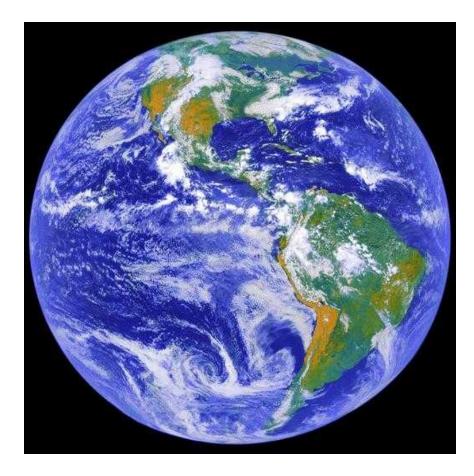
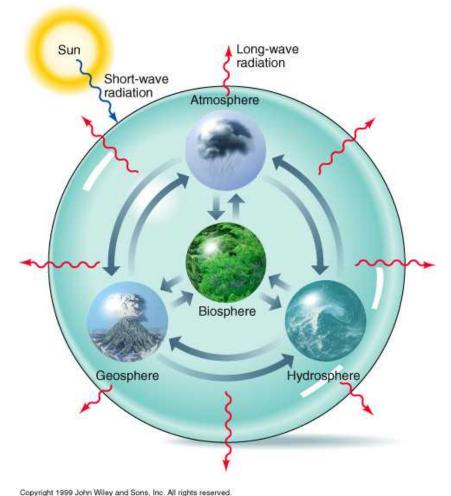
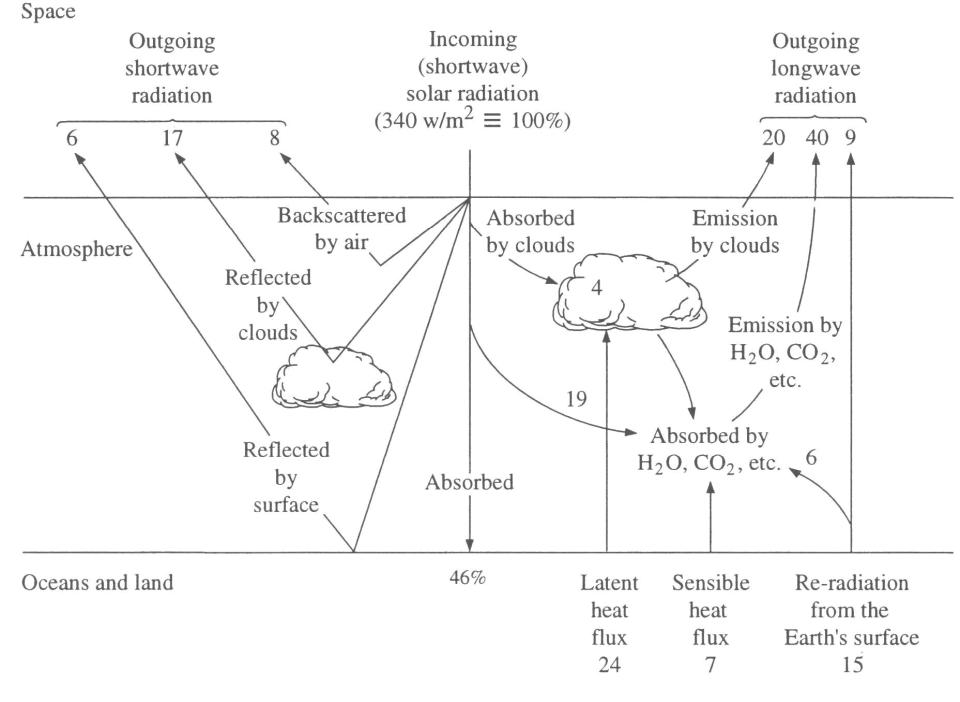
# The Atmosphere

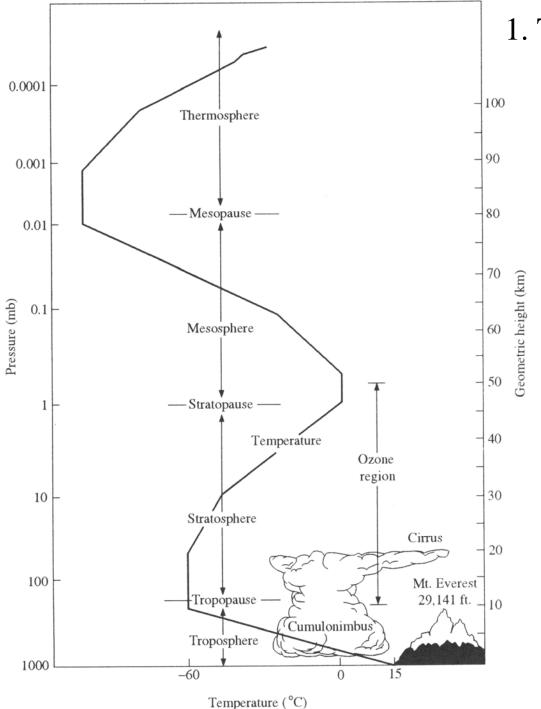
- 1. The Layered Structure
- 2. Composition
- 3. Biogeochemical Reactions in the Troposphere
- 4. Biogeochemical Reactions in the Stratosphere
- 5. Atmospheric Deposition
- 6. Brief Introduction to the Global Climate





Surface area:  $510 \times 10^{12} \text{ m}^2$ Copyright 1999 John Wiley and Sons, Inc. All rights reserved.Oceans:  $360 \times 10^{12} 70\%$ Land:  $150 \times 10^{12} 30\%$ More land surface in the Northern Hemisphere than in the Southern HemisphereHighest point of land (Mt. Everest): 8935 metersAverage height of land: 800 metersAverage depth of the ocean: 3800 meters

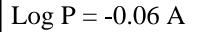




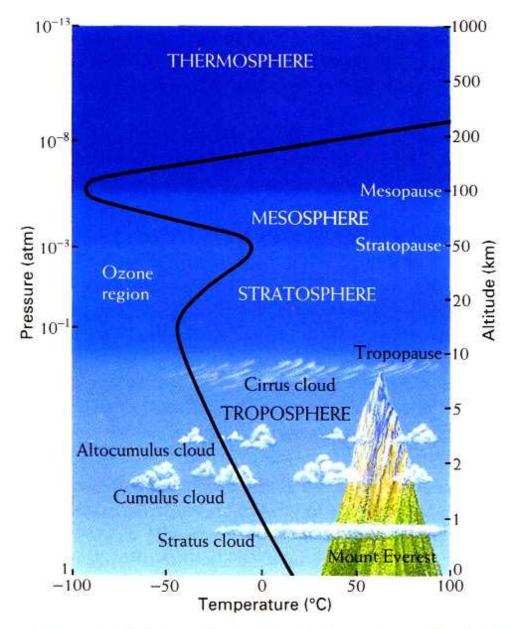
## 1. The Layered Structure

F = M(g)

