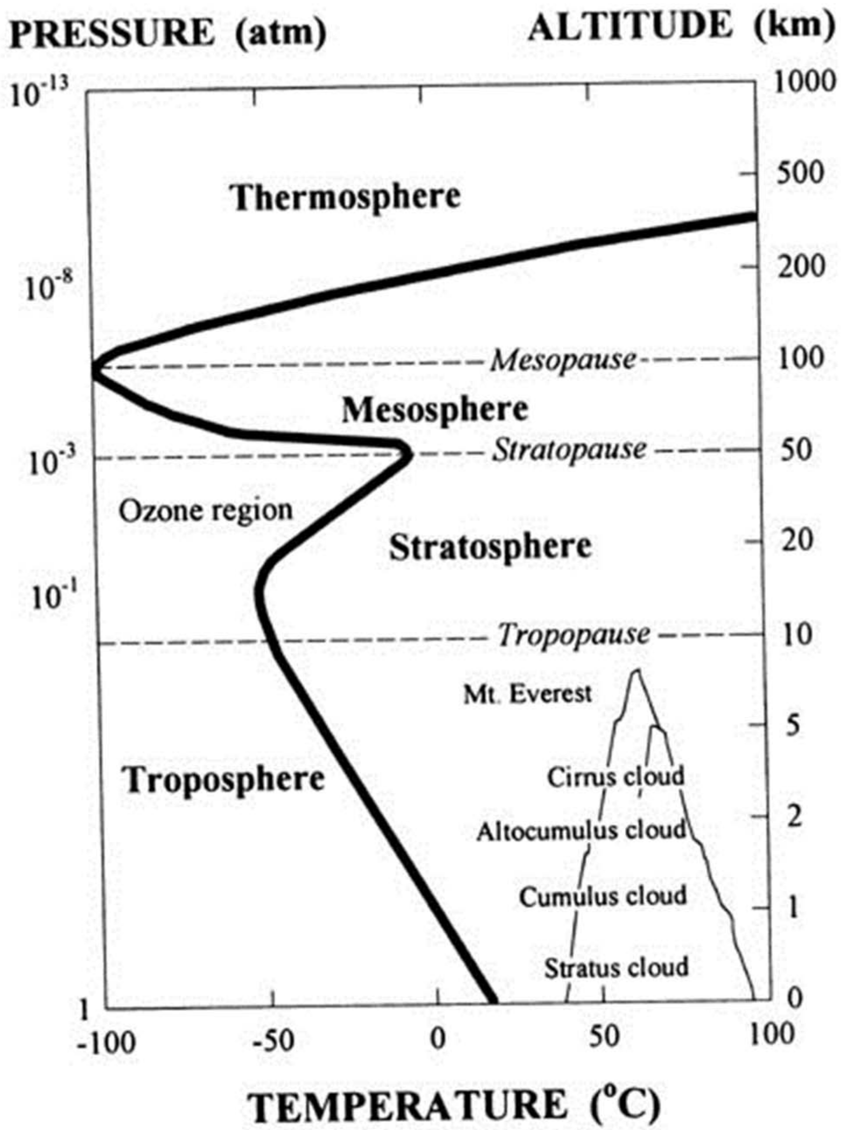
Atmospheric Chemistry

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



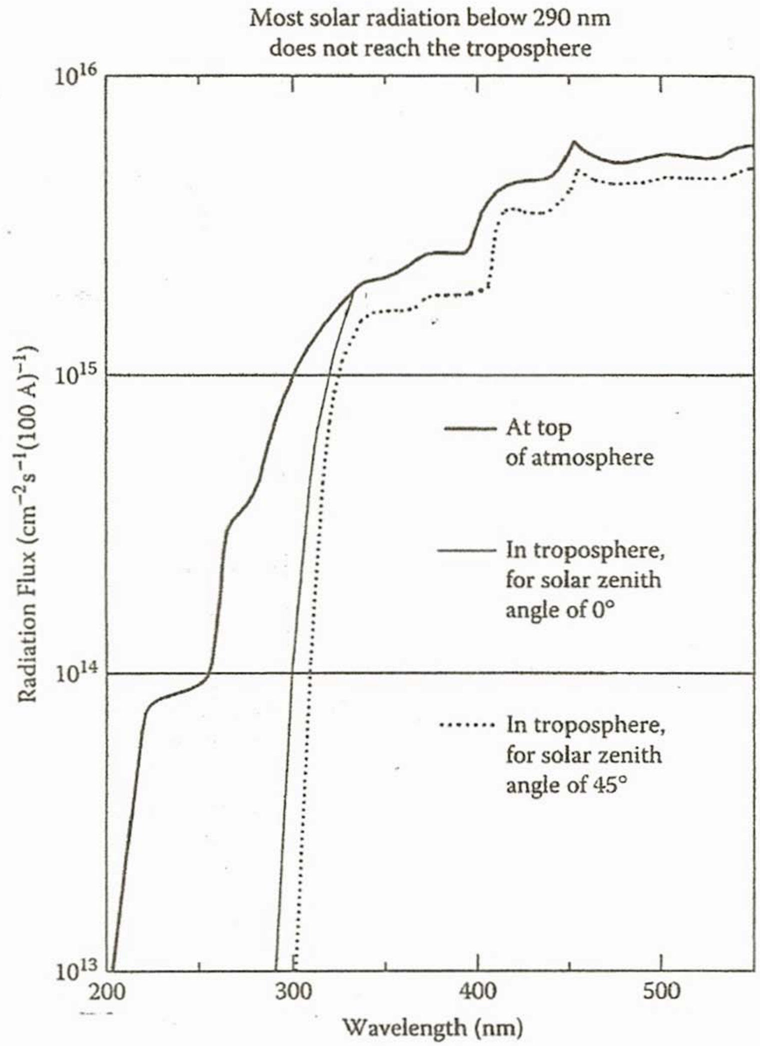


FIGURE 5.1. Changes in temperature in the layers of the atmosphere.

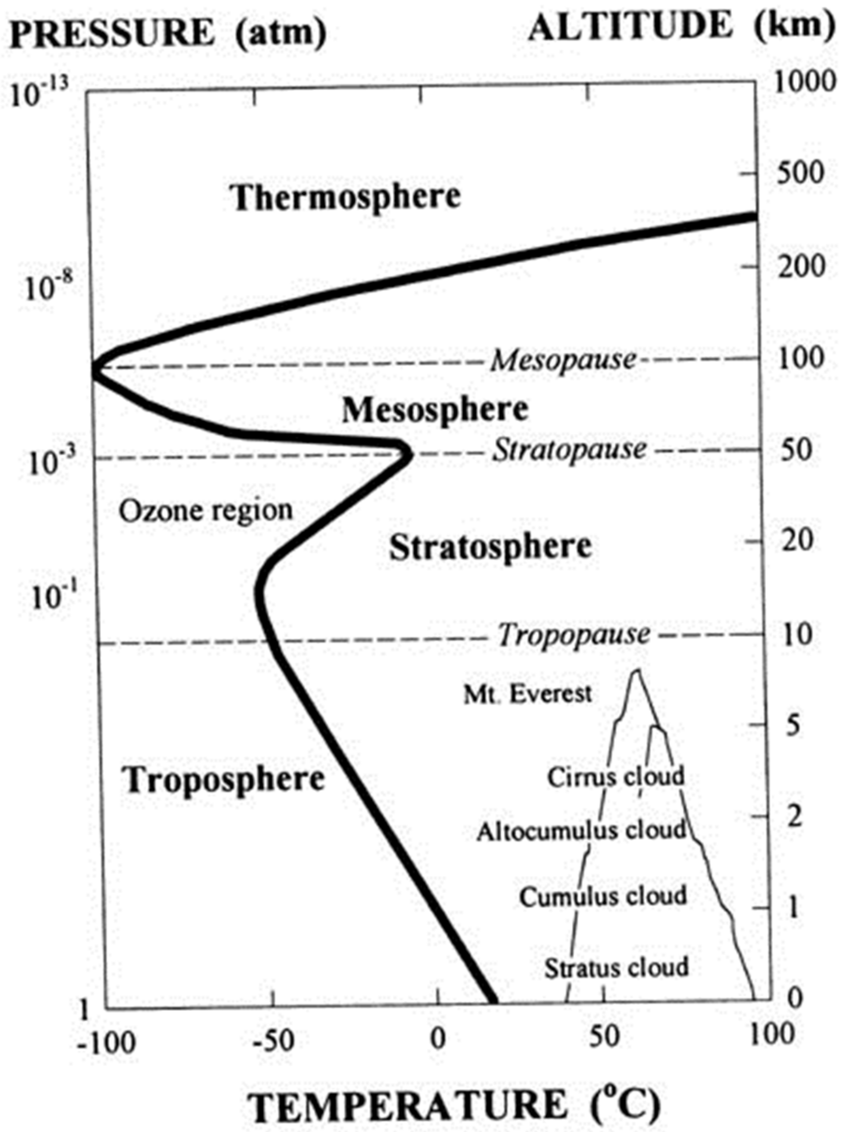


FIGURE 5.1. Changes in temperature in the layers of the atmosphere.

