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SMR/760-22

**"College on Atmospheric Boundary Layer
and Air Pollution Modelling"
16 May - 3 June 1994**

"Global and Regional Changes in Atmospheric Composition: Precipitation Chemistry"

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Precipitation
chemistry

Global and Regional Changes in Atmospheric Composition

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4

Removal of Trace Substances from the Atmosphere

4.1 DRY DEPOSITION

4.1.1 General

Except the escape of some hydrogen (which is balanced by the input of solar protons) after a definite time interval (residence time) atmospheric elements* leave the atmosphere to be deposited onto the Earth's surface. Deposition can occur under dry weather conditions or together with precipitation fall. These two removal types are termed the dry and wet deposition, respectively. More specifically, "*dry deposition* is the aerodynamic exchange of trace gases and aerosols from the air to the surface as well as the gravitational setting of particles" (Hicks et al., 1988). The transfer of gases and fine particles in the direction of the surface is controlled by turbulent diffusion, while gases and particles must be transferred through a thin laminar layer covering all surfaces by, e.g., molecular diffusion or Brownian motion. On the other hand, settling of coarse aerosol particles is the result of the gravitational field.

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* Note that chemical reactions in the air provide a sink for compounds but not for elements.

Dry deposition due to turbulent transfer is generally determined by multiplying the surface air concentration by the dry deposition velocity deduced from special micrometeorological measurements made over homogeneous surfaces. Settling velocity of coarse particles can be calculated by balancing the gravitational force with the drag force acting on the particles. Obviously, the settling velocity, V_s, of aerosol particles deduced in this way is a function of their radius, r:

$$V_s = \frac{2}{9}\frac{r^2 \rho_p g}{\mu} \tag{4.1}$$

where g and ρ_p are the gravitational constant and particle density, respectively, and μ is the dynamic gas viscosity (equal to 1.815×10^{-5} N sm^{-2} at a temperature of 20°C).

Dry deposition of gases can be a very effective process if the surface or the ecosystems on the surface remove the molecules considered (e.g., calcareous soils with high alkalinity absorb sulfur dioxide and other acidic species). Further, if the concentration of a compound is high (e.g., in the vicinity of sources) dry deposition is significant and can exceed wet deposition. Generally speaking, dry deposition of gases and particles depends on the state of the atmosphere, the type of underlying surface, and the chemical species. Consequently, its measurement is not an easy task, and dry deposition values must be considered with caution. This means that the precision of global terms discussed below is not better than a factor of 2 or 3.

Finally, we note that by increasing the concentration of different compounds in the air, human activities modify the quantity and quality of atmospheric deposition as well. While deposition is a sink for the atmosphere, it transports materials to aquatic and terrestrial ecosystems altering life processes of plants and animals. The danger caused by man-made modifications is particularly great in the case of acidic substances and toxic metals as will be discussed in Section 6.2.

4.1.2 Trace Gases

Table 4.1 gives the possible magnitude of dry deposition of various trace gases. Values tabulated in the first two lines are taken from the work of Seiler and Conrad (1987). Deposition velocities of SO_2 and NH_3 are based on information published by Beilke and Gravenhorst (1987), while those for nitrogen dioxide and nitric acid vapor are typical values chosen by Penner et al. (1991). Finally, concentration data for gases other than CH_4 and CO are estimated by using the compilation of Mészáros (1992).

Table 4.1 Dry Deposition Velocity (V_d), Concentration (C_A), Dry Deposition Rate (D_d), and Global Dry Deposition (D_{dg}) of Different Atmospheric Trace Gases

Gas	V_d(cm s^{-1})	C_A(μg m^{-3})	D_d(g m^{-2} yr^{-1})	D_{dg}(Tg yr^{-1})
CH_4	1.6×10^{-4}	1.2×10^3	5.9×10^{-2}	30 (22.5)
CO	3.0×10^{-2}	8.0×10^1	0.76	390 (167)
SO_2	0.8	0.2; 2.0	0.05; 0.5	92 (46)
NO_2	0.25	0.05; 0.5	3.9×10^{-3}; 3.9×10^{-2}	7.1 (2.2)
HNO_3	0.5	0.05; 0.5	7.9×10^{-3}; 7.9×10^{-2}	15 (3.3)
NH_3	1.0	0.01; 0.1	3.1×10^{-3}; 3.1×10^{-2}	5.7 (4.7)

Note: If two concentration values are given, the first refers to oceanic air and the second to continental atmosphere. D_d is calculated by the formula: $D_d = V_d \times C_A$.

[a] The values in parentheses are expressed in C, S, and N.

Bearing in mind that the values in Table 4.1 are tentative, one can see that gases determining the acidity of the deposition like SO_2, NO_2, HNO_3, and NH_3 are deposited rather quickly from the air, relative to methane and carbon monoxide. As we have seen, the major part of these latter two species are removed by chemical sinks. Considering the table it should be noted that the vertical flux of ammonia is bidirectional; soils and ocean water may act as sources and sinks depending on the characteristics of the air and underlying surface.

4.1.3 Aerosol Particles

Figure 4.1 represents the dry deposition velocities of aerosol particles measured in wind tunnel experiments over water and grass surfaces by Chamberlain (see Beilke and Gravenhorst, 1987). In the figure the gravitational settling velocity calculated by Equation 4.1 is also plotted. It can be seen that with decreasing particle size the deviation between actual deposition and settling is more and more important. In agreement with our previous discussion, it is believed that this deviation is caused by deposition due to turbulent diffusion. Wind tunnel studies

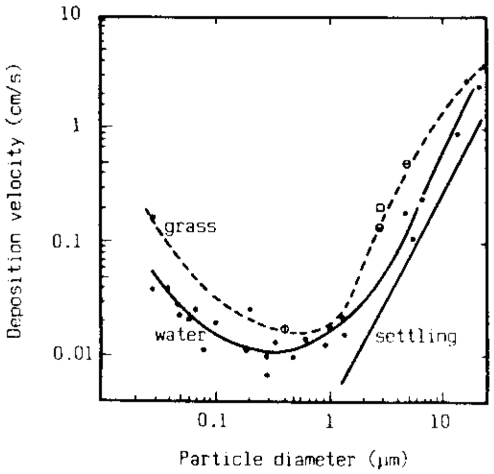

Figure 4.1 Deposition velocities of aerosol particles measured by Chamberlain (see Beilke and Gravenhorst, 1987) in a wind tunnel over smooth surface (water and short grass). The curve settling refers to spherical particles of unit density.

also indicate that the dry deposition velocity increases with decreasing size in the range where Brownian motion becomes important.

We have seen previously that fine tropospheric particles consist mainly of ammonium sulfate (sulfuric acid) and nitrate. Considering that the maximum of the mass of fine particles is in the size range of 0.1 to 0.5 µm (see Figure 3.4) it seems reasonable to suppose on the basis of Figure 4.1 that their dry deposition velocity cannot be greater than 0.1 cm s^{-1}. This is in good agreement with the estimate of Garland (1978) and the observation of Davies and Nicholson (1982), giving an average value of 0.08 cm s^{-1} for sulfate particles. If, on the basis of Figure 4.1, we assume an average of 0.03 cm s^{-1} and take into account appropriate atmospheric concentrations for nonpolluted tropospheric air (see Mészáros, 1991a), we can state that the dry deposition of fine particles can be neglected on a larger scale compared to that of precursor gases. Low dry depositions also mean that the vertical flux of fine particles is controlled by wet removal processes as we will see in the next subsections. Before a final conclusion, however, it should be considered that some field observations resulted in higher dry deposition rates than the above value as compiled by Voldner et al. (1986). The reason for this disagreement is not clear and its explanation needs further efforts.

On the other hand, it is generally accepted that the dry deposition of coarse particles is significant. The deposition of dust particles originating from Asian deserts and the Sahara can be significant under suitable weather conditions, even rather far from the source regions (see Section 2.5.2). According to a recent study of Schneider et al. (1990) carried out in Central North Pacific, dust particles in the size range 2 to 4, 4 to 8, and 8 to 15 µm have a deposition velocity of 0.3, 1.2, and 2.6 cm s^{-1}, respectively. Since human activities in semiarid areas (e.g., burning of vegetation, grazing) lead to desertification, it cannot be excluded that the windblown dust burden in the air, and consequently the dust deposition, will be increased in the future.

4.2 WET SCAVENGING OF TRACE SUBSTANCES

4.2.1 In-Cloud Scavenging of Aerosol Particles

Wet removal of trace substances takes place partly in clouds and partly below the clouds. In the first case, called the "in-cloud scavenging", aerosol particles and trace gases are removed from the air by cloud droplets and ice crystals, while in the second trace materials are scavenged by falling precipitation elements (rain drops and snow flakes). This latter type of wet removal is termed the sub-cloud scavenging.

The removal of aerosol particles begins together with cloud formation. Cloud droplets form on special aerosol particles, called the *cloud condensation nuclei* (CCN). Generally speaking, the nuclei consist of water soluble particles, mostly sulfates, since soluble nuclei are more active in condensation than insoluble particles. This means that droplets come into being at lower supersaturations on soluble particles than on insoluble ones. In other words soluble CCN have lower critical supersaturation. Particle size is also an essential parameter, owing to the fact that larger particles have higher activity in cloud formation than smaller nuclei.

Cloud formation is the result of the updraft of humid air, which is warmer than its surroundings. Because of cooling, the air becomes supersaturated with respect to water vapor. The supersaturation first increases then decreases due to water vapor consumption by nuclei. Only those particles whose critical supersaturation is equal to or less than the maximum supersaturation reached can serve as CCN. If the number of such CCN is high the water vapor quantity available for condensation is distributed on many nuclei. Consequently, the cloud is composed of small droplets with high concentration. Since the probability of precipitation formation by collision of cloud droplets is directly proportional to their size, the precipitation formation ability of such clouds is low and their lifetime is long relative to clouds consisting of larger droplets of low concentration.

The number of active nuclei depends on the properties of the particles and on the updraft velocity. However, one can postulate that soluble particles having a dry radius* larger than ~0.01 to 0.05 μm are activated under normal conditions. Since the major part of the mass of fine particles is above this size, we can conclude that soluble particles are removed very effectively by condensation. It goes without saying that coarse soluble nuclei like sea salt particles serve always as CCN, but they give only a minor fraction of CCN due to their low number concentration relative to the number of cloud droplets in clouds. However, sea salt particles can play a certain role in the formation of larger cloud droplets important for rain formation (the details of the above discussion can be found in Mészáros, 1991b).

The presence of ice crystals in clouds may also initiate rain formation. Ice crystals have a lower saturation level than supercooled liquid droplets. Consequently, the crystals absorb water vapor molecules, which lowers the vapor pressure in their surroundings. In this environment the droplets evaporate while the crystals grow. Ice crystals form on special aerosol particles called ice nuclei. The activity of particles in ice formation and their mode of action depend on many factors, but it is well documented that their number increases with decreasing temperature (see Vali, 1991).

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* The actual radius of soluble particles depends on the relative humidity of the air, since they occur in liquid phase even below the saturation level.

This short discussion shows that cloud droplets and ice crystals contain foreign materials even at the beginning of cloud formation; however, still numerous particles remain in the cloudy air (interstatial particles). Very small particles, nonactivated in condensation, have an important Brownian motion and may have a relatively high number of concentrations depending on the age of the aerosol. For these reasons they coagulate with cloud droplets and ice crystals, and their number decreases exponentially with time. Thus, due to coagulation they are also removed from the air and are imbedded in cloud elements. Finally, an important part of aerosol particles is transferred from the air to cloud water. The fraction removed is significant, in particular, in clean air under remote conditions.

4.2.2 In-Cloud Scavenging of Trace Gases

After cloud formation the sorption of soluble trace gases begins immediately. Under ideal conditions the concentration in liquid phase can be calculated by Henry's law, which shows that the concentration of the gas in liquid phase is directly proportional to the partial pressure in the gas phase. Gas scavenging is particularly important in those cases in which an absorbed gas reacts irreversibly in the liquid phase with another constituent. Example of this type of transformation is provided by the conversion of sulfur dioxide into sulfuric acid (sulfate ions). Since all the processes taking place in clouds depend on the concentration of hydrogen ions, the determination of pH (the negative exponent of the hydrogen ion concentration) is essential to evaluate the efficiency of gas scavenging.

The pH of cloud water is first of all controlled by the absorption of carbon dioxide molecules, which yields by dissociation bicarbonate and carbonate ions. The hydrogen ion concentration (bracket denotes molar concentration: M = mole per liter) in equilibrium is

$$\left[H^+\right] = \left[OH^-\right] + \left[HCO_3^-\right] + 2\left[CO_2^{2-}\right] \tag{4.2}$$

By using appropriate physicochemical data and atmospheric CO_2 concentrations, the equilibrium $[H^+]$ can be calculated. The result is a pH value of 5.6 at a temperature of 10°C. This

Table 4.2 Numerical Values of Rate Constants in Reactions 4.3 and 4.4 at 25°C[a]

Rate Constants	Numerical Values[b]
k_a	2.0×10^4
k_b	3.2×10^5
k_c	1.0×10^9
k_d	5.6×10^9

[a] Data taken from Warneck, 1988.
[b] Expressed in L mol^{-1} or L^2 mol^{-2} where applicable.

pH value is considered as the atmospheric neutral point. This means that atmospheric waters (clouds, fogs, precipitation) are acidic if their pH is lower than the above value.

When sulfur dioxide is absorbed by cloud droplets, bisulfite (HSO_3^-) and sulfite (SO_3^{2-}) ions are formed from aqueous SO_2 molecules (SO_{2aq}). Many research efforts have been done to determine the details of the oxidation of these species. It is now well documented (e.g., Penkett et al., 1979) that their oxidation to form sulfate ions proceeds through the action of oxidizing agents like ozone and hydrogen peroxide* (also absorbed by the liquid phase). Their loss is given by the following rate expressions (Warneck, 1988)

$$-\frac{d[S(IV)]}{dt} = k\left[O_{3aq}\right][S(IV)] = \left[O_{3aq}\right]\left[k_a\left(SO_{2aq}\right) + k_b\left(HSO_3^-\right) + k_c\left(SO_3^{2-}\right)\right] \tag{4.3}$$

$$-\frac{d[S(IV)]}{dt} = k'\left[H_2O_2\right][S(IV)] = \frac{k_d\left[HSO_3^-\right]\left[H_2O_2\right]\left[H^+\right]}{0.1 + \left[H^+\right]} \tag{4.4}$$

where S(IV) denotes sulfur of four valances (SO_2, bisulfite, and sulfite). The rate constants of these processes are given in Table 4.2. It follows from these reactions and rate constants tabulated that ozone oxidizes first of all sulfite ions, while hydrogen peroxide reacts solely with bisulfite. The process (Reaction 4.3) is more rapid at high pH, when sulfite formation is important. On the other hand, the rate of Reaction 4.4 is directly proportional to [H^+] for [H^+] < 10^{-2}(pH > 2). This means that at high pH values Reaction 4.3 is dominant, while for pH below 5.4 the process (Reaction 4.4) controls the formation of sulfate ions (see Figure 4.2). Considering the fact that the pH of cloud water is generally below 5.4, it can be concluded that hydrogen peroxide plays an important part in the oxidation of SO_2 in clouds.

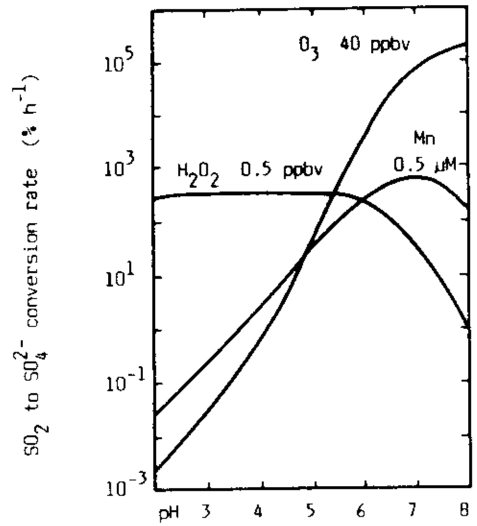

Figure 4.2 Aqueous oxidation of SO_2 in clouds as a function of pH; relative rates for reactions of dissolved SO_2 with ozone, H_2O_2 and oxygen, the latter catalyzed by manganese for the concentrations indicated (Warneck, 1988).

It can be noted that the catalyzed oxidation of S(IV) in cloud water is also possible. Such a catalyst can be provided by iron or manganese. As Figure 4.2 shows under atmospheric conditions (pH below 5.6) the rate of this reaction depends strongly on pH. Its effects can be generally neglected, except on local scale when the air is polluted by the catalytic elements in question.

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* Hydrogen peroxide is formed in the air by the reaction $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ (e.g., Logan et al., 1981).

While the oxidation of NO_2 absorbed by cloud water is theoretically possible, it can be demonstrated that NO_2 is transformed more effectively to nitric acid in gaseous phase as discussed in Section 3.3.1. This implies that the nitrate content of cloud water originates mainly from the removal of HNO_3 vapor (e.g., Chang, 1984).

Parallel with the removal of SO_2 and HNO_3, ammonia gas is also absorbed by cloud water. Ammonia, the only gaseous alkaline species, dissociates in aqueous phase to give ammonium ions:

$$NH_3 \cdot H_2O \rightarrow NH_4^+ + OH \tag{4.5}$$

This results in the neutralization of sulfuric and nitric acid. It is believed that this process removes a significant part of NH_3 molecules from the atmosphere.

4.2.3 Sub-Cloud Scavenging

There are two possibilities concerning the future fate of clouds. One possibility is that the cloud evaporates and absorbed trace constituents again become airborne. However, a new aerosol is produced in this way compared to the size distribution before cloud formation, since one drop generally captures several aerosol particles and reactive trace gases (SO_2, NH_3, HNO_3) are transformed in cloud water. At the same time after dissipation the concentration of reactive gases is lower than before cloud formation owing to irreversible removal processes.

On the other hand, if the cloud precipitates, the materials absorbed are carried out by precipitation to the surface of the Earth; they are definitively removed from the air. We have to emphasize that precipitation elements further scavenge trace materials from the air between the cloud base and the surface. The quantity of substances scavenged in this way is added to the material amount removed in clouds. If the air is not saturated below the clouds, which is generally the case at the beginning of rainfall, the partial evaporation of drops increases the concentrations. Thus, the concentration of different substances in precipitation collected at the surface is the result of three processes: in-cloud and sub-cloud scavenging as well as drop evaporation.

Aerosol particles below the clouds are captured by precipitation elements owing to the difference between falling speeds of the aerosol particles and the raindrops or snow crystals. More precisely, precipitation elements overtake the particles, which are impacted against the drops due to their inertia; the higher the inertia (size) of the particle the higher the probability of such a collision. For this reason mostly coarse particles are removed by sub-cloud scavenging. In other words, the concentration of sea salt particles (oceanic conditions) and particles of soil origin (continental conditions) is efficiently lowered by the process. Since these particles are generally alkaline, sub-cloud scavenging increases the pH of precipitation under normal conditions.

The absorption of trace gases below the cloud base is controlled by the same processes as in-cloud scavenging. The sub-cloud scavenging of trace gases may be important, in particular, if the concentration of the gas considered increases with decreasing height—that is in more polluted air—where sources can be found at the surface.

4.2.4 Wet Deposition Modeling

If we want to describe theoretically the wet deposition, D_w, as a whole, we assume that in an air layer with a depth of h it depends only on two parameters: the concentration in the air, C_A, of the substance considered and the rainfall rate, R (see, e.g., the recent review of Smith, 1991):

$$D_w = C_L R = \omega C_A R \tag{4.6}$$

where ω is the so-called washout ratio defined as the ratio of the concentration in liquid water, C_L, and in the air of the species considered. By analogy to the dry deposition velocity

$$\frac{dD_w}{dt} = v_w C_A = \omega C_A \frac{dR}{dt} \tag{4.7}$$

Thus, for characterizing the dynamics of the wet deposition it is crucial to determine the value of the washout ratio. Without further details we note that its magnitude is around 10^5 if C_A and C_L are expressed in g m^{-3}. If the washout ratio is known from independent atmospheric observations or laboratory experiments, by means of Equation 4.7, we can simulate in a simple way the variation of the wet deposition.

4.2.5 The Magnitude of Wet Removal: Precipitation Chemistry Measurements

The chemical composition of precipitation water gives information on the self-cleansing rate of the atmosphere. Additionally, precipitation chemistry observations provide data on the material quantity received by different ecosystems from the atmosphere. For these reasons many national and international research and monitoring programs have been initiated to measure the chemical composition of precipitation (see Mészáros, 1992). Special attention has been devoted to the measurement and interpretation of hydrogen ion concentration as we will see in Section 6.2.

When measuring the composition of precipitation, the concentrations of different ions (sulfate, nitrate, chloride, ammonium, sodium, and soil derived species) in unit volume of the water is determined. If it is multiplied by the amount of precipitation fallen during the sampling time, the *wet deposition* is obtained (see Equation 4.6). The unit of wet deposition (g m^{-2} yr^{-1}) may be similar to the rate of dry deposition used in Table 4.1.

The chemical composition of precipitation water is relatively well-known for Europe and North America (Nodop, 1986; Barrie and Hales, 1984). As an illustration, typical data obtained in Southern Sweden and New Hampshire are presented in Table 4.3. For the evaluation of anion concentrations we note that sulfate and nitrate ions come mostly from anthropogenic aerosol particles and precursor gases, while on a larger scale the major part of chloride ions originates from sea salt containing sodium chloride. If we suppose that sodium is entirely of maritime origin, from the data tabulated for Sweden and New Hampshire a continental chloride concentration of 3 μ eq L^{-1} and 9 μ eq L^{-1} is calculated, respectively. This means that some chloride of continental (anthropogenic?) origin can also be detected in precipitation. Among cations, ammonium is a biogenic product; however, its biological sources are modified significantly by man, as we have previously seen. Other cations, except sodium, are obviously of soil origin. Data tabulated make it evident that the high concentration of hydrogen ions (low pH) is due to sulfuric and nitric acid. The sum of anions and cations are nearly equal at both places, indicating that all essential components were analyzed. This means implicitly that the role of other species, like organic acids important under tropical conditions (Galloway et al., 1982), is insignificant over Europe and North America.

Table 4.3 **Average Concentration of Precipitation Water Collected in Southern Sweden[a] and in New Hampshire[b]**

Ions	Sweden	New Hampshire
H^+	52 (pH = 4.28)	74 (p = 4.13)
Ca^{2+}	14	8
Mg^{2+}	8	4
K^+	3	2
Na^+	15	5
NH_4^+	31	12
Sum of cations	123	105
SO_4^{2-}	70	60
NO_3^-	31	23
Cl^-	18	14
Sum of anions	119	97

Note: The values are expressed in μeq L^{-1}. For univalent ions 1 eq is equal to 1 mol while for bivalent ions (calcium, magnesium, and sulfate) the number of moles must be multiplied by two to obtain the number of equivalents.

[a] Swedish Ministry of Agriculture, 1982.

[b] Likens et al., 1977.

In contrast to Europe and North America the distribution of wet deposition on a worldwide scale is not well established. However, in spite of the small data base, efforts were made to determine the global distributions of sulfur and nitrogen containing ions due to the importance of the question. Figures 4.3 through 4.5 show the results obtained by Georgii (1982) and Böttger et al. (1978). Although these distribution patterns should be considered with caution, on the basis of Figure 4.3 we can assume that the oceanic wet deposition of sulfate (expressed in sulfur) is around 0.05 g S m^{-2} yr^{-1}, while the corresponding figure for the continents is 0.3 g S m^{-2} yr^{-1}. This difference is obviously explained by the distribution of anthropogenic sources on the Earth's surface. Further, according to Figure 4.4 one can estimate that the oceanic and continental wet deposition rates of ammonium-nitrogen are equal to 0.02 and 0.2 g N m^{-2} yr^{-1}, respectively. Finally, data in Figure 4.5 make it possible

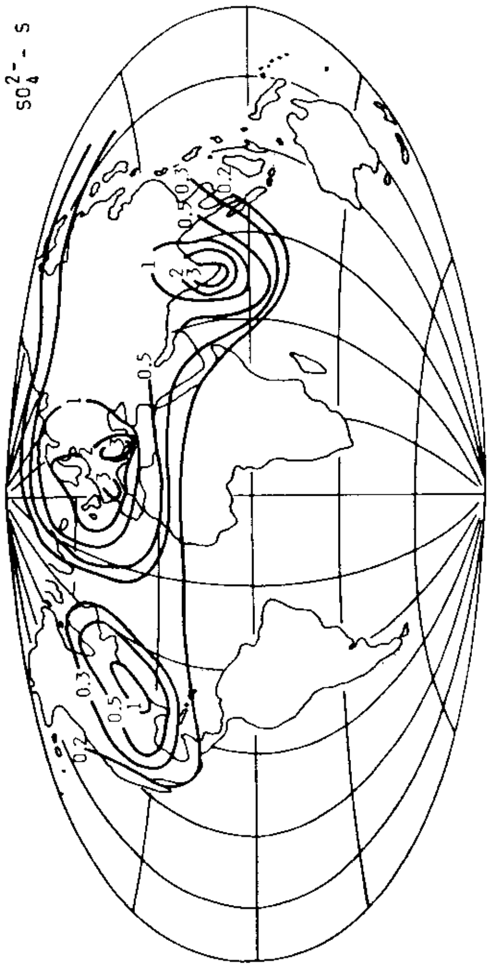

Figure 4.3 Sulfate in rain water. Deposition in units of g S m^{-2} yr^{-1} (from Georgii, 1982).

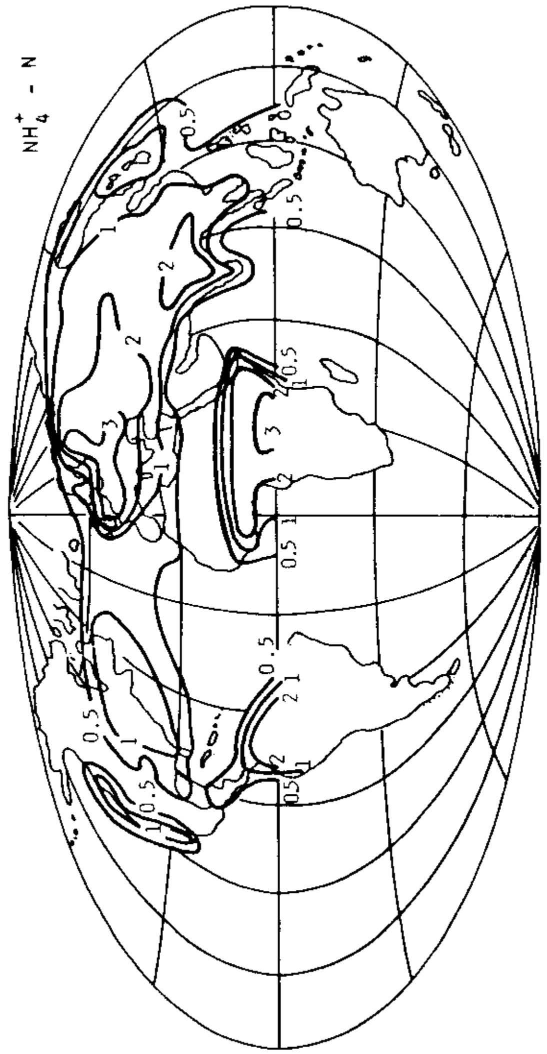

Figure 4.4 Global distribution of wet NH_4^+ deposition according to Böttger et al. (1978), derived from measurements during the period 1950–1977. The deposition rate in units of 100 mg m^{-2} yr^{-1}.

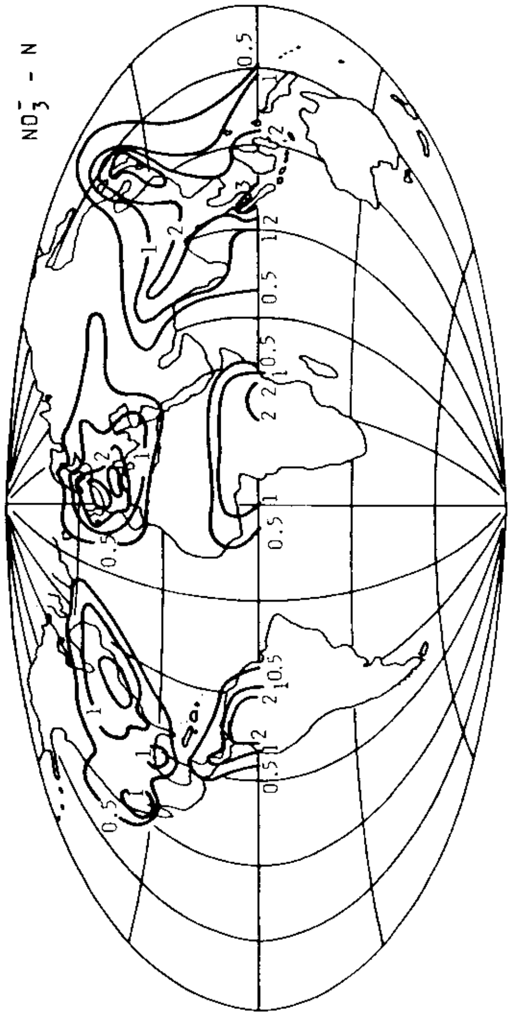

Figure 4.5 Global distribution of the wet deposition rate of NO_3^- nitrogen for the Nothern Hemisphere in units of 100 mg m^{-2} yr^{-1}, derived by Böttger et al. (1978) from measurements during the period 1955–1977.

Table 4.4 Wet Deposition Rate (D_w) and Global Wet Deposition (D_{wg}) of Sulfur and Nitrogen

Species	$D_{w\ ocean}$ (g m^{-2} yr^{-1})	$D_{w\ cont.}$ (g m^{-2} yr^{-1})	D_{wg} (Tg yr^{-1})
SO_4^{2-}-S	0.05 (3.1)[a]	0.3 (19)	62
NH_4^+-N	0.02 (1.4)	0.2 (14)	37
NO_3^--N	0.02 (1.4)	0.2 (14)	37

[a] Data in parentheses expressed in milliequivalents per square meter per year.

that the nitrate-nitrogen wet deposition rates are similar to those proposed for ammonium-nitrogen.

Table 4.4 summarizes this tentative information on wet deposition rates together with the global values calculated. Comparing these values with data tabulated in Table 4.1 one can conclude that wet deposition is the main removal process of sulfur and nitrogen compounds on a global scale. While direct estimations are not available, it is obvious that the anthropogenic fractions of these deposition terms is identical with those calculated for the emissions (see Table 2.8).

As it was mentioned in Section 2.1 the analyses of snow samples from Greenland indicate that the concentration of sulfate and nitrate ions in wet deposition has increased in the Northern Hemisphere since the end of the last century (Nefter et al., 1985). This is due to the intensification of the strength of anthropogenic emission of SO_2 and NO_x. A second reason may be the increase in the concentration of H_2O_2 in clouds and precipitation, also demonstrated by the analyses of ice core samples collected in Greenland (Sigg and Nefter, 1991). Higher hydrogen peroxide concentration has led to higher oxidation capacity of atmospheric waters as discussed in the previous subsection.

Since the time period of precipitation chemistry measurements, several studies have been made to look for possible trends in data. Thus, it was found (Brimblecombe and Pitman, 1980) that in England nitrate concentration has increased from the end of the last century until now, mainly in spring months. A similar trend was reported on the basis of the results of Hungarian observations (Horváth, 1983). Hungarian data also reveal that during this century the ammonium level of precipitation has remained essentially constant. Precipitation chemistry measurements carried out in New Hampshire since 1964 indicate some increase in nitrate concentration and a relatively constant pH level (Stensland et al., 1986). At the same time the concentration of sulfate ions has decreased significantly (2% per year) in accordance with the trend of SO_2 emissions in the northeastern part of the U.S. (Husar, 1986). According to studies made in Scandinavia the sulfate concentration in precipitation increased by 50% during the late 1950s and 60s, while it declined by 20% since the early 1970s in agreement with changes in SO_2 emissions (Rodhe and Granat, 1984). All these data demonstrate anthropogenic modifications of sulfur and nitrogen wet deposition. Among other things, these modifications resulted in the acidification of the environment on regional and continental scales.

Beside the main components discussed above the study of the deposition of carbonaceous materials and different metals is also important in solving environmental problems. The deposition rate of elemental carbon, occurring only in the aerosol phase, was determined by Ogren et al. (1984). They found that in Seattle, Washington and at a rural site in Sweden the wet deposition flux of elemental carbon is equal to 0.05 $g\ m^{-2}\ yr^{-1}$. The deposition rates of atmospheric trace metals measured under different conditions are evaluated by Galloway et al. (1982). According to their compilation at remote places, the bulk (dry + wet) deposition of, e.g., lead and copper, is around $10^{-4}\ g\ m^{-2}\ yr^{-1}$. On the other hand, Duce (1986) proposes a mean Al deposition rates with a magnitude of $10^{-2}\ g\ m^{-2}\ yr^{-1}$ for the air above the tropical North Pacific, while the corresponding value he gives for the tropical North Atlantic is about four times greater.

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ATMOSPHERIC ACIDITY
Sources, Consequences and Abatement

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1.3.3 Aqueous compounds

On condensation, cloud and fog droplets form on condensation nuclei consisting of water-soluble aerosol particles. After cloud and fog formation the sorption of soluble gases begins immediately. A part of the gases incorporated into the aqueous phase is converted irreversibly in water (e.g. SO_4^{2-} can be formed from SO_2 absorbed). On the other hand, small aerosol particles, remaining airborne after cloud/fog formation, are captured by water droplets or ice crystals due to their Brownian motion. These removal processes taking part in the clouds are termed *in-cloud scavenging*, or *rainout*.

There are two possibilities concerning the future fate of a cloud or fog. One possibility is that cloud and fog elements evaporate and the substances scavenged again become airborne. The other possibility is that the fog and cloud droplets and crystals grow into drizzle or precipitation elements which are deposited onto the earth surface. Below the cloud base raindrops and snowflakes incorporate further materials. This so-called *below-cloud scavenging* or *washout* can be particularly significant in the polluted atmosphere.

The above process, removing different species from the air and carrying them to the surface; is termed *wet deposition*. A special form of wet deposition is when cloud and fog droplets are captured from the air by trees or by any object on the surface (interception). It is also possible that water vapor condenses directly on the surface of the vegetation (or on other surfaces) to form liquid water in the form of dew.

Due to wet deposition an important part of acidifying substances and acid species is removed from the air. While wet deposition is a sink of atmospheric gases and particles, it creates an important material flux from the air to other media of our environment. Consequently, the study of the composition of atmospheric liquid waters is of crucial importance for estimating the acidification of soils and natural waters.

Owing to its significance in acidification processes, several programs have been performed during the last years to investigate the chemical composition of *fogwater*. The results of these programs demonstrate that fogwater is generally rather polluted and its H^+ ion concentration is high. Thus, in the Po Valley, Italy, pH values in fogwater between 3·49 and 4·32 and SO_4^{2-}, NO_3^- and NH_4^+ concentrations in the range of 100–1000 μeq liter^{-1} were observed.[70] In southern California a median pH value of 3·32 was measured,[71] while the lowest figure was as low as 2·7. Even a pH of 2·2 was detected in a dissipating fog under urban conditions in California.[72] In the Po Valley the SO_4 concentration was generally higher than that of NO_3^- ions, but in California the inverse was observed. The mean NO_3^- concentration in fog is equal to 1110 μmol liter^{-1},[71] while the corresponding figure for SO_4^{2-} is 292 μmol liter^{-1}. The high NO_3^- content in California is obviously due to the large traffic density and the intense photochemical activity of the area.

In California and in the Po Valley the organic acid content of fog droplets was also investigated. In California the HCOOH and CH_3COOH concentration varied between 45–142 μeq liter^{-1} and 1–134 μeq liter^{-1}, respectively.[73] Similar to these findings the results of the study carried out in Italy show that the HCOOH concentrations in fogwater range from 11 to 175 μmol liter^{-1},[74] while the corresponding interval for CH_3COOH is 10–269 μmol liter^{-1}. In agreement with previous discussions these levels are much lower than the concentrations of inorganic acidic compounds.

Some studies have also been made to determine the composition of *dew* as summarized by Ref. 75. Owing to the effects of biologically derived alkaline ions rather high pH values are generally reported in dewwater. Thus, at a site in Warren (Michigan, USA) a median pH value of 6·5 was measured in natural dew.[75] This was due to the very high calcium concentration (690 μeq liter^{-1} on average) and to the relatively 'low' SO_4^{2-} concentration (242 μeq liter^{-1}). Dew was found to be much more concentrated than rainwater, except for H^+ ions. The study also showed that dew enhances considerably the dry deposition of different materials from the air as compared to the flux over dry surfaces.[75]

The composition and acidity of *cloudwater* have been measured by several research workers.[76] The significance of such measurements for our subject is the fact that in mountainous areas the acid input to the ecosystems by the interception of cloud droplets may be more important than the deposition due to falling precipitation. This concept was formulated on the basis of the results obtained in the Adirondack Mountains of New York State, USA, according to which the pH of cloudwater was found to

Table 1.4
The chemical composition of cloudwater in Sweden[79] according to wind trajectories at 1000 hPa

Sector	*No. of samples*	*Composition* ($\mu eq\ liter^{-1}$)								
		H^+	NH_4^+	Na^+	K^+	Mg^+	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}
NE	47	33	17	7	< 0·8	1	0·6	6	9	34
NW	41	13	0·5	< 0·4	< 0·8	< 0·2	0·3	0·8	2	6
W	33	38	1	5	< 0·8	0·6	0·8	4	10	30
S	4	370	—	33	6	12	22	19	68	700

Reproduced with permission from Ref. 79.

be rather low; it was in the range of 2·66–4·66 in 90% of the cases.[77] These results are supported by more recent observations made at Whiteface Mountain (New York, USA).[78]

The chemical composition of cloudwater formed in air masses of different origin can be estimated on the basis of recent Swedish observations carried out at Areskutan (63°26′ N, 13°6′ E) at an altitude of 1250 m.[79] The authors divided their results according to the air trajectories arriving at the sampling site from different directions as shown in Table 1.4. It can be estimated that the composition of the NW sector refers to the hemispheric background, while the results gained on the occasion of S polluted continental air (compare these figures with precipitation chemistry data tabulated in Table 1.1). In the other two sectors transitional composition was measured.[80]

Owing to the importance of cloud chemistry a program was started in the US to regularly monitor cloud composition on six mountain summits. The results obtained in 1986 at one of these stations (Mt. Mitchell, State Park, North Carolina, USA)[81] show that the average pH in precipitation is about 4·4 while it ranges from 2·2 to 5·4 in cloudwater. On the basis of their observations, the authors estimate that the deposition caused by cloud interception is two to five times the deposition in form of precipitation.

It goes without saying that this conclusion is valid only for mountainous regions. In other areas the wet deposition is controlled by the composition and quantity of *precipitation water* (the deposition is the product of the concentration and precipitation amount), except during relatively infrequent foggy conditions. For this reason many national and international research and monitoring programs were initiated to measure the chemical composition of precipitation, including the European Atmospheric Chemistry Network (EACN) organized by Swedish scientists,[82] the National Acid Deposition Program in the US (NADP), the Canadian Network for Sampling Precipitation (CANSAP), the European Monitoring and Evaluation Programme (EMEP) of the Economic Commission for Europe and the Background Air Pollution Monitoring Network (BAPMoN) of the World Meterological Organization. The results of NADP and CANSAP are summarized by Refs 83 and 84, EMEP data are evaluated by Refs 7, 21 and 52, while precipitation chemistry data gained in BAPMoN are discussed by Refs 85 and 86. As an example Figs 1.6–1.9 illustrate the spatial distribution of pH, SO_4^{2-}, NO_3^- and NH_4^+ concentrations according to the data obtained in 1980 by NADP and CANSAP and by some smaller networks,[83] while Table 1.5 gives the range of the

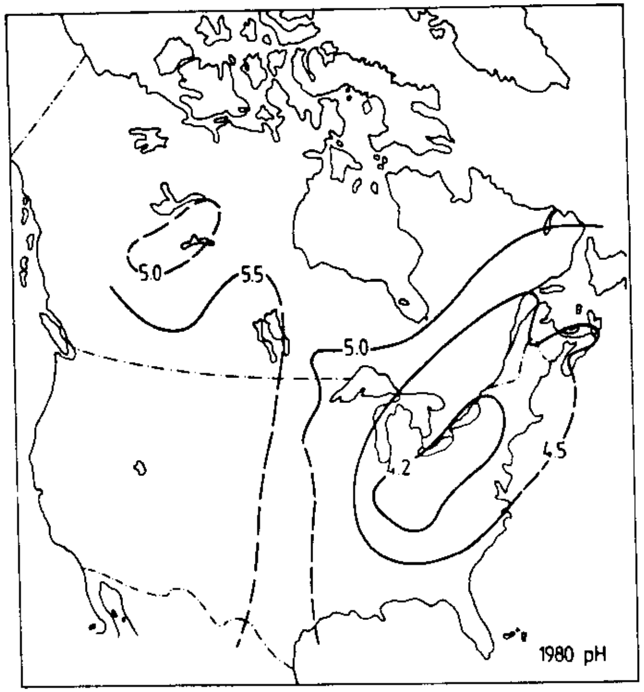

Figure 1.6. Spatial distribution of pH of precipitation water collected in North America. (Reproduced with permission from Ref. 83.)

wet deposition of these ions for eastern (north-eastern US and south-eastern Canada) and western parts of the territory where the minimum and maximum pH values occur. First of all, it should be mentioned that these values are very similar to those reported for Europe.[52] Secondly, maximum H^+, SO_4^{2-} and NO_3^- ion concentrations are found in areas with high SO_2 and NO emissions.[55] Thirdly, the spatial distribution of the concentration of NH_4^+ ions in precipitation is different from that of SO_4^{2-} and NO_3^+ ions. This is not surprising since NH_3 molecules are released from different sources than sulfur and nitrogen oxides. Thus, maximum NH_4 concentrations were found in the north central US where livestock feedlots are concentrated. On the other hand, the comparison of data in Tables 1.3 and 1.5 indicates that dry deposition of different acidifying species is comparable to their flux due to wet deposition.

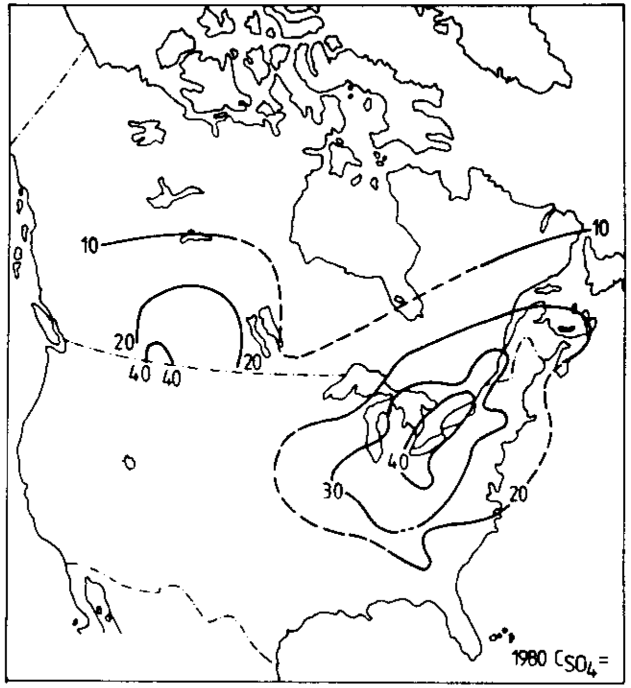

Figure 1.7. Spatial distribution of the concentration of SO_4^{2-} ions in precipitation water (expressed in μmol liter^{-1}) collected in North America. (Reproduced with permission from Ref. 83.)

Since the time period of precipitation chemistry measurements is longer than the interval of gas and aerosol phase observations, several studies have been made to estimate the possible trend in precipitation chemistry data. Thus, it was found that data obtained at Rothamsted (UK) show an increase of NO_3^- concentration from the end of the last century until now, mainly in the spring months.[87] A similar trend was reported on the basis of the results of Hungarian observations.[88] Hungarian data also reveal that since the turn of the century the NH_4^+ level of precipitation has remained practically constant. Precipitation chemistry data measured at Hubbard Brook (New Hampshire, USA) since 1964 were studied by several authors. The results indicate some increase in NO_3^- concentration and a relatively constant pH level.[84] At the same time the

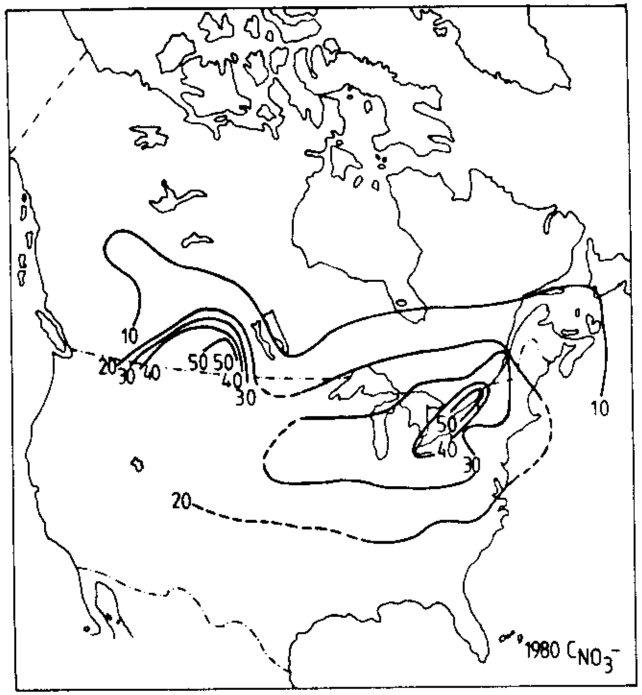

Figure 1.8. Spatial distribution of the concentration of NO_3^- ions in precipitation water (expressed in μmol liter^{-1}) collected in North America. (Reproduced with permission from Ref. 83.)

concentration of SO_4^{2-} ions has decreased significantly (2% per year) in accordance with the trend of SO_2 emissions in the north-eastern part of the US.[55] According to the analysis of EACN data obtained between 1955 and 1982 in Scandinavia, the SO_4^{2-} concentration in precipitation increased by 50% during the late-1950s and 1960s, while it declined by 20% since the early-1970s in agreement with changes in SO_2 emissions.[82]

Measurements of HCOOH and CH_3COOH in precipitation water were reviewed in several papers.[18,89] They demonstrate that, with the exception of one site in Virginia (USA) where samples were influenced by anthropogenic emissions, the concentration of these acids is high in particular in tropical and subtropical regions (ranging from 20 to 30 μmol liter^{-1}). At other continental and marine locations they vary between 5 and 20 μmol liter^{-1}. Under continental condititons the concentrations exhibit a maximum during the growing season supporting the existence of natural biogenic sources.

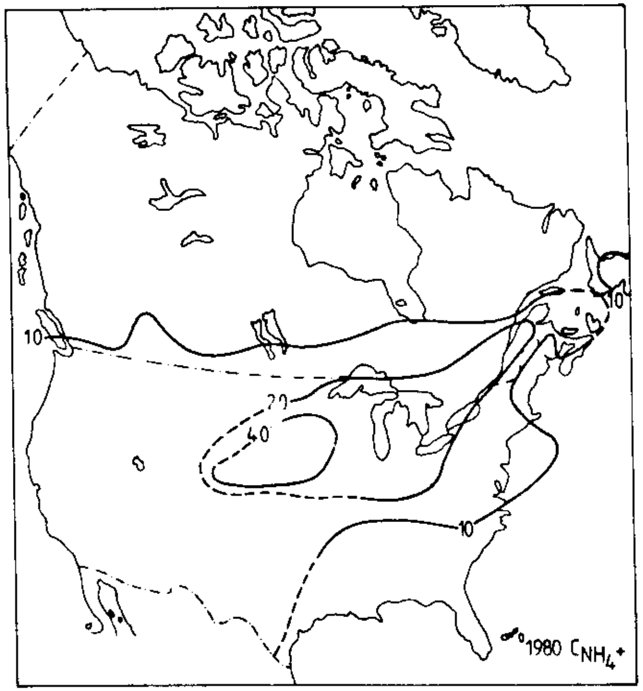

Figure 1.9. Spatial distribution of the concentration of NH_4^+ ions in precipitation water (expressed in μmol liter^{-1}) collected in North America. (Reproduced with permission from Ref. 83.)

Table 1.5
Wet deposition of different ions in eastern (Max.) and western (Min.) North America

Species	*Max.* (~~μ~~n mol m^{-2})	*Min.* (~~μ~~n mol m^{-2})
H^+	40–80	1–10
NH_4^+	20–30	1–15[a]
SO_4^-	30–50	2–20
NO_3^-	20–40	1–10

[a] Some high data which are inconsistent with other results are not considered. (Data taken from Ref. 83.)