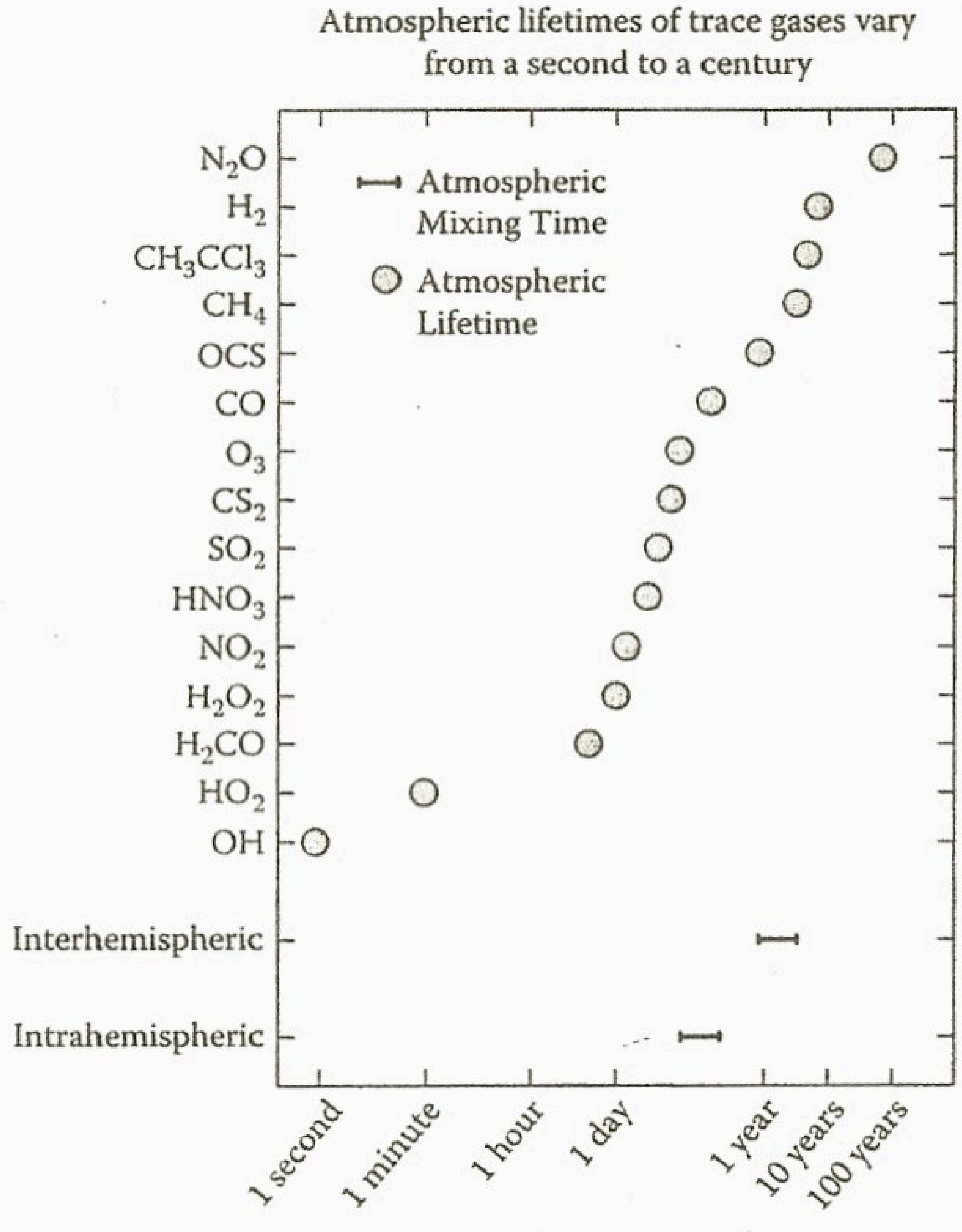
TABLE 5.1
Abundance of the Major Conservative Atmospheric Gases[a]

Gas	Mole fraction in dry air (X_i)
N_2	0.78084 ± 0.00004
O_2	0.20946 ± 0.00002
Ar	$(9.34 \pm 0.01) \times 10^{-3}$
CO_2	$(3.5 \pm 0.1) \times 10^{-4}$
Ne	$(1.818 \pm 0.004) \times 10^{-5}$
He	$(5.24 \pm 0.004) \times 10^{-6}$
Kr	$(1.14 \pm 0.01) \times 10^{-6}$
Xe	$(8.7 \pm 0.1) \times 10^{-8}$

[a] Kester (1975).

TABLE 5.2
The Composition of Minor Gases in the Atmosphere

Species	X_i actual	Reliability	Source	Sink
CH_4	1.7×10^{-6}	High	Biog.	Photochem.
CO	$0.5–2 \times 10^{-7}$	Fair	Photo., anthr.	Photochem.
O_3	5×10^{-8} (clean)	Fair	Photo	Photochem.
	4×10^{-7} (polluted)			
	10^{-7} to 6×10^{-6} (stratosphere)			
$NO + NO_2$	$10^{-12}–10^{-8}$	Low	Lightn., anthr. photo.	Photochem.
HNO_3	$10^{-11}–10^{-9}$	Low	Photo.	Rainout
NH_3	$10^{-10}–10^{-9}$	Low	Biog.	Photo., rainout
N_2O	3×10^{-7}	High	Biog.	Photo.
H_2	5×10^{-7}	High	Biog., photo.	Photo.
OH	$10^{-15}–10^{-12}$	Very low	Photo.	Photo.
HO_2	$10^{-11}–10^{-13}$	Very low	Photo.	Photo.
H_2O_2	$10^{-10}–10^{-18}$	Very low	Photo.	Rainout
H_2CO	$10^{-10}–10^{-9}$	Low	Photo.	Photo.
SO_2	$10^{-11}–10^{-10}$	Fair	Anth., photo.,	Photo., volcanic
CS_2	$10^{-11}–10^{-10}$	Low	Anthr., biol.,	Photo.
OCS	5×10^{-10}	Fair	Anthr., biol., photo.	Photo.
CH_3CCl_3	$0.7–2 \times 10^{-10}$	Fair	Anthropogenic	Photo.