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 of 120 kcal bond strength

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

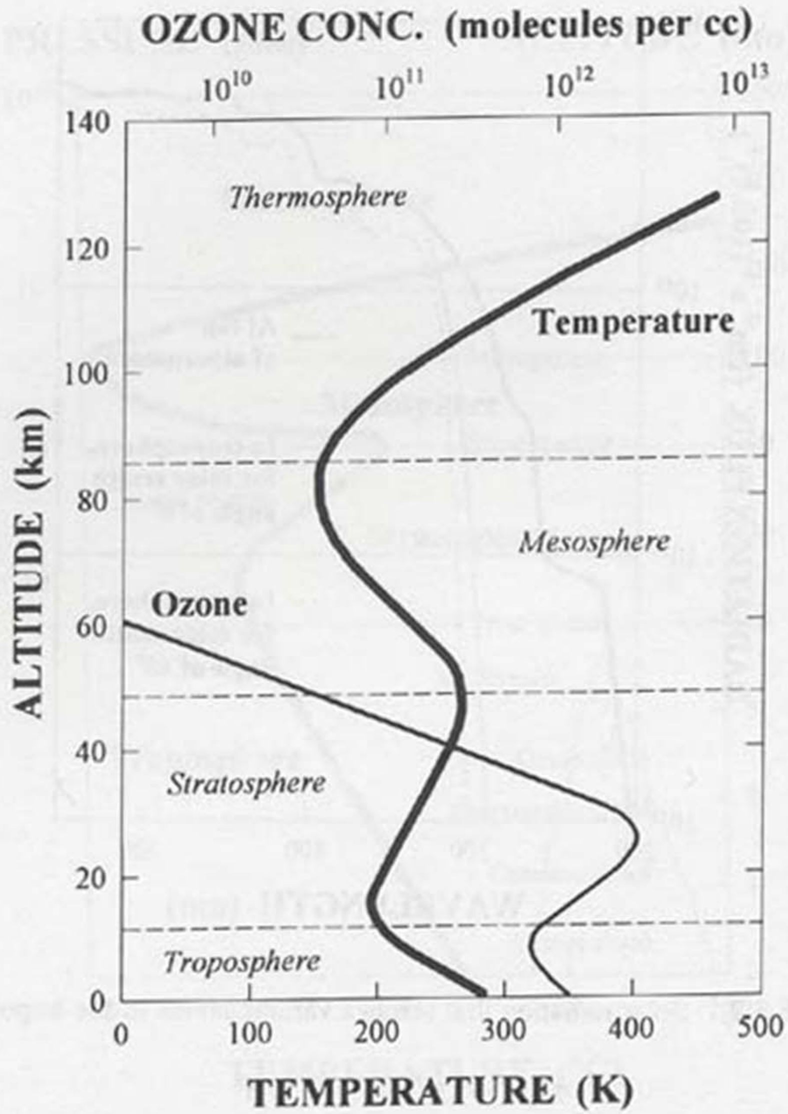
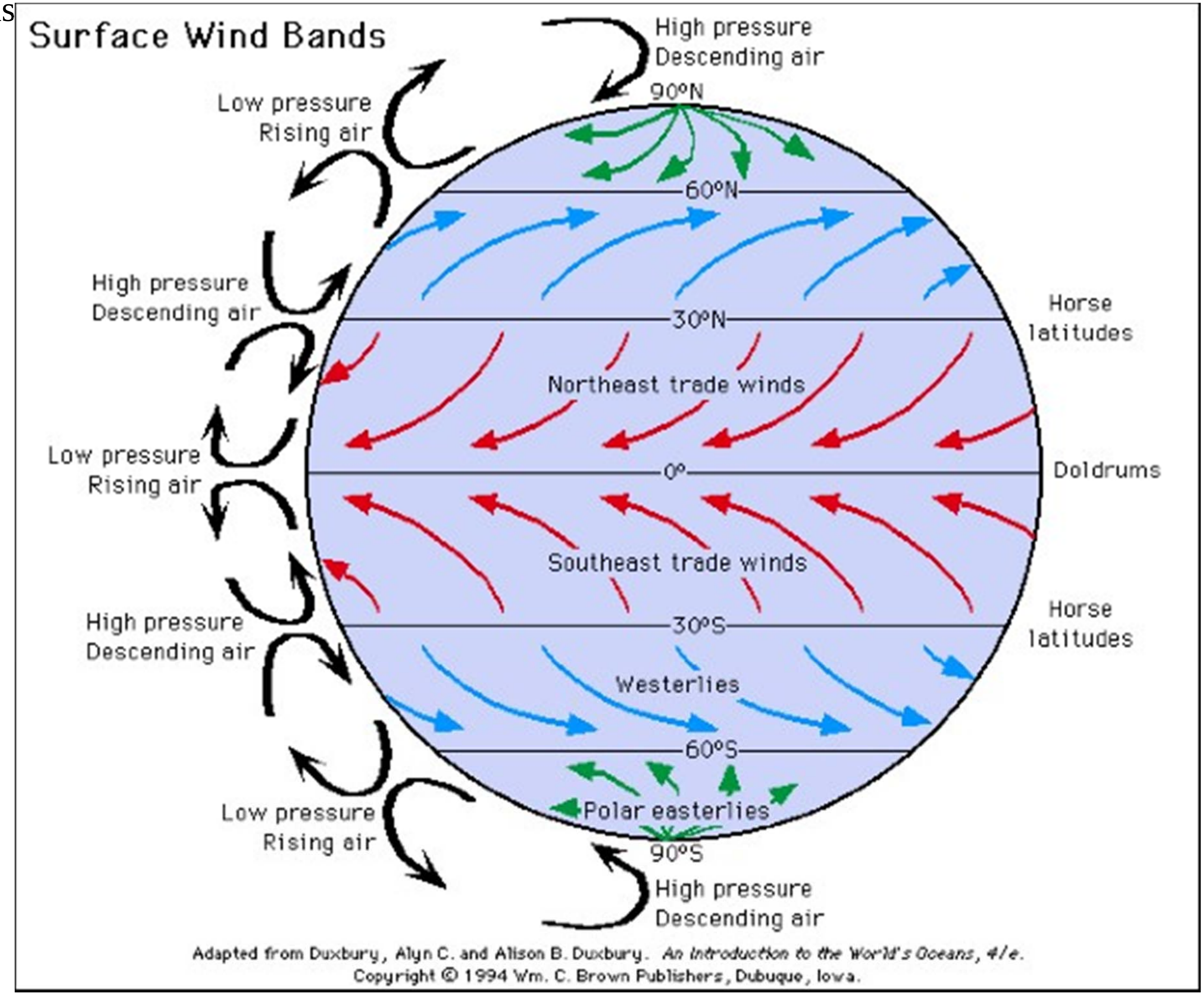


FIGURE 5.3. Concentration of ozone in various layers of the atmosphere.

Winds


Surface Wind Bands
High pressure
Descending air
90°N
Low pressure
Rising air
60°N
High pressure
Descending air
30°N
Horse
latitudes
Northeast trade winds
Low pressure
Rising air
0°
Doldrums
Southeast trade winds
High pressure
Descending air
30°S
Horse
latitudes
Westerlies
60°S
Low pressure
Rising air
Polar easterlies
90°S
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.

