Part 1. The Earth's Atmosphere

Chapter 5. Tropospheric Chemistry: Precipitation

Chapter 5. Tropospheric Chemistry: Precipitation

5.1 The Composition of rain

- Precipitation:

  -wet deposition: rain, snow, sleet, hail, etc.

  -dry deposition: SO_2, dust, etc.

- Composition of rain (table 5.1 and table 5.2)

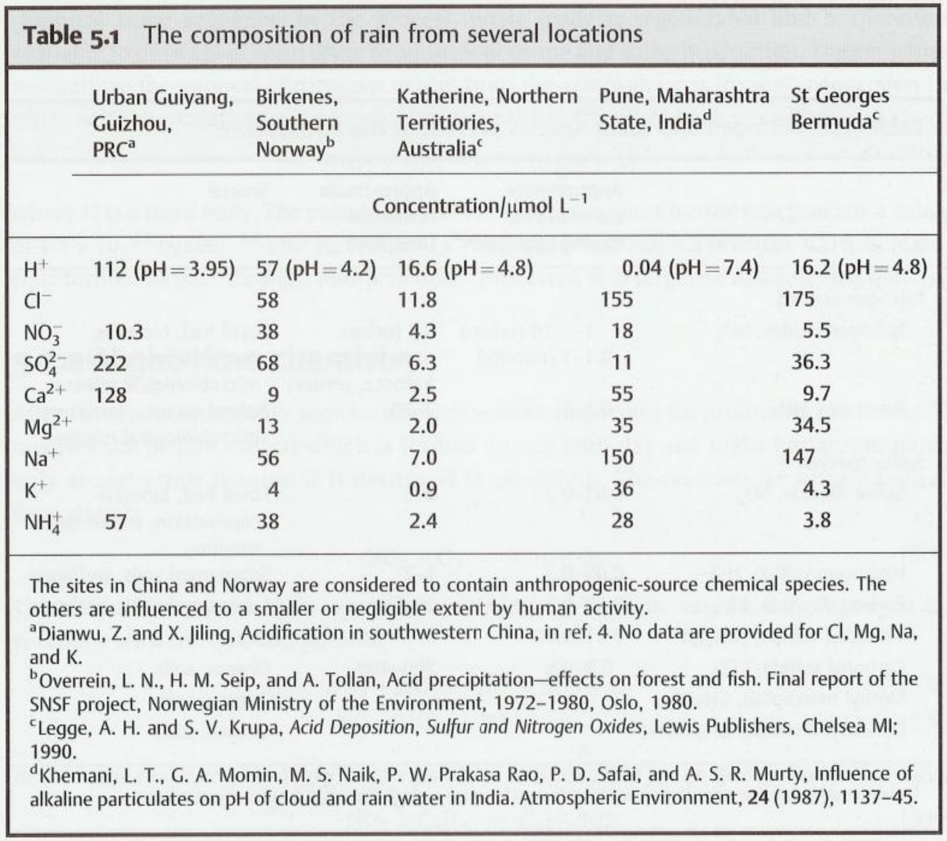

Table 5.1 The composition of rain from several locations

	Urban Guiyang, Guizhou, PRC[a]	Birkenes, Southern Norway[b]	Katherine, Northern Territories, Australia[c]	Pune, Maharashtra State, India[d]	St Georges Bermuda[c]
	Concentration/µmol L^{-1}				
H^+	112 (pH = 3.95)	57 (pH = 4.2)	16.6 (pH = 4.8)	0.04 (pH = 7.4)	16.2 (pH = 4.8)
Cl^-		58	11.8	155	175
NO_3^-	10.3	38	4.3	18	5.5
SO_4^{2-}	222	68	6.3	11	36.3
Ca^{2+}	128	9	2.5	55	9.7
Mg^{2+}		13	2.0	35	34.5
Na^+		56	7.0	150	147
K^+		4	0.9	36	4.3
NH_4^+	57	38	2.4	28	3.8

The sites in China and Norway are considered to contain anthropogenic-source chemical species. The others are influenced to a smaller or negligible extent by human activity.

[a] Dianwu, Z. and X. Jiling, Acidification in southwestern China, in ref. 4. No data are provided for Cl, Mg, Na, and K.