Atmospheric lifetimes of trace gases vary
from a second to a century
Atmospheric Mixing Time
Atmospheric Lifetime
N2O
H2
CH3CCl3
CH4
OCS
CO
O3
CS2
SO2
HNO3
NO2
H2O2
H2CO
HO2
OH
Interhemispheric
Intrahemispheric
1 second
1 minute
1 hour
1 day
1 year
10 years
100 years

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Production of OH Radicals

$$O_3 + h\nu\ (< 315\ nm) \rightarrow O(^1D) + O_2$$

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

$$H + O_2 \rightarrow HO_2$$

$$HO_2 + NO \rightarrow NO_2 + OH\cdot$$

$$HO_2 + O_3 \rightarrow 2\ O_2 + OH\cdot$$

Removal Of OH Radicals

$$CO + OH\cdot \rightarrow CO_2 + H\cdot$$

$$CH_4 + OH\cdot \rightarrow \cdot CH_3 + H_2O$$

$$HO_2 + OH\cdot \rightarrow H_2O + O_2$$

SUMMARY OF IMPORTANT NITROGEN OXIDE REACTIONS

(Species NO, NO_2, HNO_3)

Gas Phase

$N_2 + O_2 \longrightarrow 2\,NO$ High Temperatures

$NO + HO_2\,(RO_2) \longrightarrow NO_2 + OH^{\cdot}\,(RO^{\cdot})$

$NO_2 + h\nu \longrightarrow NO + O^{\cdot}$

$O_2 + O^{\cdot} + M \rightarrow O_3 + M$

$NO_2 + OH^{\cdot} \longrightarrow HNO_3$

Aqueous Phase

$NO_2 + O_3 \longrightarrow NO_3 + O_2$

$NO_3 + NO_2 \longrightarrow N_2O_5$

$N_2O_5 + H_2O \longrightarrow 2\,HNO_3$

$2\,NO_2 + O_3 + H_2O \longrightarrow 2\,HNO_3 + O_2$

Most important source of O_3 and other oxidants in the Troposphere.
Hydrocarbons are needed to produce HO_2.