## g=980 cm/Sec2



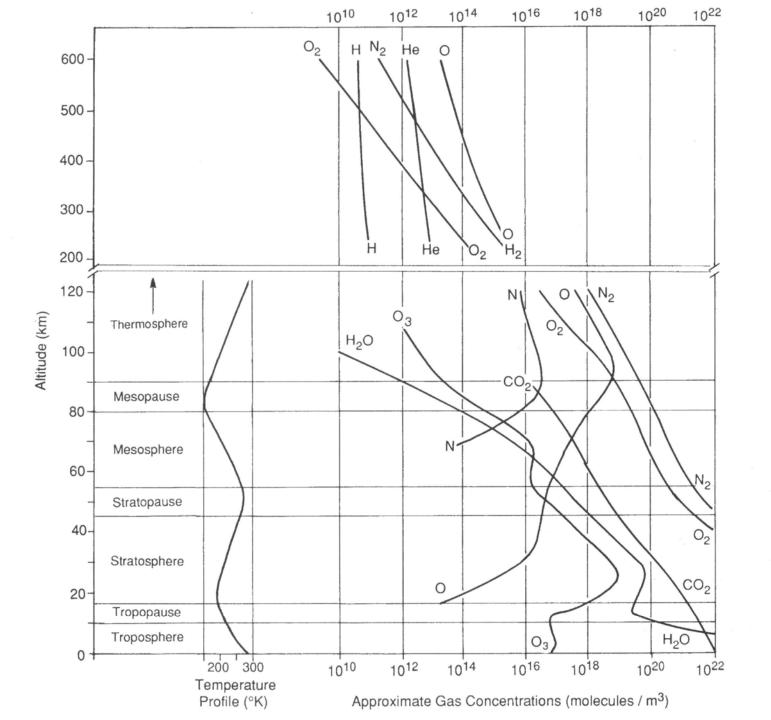
P: pressure in bars A: altitude in km

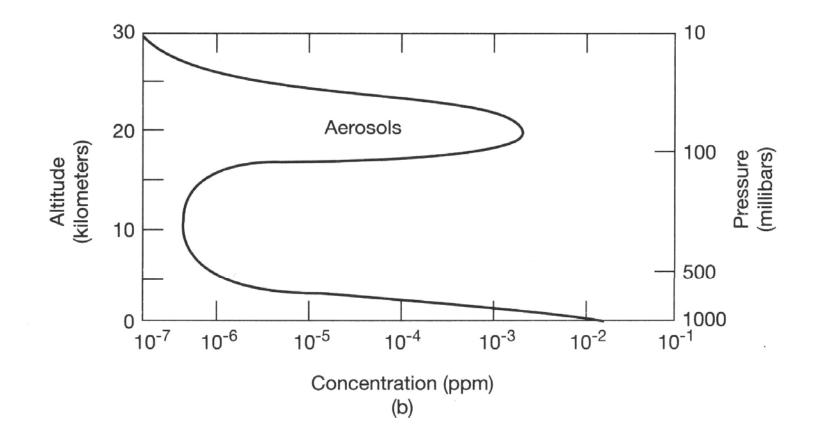


The variation of atmospheric pressure and temperature with altitude above Earth's surface. The regions of the atmosphere are noted, and the Himalayas are drawn in for perspective.

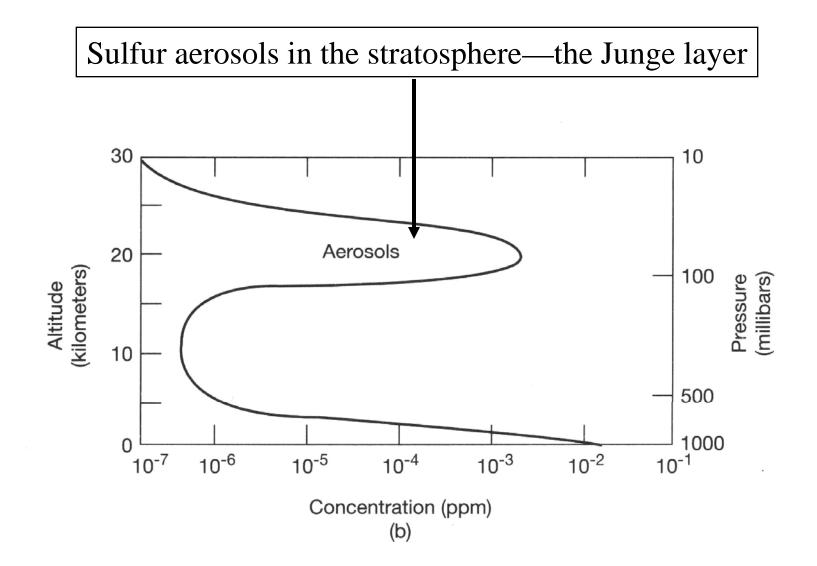


Sunset, June 15, 1991. Following the Mt. Pinatubo eruption, the Space Shuttle *Atlantis* imaged volcanic dust in the atmosphere. Most of the ejecta was in two layers at about 32 km. The roofs of the convection-driven thunderstorm clouds mark the top of the troposphere at approximately 13 km. (Image from NASA).





From: F. T. Mackinzie 2002



From: F. T. Mackinzie 2002

# The Material Composition of the Atmosphere

Compounds	Formula	Concentration	Total mass (g)	
Major constituents (%)				
Nitrogen	$\mathbf{N}_2$	78.084	$3.87 imes10^{21}$	
Oxygen	$O_2$	20.946	$1.19 imes10^{21}$	
Argon	Ar	0.934	$6.59 imes10^{19}$	
Parts-per-million constitu	ients (ppm $= 10^{\circ}$	-6)		
Carbon dioxide	$\mathrm{CO}_2$	360	$2.80 imes10^{18}$	
Neon	Ne	18.2	$6.49 imes10^{16}$	
Helium	He	5.24	$3.70 imes10^{15}$	
Methane	$\mathrm{CH}_4$	1.75	$4.96  imes 10^{15}$	
Krypton	Kr	1.14	$1.69  imes 10^{16}$	
Parts-per-billion constitu	ents (ppb = $10^{-9}$	))		
Hydrogen	$H_2$	510	$1.82 imes10^{14}$	
Nitrous oxide	$N_2O$	311	$2.42 imes10^{15}$	
Xenon	Xe	87	$2.02  imes 10^{15}$	
Parts-per-trillion constitu	tents (ppt = $10^{-1}$	<sup>2</sup> )		
Carbonyl sulfide	COS	500	$5.30 imes10^{12}$	
Chlorofluorocarbons				
CFC 11	$CCl_3F$	280	$6.79 imes10^{12}$	
CFC 12	$CCl_2F_2$	550	$3.12 imes10^{13}$	
Methylchloride	CH <sub>3</sub> Cl	620	$5.53 imes10^{12}$	
Methylbromide	$CH_3Br$	11	$1.84  imes 10^{11}$	

# Table 3.1 Global Average Concentration of Well-Mixed Atmospheric Constituents<sup>a</sup>

<sup>*a*</sup> Those with a mean residence time >1 year. Assuming a dry atmosphere with a molecular weight of 28.97. The overall mass of the atmosphere sums to 514  $\times$  10<sup>19</sup> g (Trenberth and Guillemot 1994).

Source	Global flux $(10^{12}g/yr)$
Natural sources	
Primary aerosols	
Soil dust	1500
Seasalt	1300
Volcanic dust	33
Organic particles	50
Secondary aerosols	
Sulfates from volatile organic sulfides (e.g., (CH <sub>3</sub> ) <sub>2</sub> S)	90
Sulfates from $SO_2$	12
Organic condensates	55
Nitrates from NO <sub>x</sub>	22
Sum of natural sources	3070
Anthropogenic sources	
Primary aerosols	
Industrial particles	100
Soot	20
Particles from forest fires	80
Secondary aerosols	
Sulfates from $SO_2$	140
Nitrates from NO <sub>x</sub>	36
Organic condensates	10
Sum of anthropogenic sources	390
Total	3460

**Table 3.2**Global Emissions of Aerosols<sup>a</sup>

<sup>a</sup> From Jonas et al. (1995).

Constituent	Particulate sample	Average ash	
	Major elements (%)		
$SiO_2$	=65.0	65.0	
$Fe_2O_3$	6.7	4.81	
CaO	3.0	4.94	
$K_2O$	2.0	1.47	
$TiO_2$	0.42	0.69	
MnO	0.054	0.077	
$P_2O_5{}^b$		0.17	

**Table 3.3**Composition of an Airborne Particulate Sample Collected during the Eruption of Mt. St. Helens on May 19, 1980<sup>a</sup>

S	3220	940
Cl	1190	660
Cu	61	36
Zn	34	53
Br	$<\!\!8$	$\sim 1$
Rb	$<\!\!17$	32
Sr	285	460
Zr	142	170
Pb	36	8.7

"Average ash is shown for comparison. From Fruchter et al. (1980).

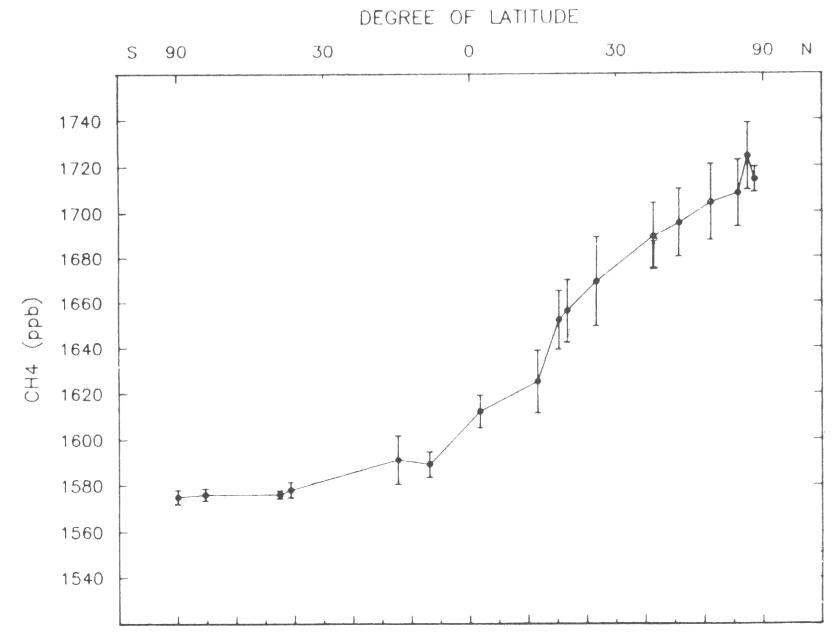
<sup>b</sup> From Hooper et al. (1980). Copyright 1980 by the AAAS.