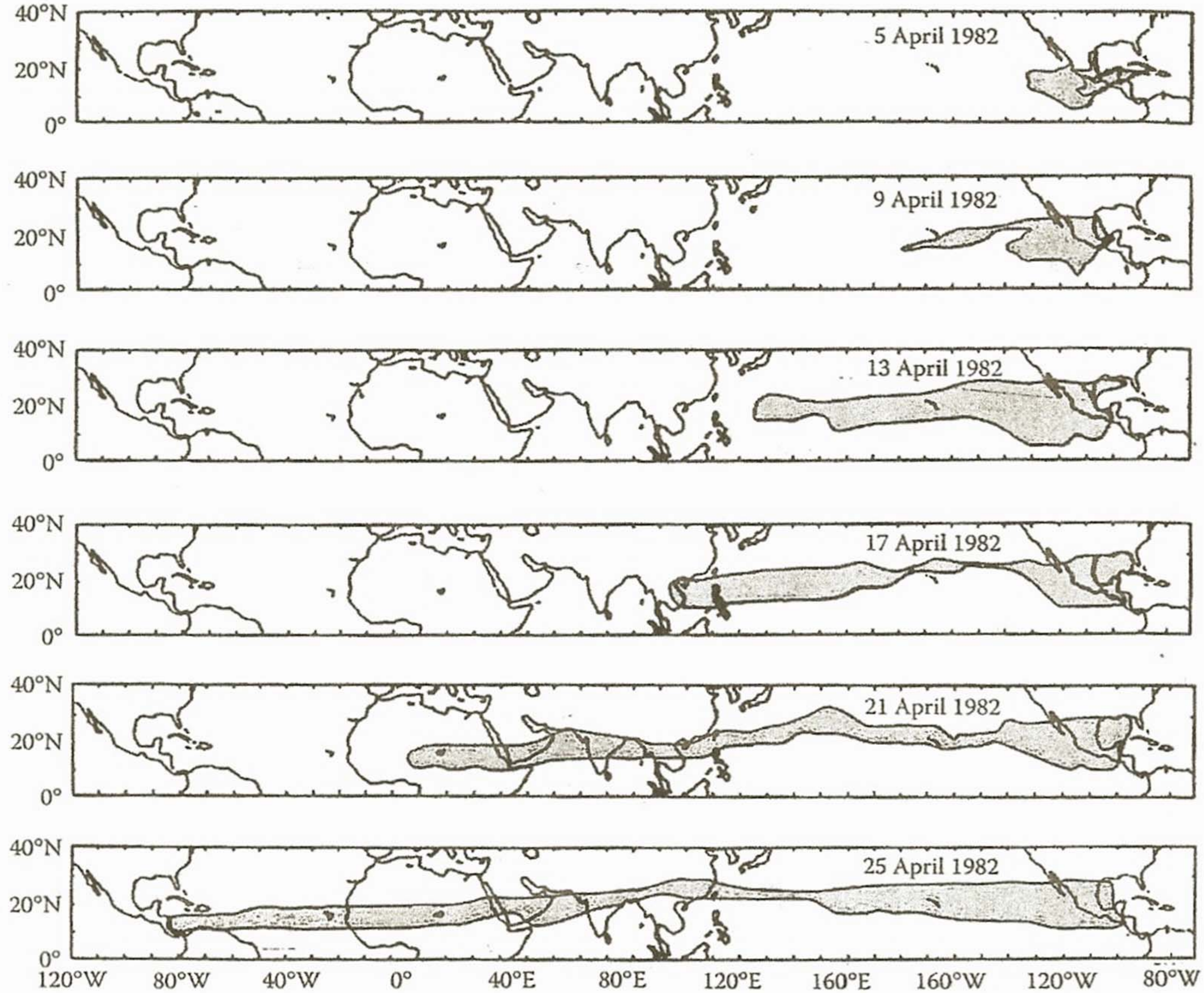


FIGURE 5.9
The movement of dust and particles in the northern hemisphere after the El Chichon Volcano eruption.

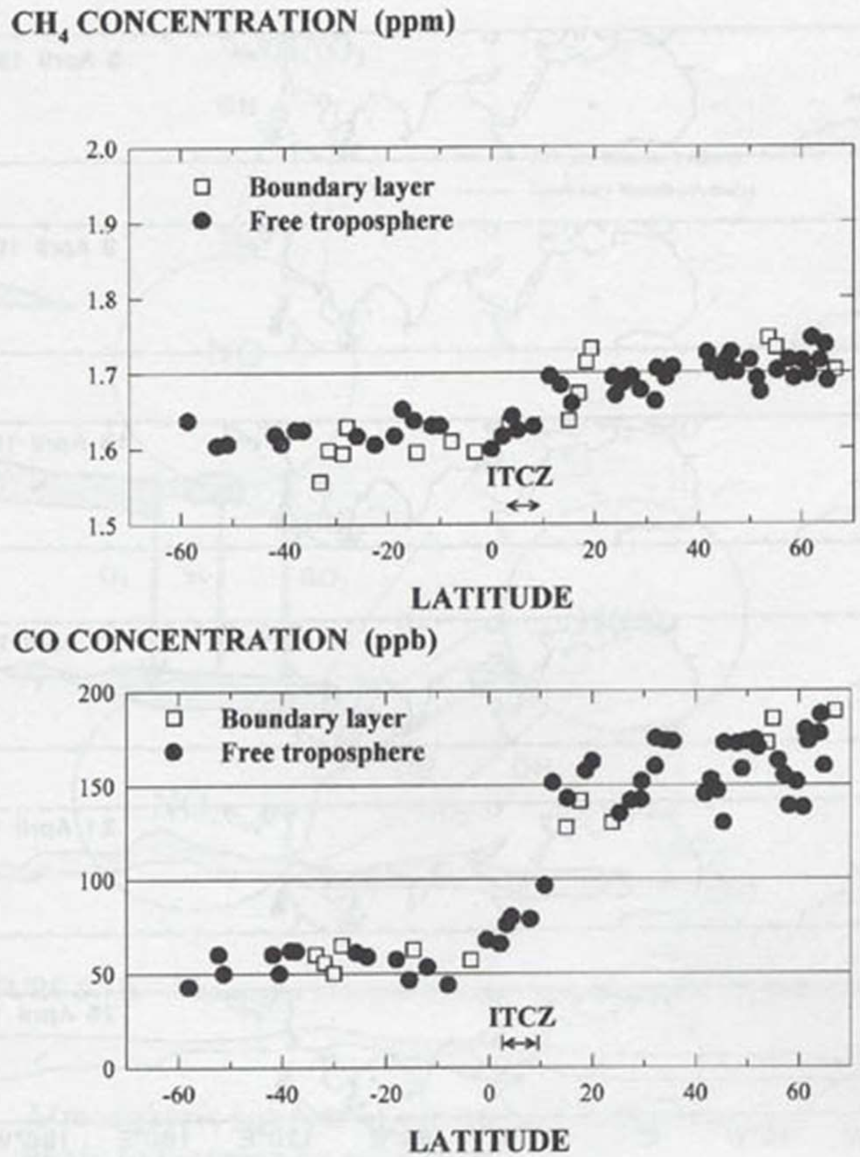


FIGURE 5.8. Distribution of methane (top) and carbon monoxide (bottom) between the hemispheres.

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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 6.2
Isotopic Abundance of Atmospheric Gases[a]

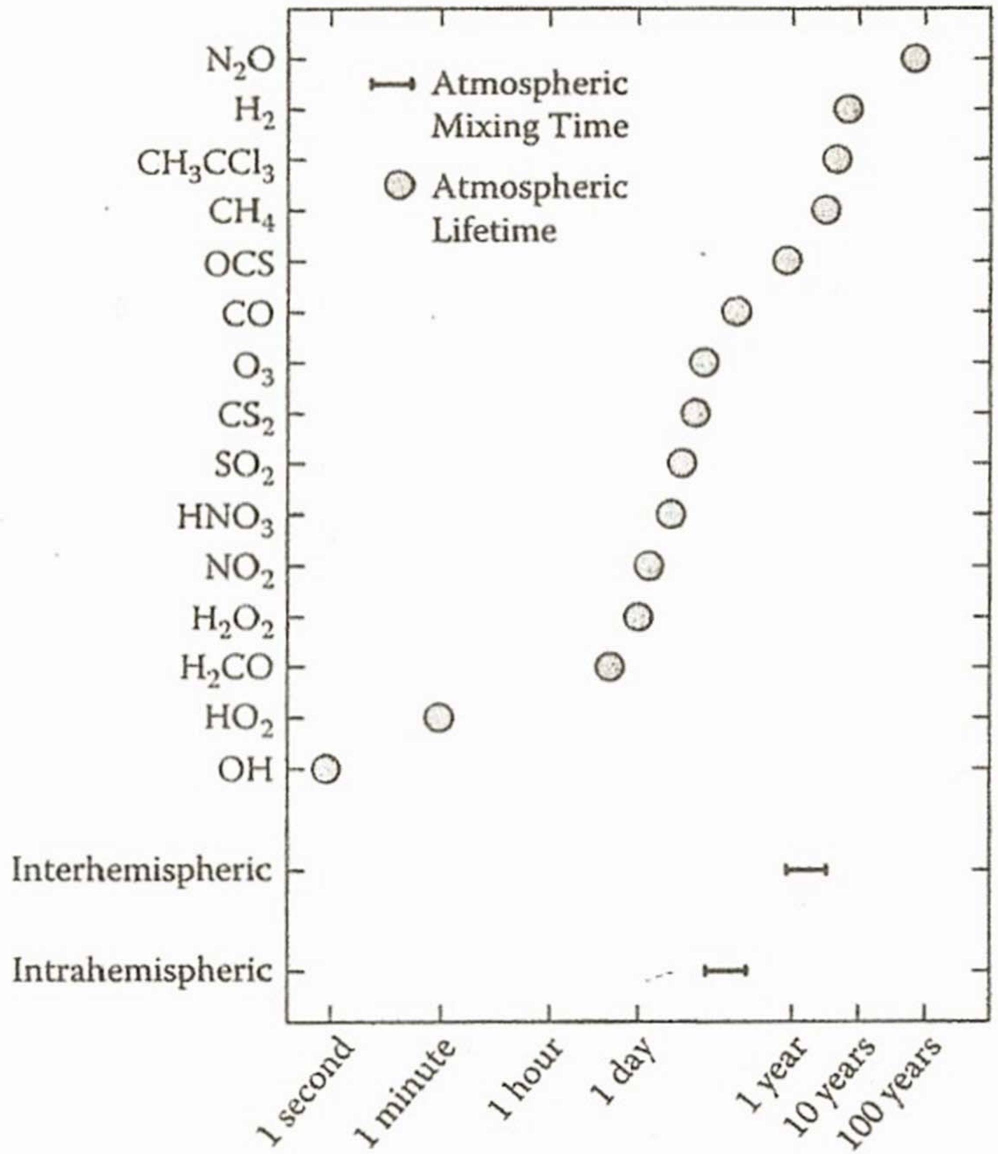
Element	Mass number	Mole %	Element	Mass number	Mole %
H (in H_2O)	1	99.98	Kr	78	0.354
H (in H_2O)	2	0.02	Kr	80	2.27
He	3	1.1×10^{-4}	Kr	82	11.56
He	4	100.0	Kr	83	11.55
C (in CO_2)	12	98.9	Kr	84	56.90
C (in CO_2)	13	1.1	Kr	86	17.37
C (in CO_2)	14	9.5×10^{-13}			
N	14	99.62	Xe	124	0.096
N	15	0.38	Xe	126	0.090
O	16	99.757	Xe	128	1.919
O	17	0.039	Xe	129	26.44
O	18	0.204	Xe	130	4.08
Ne	20	90.92	Xe	131	21.18
Ne	21	0.257	Xe	132	26.89
Ne	22	8.82	Xe	134	10.44
Ar	36	0.337	Xe	136	8.87
Ar	38	0.063			
Ar	40	99.600			