SULFUR OXIDE CHEMISTRY

Gas

$SO_2 + OH\cdot \rightarrow HOSO_2$

$HOSO_2 + O_2 \rightarrow SO_3 + HO_2$

$SO_3 + H_2O \rightarrow H_2SO_4$

Aqueous

$SO_2 + H_2O \rightarrow HSO_3^- + H^+ \rightarrow SO_3^{-2} + H^+$

$HSO_3- + H_2O_2 \rightarrow SO_4^{-2} + H^+ + H_2O$

$SO_3^{-2} + O_3 \rightarrow SO_4^{-2} + O_2$

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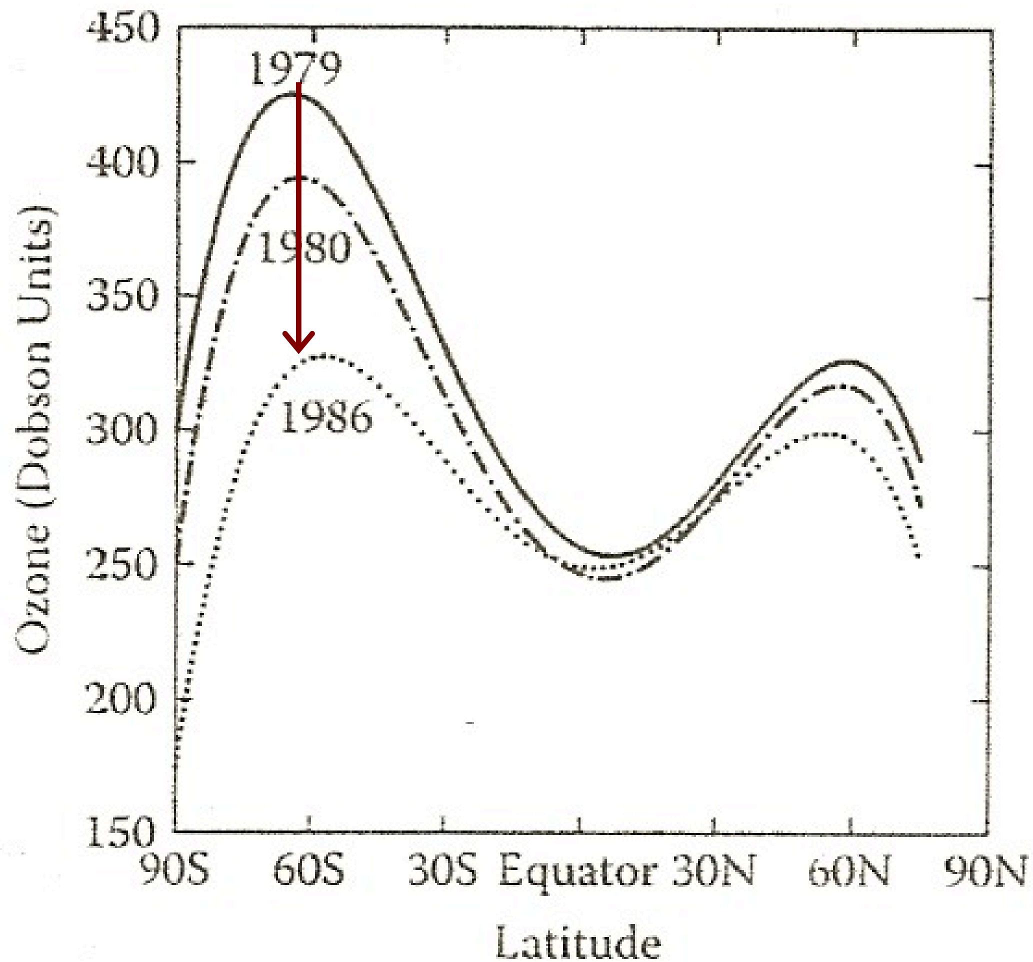
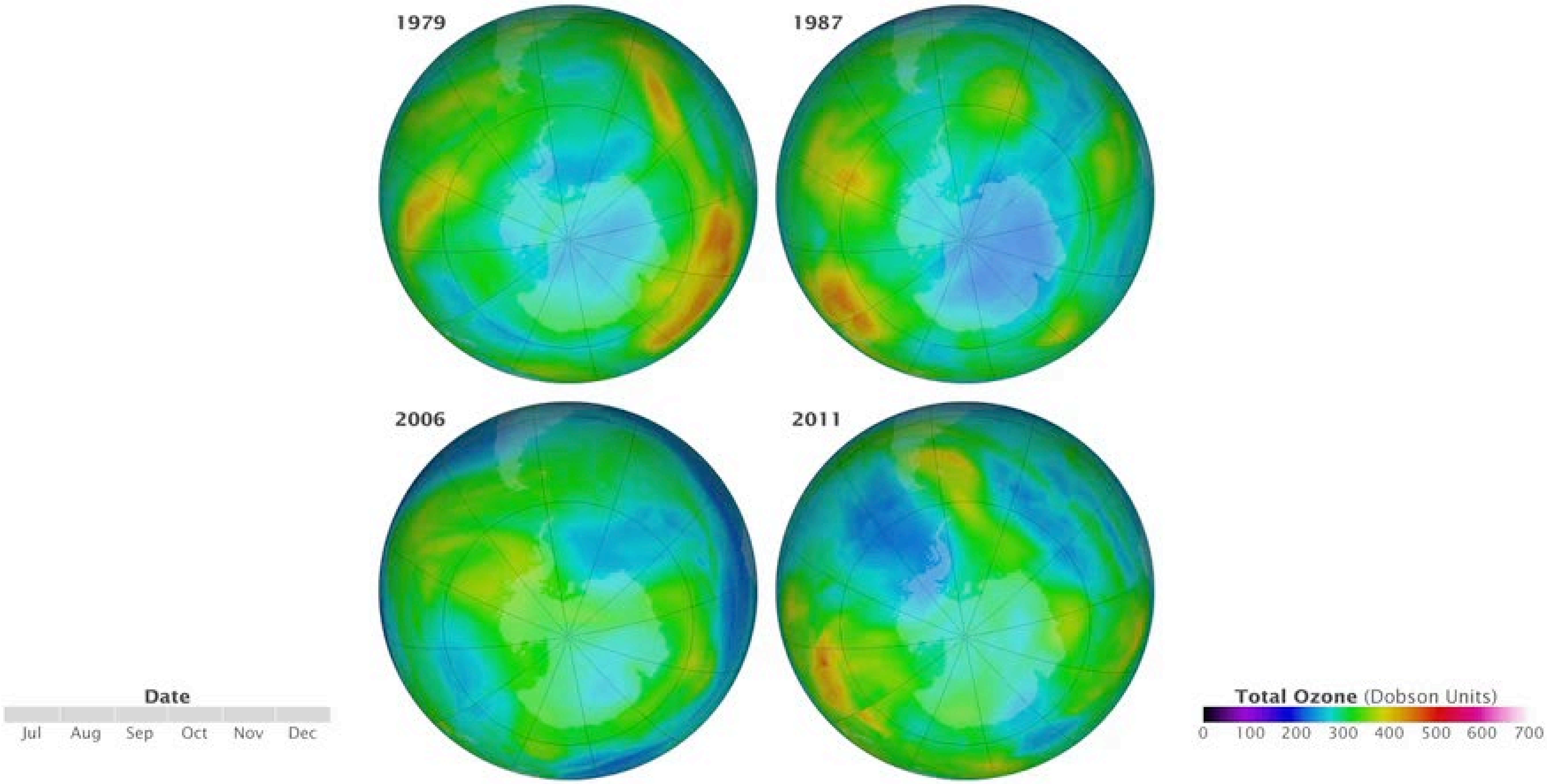
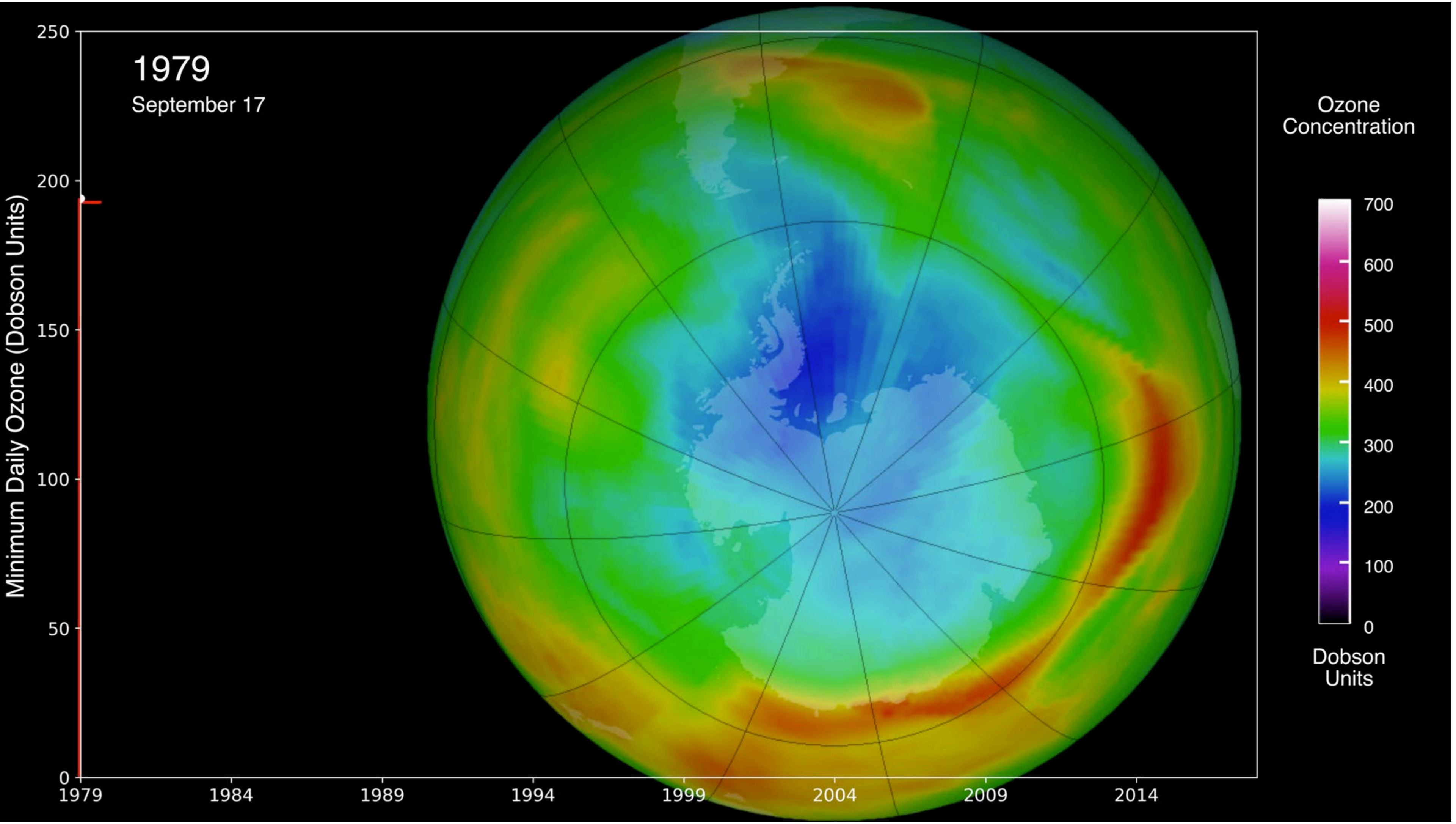