	Concent		ation (ppb)	Mean residence	Percentage of sink
Compound F	Formula	Expected <sup>a</sup>	$Actual^b$	time	due to OH
Carbon compounds					
Methane	$\mathrm{CH}_4$	$10^{-148}$	1750	9 yr	90
Carbon monoxide	CO	$10^{-51}$	45-250	60 days	80
Isoprene $CH_2 = C$	$C(CH_3)-CH=$	$= CH_2$	0.2 - 10.0	<1  day	100
Nitrogen compounds					
Nitrous oxide	$N_2O$	$10^{-22}$	311	120 yr	0
Nitric oxides	NO <sub>x</sub>	$10^{-13}$	0.02 - 10.0	1 day	100
Ammonia	$\mathrm{NH}_3$	$10^{-63}$	0.08 - 5.0	5 days	<2
Sulfur compounds					
Dimethylsulfide	$(CH_3)_2S$		0.004-0.06	1 day	50
Hydrogen sulfide	$H_2S$		< 0.04	4 days	100
Carbonyl sulfide	COS	0	0.50	5 yr	22
Sulfur dioxide	$\mathbf{SO}_2$	0	0.02-0.10	3 days	50

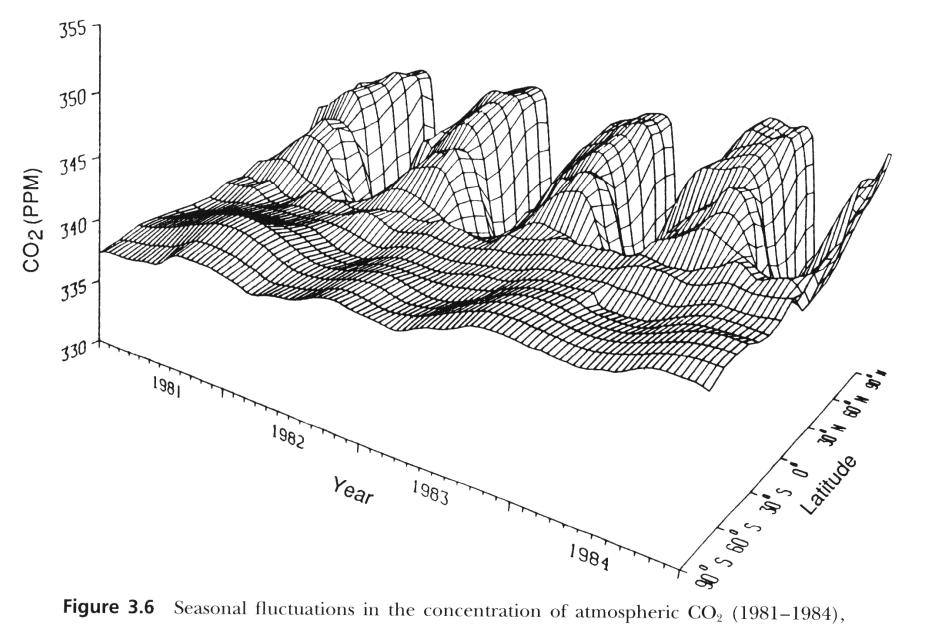
**Table 3.4**Some Trace Biogenic Gases in the Atmosphere

<sup>*a*</sup> Approximate values in equilibrium with an atmosphere containing 21%  $O_2$  (Chameides and Davis 1982).

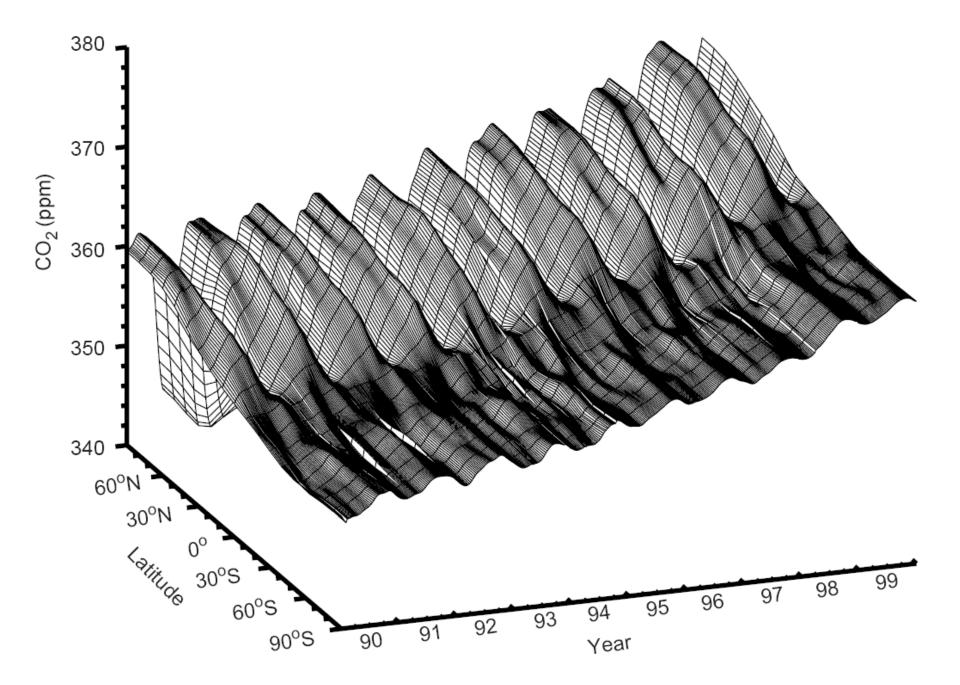
 $^{b}$  For short-lived gases, the value is the range expected in remote, unpolluted atmospheres.

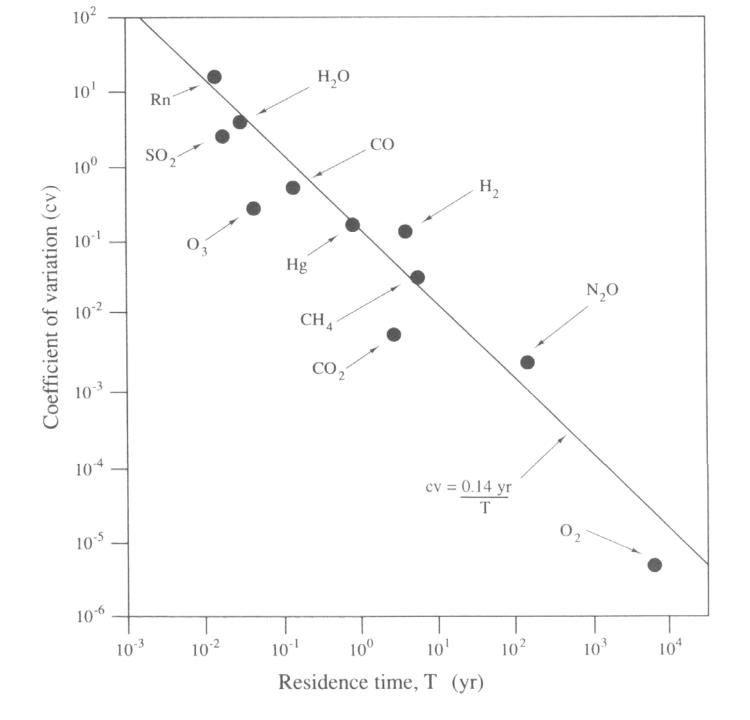


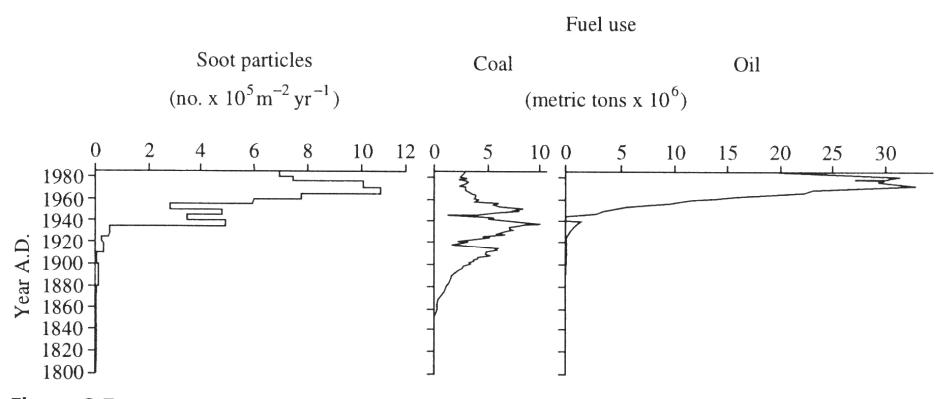
**Figure 3.4** The latitudinal variation in the mean concentration of  $CH_4$  (methane) in Earth's atmosphere. From Steele et al. (1987).