[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



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Production of OH Radicals

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

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

$$H + O_2 \rightarrow HO_2$$

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

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

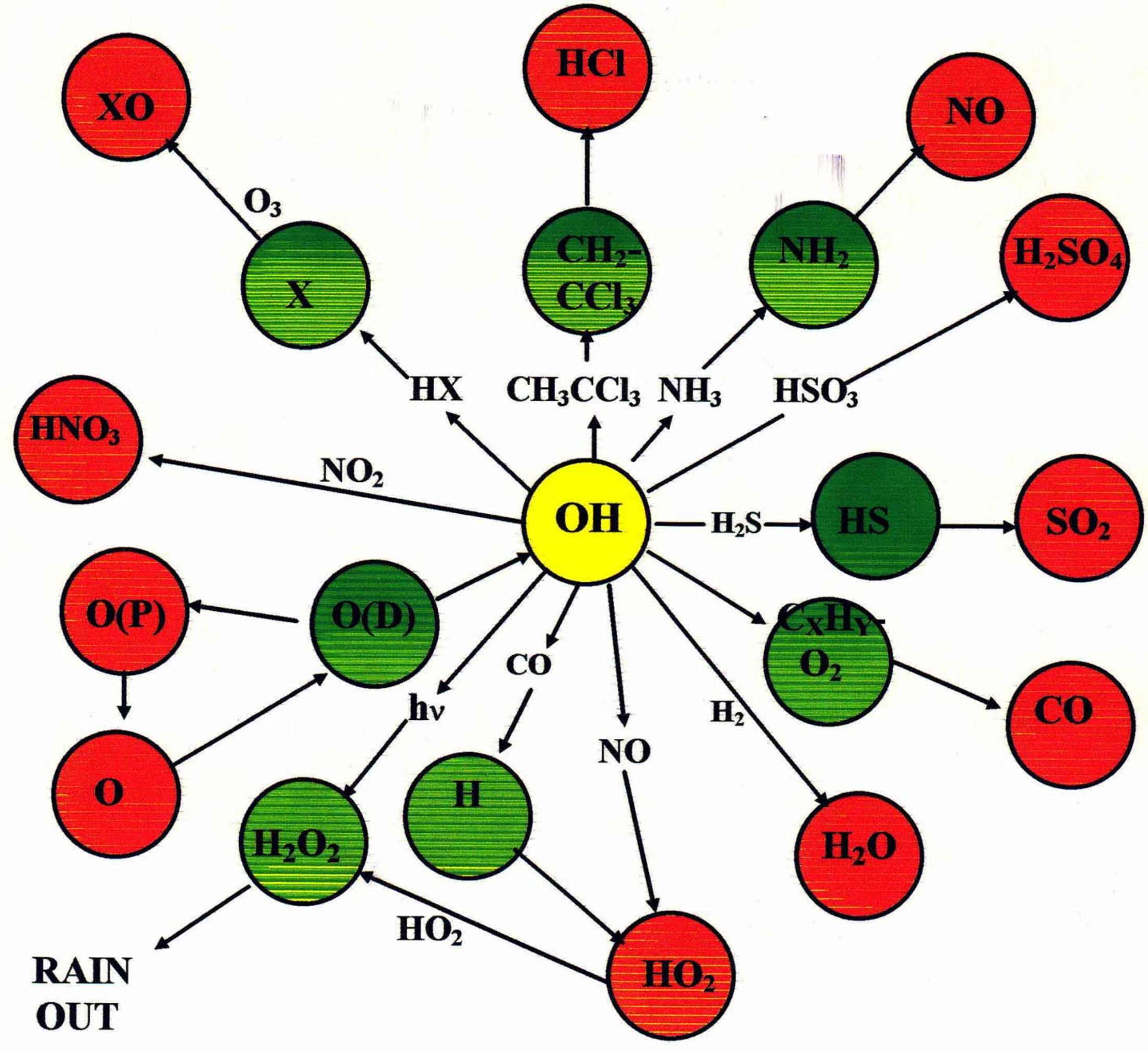
Removal Of OH Radicals

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

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

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

PHOTOCHEMISTRY OF THE OH RADICAL



SUMMARY OF IMPORTANT NITROGEN OXIDE REACTIONS

(Species NO, NO_2, HNO_3)

Gas Phase

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

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

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

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

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

Aqueous Phase

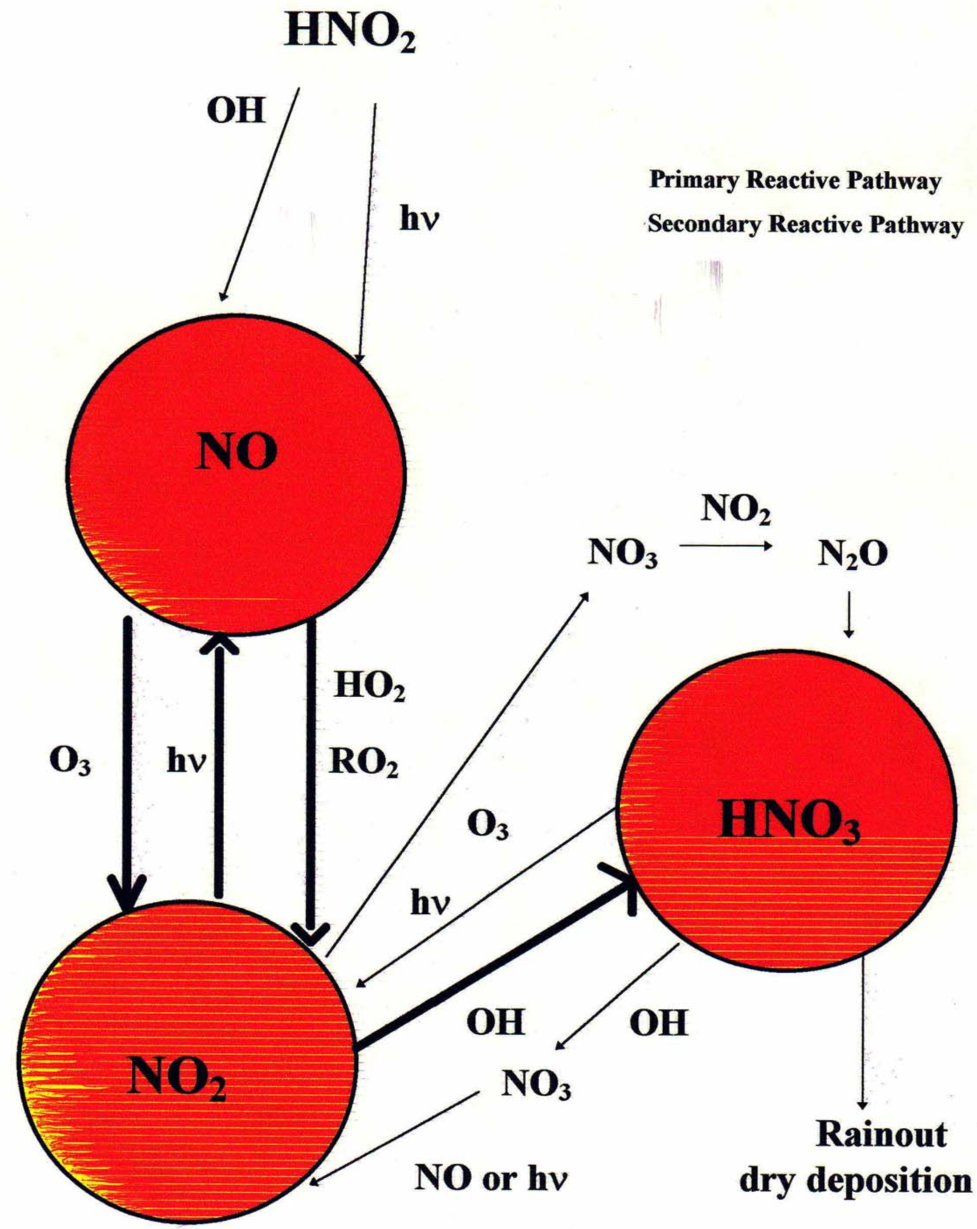
$NO_2 + O_3 \longrightarrow NO_3 + O_2$

$NO_3 + NO_2 \longrightarrow N_2O_5$

$N_2O_5 + H_2O \longrightarrow 2\,HNO_3$

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

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


HNO2
OH
hν
Primary Reactive Pathway
Secondary Reactive Pathway
NO
NO2
NO3
N2O
HO2
RO2
O3
hν
O3
hν
HNO3
OH
OH
NO3
NO2
NO or hν
Rainout
dry deposition