[b] Overrein, L. N., H. M. Seip, and A. Tollan, Acid precipitation—effects on forest and fish. Final report of the SNSF project, Norwegian Ministry of the Environment, 1972–1980, Oslo, 1980.

[c] Legge, A. H. and S. V. Krupa, *Acid Deposition, Sulfur and Nitrogen Oxides*, Lewis Publishers, Chelsea MI; 1990.

[d] Khemani, L. T., G. A. Momin, M. S. Naik, P. W. Prakasa Rao, P. D. Safai, and A. S. R. Murty, Influence of alkaline particulates on pH of cloud and rain water in India. Atmospheric Environment, **24** (1987), 1137–45.

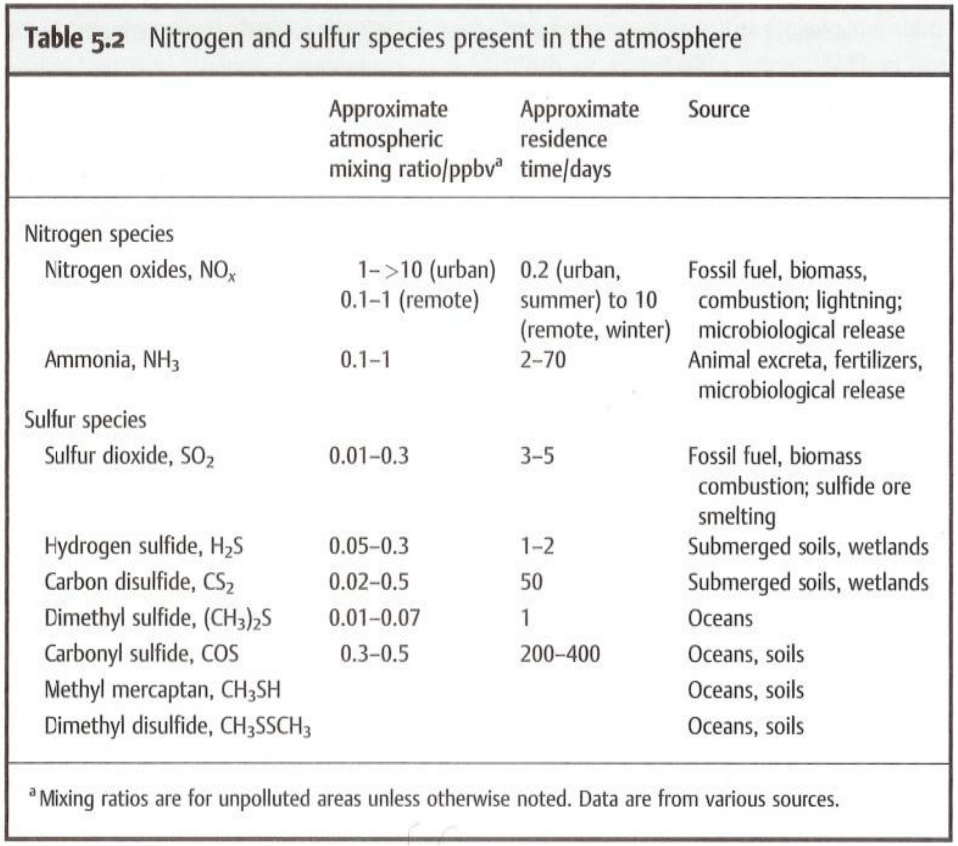

Table 5.2 Nitrogen and sulfur species present in the atmosphere

	Approximate atmospheric mixing ratio/ppbv[a]	Approximate residence time/days	Source
Nitrogen species			
Nitrogen oxides, NO_x	1–>10 (urban) 0.1–1 (remote)	0.2 (urban, summer) to 10 (remote, winter)	Fossil fuel, biomass, combustion; lightning; microbiological release
Ammonia, NH_3	0.1–1	2–70	Animal excreta, fertilizers, microbiological release
Sulfur species			
Sulfur dioxide, SO_2	0.01–0.3	3–5	Fossil fuel, biomass combustion; sulfide ore smelting
Hydrogen sulfide, H_2S	0.05–0.3	1–2	Submerged soils, wetlands
Carbon disulfide, CS_2	0.02–0.5	50	Submerged soils, wetlands
Dimethyl sulfide, $(CH_3)_2S$	0.01–0.07	1	Oceans
Carbonyl sulfide, COS	0.3–0.5	200–400	Oceans, soils
Methyl mercaptan, CH_3SH			Oceans, soils
Dimethyl disulfide, CH_3SSCH_3			Oceans, soils

[a] Mixing ratios are for unpolluted areas unless otherwise noted. Data are from various sources.