FIGURE 5.37
The levels of ozone as a function of latitude.


1979
1987
2006
2011
Date
Jul Aug Sep Oct Nov Dec
Total Ozone (Dobson Units)
0 100 200 300 400 500 600 700



1979
September 17
Minimum Daily Ozone (Dobson Units)
250
200
150
100
50
0
1979
1984
1989
1994
1999
2004
2009
2014
Ozone Concentration
700
600
500
400
300
200
100
0
Dobson Units

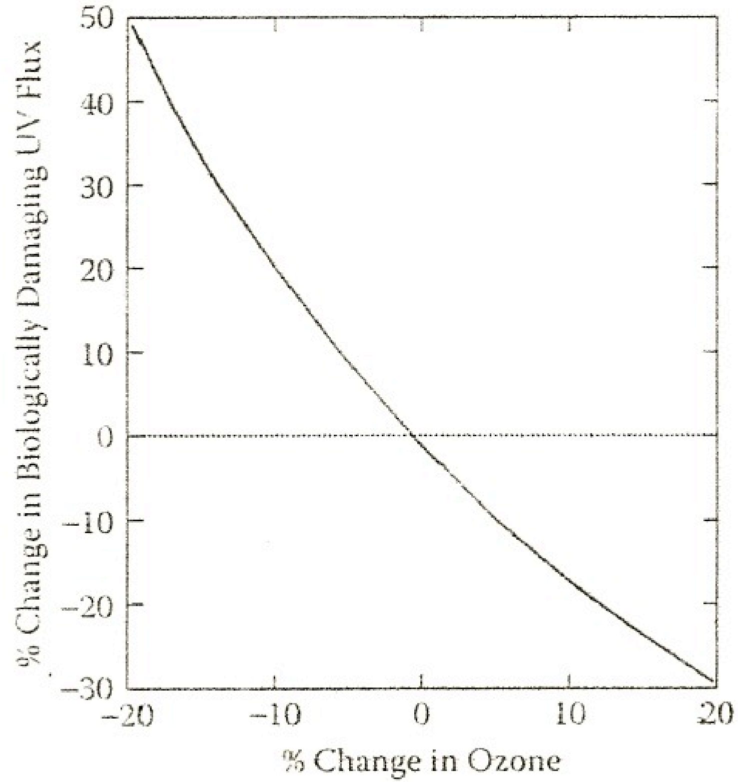


FIGURE 5.34
The changes in the biologically damaging ultraviolet (UV) flux as a function of changes in ozone levels.