SULFUR OXIDE CHEMISTRY

Gas

$SO_2 + OH\cdot \longrightarrow HOSO_2$

$HOSO_2 + O_2 \longrightarrow SO_3 + HO_2$

$SO_3 + H_2O \longrightarrow H_2SO_4$

Aqueous

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

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

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

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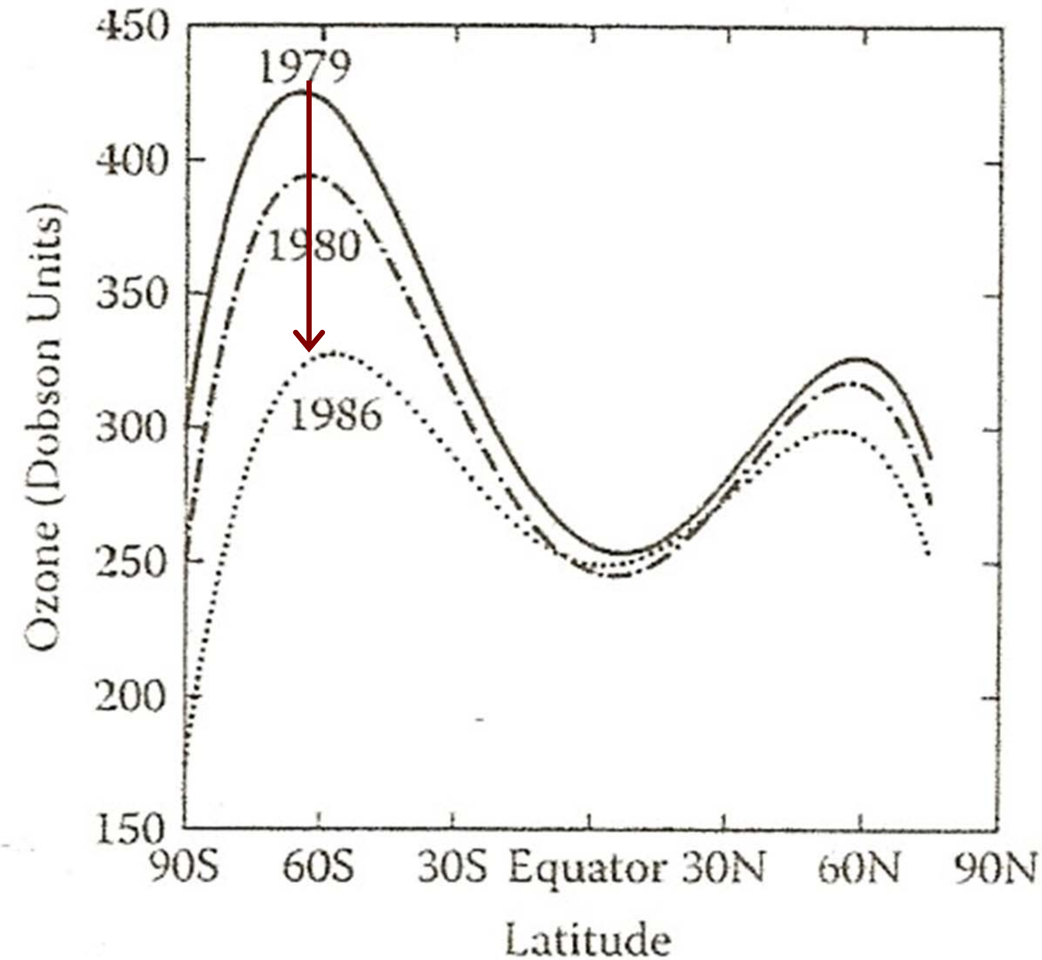
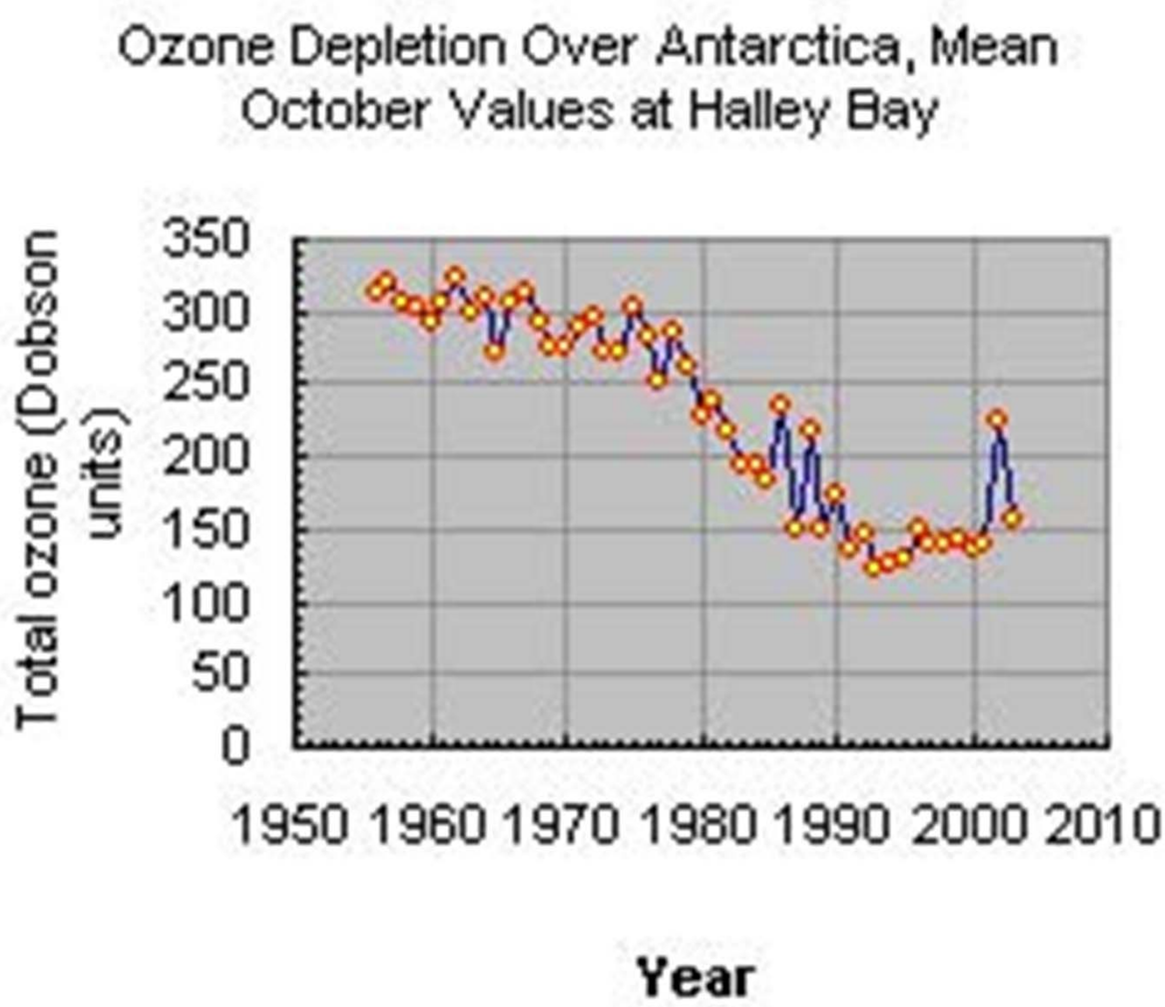


FIGURE 5.37
The levels of ozone as a function of latitude.

An animation of the development of the Antarctic ozone hole can be seen at:

http://www.youtube.com/watch?v=o7Yna4YOvM4



Ozone Depletion Over Antarctica, Mean
October Values at Halley Bay
Total ozone (Dobson units)
350
300
250
200
150
100
50
0
1950
1960
1970
1980
1990
2000
2010
Year

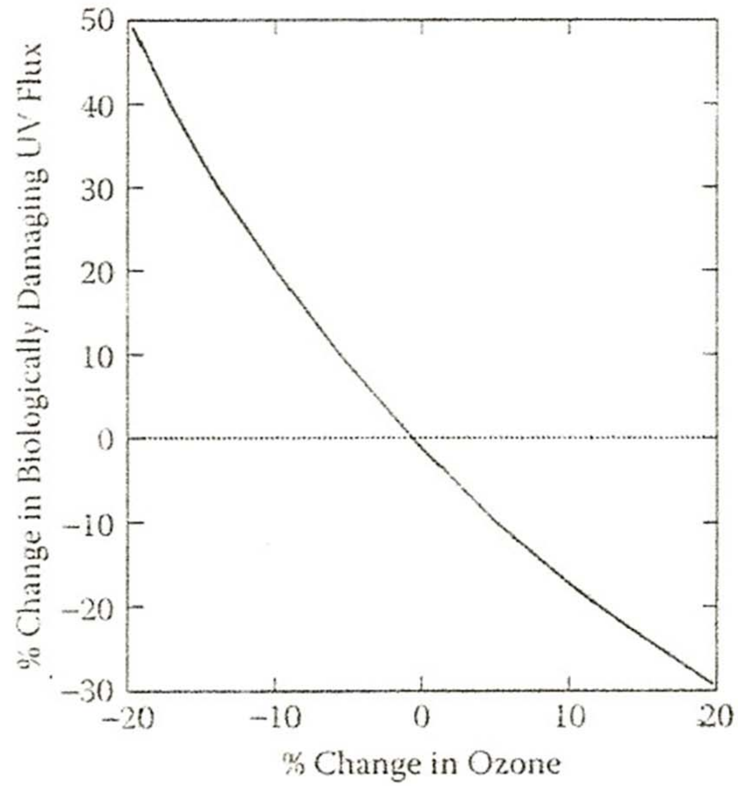


FIGURE 5.34
The changes in the biologically damaging ultraviolet (UV) flux as a function of changes in ozone levels.