Chapter 5. Tropospheric Chemistry: Precipitation

5.2 Atmospheric production of nitric acid

- Daytime chemistry: NO is oxidized by O_2, O_3, or ROO• to produce HNO_3

$NO + O_3 \rightarrow NO_2 + O_2$

$•NO_2 + •OH + M \rightarrow HNO_3 + M$: $k = 1.2 \times 10^{-11}(T/298)^{-1.6}$ cm^3 molecule^{-1} s^{-1}

- Night-time chemistry

$•NO_2 + O_3 \rightarrow •NO_3 + O_2$ (5.3)
$NO_3 + NO_2 \rightarrow NO + NO_2 + O_2$ (5.4)
$NO_3 + NO \rightarrow 2NO_2$ (5.5)
$•NO_3 + C_nH_{2n} \rightarrow •C_nH_{2n}NO_3$ (5.6)
$•NO_3 + RCHO \rightarrow R•CO + HNO_3$ (5.7)
$•NO_3 + RH \rightarrow R• + HNO_3$ (5.8)
$NO_3 + NO_2 \leftrightarrow N_2O_5$ (5.9)
$N_2O_5 + H_2O \rightarrow 2HNO_3$ (5.10)
$RC(O)OO• + •NO_2 \rightarrow RCOO_2NO_2$ (5.11)

- Removal of HNO_3

$NH_3 + HNO_3 \rightarrow NH_4NO_3$ (5.12)

Chapter 5. Tropospheric Chemistry: Precipitation

5.3 Atmospheric production of sulfuric acid

- Oxidation of reduced sulfur species: HS, COS, CS_2, H_2S, CH_3SH, etc.

$H_2S + \bullet OH \rightarrow H_2O + \bullet SH$ (5.13)

$CS_2 + \bullet OH \rightarrow COS + \bullet SH$ (5.14)

$COS + \bullet OH \rightarrow CO_2 + \bullet SH$ (5.15)

$\bullet SH + O_2 \rightarrow SO + \bullet OH$ (5.16)

$\bullet SH + O_3 \rightarrow SHO\bullet + O_2$ (5.17)

$SHO\bullet + O_2 \rightarrow SO + \bullet OOH$ (5.18)

$SO + O_2, O_3, NO_2 \rightarrow SO_2$ + other product (5.19)

$(CH_3)_2S + \bullet OH \rightarrow CH_3SCH_2\bullet + H_2O \rightarrow$ methane sulfonic acid (5.20)

$\rightarrow CH_3S\bullet(OH)CH_3 \rightarrow CH_3SOCH_3$ (5.20)

Chapter 5. Tropospheric Chemistry: Precipitation

5.3 Atmospheric production of sulfuric acid

- Oxidation of SO_2 by homogeneous rxns

$SO_2 + \bullet OH + M \rightarrow HOS\bullet O_2 + M$ (5.21)

$HOS\bullet O_2 + O_2 + M \rightarrow HOO\bullet + SO_3 + M$ (5.22)

$SO_3 + H_2O \rightarrow H_2SO_4$ (5.23)

$NO + HOO\bullet \rightarrow NO_2 + \bullet OH$ (5.24)

$\bullet NO_2 + \bullet OH + M \rightarrow HNO_3 + M$ (5.25)