SUMMARY OF OZONE CHEMISTRY

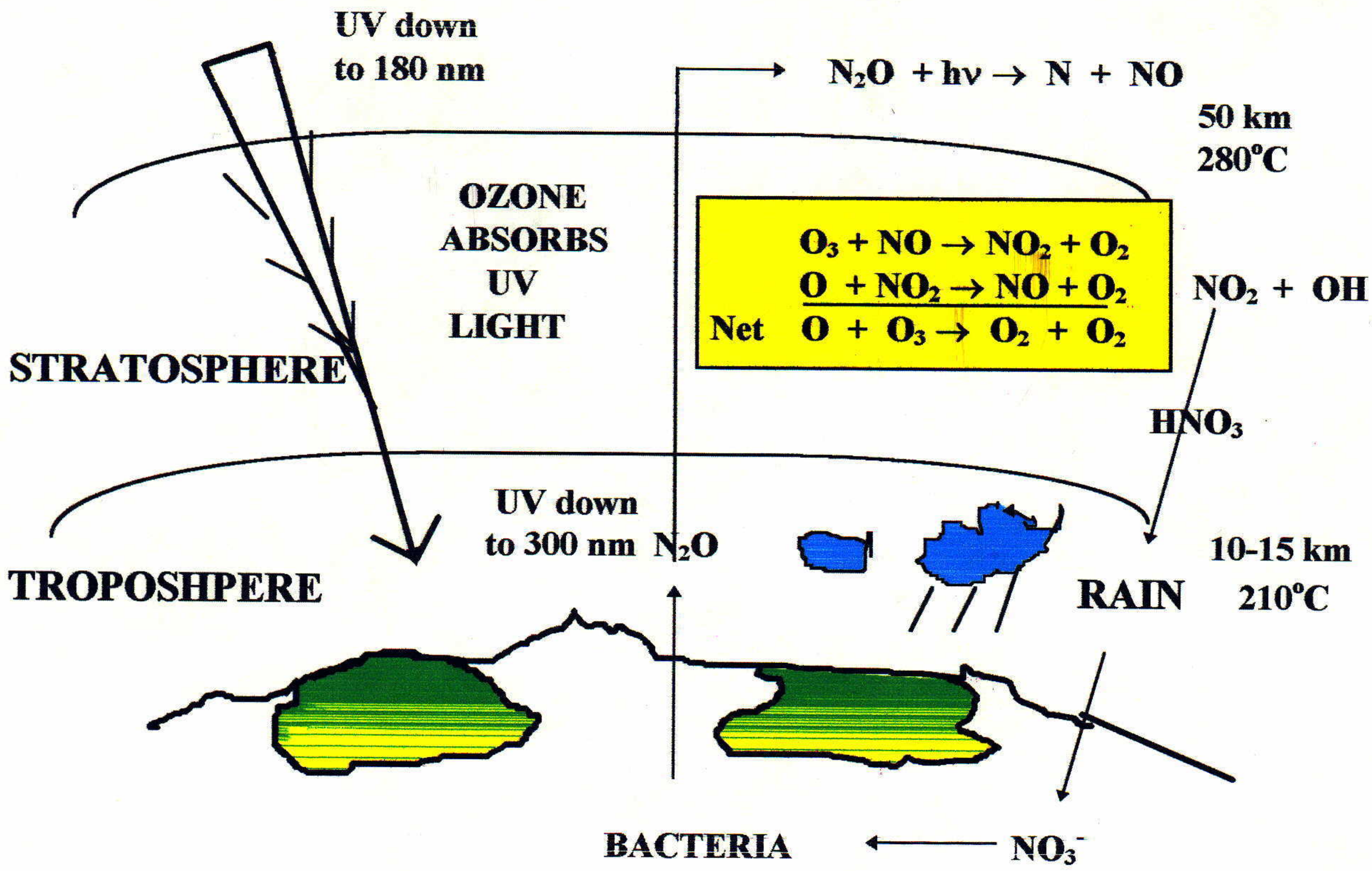
FORMATION

$O_2 + h\nu\ (< 240\ nm) \rightarrow 2\ O\cdot$

$O_2 + O\cdot \rightarrow O_3$

$O_3 + h\nu\ (240\text{-}300\ nm) \rightarrow O(^1D) + O_2$

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


UV down
to 180 nm
N2O + hν → N + NO
50 km
280°C
OZONE
ABSORBS
UV
LIGHT
O3 + NO → NO2 + O2
O + NO2 → NO + O2
Net O + O3 → O2 + O2
NO2 + OH
STRATOSPHERE
HNO3
UV down
to 300 nm N2O
10-15 km
210°C
TROPOSHPERE
RAIN
BACTERIA
NO3-

LOSS OF OZONE IN STRATOSPHERE

Chlorofluoro Carbons (CFC' s)

$CFCl_3$ (CFC-11) t = 75y
CF_2Cl_2 (CFC-12) t = 110 y

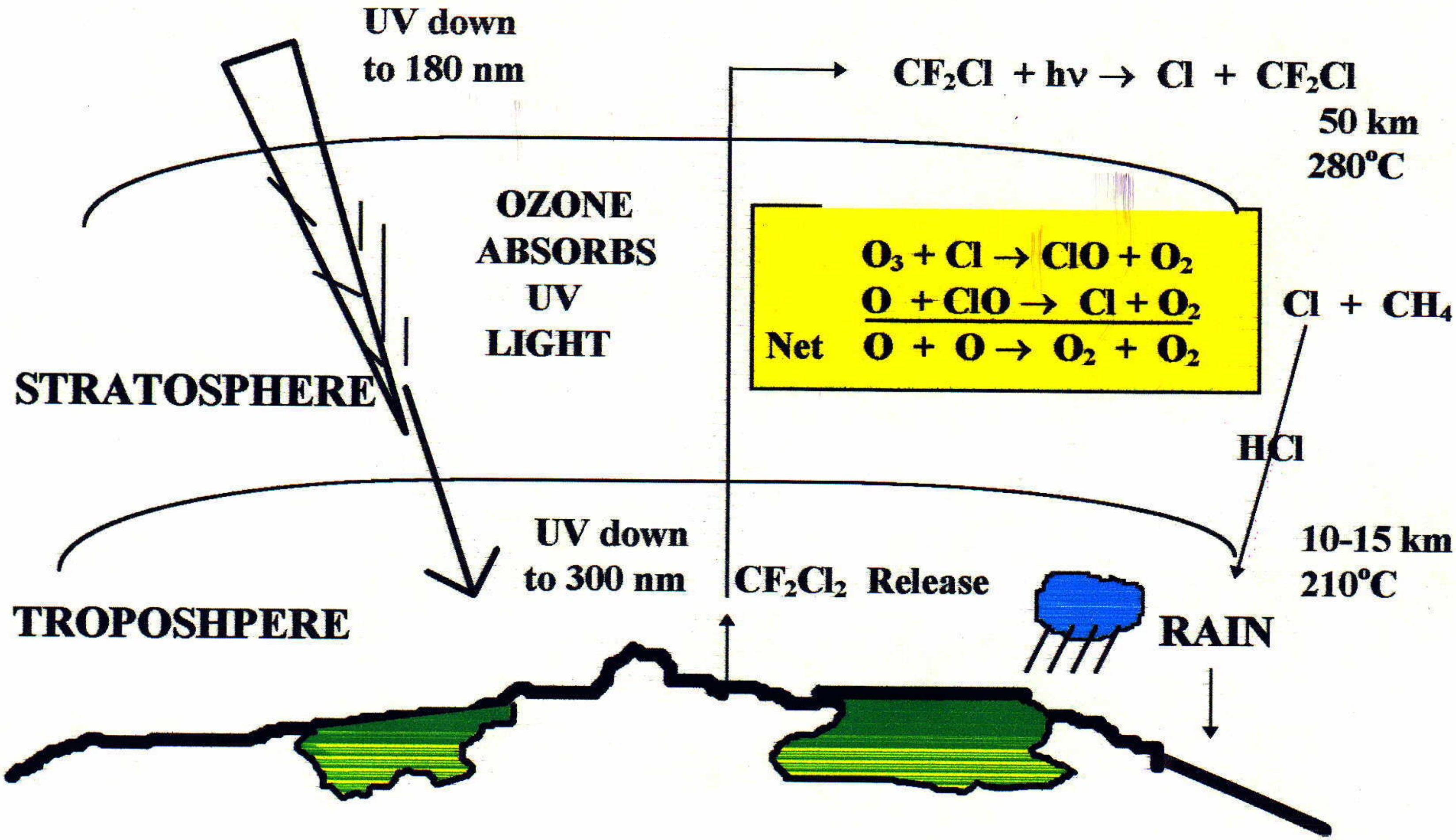
$$CFCl_3 + h\nu \rightarrow CFCl_2 + Cl\cdot$$