SUMMARY OF OZONE CHEMISTRY

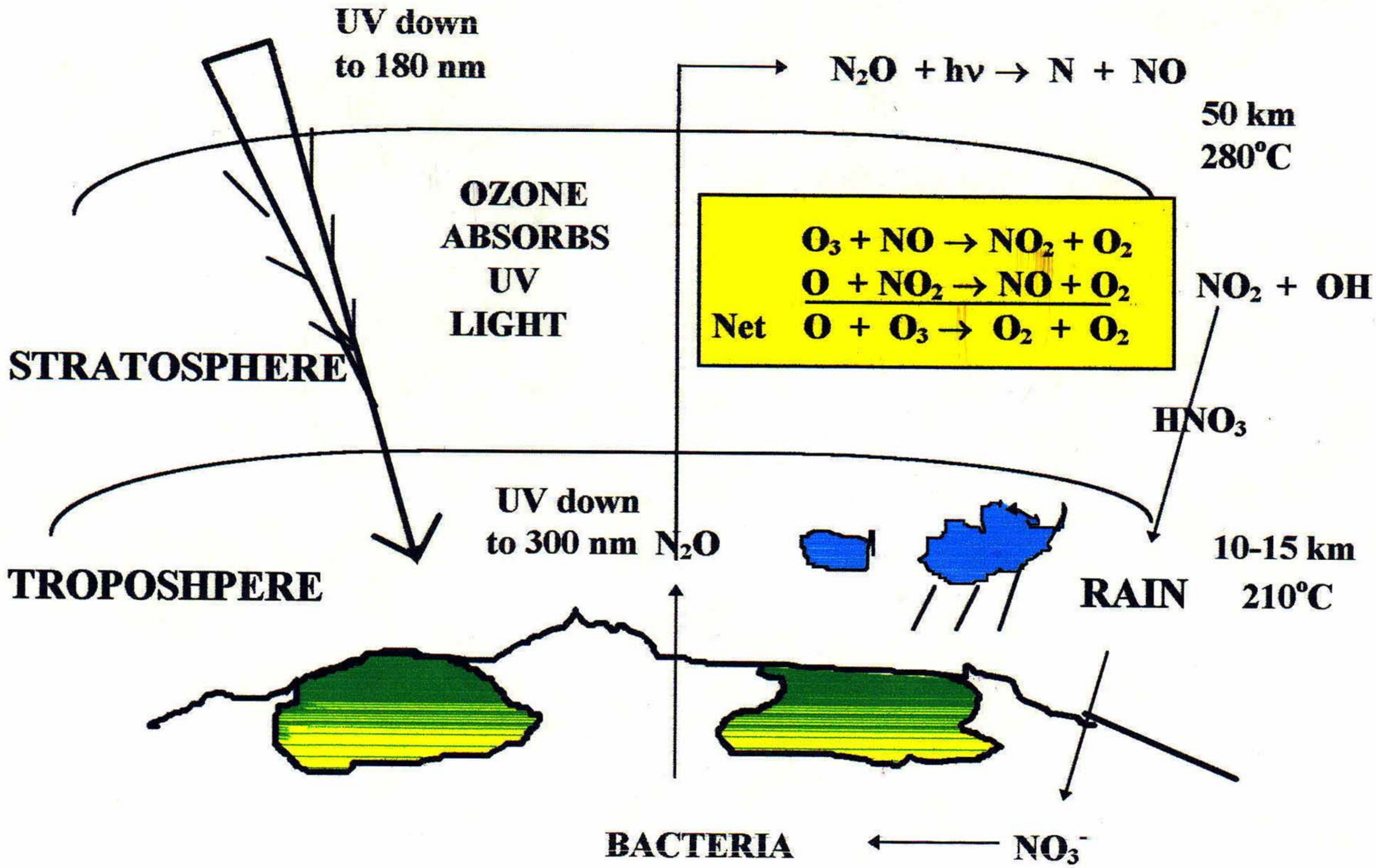
FORMATION

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

$O_2 + O\cdot \rightarrow O_3$

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

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



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
TROPOSHPERE
RAIN
210°C
BACTERIA
NO3-

LOSS OF OZONE IN STRATOSPHERE

Chlorofluoro Carbons (CFC's)

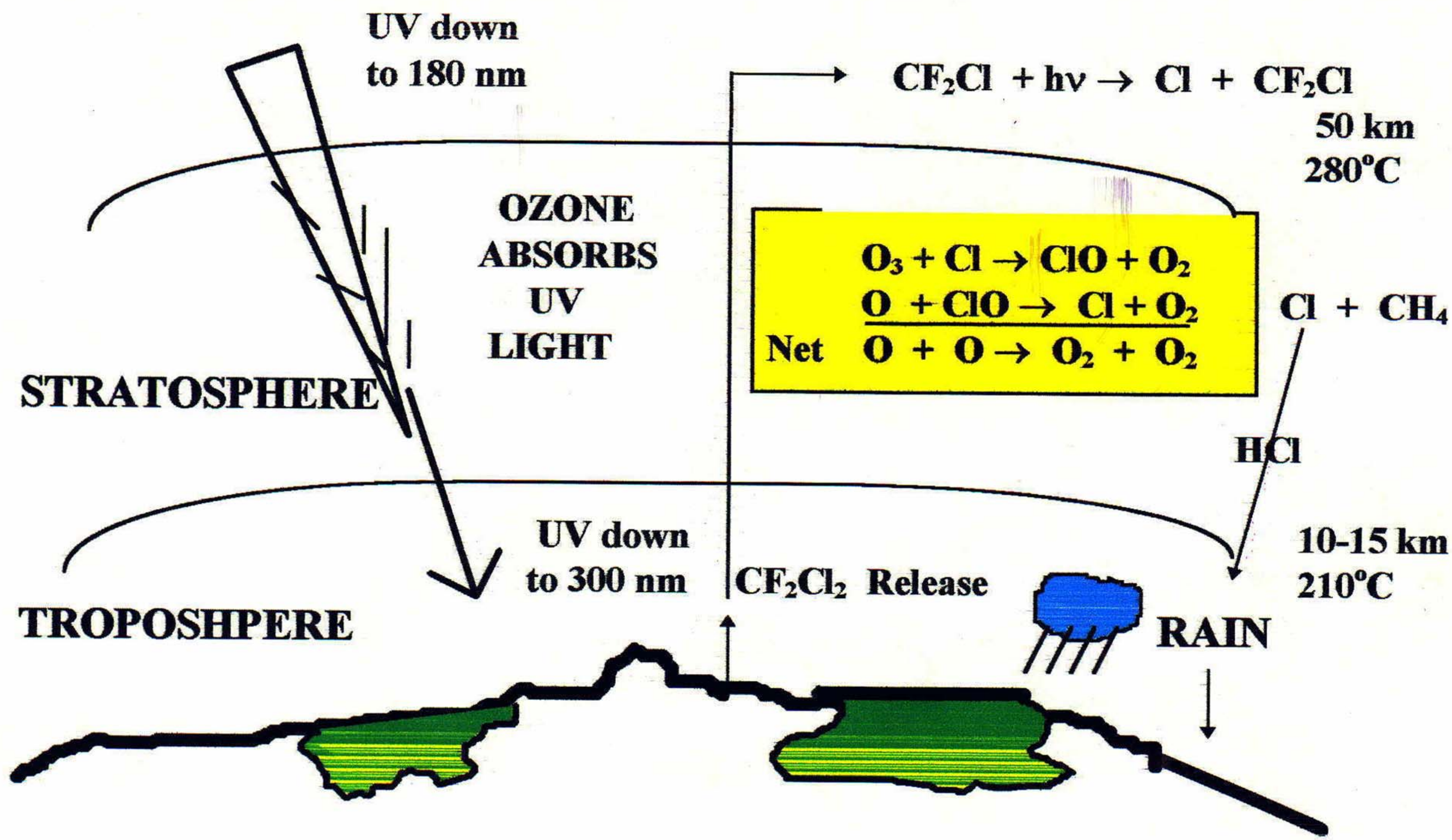
$CFCl_3$ (CFC-11) t = 75y
CF_2Cl_2 (CFC-12) t = 110 y

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

$$Cl\cdot + O_3 \rightarrow ClO + O_2$$
$$ClO + O \rightarrow Cl\cdot + O_2$$
$$\overline{O + O_3 \rightarrow 2\,O_2} \quad \text{Net}$$