Kinetic constant changes-see Fig. 5.1

Chapter 5. Tropospheric Chemistry: Precipitation

5.3 Atmospheric production of sulfuric acid

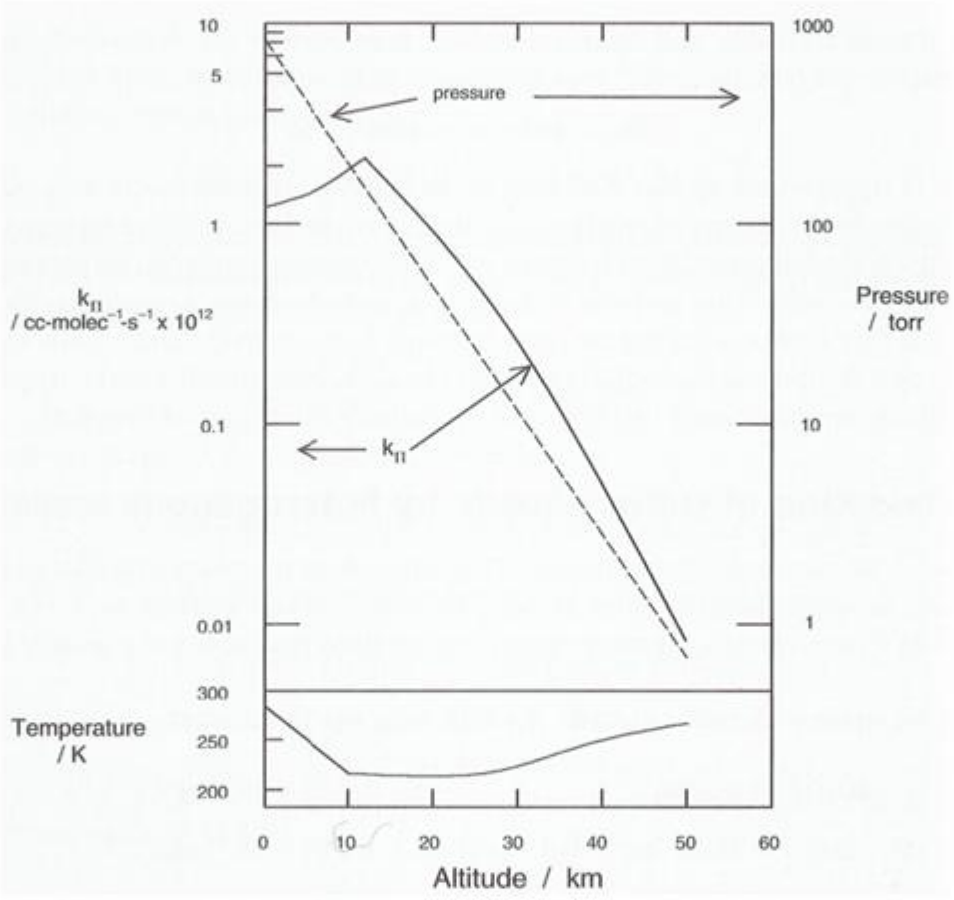

Fig. 5.1 Variation in the second order rate constant for the production of $HO\dot{S}O_2$ as a function of altitude in the troposphere and stratosphere. (Redrawn from J. G. Calvert, and W. R. Stockwell, Mechanisms and rates of the gas-phase oxidations of sulfur dioxide and nitrogen oxides in the atmosphere, in ref. 2.)

Chapter 5. Tropospheric Chemistry: Precipitation

5.3 Atmospheric production of sulfuric acid

- Oxidation of SO_2 by heterogeneous rxns

$SO_2(g) \leftrightarrow SO_2(aq)$ $K_H = 1.81 \times 10^{-5}$ mol L^{-1} Pa^{-1} (5.25)

$SO_2(aq) + 2H_2O \leftrightarrow HSO_3^-(aq) + H_3O^+(aq)$ $K_{a1}=1.27\times10^{-2}$ mol L^{-1} (5.26)

$HSO_3^-(aq) + H_2O \leftrightarrow SO_3^-(aq) + H_3O^+(aq)$ $K_{a2}=6.43\times10^{-8}$ mol L^{-1} (5.27)