**Figure 3.6** Seasonal fluctuations in the concentration of atmospheric  $CO_2$  (1981–1984), shown as a function of 10° latitudinal belts (Conway et al. 1988). Note the smaller amplitude of the fluctuations in the southern hemisphere, reaching peak concentrations during northern hemisphere minima.







**Figure 3.7** Annual deposition of soot in Lake Koltjarn, as recorded in sediment layers, and the annual consumption of coal and oil in Sweden since 1800. The use of fossil fuel and the deposition of soot have both declined in recent years. From Renberg and Wik (1984).

# 3. Biogeochemical Reactions in the Troposphere

(1). Ozone and Hydroxyl radicals

Given that some ozone is mixed into the troposphere from the stratosphere, photochemical reactions can add more ozone to the troposphere, such as these even in relatively clean air:

 $NO_2 + hv$  (sunlight)  $\Leftrightarrow NO + O$ 

and,  $O + O_2 \Leftrightarrow O_3$ ,

so the net reaction is:

 $NO_2 + O2 \Leftrightarrow NO + O_3$ 

It follows approximately this quantitative relationship:

 $O_3 (ppm) = 0.02 [NO_2] / [NO]$  Seinfield (1989)

 $NO_2$  and NO together are called  $NO_x$ . Some pollutants act like  $NO_x$ .

3. Biogeochemical Reactions in the Troposphere-continues

(2). Hydroxyl radicals

Once certain level of ozone presents in the air hydroxyl radicals are produced:

```
O_3 + hv (sunlight) \Leftrightarrow O_2 + O ('D)
and, O('D) + H_2O \Leftrightarrow 2OH,
and, 2OH + 2O_3 \Leftrightarrow 2HO_2 + 2O_{2},
and, 2HO_2 \Leftrightarrow H_2O_2 + O_2
```

All these hydroxyl radicals are short-lived oxidizing agents which react with many other compounds (CO,  $CH_4$ ,  $NO_2$ ,  $SO_2$ , and hydrocarbons) in the air.

When the air is polluted with more  $NO_x$ , hydrocarbons, or other similar pollutants, but without clouds, many photochemical reactions are elevated and entangled, and more ozone is produced as a result. So a clear sky and a heavily polluted troposphere is proven harmful to human health.

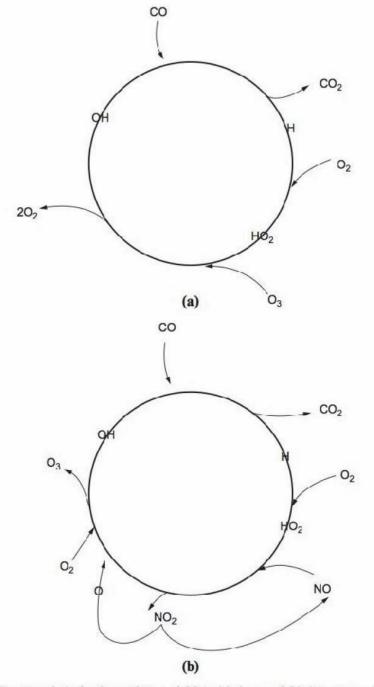


FIGURE 3.8 Reaction chain for the oxidation of CO in (a) clean and (b) dirty atmospheric conditions.

Source or sink	<b>Pre-industrial</b>	Present	Human impact
Stratospheric injection	+696	+696	0
Tropospheric production (i.e., dirty atmosphere reactions)	+199	+686	+487
Tropospheric sink (i.e., clean atmosphere reactions)	-435	-558	-123
Dry deposition	-459	-825	-366

### TABLE 3.6 Tropospheric Ozone Budget

Note: All values in Tg ( $10^{12}$  g) of O<sub>3</sub>/year. Source: From Lety et al. (1997).

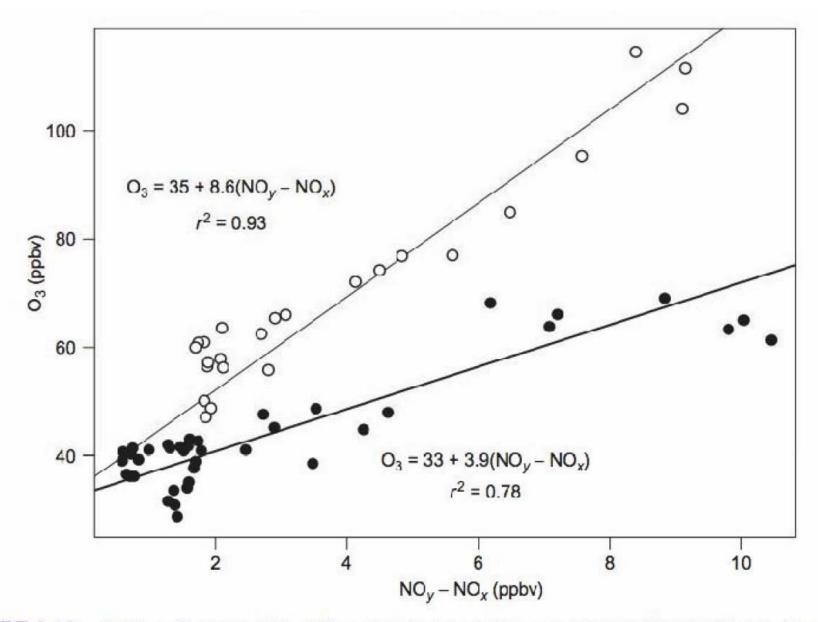
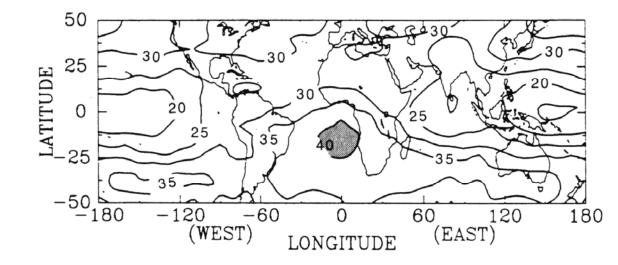


FIGURE 3.10 Ambient O<sub>3</sub> versus NO<sub>y</sub>-NO<sub>x</sub> concentrations in the atmosphere at Harward forest in northern Massachusetts in the United States, May 6–12, 1990 (•) and August 24–30, 1992 (0). Source: From Hirsch et al. (1996). Used with permission of American Geophysical Union.



**Figure 3.8** Distribution of tropospheric ozone during September through November, for the years 1979 to 1989 as determined by satellite measurements. Note the high concentration downwind (west) of central Africa, where biomass burning is widespread. From Fishman et al. (1990).

A *Dobson* unit (DU) is the most basic measure used in ozone research. The unit is named after G.M.B. Dobson, one of the first scientists to investigate atmospheric ozone (~1920 - 1960). He designed the 'Dobson Spectrometer' - the standard instrument used to measure ozone from the ground. 1 DU = 0.01 mm thickness of pure  $O_3$  at STP (0°C &1 atm pressure) for the whole column of air. A global mean concentration of 1 ppb of tropospheric  $O_3 = 0.65$  DU.