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

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

Scientific Support

F is found in Stratosphere
ClO appearance and O_3 loss in Antarctic


UV down
to 180 nm
CF2Cl + hν → Cl + CF2Cl
50 km
280°C
OZONE
ABSORBS
UV
LIGHT
O3 + Cl → ClO + O2
O + ClO → Cl + O2
Net O + O → O2 + O2
Cl + CH4
STRATOSPHERE
HCl
UV down
to 300 nm
CF2Cl2 Release
10-15 km
210°C
RAIN
TROPOSHPERE

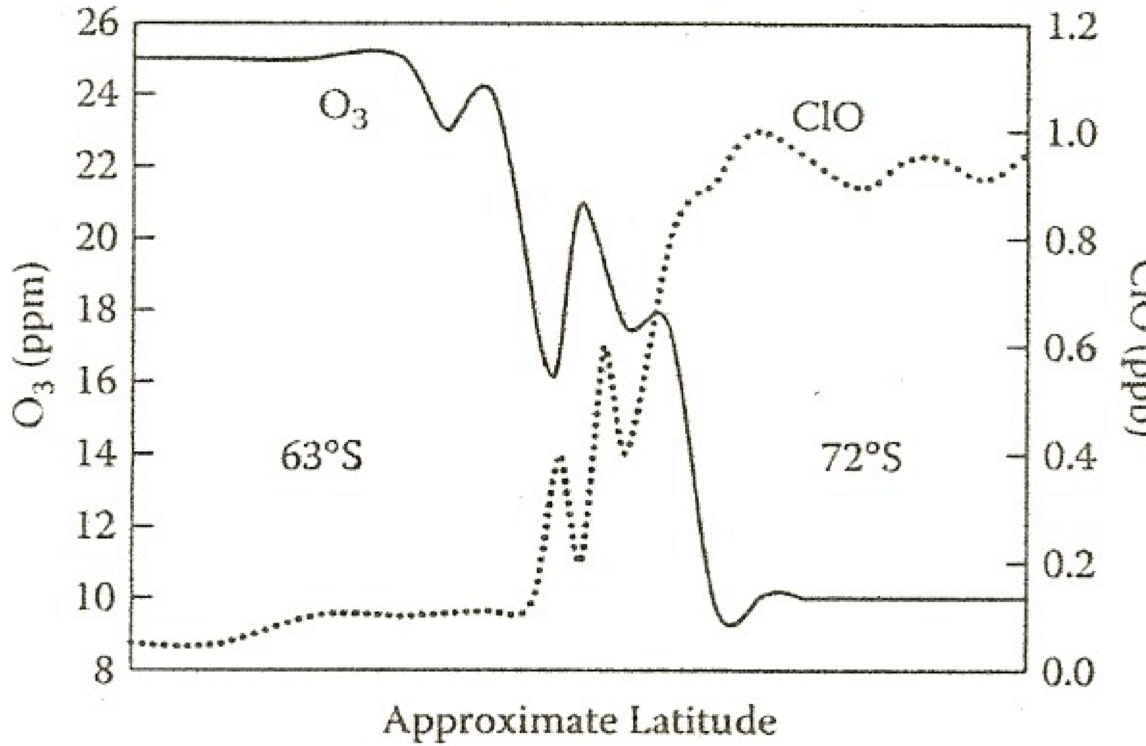
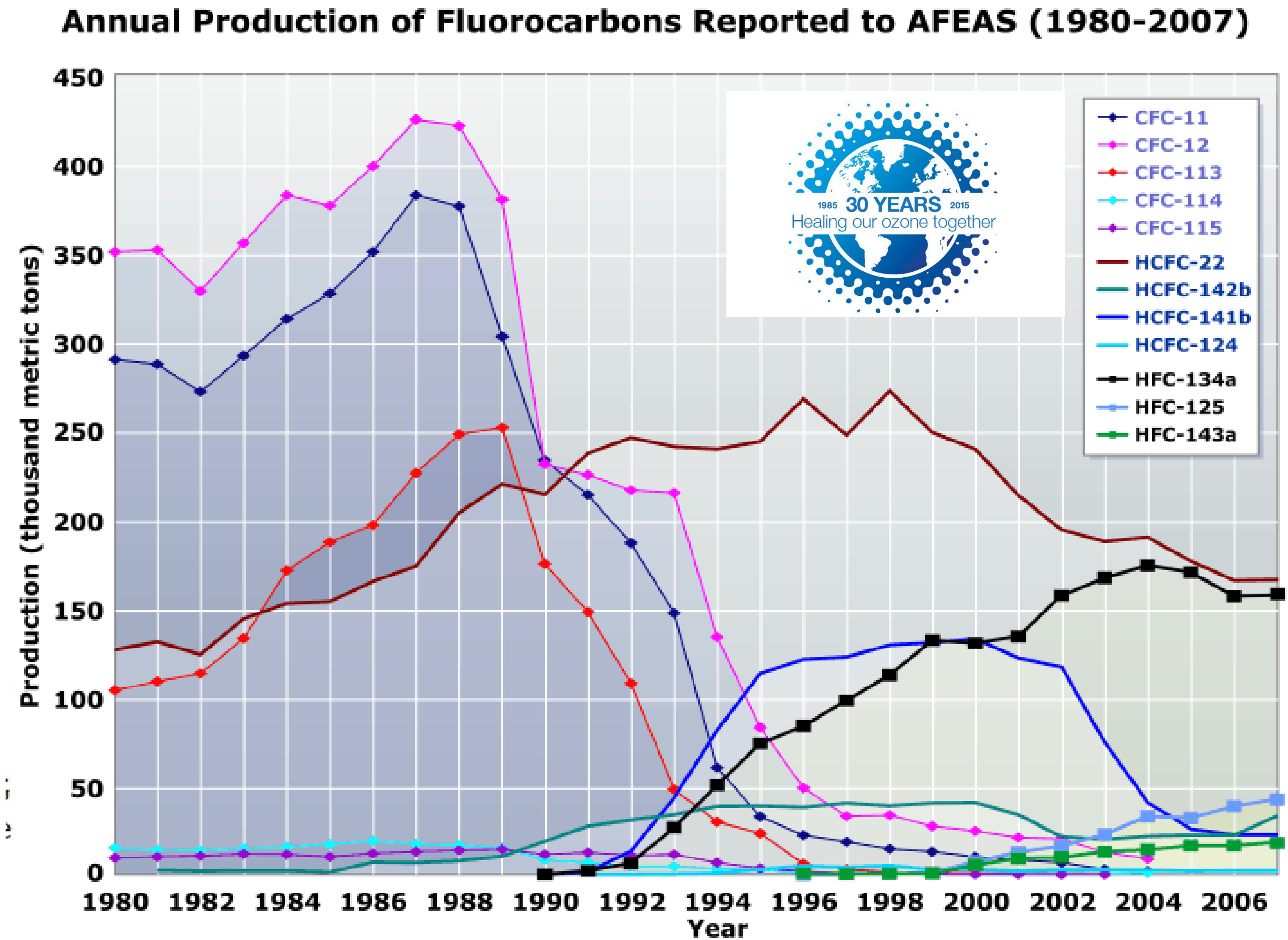
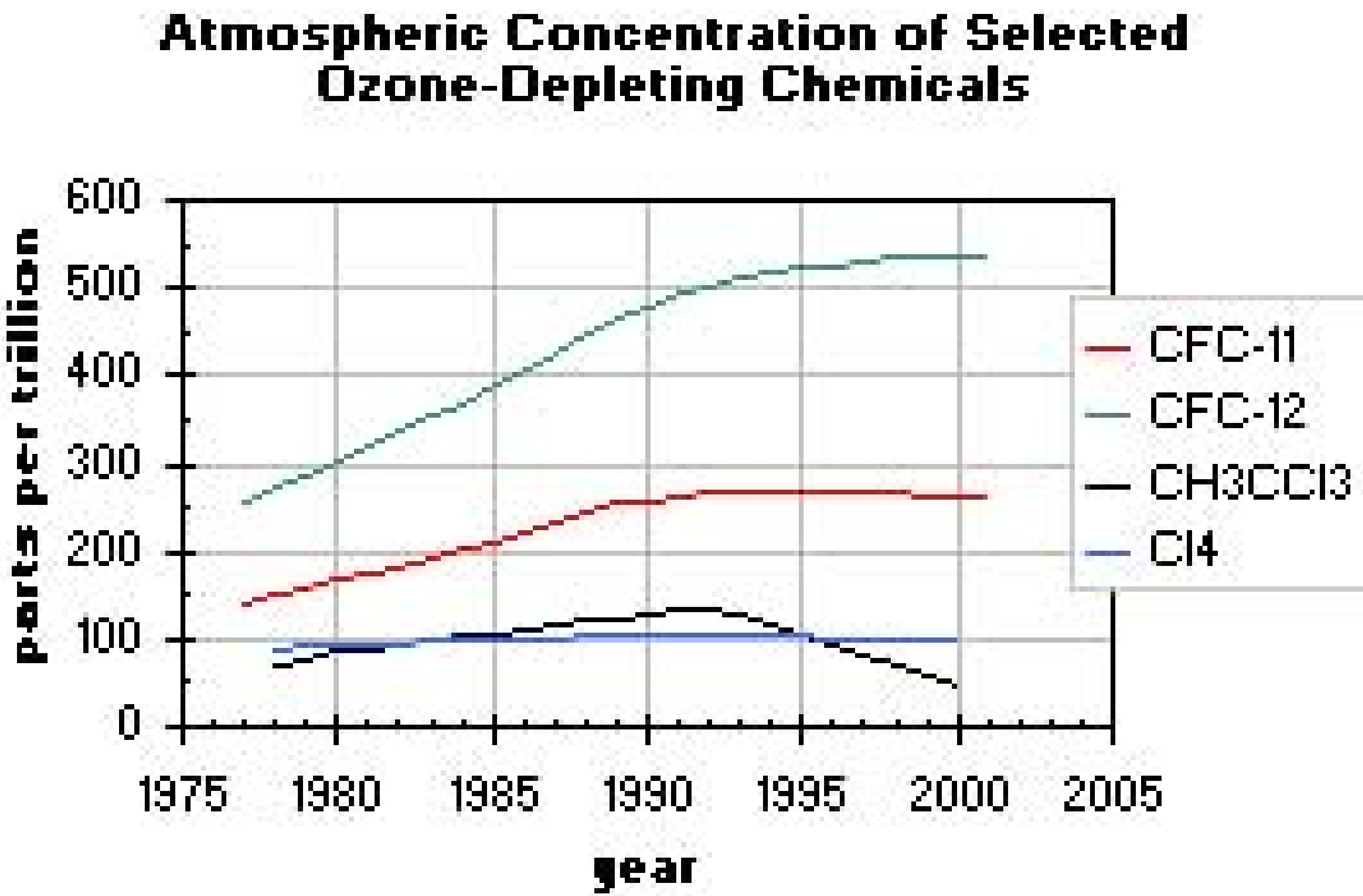
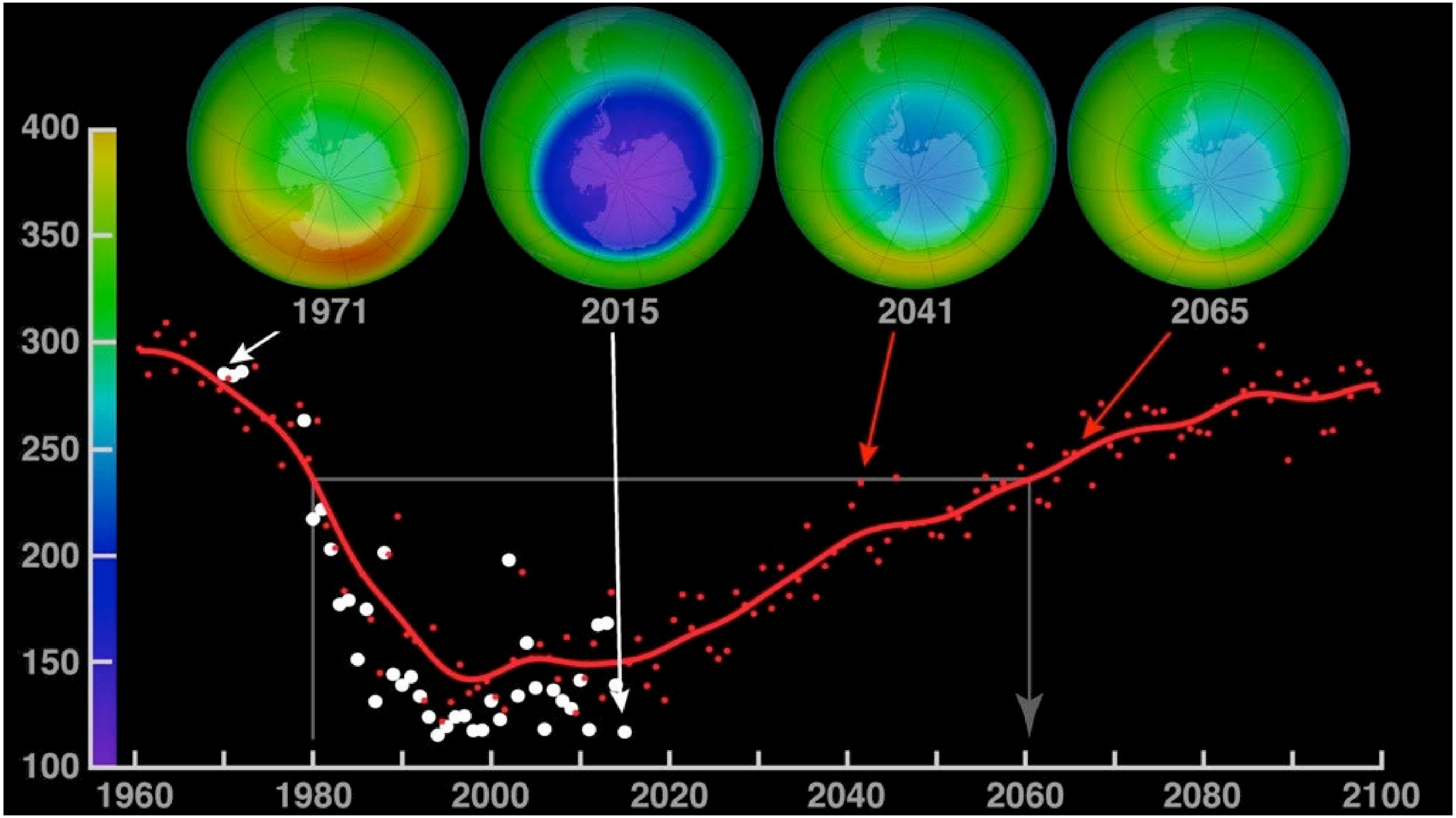


FIGURE 5.40
The relationship between O_3 and ClO in the Antarctic.


Annual Production of Fluorocarbons Reported to AFEAS (1980-2007)
450
400
350
300
250
200
150
100
50
0
Production (thousand metric tons)
1980
1982
1984
1986
1988
1990
1992
1994
1996
1998
2000
2002
2004
2006
Year
1985 30 YEARS 2015
Healing our ozone together
CFC-11
CFC-12
CFC-113
CFC-114
CFC-115
HCFC-22
HCFC-142b
HCFC-141b
HCFC-124
HFC-134a
HFC-125
HFC-143a



Atmospheric Concentration of Selected Ozone-Depleting Chemicals
parts per trillion
600
500
400
300
200
100
0
1975
1980
1985
1990
1995
2000
2005
year
CFC-11
CFC-12
CH3CCl3
Cl4



1971
2015
2041
2065
400
350
300
250
200
150
100
1960
1980
2000
2020
2040
2060
2080
2100