- aqueous solubility of SO_2

E.g. if atmospheric mixing ratio of SO_2=10 ppbv at P^0,

solubility(at pH=4) = 2.2×10^{-6} mol L^{-1}

solubility(at pH=7) = 2.2×10^{-3} mol L^{-1}

- $HSO_3^-(aq) + H_2O_2(aq) \leftrightarrow HOOSO_2^-(aq) + H_2O(aq)$ $(\rightarrow k_1, \leftarrow k_2)$ (5.28)

atmospheric mixing ratio of H_2O_2=1~2 ppbv,

readily soluble in water with $K_H = 7.0 \times 10^{-1}$ mol L^{-1} Pa^{-1}

$HOOSO_2^-(aq) + H_3O^+(aq) \rightarrow H_2SO_4(aq) + H_2O$ $(\rightarrow k_3)$ (5.29)

$$\frac{d[H_2SO_4]}{dt} = k_3[HOOSO_2^-][H_3O^+] \qquad (5.30)$$

Chapter 5. Tropospheric Chemistry: Precipitation

5.3 Atmospheric production of sulfuric acid

- Assuming a steady state conc. of HSO_4^-
- $\dfrac{\mathrm{d}[\mathrm{HOOSO_2^-}]}{\mathrm{d}t} = 0 = k_1[\mathrm{HSO_3^-}][\mathrm{H_2O_2}] - k_2^{'}[\mathrm{HOOSO_2^-}] - k_3[\mathrm{HOOSO_2^-}][\mathrm{H_3O^+}]$ (5.32)

Here, $k_2^{'} = k_2[\mathrm{H_2O}]$ since $[H_2O]>>[HOOSO_2]$

$$[\mathrm{HOOSO_2^-}] = \frac{k_1[\mathrm{HSO_3^-}][\mathrm{H_2O_2}]}{k_2^{'} + k_3[\mathrm{H_3O^+}]} \qquad (5.33)$$

$$\mathrm{rate} = \frac{\mathrm{d}[\mathrm{H_2SO_4}]}{\mathrm{dt}} = \frac{k_1k_3[\mathrm{HSO_3^-}][\mathrm{H_2O_2}][\mathrm{H_3O^+}]}{k_2^{'} + k_3[\mathrm{H_3O^+}]} \qquad (5.34)$$

$$\mathrm{rate} = \frac{k_1k_3[\mathrm{HSO_3^-}][\mathrm{H_2O_2}][\mathrm{H_3O^+}]}{k_2^{'}}$$

k_1=5.2 x 10^6 L/mol/s and $k_2'/k_3=10^{-1}$

When pH>2, $k_3[H_3O^+]<<k_2'$

$$[\mathrm{H_3O^+}][\mathrm{HSO_3^-}] = K_\mathrm{H}K_{a1}P_{SO_2}$$

$$\mathrm{rate} = \frac{k_1k_3K_HK_{a1}}{k_2^{'}}[\mathrm{H_2O_2}]P_{SO_2}$$

$$= k^{'}[\mathrm{H_2O_2}]P_{SO_2}$$

Chapter 5. Tropospheric Chemistry: Precipitation

5.3 Atmospheric production of sulfuric acid

- A second heterogeneous pathway involves ozones as the oxidant
- $HSO_3^-(aq) + O_3 \rightarrow SO_4^{2-}(aq) + H_3O^+(aq) + O_2$ (5.39)

  $SO_3^-(aq) + O_3 \rightarrow SO_4^{2-}(aq) + O_2$ (5.40)

Chapter 5. Tropospheric Chemistry: Precipitation

5.4 Acidifying agents in rain

- Refer to Table 5.1
- Cations: Na^+, K^+, Ca^{2+}, Mg^{2+} ions of strong bases
- Anions: Cl^-, NO_3, SO_4^{2-} ions of strong acids
- These are all balanced in water, so the only major ions perturbing the acid-base balance of the water are NH_4^+ and H_3O^+
- NH_4^+ is an important contributor to the soil acidification.