~36 DU for Northern Hemisphere (1999); ~32 DU for Southern Hmisphere; ~25 DU pre-industrial

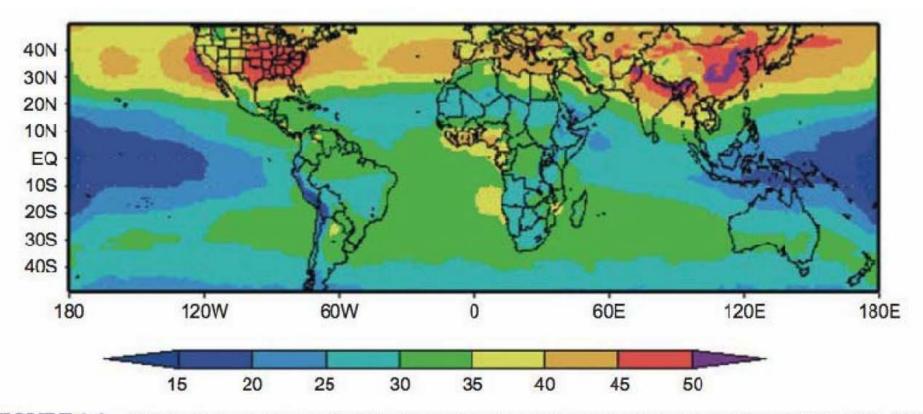
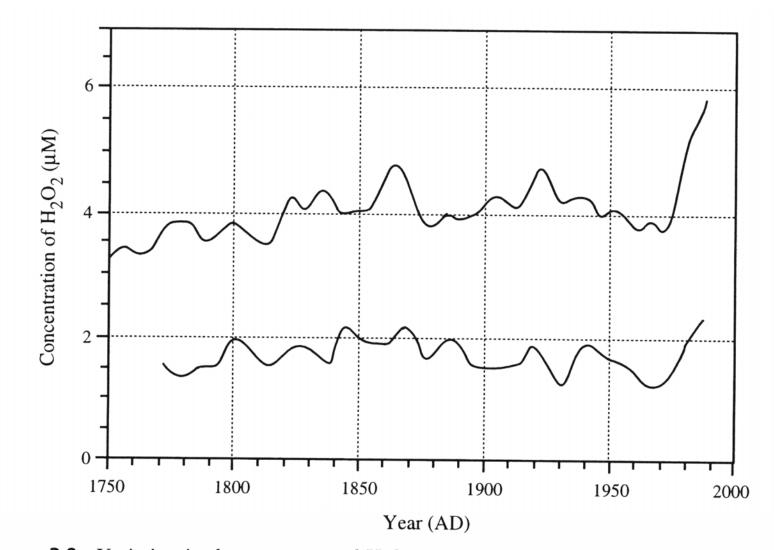


FIGURE 3.9 Distribution of ozone in Earth's atmosphere, for summer months, averaged over 1979–1991. Note high ozone concentrations over the eastern United States and China. Data are in Dobson units (see page 85). Source: From Fishman et al. (2003). Used with permission of European Geosciences Union.



**Figure 3.9** Variation in the mean annual  $H_2O_2$  concentration in two cores from the Greenland ice pack over the past 200 years. Modified from Sigg and Neftel (1991).

# 4. Biogeochemical Reactions in the Stratosphere

#### **Ozone Generation and Destruction:**

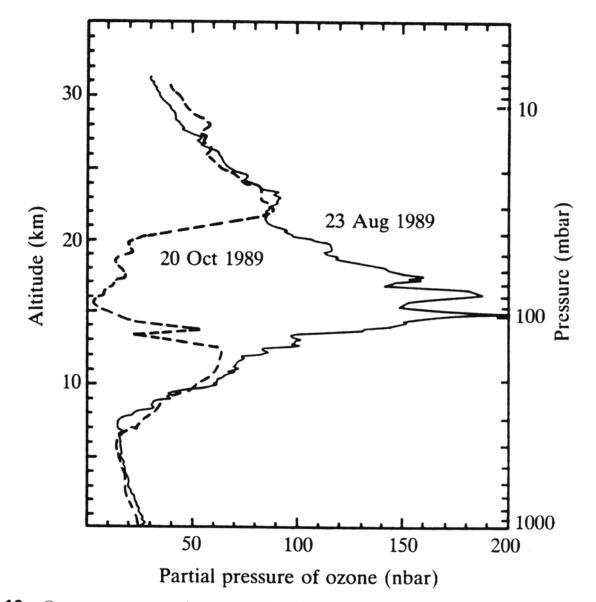
In the stratosphere, oxygen absorbs ultraviolet sunlight (hv) in the wavelengths of 180-240 nm and produces ozone:

 $O_2 + hv \Leftrightarrow O + O,$ and  $O + O_2 \Leftrightarrow O_3$ 

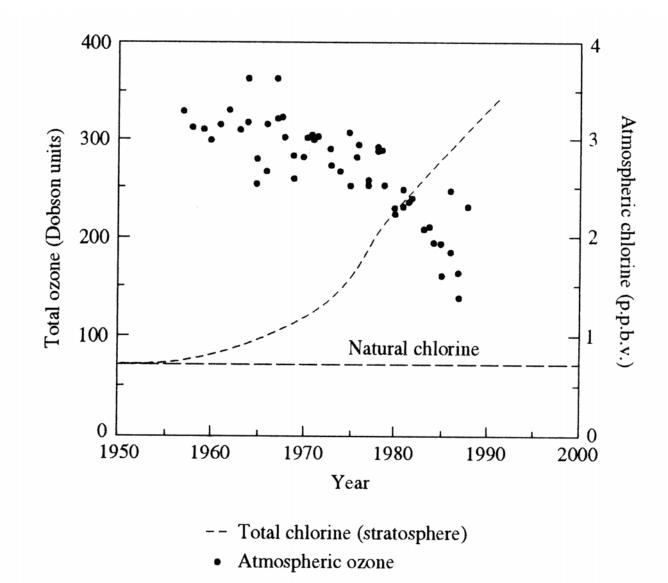
Concurrently, ozone is destroyed when it absorbs uvB (200-320 nm):

$$O_3 + hv \Leftrightarrow O_2 + O$$
  
and  
 $O + O_3 \Leftrightarrow 2O_2$ 

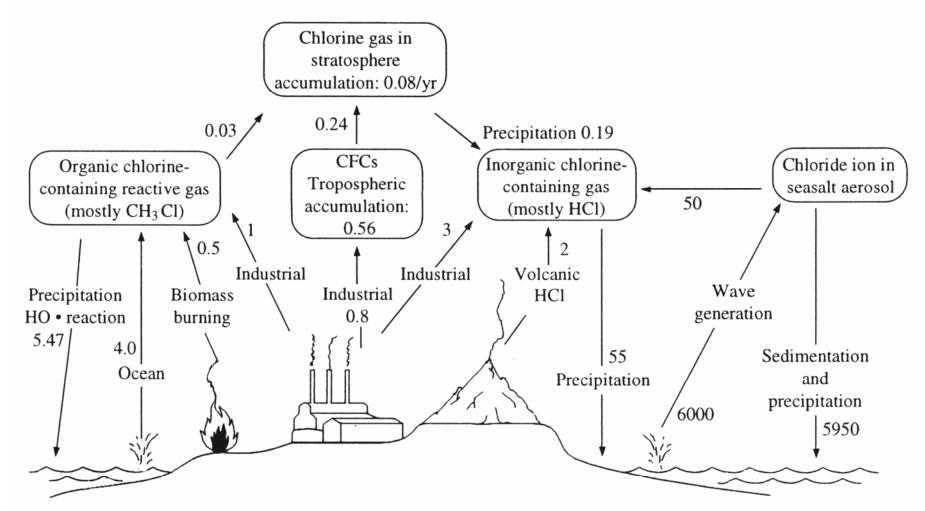
Ozone in the stratosphere can be destroyed faster when some catalyst-like agents are present such as NO (from oxidation of  $N_2O$ ), OH, and Cl/F (from CFCs).



**Figure 3.10** Ozone concentrations over McMurdo station, Antarctica in the spring of 1989. Note the near-complete loss of ozone at 15 km altitude (Deshler et al. 1990).

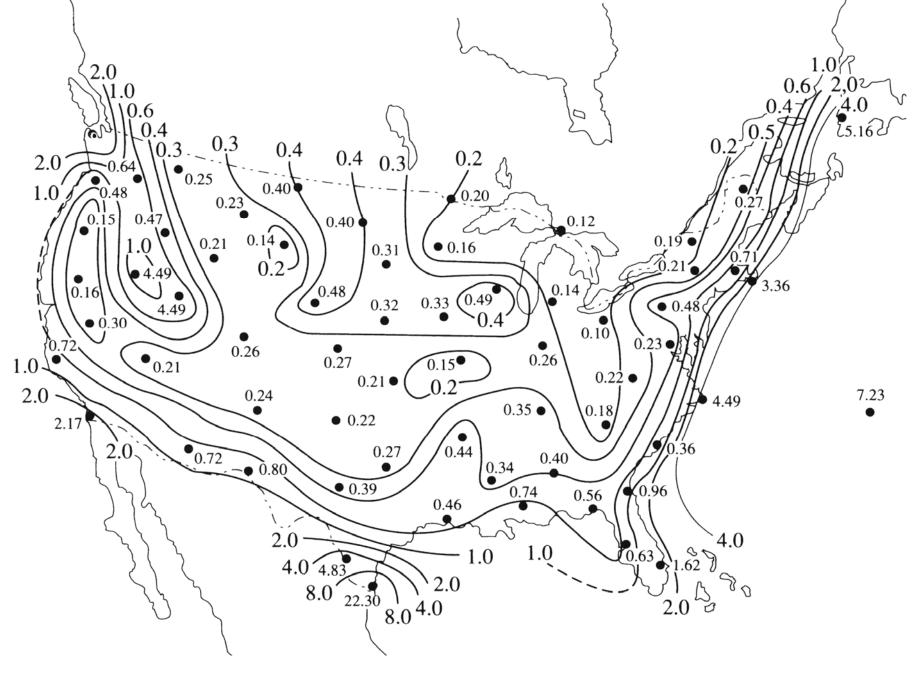


**Figure 3.11** The decline in atmospheric  $O_3$  ( $\bullet$ ) over Antarctica since 1958 corresponds to an increase in chlorine (—) in the stratosphere. The customary unit for the total number of ozone molecules in an atmospheric column, the Dobson, is equivalent to  $2.69 \times 10^{16}$  molecules/cm<sup>2</sup> of the Earth's surface. Modified from Solomon (1990).