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
TROPOSHPERE
RAIN

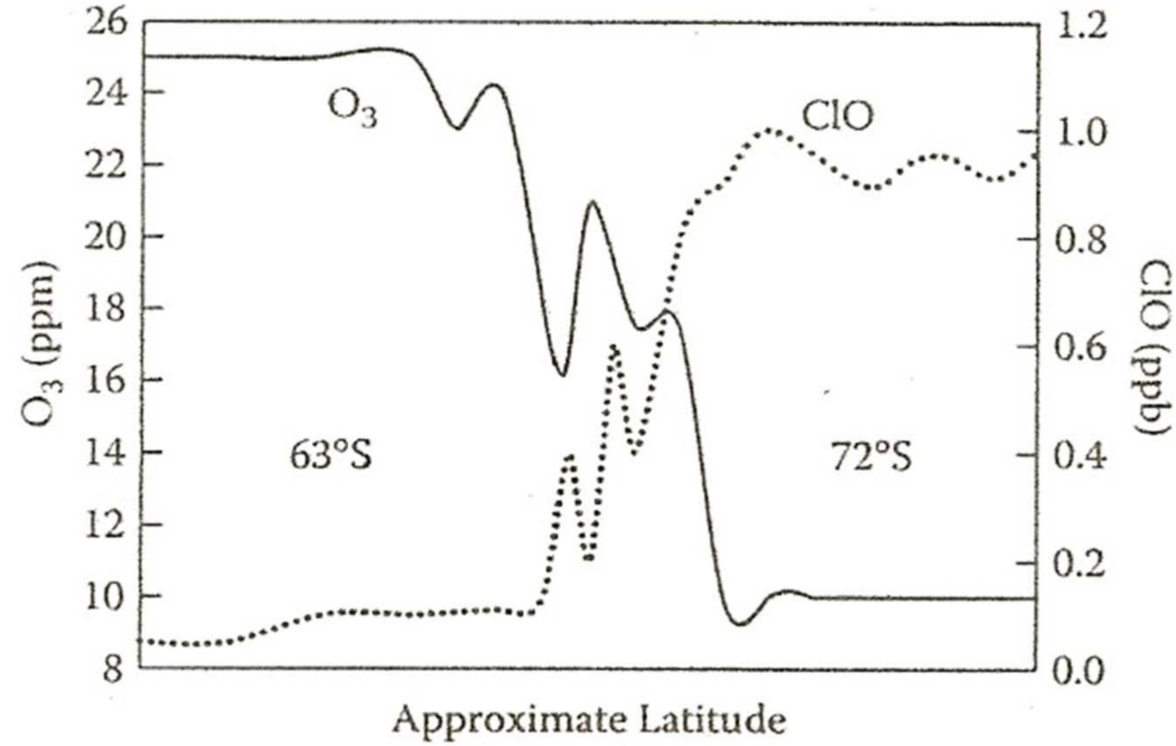


FIGURE 5.40
The relationship between O_3 and ClO in the Antarctic.

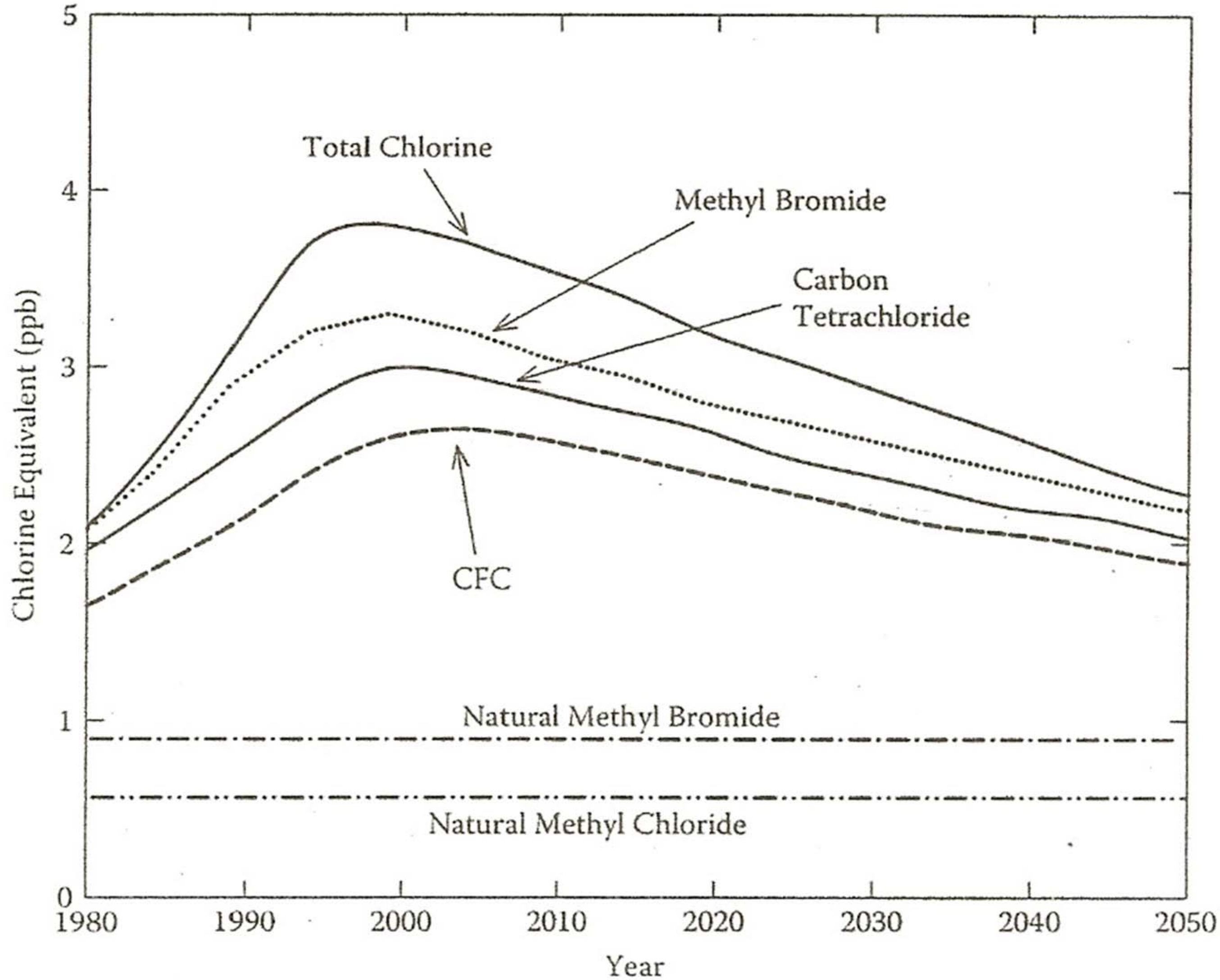
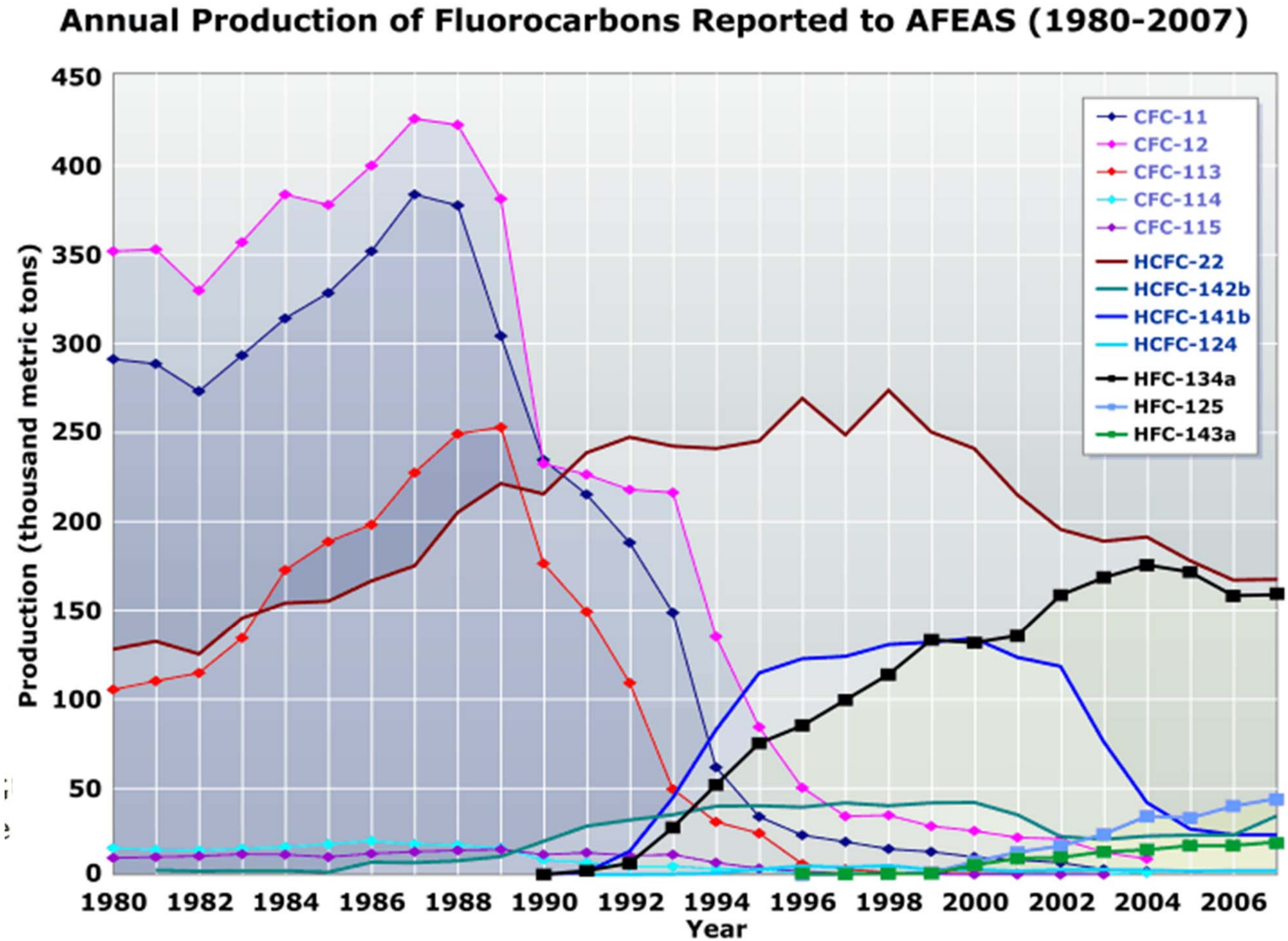
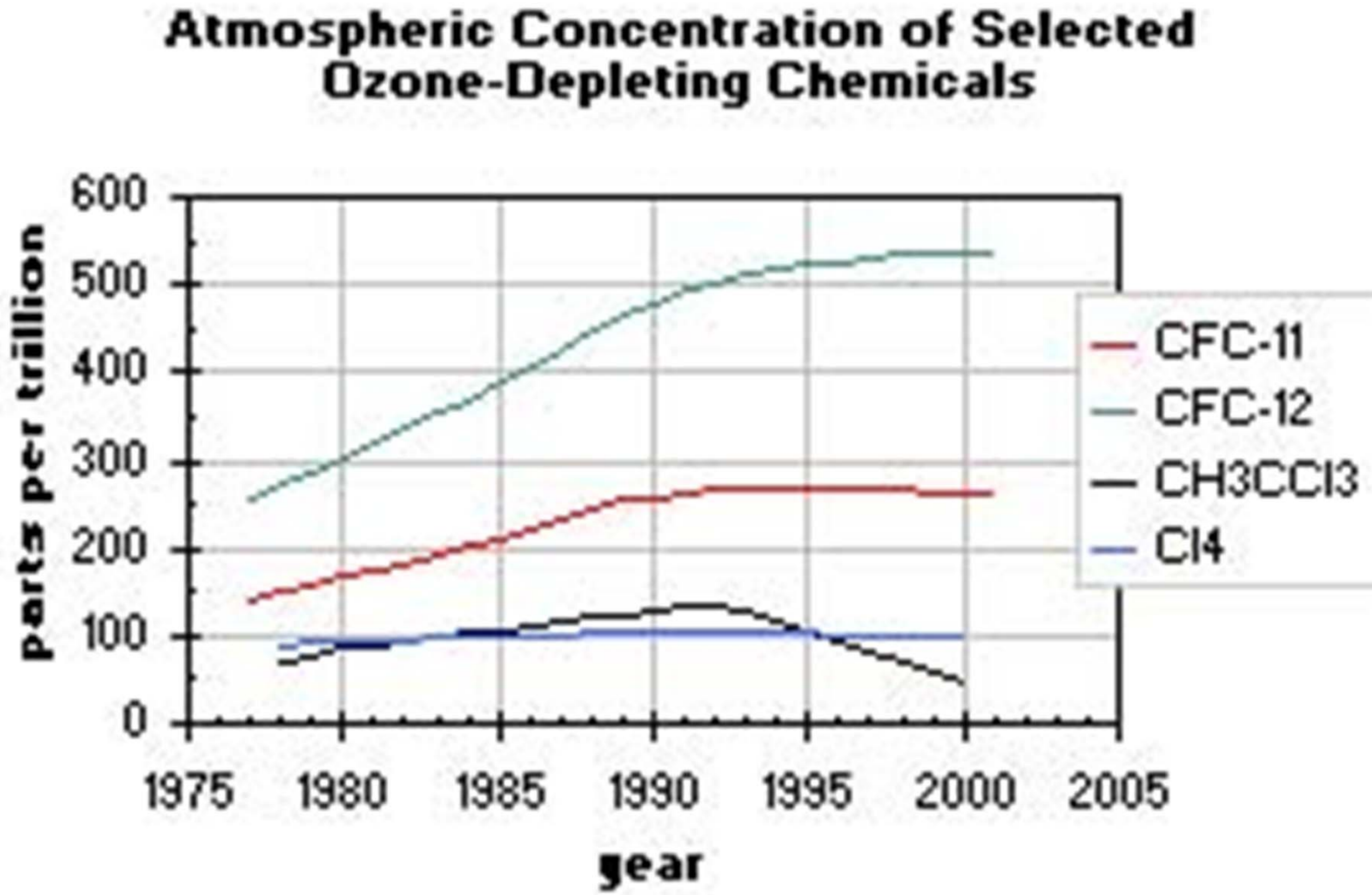


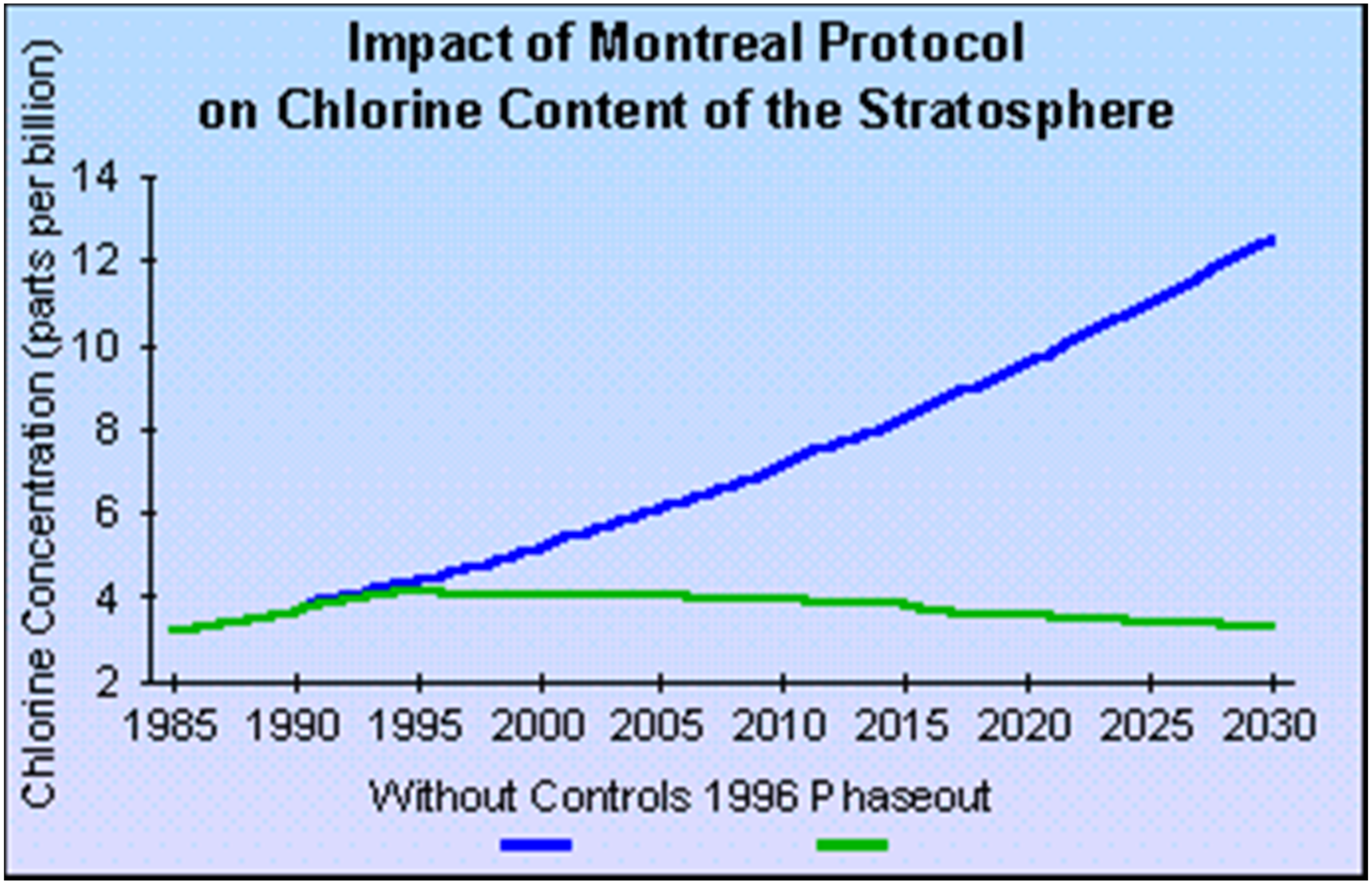
FIGURE 5.41
The levels of chlorine in the stratosphere as a result of the Montreal Protocol.



Annual Production of Fluorocarbons Reported to AFEAS (1980-2007)
Production (thousand metric tons)
Year
0
50
100
150
200
250
300
350
400
450
1980
1982
1984
1986
1988
1990
1992
1994
1996
1998
2000
2002
2004
2006
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


Impact of Montreal Protocol
on Chlorine Content of the Stratosphere
Chlorine Concentration (parts per billion)
14
12
10
8
6
4
2
1985
1990
1995
2000
2005
2010
2015
2020
2025
2030
Without Controls 1996 Phaseout