$$NH_4^+(aq) + 2O_2 + H_2O \rightarrow \rightarrow \rightarrow \rightarrow \rightarrow \rightarrow NO_3^-(aq) + 2H_3O^+(aq)$$

microorganisms

Chapter 5. Tropospheric Chemistry: Precipitation

5.5 Sources and sinks of N and S emissions

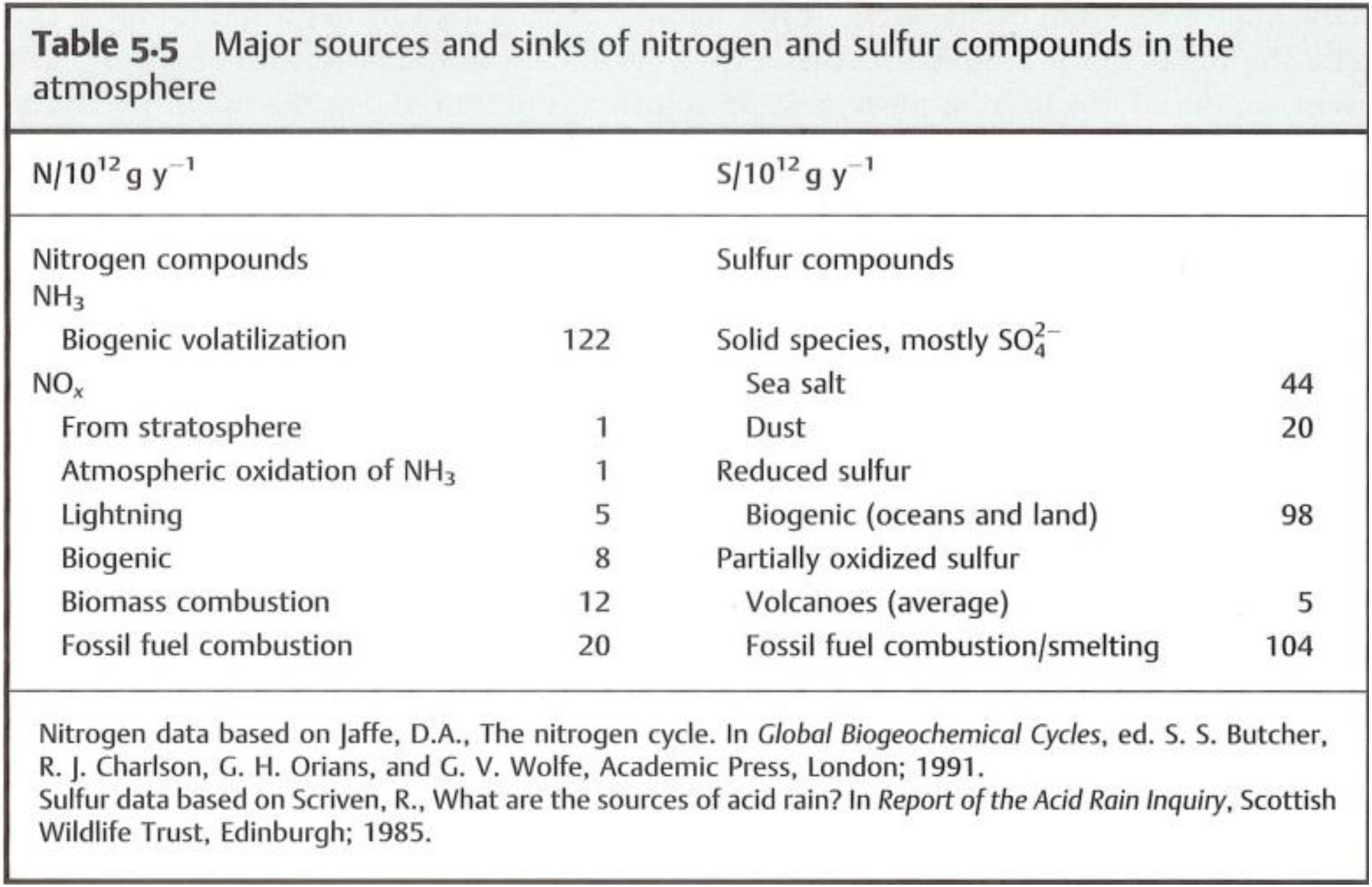

Table 5.5 Major sources and sinks of nitrogen and sulfur compounds in the atmosphere