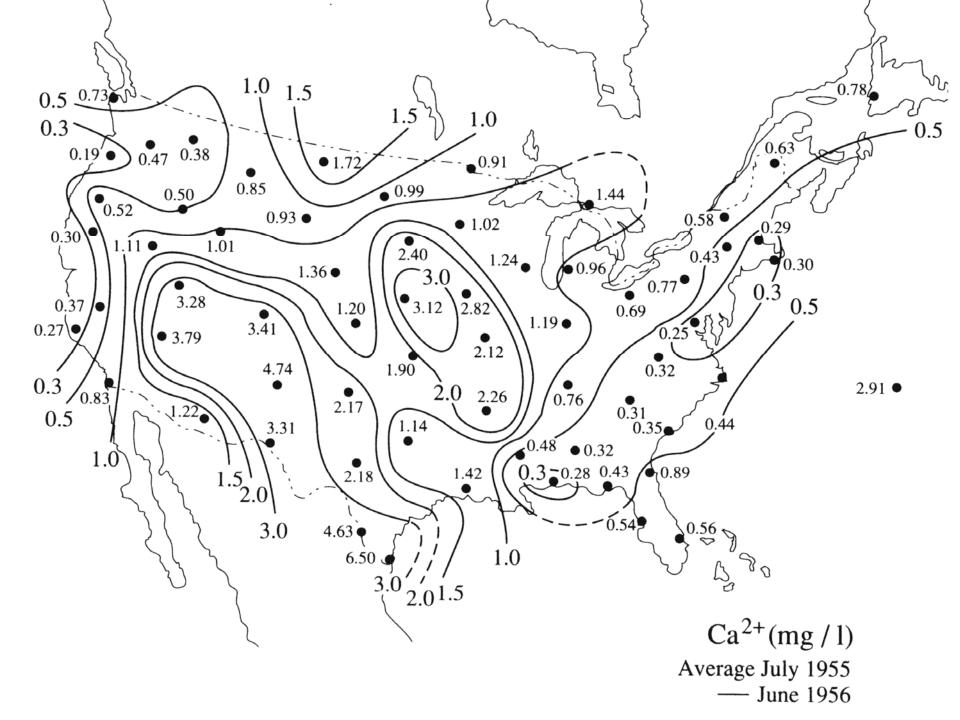


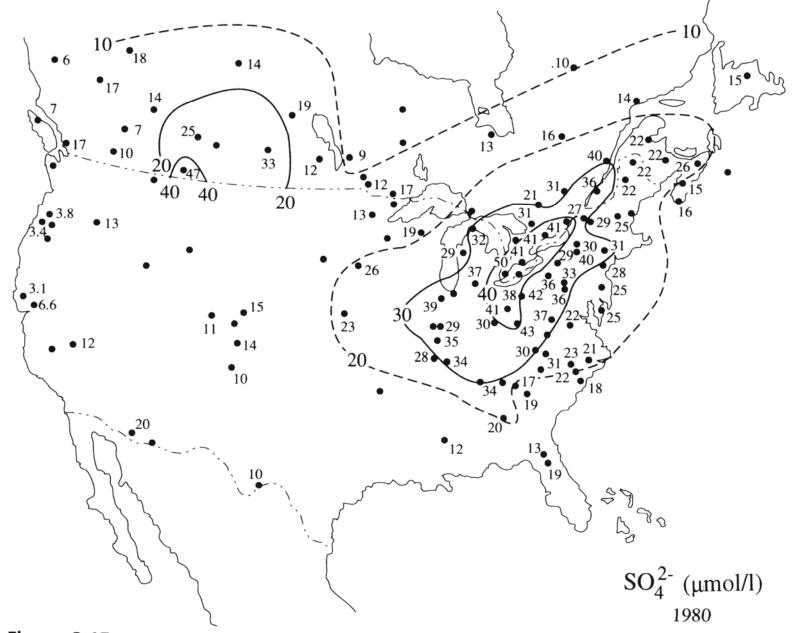
**Figure 3.12** A global budget for Cl in the troposphere and the stratosphere. All data are given in  $10^{12}$  g Cl/yr. Modified from Graedel and Crutzen (1993) and Graedel and Keene (1995).

5. Atmospheric Deposition

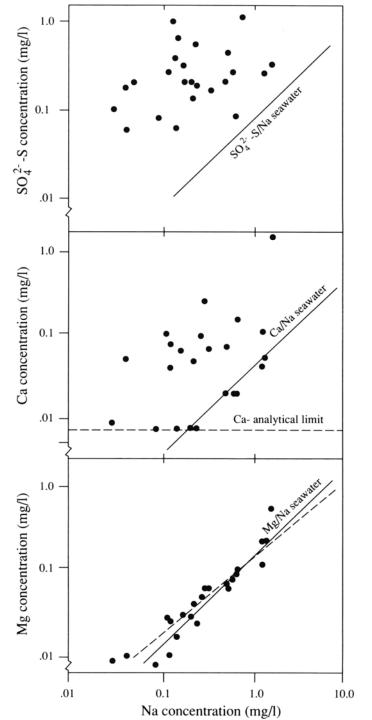


Na<sup>+</sup> (mg/L) Average July 1955-June 1956



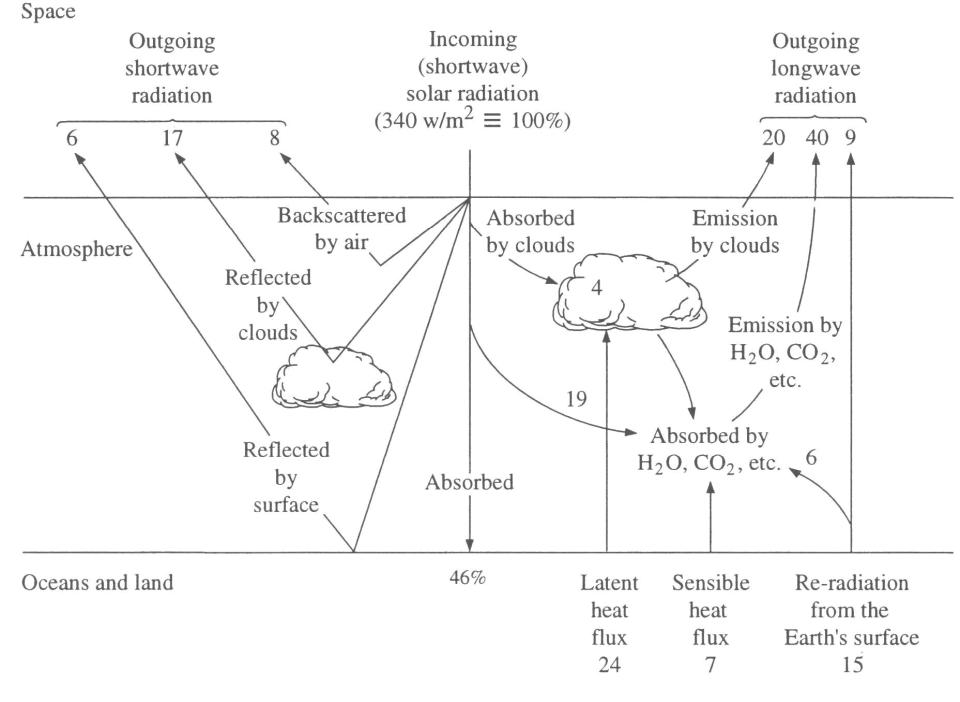


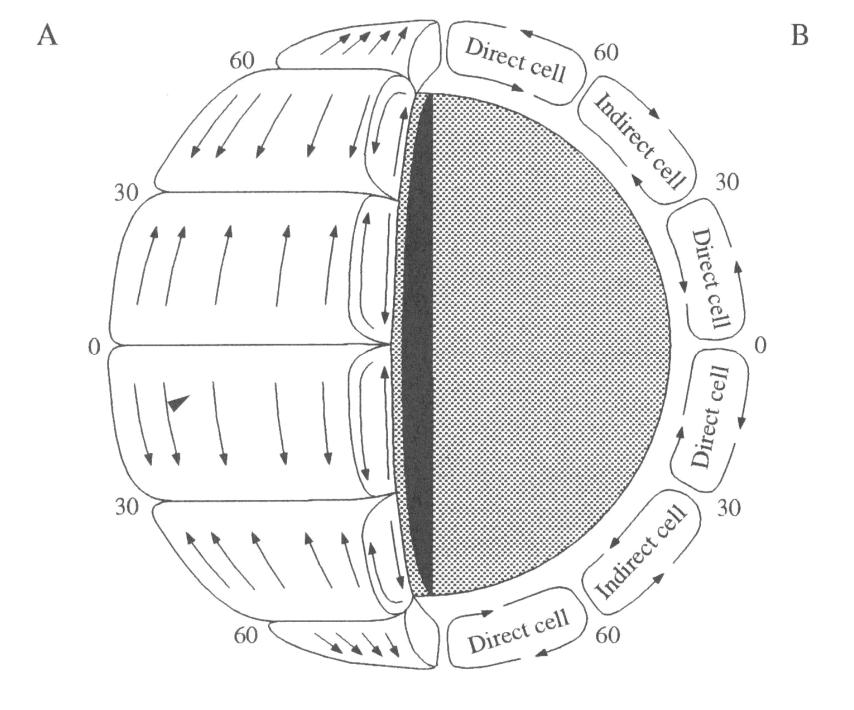
**Figure 3.15** Geographic pattern in the concentration of some major constituents in U.S. precipitation. Na and Cl are from Junge and Werby (1958) and  $SO_4$  is modified from Barrie and Hales (1984).

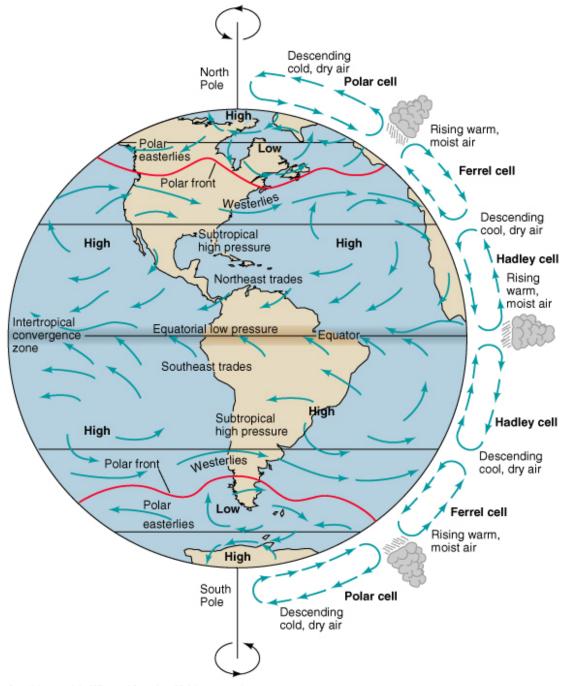


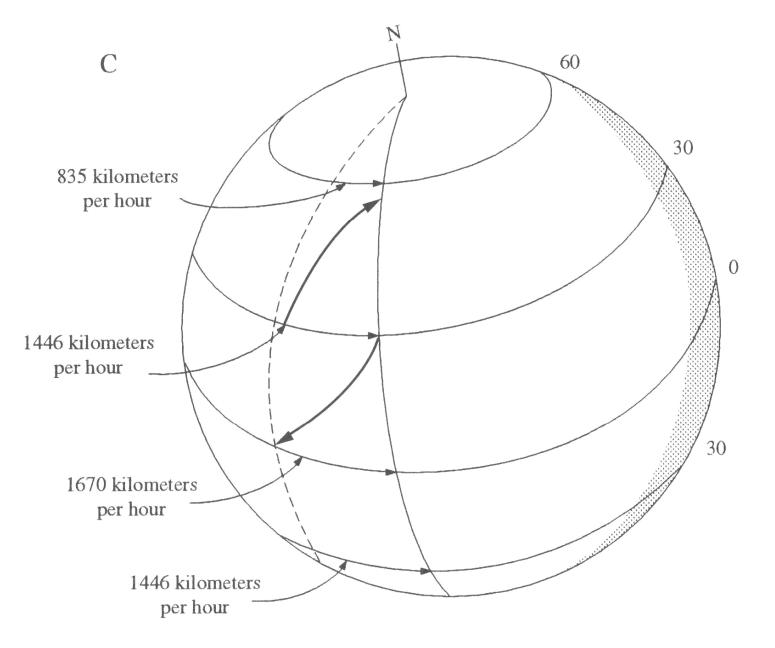
California, plotted as a logarithmic function of Na concentrations in the same collections Concentrations of SO<sub>4</sub>, Ca, and Mg in wetfall precipitation near Santa Barbara, (Schlesinger et al. 1982). The solid line represents the ratio of these ions to Na in seawater. Ca and SO4 are enriched in wetfall relative to seawater, whereas Mg shows a correlation (dashed) that is not significantly different from the ratio expected in seawater. Figure 3.16

## 6. Brief Introduction to the Global Climate



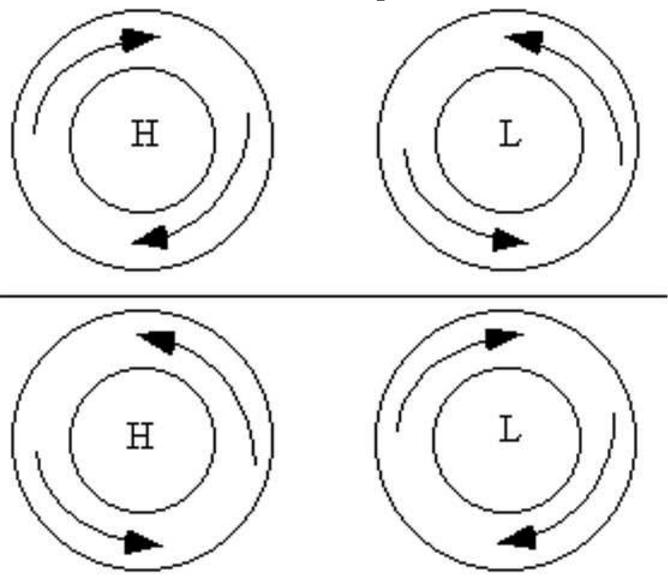






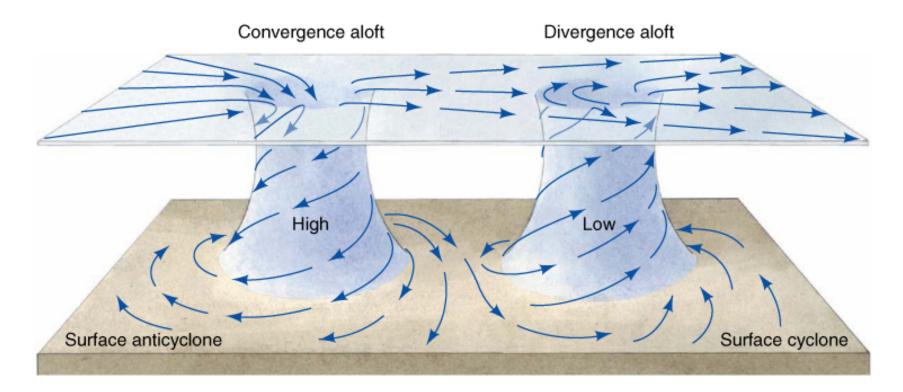
**Coriolis Effect** 

## Northern Hemisphere

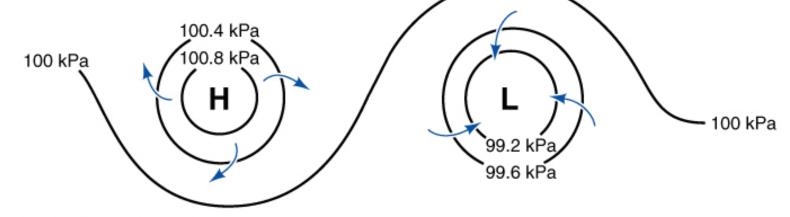


Southern Hemisphere

**Coriolis Effect** 

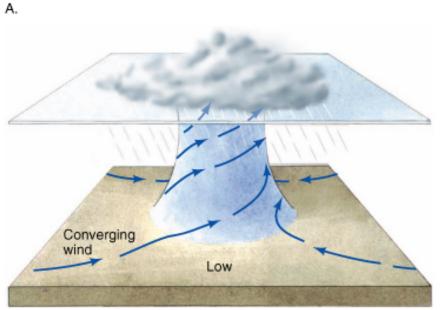


Surface isobars as they appear on a map

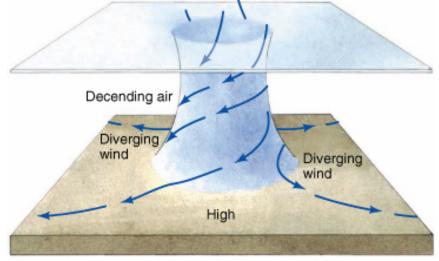


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## **Coriolis Effect**



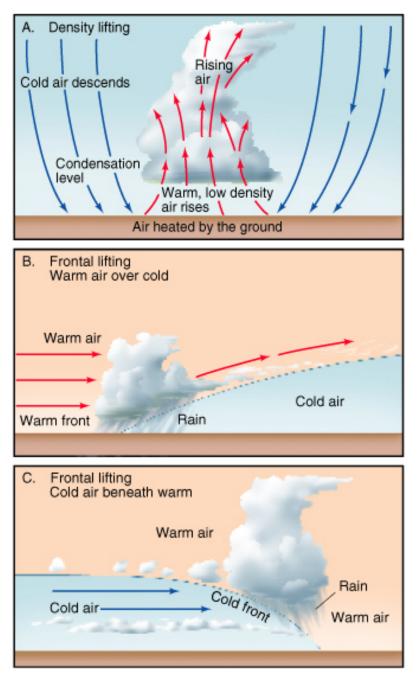


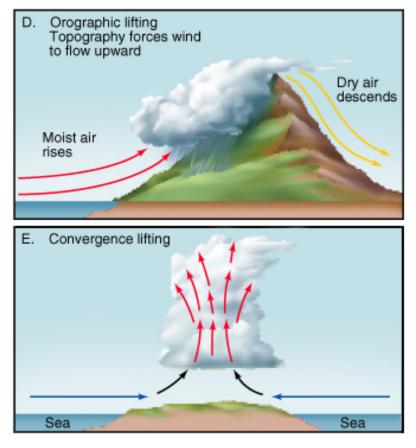


Anticyclone

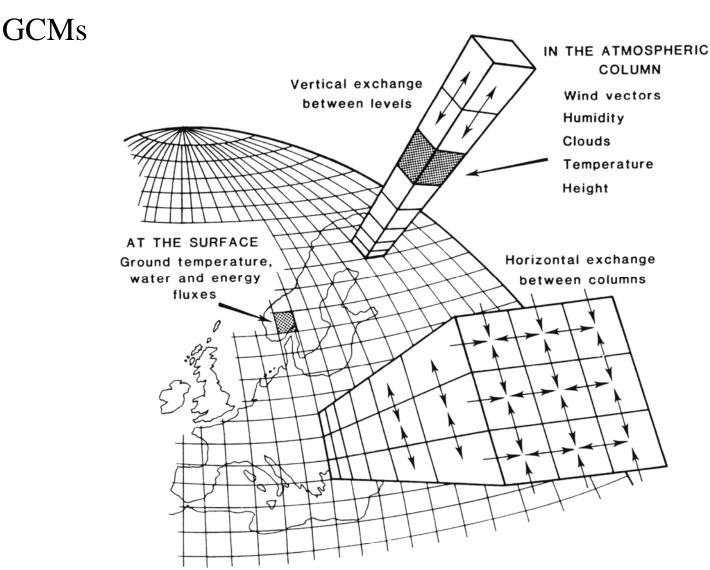
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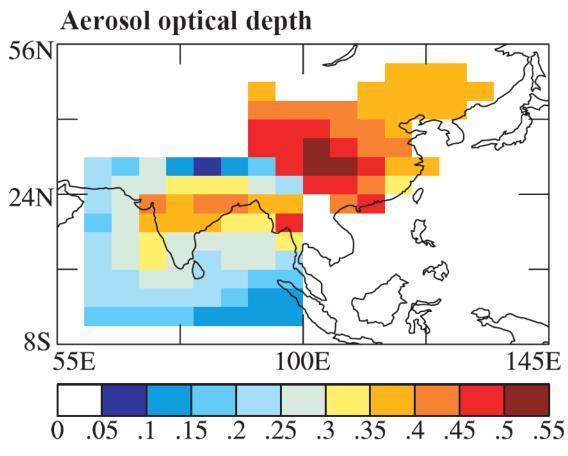




Grid spacing  $\sim 3^{\circ} \times 3^{\circ}$ 

**Figure 3.13** Conceptual structure of a dynamic, three-dimensional general circulation model for the Earth's atmosphere, indicating the variables that must be included for a global model to function properly. From Henderson-Sellers and McGuffie (1987).

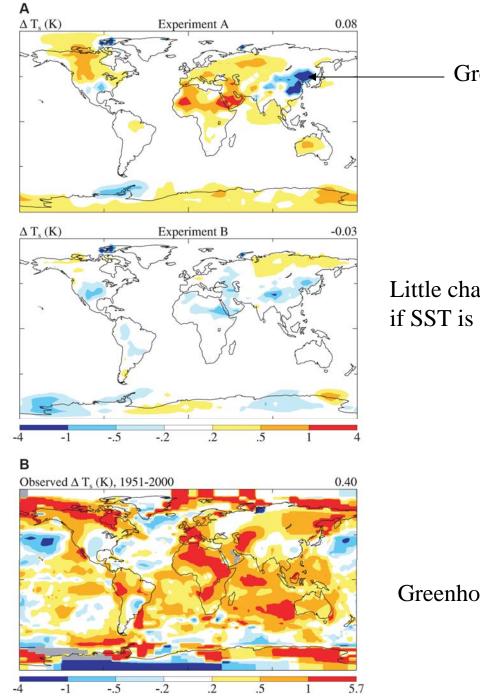
Let us discuss the research paper on black carbons in the air



**Fig. 1.** Incremental aerosol optical depth  $\Delta \tau_{aer}$  (0.55  $\mu$ m), which is used to drive the climate change simulations. Latitude and longitude are denoted.

Aerosol optical depth gives a measure of opaqueness caused by aerosols in a medium (atmosphere) to radiation passing through it.

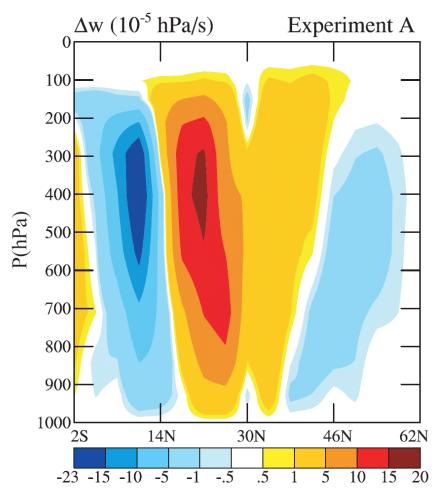
Fig. 2. (A) Simulated JJA surface air temperature change ( $\Delta T_{\rm s}$ ) for experiments A and B. The significance of these changes is shown in fig. S2. (B) Observed JJA  $\Delta T_{\rm s}$  between 1951 and 2000, based on the linear trend. Global mean changes are in the upper right corner.



Greenhouse effect excluded?

Little changes with "white" aerosols if SST is fixed.

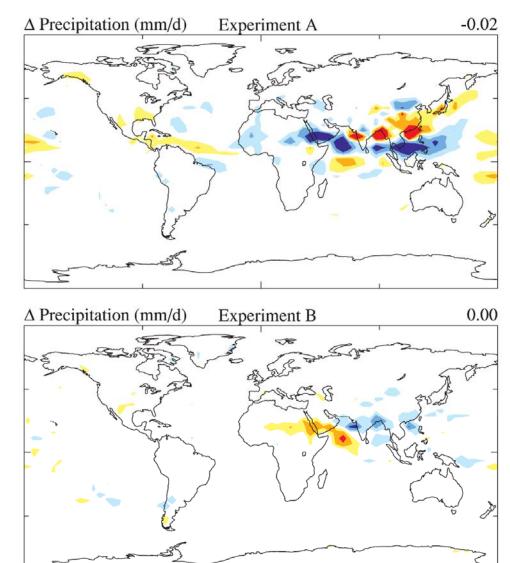
Greenhouse effect is included.



**Fig. 4.** Simulated JJA vertical velocity change  $(\Delta w)$ , as a function of latitude and height, averaged over 90° to 130°E for experiment A.

BC heats the air, strengthens local convection and precipitation, and causes surface cooling.

**. 3.** Same as Fig. 2A, for precipitation. The nificance of these anges is shown in fig.



.2

.5

-.5

-1

-4

-.2

Increased precip. is reproduced if BC is included.

Increased precip. is not reproduced if BC is excluded.