$N/10^{12}$ g y^{-1}		$S/10^{12}$ g y^{-1}	
Nitrogen compounds		Sulfur compounds	
NH_3			
Biogenic volatilization	122	Solid species, mostly SO_4^{2-}	
NO_x		Sea salt	44
From stratosphere	1	Dust	20
Atmospheric oxidation of NH_3	1	Reduced sulfur	
Lightning	5	Biogenic (oceans and land)	98
Biogenic	8	Partially oxidized sulfur	
Biomass combustion	12	Volcanoes (average)	5
Fossil fuel combustion	20	Fossil fuel combustion/smelting	104

Nitrogen data based on Jaffe, D.A., The nitrogen cycle. In *Global Biogeochemical Cycles*, ed. S. S. Butcher, R. J. Charlson, G. H. Orians, and G. V. Wolfe, Academic Press, London; 1991.
Sulfur data based on Scriven, R., What are the sources of acid rain? In *Report of the Acid Rain Inquiry*, Scottish Wildlife Trust, Edinburgh; 1985.

Chapter 5. Tropospheric Chemistry: Precipitation

5.6 Control of anthropogenic N and S emissions

- Four approaches to reduce N and S emissions:
  1. Decrease energy use by various efficiency measures
  2. Produce energy via non-combustion processes
  3. Prevent emissions of the problem gases
  4. Remove gases after they have been generated
- Fluidized-bed combustion: to enhance the efficiency of coal combustion and of heat transfer and therefore to minimize fuel use

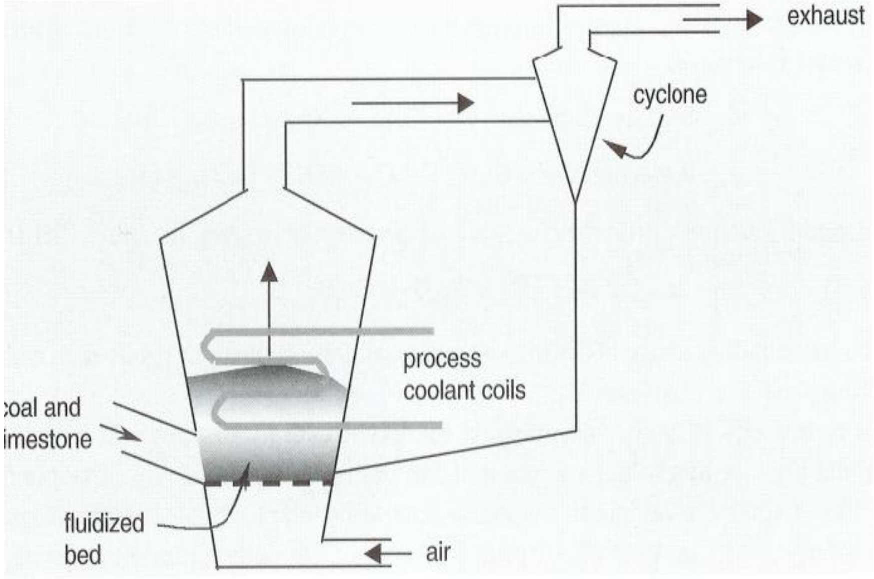

Fig. 5.3 A fluidized-bed combustion unit with a cyclone device for removal of particulate material in the flue gases.

Chapter 5. Tropospheric Chemistry: Precipitation

5.6 Control of anthropogenic N and S emissions

- Retrofitted flue gas desulfurization: combustion gas passes through an aq. slurry, then the following rxns will produce $CaSO_3$.

  with hydrated lime slurry $Ca(OH)_2 + SO_2 \rightarrow CaSO_3 + H_2O$ (5.45)

  with limestone slurry $CaCO_3 + SO_2 \rightarrow CaSO_3 + CO_2$ (5.46)

  $CaSO_3 + ½\ O_2 + 2H_2O \rightarrow CaSO_4 \bullet 2H_2O$ (5.47)

- The SONOX process:

  $CaCO_3$ (aq. slurry) $\underset{900\sim1350\ ^0C}{\rightarrow \rightarrow \rightarrow \rightarrow} CaO + CO_2$ (5.43)

  $CaO + SO_2 + ½\ O_2 \rightarrow CaSO_4$ (5.44)

  $NH_2CONH_2 + 2NO + ½\ O_2 \rightarrow 2N_2 + CO_2 + 2H_2O$ (5.48)

- Conversion of coal to gaseous and liquid forms: