GLOBAL ACID DEPOSITION ASSESSMENT

(Edited by D.M. Whelpdale and M.S. Kaiser)
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FOREWORD

Over the last thirty years, the question of the impact of acid deposition has been one of the leading environmental issues both for scientists and the general public alike. In the seventies and eighties, much of the research work undertaken was focused on “acid rain” first in Europe and then in North America. For much of the period, acid rain was considered one of the most critical pollution problems to be dealt with by governments. Extensive studies were undertaken in both regions to understand how acid forming precursor gases (SO₂ and NOₓ) would be deposited in the environment. Extreme concern was expressed regarding acid deposition and its impact on terrestrial and aquatic ecosystems. Eventually, control strategies were put into place leading to a reduction in sulphur dioxide emissions and a levelling off of nitrogen oxide in the areas concerned.

Through the studies mentioned above, it was realized that acid deposition was not limited to Europe and North America. In fact, at the 5th International Conference on Acidic Deposition (Sweden, June 1995) a number of the six hundred scientists in attendance were from Asia, southern Africa and parts of Central and South America. It was pointed out that emissions of precursor gases are rapidly increasing in these regions and are expected to double or triple in the next twenty years.

The present report is the first attempt at a detailed global assessment of acid deposition. A major problem encountered, however, is the scarcity of wet and dry deposition measurements outside Europe and North America. Even if data were available from remote areas, their quality had to be established.

I wish to thank the various authors involved for their efforts in drafting the individual chapters. I have no doubt that this publication will constitute an important reference on acid deposition for years to come.

I also wish to acknowledge with appreciation the financial support provided by the United Nations Environment Programme (UNEP).

(G.O.P. Obasi)
Secretary-General

GENEVA, December 1996
CHAPTER 1: INTRODUCTION
D. M. Whelpdale, J. M. Miller, C. C. Wallén

1.1 BACKGROUND

This report provides a critical review of worldwide acidic atmospheric deposition. We have examined the magnitude, the geographical distribution, and the temporal changes in acid deposition in all regions of the globe for which data were available. Our objectives were twofold: The first was to provide a scientifically sound, up-to-date analysis of the phenomenon of acid deposition; the second, to assist in the widespread dissemination of current knowledge of acidic deposition. This assessment was intended to be the basis for additional national and international scientific and policy initiatives designed to further understand and reduce the adverse effects of acid deposition.

This project was initiated by the United Nations Environment Program (UNEP) as one of several global assessments of the scientific status of current environmental problems. The World Meteorological Organization (WMO) is the agency responsible for conducting the project through its Executive Council Panel/Commission for Atmospheric Sciences Working Group on Environmental Pollution and Atmospheric Chemistry. A scientific steering committee consisting of the following members was appointed to carry out the assessment:

R. S. Artz, National Atmospheric and Oceanic Administration, USA
G. Ayers, Commonwealth Scientific and Industrial Research Organization, Australia
H. Dovland, Norwegian Institute for Air Research, Norway
J. N. Galloway, University of Virginia, USA
J. M. Miller, World Meteorological Organization, Switzerland
P. W. Summers, Atmospheric Environment Service, Canada
D. M. Whelpdale, Atmospheric Environment Service, Canada

Additional experts in atmospheric chemistry from other parts of the world were invited to bring special knowledge of their own regions to the assessment. All contributing experts (Annex III) participated in a workshop at the Bermuda Biological Station for Research, Inc., in November 1992, where draft sections of the report were presented, discussed, and revised.

In 1969 the Executive Committee of WMO, upon the recommendation of its Working Group on Atmospheric Chemistry and Air Pollution, agreed to establish a permanent network of stations to monitor precipitation chemistry and air pollution at background level around the globe. Each WMO member was asked to establish at least one regional station for each 500,000 km² of its territory to measure precipitation chemistry according to specified protocols. At the time, it was expected that a network of about 150 stations covering the world would be established in relatively short order. In addition, countries having the scientific and financial means were requested to set up several baseline stations to monitor air pollution and atmospheric constituents of particular global interest, such as CO₂, in remote areas.

The network was called the Background Air Pollution Monitoring Network (BAPMoN) [WMO, 1978] and it has been operating since that time. Unfortunately, despite efforts by both WMO and UNEP, it has not yet been possible to obtain station coverage in all developing areas of the world. The North American and European continents are well covered, but Africa and South America, for example, still do not have enough stations.

An interim review of BAPMoN [Georgii, 1982] stressed the need for continuing and improving the network. UNEP contemplated a worldwide assessment of acid deposition as early as 1985 because it was felt that BAPMoN could provide sufficient data. A preliminary study in 1985-86 [Wallén, 1986] showed, however, that the BAPMoN data in many areas of the world were
insufficient for the above purpose and, in addition, that a fundamental review of their quality would be required before they could be used for an assessment. In 1986 UNEP organized an expert meeting on acid deposition assessment that recommended that WMO thoroughly review the existing BAPMoN data first. Only after completion of this review should an acid deposition assessment exercise start, using the available global, regional, and national data to reach the best possible coverage of the world. In 1992, Miller completed a thorough review of the BAPMoN data, and since then various regional and national monitoring networks have provided several extensive new data sets that could be included in a current assessment.

Precipitation composition was initially monitored in BAPMoN as one of a few measurements to characterize atmospheric composition and its changes. With the appearance of the phenomenon of acid precipitation, this type of monitoring took on increased importance. In view of national and international efforts to reduce acid deposition, precipitation-composition monitoring in BAPMoN is still a high priority. However, many other environmental issues have now appeared, and acid deposition can no longer be considered in isolation. It is important that this broader context be noted and that appropriate linkages be developed. For example, sulphur dioxide emissions contribute to the overall acidity of the atmosphere. Increases in this acidity affect the rate at which many chemical reactions progress in the atmosphere and thus also influence the lifetime of atmospheric species. Sulphate, a major component of acid rain, also plays a significant role in the atmospheric radiation balance. As effective cloud-condensation nuclei, sulphate aerosols affect cloudiness and planetary albedo; and, as a major component of atmospheric aerosol, sulphate contributes to the direct absorption and scattering of radiation and is thus linked to global climate change. Atmospheric deposition is also known to provide a primary pathway for the entry of nutrients and toxic chemicals (synthetic organics and trace metals) into terrestrial ecosystems and oceans. Thus, the assessment of the state of the science in acid deposition is not being done in isolation; it also has important implications for many other environmental issues.

1.2 WHAT IS ACID DEPOSITION?

Damage to lakes and fish in Scandinavia from acid deposition first became a concern in the late 1960s. Since that time, the nature and extent of the phenomenon and its effects have become much better understood. We now know acidic materials can be transported over thousands of kilometres through the atmosphere to affect sensitive receptors through the processes of wet deposition and dry deposition far from their source. We know enough about the acidification phenomenon to implement controls and international agreements to reduce its precursor emissions. Although eastern North America and northern Europe are now the most affected regions, there is much concern for the future of southeast Asia and the tropics.

Damage from acid deposition is most evident in freshwater lakes, forest vegetation, and soils in poorly buffered regions. However, adverse health effects, damage to materials, and disruptions of marine ecosystems have also been documented. The term acid deposition is now used in a much broader sense to include many aspects of problems caused by sulphur and nitrogen oxides as well as other acidic species in the environment.

The atmosphere is an effective medium for the delivery of acidic materials and their precursors to surface ecosystems. The two major deposition processes are wet deposition and dry deposition. Wet deposition occurs when material incorporated into precipitation elements in the atmosphere reaches the surface in rain or snow. Dry deposition comprises several processes by which pollutant gases and aerosols are brought directly into contact with vegetation, soil, water surfaces, or structures. Although wet deposition is more easily measured than dry, we estimate that these two major processes are of comparable magnitude over large regional and global scales. Closer to emission sources, dry deposition dominates; further away, wet deposition becomes more important.
The oxides of sulphur (sulphur dioxide, sulphate, and sulphuric acid) and nitrogen (nitric oxide, nitrogen dioxide, nitrate, and nitric acid) are the primary acidifying species. Ammonia, ammonium, some organic nitrogen species (e.g., peroxacetyl nitrate, PAN) and organic acids (e.g., formic and acetic) also contribute to acidification. In certain regions hydrochloric acid may also be important. Several other chemical species also play a role in that they react with and buffer these acid-forming species. The alkaline species such as calcium, magnesium, and bicarbonate are in this category.

The concentration of hydrogen ions, frequently expressed in terms of pH (the negative logarithm of the hydrogen ion concentration), is the measure of acidity commonly used. However, the actual mechanisms of adverse effects from acidification are more clearly understood in terms of the individual chemical species. For example, lake acidification results from a series of processes in both a watershed and a lake that have been influenced by the chemical characteristics of both the deposition and the watershed. These chemical characteristics in turn depend on the amounts of sulphate, nitrate, ammonium, and neutralizing species and not just on the concentration of hydrogen ions. This report emphasizes the key individual species involved in acidification rather than focusing only on hydrogen ion, or pH. When controls to reduce acidification are considered, it is important to remember that only the emissions of the precursors, the sulphur and nitrogen oxides, can be reduced; emissions of the hydrogen ion cannot.

1.3 CONTENTS

We have focused this report on the magnitude of acid deposition and its spatial and temporal variations around the world. Following this introduction, two chapters, one on atmospheric processes and one on acid deposition effects, provide a context for the subsequent detailed analyses of acid deposition. Because this is not a policy document, we did not consider damage costs in the chapter on effects. Subsequent chapters examine acid deposition in various regions of the world, namely

- Europe
- North America
- the Middle East
- the former Soviet Union
- East Asia and Oceania
- South and Central America
- Africa
- Polar Regions
- Marine Regions

These regions are outlined in Figure 1.1, which also shows the spatial distribution of the world’s population.

We then combined the information from these regional analyses into a synthesis chapter (Chapter 13) that provides some insight into the present global situation and the future of acid deposition. A final chapter contains our conclusions on the project and our recommendations.

The regional chapters follow a common structure. Wet deposition is examined first and dry deposition second. For each, the sources of the information, including type and quality, are given before the available information is summarized. In examining the constituents of acid deposition, we begin with sulphur, followed by nitrogen and then other constituents. The spatial and temporal characteristics of concentration and deposition for each constituent are examined in sequence.
Data for all constituents are essential for a comprehensive analysis and understanding of acid deposition in each region. However, we did not have information on all species for all regions. For graphical presentation of information, we gave priority to:

- Precipitation: amount, non-sea-salt (nss) sulphate, nitrate
- Gases: sulphur dioxide, nitric acid
- Particles: non-sea-salt sulphate, nitrate

We have discussed other species where data have permitted and have tried to use the most recent data available, relying for the most part on data collected over approximately the past decade. We were also concerned about the dichotomy between the types of stations used in those areas with well-established precipitation chemistry networks and those in much of the developing world. In the former case, stations tended to be away from source regions so that they represented broad regional conditions. In the developing world, however, stations were often in or near cities and areas of heavy industry. Consequently direct comparisons of precipitation concentration and deposition values among regions may not be appropriate. In each chapter, we have clearly stated the nature of the data used.

Molar units are used throughout the report. Thus, for example, precipitation concentration and deposition are in units of μmol L⁻¹ and mmol m⁻² yr⁻¹ respectively. Air concentration and dry deposition are in units of nmol m⁻³ and mmol m⁻² yr⁻¹ respectively.

In addition to measurements, we have used the results from model calculations throughout the report. Models are now used extensively in acid deposition studies in North America and Europe. In addition, hemispheric and global chemical transport models are being applied to the study of sulphur and nitrogen cycles. Model results complement available measurements in some regions and provide valuable insights into concentration and deposition fields in data-poor areas.
1.4 REFERENCES


Wallén, C-C., Regional and global trends of acidity in precipitation, Draft Rep., 125 pp., UNEP, Geneva, Switz., 1986

2.1 INTRODUCTION

Atmospheric constituents follow a series of steps or processes from the time of their introduction into the atmosphere until their eventual removal from it. This atmospheric pathway is but one portion of the overall biogeochemical cycle that links the origins and fates of all environmental chemicals. The main processes that comprise the atmospheric pathway are emissions, transformation, transport, and deposition (Fig. 2.1). Understanding the atmospheric pathways of important species and quantifying the flux of material along these pathways are fundamental to the study of atmospheric chemistry.

Figure 2.1: Schematic representation of (A) the atmospheric cycle and (B) its component processes
The atmosphere is only one environmental compartment or reservoir; others are the biosphere, the oceans, the lithosphere, and the cryosphere. The biogeochemical cycle of any individual chemical species may include several or all of these compartments. The amount of material and the characteristic time spent in different reservoirs vary tremendously. The global oceans, for example, contain about $4 \times 10^{19}$ mol (about $10^{21}$ g) of sulphur with a residence time of $3 \times 10^6$ yr, whereas the global troposphere contains about $10^{17}$ mol (about $4 \times 10^{12}$ g) of sulphur with a residence time of only a few weeks [Schlesinger, 1991]. Within each reservoir, many chemical species can be involved in storing and transporting individual elements. Gaseous sulphur dioxide and particulate sulphate are the most dominant reactive sulphur species in the atmosphere, although carbonyl sulphide is the most abundant. In the oceans much of the sulphur resides in organically linked forms, some of which enter the atmosphere as dimethyl sulphide (DMS). Nitrogen compounds are similarly diverse.

Before industrialization, biogeochemical cycles functioned in what is known as a background state, that is, without significant human-induced perturbation. With the impact of such human activities as fossil-fuel burning and smelting as well as other industrial processes, many biogeochemical cycles have become significantly perturbed. The most affected cycles are sulphur, nitrogen, and carbon; the most striking result is acid deposition.

The study of acid deposition involves primarily the cycles and pathways of sulphur and nitrogen in their various chemical forms while at the same time considering potentially neutralizing species such as base cations. Acid deposition is a problem when it damages a receptor. A receptor, whether material, plant, aquatic, or animal (including humans), is part of an environmental compartment other than the atmosphere. Thus, the study of acid deposition considers the transfer or flux of material across the interface between the atmosphere and another environmental compartment. For example, how much sulphate or nitrate is deposited on a particular soil or lake? This means that the study of acid deposition, as its name suggests, focuses on that part of the atmospheric pathway comprising the deposition processes and specifically considers the amount and chemical composition of the material being deposited.

The sulphur cycle can be taken as an example: Langner and Rodhe [1991] estimate that globally anthropogenic sulphur emissions in the 1980s were approximately $2.3 \text{ Tmol S yr}^{-1}$, three times the natural emission of $0.8 \text{ Tmol S yr}^{-1}$ (73 and 25 Tg S yr$^{-1}$ respectively). In other words almost four times as much sulphur now passes through the atmosphere as did before the industrial revolution. Even in such remote areas as the mid-Pacific and Antarctica, the human perturbation of the sulphur cycle, although small, is still measurable. Of course, in industrial regions anthropogenic sulphur emissions dominate the sulphur cycle. Galloway et al. [1984] estimate that anthropogenic emissions in eastern North America and western Europe are 10 to 20 times greater than natural emissions. In such areas, the atmospheric deposition of sulphur can now be more than an order of magnitude above that of the background (preindustrial) atmosphere. Such a simple example clearly demonstrates the impact of human activity and illustrates why acid deposition is of such worldwide concern.

In this chapter, each major component of the atmospheric pathway--emissions, transport, transformation, and deposition--is briefly described to provide a suitable context for the extended discussion of the magnitude, distribution, and change in acid deposition. A final section introduces some scientific tools, models, and budgets commonly used to organize and integrate acid deposition information.

2.2 EMISSIONS

To understand the origin of the chemical species deposited from the atmosphere to the earth at a specific point or over a region, one needs a comprehensive knowledge of the emissions of these species and their precursors both regionally and globally. This knowledge is not easy to obtain. Emissions have been directly measured by in-stack sampling for only a few large point sources such as smelters or power plants. Automobile exhausts have been analysed in test
facilities and some road tunnel studies, but extrapolation to the real world of millions of vehicles is very difficult, involving complex models with many assumptions. Nevertheless, large-scale regional and national anthropogenic emissions have been estimated by several empirical techniques based on such parameters as total combustion figures, fuel characteristics, amounts of raw materials processed, vehicle-kilometres driven, and biomass-burning areas.

Biogenic emissions have been measured at a few field experimental sites. Without direct measurements, regional and global natural emissions are estimated using land-use data and ocean characteristics combined with surface meteorological parameters, records of volcanic activity, frequencies and distribution of thunderstorms, and other such information. To make these estimates, heavy reliance has been placed on large statistical data bases compiled by governments and based on information that is often incomplete. (Data obtained from satellite imagery and geographical information systems, however, are becoming more and more useful for estimating some input parameters such as land use.) The completeness and accuracy of the resulting emission estimates are often highly variable. Many papers have been published over the last 20 years containing estimates of global emissions of sulphur and nitrogen and more recently of other species. As more detailed and accurate data become available, these emission figures are being refined and the range of uncertainty decreased; nevertheless, most emission figures available today are based on statistical data from the 1980s.

Anthropogenic emissions of sulphur are primarily in the form of SO₂ from fossil-fuel combustion, smelting, and other industrial processes, with a small fraction (<5%) in the form of particulate sulphate. Natural emissions of organic species such as DMS and H₂S come from marine biogenic sources and from soils and plants; both SO₂ and volatile organic species are emitted from volcanoes. Some of the most recent estimates of global sulphur emissions, representative of the decade of the 1980s, are given in Table 2.1. Approximately 80% of the global sulphur is emitted in the northern hemisphere; over 90% of manmade industrial emissions occur there and both volcanic and terrestrial ecosystem emissions are greater. About 60% of marine biogenic emissions appear to occur in the southern hemisphere, and emissions from biomass burning are also somewhat greater in the South. Except for volcanoes, which are both strong intermittent and continuous low-rate sources, natural emissions tend to be widely spread at a low rate over both hemispheres. In contrast, manmade emissions are heavily concentrated in three regions around the northern hemisphere: Europe, including the region of the former Soviet Union west of the Urals; eastern North America, and eastern Asia. Figure 2.2 shows the recent global distribution of annual non-sea-salt sulphur emissions.

The main anthropogenic sources of nitrogen oxide emissions are fossil-fuel combustion from ground-based sources, aircraft traffic, and biomass burning. The main natural sources of nitrogen oxide emissions are soils, stratospheric air injected into the troposphere, and lightning. Recent estimates of global nitrogen oxide emissions are shown in Table 2.2. As is the case with sulphur emissions, human activities contribute between 75% and 80% of total global nitrogen oxide emissions. Emissions from fossil-fuel combustion are distributed around the globe approximately the same as are anthropogenic sulphur emissions; both depend strongly on the distribution of population and the degree of industrialization. Emissions from biomass burning and lightning are concentrated in tropical and subtropical regions. Soil microbiological emissions are higher in the northern hemisphere because of the larger landmass. Figure 2.3 shows the recent global distribution of total annual nitrogen oxide emissions. Additional details of global sulphur and nitrogen emissions are given in Annexes I and II, including estimates of the global distributions of emissions for preindustrial times and the year 2020.
Table 2.1: Global emissions of sulphur from the early 1980s (Tmol S yr\(^{-1}\))

<table>
<thead>
<tr>
<th>Emission</th>
<th>Global</th>
<th>Range</th>
<th>Northern</th>
<th>Southern</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass burning</td>
<td>0.08</td>
<td>0.07-0.09</td>
<td>0.03</td>
<td>0.04</td>
<td>Andreae, 1990; Langner &amp; Rodhe, 1991; Spiro et al., 1992</td>
</tr>
<tr>
<td>Industrial(^a)</td>
<td>2.19</td>
<td>1.94-2.50</td>
<td>2.00</td>
<td>0.19</td>
<td>Hameed &amp; Dignon, 1988; Langner &amp; Rodhe, 1991; Möller, 1984; Spiro et al., 1992; Varhegyi, 1985</td>
</tr>
<tr>
<td>Volcanoes(^b)</td>
<td>0.27</td>
<td>0.23-0.29</td>
<td>0.18</td>
<td>0.08</td>
<td>Andreae, 1990; Stoiber et al., 1987</td>
</tr>
<tr>
<td>Oceans</td>
<td>0.50</td>
<td>0.25-1.59</td>
<td>0.22</td>
<td>0.28</td>
<td>Andreae, 1990; Bates et al., 1987; Spiro et al., 1992</td>
</tr>
<tr>
<td>Soil, plants</td>
<td>0.03</td>
<td>0.01-0.13</td>
<td>0.02</td>
<td>0.01</td>
<td>Andreae, 1990; Bates et al., 1992; Langner &amp; Rodhe, 1991; Spiro et al., 1992</td>
</tr>
</tbody>
</table>

| TOTALS         | 3.07   | 2.45        | 0.61     |          |

\(^a\)5% is emitted as SO\(_4\)\(^2-\).

\(^b\)The fraction emitted into the troposphere.

Figure 2.2: Global distribution of annual nss-sulphur emissions (mmol m\(^{-2}\)) for 1980 from the three-dimensional global chemistry transport model MOGUNTIA.
Table 2.2: Past, present, and future nitrogen oxide emissions (Tmol N yr\(^{-1}\))

<table>
<thead>
<tr>
<th>Source</th>
<th>Preindustrial</th>
<th>Present</th>
<th>Year 2020</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fossil-fuel combustion</td>
<td>0</td>
<td>1.5</td>
<td>3.3</td>
</tr>
<tr>
<td>Aircraft</td>
<td>0</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>Biomass burning</td>
<td>0.06</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>Biogenic soil activity</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>Lightning</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Stratospheric injection</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>0.7</strong></td>
<td><strong>2.8</strong></td>
<td><strong>4.6</strong></td>
</tr>
</tbody>
</table>

Source: Present-day data from Levy and Moxim [1989], Kasibhatla et al. [1993], Levy et al. [1991]; year 2020 data from Galloway et al. [1994].

Figure 2.3: Global distribution of annual nitrogen oxide emissions (mmol m\(^{-2}\)) for 1980 from the NOAA/GFDL three-dimensional chemistry transport model.

Ammonia emissions are particularly interesting in relation to acid deposition because they are the primary sources of alkalinity in the atmosphere. Conversion to ammonium in precipitation and subsequent wet deposition is the main removal pathway for atmospheric ammonia. Ammonia is emitted from combustion, bacterial decomposition of animal excreta, and soils [Warneck, 1988]. The main combustion sources are coal and biomass burning. Domestic animals are the largest sources of ammonia emissions, accounting for about 40%, but wild animals and humans also contribute. The volatilization of ammonia from high pH soils is the second largest source (28%); release from fertilizer application also contributes. Global ammonia emissions are estimated at about 3 Tmol yr\(^{-1}\) (50-55 Tg NH\(_3\) yr\(^{-1}\)) [Warneck, 1988]. Estimates of the latitudinal distribution
of ammonia emissions show that emission rates are high in two broad bands from 10-50° N and from 20-40° S [Warneck, 1988]. Since ammonia has a relatively short residence time of a few days and is removed primarily by precipitation, wet-deposition patterns of ammonium ion reflect source regions reasonably well. Global deposition maps of Böttger et al. [1981] suggest that ammonia emissions are greatest in Europe, northern India, and equatorial Africa. In Europe, for example, ammonia emission densities range from 0.02 mol m² yr⁻¹ in Norway to 0.4 mol m² yr⁻¹ in the Netherlands [Buijsman et al., 1987].

Hydrochloric acid may also contribute to acid deposition in some locations. It is emitted into the atmosphere from solid-waste incineration plants, some power-generation facilities that burn coal with high levels of chloride, and volcanoes. For example, Sakurajima, a large active volcano in southern Japan, is estimated to inject as much as 10⁹ mol (=4 × 10¹⁰ g) HCl annually into the atmosphere [H. Hara, personal communication, 1993]. HCl is also formed in the atmosphere through the reaction of sulphuric acid with sea-salt particles:

\[ \text{H}_2\text{SO}_4 + 2\text{NaCl} \rightarrow \text{Na}_2\text{SO}_4 + 2\text{HCl} \]  \hspace{1cm} (Eq. 2.1)

This process could be significant in polar regions as well as in some coastal environments. In essence, this process converts particulate acid to gaseous acid, which will then be subjected to different atmospheric scavenging processes than those that affect the particles.

Up-to-date information on emission rates and geographical distributions is essential if we are to understand completely the atmospheric pathways and effects of acidifying species. Information on anthropogenic emissions of sulphur and nitrogen species continues to improve as more countries make available reliable emission figures. Estimates of natural emissions continue to improve as well; however, producing reliable, comprehensive inventories remains a substantial scientific challenge. A recent paper by Graedel et al. [1993] compiles and assesses existing emission inventories.

2.3 ATMOSPHERIC TRANSPORT

2.3.1 Introduction

The transport portion of the atmospheric pathway consists of those processes that mix material through the troposphere, or occasionally even the stratosphere, and that carry material from where it is injected into the atmosphere to where it is eventually deposited on the earth's surface. The initial mixing of emissions, vertical-exchange processes, clouds, and advection are all important aspects of this part of the atmospheric cycle. The relative importance of various physical processes that influence transport depends on the spatial scale of the transport. The degree of influence any individual process has on transport depends on how far material is transported.

The range of influence of a chemical species emitted into the atmosphere depends on both the atmospheric residence time of the species and the prevailing meteorological regime. A chemical species may reside in the atmosphere for as short a time as a second to as long as several centuries. In the context of acid deposition, the important contributors, i.e., gaseous sulphur dioxide, nitric oxide, and ammonia, tend to have relatively short residence times of approximately a day. Oxidation products, such as particulate sulphate and nitrate or sulphuric acid and nitric acid, have longer residence times of a few days. The range of influence of a species with a short residence time depends on wind speed and atmospheric stability near the source. A species with a longer residence time can be distributed over hundreds and thousands of kilometres by large-scale meteorology. Meteorological factors are less important for a longer-lived species that has been distributed throughout the hemispheric or global atmosphere. Because the chemical species most involved in acid deposition generally reside in the atmosphere from several hours to several days, meteorology is crucial in their distribution over tens to thousands of kilometres.
2.3.2 Initial Mixing

Near either natural or anthropogenic emission sources, source characteristics (height of release, temperature, and buoyancy of the emissions) and meteorological factors (atmospheric stability, small-scale turbulence, and local wind conditions) control the initial mixing and transport of the emitted material. A stable atmosphere generally inhibits vertical mixing, which results in reduced transport and relatively high ambient concentrations. Materials are more rapidly dispersed through the mixed layer and, consequently, may be more effectively transported when emitted into a well-mixed atmosphere. The stable conditions that result in poor initial mixing occur at night with low wind speeds and temperatures. On the other hand, effective initial mixing occurs with strong, gusty winds or in convective atmospheres. The relative frequencies of such conditions vary around the world depending on the time of day, the season, and the meteorological condition.

Close to a source, turbulent eddies are important in determining the horizontal and vertical distributions of emitted material. Such eddies last several minutes, in which time they distribute material uniformly throughout the mixed layer but over a short distance. As the depth of this mixed region above the surface expands and contracts, for example, in response to the diurnal variation in heating, the emitted substances are detrained from the boundary layer and escape into the free troposphere.

Between the eddy-diffusion scale and larger scales where advection by the mean wind dominates, dispersion is affected by mesoscale features of wind systems, for example, land/sea breezes, mountain/valley winds, other topographic features, and local modifications of the boundary layer depth, particularly in urban regions. These all influence transport over several tens of kilometres. Although acid deposition is primarily a regional to long-range problem, such mesoscale transport features exert important influences on dry-deposition removal near the source and the transport of pollutants before their eventual deposition elsewhere.

2.3.3 Vertical Exchange

In addition to factors that affect the initial mixing of emissions, other mechanisms that vertically redistribute material significantly influence the efficiency of large-scale transport [e.g., Hasse, 1983; Whelpdale and Moody, 1990]. Over land the strong diurnal cycle of surface heating results in a similar cycle of stability in the near-surface layer of the atmosphere. In the daytime, turbulent mixing and rising motions throughout the mixed layer, typically a few hundred to a few thousand metres deep, cause effective vertical exchange. Where convection is strong enough, buoyant boundary layer air may penetrate into the free troposphere, bringing along contaminants from lower levels. At night, the stability of the lower atmosphere suppresses vertical motion. Under such conditions decoupling of the large-scale flow can occur above the surface-based nighttime inversion; material tends to remain at the level at which it was injected until the stability changes.

Air from the free troposphere is entrained into the turbulent boundary layer with the result that boundary layer concentrations are diluted as the depth of the boundary layer increases. Such entrainment occurs at the interface between two regions, for example, when air in the lower free troposphere sinks as a result of radiative cooling or cooling from evaporation of recently entrained cloudy air. Frontal uplifting is also an effective vertical exchange mechanism. Clouds and associated precipitation are caused by this uplifting, and boundary layer air is lifted into the free troposphere by this process. This mechanism is most effective with travelling midlatitude and tropical disturbances.

The downward exchange of air typically differs from the upward because the energetics of the transfers are different. Downward transfer by turbulence is effective on small scales as long as there is a vertical gradient in the substance being transferred. For strong regional convection, downdraughts usually occur over a much wider area and have lower velocities. An example is the
slow sinking motion between cumulus clouds. Large-scale subsidence in high-pressure cells is also less energetic than the upward motions.

In summary, the potential for large-scale transport increases when vertical exchange processes transport material from elevations with low wind speeds and efficient surface removal mechanisms into regions of higher winds, vertical stability, and less efficient removal. This often happens with vertical transfer from the surface boundary layer into the free troposphere, where residence times and transport distances are longer. Such transfers are most often accomplished by convection and frontal lifting.

2.3.4 Role of Clouds

At any given time, about 60% of the earth's surface is covered by cloud, but clouds occupy only some 10-30% of the total volume of air below 500 hPa. Lelieveld et al. [1989] estimate that globally, except for the Antarctic, a parcel takes 3.5-4.0 hours to pass through a cloud compared to 10-20 hours spent in the intervening free air. These times vary considerably, depending on cloud type, geographical location, and season. Despite the relatively short time air spends in cloud, clouds play an important global role in vertically redistributing atmospheric constituents.

The interactions between cloud dynamics and atmospheric constituents can be very complex. Below, we have briefly described the main features for the most important cloud types (for detailed descriptions and references, see Summers [1991]).

Small cumulus clouds grow at the top of thermals rising through the surface mixed layer. These thermals carry with them trace substances from the surface mixed layer. When the clouds evaporate, they leave the constituents higher in the atmosphere. This mild, thermally driven, convective activity redistributes material through a slightly deeper layer and, since wind speed generally increases with increasing altitude, slightly enhances the potential for long-range transport.

Strong convection results in clouds processing huge volumes of air drawn out of the subcloud layer. Because of the strong updraughts, the time of transit through the cloud is short. Nevertheless, the heavy rainfall of such clouds probably scavenges 50-100% of the contaminants. The remaining material is carried out through the cloud top into the upper troposphere and lower stratosphere or remains in the troposphere after the clouds evaporate. These cumulonimbus clouds are often part of a larger storm complex, such as the Intertropical Convergence Zone (ITCZ), or a midlatitude cold front and squall line. In these cases, the intercloud dynamics, although more complex, still consist of a series of strong updraught cores that pump atmospheric constituents upward. The other main feature of these cloud systems is downdraughts that consist of mid- to upper-tropospheric air entering the rear of the system and the slower sinking motions between the clouds bringing cleaner air down to the lower troposphere.

The main feature of warm frontal systems is a slow lifting of advancing warmer air over the cooler air ahead of the system. Such systems efficiently produce precipitation; material emitted at low level into the warm-sector is slowly carried upward where the stronger airflow can move it as far as 1000 km before it is scavenged by precipitation. The strong wind shear of such systems causes the transport direction associated with the warm frontal uplifting to be significantly different from that in the surface layer.

The two major types of cyclonic storm systems are the commonly occurring "depressions" or "lows," which travel along midlatitude frontal zones, and tropical cyclones. At any given time, there may be between 10 and 20 lows around the globe. Because these two types typically contain both warm and cold fronts, their effect on transport combines the effects we have just described. Tropical cyclones are the most vigorous of atmospheric circulations. Their circulation can result in a strong overturning of the atmosphere and a significant exchange of material between air over the tropical oceans and air at 10-15 km altitude.
Mountain ranges, which constrain airflow in many regions of the globe, produce forced lifting. Transport is strongly dominated by terrain features, and any contaminants in the lower-level air on the upwind side are carried along with the flow. Clouds and precipitation over a mountain range determine to what extent material passing over the orographic feature is modified or deposited. Thus the main impact of any orographic cloud formation is in determining whether material is transported beyond the mountains.

How much influence a cloud may have depends on its vertical motions, location, vertical and geographical dimensions, and liquid water and ice content. The clouds responsible for most precipitation cover only a small fraction (5-10%) of the globe. The convective cumulonimbus clouds have a maximum coverage in equatorial regions, and nimbostratus clouds have maximum coverage in the midlatitude cyclone belts and in the Arctic. Weaker convection cumulus clouds, which produce far less precipitation, also have maximum coverage in the equatorial regions. The most prevalent clouds, in terms of average global coverage are the non-precipitating stratus and stratocumulus; they are common at all latitudes, except in the Antarctic, with a slight maximum in the midlatitudes and the Arctic.

In summary, clouds are important to both the dynamics and chemistry of atmospheric constituents. Usually (70-90% of the time) pollutants move with the air flow through cloud-free air. Clouds alter this flow of materials the other 10-30% of the time when vertical motions redistribute material to different transport regimes. However, since any substantial upward motion usually produces precipitation as well as clouds, much of the redistributed material is soon removed by precipitation. Therefore, the most important material is that remaining high in the atmosphere after both cumulus and cumulonimbus convective clouds have evaporated. These clouds prevail in equatorial and subtropical regions and in the summer over the continents in the northern hemisphere. Because wind speed usually increases and changes direction with height, material transport is affected by even the slightest upward motion.

2.3.5 Transport

Long-range material transport, over distances of several hundred to a few thousand kilometres, is primarily controlled by large atmospheric circulation patterns and the synoptic systems embedded within them. Large-scale circulation in each hemisphere is characterized by a band of fairly stable, light, easterly winds between approximately the equator and 30°, by a band of westerly winds in the temperate latitudes, and by light easterly winds at the poles. Within these flow regimes are large, semipermanent high- and low-pressure cells such as the Bermuda high and the Aleutian low. Superimposed on these features are secondary, usually seasonal circulation patterns (such as the Asian monsoon) and travelling disturbances (such as tropical cyclones and the high-pressure cells and depressions of the midlatitudes) that bring much of the day-to-day variability of the weather.

The scales and regularities of these features determine the average atmospheric pathway of a constituent. However, average conditions or patterns do not reflect the high degree of temporal variability in the atmosphere. How effectively material is transported over long distances depends on diurnal and seasonal cycles as well as such smaller scale features as the intensity of vertical exchange processes and precipitation scavenging. One consequence of the high temporal variability in the atmosphere is the sporadic nature of acid deposition.

In view of the highly variable nature of the atmosphere, transport around the world is difficult to characterize. In the northern midlatitudes, moderately strong westerly winds and frequent precipitation result in substantial acid deposition for up to about two thousand kilometres downwind of sources. Anthropogenic emissions have also been transported over thousands of kilometres across the Atlantic [Tarrason and Iversen, 1992] and from Africa to Amsterdam Island in the Indian Ocean [Moody et al., 1991]. Because of the generally less vigorous winds, strong convection, and intense precipitation in the tropics and subtropics, materials are probably not transported as far there as in the midlatitudes—unless, of course, the material rises above the
trade-wind inversion (as does Saharan dust). Because of the atmospheric stability and low precipitation at the poles, atmospheric pollutants in polar regions have relatively long lifetimes. For example, the sulphate component dominating Arctic haze is the result of sulphur transported to the Arctic from sources in Europe and the former Soviet Union [Barrie et al., 1989]. Clearly, in dry regions where wet removal processes are ineffective, materials are transported over larger distances.

The size of an area affected by acid deposition depends on the meteorological regime of the region. With atmospheric lifetimes of hours to several days, most of the important species related to acid deposition are deposited regionally, usually from several hundred to a few thousand kilometres downwind of their source. Transport is the prime determinant as to whether a specific receptor is affected by a given source; the other processes then determine the concentrations, species, and efficiency of the deposition. However, what impact the deposition may have depends both on the pattern and intensity of the deposition and on the sensitivity of the biotic and nonbiotic resources that receive it.

2.4 CHEMICAL TRANSFORMATIONS

2.4.1 Introduction

The chemical species that are the components of acid deposition may differ from those originally emitted. Pollutants released into the atmosphere from a given source may undergo reactions with each other and with other naturally occurring and anthropogenically produced species. This web of reactions controls the rate at which acidic species are generated in the atmosphere. In addition, since chemical reactivity, dry deposition, scavenging rate, and water solubility are all species-dependent, chemical reactions play a large role in determining the scale of the acid deposition. Important reactions occur in the gas phase (homogeneous) and in the aqueous and particulate phases (heterogeneous); all need to be considered. The relative importance of reactions involving one or more of these three phases depends heavily on the chemical species and on the environmental conditions. Many species that contribute to heterogeneous oxidation processes originate in the gaseous phase.

2.4.2 Gas-Phase Chemistry

2.4.2.1 Oxidants

Atmospheric oxidants are instrumental in converting both naturally and anthropogenically produced precursor chemicals to weak and strong acids. The major oxidants in the atmosphere are ozone (O₃), the hydroxyl radical (OH), the hydroperoxy radical (HO₂), organic peroxy radicals (RO₂), peroxyacetyl nitrate (PAN), hydrogen peroxide (H₂O₂), organic hydroperoxides (ROOH), and the nitrate radical (NO₃). The hydroxyl radical is the most reactive, followed by ozone and the nitrate radical.

With high-energy solar radiation, typically at wavelengths shorter than 315 nm, reactions generally drive the production of oxidants by generating oxidizing free radicals. As well as helping produce nonradical oxidants such as hydrogen peroxide and ozone, these radicals can also react with volatile organic compounds (VOCs), which themselves have both natural and anthropogenic sources, to produce organic acids. Many different classes of VOCs are important in this role, from alkanes to aldehydes, esters, and alcohols. Although we currently know little of VOC reactions, we do know that the chemical reactivities vary considerably and their chemical lifetimes are probably short. The energy and transport industries emit significant amounts of VOCs through supply ventilation, exhaust emissions, and natural-gas escape. Oxidant radicals react with nitrogen oxides to produce nitric acid (HNO₃), PAN, and other organic nitrates and with sulphur dioxide (SO₂) to produce sulphuric acid (H₂SO₄).
Several key atmospheric oxidants are subject to strong diurnal cycles that control their effectiveness. Hydroxyl, hydroperoxy, and organic peroxyl radicals are produced only during the day and undergo a rapid net consumption at night. The nitrate radical formed from the reaction of nitrogen dioxide with ozone contributes greatly to nighttime oxidation, but its influence is negligible during the day because of its photochemical destruction. The following reactions show why daytime oxidation by the hydroperoxy and organic peroxyl radicals is important:

\[ \text{NO} + \text{RO}_2 \rightarrow \text{NO}_2 + \text{RO} \]  \hspace{1cm} (Eq. 2.2)
\[ \text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH} \]  \hspace{1cm} (Eq. 2.3)
\[ \text{NO}_2 + \text{hv} \rightarrow \text{NO} + \text{O} \]  \hspace{1cm} (Eq. 2.4)

where \( \text{hv} \) represents solar energy and

\[ \text{O} + \text{O}_2 \rightarrow \text{O}_3 \]  \hspace{1cm} (Eq. 2.5)

These reactions are fundamental in that they result in net ozone formation. Since chemical lifetimes of the radicals are only a few minutes, their concentrations are essentially governed by local photochemistry; transport on a regional scale is negligible. On the other hand, with chemical lifetimes of several days, hydrogen and organic peroxides are transported regionally, particularly during winter and in the free troposphere.

Once above the boundary layer, the subsequent lifetimes of these species depend on whether or not they are entrained into clouds where aqueous-phase processes may rapidly consume them. The lifetimes of organic peroxide nitrates such as PAN are also extended under winter, free-troposphere conditions, making them important long-range transport reservoirs for nitrogen oxide compounds. This contrasts sharply with their lifetimes of just a few hours during summer in the boundary layer.

Under natural conditions the production and the destruction of tropospheric ozone are generally balanced. The dominant natural sources of ozone are stratospheric injection and photochemical production from natural ozone precursors such as nitrogen oxides, carbon monoxide, methane, and VOCs; surface deposition and destruction are the sinks. The resulting background ozone concentration depends on the relative strength of these source and sink processes, a balance that varies temporally and spatially. We also know that there are many sources of anthropogenic ozone precursors. Therefore, summertime ozone concentrations are likely to be higher in and downwind of industrialized regions where both \( \text{NO}_x \) and VOCs are emitted.

2.4.2.2 Acidic species production

Sulphuric and nitric acids dominate acid deposition within and downwind of most industrialized regions of the world. In some areas, for example, close to sources such as power plants fuelled by high-chloride coal and some chemical industries, nonmarine chloride may contribute significantly to rainwater acidity in the form of hydrochloric acid (HCl) [UKRGAR, 1990]. We know that organic acids, in particular formic and acetic acids, contribute significantly to precipitation acidity in remote locations. These may be generated in both gaseous and aqueous phases, and we think that natural hydrocarbons in these remote regions are also important in the formation of organic acids [Keene and Galloway, 1988].

Nitric acid. Nitric oxide (NO) is the primary precursor for nitric acid production. It is oxidized to nitrogen dioxide (\( \text{NO}_2 \)) by ozone and by peroxy radicals. In the daytime, nitrogen dioxide is then oxidized to nitric acid (\( \text{HNO}_3 \)) mainly by hydroxyl radicals. Seasonal variations in the availability of hydroxyl radicals lead to rapid nitrogen oxide oxidation during summer and the potential export from source regions during winter. The atmospheric chemistry of nitrogen oxides tends to be more complex than that of sulphur oxides, mainly because of its inherent nonlinear nature: hydroxyl radical and ozone concentrations themselves depend on the nitrogen oxide concentration.
There is a further confounding fact in the atmospheric chemistry of nitrogen oxides. Reaction rates, and thus reaction pathways, vary diurnally. It is thought that reactions involving the nitrate radical govern the nocturnal conversion of nitrogen oxides to nitric acid and, furthermore, that this reaction rate is comparable to the daytime rate during the summer and an order of magnitude more efficient during the winter. Since nitrogen oxide emissions in North America are not seasonal, the nocturnal conversion of nitrogen oxides to nitric acid must account for part of the seasonal asymmetry in nitrate concentrations.

**Sulphuric acid.** In industrialized regions, sulphur dioxide is the main precursor of sulphur-containing acidic species. In more remote areas, the natural emissions of reduced sulphur species, such as carbonyl sulphide (COS), hydrogen sulphide (H₂S), and dimethyl sulphide (DMS), are relatively more important. Volcanoes are both continuous and strong episodic sources of sulphur oxides. The oxidation of reduced sulphur species in the atmosphere contributes little to the generation of sulphur-based acidity in nonremote regions except under specific conditions. For instance, Leck and Rodhe [1991] estimate that in summer months, biogenic sulphur emissions from the seas surrounding Scandinavia may contribute an amount equivalent to 20-70% of Scandinavian anthropogenic sulphur emissions. In the context of annual European sulphur emissions, this source represents less than 1%. In remote marine areas, however, the relative importance of these natural reduced sulphur species to the production of atmospheric acidity increases.

The hydroxyl radical is of paramount importance in the initial stage of sulphur dioxide oxidation:

\[ \text{OH} + \text{SO}_2 \rightarrow \text{H}_2\text{SO}_3 \]  
*(Eq. 2.6)*

Subsequent conversion is as follows:

\[ \text{H}_2\text{SO}_3 + \text{O}_2 \rightarrow \text{H}_2\text{O}_2 + \text{SO}_3 \]  
*(Eq. 2.7)*

\[ \text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 \]  
*(Eq. 2.8)*

Therefore, in contrast to the atmospheric chemistry of nitrogen, the significance of this set of reactions is conservation of odd hydrogen radicals, simplifying the oxidation process to a linear one [Stockwell and Calvert, 1983]. Neuman's [1981] field studies indicate that clear-sky oxidation rates are typically in the range of a few percent an hour; they obviously depend on ambient hydroxyl radical concentrations that in turn depend on the amount of sunshine (and thus on latitude and water vapour levels).

### 2.4.3 The Role of Ammonia

Ammonia is the most common basic gas found in the atmosphere; it originates mainly from biological activity and deposits rapidly upon contact with the ground or vegetation. Hence, ammonia tends to be of more local concern than sulphur and nitrogen species. Ammonia is quickly taken up by cloud droplets and is deposited as ammonium ion, usually directly associated with sulphate. In air, there is frequently some ammonium sulphate in particulate form, and in some regions, where both ammonia and nitric acid vapour concentrations are high enough, particulate ammonium nitrate can form. Although they are essentially basic compounds in air, deposition ammonium enters into reactions involving plants that result in a net acidification of soils. Thus the roles of ammonia and ammonium in the context of acidic and acidifying deposition are highly complex. This is especially the case in western Europe, where population densities and agricultural practices lead to production rates of ammonia far exceeding those in North America, and consequently, ammonia and ammonium affect air chemistry and even dry deposition in western Europe to a much greater extent. Similar situations are inevitable in other areas of the globe with similar stresses on regional environments, such as in large areas of Africa, on the Indian subcontinent, and in Asia generally.
2.4.4 Aqueous-phase Chemistry

This section concentrates on oxidation and the production of acidic species within the aqueous phase. However, we begin with a brief discussion of the other important processes involving the particulate and gaseous phases and their subsequent incorporation into hydrometeors.

A major pathway for the incorporation of aerosol particles into the aqueous phase is by way of their role as cloud-condensation nuclei (CCN). Most of the total particulate mass that enters droplets does so in this fashion, with only a small addition of further mass by the subsequent scavenging of other particulate matter. An important difference between polluted continental regions and the relatively clean marine environment is that in the former, anthropogenically derived nitrate and sulphate aerosols contribute a greater portion of CCN.

Nitric acid formed in the gas phase can exist as a vapour or particle. Sulphuric acid, in contrast, is generated in the gas phase but exists primarily in particle form. Gas-phase acids can be effectively neutralized through condensation on the surfaces of basic particles and by reaction with ammonia gas that produces particles. In general, coarse particles tend to be basic whereas finer particles are more likely to have a strong acidic component. Since fine and coarse particles do not coagulate efficiently, they may coexist. Once aerosol droplets are formed, oxidation can proceed in the liquid phase.

Some acidic gases, such as the highly soluble nitric acid, can be taken up by cloud droplets and thereby contribute directly to cloud-water acidity. Organic acids generated in the gas phase can also contribute to acidity in this manner. In industrialized regions their low concentrations and the relatively low pH of the cloud water result in their contributing little to total cloud acidity. Depending on the specific gases and the pH of the precipitation, gas uptake can be enhanced during precipitation, as droplets are continuously exposed to air that, unlike that in the cloud environment, has not previously been depleted of its pollutants. We still do not know how important the ice phase is to in-cloud chemical reaction. We think that gaseous nitric acid is incorporated efficiently into the ice phase, but sulphur dioxide is probably not [Lee and Kinsley, 1986]. There are probably few, if any, oxidation reactions in the ice phase.

The distinction between the direct contribution to cloud-water acidity and the indirect contribution, which requires aqueous-phase oxidation of dissolved gases, is clear in the case of sulphur dioxide. Sulphur dioxide is the anhydride of the weak sulphurous acid, which, having formed in the gas phase, can also contribute to cloud acidity by mass transport in the same manner as nitric acid and the organic acids described above. However, this contribution is generally much less than that from the subsequent aqueous-phase oxidation of sulphur dioxide to sulphuric acid, a more soluble and stronger acid. By contrast, nitrogen oxides are not anhydrides of weak acids and cannot contribute to cloud-water acidity without oxidation to nitric acid.

Three different oxidants are important for the aqueous-phase oxidation of sulphur dioxide. The first, molecular oxygen, requires metal catalysts and is now believed to be a less efficient pathway for oxidation, especially where the other two major oxidants, hydrogen peroxide and ozone, are plentiful [Penkett et al., 1979].

It is interesting to contrast the pH-dependence of the oxidation processes of the other two oxidants, ozone and hydrogen peroxide, with sulphur dioxide in the aqueous phase. The hydrogen peroxide-sulphur reaction is acid-catalysed. Combined with the lower solubility of sulphur dioxide in more acidified droplets, this leads to an essentially pH-independent oxidation rate relative to the gas-phase sulphur dioxide concentration. Further, this reaction rate increases as temperature decreases because sulphur dioxide solubility increases more rapidly than the reaction-rate coefficient decreases. However, because there is a net consumption of hydrogen peroxide in this process, the reaction rate depends critically on the further entrainment of hydrogen peroxide into the cloud environment. Methylyhydroperoxide and peroxyacetic acid can play a similar role to hydrogen peroxide, although probably only under circumstances where the latter is depleted.
Unlike the hydrogen peroxide reaction, the rate for the ozone - S(IV) reaction is in phase with the reduced solubility of S(IV) in more acidic solutions, producing a strong dependence of the reaction rate on solution pH. Interestingly, under reaction-promoting conditions of high pH, the reaction rate is faster than that for hydrogen peroxide. This may not persist, however, since the acidity produced by the reaction quickly reduces the pH and decreases the reaction rate.

Despite the efficiencies of the hydrogen peroxide and ozone pathways for sulphur dioxide oxidation, it is important to recall that clouds and rain occur only for a relatively small fraction of the time. Homogeneous oxidation of sulphur dioxide remains important. Nitrogen oxides generally have low solubilities. Hence, although dissolved nitrogen dioxide is believed to react rapidly with water to form nitric acid, this is not thought to be an important pathway for cloud-water acidification. Under conditions in which the oxidation of acid precursors is predominantly in the aqueous phase, large differences in oxidation rate may occur in some parts of the world, depending on the abundance of oxidants such as $\text{H}_2\text{O}_2$.

2.5 DEPOSITION

There are two pathways by which chemical species are removed from the atmosphere: wet deposition, which is removal by precipitation scavenging and, to a lesser extent, impaction of fog or cloud droplets on vegetation; and dry deposition, which includes the uptake of gases at the surface and the settling and impaction of particles. On a global scale, precipitation scavenging and dry deposition are by far the most important; fog and droplet deposition can be locally important, especially in cloudy, high elevation regions.

2.5.1 Wet Deposition

Precipitation scavenging is an effective mechanism for removing soluble trace gases and small particles from the troposphere. The gases and particles are incorporated into cloud droplets and falling precipitation in several ways. Those trace particles in the atmosphere that act as ice-forming nuclei or condensation nuclei can be incorporated into hydrometeors during the nucleation process itself. This is the process that generates cloud droplets from which raindrops form. In many parts of the world, sulphate particles are the most commonly found condensation nuclei in the atmosphere. The cloud droplets that are generated continue to scavenge gases and particles in cloud as they grow in size. As they grow, the droplets fall faster until they leave the cloud base and are deposited as rain, carrying all of the scavenged pollutants with them. It is not only particulate sulphate that is scavenged in this way; gaseous sulphur dioxide can be dissolved in cloud droplets, whereupon it can be oxidized to sulphate by aqueous-phase chemical reactions (see section 2.4.4).

The hydrometeors falling from the cloud can scavenge other pollutants with which they come in contact. This subcloud scavenging is often relatively inefficient in comparison to in-cloud processes, especially in the case of convective cells. In these, clouds "process" a steady stream of air as it passes through them and scavenge pollutants from this stream in a continuing, dynamic process. Convective precipitation cells are among the most efficient mechanisms for cleaning the atmosphere.

Clearly, the actual wet-deposition flux of chemical species to the surface depends on many factors. The most important ones are precipitation form (rain, snow, etc.) and precipitation rate, both of which are strongly related to cloud type, and the ambient air concentrations within and below cloud. These complex physicochemical processes can be integrated into several parameters such as scavenging ratio, scavenging efficiency, and scavenging rate. These quantities have varying degrees of applicability, depending on the kind of precipitation system that is considered, but all can be formulated from observations and give the "bulk" characteristics of precipitating weather systems. For example the mass scavenging ratio ($S_m$) is defined as the concentration of
the dissolved chemical species per unit mass of cloud water or rain \((C_r)\) divided by the concentration of the same species (or its precursor) per unit mass of ambient air \((C_a)\):

\[
S_R = \frac{C_r}{C_a}
\]  
(Eq. 2.9)

The typical liquid water content of precipitating clouds is 1 g of water per 1 m\(^3\) of air (but ranges from 0.1 to 5.0). Since 1 m\(^3\) of air weighs approximately 1 kg, if all the trace species in 1 m\(^3\) of air were dissolved in the cloud water (i.e., 100% scavenging efficiency), the species concentration in the rain would be magnified by a factor of 1000 and the scavenging ratio would be 1000. In practice, the efficiency of removal of either pollutants or of water itself is not 100%, and hence the scavenging ratio can vary greatly. At a few locations in North America (Barrie, 1988) and Europe where concentrations of sulphur and nitrogen species have been simultaneously measured in the air and precipitation, values of \(S_R\) vary from 100 to a few thousand.

The wet-deposition rate \((D_w)\) is given by the precipitation rate \((R)\) times the species concentration in the rain \((C_r)\):

\[
D_w = C_rR = S_RRC_a
\]  
(Eq. 2.10)

The ratio \(S_R/R\) is thus analogous to the dry-deposition velocity in the formulation of the dry-deposition flux (see next section). However, for wet deposition, \(C_a\) refers to the air concentrations at various atmospheric elevations where the species are being incorporated into the cloud- and rainwater, whereas for dry deposition, \(C_a\) refers to the air concentration immediately above the surface.

2.5.1.1 Calculation and variability of wet deposition

The wet deposition in a given precipitation event is calculated as the product of the total precipitation \((P)\) times the measured concentration \((C_r)\) of the species in the precipitation. In addition to the "chemical" collector, most precipitation chemistry monitoring sites are equipped with standard rain and, if necessary, snow gauges.

Over distance scales of 100-1000 km, data from monitoring networks indicate that values of \(C_r\) especially for oxidized species such as SO4\(^{2-}\) and NO3\(^{-}\), are spatially coherent and have regional patterns that vary in a smooth and systematic way over the course of a season or year. On the other hand, the precipitation amount \((P)\) shows more regional variability especially in regions where convective rain predominates. Thus, in regions with dense precipitation-monitoring networks, such as those operated by meteorological services, regional wet deposition can be more accurately estimated by combining the gridded fields of \(C_r\) and \(P\). Because concentration and precipitation tend to be correlated, a small systematic error might arise in combining the two data fields in this way. In essence, the longer the averaging time that is used, the lower the correlation coefficient and the smaller the magnitude of any errors that might arise. In all cases, care should be taken to avoid biases whenever such data fields are combined and there is need to interpolate one to meet the finer grid detail of the other.

In many regions the day-to-day variation in wet-chemical deposition is controlled more by the precipitation amount than by the trace-chemical concentrations.

2.5.1.2 Mountain effects

In mountainous regions, there are strong vertical gradients with the precipitation amount increasing with increasing elevation up to some height (usually one or two kilometres above the typical cloud base) and then decreasing again. Forested mountain tops frequently bathed in clouds (at elevations typically above 1 km) act as very efficient collectors of cloud water (or rime ice), and in some regions (e.g., New England), the water input to the ecosystem via this mechanism is comparable to that of rainfall. The input of chemical species to the higher elevations by cloud,
fog, or "occult" deposition, as the process is sometimes known, plus that from the additional precipitation is much higher than in the intervening valleys. These effects are very important locally and have been strongly implicated as a contributing cause in the decline of high-elevation forests. However, this amounts to only 5% of the global budget of total wet-deposition flux.

2.5.1.3 Episodicity

One overwhelming characteristic of wet deposition is how much the total wet deposition of one chemical species can vary from one event to another. Precipitation itself is a highly intermittent phenomenon occurring about 5% of the time in the midlatitude cyclonic belt, with amounts varying between a trace to several centimetres from one event to the next; the concentration of a chemical species can vary by an order of magnitude. The largest difference between events is on the periphery of industrial regions where emission rates are high. There, depending on air-mass trajectories, the air can be clean or heavily polluted. Within regions with high emissions and in cleaner remote areas, the concentrations vary less. Thus, in southeast Canada and southern Scandinavia, wet-deposition episodicity is highest, with typically less than 10% of the wet days accounting for 50% or more of the annual wet deposition of $\text{SO}_4$. In extreme cases a single precipitation event can contribute up to 30% of the annual chemical deposition.

2.5.1.4 Application of wet-deposition data

This assessment focuses on the large-scale meteorological/climatological aspects of acid deposition. Figure 2.4 shows the global distribution of annual precipitation. An examination of this map, along with the emissions in Figures 2.2 and 2.3, provides an overall impression of regions of the world where wet deposition is potentially important. Data and maps presented in subsequent chapters yield detailed information on wet deposition in various broad regions of the globe. However, for a single location one needs to be careful in reading data off, or interpolating from, these maps. For studying impacts at specific sensitive receptors, one needs actual on-site data, including the siting criteria and sampling protocol used. In North America and Europe, such detail is available for extensive monitoring networks.

![Global distribution of annual precipitation (cm). (Adapted from de Blij and Muller [1993].)]
2.5.2 Dry Deposition

Dry deposition must always be considered in any calculation of total deposition of an acidifying compound, whether to a specified receptor or a large area. In some areas, especially near large sources, dry deposition is at least as important as wet deposition. The dry-deposition process involves a close interaction between the atmosphere and the surface in which the characteristics of individual underlying surfaces often determine the mass-transfer rates. Depending on the characteristics of the surface, the ability to "capture" pollutants from the air may vary by more than an order of magnitude, causing highly varied dry-deposition rates even over small scales. Forests, especially coniferous forests, normally receive relatively high dry deposition of acidifying compounds, whereas lake surfaces receive much lower. Deposition extremes are often observed at forest edges or in forests on mountain slopes.

The following discussion concentrates on sulphur and nitrogen compounds, as does the rest of this report. Base cations are also very important; however, because of the limited available data, we were unable to substantiate the same broad categorizations as those that follow for sulphur and nitrogen compounds.

2.5.2.1 Quantification of dry deposition

Dry deposition can be measured directly in only a few, selected situations. Except for a few rare efforts, no direct measurements of dry deposition lend themselves to direct incorporation into the present assessment; instead, all dry-deposition estimates had to be inferred from other information. The difficult question was how to make this inference.

In any circumstance dry-deposition rates are proportional to the concentrations in air immediately above (or surrounding) the receptor of concern. The "constant" of proportionality is referred to as a deposition velocity \( V_d \) that depends on factors (mainly associated with turbulence; see, e.g., Wesely and Hicks, [1977]) related to characteristics of air near the surface and the composition of the surface itself. Depending on the chemical in question, different factors assume important roles in determining the magnitude of \( V_d \). For sulphur dioxide, for example, the surface wetness and the photosynthetic activity of vegetation are important: the dominant terrestrial surface sink for sulphur dioxide is via open stomata into plant mesophyll tissue. For nitric acid vapour, however, the controlling property is atmospheric [Huebert and Robert, 1985], because the vapour is readily captured upon contact with any natural surface. In practice, using a standardized deposition velocity in numerical models is an engineering approximation that is particularly attractive in large-scale simulations because it combines the effects of many complex processes into a single term. As will be seen later, reliance on a simple deposition-velocity approach, although attractive in its simplicity, can lead to problems when interest relates to specific surfaces or subgrid-scale areas.

Rather than being quantified directly from field measurements, dry-deposition rates are usually deduced from measurements of air concentration and of factors that control \( V_d \). In practice, \( V_d \) is of the order of a centimetre per second—somewhat lower for stomately controlled gases like \( \text{SO}_2 \) and \( \text{NO}_2 \) and somewhat higher for easily captured gases like \( \text{HNO}_3 \) (and \( \text{NH}_3 \)). For sulphur and nitrogen particles relevant to assessing acid deposition, values of \( V_d \) are typically lower. (The case of base cations is different but will not be addressed here.) At sea, however, interactions with sea salt may cause the particle-size distribution associated with sulphur and nitrogen compounds to be skewed towards larger sizes, thereby increasing the deposition velocity.

2.5.2.2 The specification of air concentrations

Clearly, atmospheric concentrations must be correctly quantified to ascertain accurate wet-deposition values. Although not always easily measured, atmospheric concentrations of pollutants to which sensitive systems are exposed can be measured. Therefore, if one's goal is to assess deposition to a specific area, one should locate a concentration monitoring device at that location.
The modelling equivalent would be to arrange model inputs and outputs to focus on the area in question. Such targeted modelling is sometimes difficult to arrange, especially when the model's grid cell is large. If errors of approximately 10% are acceptable because of the uncertainties associated with dry deposition, then a target upper limit for the grid size of approximately 50 km results. This would be a challenge for the numerical modelling community, where much larger grid sizes are commonly used.

2.5.2.3 The determination of deposition velocity

Some surfaces are far more efficient "receptors" of dry deposition than others. Actively respiring vegetation presents a good sink for SO₂, whereas the same vegetation suffering under water stress does not. In this context (and for other chemical species, such as NO₂ and O₃), it is the stomatal opening that is important. Dry deposition is partially controlled by surface characteristics, often biological or soil-related rather than purely atmospheric [Baldocchi et al., 1987]. Because many different kinds of "surfaces" may be contained within a grid cell of a numerical model, an appropriate deposition velocity for the entire grid cell becomes not only difficult to specify but also questionable. If one were to consider a certain kind of receptor within a specific grid cell, one could feasibly ask a much simpler question. However, the answer to this simplified question could not be considered indicative of the average areal deposition.

Contemporary models often use a land-use formulation to account for different surfaces [Sheih et al., 1979; Chang et al., 1987]. Deposition velocities are computed for each kind of surface; an areal average is obtained by weighting according to the land-use apportionment. The average dry-deposition rate that results is relatively crude yet provides acceptably accurate estimations of local concentrations. Of course, any single land-use category could be so complex as to further influence the accuracy of deposition predictions for specific kinds of surface. For example, the category of "farmland" could contain land that is fallow, green, or senescent during the growing season. Various fields might have widely differing ratios of uptake at soil surfaces to uptake via plant stomata, and different plant species have different responses to water stress.

If a specific receptor is to be addressed at the subgrid-scale level of resolution, then one needs to use a site-specific methodology driven by the concentrations (and perhaps the meteorological information) yielded by a larger-scale numerical model. As mentioned above, the handover from one kind of model to the other would optimally be at a scale of about 50 km.

To address site-specific dry deposition, direct measurements of relevant on-site properties are clearly most desirable. In their absence, models can be used to produce relevant information from which site-specific deposition values can then be estimated. However, the dry-deposition averages derived from large-scale models are not appropriate to address smaller-scale practical problems. Instead, the outputs of these larger-scale models should be used to drive more detailed models that can handle factors such as variations in local conditions, which typically determine the locally appropriate deposition velocity.

2.5.2.4 Practical application

The fundamental set of information required to estimate global dry-deposition rates is near-surface air concentrations. A limited amount of such data is reported in the following chapters. The practical application of our reasonably detailed understanding of processes controlling dry deposition involves the use of an appropriate deposition velocity (Table 2.3), which depends on the nature of the underlying surface.

The values tabulated are approximate annual averages and hence may be subject to considerable error. The uncertainties associated with the SO₂ values are estimated to be approximately ±40%. In general, data are as yet insufficient to quantify uncertainties for HNO₃ and particles. The controlling factor for HNO₃ dry deposition is atmospheric turbulence, which can be estimated quite well over uniform surfaces. However, terrain complexity is likely to have a
greater influence on the deposition velocity for HNO₃ than on that for SO₂, NO₂, O₃, or particles, because \( V_d(HNO₃) \) is dominated by atmospheric terms that strongly depend on terrain complexity. Particles are worthy of special attention because the amount of field data suitable for refining understanding of their deposition velocities is exceedingly limited.

It is possible that the error in deposition velocity may be organized, with bias correlated with latitude or location. For example, surface wetness is highly variable in time and space; its variations could cause regionally high (or low) deposition to occur. Likewise, areas with high ammonia emissions could have SO₂ deposition velocities larger than those tabulated, because ammonia deposited on plant surfaces provides an opportunity for direct capture of SO₂ molecules and thus a dry-deposition pathway in addition to the usual stomatal exchange.

The values in Table 2.3 smooth out the strong diurnal cycle that characterizes dry deposition to terrestrial surfaces. It is well known that the daytime deposition velocity for SO₂ is approximately 1 cm s⁻¹ in most terrestrial circumstances. The values provided are smaller as a result of considering the entire diurnal cycle.

In conclusion, we note that the use of a deposition velocity approach in large-scale numerical models is a simplification of complicated processes that results in substantial computational convenience. This is in contrast to the complexity with which chemical reactions are addressed in advanced Eulerian models. If deposition processes were described with the detail permitted by current understanding, much greater surface detail would be required and computation time would be increased considerably.

2.5.3 Relative Importance of Wet and Dry Deposition

As discussed earlier in the sections on wet deposition and dry deposition, the processes have some similar but also some quite different characteristics in terms of their spatial and temporal behaviour. Both wet and dry depositions of trace species to the earth’s surface are directly related to ambient air concentrations of the same species or their precursors. However, the relative contribution to total deposition at a given point or over a given region depends on many surface factors and meteorological parameters, and thus only general statements can be made. In regions for which information is available, dry deposition dominates close to large sources of SO₂ and NOₓ, but as these species become oxidized further downwind wet deposition dominates. Atmospheric budget estimates for large regions such as eastern North America or Europe indicate that approximately one third of the emissions are deposited back on the region by wet deposition, one third are deposited by dry deposition, and the remaining one third are transported out of the region.

As the discussion above has already indicated, wet deposition is generally better understood than dry. However, we know that there are important differences in the basic character of these two phenomena that have far-reaching repercussions. Wet deposition has many of the same characteristics as rain; although deposition is often highly variable over the short term, it shows consistency for a particular location when considered over a longer period. Consequently, annual and even seasonal maps of deposition rates are meaningful and permit ready interpolation to address situations at locations from which there are no direct measurements. Although wet deposition is a highly irregular process, it is controlled by the atmosphere and averaging smooths out the short-term variability.

In contrast, dry deposition is largely controlled by the nature of the underlying surface, with the result that its spatial variability is not reduced by time-averaging. A consequence is that the model estimates of areal average dry deposition are not suitable for deriving site-specific values at the subgrid scale unless proper allowance is made for the particular site characteristics. Similarly, contoured dry-deposition fields are far less meaningful than those for wet deposition. For these reasons, displaying total (i.e., dry plus wet) deposition as fields on a map to assist in consideration of “critical loads” is not desirable; the approach would necessarily eliminate the
possibility of identifying local "hot-spots," which are precisely the locations where critical loading
communications are more properly directed.

Although such arguments can be strongly made for the terrestrial case, surface homogeneity
in the marine case imposes much less dry-deposition variability, and the uncertainties mentioned
above are then greatly reduced.

### Table 2.3: Estimated long-term average deposition velocities

<table>
<thead>
<tr>
<th></th>
<th>Tropical, Subtropical</th>
<th>Dry, Arid</th>
<th>Temperate</th>
<th>Polar</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sulphur Dioxide</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bare soil</td>
<td>-</td>
<td>0.2-0.3</td>
<td>0.3-0.4</td>
<td></td>
</tr>
<tr>
<td>Grass, heath</td>
<td>-</td>
<td>0.3-0.4</td>
<td>0.3-0.5</td>
<td>-</td>
</tr>
<tr>
<td>Farmland</td>
<td>0.4-0.5</td>
<td>0.3-0.4</td>
<td>0.3-0.5</td>
<td>-</td>
</tr>
<tr>
<td>Forests</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Deciduous</td>
<td>0.3-0.5</td>
<td>0.3-0.4</td>
<td>0.3-0.4</td>
<td>-</td>
</tr>
<tr>
<td>Coniferous</td>
<td>0.3-0.5</td>
<td>0.3-0.4</td>
<td>0.3-0.4</td>
<td>-</td>
</tr>
<tr>
<td>Polar</td>
<td>-</td>
<td></td>
<td></td>
<td>0.1</td>
</tr>
<tr>
<td><strong>Nitric Acid Vapours</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil, grass, heath, farmland</td>
<td>1-3</td>
<td>1-3</td>
<td>1-3</td>
<td>-</td>
</tr>
<tr>
<td>Forests</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Deciduous</td>
<td>2-4</td>
<td>2-4b</td>
<td>2-4b</td>
<td>-</td>
</tr>
<tr>
<td>Coniferous</td>
<td>2-4</td>
<td>1-2e</td>
<td>1-2e</td>
<td>-</td>
</tr>
<tr>
<td>Polar</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Particulate Sulphate</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bare soil</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>Grass, heath</td>
<td>0.1-0.2</td>
<td>0.1-0.2</td>
<td>0.1-0.2</td>
<td>-</td>
</tr>
<tr>
<td>Farmland</td>
<td>0.1-0.2</td>
<td>0.1-0.2</td>
<td>0.1-0.2</td>
<td>-</td>
</tr>
<tr>
<td>Forests</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Deciduous</td>
<td>0.2-0.3</td>
<td>0.2-0.3</td>
<td>0.2-0.3</td>
<td>-</td>
</tr>
<tr>
<td>Coniferous</td>
<td>0.3-0.4</td>
<td>0.3-0.4</td>
<td>0.3-0.4</td>
<td>-</td>
</tr>
<tr>
<td>Polar</td>
<td>-</td>
<td></td>
<td></td>
<td>0.1</td>
</tr>
</tbody>
</table>

**Note:** Values for NO₂ are probably about the same as for SO₂ except for water (or wetted vegetation surfaces) for which Vₐ(NO₂) is probably close to zero.

*For water bodies, deposition velocities depend on wind speed and climatology; if the water body is large enough, air becomes equilibrated with the water surface and open-ocean conditions (5 m s⁻¹ = 0.5-1.0, 10 m s⁻¹ = 1.5-2.0; 15 m s⁻¹ = 2-3) apply. Otherwise, values may be considerably lower.

*Winter.

*If T < -5°C, deposition is known to be reduced, but we do not know by how much.

*For water bodies, deposition velocities depend on particle size and climatology; if the water body is large enough, air becomes equilibrated with the water surface and open-ocean conditions (5 m s⁻¹ = 0.1, 10 m s⁻¹ = 0.2; 15 m s⁻¹ = 0.3) apply. Otherwise, values may be considerably lower.

*Particulate nitrate probably provides an important deposition mechanism for nitrate ion at sea. Appropriate deposition velocities are probably greater than shown here because of the greater particle sizes involved.

#### 2.6 SYNTHESIS TOOLS

##### 2.6.1 Introduction

In earlier sections of this chapter, we briefly described the processes involved in the different parts of the atmospheric pathway. Acid deposition, which became a concern in the early 1960s, was one of the first regional-scale pollution issues to attract the attention of scientists and policy
makers in many parts of the world, and it continues to do so today. The interest in this phenomenon, which has now lasted more than three decades, has resulted in the extensive study of the basic processes involved in acid deposition and in the collection of many sets of short- and long-term measurements. Other important outcomes have been the development and application of methods to synthesize the acquired knowledge, to simulate major aspects of the phenomenon, and even to predict possible future responses of the system with the implementation of emission controls on acid-precursor species. In this section, we briefly describe two main types of synthesis tool, mathematical models and budgets.

2.6.2 Atmospheric Models

The information in this report is primarily based on measurements. However, because regional-scale transport and deposition models have been used so widely in the study of acid deposition and because, to a large extent, their development has been a consequence of work on the acid-deposition issue, we describe them briefly here.

Atmospheric tracers have been used to gather information about atmospheric transport, transformation, and deposition processes and to evaluate models. Tracers used in the study of transport processes are assumed not to affect atmospheric behaviour, and they are preferably inert and nondepositing, so that their concentration downwind depends only on dispersion. Tracers of opportunity have included smoke, photochemical smog, ozone and $^7$Be (which can sometimes be used to detect stratospheric intrusions), chlorofluorocarbons, and emissions from accidents such as Chernobyl. Isotopes of sulphur [Krouse and Grinenko, 1991] and of lead in aerosols [Hopper et al., 1991] have also been used to identify pollutant source regions.

In the late 1970s perfluorocarbons began to be used specifically as tracers of atmospheric motions. These chemicals have many advantages: They are nondepositing and inert, they have extremely low background concentrations (3 parts in $10^{15}$), and they can be measured with precision at these concentrations. They have proved useful in developing and testing atmospheric transport models over distances of up to a few thousand kilometres, based on experiments like the Cross Appalachian Tracer Experiment (CAPTEX) [Haagenson et al., 1988; Draxler and Stunder, 1988], the Across North America Tracer Experiment (ANATEX) [Draxler, 1991], and the European Tracer Experiment (ETEX) [Klug et al., 1993].

Atmospheric models used in the study of pollutant transport and deposition are of three kinds. The simplest are statistical in nature. They use either mean wind directions with plume standard deviations to represent horizontal fluctuations or wind-direction frequency classifications to assess the likelihood of dispersion in different directions. Because such models depict only mean large-scale meteorology, they are useful for approximating pollutant transport over periods of a year or more [Venkatram, 1986].

Lagrangian models are more suited to shorter time scales. They simulate transport using either dynamic or kinematic air parcel trajectories. The dynamic approach uses pressure and temperature fields to compute wind fields. These are usually geostrophic and are used to compute trajectories of passive materials. The kinematic approach requires measured, gridded, multilevel wind fields. Trajectories are further classified as representing (1) motion on a constant-pressure surface (isobaric), (2) average motion over a depth of the atmosphere (usually the mixed layer), or (3) adiabatic three-dimensional motion of an air parcel (isentropic) [Danielsen, 1961; Heffter and Stunder, 1987; Draxler, 1990]. The choice of a trajectory technique depends on the meteorological information and computing resources available and on the required accuracy of the resulting predictions. In data-sparse regions of the world, for example, a complex trajectory calculation procedure may be neither warranted nor feasible.

Several Lagrangian models have been developed and used to study acid deposition in Europe and North America [e.g., Eliassen and Saltbones, 1983; Voldner et al., 1981; Clark and Clark, 1984; Shannon and Lesht, 1986]. They provide concentration and deposition fields of key
species, regional inflows and outflows, and source-receptor relationships; they are also used to develop and test policy options.

The accuracy of computed trajectories depends strongly on prevailing meteorological conditions and on the temporal and spatial resolution of the input data. Contemporary trajectory computation techniques typically use data assimilation (by which additional data relevant to the area of specific interest are used to refine local wind fields), higher-resolution analytical products available from weather-forecasting sources, and results of field experiments such as CAPTEX, ANATEX, and ETEx designed specifically for model evaluation.

In Lagrangian models chemical and deposition processes are parameterized in a simplified way and a mass balance of inputs and outputs of various species is maintained as the air parcel moves along the meteorologically determined trajectory. Emission input fluxes are averaged over grid squares, which are typically 127 km on a side. Diurnal and seasonal grid-square averages of key meteorological parameters such as stability, turbulence, mixing height, precipitation, and solar radiation are used to parameterize clear-air and aqueous-phase conversion rates (e.g., SO₂ to SO₄²⁻), dry-deposition velocities (based on land use) and fluxes, scavenging rates, and wet-deposition fluxes. The mass balance (e.g., for sulphur) is then maintained by using two coupled equations for the temporal rate of change of SO₂ and SO₄²⁻ along the trajectory.

Model applications during the Kuwait oil-fire emergency revealed that available models were not capable of simulating local circulations in the absence of indicative local observations nor were they able to handle the situation of a dense pollution cloud that modified the radiation field sufficiently to dampen convective mixing and so slow down dispersion to the ground. Recent models contain new formulations that account for such behaviour [McQueen and Draxler, 1994]. Despite the limitations of Lagrangian models (e.g., their limited temporal and spatial resolution) and their highly simplified chemistry, they are easier and less expensive to use than the more sophisticated Eulerian models.

Eulerian models, the third type of atmospheric model, are able to incorporate the complexity of chemical and physical processes more realistically and to provide greater temporal resolution [Chang et al., 1987; Misra et al., 1989]. In acid deposition applications, for example, they permit detailed simulation of the complicated interactions of nitrogen, sulphur, and oxidant species that occur while transport is taking place. They also provide a better computational framework for the necessary calculation capability.

Eulerian models operate on a grid system with adequate spatial resolution to resolve the advective portion of the flow field explicitly, but they use a three-dimensional eddy diffusivity to model subgrid-scale turbulence. Pollutant transport can be computed at many different vertical levels. One problem with Eulerian models is that the computational methods used to describe diffusion processes in a discrete grid system may cause artificial diffusion. Sophisticated advection/diffusion algorithms have to be developed to minimize this problem. These models are also computationally expensive and require detailed meteorological information. This information can consist of (1) observational data interpolated in space and time, (2) forecast data from, for example, a numerical weather prediction (NWP) model, or (3) a combination of the two. The last option, known as four-dimensional data assimilation (FDDA) is preferred because observational data are often sparse in time and space and interpolation methods are approximate.

Hemispheric-scale models have been developed to simulate the very large-scale distribution and transport of sulphur and nitrogen species in the atmosphere. They have been used in studies of acid deposition and the hemispheric transport of volcanic emissions and to determine sulphate-aerosol distributions for radiative transfer calculations related to climate warming. The global-scale models of Langner and Rodhe [1991] and Levy and Moxim [1989] were used in this study to portray likely preindustrial, current, and future deposition fields based on respective emission scenarios (see Annexes I and II).
Because the atmospheric behaviour of chemicals can be so complex, no single description (model) is likely to meet the needs of all applications. This is why so many numerical models have been developed for the acid deposition issue. Although it may not be possible to select the best model for a particular application, it is usually possible to judge which kind of model best describes the relevant processes for a particular investigation. Model testing against field data is also problematic because such evaluations demonstrate the applicability of the model in the particular circumstances of the test. Most model testing focuses on the capability to describe changes in air quality rather than in total acid deposition. This is not necessarily inappropriate, but it does point out the need for improved model-evaluation methods and the wisdom of using additional sources of independent information, particularly when costly decisions are likely to be influenced. In the present context, then, models are but one "synthesis tool" that must be considered.

2.6.3 Atmospheric Budgets

A second type of synthesis tool is the atmospheric budget. This is a means of accounting for all known inputs and outputs of a substance, such as sulphur or nitrogen, for a region of the atmosphere (e.g., western Europe, eastern North America, southeast Asia). In a budget analysis, an attempt is made to identify all emissions, inflows, outflows, and depositions and then to quantify the fluxes along these pathways with a view to seeking a balance between inputs and outputs. Such an exercise is often useful for synthesizing available information and providing an overview of what is known and what is not known about the atmospheric pathways in a particular region.

It is not always possible to determine directly the various flux terms in a budget. They may be derived from measurements, from model calculations, from a combination of the two, or as a last resort, from the difference between inflows and outflows. (For a review of regional pollutant budgets for many areas of the world, see Galloway and Rodhe [1991].) Experience from North American budget work has shown that quantification of flux terms provides valuable insight into the important pathways and fluxes of pollutants within a region and between neighbouring regions. However, it is clear that contemporary knowledge is not adequate to specify reliable levels of uncertainty for several of the critical terms in such budget calculations. For example, the uncertainty associated with average dry deposition is roughly three to four times that appropriate for wet deposition. When determined on an annual basis, budgets do not reflect the seasonality inherent in the various flux terms, such as the outflow of sulphur to the Atlantic.

Some examples of the application of regional budgets are given in the chapters describing acid deposition in individual regions and in Chapter 13.

2.7 REFERENCES


CHAPTER 3: EFFECTS OF ACIDIC DEPOSITION
P. Grennfelt and J. N. Galloway

3.1 INTRODUCTION

Acid deposition and accompanying effects were first noticed as a large-scale environmental problem at the end of the 1960s [Odén, 1968; Hultberg and Stensson, 1970]. Odén observed that acid precipitation over large areas in Europe was accompanied by an ongoing acidification of lakes and streams, especially in Scandinavia. In his first publications he pointed out possible effects such as depletion of base saturation in soils causing decreased forest production and increased corrosion. He also coupled the acidification to observed disappearances of fish populations in Norway and Sweden. Hultberg and Stensson showed that the perch population had disappeared and pike reproduction stopped in Swedish lakes over a period when the pH of the lakes dropped by 1.0-1.3 pH units.

Effects in terms of losses in fish populations were, however, not a new phenomenon, even though nobody had previously linked the losses to the deposition of acidifying substances. Losses in fish populations were already being observed during the 1920s in Norway, where the Atlantic salmon population decreased in connection with low pH [Jensen and Snevik, 1972]. Losses in fish populations associated with acid deposition were also reported from Germany during the 1930s [Hultberg, 1983], where brown trout disappeared in streams draining forested catchments.

During the 25 years since they were originally observed, acidification effects have occurred in many ways and in various ecosystems. Early observations of acidification effects in lakes and streams were followed by later observations of groundwater acidification and, later still, soil acidification. Acid deposition has also caused severe effects on materials.

Acidification effects are primarily associated with the atmospheric deposition of sulphur and nitrogen compounds. Deposition may occur in the form of strong acids (sulphuric acid, nitric acid, and sometimes also hydrochloric acid) or compounds, which, after deposition, may be converted to strong acids (e.g., sulphur dioxide and nitrogen dioxide). In this context ammonia is also a potentially strong acid. In soils it may be converted to nitric acid and thus cause acidification. In tropical areas organic-acid deposition may contribute as much as 50% of the deposition of acids in precipitation. It is, however, assumed that these acids are absorbed or oxidized in soil and will not contribute to soil acidification [McDowell, 1988].

Acid deposition has been of interest not only for its role in acidification but also for effects associated with the deposition of nitrogen as a nutrient. Also, direct effects from sulphur dioxide and nitrogen oxides have sometimes been considered as acidification effects. In this chapter the effects of sulphur and nitrogen deposition leading to acidification and nutrient effects in ecosystems will be considered, as well as effects on materials. Health effects will only be considered in connection with the acidification of drinking water. It is, however, important to note that, in many areas of the world, concentrations of sulphur and nitrogen oxides exceed ambient air quality standards, and considerable emission reductions are necessary to protect human health. Sulphur and nitrogen compounds may also affect physical and chemical properties of the atmosphere [Isaksen and Hov, 1987; Langner et al., 1992].
3.2 PATHWAYS IN THE ECOSYSTEMS: MECHANISMS OF ACIDIFICATION

3.2.1 Pathways of Sulphur and Nitrogen Deposition

Anthropogenic sulphur is mostly deposited from the atmosphere as S (VI) (sulphates or sulphuric acid) and S (IV) (sulphur dioxide). Sulphur dioxide is deposited as dry deposition, mainly by direct uptake by plants through their stomata. After uptake, sulphur dioxide is, to a large extent, oxidized to sulphuric acid, which may be transferred to the surface of the leaves and then washed off by precipitation. Particulate sulphur is deposited to the ground by different mechanisms (e.g., turbulent diffusion and sedimentation). Rough surfaces, such as forests, receive relatively more dry deposition than open flat areas such as agricultural land. Much of the sulphur deposited on vegetation is washed off by precipitation [Hultberg and Grennfelt, 1991].

Nitrogen oxides are not easily deposited to the ground. Nitrogen dioxide is taken up by stomata, and nitric oxide shows low-deposition velocities to most receptors. Instead nitrogen oxides need to be converted to nitric acid and nitrates to be easily deposited. Nitric acid has a very high solubility and sticks to almost all surfaces. Reduced nitrogen may be deposited as gaseous ammonia and aerosol ammonium in precipitation.

Dry deposition varies considerably depending on the receptor type. This has been treated in detail in Chapter 2 but may also be considered in connection with the assessment of effects. Some receptors that are at risk from acidification effects may themselves increase dry deposition. This is the case with coniferous forests, which may increase their relative sensitivity to damage because of their high filtering efficiency. Dry deposition to such receptors may be more than twice the wet deposition, although the dry deposition to adjacent open land may only be a small fraction of the wet deposition. Deposition to forests may be enhanced at forest edges or to forests growing on slopes or ridges in mountain areas ([Ivens, 1990; Fowler et al., 1993]).

Monitoring sulphur deposition to boreal ecosystems shows that sulphur almost quantitatively passes through the ecosystems. In fact, sulphur transport in throughfall often equals the outflow from forested catchments, and sulphur flux in throughfall is widely used as a method of determining sulphur deposition [Hultberg and Grennfelt, 1991; Ivens, 1990].

In tropical or other well-weathered soils, significant sulphur deposited from the atmosphere is retained in soil [Eriksson, 1988; Galloway, 1988; Sanhueza et al., 1988]. Retention of sulphate is accompanied by retention of an equal amount of hydrogen ions; sulphate retention may then be regarded as retention of sulphuric acid [Eriksson, 1988].

Nitrogen deposition is retained in almost all terrestrial ecosystems. In areas with low nitrogen deposition, retention may be 80% or more, although in areas that have received high quantities of nitrogen over a long period, retention is much smaller. In boreal ecosystems, nitrogen input is retained in soil and an increasing biomass [Gundersen, 1992]. Leaching of nitrogen from soils occurs primarily as nitrate, although in areas with very high input of reduced nitrogen even leaching of ammonium may occur [Heij et al., 1991].

3.2.2 Acidification Mechanisms

Acidification is a dynamic process causing chemical changes in soils and waters that, in turn, cause effects on biota and materials. In buffered soils an input of acid may be neutralized by alkaline ions, raising the pH of passing water. Neutralization takes place by ion exchange between H⁺ and alkaline cations on surfaces of soil particles. If weathering is high, soil generates new cations and keeps the soil well buffered. In slowly weathered poor soils, soil may continuously lose cations from particle surfaces, and cation sites will successively be filled by hydrogen ions (Fig. 3.1). The proportion of sites occupied by alkaline ions determines the degree of base saturation; during soil acidification, soil loses its base saturation.
Figure 3.1: Soil acidification by sulphur for (A) highly weathered, well-buffered soil (base saturation >20%) and (B) slowly weathered, poor soil (base saturation <20%).

When base saturation has decreased to low values, the acid may release ions from the structure of soil particles, usually inorganic aluminium ions. The acidification of soils is often considered to be the loss of base saturation, which leads to a decreased pH of soil water and, at pH less than approximately 4.5, to a release of inorganic metal ions (Fig. 3.1).

Acidification processes may occur naturally. The growth of plants—especially forest trees—is accompanied by a long-term accumulation of alkaline ions in the biomass that, in the case of forest harvesting, may be taken away from the system.

The role of nitrogen in the acidification process is more complicated. Acidification may occur, in the same way as it does for sulphate, when nitrate is leached from the soil. However, because the biological productivity of most terrestrial ecosystems is limited by the amount of nitrogen available, deposition of nitrogen (in oxidized or reduced form) acts primarily as a fertilizer. Some nitrogen is also absorbed in soils as organic nitrogen (Fig. 3.2).
Figure 3.2: Many terrestrial ecosystems have a substantial capacity to take up and immobilize nitrogen deposited from the atmosphere. In Scandinavia (A), up to 140 mmol N m$^{-2}$ are deposited annually, but most of the nitrogen is absorbed by vegetation and soils, and leaching is typically far less than 5% of the total deposition. In central Europe (B), where annual deposition is often of the order of 140-700 mmol N m$^{-2}$, a substantial fraction (10-50% or more) of the deposited nitrogen is leached to groundwater or picked up by surface water runoff.

The acidification effect of nitrogen may, therefore, be primarily expressed as the leaching of nitrate from ecosystems. Significant ammonium leaching seldom occurs, except in areas with very high ammonium deposition. If not incorporated in the biota, ammonium is instead converted to nitrate.

The relative acidification effect from nitrogen varies considerably in different areas due to differences in the deposition of nitrogen. In areas with high sulphur and nitrogen deposition (e.g., central Europe), nitrogen may contribute 30-50% of acidification; in more remote areas, it contributes less than 20% (Table 3.1). Table 3.1 shows that most nitrogen is retained in the soil in more remote areas in Europe, although a substantial fraction passes through the soil to groundwater and runoff in central Europe. Since nitrogen output is usually dominated by nitrate, Table 3.1 also indicates the relative importance of nitrogen for the acidification of soils.
Table 3.1: Typical input/output values for forested areas in Europe.

<table>
<thead>
<tr>
<th></th>
<th>Input (kg ha⁻¹ yr⁻¹)</th>
<th>Output (kg ha⁻¹ yr⁻¹)</th>
<th>N Fraction in Output (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sulphur</td>
<td>Nitrogen</td>
<td>Sulphur</td>
</tr>
<tr>
<td>Scandinavia</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>North/Central</td>
<td>0.3</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>South</td>
<td>1-1.5</td>
<td>0.7-1.5</td>
<td>1-1.5</td>
</tr>
<tr>
<td>Central Europe</td>
<td>2-4</td>
<td>1-3</td>
<td>2-4</td>
</tr>
<tr>
<td>The Netherlands</td>
<td>2-4</td>
<td>3-6</td>
<td>2-4</td>
</tr>
</tbody>
</table>

Note: The column to the right gives the N fraction of the S + N output from the systems.

Tropical soils, as well as soils not covered during the last glaciation, are often well weathered and thus have a low buffering capacity, although they can have a very high sulphate adsorption capacity (section 3.2.1). Leaching of ions from these soils is often accompanied by aluminium ions, a situation that has made many tropical species relatively insensitive to aluminium.

During the last century in areas receiving high sulphur and nitrogen deposition, glaciated mineral soils lost a substantial fraction of their neutralizing capacity; that is, base saturation decreased. Soil samples analysed decades ago often show a substantially higher base saturation than present-day soils, with soil pH having often decreased by 1.0-1.5 pH units.

3.3 ACID DEPOSITION EFFECTS

3.3.1 Plants and Vegetation

Acidic gases, especially sulphur dioxide, are toxic to plants. High concentrations of sulphur dioxide cause acute toxic effects such as reduced photosynthesis, which generally occurs at concentrations of 8-16 μmol m⁻³ [Darrall, 1989]. Other effects may occur from long-term exposure at much lower concentrations. Conifers are more sensitive than deciduous trees and agricultural crops, and effects are assumed to occur at long-term concentrations below 0.3-0.5 μmol m⁻³ [Krause, 1988]. It is also assumed that SO₂ and other gaseous pollutants may increase the susceptibility of plants to climate stresses such as low temperatures [Wolfenden and Mansfield, 1991].

Nitrogen dioxide may cause direct effects to plants, although the acidifying and fertilizing effects of nitrogen are normally considered more important. Synergistic effects may often occur between SO₂ and NO₂, SO₂ and ozone, and other gases. In addition to the direct effects of gases, acid rain and direct deposition of fog and cloud droplets affect the structure of leaf surfaces, notably the cuticles of coniferous needles [Riederer, 1989]. Deposition of fog and cloud droplets may generate very acidic conditions on leaf surfaces. Experiments with acid fog in combination with ozone and/or sulphur dioxide indicate increased nutrient leaching [Krause, 1988].

3.3.2 Terrestrial Ecosystems

Acidification of mineral soils leading to a loss of alkaline ions (K⁺, Mg⁺⁺, Ca⁺⁺) may cause a nutrient deficit. Magnesium deficit, for example, causes forest damage in central Europe [Hüttl, 1989, 1990]. A main concern related to the acidification of soils is the release of aluminium to soil water, an hypothesis put forward by Ulrich and coworkers [e.g., Ulrich and Matzner, 1983]. Aluminium toxicity thresholds for various species vary widely, from less than 1.5 mg L⁻¹ to more than 30 mg L⁻¹ [e.g., McCormack and Steiner, 1978; Ryan et al., 1986a, 1986b; Thornton et al., 1987; Smit et al., 1987; Joslin and Wolfe, 1988]. Most data are based on studies of seedlings grown in well-controlled experimental systems and are difficult to extrapolate to mature trees growing under natural conditions. Red spruce is one of the most sensitive tree species, with an
observed reduction in biomass production starting at a concentration of 2.5 mg L\(^{-1}\) of labile aluminium [de Vries, 1991]. In addition to aluminium concentration, the Al\(^{3+}\):Ca\(^{2+}\) ratio is an important determinant of toxicity to roots [Rost-Seibert, 1983; Roelofs et al., 1985]. An Al\(^{3+}\):Ca\(^{2+}\) molar ratio of 1.0 has been proposed as a critical threshold of toxicity for tree roots [Ulrich and Matzner, 1983; Boxman et al., 1988].

Deposition of reduced and oxidized nitrogen may cause a series of long-term ecosystem effects, as systems that were once nitrogen poor acquire a surplus of nitrogen. Biological effects pass through different stages, including increases in growth, changes in structures, and finally destabilization of the ecosystem (Fig. 3.3). Ecosystem effects from high nitrogen input have been observed in many areas, especially where heavy emissions of ammonia from intensive farming have caused vegetation changes. In the Netherlands, substantial parts of the heaths have turned from caluna heaths to grasslands [Boxman et al., 1988]. High nitrogen input may also increase frost sensitivity [Soikkeli and Kärenlampi, 1984], while ammonium deposition may cause critical nutrient imbalances, such as in the NH\(_4^+\):Mg\(^{2+}\) ratio [Schulze, 1989].

Figure 3.3: Hypothetical time course of forest ecosystem response to chronic nitrogen additions. Relative changes (A) in rates of nitrogen cycling and nitrogen loss and (B) in plant condition (e.g., foliar biomass and nitrogen content, fine-root biomass) and function (e.g., net primary productivity--NPP--and nitrate assimilation) in response to changing levels of nitrogen availability (adapted from Aber et al. [1989]).

At the final stage, when most nitrogen is leached as nitrate, nitrogen contributes to acidification in the same way that sulphur does.
3.3.3 Forest Damage

Damage to vegetation, especially forests, was observed and documented in the early stages of industrialization and was easily related to toxic concentrations of primary pollutants, most often sulphur dioxide [Guderian, 1977]. Severe effects on forests and other vegetation have also been seen close to very large sulphur sources, such as smelters in Sudbury (Canada) and Nikel (on the Kola peninsula, Russia). In such areas forest deaths have been observed over large areas.

In the early 1980s new types of forest damage were observed over large areas of western Germany and adjacent areas in central Europe as well as in other parts of Europe and large parts of eastern North America. This damage could not be related to any obvious pollutant stress [Cowling, 1988].

Several hypotheses have been put forward, most related to the stress of air pollution. Although much research has been done, causes of this regional stress have only partly been shown. However, several experiments show that air pollution stresses forests in different ways. The most important involve aluminium toxicity to roots, shortages in nutrients (e.g., magnesium, calcium, and phosphorus) because of acidic deposition, nutrient imbalances (especially NH$_4^+$:K$^+$ and NH$_4^+$:Mg$^{2+}$ ratios), direct effects of ozone, and effects of acidic fog and cloud droplets on the cuticles of needles and leaves [Schulze and Freer-Smith, 1991].

3.3.4 Groundwater

Groundwater acidification threatens human health primarily because of metals released from soils or from water supply pipes. Corrosion of water supply pipes and of metal equipment and material in soils may be economic problems in areas subject to severe soil acidification [Kucera, 1990].

The greatest threat of groundwater acidification is in shallow groundwater aquifers. Water supply in rural areas is often derived from such sources, especially in Canada and northern Europe. High concentrations of aluminium in these waters have been suggested as a risk for human health. Infants and children are especially susceptible to illnesses caused by high copper concentrations released from supply pipes [Grant et al., 1991].

3.3.5 Lakes and Running Waters

Earlier in this chapter early observations of fish losses in lakes and streams subject to acid precipitation were mentioned. These observations indicated that biological systems in surface waters were very sensitive to acidification and related chemical changes.

When considering the sensitivity of a lake or a stream to acidification, the variable usually considered is the acid-neutralizing capacity (ANC). Waters with low ANC (<50 μeq L$^{-1}$) normally have very little ability to neutralize added acids. Waters with low ANC values are found in areas with poor soils on granite bedrock. Generally lakes and streams closer to the origin of the system have lower ANCs than lakes further down. Lakes with small drainage areas are also usually more sensitive than those with large ones.

The historical development of acidification can be followed by paleolimnological studies. By determining the diatom composition of lake sediments, a record of pH development of a lake can be established for several thousand years [Battarbee, 1984; Renberg and Hellberg, 1982]. Lakes on weakly buffered soils covered by the last glaciation have undergone a slow acidification from when they were formed up to the beginning of this century. In areas subject to large anthropogenic deposition during recent decades, the lake pH has changed dramatically.

Biological systems in surface waters are very sensitive to acidification and related chemical changes. Fish losses are the most obvious effect. The threat to fish is not only from low pH but
also from low Ca\(^{++}\) and high Al\(^{+++}\). Laboratory experiments with brown trout show that fish survival decreases with decreasing pH and increasing Al\(^{+++}\) and that toxic effects are enhanced by low Ca\(^{++}\) [Brown, 1982]. In a Norwegian field investigation [Hultberg, 1988], more than 600 lakes were investigated between 1978 and 1983. Perch and trout populations decreased with decreasing pH and Ca\(^{++}\) and increasing labile Al\(^{+++}\). Most fish species in acidified regions have a survival threshold in the pH range 5-6 [Hultberg, 1988] (Table 3.2).

Table 3.2.: Critical pH and labile Al\(^{+++}\) concentrations from some organisms sensitive to acid water (Ca\(^{++}\) 50 \(\mu\)eq L\(^{-1}\))

<table>
<thead>
<tr>
<th>Organism</th>
<th>Effect</th>
<th>Critical pH/Labile Al(^{+++}) ((\mu)g L(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phytoplankton</td>
<td>Species composition changes</td>
<td>6.0-5.5</td>
</tr>
<tr>
<td>Zooplankton</td>
<td>Species composition changes</td>
<td>6.0-5.5</td>
</tr>
<tr>
<td>Filamentous algae</td>
<td>Forms mats on shallow bottoms</td>
<td>5.8</td>
</tr>
<tr>
<td>Mougeotia sp.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sphagnum sp.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Freshwater shrimp*</td>
<td>Total decline</td>
<td>5.9</td>
</tr>
<tr>
<td>Crayfish</td>
<td>Recruitment failure, disappearance</td>
<td>5.6-5.0</td>
</tr>
<tr>
<td>Molluscs</td>
<td>Many species disappear</td>
<td>5.5</td>
</tr>
<tr>
<td>Ephemeroïds</td>
<td>Many species disappear</td>
<td>6.0-5.5</td>
</tr>
<tr>
<td>Chironomids</td>
<td>Some species increase/decrease in abundance</td>
<td>6.0-5.0</td>
</tr>
<tr>
<td>Atlantic salmon</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lake trout</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sea trout</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Arctic char</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brown trout</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Roach</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Perch</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Northern pike</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: Streams and rivers often show episodic changes in water chemistry. Fish species spawning in running waters (Atlantic salmon, sea trout, and brown trout) are, therefore, more exposed to toxic changes in pH and labile Al compared to fish species spawning in lakes.

*Mysis sp. Gammarus

Surface waters often show decreases in pH with snowmelt or heavy rain. Such acidic episodes may occur in many lakes and streams with a stable summer pH greater than 6.0 [Leivestad and Muniz, 1976].

Not only fish populations are affected by acidification. Crayfish and freshwater shrimp (Mysis sp. Gammarus) decline and disappear in lakes and streams because of acidification (Table 3.2). Even the lake flora are influenced, and one of the most obvious acidification effects in northern lakes is the increased growth of sphagnum, which may form mats on shallow bottoms [Hultberg and Grahn, 1975].

3.4 MARINE ECOSYSTEMS

Although several nutrients have been investigated as limiting agents for biological productivity in the ocean (e.g., phosphate and iron [Broecker and Peng, 1982; Martin and Fitzwater, 1988]), the prevailing view is that the supply of inorganic nitrogen to the illuminated upper ocean (euphotic zone) regulates the oceanic carbon cycle [Epplle and Peterson, 1979]. Only through the supply of additional nitrogen from outside the euphotic zone (exogenous input) can rates of primary production increase (spring blooms) or organic material be exported from the surface ocean without continuously diminishing the stock of organic material in the system. Production of plant biomass from these exogenous nutrients is termed new production [Dugdale and Goering, 1967], which, given steady state conditions, will equal nitrogen losses from the euphotic zones. The principle source of new nitrogen is vertical mixing of nitrate from water below the euphotic zone, where concentrations range from 20 \(\mu\)mol in the Atlantic Ocean to more than 40 \(\mu\)mol in the
Pacific Ocean. Fixation of atmospheric nitrogen to ammonium by marine cyanobacteria is probably a minor source of new nitrogen [Carpenter, 1983], but recent measurements of higher rates may require a reevaluation of this conclusion [Martinez et al., 1983; Carpenter et al., 1987; Scranton et al., 1987].

Atmospheric inputs of biologically usable nitrogen (regardless of the form) are classified as exogenous nutrient sources to the surface ocean. Logically then, for estimating their relative importance to primary production in the ocean, rates of atmospheric deposition must be compared with production rates caused by new nitrogen. Nitrogen from atmospheric sources is a relatively minor exogenous source to the ocean on a yearly basis [Knap et al., 1986], although on an event basis it may be significant [Parré, 1985; Owens et al., 1992; Michaels et al., 1993].

To determine the role of atmospheric deposition of nitrogen and its relative importance to oceanic primary productivity, estimates of new production can be compared to estimated nutrient inputs from the atmosphere in a specific region. In the following sections, we discuss a case from the Atlantic Ocean, where acid deposition from the United States is high and hence any impact would be enhanced.

Previous estimates of the importance of deposition events to the productivity of the Sargasso Sea have compared measured deposition with estimated new production derived from historical comparisons [Knap et al., 1986; Owens et al., 1992]. Knap et al. [1986] compared deposition with the annual new production estimated from measurements of total production [Menken and Ryther, 1961; Knap et al., 1986] and large-scale indirect methods [Jenkins and Goldman, 1985] and found that total deposition is insignificant compared to other sources of new nutrients. Owens et al. [1992] compared an updated version of the same deposition record with estimates of new production from historical production rates and assumed f-ratios (ratio of new production to total production). They suggested that many individual deposition events are important in stimulating short-lived pulses of new and total production.

A recent paper by Michaels et al. [1993] compares simultaneous collections of atmospheric samples and ocean nitrogen-cycle measurements for the area around Bermuda. They found that nitrogen deposition is a small fraction of the annual new nitrogen uptake at the BATS site, whether predicted from carbon-fixation rates and sediment-trap data or from tracing oxygen budgets. The annual nitrogen deposition accounts for only 0.4% of the total production and 5.8% of the sediment-trap-determined nitrogen flux.

On shorter time scales, nitrogen deposition events are a larger fraction of the sediment-trap-measured daily fluxes. Deposition events ranged from 0.3% to 271.4% of the daily sediment flux, with a mean and median contribution of 30% and 17% respectively. In 16 events (an average of 1.6% of the days each year), the deposition event equalled the daily particulate nitrogen flux. However, this conclusion must be tempered by evidence suggesting that trap data underestimate true new production values.

Wet deposition of nitrate and ammonia is only part of the atmospheric nitrogen supply to the upper ocean. Dry deposition and wet deposition of dissolved organic nitrogen (DON) should also be considered [Knap et al., 1986]. Thus, it is imperative that the total nitrogen content of rainwater be measured to make the kinds of comparisons done here and elsewhere accurately. However, in most cases, DON measurements are not included in studies of the nitrogen composition of rainwater. Furthermore, the supply of other nutrients present in the ocean at near-limiting concentrations (e.g., phosphate, iron) needs to be assessed, as these nutrients are also required for phytoplankton growth and may play a significant role in determining the fate of atmospheric nitrogen. Phytoplankton blooms may only develop in the subset of nitrogen deposition events that are accompanied by adequate phosphate and trace elements.

Direct comparisons of atmospheric wet deposition of nitrogen with concurrent measurements of nitrogen cycling, such as were performed in the Sargasso Sea, indicate that nitrogen deposition
events are only rarely important in upper ocean biogeochemistry. Although atmospheric sources of new nitrogen can lead to the formation of near-surface phytoplankton blooms [Glover et al., 1988], the above analysis indicates that nitrogen deposition events are too rare and too small to make any significant contribution to ocean nitrogen cycling. They only rarely contribute adequate nitrogen to change stocks of particulate nitrogen or phytoplankton in the entire mixed layer. However, when deposition is confined to the near-surface layer by strong salinity or temperature stratification, it can cause a shallow, local bloom.

Atmospheric deposition of nitrogen has been increasing over the past decade and is likely to continue to increase as human populations and their relative levels of industrial development increase. We expect that the relative importance of atmospheric nitrogen inputs to the surface ocean will also increase. To become an important source of new nitrogen to the ocean, this increase would have to be substantial or oceanic rates of new production would have to decrease from their current values. If wind patterns shift, leading to increased deposition over oceanic provinces that are oligotrophic year-round, atmospheric deposition could have the potential to increase new production.

3.5 REGIONAL ACID DEPOSITION PROBLEMS

3.5.1 Introduction

In Europe and North America acid deposition has been a major environmental interest for two decades. In North America this problem and its related effects have been compiled in several assessment studies such as the U.S. National Acid Precipitation Assessment Program [Irving, 1991].

Acid deposition and its effects in the tropics were assessed in an international workshop [Rodhe and Herrera, 1988]. In the workshop report, effects in some tropical regions were analysed.

3.5.2 Europe

Acidification effects in Europe, although severe and extensive, have not been monitored on a European scale. Forest conditions in terms of defoliation and discolouration of the tree canopies, however, have been investigated yearly in a joint network covering most of the continent. These studies indicate that 25-50% of forest trees in many European countries show a pronounced defoliation (>25%) (Table 3.3) [UN ECE, 1992]. From these inventories observed effects cannot be allocated to any specific pollution or climate stress or combination of stresses (see section 3).

Several countries have made national inventories of acidification effects such as lake or soil acidification. Such inventories usually include only physical and chemical parameters (pH, main anions and cations, inorganic aluminium, etc.) and biological parameters. Lake acidification inventories are available in the Scandinavian countries and in the United Kingdom. In Norway many lakes were inventoried in 1974 and 1986. During this 12-year period sulphate concentrations did not change significantly, but aluminium and nitrate concentrations increased markedly, indicating ongoing acidification [Henriksen et al., 1988].
Table 3.3.: Conifer and broadleaf defoliation (in percent) according to the 1990 forest inventory within the UN ECE convention on long-range transboundary air pollution.

<table>
<thead>
<tr>
<th>Country</th>
<th>Conifers</th>
<th>Broadleaves</th>
</tr>
</thead>
<tbody>
<tr>
<td>Austria</td>
<td>8.3</td>
<td>14.9</td>
</tr>
<tr>
<td>Belgium</td>
<td>10.7</td>
<td>5.2</td>
</tr>
<tr>
<td>Bulgaria</td>
<td>37.4</td>
<td>17.3</td>
</tr>
<tr>
<td>Byelorussia</td>
<td>57.0</td>
<td>45.0</td>
</tr>
<tr>
<td>St. Petersburg</td>
<td>32.7</td>
<td>10.2</td>
</tr>
<tr>
<td>Czechoslovakia</td>
<td>50.3</td>
<td>33.9</td>
</tr>
<tr>
<td>Denmark</td>
<td>18.8</td>
<td>25.4</td>
</tr>
<tr>
<td>Estonia</td>
<td>20.0</td>
<td>---</td>
</tr>
<tr>
<td>Finland</td>
<td>18.0</td>
<td>11.6</td>
</tr>
<tr>
<td>France</td>
<td>6.6</td>
<td>7.7</td>
</tr>
<tr>
<td>Germany</td>
<td>15.0</td>
<td>23.8</td>
</tr>
<tr>
<td>Greece</td>
<td>10.0</td>
<td>26.5</td>
</tr>
<tr>
<td>Hungary</td>
<td>23.3</td>
<td>21.5</td>
</tr>
<tr>
<td>Ireland</td>
<td>5.4</td>
<td>---</td>
</tr>
<tr>
<td>Italy</td>
<td>13.8</td>
<td>16.7</td>
</tr>
<tr>
<td>Latvia</td>
<td>43.0</td>
<td>27.0</td>
</tr>
<tr>
<td>Lithuania</td>
<td>22.9</td>
<td>15.8</td>
</tr>
<tr>
<td>Netherlands</td>
<td>21.4</td>
<td>11.5</td>
</tr>
<tr>
<td>Norway</td>
<td>17.1</td>
<td>18.2</td>
</tr>
<tr>
<td>Poland</td>
<td>40.7</td>
<td>25.6</td>
</tr>
<tr>
<td>Portugal</td>
<td>25.7</td>
<td>34.1</td>
</tr>
<tr>
<td>Spain</td>
<td>3.1</td>
<td>4.4</td>
</tr>
<tr>
<td>Sweden</td>
<td>16.1</td>
<td>22.1</td>
</tr>
<tr>
<td>Switzerland</td>
<td>19.0</td>
<td>12.0</td>
</tr>
<tr>
<td>Ukraine</td>
<td>3.0</td>
<td>2.7</td>
</tr>
<tr>
<td>United Kingdom</td>
<td>45.0</td>
<td>28.8</td>
</tr>
<tr>
<td>Yugoslavia</td>
<td>34.6</td>
<td>4.4</td>
</tr>
</tbody>
</table>

Notes: Conifer defoliation for Italy is for 1991; Croatia and Slovenia were not included in Yugoslavian defoliation values.

For forest soils in Europe several investigations indicate substantial leaching of nitrate, as shown in Figure 3.3. Long time series indicate that leaching is increasing and consequently contributing more to soil acidification from nitrate. Increased nitrate leaching may also have consequences for the acidification and eutrophication of lakes, but it is probably most important for the nitrogen loading and thus the eutrophication of coastal waters.

3.5.3 North America

The first thorough documentation of acid deposition in North America [Likens et al., 1972] discussed its distribution and possible environmental consequences. Cowling [1982] compiled an excellent history of acid deposition, including North America. Following a period of rapid advancement in the state of knowledge about acid deposition and its effects in North America, both the Canadian and the United States governments initiated extensive programmes to document the extent of effects in the two countries. The Canadian Long Range Transport of Air Pollutants [LRTAP] programme and the U.S. National Acid Precipitation Assessment Program [NAPAP] both began in about 1980. LRTAP issued a major report of its findings in 1990 [RMCC, 1990]; NAPAP issued a similar report in 1991 [Irving, 1991]. The geographical situation in North America is similar to that in Europe. In both cases, regions with large emissions of SO₂ and NOₓ are upwind of regions with extensive sensitive ecosystems [Likens et al., 1979].

Both the LRTAP and NAPAP programmes showed that acid deposition is present in large regions of eastern North America and is primarily due to U.S. emissions. The two programmes supported findings of earlier studies [e.g., Galloway and Whelpdale, 1980] that there was extensive transport of acid deposition precursors from the U.S. to Canada.
Both Canada and the U.S. have extensive regions with sensitive aquatic ecosystems. RMCC [1990] estimates that east of the Manitoba/Ontario border and south of James Bay half the approximately 800,000 water bodies greater than 0.18 ha are sensitive to acid deposition. In the United States, many sensitive aquatic systems were found in the northeast, the mid-Atlantic states, the upper Midwest, and the west. Using historical information, it has been possible to document the extent of acidification in some regions (e.g., about 15% of Adirondack lakes larger than 4 ha have had a pH decrease of more than 0.28 pH units). In both countries research has shown that, once a water body acidifies, many aquatic organisms suffer adverse effects starting at pH values below 6.0.

For terrestrial ecosystems, Irving [1991] concluded that the vast majority of forests were not declining in health or productivity due to acid deposition or any other stress factor. However, some sensitive species in forested ecosystems in high-deposition regions were declining, and it was concluded that acid deposition may be a contributing factor (e.g., red spruce at high elevations in the northern Appalachian Mountains.) RMCC [1990] identified a possible link between increased acid deposition and O₃ levels and an observed decline in maple trees. One of the more intriguing findings of the programmes was that increased deposition of nitrogen results not only in impacts on forests but also in saturation of ecosystems with nitrogen, resulting in damage to downstream ecosystems (e.g., Aber et al., 1989). As both studies stress, identifying cause-effect relationships between changes in atmospheric composition and forested ecosystems is especially difficult because of the complexity of forests and their natural slow growth.

In summary, acid deposition is prevalent over large regions of North America. Effects on aquatic ecosystems are well documented. Effects on terrestrial ecosystems are more subtle and occur in concert with other pollutants (e.g., O₃) but are possibly more extensive.

3.5.4 Asia

Knowledge of the effects of acid deposition in Europe and North America cannot be directly transferred to other areas of the world to assess potential damage or future risks. In Asia several regions, especially in the southeast, are experiencing increased acidic deposition and the subsequent effects.

Adverse effects of high levels of acidifying air pollutants have been documented in southwestern China, especially in the regions of Guizhou, Hunan, and eastern Sichuan [Cao, 1989; Zhao and Kiong, 1988]. Most relate directly to high levels of sulphur dioxide, but the low pH of rain (4.1-4.5) and the high acid deposition (up to 2 kmol S ha⁻¹ yr⁻¹) might have severe effects on soils and biota. Substantial decreases in forest production have been observed in regions where rain pH is less than 4.5 compared to regions with rain pH greater than 4.5.

In Japan some acidification effects have been observed. They pertain mainly to acidification of some mountain lakes where pH has dropped approximately 0.6 pH units over 10 years [Kurita et al., 1990].

Sensitivity to soil acidification in southeast Asia has been evaluated by Kuylenstierna et al. [1992] based on geological and climatological data. This study made a distinction in sensitivity between areas that were glaciated and those that were not during the last glaciation.

3.5.5 Other Areas

There is little evidence for regional acidification effects in areas of the world other than those mentioned above. However, the acidification problem probably extends to other areas. Two conditions must be met if acidification effects are to occur: (1) emission density must be high over a substantial area, and (2) soils and ecosystems must be sensitive to acid deposition. The investigation by Kuylenstierna et al. [1992] cited above gives a detailed study of sensitivity to acidification in southwestern Asia. Rodhe et al. [1988] offer a more qualitative analysis of the
sensitivity on a global scale. They point out areas with soils sensitive to acidification and areas with high emission densities. They conclude that areas with potential problems are in northern and southeastern South America, in southwestern Asia (Indonesia, Malaysia, Thailand), and in Central Africa (Nigeria) (Fig. 3.4).

Figure 3.4: Regions with current acidification problems and those where acidification might become severe because of soil sensitivity, expected future emissions, and population density. Present emissions are designated by \|
, sensitive soils by /\, present problem areas by solid-line circles, and potential problem areas by dashed-line circles. (Figure adapted from Rodhe and Herrera [1988].)

3.6 EFFECT-BASED CONTROL STRATEGIES FOR ACID DEPOSITION: THE CRITICAL LOAD CONCEPT

The reason for controlling emissions of acidifying substances is to avoid effects from acid deposition. Although most effects are related to long-term doses, control strategies must take account of effects occurring over the short term as well. One approach to controlling acidification and nutrient effects is the concept of critical loads developed by Nilsson and Grennfelt [Nilsson, 1986; Nilsson and Grennfelt, 1988]. Critical load is defined as a quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur, according to present knowledge.

The concept was accepted in 1988 as a basis for the development of control strategies and further agreements on emission reductions under the UN ECE Convention on Long-Range Transboundary Air Pollution. Based on this concept, critical-load maps have been developed for acidification and for sulphur and nitrogen deposition for large parts of Europe. By using the maps and source-receptor matrices for sulphur and nitrogen emissions in Europe, control strategies are presently being developed.

At a workshop in 1988, a set of critical-load values for acidification and nitrogen deposition to terrestrial ecosystems was derived. For acidification these values were based on soil mineralogy (Table 3.4). For nitrogen two different concepts were studied—one based on observed ecosystem
effects and one based on long-term nitrogen balances within the actual system. Later, more sophisticated methods were developed using static and dynamic models of the processes involved.

**Table 3.4.: Critical loads for the acidification of forest soils.**

<table>
<thead>
<tr>
<th>Class</th>
<th>Minerals Controlling Weathering</th>
<th>Usual Parent Rock</th>
<th>Total Acidity (kmol H⁺ km⁻² yr⁻¹)</th>
<th>Equivalent Sulphur (kg ha⁻¹ yr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Quartz, K-feldspar</td>
<td>Granite, quartzite</td>
<td>&lt;20</td>
<td>&lt;3</td>
</tr>
<tr>
<td>2</td>
<td>Muscovite, plagioclase, biotite (&lt;5%)</td>
<td>Granite, gneiss</td>
<td>20-50</td>
<td>3-8</td>
</tr>
<tr>
<td>3</td>
<td>Biotite, amphibole (&lt;5%)</td>
<td>Granodiorite, gray-wacke, schist, gabbro</td>
<td>50-100</td>
<td>8-16</td>
</tr>
<tr>
<td>4</td>
<td>Pyroxene, epidote, olivine (5%)</td>
<td>Gabbro, basalt</td>
<td>100-200</td>
<td>16-32</td>
</tr>
<tr>
<td>5</td>
<td>Carbonates</td>
<td>Limestone, marlstone</td>
<td>&lt;200</td>
<td>&lt;32</td>
</tr>
</tbody>
</table>

Critical loads for acidification of soils are usually based on the concept of aluminium toxicity. Generally, Al⁺⁺⁺ concentrations are set to 0.2 mmol L⁻¹ or a critical Al⁺⁺⁺ :Ca⁺⁺ molar ratio is usually set to 1.0 [Hettelingh et al., 1991; de Vries, 1991]. For nitrogen a mass-balance criterion is normally based on either maximum allowed leaching of nitrate or a maximum long-term build-up of nitrogen in the ecosystem [Grennfelt and Thörnelöf, 1992]. In most cases, critical loads for lakes are based on critical levels of alkalinity, which may be set to 0-50 μeq L⁻¹ [Hettelingh et al., 1991]. Although the critical-load concept has not been applied to marine areas the concept might be useful as a tool for assessing the importance of atmospheric deposition for the eutrophication of marine estuaries and coastal areas [Grennfelt and Thörnelöf, 1992].

The critical-load concept has been used to map critical loads in Europe, in parts of North America, and to a minor extent in southeast Asia [Hettelingh et al., 1991; de Vries et al., 1992; Kuylenstierna et al., 1992]. Mapping for southeast Asia is based on a judgment of relative sensitivity based on soil type, rock type, land use and vegetation, and the ratio of precipitation to potential evapotranspiration (Fig. 3.4).

The critical-load concept is susceptible to criticism because the determination of a numerical value requires specification of the total deposition from all mechanisms. Quantification of wet deposition is relatively straightforward; however, dry deposition and deposition by fog are much harder to quantify. This is not very important in regions distant from sources (such as Scandinavia and much of Canada), where wet-deposition rates dominate, but in other areas, dry deposition is important and may well constitute most of the deposition that defines a relevant critical load.

To apply the critical-load concept, we must first consider whether dry deposition can be accurately taken into account. A key factor is the simple observation that wet deposition at one location tends to be much the same as that at a neighbouring site, providing the averaging time is long enough; however, this does not apply for dry deposition. Although areal isopleth maps of wet deposition are meaningful and useful, spatial contouring of dry deposition is questionable. In fact, time-averaging helps reveal differences between neighbouring locations and does not smooth dry-deposition patterns. Because it is fundamentally not possible to draw isopleth diagrams of dry deposition in the same way as is done for wet deposition, easy application of the critical-load concept is not possible.

Although these difficulties are well known, the concept of critical loads has been widely adopted. To bypass obstacles imposed by the fundamental physics of the problem, perhaps a
philosophy similar to that used in the case of regulatory air-pollution models, might be profitably employed; that is, recognize the limitations of the model and, in the absence of site-specific total deposition data, focus instead on predicting the probability that deposition will fall in specific ranges. If there is a high probability that critical limits will be exceeded, then appropriate actions can be contemplated.

Control can also be approached in terms of the analogous concept of critical levels, which were established as a tool for developing control strategies for direct effects of air pollutants on ecosystems and materials. A first set of critical levels was formulated in 1988 [UN ECE, 1988], including those for sulphur dioxide, nitrogen dioxide, and ammonia. In 1992 these were revised and extended to include direct effects of acidic particles. Critical levels for sulphur dioxide are only exceeded in areas close to low-level sulphur dioxide sources or near very large emissions (e.g., the lignite coal area in northern Bohemia). Critical levels for NO₂ may be exceeded in urban areas, and those for ammonia may be exceeded in areas with intense farming. Critical levels for the direct impact of acid particles may, however, be exceeded in more remote areas—especially in mountainous areas where the topography may increase fog and cloud-water deposition.

Critical levels are still uncertain and need further development. Synergistic effects, which are known to occur, are only included to a limited extent. If critical levels for sulphur dioxide and ammonia are compared to the deposition that would be caused by such concentrations, the dry deposition of these compounds would be sufficiently large to account for all or most of the allowed deposition. The critical load would, thus, in many areas of Europe, be a stronger control criterion than critical levels. This may not be the case for all parts of the world.

3.7 REVERSIBILITY AND MITIGATION

To what extent and how fast damaged systems will return to preacidification conditions are important questions relevant to the control of acid deposition. These are particularly important issues for soils in glaciated areas where the loss of base saturation has been the most dominant effect. Experimental studies of reduced sulphur and nitrogen inputs have been started in several areas that experience pronounced acidification. At present the few existing results indicate that soils will respond quickly with respect to the transport of sulphur and nitrogen through the ecosystems, leading to a rapid decrease in anion transport. The soil system will then turn to a situation where base cations (weathered or deposited) are being accumulated. However, the base saturation in soils will probably take a long time to recover.

The recovery of acidified lakes when atmospheric deposition has decreased has been studied around the smelters near Sudbury, Canada. These studies showed that lake-water sulphate concentrations decreased along with emissions and deposition and that the reduced sulphate concentrations were followed by a comparative increase in pH [Dillon et al., 1986].

The only long-term way of reducing effects of acid deposition is by eliminating emissions. However, in many areas acidification is so severe that acidified soils and waters have been treated to mitigate acidification effects.

Soil base saturation losses and leaching of aluminium may be treated by alkaline agents. The short-term purpose of such treatments is to increase soil-water pH and thus decrease aluminium toxicity; the long-term goal is to increase base saturation. Experiments with calcium minerals (limestone, etc.) [e.g., Westling and Hultberg, 1991] indicate that it will take a very long time before the limestone penetrates the soil profile and even longer before the response is seen in water outputs. Treatments with more soluble magnesium and potassium show a much shorter response time. Treatments with soluble salts on acidified soils may, however, result in a short-term acid peak in the outflow since the alkaline ions will replace hydrogen ions in the soil profile.

In some countries, particularly Sweden and to a lesser extent Norway and Finland, liming has become a common practice to keep natural fish populations in acidified lakes and streams.
Although liming will not restore a lake or stream to a pre-acidification condition, it will increase pH and calcium, precipitate aluminium, and make it possible for all natural fish to survive and reproduce. In Sweden approximately 6000 lakes are limed [Thörnlof and Degerman, 1991]. Lake liming is, however, only a temporary solution and needs to be repeated frequently, depending on the size and turnover time of the lake. Liming of soils to improve the quality of surface waters is normally not successful because of the slow transport of calcium ions in soils. Liming of bogs and other wetlands may, however, be successful in improving water quality.

3.8 CONCLUSIONS

Many effects may occur from the atmospheric deposition of acidifying compounds. These include:

- direct effects to vegetation, most likely in source areas;
- acidification of soils, which on weakly buffered soils may result in depletion of base saturation and nutrients and, in weathered soils, in increased metal (especially Al$$^{+++}$$) leaching. The effects in soils may lead to decreased forest production, changes in ecosystem composition, and, in severe cases, to ecosystem breakdowns;
- acidification of surface waters, which may lead to the disappearance of populations of fish and other species;
- eutrophication or other nutrient imbalance effects in terrestrial and marine ecosystems;
- corrosion and other effects on materials exposed to the atmosphere or to acidified soils and waters;
- health effects in the form of direct effects from high atmospheric concentrations of primary pollutants (not considered in this report) as well as effects through acidified drinking water that may contain high concentrations of toxic metals (released from the soil as well as from water supply systems).

These effects may be quantified to use such information for emission control strategies. This is currently being done in Europe and North America by the application of the critical-load concept.

Emission reductions have improved the acidification situation with respect to soils and surface waters. It is not yet known, however, to what extent damaged ecosystems will fully recover if emissions are adequately reduced.

Repeated liming is an effective method for restoring damaged surface waters to keep fish populations productive and vital.

3.9 REFERENCES


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CHAPTER 4: ACID DEPOSITION IN EUROPE
H. Dovland and U. Pedersen

4.1 BACKGROUND

Acid deposition in Europe is mainly caused by anthropogenic emissions of sulphur and nitrogen oxides from the combustion of fossil fuels. The main source of sulphur dioxide is the sulphur in fossil fuels used in power plants. Nitrogen oxides are emitted from all combustion processes; thus traffic, power generation, and domestic heating are important sources. The main source of ammonia emissions to the atmosphere is agriculture, particularly the storage and spreading of animal manure. On a European scale, anthropogenic emissions of acidifying components far outweigh emissions from natural sources.

Through the international exchange of relevant emission figures and statistical data, emissions of pollutants relevant to acid deposition in Europe are now reasonably well known. Total European emissions of these components have greatly increased during this century. Sulphur dioxide emissions approximately doubled from 1950 to 1970, were relatively stable during the 1970s, and then decreased to the present level of about 0.6 Tmol (20 Tg S) per year (including the European part of the former Soviet Union). The decrease during the 1980s follows international agreements on emission reductions [see e.g., United Nations, 1992; Sandnes and Styve, 1992]. We know less about nitrogen oxide emissions. However, European emissions of nitrogen oxides have increased dramatically during the last decades, probably by a factor of five from 1955 to the present annual level of about 0.5 Tmol (7 Tg N). Most of the increase occurred before 1970. During the last decade the increase has probably been less than 5% [Pacyna et al., 1991; Sandnes and Styve, 1992]. Ammonia emissions have probably also increased during recent decades because of more intensive agricultural production. Quantitative information on ammonia emissions is, however, scarce.

Acid deposition has caused severe ecological damage in large parts of Europe. The acidification of freshwater has resulted in thousands of lakes, mainly in Scandinavia, being practically devoid of fish. Acid deposition has caused soil acidification and probably plays an important role in forest damage, mainly in central Europe. Significant research and monitoring activities related to acid deposition have been carried out in response to public and political concerns about the damage. Results from these programmes are being actively used in developing international agreements to reduce emissions of air pollutants in Europe.

4.2 DATA SOURCES

Information on air and precipitation chemistries in Europe has been provided through several international networks, namely

- the European Air Chemistry Network (EACN), which was established in the 1950s [e.g., Rodhe and Granat, 1984]
- the Background Air Pollution Monitoring Network (BAPMoN), which was established in 1972
- the Organization for Economic Cooperation and Development (OECD) study on "Long-Range Transport of Air Pollutants" network, which operated in 10 western European countries from 1972 to 1975 [OECD, 1977]
- the Cooperative Programme for Monitoring and Evaluation of Long-Range Transmission of Air Pollutants in Europe (EMEP), which was established in 1977 and organized under the auspices of the United Nations Economic Commission for Europe (ECE) in cooperation with UNEP and WMO. EMEP is now an integral part of the cooperation under the 1979 Geneva Convention on Long-Range Transboundary Air Pollution.
Some European countries have reported data from the same sites to several networks; others have assigned separate stations for separate networks. Several European countries have national networks that complement the sites reporting to the international networks, and results from these national networks are often published in national reports. Data and data evaluations are also available from various shorter-term scientific studies.

We have based our assessment of acid deposition (wet and dry) over Europe on EMEP data for the following reasons:

- EMEP covers the largest area.
- Established quality-assurance procedures are implemented both locally and centrally.
- Experts from EMEP's Chemical Coordinating Centre (CCC) have visited most laboratories and several sites.
- All laboratories participate in annual interlaboratory tests [e.g., Hanssen, 1990; Hanssen and Skjelmoen, 1992].
- The Steering Body of EMEP regularly evaluates and reports on the quality of the data.
- Model calculations are routinely compared to measured data. EMEP employs models using emission data, meteorological data, and transformation and removal parameters to provide concentration and deposition fields for sulphur and nitrogen oxides as well as transfer matrices [e.g., United Nations, 1991; Sandnes and Styve, 1992].

Sampling and chemical analyses are carried out by national laboratories. Methods for sampling and chemical analysis are not strictly standardized, but most laboratories follow a manual of recommended procedures. To check the analytical performance of the participating laboratories, interlaboratory tests are undertaken and results reported annually. Three field tests have been undertaken for comparison of air samplers. The quality assurance procedures include collection and storage of detailed information on each site and its surroundings, sampling equipment, and analytical methods; an audit programme with site and laboratory visits; and detailed data checking (for ionic balance, outliers, etc.).

Ideally, EMEP sites should be located so as to represent areas of about 150 km × 150 km to provide a sound basis for comparison with model calculations. However, because emission densities vary considerably over Europe, strict siting criteria cannot be set. In several cases, sites may underrepresent deposition in their region, since they were deliberately located in areas of less intense emissions and out of the prevailing wind direction from large emissions.

Most long-term results we present here are based on the five-year period 1983-1987 evaluated and reported by Hanssen et al. [1990]. In this period, the EMEP sampling network consisted of about 100 stations (Fig. 4.1). About 80 stations reported both precipitation and air chemistry data; the remaining stations reported either only air or only precipitation data. The measurement programme, based on 24-hour sampling, included all major ions in precipitation and sulphur dioxide, sulphate, nitrogen dioxide, nitrate (\(\text{HNO}_3 + \text{NO}_3\)), and ammonium (\(\text{NH}_3 + \text{NH}_4^+\)) in air. Nitrogen components in air, however, were measured only at a few sites. Further information on the measurement programme at an individual site can be obtained from one of the reports regularly issued by the EMEP/CCC [e.g., Pedersen et al., 1992].
4.3 SUMMARY OF INFORMATION

We based the information on wet deposition and dry deposition in Europe in sections 4.3.1 and 4.3.2 respectively on measurements at EMEP sites in rural areas that were as unaffected as possible by local sources. In urban areas, concentrations of air pollutants like sulphur dioxide and nitrogen dioxide are generally significantly higher than those presented here. Annual average concentrations of sulphur dioxide in European cities have decreased during the last few decades, particularly in western Europe. When we did this assessment, annual average sulphur dioxide concentrations in many European cities were in the range of 300-600 nmol m\(^{-3}\) (20-40 µg m\(^{-3}\)), even higher in some central and eastern European cities. Typical annual averages for nitrogen dioxide ranged from 850 to 1300 nmol m\(^{-3}\) (40-60 µg m\(^{-3}\)). The increased air concentrations normally imply increased levels of dry deposition in urban areas.

Urban areas also influence the chemical composition of local precipitation. A report on urban influence by the United States National Acid Precipitation Assessment Program [Irving, 1991] concluded that precipitation components in urban areas may be between 1.5 and 2 times higher than in rural areas. The United Kingdom Review Group on Acid Rain [UKRGAR, 1990] evaluated the influence of an urban environment on precipitation quality based on data obtained in England, mainly through studies in greater Manchester and Leeds. Their main conclusion was that rainwater acidity in urban areas is not generally very different from regional patterns based on rural measurements. Calcium concentrations are, however, often elevated. In addition, the Manchester results indicated that annual mean concentrations of sulphate may be (up to 30-40%) higher and nitrate and ammonium lower than in rural areas. Our general conclusion is, therefore, that acid
deposition data for urban areas may deviate from those presented below, but the magnitude of the urban influence is variable and highly uncertain.

4.3.1 Wet Deposition

4.3.1.1 Spatial distribution

Precipitation-weighted mean concentrations of non-sea-salt sulphate, nitrate, ammonium, and non-sea-salt calcium for 1983-1987 are shown in Figures 4.2-4.5. Concentration fields were determined by ordinary kriging, a linear estimation technique that provides an unbiased estimator with a minimum estimation variance [Journel and Huijbregts, 1978]. The highest concentrations of sulphate, nitrate, and ammonium were in industrialized and densely populated areas extending from the United Kingdom to Poland and Czechoslovakia. Non-sea-salt concentrations of sulphate varied from above 80 $\mu$mol L$^{-1}$ in southeastern Europe to below 20 $\mu$mol L$^{-1}$ in northern and western Europe. Nitrate concentrations were above 50 $\mu$mol L$^{-1}$ in Germany and Poland and below 20 $\mu$mol L$^{-1}$ in the north and west. For ammonium, the concentration range was similar to that of nitrate, but the spatial distribution showed more small-scale variations.

Figure 4.2: Weighted mean concentrations of non-sea-salt sulphate in precipitation ($\mu$mol L$^{-1}$) for 1983-1987.
Figure 4.3: Weighted mean concentrations of nitrate in precipitation (µmol L\(^{-1}\)) for 1983-1987.

Figure 4.4: Weighted mean concentrations of ammonium in precipitation (µmol L\(^{-1}\)) for 1983-1987.
Figure 4.5: Weighted mean concentrations of calcium in precipitation (μmol L⁻¹) for 1983-1987.

The relative contributions to acid deposition varied somewhat over Europe because of differences in the spatial distribution of emissions. The molar ratio between nitrate and sulphate in precipitation was generally between 1.0 and 1.2 in western Europe and below 1.0 in eastern and northernmost Europe. Thus sulphur was relatively more important over eastern Europe and the nitrogen oxides were more important in the west. The nitrate:sulphate ratio increased at European sites during the 1980s, illustrating that nitrogen oxides were becoming a larger part of acid deposition.

Wet-deposition fields can be determined using the deposition measured at the EMEP sites. However, the spatial variations in the precipitation amounts were considerably larger than those in the concentration values [Granat, 1988]. Therefore, we constructed the spatial distributions of wet deposition of sulphate, nitrate, and ammonium over Europe by multiplying the concentration fields (Figs. 4.2-4.5) by a precipitation field obtained from observations at several meteorological stations in Europe (Fig. 4.6). The precipitation field, constructed by the Meteorological Synthesizing Centre-West (MSC-W) of EMEP at the Norwegian Meteorological Institute, gives the precipitation amount in each 150 km × 150 km EMEP grid square. The precipitation field is, however, based on only two years (averages of 1985 and 1987). To assess how representative these two years were compared to the 1983-1987 period, we compared precipitation amounts from the EMEP stations for the two periods. Our comparison showed that the two-year period was within ±10% of the five-year period for 77% of the stations and within ±20% for 95% of the stations, with no systematic regional differences. Therefore, we used the precipitation field from the two years as a reasonable representation of the five-year period. The resulting deposition maps (Figs. 4.7-4.9) are expected to provide a more accurate pattern than a kriging analysis of deposition as measured at the EMEP sites.
Figure 4.6: Average precipitation (mm) for 1985 and 1987.

Figure 4.7: Average wet deposition of non-sea-salt sulphate (mmol m\(^{-2}\) yr\(^{-1}\)) for 1983-1987.
Figure 4.8: Average wet deposition of nitrate (mmol m$^{-2}$ yr$^{-1}$) for 1983-1987.

Figure 4.9: Average wet deposition of ammonium (mmol m$^{-2}$ yr$^{-1}$) for 1983-1987.
4.3.1.2 Temporal variations

We illustrated the time trends simply by plotting annual mean concentrations and depositions for selected stations against the year. An alternative would have been to base the analyses on groups of stations in the same region, taking into account factors such as the distance to major emission sources and prevailing meteorological conditions. Using groups of stations [see e.g., Rodhe and Granat 1984] was probably better than relying on any single station, where local effects may have influenced time variations. However, the distance between EMEP stations varied significantly, and in most parts of Europe the network was probably not dense enough to study time trends based on area averages.

The time trends are illustrated for four stations with reliable data records and represent northern, western, central, and eastern Europe. Annual average concentrations of sulphate, nitrate, and ammonium in precipitation and wet deposition for 1981-1990 are shown in Figure 4.10 for the following four stations:

![Graphs showing annual wet depositions and concentrations for different stations](image)

**Figure 4.10:** Annual wet depositions (left column) and concentrations (right column) of (A, B) non-sea-salt sulphate; (C, D) nitrate; and (E, F) ammonium, 1981-1990, for Deuselbach (solid triangle), Birkenes (solid square), Eskdalemuir (solid diamond), and Suwalki (solid circle). (See also Fig. 4.14.)
- Birkenes, Norway (in the south about 20 km from the coast in an area forested by coniferous and deciduous trees)
- Deuselbach, Germany (in an agriculture area of mostly arable land with some planted forest on a ridge west of the river Rhine)
- Eskdalemuir, United Kingdom (an isolated observatory in an open moor and heath in southern Scotland)
- Suwalski, Poland (a rural forested area in the Mazuri lake district far (more than 200 km) from major industrial sources and used mostly for recreation)

The nitrate and ammonium concentrations were largely constant over the 10 years, except for a decrease in ammonium at the Polish station. Sulphate concentrations, however, decreased. In the same period, European sulphur emissions were reduced by about 20% (10 countries in western Europe reduced sulphur emissions by more than 50%). The NO\textsubscript{x} emissions were less well known, but they probably increased a few percent during the same period. Thus the trends in concentrations in precipitation broadly agreed with the emission trends.

Interannual variations were generally larger for wet deposition than for concentrations, but the main trends were the same. However, at Birkenes the wet deposition of nitrogen increased during this period.

Figure 4.11 illustrates the average annual variations in concentration and deposition of sulphate and nitrate at Birkenes and Deuselbach. The figure shows for each month the median, maximum, and minimum of the monthly average concentrations (precipitation weighted) and depositions. At both stations there was a late spring or early summer concentration maximum. At Birkenes, the deposition had an autumn maximum because of a large amount of precipitation, but at Deuselbach the deposition was largest in the summer.

4.3.2 Dry Deposition

No routine measurements of dry deposition in Europe were available. Instead, air concentrations were measured as a surrogate for dry deposition. We estimated dry deposition by multiplying the species concentration by the appropriate deposition velocity (see Chapter 2).

4.3.2.1 Spatial deposition

Average concentrations of sulphur dioxide and sulphate in air measured at EMEP sites are shown in Figures 4.12 and 4.13. The highest average concentrations of sulphur dioxide (exceeding 400 nmol m\textsuperscript{-3}) were over Germany, Czechoslovakia, and Poland. For sulphate, which is mainly formed in the atmosphere by oxidation of sulphur dioxide, the maximum was found further to the east, and the spatial gradients were somewhat smaller than for sulphur dioxide.

Nitrogen components in air were measured at fewer stations than sulphur dioxide, and routine measurements had only started fairly recently. Long-term mean values were, therefore, not available and the number of stations was too small to draw isolines. Nitrogen dioxide, nitrate (the sum of gaseous HNO\textsubscript{3} and nitrate on particles), and ammonium (the sum of gaseous ammonia and ammonium on particles) were measured. Table 4.1 shows the annual average concentrations in 1990 for some European countries for which such measurements were available [Pedersen et al., 1992]. For countries with more than one site, we have included the highest and the lowest annual averages. The maximum average concentrations of nitrogen dioxide were over densely populated and industrialized parts of western Europe. Both nitrate and ammonium concentrations were generally lower in northern than in southern Europe, although ammonium concentrations varied significantly over small distances. These variations were probably caused by local ammonia emissions (from agriculture) and may lead to the relocation of some EMEP sites.
Figure 4.11: Monthly averages of concentration (lower curves) and deposition (upper curves) of non-sea-salt sulphate (left column) and nitrate (right column) at (A, B) Birkenes (1981-1990) and (C, D) Deuselbach (1982-1990).
Figure 4.12: Average annual concentrations of sulphur dioxide in air (nmol m\(^{-3}\) yr\(^{-1}\)) at EMEP sites for 1983-1987.

Figure 4.13: Average annual concentrations of sulphate in air (nmol m\(^{-3}\) yr\(^{-1}\)) at EMEP sites for 1983-1987.
Table 4.1: Annual average concentrations of nitrogen compounds in air from some EMEP sites in 1990 (nmol m^-3).

<table>
<thead>
<tr>
<th></th>
<th>Number of Stations</th>
<th>NO_2</th>
<th>HNO_3 + NO_3^-</th>
<th>NH_3 + NH_4^+</th>
</tr>
</thead>
<tbody>
<tr>
<td>Norway</td>
<td>6</td>
<td>29-71</td>
<td>4-19</td>
<td>14-148</td>
</tr>
<tr>
<td>Sweden</td>
<td>5</td>
<td>14-171</td>
<td>4-59</td>
<td>9-144</td>
</tr>
<tr>
<td>Finland</td>
<td>3</td>
<td>36-136</td>
<td>6-27</td>
<td>16-68</td>
</tr>
<tr>
<td>Denmark</td>
<td>2</td>
<td>157-193</td>
<td>79-105</td>
<td>272-285</td>
</tr>
<tr>
<td>United Kingdom</td>
<td>2</td>
<td>--</td>
<td>26-54</td>
<td>66-146</td>
</tr>
<tr>
<td>Netherlands</td>
<td>2</td>
<td>407-885</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Germany</td>
<td>6</td>
<td>85-257</td>
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<td>--</td>
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<tr>
<td>Hungary</td>
<td>1</td>
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<td>54</td>
<td>149</td>
</tr>
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<td>Spain</td>
<td>4</td>
<td>214-321</td>
<td>34-81</td>
<td>101-453</td>
</tr>
<tr>
<td>Italy</td>
<td>1</td>
<td>650</td>
<td>120</td>
<td>--</td>
</tr>
</tbody>
</table>

Source: Data from Pedersen et al. [1992].

4.3.2.2 Temporal variation

Annual mean concentrations of sulphur dioxide and sulphate for 1981 through 1990 are shown in Figure 4.14 for the same four stations used in the precipitation chemistry section. Clear trends were not obvious from these data. There was a slight downward trend at most sites, with some exceptions: concentrations at the Polish site increased during the first half of the period and decreased thereafter. Relatively mild winters in Europe during the last years of the decade probably contributed to the drop in sulphur dioxide concentrations.

Figure 4.14: Average annual concentrations (1981-1990) in air of (A) sulphur dioxide and (B) sulphate for Deuselbach (solid triangle), Birkenes (solid square), Eskdalemuir (solid diamond), and Suwalki (solid circle). (See also Fig. 4.10.)
The annual variation is illustrated by the median and the maximum and minimum of the monthly values for Birkenes and Deuselbach (Fig. 4.15). At both sites, maximum monthly sulphur dioxide concentrations occurred in winter when European sulphur emissions were highest. Meteorological conditions, however, caused large variability in the average winter concentrations. At Deuselbach, the maximum sulphate concentrations occurred during winter; Birkenes showed a late spring or early summer maximum.

Figure 4.15: Monthly averages of sulphur dioxide (left column) and sulphate (right column) concentrations in air at (A, B) Birkenes (1981-1990) and (C, D) Deuselbach (1982-1990).
4.3.3 Model Calculations: Budgets

An essential element in assessing acid deposition in Europe is the use of the large-scale dispersion model. Within EMEP, two Meteorological Synthesizing Centres routinely carry out model calculations of long-range transport and deposition of sulphur oxides and oxidized and reduced nitrogen. Model results are compared with measurements at EMEP sites. In addition to providing concentration and deposition fields, the model results include data specifying the contribution of emissions in one country to the deposition in any other European country (or subarea).

The annual anthropogenic emissions of sulphur oxides in Europe were about 0.6 Tmol (19.4 Tg S), biogenic emissions from the sea were below 0.03 Tmol (1 Tg S) [Tarrason, 1991; Sandnes and Styve, 1992], and the flux of North American sulphur reaching the west coast of Europe was estimated to be 3-6 Gmol yr⁻¹ (0.1-0.2 Tg S yr⁻¹) [Tarrason and Iversen, 1992]. EMEP calculations showed that, of the sulphur emitted to the atmosphere within the EMEP area in 1991, 48% was dry deposited within the area, 28% wet deposited, and 24% transported out of the area (H. Sandnes, personal communication, 1992). Dry deposition is more important near source regions where air concentrations are highest. The EMEP calculations could also be used to describe typical dry:wet deposition ratios over Europe, although there would be local variations that would not fit a large-scale pattern. In large areas of central Europe, the dry deposition of sulphur compounds was 60-70% of total deposition. Thus, in Germany a typical large-scale value for the total annual sulphur deposition was 80 mmol m⁻², of which 50 mmol m⁻² was dry deposited and 30 mmol m⁻² was wet deposited.

Further downwind of the source regions, wet deposition becomes more important. We estimated that for southern Norway about 80% of the deposition was wet deposition; of the total annual deposition of about 25 mmol m⁻², 5 mmol m⁻² was dry deposition and 20 mmol m⁻² was wet deposition. Thus, the wet deposition in southern Norway was similar to that in Germany, but the dry deposition was only one-tenth as much. This difference in regional patterns of wet and dry deposition are illustrated by the data in Figs. 4.7 and 4.13 respectively.

For nitrogen oxides, we estimated that the emissions were about 0.5 Tmol (7 Tg N), of which 24% was dry deposited, 41% wet deposited, and 35% transported out of the area (H. Sandnes, personal communication, 1992). The calculations for nitrogen oxides are probably more uncertain than for sulphur oxides. The pattern of the wet:dry deposition ratio was different from that for sulphur oxides. According to the EMEP calculations, the wet deposition of nitrogen oxides was greater than the dry deposition all over Europe, ranging from about 50% to more than 80% of the total. A typical annual deposition value in Germany was 70 mmol m⁻², of which 60% or 40 mmol m⁻² was wet deposited and 40% or 30 mmol m⁻² was dry deposited. We estimated that the total annual deposition of nitrogen oxides in southern Norway was about 35 mmol m⁻², of which 30 mmol m⁻² or more than 80% was ascribed to wet deposition and only 5 mmol m⁻² to dry deposition.

4.4 REFERENCES


Hanussen, J. E., The eleventh intercomparison of analytical methods within the EMEP, *EMEP/CCC Rep.* 1/90, 64 pp., Chemical Coordinating Centre, Norwegian Institute for Air Research, Lillestrom, Norway, 1990.


CHAPTER 5: DEPOSITION IN NORTH AMERICA
Peter W. Summers

5.1 BACKGROUND

Extending from near the North Pole (82° N) to the subtropics (25° N), the North American continent spans many latitudes and includes a diversity of climatic conditions. In addition, the density of manmade emissions ranges from one of the highest on earth (i.e., in the lower Great Lakes region) to near zero in the remote Arctic. Further, natural emissions of many acidifying and neutralizing substances occur across the region. As a result, a wide spectrum of acidic and alkaline species is found in the deposition.

As in Europe, acidic deposition in North America is mainly caused by anthropogenic emissions of sulphur and nitrogen oxides. Over eastern North America, manmade emissions of these species are an order of magnitude higher than natural emissions. Over this same region, sulphur and nitrogen emissions are equivalent on a molar basis, and the annual average molar ratio of sulphate to nitrate in precipitation is close to unity. The main sources of SO₂ emissions are fossil fuels (especially coal) burned in power plants, ore-smelting operations, and the petrochemical industry. Nitrogen oxides are generated by all combustion processes; vehicular traffic, power generation, and, in winter, heating systems in buildings are the primary sources.

Because of the steady growth of population and industry in North America during the first half of the twentieth century, SO₂ and NOₓ emissions steadily increased. After World War II, these rates of growth accelerated, and emissions of SO₂ reached a peak in the mid-1970s of above 0.5 Tmol yr⁻¹ (15 Tg S yr⁻¹). Since then emissions have decreased to their current levels of about 0.4 Tmol yr⁻¹ (12 Tg S yr⁻¹). On the other hand NOₓ emissions, which doubled from the early 1950s to the late 1970s, have remained steady during the last 15 years at about 0.5 Tmol yr⁻¹ (7 Tg N yr⁻¹).

Concern about the ecological effects of acid deposition developed in the 1970s with the recognition that deposition rates and soil sensitivities in eastern North America were very similar to those in regions of Europe where serious effects were already being documented. As a result, monitoring and research activities expanded dramatically in the 1980s, leading to agreements in Canada and the United States to reduce SO₂ emissions.

5.2 WET DEPOSITION

5.2.1 Sources of Information

Most wet-deposition information in North America comes from several national and regional precipitation chemistry monitoring networks. Because of concern about the long-range transport of pollutants and the effects of acid deposition, the modest sampling density in the 1970s expanded rapidly in the 1980s, reaching a peak near the end of the decade. Because spatial patterns were established and other issues such as air toxics and global change were competing for resources, the number of sampling stations was cut back. Descriptions of the main networks in the United States and Canada and their research results are documented in reports from the two major programmes: the National Acid Precipitation Assessment Program [Sisterson et al., 1989] and the Long-Range Transport of Air Pollutants programme [RMCC, 1990], respectively. Most networks have had rigorous quality control and assurance (QC/QA) programmes, and different samplers have been compared at several sites to ensure data compatibility. The multiyear composite wet-deposition isopleth maps in this chapter are based on those stations shown in Figure 5.1 (about 90% of the total) that meet stringent record completeness and siting criteria. The number of stations increased from about 100 in 1982 to about 200 in 1987; the stations in Figure 5.1 were active in 1988.
Several hundred scientific papers and reports describing many aspects of wet deposition in North America have been published over the last decade. These have not been summarized here. Instead, key aspects of the spatial and temporal behaviour of the main chemical species found in North America are presented so that the results can be compared to other regions of the globe for which there is less information.

To illustrate the temporal variations, six sites (Fig. 5.1) were chosen to represent regions in North America that have differing influences of manmade emissions. The four U.S. sites (weekly sampling) are:

- Hopland (HOP), California, which is about 55 km inland and about 130 km north-northwest of the San Francisco Bay area and is exposed to air masses arriving from the Pacific Ocean
- Mead (MEAD), Nebraska, in the centre of a widespread agricultural area in the high plains continental interior
- Wooster (WSTR), Ohio, located in the industrial heartland of North America where wet deposition of anthropogenic SO$_4^{2-}$ and NO$_3^-$ is highest
- Organ Pipe National Monument (OPNM), Arizona, which is located in the dry interior of the southwestern United States and also represents conditions in northern Mexico (no data are available from Mexico)

The two Canadian sites (daily sampling) are:
The Experimental Lakes Area (ELA), Ontario, which is situated in a remote boreal forest region, well removed from significant anthropogenic sources, and is representative of "background" conditions across central and northwestern Canada.

Longwoods (LWD), Ontario, located in an agricultural region of southwestern Ontario that is heavily impacted by anthropogenic deposition from surrounding high-density emission source regions.

5.2.2 Information Quality

A report on the Global Precipitation Chemistry Programme of BAPMoN [Miller, 1992] examined the quality of the data from various regions of the world. BAPMoN stations in North America, which are a subset of stations from the major national networks in Canada and the United States, were rated as being of high quality. The quality of the complete networks is assumed to be similar. Sampler collection efficiencies ranged from 83% to 100%, with a network average of 92%. The difference between measured anions and cations was well under 10% at most stations, and the network average was about 5%. North American laboratories consistently ranked in the top 10, and often in the top 5, of the over 30 laboratories involved in BAPMoN worldwide.

5.2.3 Sulphate

Spatial distribution. Sulphate is the main ion contributing to the acidity of deposition over North America, especially in the northeast where the average annual molar ratio of $\text{SO}_4^{2-}:\text{NO}_3^-$ is about 1; in winter snowfall, the ratio is closer to 0.5. The six-year average (1982-1987) concentration and deposition patterns for excess (or non-sea-salt) $\text{SO}_4^{2-}$ for eastern North America are shown in Figure 5.2. Both concentration and deposition were at their maximum over and immediately downwind (towards the northeast) of the region with maximum anthropogenic $\text{SO}_2$ emissions. Over the remainder of North America the sulphate concentration was generally less than 10 $\mu$mol L$^{-1}$ and the deposition was less than 10 mmol m$^{-2}$ yr$^{-1}$, except in the heavily populated regions of California and Seattle-Vancouver.
Temporal trends. Several stations had reliable records dating back to 1979. Time trends for these stations were studied independently in the United States and Canada using different analyses and presentations. The NAPAP analyses [Sisterson et al., 1989], fitting linear trends to data from 137 sites, show that, although most have downward slopes, only 8 have trends significant at the p < 0.05 level. In a more sophisticated approach, Sirois [1993] used a Kernel regression smoother to investigate the temporal variations and then fit a geometric time variation model to the data. This technique, applied to daily or weekly samples, produced statistically significant long-term sulphate trends at 24 monitoring sites evenly distributed over eastern North America. In nearly all cases trends were lower in the later years, 1988-1990, than in the earlier years, 1979-1982. The correlation of these trends against the trends of the annual SO₂ emissions integrated over eastern North America were statistically significant at 11 sites.

The annual averages for sulphate concentration and annual deposition are plotted against the year for five stations (Fig. 5.3a and b). Each site shows a downward tendency, with average concentrations over the last few years slightly lower than in the early 1980s.

Figure 5.3: Long-term trends in annual average volume-weighted concentrations (left column) and deposition (right column) of (A, B) sulphate, (C, D) nitrate, and (E, F) ammonium ion at Wooster, Ohio (solid triangle); Mead, Nebraska (cross); Experimental Lakes Area, Ontario (solid squares); Organ Pipe Cactus National Monument, Arizona (solid circle); and Hopland, California (asterisk); see Figure 5.1 for exact location of sites.
Annual cycle. The annual cycles for 1984-1991 for the two sites with daily sampling, Longwoods in the highest deposition region and the Experimental Lakes Area in the lowest, are shown in Figure 5.4. Figure 5.4(a) shows a maximum in the summer for both concentration and deposition at Longwoods; this pattern is typical of the northeastern United States and eastern Canada. At the Experimental Lakes Area (Fig. 5.4b), SO$_4^{2-}$ concentration reached a weak maximum in late winter but was more or less constant for the remainder of the year; the annual deposition cycle was strongly influenced by precipitation amount.

![Graph showing SO$_4^{2-}$ concentration and deposition over time](image)

Figure 5.4: The 1984-1991 monthly averages (and maximum and minimum values) of volume-weighted concentration (lower curves) and deposition (upper curves) for sulphate ion at (A) a high-deposition site (Longwoods, Ontario) and (B) a low-deposition site (Experimental Lakes Area, Ontario).

5.2.4 Nitrate

Spatial distribution. Six-year (1982-1987) average concentration and deposition patterns of NO$_3^-$ over eastern North America are shown in Figure 5.5. These patterns are similar to those for SO$_4^{2-}$ (see Fig. 5.2); the maximum occurs over regions with maximum anthropogenic NO$_x$ emissions. Note, however, that the values fall off more rapidly downwind (i.e., to the northeast) than do those for SO$_4^{2-}$ because of the shorter atmospheric residence time for nitrogen species. Except in the heavily populated regions along the west coast, concentrations in western North America were less than 16 μmol L$^{-1}$ and deposition was less than 8 mmol m$^{-2}$ yr$^{-1}$.

Temporal trends. The trend analysis for nitrate (Fig. 5.3c and d) does not indicate the same downward trend shown in the sulphate data. This conclusion was supported by the 24-station analysis by Sirois [1993].
Figure 5.5: Six-year (1982-1987) (A) concentration (µmol L⁻¹) and (B) deposition (mmol m⁻² yr⁻¹) patterns of nitrate (adapted from RMCC [1990]).

Annual cycle. Figure 5.6 shows that the annual cycles for NO₃⁻ concentration and deposition at sites with high (Longwoods) and low (Experimental Lakes Area) deposition were not as pronounced as the SO₄²⁻ cycles at the same sites (Fig. 5.4). Concentrations were generally highest in late winter/early spring, although deposition had a late-spring/early-summer maximum.

Figure 5.6 The 1984-1991 monthly averages (and maximum and minimum values) of volume-weighted concentration (lower curves) and deposition (upper curves) for nitrate ion at (A) a high-deposition site (Longwoods, Ontario) and (B) a low-deposition site (Experimental Lakes Area, Ontario).
5.2.5 Ammonium

The two major cations are ammonium and calcium. Together with sulphate and nitrate anions, they account for about 80-90% of the total ions in precipitation over North America. Although clearly as important as sulphate and nitrate in determining the acidity of precipitation, neither ammonium nor calcium measurements have been as rigorously analysed.

Spatial distribution. The spatial patterns of six-year average \( \text{NH}_4^+ \) concentration and deposition (Fig. 5.7) were quite different from those of \( \text{SO}_4^{2-} \) and \( \text{NO}_3^- \). They were clearly driven by the agricultural activity in the Midwest and Great Lakes regions.

![Map](image)

Figure 5.7 Six-year (1982-1987) (A) concentration (\( \mu \text{mol L}^{-1} \)) and (B) deposition (mmol m\(^2\) yr\(^{-1} \)) patterns of ammonium (adapted from RMCC (1990))

Temporal trends. The annual values for 1979-1991 for the five sites in Figures 5.3(e) and (f) show no clear trend. More detailed statistical tests were not available.

Annual cycle. The annual cycles for Longwoods and the Experimental Lakes Area are shown in Figure 5.8. At Longwoods, concentrations were highest in spring, although deposition had both a spring and a summer peak. At the Experimental Lakes Area, concentrations were high during winter; deposition, driven by rainfall, was high in the summer.
Figure 5.8: The 1988-1991 monthly averages (and maximum and minimum values) of volume-weighted concentration (lower curves) for ammonium ion at (A) a high-deposition site (Longwoods, Ontario) and (B) a low-deposition site (the Experimental Lakes Area, Ontario).

5.2.6 Calcium

Spatial pattern. The spatial distribution of Ca\(^{++}\) concentration was somewhat similar to that of NH\(_4\)\(^+\) but was still not very coherent. A systematic emissions inventory for Ca\(^{++}\), against which to compare these patterns, was not available.

5.3 AIR CONCENTRATIONS

Except at a few research sites, the dry deposition of acid species has not been directly measured. Such measurements require detailed observations of the surface (e.g., stomatal behaviour), of atmospheric parameters immediately above the surface (e.g., wind speed, turbulence), and of the near-surface gradients of species concentration. From such research studies the concept of a deposition velocity (\(u_d\)) has developed, whereby the dry-deposition flux at a given location is calculated as the product of the species concentration and \(u_d\). As a first step in estimating dry deposition, patterns of air concentrations must be established (see Chapter 2). This section briefly summarizes some of the more important aspects of rural air concentration measurements in North America and concludes with some point estimates of dry-deposition fluxes of sulphur.

5.3.1 Information Sources

Information on regionally representative air concentrations (as distinct from those in urban areas) is limited. One source is the Air and Precipitation Network (APN), which was established in the late 1970s at six sites in eastern Canada and expanded slowly through the 1980s [Sirois and Fricke, 1992]. Another source is the research and routine monitoring networks set up in the United States in the mid- to late 1980s [Sisterson et al., 1989]. The latter networks were specifically designed to provide the basis for extending detailed air concentrations and dry-deposition calculation methods to stations where simpler measurements were made.
5.3.2 Sulphur Species

Spatial patterns. The 1989 pattern of median SO$_2$ concentration in Figure 5.9 shows that annual values of rural SO$_2$ concentrations were highest (>100 nmol m$^{-3}$) in a band across the states south of the Great Lakes and across to the east coast. Particulate SO$_4^{2-}$ concentrations (Fig. 5.10) were highest (>50 nmol m$^{-3}$) across the same region. These regions could reasonably be expected to have the highest deposition fluxes of SO$_2$ and SO$_4^{2-}$.

Figure 5.9: Median concentrations (nmol m$^{-3}$) of SO$_2$ at nonurban sites in eastern North America in 1989 (based on data from IJC (1992))

Figure 5.10: Median concentrations (nmol m$^{-3}$) of SO$_4^{2-}$ at nonurban sites in eastern North America in 1989 (based on data from IJC (1992))
Temporal trends. The U.S. network data record is too short to carry out a meaningful analysis of long-term trends at this time. Data from the six Canadian APN stations have been analysed (RMCC, 1990) using the technique described for precipitation data [Sirois, 1993]. Only one site showed a statistically significant trend in particulate SO₄²⁻ concentrations. Four stations showed significant SO₂ trends, all strongly downward from the early to late 1980s. Data from the remote (ELA) and polluted (Longwoods) sites are shown in Figure 5.11. At ELA, with near background levels of SO₂ and SO₄²⁻ of between 10 and 20 nmol m⁻³, there was considerable year-to-year variability but no evidence of a trend since 1983. At Longwoods, SO₂ has been almost constant since 1983 but SO₄²⁻ has had a slight downward trend.

Figure 5.11 Long-term trends at (A,B) a polluted site (Longwoods, Ontario; 1983-1992) and (C,D) a remote site (the Experimental Lakes Area, Ontario; 1979-1992) in annual average ambient air concentrations of SO₂ (left column) and SO₄²⁻ (right column). (Data for graph were extended three years from data in Sirois and Fricke (1992)).

Annual cycle. The annual cycle is discussed in detail in Sirois and Fricke (1992). Figure 5.12 shows the data for the two Canadian sites. At the polluted site (Longwoods), the annual SO₂ and SO₄²⁻ cycles were out of phase; SO₄²⁻ showed a maximum in summer and a minimum in early winter; SO₂ showed the reverse but with a greater amplitude. At the clean site (the Experimental Lakes Area), the SO₂ and SO₄²⁻ cycles were in phase with summer minima.
5.3.3 Nitrogen Species

Spatial patterns. In Canada the concentrations of particulate nitrate (p-NO$_3^-$), nitric acid (HNO$_3$), and ammonium (NH$_4^+$) are greatest over southwestern Ontario and fall off rapidly towards the north and northeast [Sirois and Fricke, 1992]. Annual average concentrations at the polluted and clean Canadian sites (Table 5.1) fall into the same ranges given for Europe in Table 4.1 for p-NO$_3^-$ + HNO$_3$, but the NH$_4^+$ values are lower in Canada.

<table>
<thead>
<tr>
<th>Site</th>
<th>Annual Average Concentration</th>
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<td></td>
<td>P-NO$_3^-$</td>
<td>HNO$_3$</td>
<td>NH$_4^+$</td>
</tr>
<tr>
<td>Polluted (LWD)</td>
<td>40</td>
<td>25</td>
<td>117</td>
</tr>
<tr>
<td>Remote (ELA)</td>
<td>5</td>
<td>5</td>
<td>23</td>
</tr>
</tbody>
</table>

Source: Data from Sirois and Fricke [1992].
5.3.4 Estimates of Dry-Deposition Flux

Because of the large spatial variability of the surface characteristics that affect the dry-deposition velocity (see section 2.5.2), contour maps of dry-deposition flux cannot be readily derived from the concentration fields in Figures 5.9 and 5.10. However, these fluxes can be calculated at any monitoring site where there are appropriate air concentration and meteorological measurements and local land-use classifications. Slightly different approaches have been used in Canada and the United States. In 1984, an exploratory network (CORE) was established at a few nonurban sites across the United States. Results from this network show that, averaged over two to three years, the dry deposition of sulphur and nitrogen is generally about 0.4 to 1.0 times the wet deposition [Sisterson et al., 1989]. Using the Canadian network, Sirois and Barrie [1988] estimated that dry deposition of sulphur and nitrogen is between 0.2 and 0.7 times the wet over four years. The dry-deposition velocities used by NAPAP and Sirois and Barrie are within the ranges in Table 2.3. The percentage of the total deposition that is dry tends to fall off with distance from the area of highest emission density.

Atmospheric mass budgets for sulphur can give regionally integrated estimates of dry-deposition fluxes. (Budgets are discussed in more detail in Chapter 13.) Dry deposition can be estimated from measurements as follows [RMCC, 1980]. Over the region bounded on the west by the Mississippi Valley and the Ontario/Manitoba border and on the north by latitude 55°N, annual emissions of sulphur in the mid-1980s were about 0.30 Tmol yr⁻¹ (9.6 Tg S yr⁻¹). The outflow into the Atlantic, determined from a series of WATOX measurement programmes [Galloway and Whelpdale, 1987], was 0.11 Tmol yr⁻¹ (3.5 Tg S yr⁻¹), while the amount of wet deposition measured over eastern North America was 0.10 Tmol yr⁻¹ (3.3 Tg S yr⁻¹). Neglecting smaller terms, such as inflow from the west and fog deposition at high elevation, the dry-deposition flux necessary to balance the input and output would be 0.09 Tmol yr⁻¹ (2.8 Tg S yr⁻¹). Thus, averaged over eastern North America, dry deposition was about 0.8 of wet.

5.3.5 Rural versus Urban Deposition

In North America, because of the concern about the impact of acid deposition on ecosystems, most monitoring was in rural and remote rather than urban areas. The information in this chapter is based on rural data, a fact which must be borne in mind when comparing the magnitudes of concentrations and deposition with other regions covered in this report, where mainly urban data are used.

Comparisons between urban and nearby rural wet-deposition measurements in North America are summarized in the NAPAP report [Sisterson et al., 1989]. Many factors affect the results, including the spatial configuration of emission sources, local climate, and prevailing winds. Chicago and Philadelphia, for example, two large cities cited in the NAPAP report, are both in regions with moderate regional deposition (approximately 25 nmol S m⁻² yr⁻¹). Deposition within and immediately downwind of these cities is enhanced by a factor of 1.5 to 2.0. About 25 km downwind of Halifax, Canada, where regional deposition is considerably lower (approximately 15 nmol m⁻² yr⁻¹), the urban impact is estimated at 50% of the total.

Air concentrations show bigger differences between rural and urban areas, especially for SO₂. For example, Windsor, Hamilton, Toronto, and Montreal in eastern Canada have mean annual ambient SO₂ concentrations 3 to 10 times higher than the nearby rural concentrations on which the contours in Figure 5.9 were based. For ambient SO₂ the urban enhancement is about a factor of 2 over the nearby rural areas. Large differences in roughness parameters, wind flow, and the biological characteristics of urban and rural surfaces make it extremely difficult to estimate the difference between urban and rural dry-deposition fluxes.
5.4 SUMMARY

Because of the large-scale precipitation chemistry monitoring efforts over the last decade, the extent and intensity of acidic wet deposition in North America (and western Europe) are well documented. The processes of dry acid deposition are well understood, but its measurement is more difficult and geographical variations are not well characterized. Nonetheless, the data show a strong geographical association between maximum wet and dry acid deposition and the regions of and immediately downwind of maximum SO$_2$ and NO$_x$ emissions. Approximately two-thirds of the emissions in eastern North America are being deposited back into these regions.

In response to the documented adverse ecological impacts of this deposition, the governments of Canada and the United States had by the mid-1980s and early 1990s established control strategies to decrease emissions of SO$_2$ significantly over the next decade. Future trends in the deposition of acidic sulphur species are thus expected to continue downwards. Model predictions indicate that, over most of eastern North America, wet deposition will fall below the target load of 20 kg S ha$^{-1}$ yr$^{-1}$ by early next century.

The outlook for the nitrate contribution to acidic deposition is not so clear. Present international agreements call only for freezing NO$_x$ emissions at 1987 levels and applying the best available, economically achievable technology to new sources. Both the United States and Canada continue monitoring and research programmes to assess the contribution of NO$_x$ emissions to ecological acidification and the formation of ground-level ozone. However, no large changes are expected in either NO$_x$ emissions or NO$_3^-$ deposition over the next decade.

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5.5 REFERENCES

CHAPTER 6. REGION OF THE FORMER SOVIET UNION
Richard S. Artz, Alexey Ryaboshapko, and Winston Luke

6.1 INTRODUCTION

Observations of precipitation chemistry in the Russian Federation began in the early years of the twentieth century. However, until the 1950s they were conducted sporadically. Beginning in the International Geophysical Year (1957-58), Professor Ye. S. Seleznева, and V. M. Drozdova (Drozdova et al., 1964) conducted routine and systematic precipitation chemistry observations. This network began with 13 stations, primarily in the European part of the former Soviet Union. The initial purpose was to determine the general characteristics of natural precipitation composition over large background areas and the influence of meteorological conditions on precipitation composition. The original programme has grown through Soviet participation in many international programmes such as the International Background Monitoring (IBM) network, the Background Air Pollution Monitoring Network (BAPMoN), and the Co-Operative Programme for Monitoring and Evaluation of the Long Range Transmission of Air Pollutants in Europe (EMEP). It continues to evolve as questions are raised about human impacts on the natural cycling of chemicals through the environment. Other regional programmes monitoring precipitation chemistry were also implemented [Andreev and Rozhkova, 1971; Chernjaeva et al., 1978; Sopauskiene et al., 1992].

For this publication, we refer to the following territories as the former USSR (FUSSR): Armenia, Azerbaijan, Belarus, Estonia, Georgia, Kazakhstan, Kirgiz Republic, Latvia, Lithuania, Republic of Moldova, Russian Federation, Tajikistan, Turkmenistan, Ukraine, and Uzbekistan. The FUSSR is a vast territory covering about 17% of the global land area. This territory can be subdivided into several climatological and geographical zones, ranging from deserts and subtropics in the south to the Arctic tundra in the north. Because such diverse geophysical conditions create highly variable atmospheric and precipitation chemistry, an extensive monitoring network was required to cover the entire area. Before 1975, there were 23 precipitation chemistry monitoring stations in the FUSSR and trace atmospheric composition had not been studied at the regional level. By 1990 there were 85 operational BAPMoN stations, 15 IBM stations, and 11 EMEP stations in the region. Snow-cover chemistry has been analysed annually (during the period of maximum snow accumulation) since 1979, and a 263-station national precipitation chemistry network, started in 1988, was operating in the early 1990s. Aerosols and gases were also measured at the EMEP (Table 6.1) and IBM stations (Table 6.2). Precipitation chemistry, aerosol, and gas measurements were in demand because increasing anthropogenic emissions from vehicles, power plants, and industry during the twentieth century were suspected of having adverse environmental and human health effects.

According to Rovinsky [1988] the increase in SO₂ emissions was largest between 1960 and 1979 because petroleum consumption increased. Rovinsky estimates approximately 55% of the SO₂ was from heat and power production, 44% from industrial operations, and about 1% from transportation emissions. For NOₓ, 37% of emissions were from heat and power production, 13% from industrial operations, and 50% from transportation.
Table 6.1: Precipitation, gas, and aerosol sampling and analysis techniques at the EMEP network in the former Soviet Union.

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Sampling</th>
<th>Analytical</th>
<th>Dates</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_4^{2-}$</td>
<td>Open funnel</td>
<td>Thorin; ion chromatography</td>
<td>1980-1992</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>Open funnel</td>
<td>Flame photometry; atomic absorption</td>
<td>1980-1992</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>Open funnel</td>
<td>Ion chromatography</td>
<td>1990-1992</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>Open funnel</td>
<td>Griss; ion chromatography</td>
<td>1984-1992</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>Open funnel</td>
<td>Indophenol; ion chromatography</td>
<td>1982-1992</td>
</tr>
<tr>
<td>Ca$^{++}$</td>
<td>Open funnel</td>
<td>Flame photometry; atomic absorption</td>
<td>1982-1992</td>
</tr>
</tbody>
</table>

**Gases**

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Sampling</th>
<th>Analytical</th>
<th>Dates</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_2$</td>
<td>Semi-liquid absorption</td>
<td>Tetrachloromercurate method</td>
<td>1985-1989</td>
</tr>
<tr>
<td></td>
<td>Impregnated filter</td>
<td>Thorin; ion chromatography</td>
<td>1990-1992</td>
</tr>
<tr>
<td></td>
<td>Automatic monitor</td>
<td></td>
<td>1990-1992</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>Semi-liquid absorption</td>
<td>Griss</td>
<td>1986-1992</td>
</tr>
</tbody>
</table>

**Aerosols**

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Sampling</th>
<th>Analytical</th>
<th>Dates</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_4^{2-}$</td>
<td>Watman-40 filters</td>
<td>Thorin; ion chromatography</td>
<td>1980-1992</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>Watman-40 filters</td>
<td>Griss; ion chromatography</td>
<td>1986-1992</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>Watman-40 filters</td>
<td>Indophenol; ion chromatography</td>
<td>1986-1992</td>
</tr>
</tbody>
</table>

Source: From the EMEP network in the former Soviet Union.

Table 6.2: Gas and aerosol sampling and analysis techniques used at IBM stations in the former Soviet Union.

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Sampling</th>
<th>Analytical</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_2$</td>
<td>Semi-liquid absorption</td>
<td>Tetrachloromercurate method</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>Semi-liquid absorption</td>
<td>Zaitseman</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>Hi-vol filtration</td>
<td>Turbidimetry</td>
</tr>
</tbody>
</table>

Estimates of total sulphur and nitrogen emissions were uncertain, and credible budgets for the FUSSR that could be used to support the emission or deposition values were scarce. For sulphur, Rovinsky [1988] estimated that for the European FUSSR about 0.2 Tmol (12.8 Tg) of SO$_2$ was emitted in 1980 and 0.17 Tmol (11.1 Tg) in 1985, with forecasted emissions of 0.15 Tmol (9.6 Tg) for 1990. Dignon [1992] estimated that 1980 SO$_x$ (SO$_2$ plus SO$_4^{2-}$) emissions for the entire USSR were about 0.4 Tmol yr$^{-1}$ (25.6 Tg SO$_2$). Recent assessments of anthropogenic sulphur emissions into the atmosphere over the FUSSR and Europe [Ryaboshapko et al., 1994; Mylona, 1993; Ryaboshapko, 1990] indicate that the actual emissions were probably higher than the Rovinsky estimates, which did not include emissions from small sources or military sources. Additionally, although a rapid drop in official emission values for sulphur was noted after the Economic Commission for Europe's (ECE) protocol requiring a 30% decrease in SO$_2$ emissions came into force, there was little evidence of change by the energy-production industry that would remove sulphur dioxide, even though some fuel switching may have occurred.

Estimates for total nitrogen emissions were even less certain. Rovinsky [1989] estimated that 1980 NO$_x$ emissions for the eastern FUSSR were about 0.061 Tmol (2.79 Tg NO$_x$) and 1985 emissions were about 0.064 Tmol (2.93 Tg); they have been fairly stable since. Dignon [1992] reported that NO$_x$ emissions for the entire FUSSR were about 0.31 Tmol yr$^{-1}$ (4.4 Tg N yr$^{-1}$) in
1980. Pacyna et al. [1991] estimated that NO$_x$ emissions were about 0.15 Tmol yr$^{-1}$ (7.11 Tg NO$_2$ yr$^{-1}$) for the western FUSSR, a value supported by an annual per capita emission of 0.81 kmol (37.2 kg NO$_2$ yr$^{-1}$), which is very close to the eastern European estimate of 0.79 kmol yr$^{-1}$ (36.4 kg NO$_2$ yr$^{-1}$). Considering the use of fossil fuels in the FUSSR to produce electricity and heat and the extent of gasoline and diesel oil consumption in the transport sector, the NO$_x$ emission estimates by Pacyna et al. were probably not overestimates. Contrary to Rovinsky's [1988] estimates that 50% of NO$_x$ emissions in the FUSSR were from transportation, Ryaboshapko [1990] estimates that transportation contributions did not exceed 38%. Ryaboshapko also presented stationary source, transport, and total NO$_2$ estimates for the FUSSR and notes that, as for SO$_2$, official estimates are likely to be biased low. We know of no NH$_3$ emission estimates for the FUSSR.

6.2 WET-DEPOSITION ASSESSMENT

Figure 6.1 shows the monitoring stations whose data were used for this report. Additional information regarding specific programmes is discussed below.

- EMEP
- IBM
- BAPMoN

Figure 6.1 Monitoring stations in the former Soviet Union from three precipitation chemistry networks: the Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP, solid square), International Background Monitoring (IBM, solid circle), and Background Air Pollution Monitoring Network (BAPMoN, solid star)
Sampling and analyses differed significantly between the networks, depending on the requirements of the specific international programme or on the regional problems to be studied. The precipitation sampling periods were 1 month at BAPMoN stations, 10 days at IBM stations, and 1 day at EMEP stations. The data from those stations in industrialized cities may reflect local atmospheric pollution levels. Samples were analysed using different methods, depending on the technical capabilities of the participating analytical laboratories. These circumstances affected data quality and thereby limited our use of the information for this assessment.

Concentrations of sea-salt ions in precipitation decrease very quickly away from coastal areas. Conversely, the continental atmosphere can be enriched by calcium and other elements of aeolian origin. The entrainment of eroded soils surrounding the Aral Sea into precipitation suggests high levels of sea salt, despite the fact that this area is very far from the world's oceans and that the composition of Aral Sea water does not resemble that of ocean water. Attempts to determine excess sulphate, calcium, or other ions typically found in sea water for atmospheric samples collected from interior areas of the Euro-Asian continents can lead to serious errors. We made no sea-salt corrections in the analyses for this chapter.

### 6.2.1 Data Sources

Wet-deposition data for the FUSSR were based on field observations of precipitation chemistry. For the European FUSSR, wet-deposition levels have also been calculated using numerical models operated by the EMEP programme. The calculation methods and results have been published in numerous articles and reports (see Chapter 4 for references). The field measurement programmes and resulting data sets are discussed next.

#### 6.2.1.1 National Precipitation Chemistry Monitoring Network

**Data source.** The National Precipitation Chemistry Monitoring Network, established during the late 1950s, operated as a part of the international Background Air Pollution Monitoring Network (BAPMoN) during the early years. The Main Geophysical Observatory (MGO) provided the scientific and methodological guidelines for the network. The network consisted of 263 stations designed solely to monitor and study precipitation chemistry. These stations were both in background areas and near relatively large cities (see Fig. 6.1). Specialists from the MGO divided the FUSSR BAPMoN stations into two groups, background stations and conditional background stations, where the impact of local anthropogenic emission sources on precipitation chemistry could be observed [Zaitsev and Sivistov, 1989]. To the best of our knowledge, the stations we used in this report were background stations. According to the sampling protocol, precipitation was collected by event using a bulk collector that remained covered except during precipitation events. Liquid samples were poured from a polyethylene bottle into a common container to obtain a monthly averaged sample. Frozen samples were collected in a metal snow tray, allowed to melt, and then treated as liquid samples. To exclude dry-deposited materials from the sample, the precipitation collector was opened by an operator just before precipitation started and closed just after the event was over. Artz and Lavrinenko [1993] give station-siting criteria, sampling equipment, and collection protocol.

Samples were analysed at both MGO and six regional laboratories for all major ions using the analytical chemical techniques described by Artz and Lavrinenko [1993] (Table 6.3). Results from the BAPMoN stations were issued approximately every five years in MGO reports [see Sivistov, 1985, 1986a, 1986b, 1991; Zaitsev and Sivistov, 1989].
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Technique</th>
<th>Accuracy</th>
<th>Detection Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphate</td>
<td>Estimated from the intensity of turbidity when BaCl is added*</td>
<td>±15%</td>
<td>0.1 mg⁻¹</td>
</tr>
<tr>
<td>Chloride</td>
<td>Titration using Hg(NO₃)₂</td>
<td>±10%</td>
<td>0.1 mg⁻¹</td>
</tr>
<tr>
<td>Nitrate</td>
<td>Reduction using amalgamated Cd and subsequent colorimetric estimate of nitrite ions using Griss reagent</td>
<td>±10%</td>
<td>0.05 mg⁻¹</td>
</tr>
<tr>
<td>Ammonium</td>
<td>Photometric estimate using Nessler's reagent</td>
<td>±10%</td>
<td>0.05 mg⁻¹</td>
</tr>
<tr>
<td>Sodium</td>
<td>Flame photometry</td>
<td>±8%</td>
<td>0.01 mg⁻¹</td>
</tr>
<tr>
<td>Potassium</td>
<td>Flame photometry</td>
<td>±8%</td>
<td>0.05 mg⁻¹</td>
</tr>
<tr>
<td>Calcium</td>
<td>Atomic absorption spectrometry</td>
<td>±8%</td>
<td>0.01 mg⁻¹</td>
</tr>
<tr>
<td>Magnesium</td>
<td>Atomic absorption spectrometry</td>
<td>±8%</td>
<td>0.01 mg⁻¹</td>
</tr>
<tr>
<td>Acidity/Alkalinity</td>
<td>Reverse titration in the presence of a mixed indicator of equal volumes of 0.2% methyl red and 0.1% methylene blue; positive values indicate alkalinity, negative values indicate acidity; HCO₃⁻ defined as alkalinity</td>
<td>±15%</td>
<td>1 mg⁻¹</td>
</tr>
<tr>
<td>pH</td>
<td>Electrometric estimation using reference and glass indicator electrodes; instrument is calibrated using standard buffer solutions</td>
<td>±2%</td>
<td>0.01 unit</td>
</tr>
<tr>
<td>Specific conductivity</td>
<td>Conductivity metre at 25°C; cell constant = 1.0, determined using KCl</td>
<td>±10%</td>
<td>0.1 μS cm</td>
</tr>
</tbody>
</table>

*Presence of colloidal substances makes these measurements difficult.

**Data quality.** The chemical analysis techniques used by the FUSSR BAPMoN network were not of high accuracy, although the accuracy of individual measurements of any major ion did not exceed the network limit of approximately ±30% (Table 6.3) [Rovinsky, 1989, 1990]. The quality of the chemical analyses was controlled by MGO using standard quality assurance methods such as intercalibration and blind sample analyses. The main criterion for data quality evaluation is the extent to which analysed samples deviate from the ion balance. Typical deviations at MGO were approximately ±10%. Samples analysed by the Tallinn regional laboratory had a mean deviation of less than 1% (Ryaboshapko, unpublished data, 1992). We could not find a separate list of the stations whose data were analysed at the Tallinn Laboratory.

The sampling methods used at the FUSSR BAPMoN stations posed the greatest problems for data quality. There were two potential sources of collection error. First the lid of the precipitation collector used was designed to be opened manually just before a precipitation event and closed shortly after the event. The operation was performed by an unmonitored field observer. Such a protocol is difficult to follow, especially at night when the first part of an event could easily be missed. Also, if the lid were not closed during a dry period, dry deposition could affect the sample. For instance, during the dusty periods typical of the southern semidesert and desert regions, contamination from dry deposition of large aerosol particles, which cannot be quantified, is a potentially serious problem. Second, monthly samples were not refrigerated or chemically treated to suppress biological processes. During the warm season bacteria multiply in samples and destroy biologically active substances, principally nitrogen compounds and weak organic acids. Therefore, concentration data, especially from the warm months, for nitrate, ammonium, and pH were suspect. We were unable to estimate how extensive this problem was.

**6.2.1.2 Integrated Background Monitoring (IBM) Network**

**Data source.** The IBM network, which was used to observe both atmospheric and precipitation chemistry, relied on the biosphere reserve system already in place in the FUSSR and was included in the Global Environmental Monitoring System (GEMS). The locations of some stations coincided with those of BAPMoN sites (see Fig. 6.1). The protocols for atmospheric monitoring within the
biosphere reserves were established in 1976. By 1990, there were 15 stations of this type in the FUSSR and many others in Bulgaria, Hungary, the former GDR, Poland, Romania, and the former Czechoslovakia. The Institute of Global Climate and Ecology provided scientific and methodological guidelines for this network.

The IBM observation programme included precipitation chemistry and atmospheric concentrations of sulphur dioxide, nitrogen dioxide, and sulphate aerosol (Table 6.2). Precipitation was sampled as it was for BAPMoN but for 10-day periods. Samples were refrigerated at +4°C before being analysed at the MGO or regional laboratories according to BAPMoN protocols.

Mean seasonal values derived from statistical analyses of data collected by the IBM network were published in annual reports [Israel and Rovinsky, 1992], although individual analyses were not. We found additional information in "Bulletins of the Background State of the Environment in CMEA Member Countries" [e.g., Rovinsky, 1989, 1990] and through other publications by Rovinsky [1988] and Israel and Rovinsky [1991].

Data quality. Collecting individual precipitation samples reduces errors and contamination in the field. However, since funnel lids had to be opened and closed manually, the early parts of any event, especially at night, were likely to be excluded. Refrigerating the samples in the field did inhibit biological processes, but the samples were not refrigerated during the two weeks they were in transit to the appropriate laboratories. Therefore, the same data quality problems found for the nitrogen compounds collected according to BAPMoN protocols could also be expected for the IBM network.

The reliability and compatibility of observations collected by the cooperating countries in this network were assessed through regular quality control tests [Rovinsky, 1990]. This included the use of certified references and chemical standards to calibrate instrumentation, interlaboratory analysis of uniform test solutions and natural samples, and simultaneous measurements of pollutant concentrations under field conditions. An instrument calibration was conducted in 1989 using chemically pure solutions for sulphate, nitrate, and ammonium. FUSSR samples were analysed at three regional analytical laboratories that apparently underwent interlaboratory analysis. The relative error in the measurements did not exceed the ±30% limit [Rovinsky, 1989, 1990] accepted by the experts from the cooperating countries. In addition, a bilateral intercomparison between the FUSSR and Finland in 1989 showed that measurements of sulphur and nitrogen compounds in the atmosphere and precipitation were sufficiently compatible to allow practical use of the data from both countries. Thus, despite known deficiencies in the IBM measurement protocols for these substances, the reported data were still useful.

6.2.1.3 EMEP network

Data source. Practically all stations in the Co-Operative Programme for Monitoring and Evaluation of the Long Range Transmission of Air Pollutants in Europe (EMEP) are located along the FUSSR western border. The three EMEP stations used in this analysis are shown in Figure 6.1. The EMEP stations were established at existing meteorological stations meeting the EMEP sitting criteria. By 1990, there were 11 EMEP stations in the FUSSR. (The current status of several stations is unknown; some may no longer be in operation.) The Institute of Global Climate and Ecology provided scientific and methodological guidelines for the network.

The observation programme carried out at the stations corresponded to the third phase of EMEP and included daily precipitation, gas, and aerosol sampling (see Table 6.1). For precipitation sampling, the collector surface was thoroughly cleaned every day, regardless of the occurrence of any precipitation event the previous day. This procedure significantly reduced the contribution of dry deposition to the collector surface, especially during long periods of dry weather. However, the protocol did not require refrigerating or chemically preserving collected samples.
Until recently, all samples from the EMEP network in the FUSSR were analysed at a specialized laboratory in Latvia. Samples from three top-priority stations (Janiskoski, Lahemaa, and Syrve) were also partly analysed at the central chemical laboratory in Moscow. More recently, EMEP precipitation samples have been analysed in laboratories in each of the three Baltic states and in the Russian Federation. At some stations, precipitation pH was measured at the sampling station immediately after collection. The analytical techniques used for precipitation chemistry, gas, and aerosol samples in the EMEP network are summarized in the 1989 EMEP data report (Table 6.1) [Schaug et al., 1991].

Recent data for the Russian EMEP stations have not been published in the EMEP data reports. However, they were available either through the EMEP Chemical Coordinating Centre (CCC) or from the Institute of Global Climate and Ecology in Moscow. Monthly, seasonal, and annual data summaries were published in the EMEP CCC Annual Reports [e.g., Pederson et al., 1992].

Data quality. Precipitation sampling and collection techniques used by the EMEP network should have adequately prevented dry deposition from contaminating precipitation samples. The chemical analyses should have been more reliable than for other FUSSR precipitation chemistry networks. The manual "wet" chemistry techniques used ensure that any single measurement of major ion concentration in precipitation is accurate to within ±30% and that the mean monthly values calculated from the daily sample data are accurate to within ±10%. The quality of analyses within EMEP was controlled through intercalibrations that routinely indicated that many analyses were within 10% of the expected value, although there were frequent outliers.

Unfortunately, the Russian EMEP network was suffering from the same problem of degradation of nitrogen compounds that was plaguing the BAPMoN and IBM networks. Although precipitation samples were refrigerated at the stations and laboratory, they could not be kept cool during the approximately two weeks it took for them to be transferred from field to laboratory.

6.2.1.4 Snow-pack monitoring

One network in the FUSSR monitored air pollution and acid deposition to snow cover; it consisted of 933 stations, 457 of which were in the European FUSSR. Many stations were located where no observations of pollution had been previously made. The network was developed around the existing Snow Survey Network of Goskomhydromet, which was designed to measure the physical parameters of the snow cover. Samples were collected through the entire depth of the snow cover, melted, filtered, and sent to chemical laboratories where SO₄²⁻, NO₃⁻, NH₄⁺, pH, and several metals and organic compounds were measured. Results from the snow-core analyses generally agreed with comparable precipitation chemistry and aerosol measurements, indicating higher levels of anthropogenic materials in the western FUSSR relative to Asian sections of the Russian Federation and somewhat higher levels near large cities relative to agricultural or remote areas. The network was useful in identifying areas of strong transboundary fluxes of anthropogenic SO₄²⁻ and NO₃⁻ and in tracking the deposition and flux of soil materials [Vasilenko et al., 1987]. Even though the network had begun operating in 1980, few data are available and there is little information on the movement of ionic materials between soils and snow pack. No attempt was made to assimilate the snow-pack chemistry measurements into the current study.

6.2.1.5 Results

There were serious problems with the quality of the data from the three FUSSR sets, several of which were common to all three national networks, and quality seemed to decline as sampling periods lengthened. We had to assume that using manual collectors did not completely compromise the data and that the two-week unrefrigerated mailing period did not cause major chemical changes in the samples. We also had to assume that BAPMoN and, to some extent, IBM sample quality was not compromised by the amount of time samples were in the field before being analysed.
The same evaporation problems found in the FUSSR monitoring programmes have also been encountered in North America. A Canadian study cited by Chan et al. [1985] documented summertime evaporative losses of close to zero for 1-day sampling periods and up to 26% for 28-day sampling periods. They estimated seasonal evaporative losses of from 0.6% to 5%, depending on the effectiveness of the lid seal when using the 28-day sampling period. In the FUSSR, the designated protocols, when followed, kept sample evaporation from being a problem at the EMEP and BAPMoN stations. However, at the IBM stations, where samples were collected only every 10 days, they suffered from evaporative and snow losses.

Several studies [Willoughby et al., 1990; Tang et al., 1987; de Pena et al., 1985; Keene et al., 1983; and Hutzinger, 1991] have documented chemical changes in precipitation chemistry samples from volatilization, chemical conversion, particle dissolution, biological uptake or conversion, and adsorption/desorption on the collection vessel walls. Except for the results in the de Pena et al. [1985] study, indications are that weekly and longer sampling periods produce higher ion concentrations than daily sampling, except for hydrogen ion and ammonium, which have lower concentrations.

Based on information in the above-cited studies, we expected some contamination from dry deposition on the collectors, even if the observers had strictly followed sampling protocols. Changes to sample chemistry were also likely because of the long intervals between sample collection and analysis. Therefore, we concentrated our efforts on understanding the more stable ionic components and avoiding the most labile species. Below we present only sulphate, nitrate, and calcium information from all three networks and do not consider the ammonium or pH records. Nitrate values were probably not too reliable, but the cold climate at most FUSSR sites would have helped ensure reasonable data quality.

Figure 6.2 shows the precipitation-weighted mean concentrations of sulphate, nitrate, and calcium for a subset of stations from each network for five years, 1981-1985, where possible. Even though the regional differences were clear, we chose not to contour the plots because of differences among the networks. The highest concentrations of sulphate and nitrate were in the European sector of the FUSSR. The data for all ions from Shahrinau (far southwestern FUSSR) were suspect, and data for sulphate and calcium from Ust-Bolsheretsk (Far East) were extremely high.

The wet-deposition data for the same components and stations are shown in Figure 6.3. These have been constructed by multiplying the precipitation concentration fields referred to above by precipitation measurements recorded at the same stations for the same periods. Calcium deposition tended to be lower in Siberia than in other areas; sulphate and nitrate deposition values, as expected, were higher in more industrialized eastern Europe.

We graphed the annual average concentrations for sulphate, nitrate, and calcium in precipitation for those periods available between 1971 and 1991. Figure 6.4 shows the values for five stations falling generally along the latitude band of approximately 60° N; Figure 6.5, for five stations falling generally along the latitude band of approximately 45°N. Nitrate concentrations were highest in the European FUSSR at both latitudes and relatively low elsewhere. Sulphate concentrations were between about 20 and 40 µmol L⁻¹ except at Razdolnoye in the Far East and Svitjaz in industrialized eastern Europe. Information was not available on emission trends, and we did not try to infer trends from this data set.
Figure 6.2  Precipitation-weighted mean concentrations (μmol L⁻¹) of sulphate, nitrate (in parentheses) and calcium (in brackets) for a subset of stations from each network (see Figure 6.1) for 1981-1985 where possible.

Figure 6.3  Wet-deposition values (mmol m⁻² yr⁻¹) for sulphate, nitrate (in parentheses) and calcium (in brackets) for a subset of stations from each network (see figure 6.1) for 1981-1985 where possible.
Figure 6.4  (A) SO$_4^{2-}$, (B) NO$_3^-$, and (C) Ca$^{2+}$ in precipitation from 1971-1991 at Lahemaa (solid triangles), Siktivkar (solid circles), Turukhansk (solid squares), Suntar (asterisks), and Magadan (open triangles), all stations falling generally along the latitude band of approximately 60°N (see Figure 6.1)
Figure 6.5  (A) SO\textsubscript{4}\textsuperscript{2-}, (B) NO\textsubscript{3}\textsuperscript{−} and (C) Ca\textsuperscript{2+} in precipitation from 1971-1991 at Svityaz (solid triangles), Pyatigorsk (solid circles), Alma-Ata (solid squares), Khuzhir (asterisks), Razdolnuye (open triangles), all stations falling generally along the latitude band of approximately 45°N (see Figure 6.1)
We plotted the annual average concentrations for sulphate and nitrate from five stations in the European FUSSR (Fig. 6.6) to compare sample concentrations from nearby stations in the three networks. From this comparison we found that concentrations from the EMEP station at Lahemaa were routinely lower than those from the nearby BAPMoN stations. Those from the BAPMoN station at Voelikovo agreed well with those from the IBM station at Valday (for 1991 only). Arzt and Lavrinenko [1993] found that precipitation chemistry concentrations tend to be overestimated at FUSSR stations.

![SO₄²⁻ Concentration, μmol L⁻¹](image1)

![NO₃⁻ Concentration, μmol L⁻¹](image2)

Figure 6.6  (A) SO₄²⁻, (B) NO₃⁻ in precipitation from 1971-1991 at Valday (solid triangles), Prella (solid circles), Shilute (solid squares), Voelikovo (asterisks), and Lahemaa (open triangles) (see Figure 6.1)

We also plotted the corresponding annual average depositions for sulphate, nitrate, and calcium in precipitation for those periods available between 1971 and 1991 for the latitude bands of approximately 60°N (Fig. 6.7) and approximately 45°N (Fig. 6.8). Figures 6.7 and 6.8 suggest that deposition of sulphate was higher in the European FUSSR and in the Far East and somewhat lower in the interior areas of Asia. Nitrogen deposition was highest in the European FUSSR and generally very low elsewhere; calcium deposition was higher in the south than in the north. As before, we did not try to infer trends from this data set.

Figures 6.9-6.11 illustrate the average intra-annual variations in concentrations and deposition for six selected stations for 1981-1985, except for Lahemaa where the period was 1985-1990 and for Magadan where the 1983 data were missing. Figures 6.9-6.11 show the maximum and minimum monthly concentrations and deposition as well as the volume-weighted mean monthly concentrations and arithmetic mean depositions. Concentrations were generally lowest in the summer for sulphate, nitrate, and calcium ions and highest in the spring and fall. Highest concentrations and depositions were in the European FUSSR for sulphate and nitrate, with occasional exceptions along the Pacific coast. Deposition values for the whole territory tended to be at a maximum during the summer because of the heavy summer precipitation.
Figure 6.7: Annual average deposition from 1971-1991 for (A) sulphate, (B) nitrate, and (C) calcium in precipitation at Lahemaa (solid triangles), Siktivkar (solid circles), Turuhansk (solid squares), Suntar (asterisks), and Magadan (open triangles), all stations falling generally along the latitude band of approximately 60° N (see Fig. 6.4).
Figure 6.8: Annual average deposition from 1971-1991 for (A) SO\textsubscript{4}\textsuperscript{2-}, (B) NO\textsubscript{3}\textsuperscript{-}, and (C) Ca\textsuperscript{2+} in precipitation at Svityaz (solid triangles), Pyatigorsk (solid circles), Alma-Ata (solid squares), Khuzhir (asterisks), Razdelnoye (open triangles), all stations falling generally along the latitude band of approximately 45° N (see Fig. 6.5).
Figure 6.9: Average monthly concentration (lower curves) and deposition (upper curves) for $\text{SO}_4^{2-}$ (left column) and $\text{NO}_3^-$ (right column) at (A, B) Lahema (1987-1991) and at (C, D) Pyestigorsk (1981-1985).

Figure 6.10: Average monthly concentration (lower curves) and deposition (upper curves) for $\text{SO}_4^{2-}$ (left column) and $\text{NO}_3^-$ (right column) at (A, B) Turuhansk (1981-1985) and at (C, D) Pyestigorsk (1981-1985).
Figure 6.11: Average monthly concentration (lower curves) and deposition (upper curves) for $\text{SO}_4^{2-}$ (left column) and $\text{NO}_3^-$ (right column) at (A, B) Magadan (1981-1988) and (C, D) Razdolnoye (1981-1986).
6.3 DRY-DEPOSITION ASSESSMENT

6.3.1 Introduction

Most of the world's dry deposition estimates are based on the calculation of the product of air concentration and an estimated dry-deposition velocity. Very few programmes measure dry deposition directly. This was also true in the FUSSR, where dry-deposition estimates were the product of atmospheric concentration values determined as part of the EMEP and IBM programmes and deposition velocities gleaned from the literature and sporadic field programmes. Estimates have typically been made for sulphate, nitrate, sulphur dioxide, and nitric acid. We knew of no comprehensive study where dry deposition had been estimated for the entire FUSSR. As a result, we discuss only the major air concentration programmes below and give one example where actual dry-deposition estimates had been made.

6.3.2 Organized Atmospheric Concentration Measurement Programmes

6.3.2.1 EMEP programme

Air concentration measurements within EMEP are discussed in Schaug et al. [1991]. The analytical laboratories for these measurements are in Latvia and Moscow. The filter-pack method used to measure sulphur dioxide from 1980 to 1989 tended to underestimate sulphur dioxide concentrations because samples were not refrigerated during the mailing period. The Soviet EMEP network used the West and Gaeke (or tetrachloromercurate) method for measuring SO$_2$. The new, more reliable impregnated-filter technique provides sulphur dioxide concentration measurements accurate to ±40% and mean monthly values to ±25%. The use of an automatic SO$_2$ gas analyser at the Janiskoski station improved the estimated accuracy to approximately ±10%. Sampling and analysis techniques for the other gaseous pollutants measured by the FUSSR EMEP programme resulted in accuracies of ±50% at best.

The measurement accuracy of sulphate and other aerosols depends upon the chemical analysis technique used. Manual (wet chemical) techniques are accurate to within ±40%, while ion chromatography is accurate to within ±30% for a single measurement.

6.3.2.2 IBM network

Analysis of mean daily gas and aerosol samples is carried out directly in the biosphere reserve just after sampling. Sampling was done using semiluid absorption or high-volume filtration techniques. Analytical techniques included a tetrachloromercurate method for SO$_2$, the Saltsman method for NO$_2$, and a turbidimetry method for SO$_4$$^{2-}$.

The estimated error for individual sample concentration measurements for sulphur dioxide, nitrogen oxides, and sulphate aerosol was about ±30%. Assuming a log-normal frequency distribution of pollutant concentrations at background stations, the error of a mean monthly value should not have exceeded ±10%.

6.3.3 Dry-Deposition Estimates

As stated above, dry deposition was not directly measured in these networks; only trace gas and aerosol concentrations were. Dry deposition of sulphur and nitrogen over the European part of the country has been modelled within the framework of EMEP. In some regions, such as Estonia, the Leningrad District, and the Kola Peninsula, special studies have attempted to assess the magnitude of dry deposition and its contribution to the total flux of pollutants from the atmosphere.

As an example of the potential importance of dry deposition, we examine one such study [Tuovinen et al., 1993; Sivertsen et al., 1992] which estimated dry deposition of sulphur over the
Kola Peninsula. Annual sulphur dioxide emissions, which exceed 0.008 Tmol yr⁻¹ (0.5 Tg yr⁻¹) are from a few point sources. Deposition is controlled by the nature of underlying surfaces (lakes, soils, vegetation) and by meteorological conditions (see Table 6.4). Long summer hours of sunlight are conducive to plant respiration, while long polar nights have high atmospheric stability and high aerodynamic resistance to deposition. Because of frequent summer rains, underlying surfaces are continually wet. The sulphur dioxide concentration field, determined from a semiempirical climate model, showed an area of approximately 8000 km² (including approximately 1500 km² in Norway) with levels above 0.3 μmol m⁻³ (20 μg m⁻³), the level considered hazardous for terrestrial ecosystems on the Kola Peninsula. Based on the results of Tuovinen et al. (1993) and Sivertsen et al. (1992), we estimated that an area of approximately 150,000 km² (including 20,000 km² in Norway and 30,000 km² in Finland) had dry deposition in excess of 9 mmol m⁻² yr⁻¹ (0.3 g S m⁻² yr⁻¹), a level generally considered hazardous for terrestrial ecosystems. If the threshold levels for concentration and deposition are indeed correct, dry deposition poses a greater environmental threat here than do ambient concentrations. Most dry deposition occurred with wet vegetated surfaces, indicating that an exceptionally acidic solution formed on the surfaces of leaves and needles. Dry deposition is estimated to exceed 50% of the total deposition on the Kola Peninsula and to be as much as 90% near sources. Regional precipitation was not highly acidic: the mean annual pH at the EMEP station closest to the emission sources, Janiskoski, was between 4.7 and 4.9, and the snow-cover pH was even higher.

Table 6.4: Seasonal dry-uptake velocities for sulphur.

<table>
<thead>
<tr>
<th>Velocities (cm s⁻¹)</th>
<th>Warm</th>
<th>Transitional</th>
<th>Cold</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₂</td>
<td>1.0</td>
<td>0.8</td>
<td>0.2</td>
</tr>
<tr>
<td>SO₄⁻</td>
<td>0.15</td>
<td>0.1</td>
<td>0.005</td>
</tr>
</tbody>
</table>

Note: The warm months are June, July, August, September; the transitional months are May and October; the cold months are January, February, March, April, November, and December.

6.4 CONCLUDING REMARKS

Although more wet- and dry-deposition information was available for the FUSSR than for some areas of the developing world, much of it was difficult to interpret and of poorly characterized quality. The data could be improved by

- establishing a central computerized data base to catalogue and assess the quality of all existing data. It was extremely difficult to acquire and process what was mostly a hard-copy data set with no central source;
- expanding the EMEP programme to provide daily precipitation, aerosol, and gas concentration information for use in process-oriented studies. Although this is a difficult task, such information is essential for the generation of chemical transport information and for the development of credible chemical budgets;
- updating field and laboratory protocols. Automated programmes incorporating thoroughly tested, durable equipment should replace manual field-sampling techniques and chemical bench-top analyses. Samples should only be analysed at a few central laboratories;
- establishing nested networks. High emissions of sulphur and nitrogen compounds, heavy metals, and other environmentally important materials currently occur on the Kola Peninsula, in the Ural Mountain region, around Norilsk, and in other areas. Special monitoring programmes should be developed so that the impacts of these emissions can be determined. Special consideration should be given to enhancing monitoring efforts in areas where significant growth is expected over the next several decades.
6.5 References


Ryaboshapko, A., V. V. Sukhenko, and S. G. Paramonov, Assessment of wet sulphur deposition over the former USSR, Tellus, 46B, 205-219.


CHAPTER 7: THE MIDDLE EAST
Richard S. Artz

7.1 INTRODUCTION

Few measurements of precipitation chemistry, aerosols, or gas concentrations are available for this region. The information presented below is from the published literature. With the generally high population growth rate and rapid industrial development in parts of the region, new monitoring programmes and environmental issues will require greater attention in the coming decade.

7.2 EMISSION ESTIMATES

Emissions of nitrogen and sulphur oxides in the Middle East have increased sharply since the early 1970s, particularly in areas where petroleum resources have been developed. Ahmed [1990] reported that total SO$_2$ and NO$_x$ emissions in Saudi Arabia increased sharply between 1974 and 1980, although from 1980 to 1984 total SO$_2$ emissions increased gradually and NO$_x$ emissions decreased. NO$_x$ decreases resulted from the reduced flaring of natural gas. Ahmed also reported that emissions in 1986 were about 16 times higher than in 1971 and that they were consistently higher than those of several European nations. Based on 1980 data Spiro et al. [1992] estimated that total Middle East (Bahrain, Iran, Iraq, Israel, Kuwait, Lebanon, Saudi Arabia, Syria, and South Yemen) SO$_2$ emissions were about 0.045 Tmol yr$^{-1}$ (1.45 Tg S yr$^{-1}$), with almost all from petroleum combustion. Saudi Arabia accounted for about 24% of the total. Ahmed [1990] estimated that 1986 emissions from Saudi Arabia were 0.036 Tmol S (1.15 Tg S) and about 0.017 Tmol NO$_x$ (0.77 Tg NO$_x$).

7.3 PRECIPITATION CHEMISTRY MEASUREMENTS

7.3.1 Israel

Israel's population is about four and a half million people with a population density exceeding two hundred per square kilometre. The two major urban areas along the coast around Tel Aviv and Jerusalem contain over half the population. The main industrial base of Israel is along the coast near Tel Aviv. Precipitation amounts range from about 65 cm annually along the coast to about 50 cm near Jerusalem. Three important factors affect the precipitation chemistry over much of Israel: Saharan dust, Mediterranean aerosols, and anthropogenic emissions from the industrial areas near Tel Aviv.

According to Levin and Lindberg [1979] and Ganor and Mamane [1981], over 20 million tonnes of Saharan dust reach the east coast of the Mediterranean each year. Advedted materials include silicon, aluminium, and calcium, with lesser amounts of potassium, sodium, and chloride; these are wet and dry deposited in the form of quartz, calcite, dolomite, feldspar, and several other materials. Schutz [1980] reported that Saharan dust outbreaks called "Khamsin depressions" are important in the spring. They travel over the eastern Mediterranean and lead to dust-deposition rates of about 0.5-2.5 tonnes km$^{-2}$ hr$^{-1}$ for average Khamsin storms that usually last about one day. Roughly 15 storms can be expected each spring. Mediterranean sea-salt aerosols are important during much of the year and contribute a great deal of the sodium, calcium, magnesium, potassium, chloride, and sulphate deposited along the coast. Mamane et al. [1980] reported that, even in areas such as Tel Aviv where some of the sulphate is likely to be from anthropogenic sources, sulphate attached to insoluble particles of desert origin accounts for much of the aerosol sulphate observed when the flow is from the Sahara via the Mediterranean Sea.

Manes and Segal [1976] analysed fifty precipitation samples collected during the winter of 1973-1974 at eight stations in Israel and reported an average concentration of sulphate of about 12.5 µmol L$^{-1}$, with a maximum concentration of about 41.7 µmol L$^{-1}$ near the Haifa Bay industrial
complex and a minimum concentration of about 3.5 \mu mol L^{-1} in the Golan Heights. They did not estimate what fraction of the sulphate could be traced to sea-salt aerosol.

Mamane [1984, 1987] reported on rainwater collected at eight sites for three hydrological years (1979-1982) using bulk collectors; one station operated daily with rain samples analysed on site according to WMO protocols. Ion balances for the entire set indicated an anion deficit; low pH events had an anion deficit of approximately 20%. The rain was alkaline with a mean pH of 6.5 ± 0.8 and a range from 4.1 to 8.7 during the winter in Israel. The natural components (sea salt and soil minerals) overwhelmed any anthropogenic contributions. Low pH cases were associated with large amounts of precipitation and were accompanied by relatively higher NH_4^+ and NO_3^− concentrations, indicating enhanced anthropogenic contributions. Using Na^+ as a tracer, the sea-salt contributions amounted to 89%, 31%, 65%, 6%, and 60% for the ions Cl^−, SO_4^{2−}, Mg^{2+}, Ca^{2+}, and K^+ respectively. The rest of the chloride fraction and most nitrates were probably associated with industrial sources; much of the remainder of the calcium, sulphate, and magnesium fractions were associated with soil particles.

Mamane et al. [1987], using the bulk event data above and air-parcel back trajectories, confirmed that most precipitation came from air masses that had passed along the Mediterranean Sea or along the North African coast. These events were high in soil and seawater components. Air flow originating in eastern Europe (less than 20% of the total) was associated with acid rain in Israel, probably because of the lack of alkaline materials. Table 7.1 gives precipitation-weighted mean concentrations (\mu mol L^{-1}) for low and high pH rain events in Israel for 1979-1982.

<table>
<thead>
<tr>
<th>pH</th>
<th>No. of Events</th>
<th>Ca^{2+}</th>
<th>Mg^{2+}</th>
<th>K^+</th>
<th>Na^+</th>
<th>NH_4^+</th>
<th>NO_3^-</th>
<th>Cl^-</th>
<th>SO_4^{2-}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low (4.7)</td>
<td>9</td>
<td>10.8</td>
<td>25.6</td>
<td>4.3</td>
<td>253</td>
<td>11.9</td>
<td>2.8</td>
<td>273</td>
<td>39</td>
</tr>
<tr>
<td>High (7.4)</td>
<td>10</td>
<td>256</td>
<td>70</td>
<td>22.1</td>
<td>233</td>
<td>10.6</td>
<td>11.1</td>
<td>392</td>
<td>72</td>
</tr>
</tbody>
</table>

7.3.2 Arabian Peninsula

The Arabian peninsula has a rapidly growing, highly urbanized population. The mean age of the population is less than twenty, and the estimated period for the population to double is about twenty years. Large cities in the region include Riyadh, with a population of about two million, and Jeddah, with a population of approximately one million. Because of the arid climate, much of the peninsula is nearly uninhabited. Annual precipitation over much of the inhabited part of the peninsula is about 10 cm.

Precipitation chemistry data from the region are nearly nonexistent. The two articles cited below give a general impression of the situation. Ahmed et al. [1990] reported on the chemistry of rainwater and atmospheric bulk deposition on the western Arabian Gulf coast. Continuous samples were collected manually on a rooftop station in Dhahran throughout the rainy season between December 1987 and February 1988. Thirteen samples (including one in March 1987) were analysed for pH and major ions. The pH ranged from 5.1 to 7.2 and sulphate, nitrate, chloride, calcium, sodium, and magnesium concentrations were all high; ammonium concentrations were moderate (Table 7.2). Total rainfall for the period was 12.4 cm.
Table 7.2: Average ion concentrations in cloud water (Dhofar, Oman) and winter rain (Arabian Peninsula).

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>Ca$^{++}$</th>
<th>Mg$^{++}$</th>
<th>K$^{+}$</th>
<th>Na$^{+}$</th>
<th>NH$_4^+$</th>
<th>NO$_3^-$</th>
<th>Cl$^-$</th>
<th>SO$_4^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cloud water</td>
<td>7.4</td>
<td>377</td>
<td>119</td>
<td>28</td>
<td>1048</td>
<td>11</td>
<td>76</td>
<td>1242</td>
<td>35</td>
</tr>
<tr>
<td>Winter rain</td>
<td>5.5</td>
<td>232</td>
<td>45</td>
<td>10</td>
<td>131</td>
<td>44</td>
<td>144</td>
<td>144</td>
<td>117</td>
</tr>
</tbody>
</table>

Schemenauer and Cereceda [1992] reported on cloud-water chemistry data near the coast of the Dhofar region of southern Oman in July 1990 using the method of Mohnen and Kadlecek [1989]. The samples came into contact with only Teflon, polyethylene, and polypropylene surfaces. The pH levels were between 7.0 and 7.9, with sulphate values around 35 μmol L$^{-1}$ and nitrate values around 76 μmol L$^{-1}$. Calcium and magnesium values were extremely high at around 9.4 μmol L$^{-1}$ and 4.9 μmol L$^{-1}$ respectively. In general, these numbers probably corresponded to meteorological systems not influenced by anthropogenic emissions and represented the expected concentration ratios from seawater plus the influence of soil cations.

Table 7.2 gives a comparison of the Dhahran and Dhofar data. Note that cloud-water samples frequently contain higher concentrations of major ions than do the rainwater samples and that the Dhahran data are from bulk samples that, in such an arid region, are likely to be contaminated with soil cations. Although the data reported are not corrected for the influence of sea-salt, the Dhahran samples have only a minor influence from seawater and the Dhofar samples have a large additional source of sodium other than seawater. Both data sets have an anion deficit of approximately 10%, suggesting that some additional chemical species were not measured. Although these data should not be overinterpreted, a comparison with the Israeli data indicates that sea-salt and soil cations control the precipitation chemistry at least for these three locations. The Dhahran data also demonstrated a moderate anthropogenic signal, perhaps from regional oil refinery emissions.

7.3.3 Tehran, Iran

Iran has a population of about 52 million, with a population density of about 32 per square kilometre. Approximately 10 million Iranians live in the three largest cities: Tehran with about 6 million and Mashad and Isfahan with about 1 million people each. Most of the country has a dry continental climate, with precipitation amounts ranging between about 20 and 40 cm annually.

The one known data set for Iran contains twelve samples from Tehran for the 1991-1992 hydrologic year (Davood Ahmadi Kermanshahi, Director of Legal and International Affairs of the Iranian Meteorological Organization, personal communication, 1993). The information includes a table describing Tehran precipitation events by date and type as well as the chemical analyses for each precipitation sample (K$^+$, Na$^+$, NH$_4^+$, Mg$^{++}$, Ca$^{++}$, Cl$^-$, NO$_2^-$, NO$_3^-$, pH, and conductivity). Copies of the ion chromatograms for each precipitation sample, calibration curves constructed for each major ion from external standards, and results from two field blanks are included.

Limitations of the data set, however, precluded a thorough analysis. The fraction of events collected was unknown, and the dates of consecutive samples were not sequential. In two cases, multiple samples were collected on the same day. In addition, precipitation amounts were not reported, neither the sample collection protocol nor the sampling equipment were known. Ion balances were poor, especially for high sulphate cases. Despite these limitations, the data set indicates that typical pH values were about 6.5, with occasional values below pH 5.0. Sodium, chloride, and magnesium values were relatively low (approximately 40 μmol L$^{-1}$ for sodium and chloride and 10 μmol L$^{-1}$ for magnesium); sulphate values ranged from about 6 μmol L$^{-1}$ to 250 μmol L$^{-1}$. Nitrate values were typically less than 10 μmol L$^{-1}$. Iranian precipitation probably contains a strong natural signal from soil cations, coupled with a strong anthropogenic signal from petroleum sources.
The few precipitation chemistry measurements available from this region of the world give the impression of precipitation composition influenced strongly by soil dust and, to a lesser extent, by marine ions and anthropogenic emissions near urban and industrial sources.

7.4 REFERENCES


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CHAPTER 8: ACIDIC DEPOSITION IN EAST ASIA AND OCEANIA
G. Ayers, R. Gillett, and H. Hara

The region covered by this chapter extends from Pakistan in the west, through to China and Japan in the east (but excludes countries of the former Soviet Union), and south through the Association of Southeast Asian Nations (ASEAN) countries to Australia and New Zealand.

Before the SCOPE Project on Acidification in Tropical Countries in the mid-1980s [Rodhe and Herrera, 1988], there had been no attempt at a systematic appraisal of the state of acidification and acidic deposition in tropical regions, including the Asian tropics. Yet the knowledge gained from acid deposition studies in Europe and North America, juxtaposed with the knowledge that world population growth, economic development, and growth in energy use are now centred on the Asian region, leads inexorably to the conclusion that the possibility of excessive acidic deposition in Asia requires immediate evaluation. Statistics quoted by Ayers [1991] underscore this point:

- Populations of the ten most populous Asian countries alone exceed 50% of the total global population.
- Most countries in the region have population growth rates at or above the global mean population growth rate of about 1.7% per year, which as a raw statistic implies a population doubling time of only 40 years.
- The region's share of world gross domestic product (GDP) increased from about 14% in 1970 to about 21% in 1988 (and continues to grow), with much of this increase powered by increasing use of fossil fuels.

It is important to translate these attention-grabbing, one-line statistics into a perspective more relevant to a scientific appraisal of acidic deposition in Asia.

Asian emissions of SO$_2$ and NO$_x$ have risen dramatically in the last decade or two and will continue to do so in the future. Based on European and North American precedents, the magnitude of emissions in the 1980s, and the predictions for early next century, acidic deposition is either already occurring or will soon be. These facts motivated the analysis in this chapter.

However, because of the limited quality and quantity of available data on atmospheric acidity, we cannot hope at present to assess properly current or likely future levels of atmospheric acidity or sulphur and nitrogen fluxes to the surface. Few countries within the region had either multisite or multイヤear data sets on acid precursors (SO$_2$ and NO$_x$) or their acidic gas, aerosol, or rainwater products. Where data were available, the geographical representativeness may not have been ideal. More importantly, data quality frequently was unknown or, where known, was poor [Miller, 1992; Ayers, 1991]. Nevertheless, the currently available data provided a starting point for a regional assessment and a base from which future observational programmes could be developed and refined. The few available, good-quality data sets confirmed the imperative outlined above: Deposition fluxes of acidic sulphur and nitrogen in parts of Asia could soon be comparable to those that have adversely affected the environment in acid-sensitive regions of the northern midlatitudes.

The remainder of this chapter is devoted to a description of data sets available from countries (Japan, Korea, China, Hong Kong, India, Malaysia, Indonesia, Australia, and New Zealand) which, at the time of writing, had at least some data relevant to the assessment of present levels of acidic deposition. Not all of the available data sets could be confirmed as ideal or adequate for use in the assessment. One difficulty was simply the paucity of relevant atmospheric composition data from the Asia/Oceania region. A second was that, where data were available, quality was often unquantifiable or demonstrably poor. A third complication was that a large portion of the few Asian data sets available were aimed primarily at urban air quality issues; the measurement sites were near strong emission sources rather than in the more regionally representative (often rural) locations typically chosen for acid deposition assessment. These complicating factors must
be borne in mind when the Asian data are compared with those from the more data-rich areas such as Europe and North America.

The role organic acids play in regulating atmospheric acidity in Asia is not explicitly addressed in this chapter. Although there was some evidence that these organic acids may contribute significantly to the overall acidity in some tropical areas, the published data were insufficient for us to assess their contribution. Chapter 13 contains a general discussion of organic acids, including those in Asia.

A small section at the end of the chapter briefly considers prospects for improvement in the number and quality of regional databases on atmospheric composition and acidic deposition.

8.1 JAPAN

8.1.1 Overview

Since the mid-1960s, a systematic programme of emission control or reduction has been implemented throughout Japan. For SO$_2$, this programme was based on importation of low sulphur fuel, desulphurization of heavy fuel oil, and flue-gas desulphurization. For NO$_x$, the control strategy was based on introducing flue-gas denitrification to stationary sources and developing low-NO$_x$ combustion technology for both stationary and mobile sources.

Monitoring of ambient levels of SO$_2$ and NO$_x$ likewise has been approached in a systematic way in Japan. By 1991, 1,694 stations in 686 municipalities were monitoring SO$_2$ and 1722 monitoring stations in 653 municipalities were monitoring NO$_2$. Figure 8.1 shows clearly how effective these control measures have been for SO$_2$. The situation was somewhat complicated for NO$_x$ because of the partitioning between NO$_2$ and NO and because the number of the mobile sources (i.e., automobiles) kept increasing. Nevertheless, the NO data show a temporal decrease (Fig. 8.1) similar to that for SO$_2$, while NO$_2$ data show evidence of a plateau in concentration with time.

![Figure 8.1: Mean annual gas concentrations of SO$_2$ (solid square), NO$_2$ (×), and NO (open square) averaged across Japanese "General Environment" air quality monitoring stations reflecting a mixture of urban and rural sites.](image)

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Systematic monitoring of acidic wet deposition began on a national scale in 1983, when the Japan Environment Agency (JEA) implemented the Phase I Survey (1983-1987) with 14 bulk deposition sites, 7 of which also had wet-only samplers. In 1985, 15 more sites were added. The Phase II Survey was started in 1988 with the distribution of wet-only samplers to the 23 stations of the Japanese National Air Pollution Surveillance Network, where SO$_2$, NO, and NO$_2$ data were available, and to 6 islands remote from the main islands of Japan. The pH and conductivity were automatically measured for every 0.5 mm of rainfall, and bivweekly (14-day) samples were collected for chemical analysis. Weekly bulk samples were also collected at 5 other stations, where environmental parameters regarding soil, vegetation, and surface water were monitored. In 1993, the Phase III Survey was to be initiated, with emphasis on evaluating critical loads and collecting data for long-range transport modelling. Further, JEA had also proposed an international monitoring network in East Asia, possibly including southeast Asia, (tentatively named the Asian Monitoring and Evaluation Programme, AMEP, after the European programme EMEP).

The Central Research Institute of the Electric Power Industry (CRIEPI) had its own nationwide monitoring network. Monitoring started in 1987 to collect fundamental data on temporal and spatial distributions of acid deposition and to provide basic data for assessing the effects of acidification on terrestrial ecosystems. Precipitation samples were collected with wet-only samplers every 10 days at 21 stations, including 5 remote islands. Gaseous SO$_2$ and major aerosol ions, such as sulphate and nitrate, were also monitored in this network. Before the JEA and CRIEPI networks began, only one station monitored rainwater composition. In 1976, the Japanese Meterological Agency (JMA) established a station at Ryori (39°02'N, 141°50'E), a coastal site several hundred kilometres north of Tokyo, as part of the WMO BAPMoN network. This site provided the longest wet-only rainwater composition record available from Japan. However, only monthly samples were collected and no complementary long-term gas or aerosol records were kept.

Thus, wet-only rainwater sampling was not common in Japan before 1988, although such data existed for the analysis presented below. This analysis should be viewed within the Japanese context defined by the interim results from the bulk sampling data set in the Phase I Survey, that is, that Japanese rainwater is acidic but at lower levels than in acid-impacted areas of Europe and North America [Hara et al., 1990].

8.1.2 Wet Deposition

8.1.2.1 Sources of information

We selected two data sets from the two major nationwide acid deposition data bases available in Japan, JEA and CRIEPI, for this study. From the JEA, we chose a four-year record (April 1984-March 1988) of wet-only, event rainwater composition data from five urban or suburban stations (Tokyo, Nagoya, Osaka, Hiroshima, and Nagasaki). From CRIEPI, we used 12 months of wet-only rainwater composition data from five remote islands, four of which were in the Japan Sea or South China Sea surrounding the main islands of Japan. The latter data were from samples accumulated over 10-day sampling periods. Because none of the JEA or CRIEPI sites was on the Japan Sea coast, we also added a prefectural data base for wet-only, event rainwater data from the Toyama site (TYM) along the coastline. The station locations are given in Table 8.1 and Figure 8.2.
Table 8.1: Japanese rainwater chemistry sites (see Fig. 8.2).

<table>
<thead>
<tr>
<th></th>
<th>Site</th>
<th>Longitude (°E)</th>
<th>Latitude (°N)</th>
<th>Altitude (m)</th>
</tr>
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<td>1</td>
<td>Tokyo</td>
<td>139.5</td>
<td>35.4</td>
<td>21</td>
</tr>
<tr>
<td>2</td>
<td>Nagoya</td>
<td>136.6</td>
<td>35.1</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>Osaka</td>
<td>135.3</td>
<td>34.5</td>
<td>79</td>
</tr>
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<td>273</td>
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<td>6</td>
<td>Toyama</td>
<td>137.1</td>
<td>36.7</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td><strong>Toyama Site</strong></td>
<td></td>
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</tr>
<tr>
<td>7</td>
<td>Oki</td>
<td>133.3</td>
<td>36.3</td>
<td>240</td>
</tr>
<tr>
<td>8</td>
<td>Tsushima</td>
<td>129.2</td>
<td>34.2</td>
<td>10</td>
</tr>
<tr>
<td>9</td>
<td>Fukue</td>
<td>128.7</td>
<td>32.7</td>
<td>10</td>
</tr>
<tr>
<td>10</td>
<td>Amami</td>
<td>129.7</td>
<td>28.5</td>
<td>20</td>
</tr>
<tr>
<td>11</td>
<td>Hachijyo</td>
<td>139.8</td>
<td>33.1</td>
<td>50</td>
</tr>
</tbody>
</table>

Samples were analysed for pH, conductivity, and concentrations of sodium, potassium, magnesium, calcium, ammonium, chloride, nitrate, and sulphate. Data quality was assessed by calculating the ratio of cation sum to anion sum and observed-to-calculated conductivity. If ratios differed from unity by more than 20%, the samples were reanalysed.

Non-sea-salt (nss) components were calculated by assuming sodium to be a conservative tracer for sea salt and estimating sea-salt contributions from the known ionic ratios in seawater [Millero, 1974].

8.1.2.2 Geographical variation

Table 8.2 gives a summary of annual average concentrations and deposition for the major ions. For nss-SO$_4^{2-}$, Tokyo had the highest concentration, an annual average of more than 60 μmol L$^{-1}$; all the other urban/suburban JEA sites had annual average concentrations of about 40 μmol L$^{-1}$, which were still considerably higher than the 10-20 μmol L$^{-1}$ concentrations at TYM and the CRIEPI island sites. The JMA site at Ryori showed a long-term mean nss-SO$_4^{2-}$ concentration near 10 μmol L$^{-1}$ [Miller, 1992], which was consistent with its location away from any immediate sources of anthropogenic emissions. Deposition at all sites ranged from 24-42 mmol m$^{-2}$ yr$^{-1}$. The deposition of nss-SO$_4^{2-}$ in Japan was rather uniform when compared with concentration. Apparently the lower concentrations at Toyama and the island sites were compensated for by higher annual rainfall amounts, which resulted in similar deposition values at all sites. In addition, there was some indication from bulk sampler data that nss-SO$_4^{2-}$ deposition was higher at sites on the Japan Sea coast. In this study, Toyama was the only site on this coast. Elevated deposition in winter was evident from wet-only data at this site.
Figure 8.2: Japanese sites listed in Table 8.1.
Table 3.2: Annual mean (A) rainwater composition, wet-deposition, and (B) air concentration values from Japan Environment Agency, Toyama, and Central Research Institute of Electric Power Industry sites.

### A. Annual mean rainwater composition and wet deposition

<table>
<thead>
<tr>
<th>Site</th>
<th>nss-SO$_4^{2-}$</th>
<th>NO$_3^-$</th>
<th>NH$_4^+$</th>
<th>nss-Ca$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>JEA Network$^1$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tokyo</td>
<td>63.0</td>
<td>79.3</td>
<td>91.9</td>
<td>61.2</td>
</tr>
<tr>
<td>Nagoya</td>
<td>43.8</td>
<td>49.4</td>
<td>55.2</td>
<td>27.7</td>
</tr>
<tr>
<td>Osaka</td>
<td>29.8</td>
<td>32.3</td>
<td>27.6</td>
<td>15.7</td>
</tr>
<tr>
<td>Hiroshima</td>
<td>38.8</td>
<td>30.6</td>
<td>59.8</td>
<td>14.9</td>
</tr>
<tr>
<td>Nagasaki</td>
<td>34.3</td>
<td>18.6</td>
<td>21.4</td>
<td>10.1</td>
</tr>
<tr>
<td>TYM Site$^2$</td>
<td>19.0</td>
<td>15.6</td>
<td>19.4</td>
<td>5.5</td>
</tr>
<tr>
<td>Toyama</td>
<td>17.6</td>
<td>13.0</td>
<td>23.2</td>
<td>5.5</td>
</tr>
<tr>
<td>CRIEPI Network$^3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oki</td>
<td>17.5</td>
<td>11.9</td>
<td>40.8</td>
<td>10.5</td>
</tr>
<tr>
<td>Tsushima</td>
<td>15.6</td>
<td>9.6</td>
<td>18.1</td>
<td>4.4</td>
</tr>
<tr>
<td>Amami</td>
<td>9.7</td>
<td>6.4</td>
<td>8.1</td>
<td>2.4</td>
</tr>
<tr>
<td>Hachijo</td>
<td>10.1</td>
<td>8.1</td>
<td>11.0</td>
<td>3.8</td>
</tr>
</tbody>
</table>

#### Rainwater Composition (μmol L$^{-1}$)

<table>
<thead>
<tr>
<th>Site</th>
<th>nss-SO$_4^{2-}$</th>
<th>NO$_3^-$</th>
<th>NH$_4^+$</th>
<th>nss-Ca$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>JEA Network$^1$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tokyo</td>
<td>38.3</td>
<td>49.8</td>
<td>60.0</td>
<td>37.8</td>
</tr>
<tr>
<td>Nagoya</td>
<td>33.4</td>
<td>27.8</td>
<td>41.8</td>
<td>14.1</td>
</tr>
<tr>
<td>Osaka</td>
<td>24.9</td>
<td>22.2</td>
<td>22.6</td>
<td>10.6</td>
</tr>
<tr>
<td>Hiroshima</td>
<td>32.5</td>
<td>7.0</td>
<td>50.5</td>
<td>9.8</td>
</tr>
<tr>
<td>Nagasaki</td>
<td>28.5</td>
<td>12.5</td>
<td>14.2</td>
<td>7.8</td>
</tr>
<tr>
<td>TYM Site$^2$</td>
<td>41.7</td>
<td>34.3</td>
<td>42.6</td>
<td>12.2</td>
</tr>
<tr>
<td>Toyama</td>
<td>32.0</td>
<td>23.7</td>
<td>42.3</td>
<td>10.0</td>
</tr>
<tr>
<td>CRIEPI Network$^3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oki</td>
<td>26.1</td>
<td>17.7</td>
<td>60.9</td>
<td>15.7</td>
</tr>
<tr>
<td>Tsushima</td>
<td>30.6</td>
<td>18.9</td>
<td>35.5</td>
<td>8.6</td>
</tr>
<tr>
<td>Amami</td>
<td>24.1</td>
<td>15.9</td>
<td>19.9</td>
<td>5.9</td>
</tr>
<tr>
<td>Hachijo</td>
<td>27.6</td>
<td>22.0</td>
<td>29.8</td>
<td>10.4</td>
</tr>
</tbody>
</table>

#### Wet Deposition (mmol m$^{-2}$ yr$^{-1}$)

<table>
<thead>
<tr>
<th>Site</th>
<th>SO$_2$</th>
<th>NO$_2$</th>
<th>nss-SO$_4^{2-}$ (aerosol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>JAE Network$^1$</td>
<td>473</td>
<td>1315</td>
<td></td>
</tr>
<tr>
<td>Tokyo</td>
<td>383</td>
<td>1166</td>
<td></td>
</tr>
<tr>
<td>Nagoya</td>
<td>196</td>
<td>353</td>
<td></td>
</tr>
<tr>
<td>Hiroshima</td>
<td>213</td>
<td>405</td>
<td></td>
</tr>
<tr>
<td>Nagasaki</td>
<td>225</td>
<td>499</td>
<td></td>
</tr>
<tr>
<td>TYM Site$^2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toyama</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CRIEPI Network$^3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oki</td>
<td>32</td>
<td></td>
<td>28</td>
</tr>
<tr>
<td>Tsushima</td>
<td>80</td>
<td></td>
<td>64</td>
</tr>
<tr>
<td>Fukue</td>
<td>90</td>
<td></td>
<td>84</td>
</tr>
<tr>
<td>Amami</td>
<td>44</td>
<td></td>
<td>42</td>
</tr>
<tr>
<td>Hachijo</td>
<td>31</td>
<td></td>
<td>28</td>
</tr>
</tbody>
</table>

Among the JEA urban/suburban stations, the nitrate concentrations followed the pattern of nss-SO$_4^{2-}$, with concentrations highest at Tokyo (≈80 $\mu$mol L$^{-1}$), followed by Nagoya (50 $\mu$mol L$^{-1}$), and then the rest of the JEA stations (20-30 $\mu$mol L$^{-1}$). The CRIEPI island stations all showed systematically lower nitrate concentrations, in the range 6-13 $\mu$mol L$^{-1}$, while the JMA site at Ryori had a long-term mean in the middle of this range [Miller, 1992]. The concentration at Toyama, 16 $\mu$mol L$^{-1}$, was slightly higher than those at the CRIEPI sites.

At the JEA stations, nitrate deposition was highest at Tokyo, much lower at Nagoya, Osaka, Nagasaki, and Hiroshima. At the five CRIEPI island sites, nitrate deposition (20 mmol m$^{-2}$ yr$^{-1}$) fell within the range of the values for Osaka and Nagasaki. Toyama had the second highest wet deposition among the 11 Japanese sites considered here, which may have been because of its heavy precipitation amount.

Both ammonium and nss-Ca$^{2+}$ had similar patterns in concentration and deposition, with concentrations generally lower at the CRIEPI sites and Toyama than at the JEA sites. However, because of the generally higher rainfall at the coastal and island sites, the deposition values in Table 8.2 are more uniformly distributed across all sites.

8.1.2.3 Temporal variation

Annual records of the monitoring results, like many data series in Japan, were compiled on the basis of the financial year, starting on 1 April. For example, published annual values for 1984 covered April-December 1984 and January-March 1985 rather than January-December 1984.

With only a relatively short four-year record available from the JEA data base, we could not reliably interpret the annual average data in terms of significant temporal trends. Within the perspective given by this caveat, the available annual averages in ion concentration and deposition (Fig. 8.3) did not show significant trends for any ions other than nitrate in Tokyo, for which the raw data exhibited an obvious increase in both concentration and deposition. We could not ascertain the significance of this behaviour, which, because of the shortness of the record, should not be overemphasized.

Over seasonal time scales, the concentration data from Tokyo, Nagoya, and Osaka showed no significant variation, although the remaining sites, both JEA and CRIEPI, showed a winter maximum that was converted at most sites to a well-defined June-July maximum in nss-SO$_4^{2-}$ deposition (Fig. 8.4) because of the characteristically strong summer maximum in rainfall at the Japanese sites. In contrast, the single year's data from the CRIEPI sites did not show a distinct summer maximum in rainfall, so this single annual cycle in deposition retained the winter maximum evident in the concentration data. We do not know how representative this single annual picture was.

The seasonal patterns in nitrate concentration and deposition across both data were essentially identical to those for sulphate, indicating a summertime maximum in deposition at the JEA sites in contrast to a wintertime maximum in concentration in the single year's data from the CRIEPI sites. The only exception was for Hiroshima among the JEA sites, for which the data suggested a wintertime maximum in nitrate deposition.

A mixed picture was apparent in the ammonium concentration data. The Osaka data showed relatively little seasonal variation, while the other JEA sites, Tokyo and Nagoya, tended towards summer maxima in concentration. In contrast, Hiroshima and Nagasaki exhibited a tendency towards a winter maximum. In terms of deposition, however, a summertime maximum for ammonium was generally evident. The CRIEPI sites had relatively low, consistent monthly concentrations, interspersed with occasional uncorrelated monthly peaks in concentration. The 12 months of deposition data from these sites showed similar characteristics, with no suggestion of strong annual cycles.
Figure 8.3: Annual mean concentrations in rainwater (left column) and deposition (right column) of (A, B) nss-SO$_4^{2-}$ and (C, D) NO$_3^-$ at Japan Environment Agency sites (Hiroshima, solid square; Osaka, open square; Nagoya, solid diamond; Tokyo, open diamond; Nagasaki, solid triangle).

Figure 8.4: Monthly (minimum, mean, maximum) nss-SO$_4^{2-}$ concentrations (lower curve) and deposition (upper curve) at Hiroshima.
The JEA sites generally showed higher concentrations of nss-Ca\(^{++}\) in winter. Of the CRIEPI sites, Oki, Tsushima, and Hachijyo showed a March peak, which especially for the first two sites could be attributed to the Kosa (dust transport) events from the Asian continent at this time of year [e.g., Suzuki and Tsunogai, 1988]. Deposition of nss-Ca\(^{++}\) was generally lower in autumn and winter at the JEA sites. At the island sites the tendency was for an April peak, except at Tsushima where the single year of available data showed a July peak.

8.1.3 Dry Deposition

8.1.3.1 Sources of information

Although dry deposition fluxes of relevant acidic and basic species were not routinely measured in Japan, concentrations of SO\(_2\) and NO\(_2\) were monitored throughout the National Air Pollution Surveillance Network and prefectural monitoring networks. Thus, data were available from the same study areas in which the JEA and TYM rainwater sampling sites were located. For the CRIEPI programme, SO\(_2\), aerosol sulphate, and nitrate concentrations were determined in conjunction with the rainwater sampling.

8.1.3.2 Geographical variation

Table 8.2 shows that the urban/suburban JEA and TYM sites generally exhibited significantly enhanced SO\(_2\) concentrations compared with the CRIEPI island sites. Among the JEA and TYM sites, Tokyo and Nagoya had the highest and second-highest mean concentrations. Among the CRIEPI stations, concentrations at Fukue and Tsushima were elevated compared with those at the other sites.

The only available aerosol nss-SO\(_4^{2-}\) data for the CRIEPI sites (Table 8.2) correlated well with the SO\(_2\) concentrations.

8.1.3.3 Temporal trends

We discerned no significant temporal trends in annual mean concentrations of SO\(_2\) during the short four-year time span covered by the JEA rainwater composition data base (Fig. 8.5). However, the long-term record of SO\(_2\) concentrations at the Japanese air quality sites showed a decrease with time (Fig. 8.1) consistent with the implementation of the national emission control strategies. Seasonal variations in SO\(_2\) concentration at all sites except Tsushima (which showed an unusual winter peak) were small, perhaps with some minor tendency towards a summer minimum.

![Figure 8.5: Annual mean SO\(_2\) concentration at Japan Environment Agency sites (Hiroshima, solid square; Osaka, open square; Nagoya, solid diamond; Tokyo, open diamond; Nagasaki, solid triangle).](image-url)
Just as with SO$_2$, we found no significant trend in annual mean concentrations in NO$_2$ in the JEA rainwater data base, although Figure 8.1 indicates a secular trend over the longer term. The NO$_2$ data did exhibit a general seasonal trend across all sites, with a summer maximum ascribed to photochemical smog processes.

The relatively small aerosol nss-SO$_4^{2-}$ data records from the CRIEPI sites suggested a significant winter peak.

### 8.1.4 Summary

Table 8.2 contains a summary of the annual average concentrations and deposition fluxes for nss-SO$_4^{2-}$, NO$_3^-$, NH$_4^+$, and nss-Ca$^{++}$ estimated from the mean annual rainfall and ion concentration data from the JEA, TYM, and CRIEPI sites. The annual wet-deposition estimates are comparable in magnitude with typical values from the acid-impacted areas of Europe and North America.

Dry-deposition data were more problematic. However, we were able to provide a rough guide to dry-deposition fluxes as a national average by combining the national average SO$_2$ concentrations with an assumed annual average dry-deposition velocity. By using annual average SO$_2$ concentrations (Table 8.2, Fig. 8.5) and a deposition velocity of 0.003 m s$^{-1}$, we estimated dry-deposition fluxes ranging from 3-45 mmol m$^{-2}$ yr$^{-1}$, which were comparable to the wet-deposition values (Table 8.2).

Gaseous nitric acid is another major dry-deposition component. The very limited concentration data, consisting of occasional observations reported for Tokyo, Osaka, and Mt. Tsukuba (Okita et al., 1976; Ohta et al., 1978; Taguchi and Oka, 1983; Harah et al., 1989), ranged from 0.3-107 nmol m$^{-3}$. When we assumed an annual concentration of 5 nmol m$^{-3}$ (5% of the maximum reported) and a deposition velocity of 0.02 m s$^{-1}$, the dry deposition was 3 mmol m$^{-2}$ yr$^{-1}$.

Considering all the data presented here, we concluded that total acid deposition fluxes over at least some Japanese sites were comparable with fluxes encountered in acid-impacted regions of Europe and northeastern North America.

### 8.2 KOREA

#### 8.2.1 Overview

Relatively few data relevant to acid deposition were currently available from Korea [see Ayers, 1991]. However, because of current interest within Korean academic and governmental institutions, much new work had just begun or was planned for the near future [MST, 1991; ME, 1991a,b]. For our analyses we had only a single 12-month (1989) data series of wet-only precipitation composition from the site at Kanghwa. The quality of the data was confirmed using the usual ion balance and conductivity checks.

SO$_2$ and NO$_2$ concentrations were available for 1991 for five major urban areas: Seoul, Pusan, Kwangju, Taegu, and Ulsan. Although the data quality was unknown, we assumed that it was potentially good since modern pulsed-fluorescence/chemiluminescence measurement techniques were used.

#### 8.2.2 Summary

##### 8.2.2.1 Wet deposition

The available concentration and deposition data from Kanghwa are plotted in Fig 8.6. Nss-SO$_4^{2-}$ and NO$_3^-$ concentrations appeared to peak in winter; NH$_4^+$ concentrations showed no systematic trend. Nss-Ca$^{++}$ concentrations were high in spring, perhaps because of Kosa dust events.
Deposition of nss-SO$_4^{2-}$ and NO$_3^-$ peaked in December, with NH$_4^+$ and nss-Ca$^{++}$ showing slightly earlier peaks in October.

8.2.2.2 Dry deposition

The available SO$_2$ data from large cities (Fig. 8.7a) indicates that Seoul has the highest concentrations, with a clear winter maximum. No such clear seasonal cycle occurs in the analogous NO$_2$ data (Fig. 8.7b). Estimated dry deposition figures can be calculated from the data in Fig 8.7a assuming a deposition velocity of 0.003 m s$^{-1}$. Values in the range 3-45 mmol m$^2$ yr$^{-1}$ result, which may be compared with the wet deposition values in Figure 8.6(b).

Clearly these data can only be seen as indicative: the overall situation in Korea cannot be assessed quantitatively at present owing to the paucity of representative data. However, the possibility that significant wet- plus dry-deposition fluxes exist in some regions is certainly reinforced by the few elements of data that are available.

8.3 CHINA

8.3.1 Overview

Acid deposition, especially in southwestern China, is a serious problem [Zhao et al., 1988]. Wet deposition of sulphuric and nitric acid and the dry deposition of sulphur dioxide and oxides of nitrogen are all implicated. The effects of pollution by acid deposition are seen mainly in forests and on corroded metal and concrete structures. The major source of atmospheric acidity in the form of sulphur and nitrogen species is the burning of fossil fuels, mainly coal for electricity and domestic heating and cooking.

Research into acidic deposition in China began in 1982. During the seventh five-year plan (1986-1990), a research project, National Acid Rain Research, was implemented in four provinces in southwest China. During the eighth five-year plan (1991-1995), the study was expanded to cover the eastern areas of China and to include the transport of acidifying pollutants, technological development, and control strategies such as critical-load mapping.

Coal consumption in China has increased by an order of magnitude from 1953 until 1982, when 71.5 Mt and 641 Mt respectively of coal were consumed. Burning coal accounted for about 74% of the energy produced in 1982 in China; the rest was produced from oil, gas, and hydro power [Zhao et al., 1988]. China has undergone a rapid increase in industrial development and has an economic growth rate above 7% per year. Such economic activity will inevitably increase the installed coal-fired generating capacity from 76 GW in 1990 to a predicted 160 GW in 2000 and 400 GW in 2020 [Liu and McLean, 1992]. Foell and Green [1991] predicted that, under a "business-as-usual" scenario, coal consumption in China will increase to more than 1200 Mt and that SO$_2$ emissions will increase from a 1987 level of 0.3 Tmolyr$^{-1}$ (20 Mt yr$^{-1}$) to near 0.8 Tmolyr$^{-1}$ (50 Mt yr$^{-1}$) by 2020.

The problem in China is exacerbated both because much of the coal is burned in urban areas in small and medium boilers and household stoves and because the sulphur content of the coal is significant. Kato and Akimoto [1992] estimate the weighted average sulphur content of coal used throughout China is 1.35%; however, levels in acid-impacted areas such as the southwest and Shandong Province are considerably higher, at 3-5%. Although the small and medium boilers have some dust-removal equipment, neither they nor the household stoves remove any sulphur dioxide or nitrogen oxides. Since most gases are emitted through short chimneys near ground level, severe pollution episodes result when unfavourable meteorological conditions, such as inversions, prevail.
Figure 8.6: Monthly mean (A) rainwater ion concentrations and (B) wet-deposition values for Kanghwa, Korea, in 1989 (NO$_3^-$, solid triangle; nss-SO$_4^{2-}$, solid square; NH$_4^+$, solid diamond; nss-Ca$^{2+}$, open diamond).
Figure 8.7: Monthly mean (A) SO₂ and (B) NO₂ data from six Korean cities for 1991 (Seoul, solid square; Pusan, open square; Kwangju, solid diamond; Taegu, solid triangle; Taegon, open diamond; Ulsan, open triangle).
Table 8.3 presents annual average concentrations of sulphate, nitrate, ammonium, and calcium in rainwater and the corresponding annual average depositions (where rainfall data were available). The data were taken over three years: 1982, 1984, and 1985. Rainwater samples were collected manually in polythene containers by event. The event samples were then composited and analysed monthly. Sulphate, nitrate, and ammonium were measured by ion chromatography, and calcium, by atomic absorption spectroscopy.

Table 8.3: Annual median concentrations of selected ions and deposition of selected rainwater species in China: 1982-1985.

<table>
<thead>
<tr>
<th></th>
<th>nss-SO\textsubscript{4}\textsuperscript{2-}</th>
<th>NO\textsubscript{3}\textsuperscript{-}</th>
<th>NH\textsubscript{4}\textsuperscript{+}</th>
<th>nss-Ca\textsuperscript{2+}</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Concentrations (\textmu mol L\textsuperscript{-1})</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>North China (16 sites)</td>
<td>66.6</td>
<td>18.1</td>
<td>74.5</td>
<td>93.4</td>
</tr>
<tr>
<td>South China (15 sites)</td>
<td>83.5</td>
<td>21.1</td>
<td>116.7</td>
<td>64.5</td>
</tr>
<tr>
<td>Rural (3 sites)</td>
<td>64.0</td>
<td>8.2</td>
<td>23.4</td>
<td>47.2</td>
</tr>
</tbody>
</table>

| **Deposition (mmol m\textsuperscript{-2} yr\textsuperscript{-1})** | |
| North China (16 sites) | 66.6                           | 18.1            | 74.5            | 93.4            |
| South China (15 sites)  | 83.5                           | 21.1            | 116.7           | 64.5            |
| Rural (3 sites)               | 64.0                           | 8.2             | 23.4            | 47.2            |

Sources: Galloway et al. (1987); Dianwu Zhao (personal communication, 1992).

8.3.2 Wet Deposition

The measured annual average rainwater SO\textsubscript{4}\textsuperscript{2-} concentrations in China varied widely from 1.4 \textmu mol L\textsuperscript{-1} at a background site in southwest China to 288 \textmu mol L\textsuperscript{-1} at Dalian in northern China. Acidic deposition is generally thought to be greatest southwest of the Yangtze River than north of it. This was obvious from a comparison of Beijing and Guiyang, which have mean sulphate concentrations of about 90 and 210 \textmu mol L\textsuperscript{-1} respectively, but not so obvious when comparing other southern areas with Beijing. In fact, Table 8.3 shows that average concentrations of sulphate in rainwater in northern China were higher than in southern China. Wet deposition of SO\textsubscript{4}\textsuperscript{2-} also varied widely from 2.4 mmol m\textsuperscript{-2} yr\textsuperscript{-1} at Qiinghaer to 266 mmol m\textsuperscript{-2} yr\textsuperscript{-1} at Dalian, both in the north of China. Table 8.3 also shows that the median wet sulphate deposition in southern China (84 mmol m\textsuperscript{-2} yr\textsuperscript{-1}) is greater than in northern China (67 mmol m\textsuperscript{-2} yr\textsuperscript{-1}).

Table 8.3 shows that nitrate concentrations in rainwater were significantly lower than the corresponding sulphate concentrations. In fact the mean sulphate:nitrate molar ratio for the individual sites was 5.7:1, indicating that sulphuric acid was the main contributor to the acidity of rainwater. As we expected, the wet deposition of nitrate was also significantly lower than sulphate. The annual median depositions of nitrate were 18 and 21 mmol m\textsuperscript{-2} yr\textsuperscript{-1} in the north and south of China respectively, compared with sulphate values of 67 and 84 mmol m\textsuperscript{-2} yr\textsuperscript{-1} respectively (Table 8.3). Nitrate deposition at individual sites in China ranged widely, from 0.2 mmol m\textsuperscript{-2} yr\textsuperscript{-1} at Jian to 96.9 mmol m\textsuperscript{-2} yr\textsuperscript{-1} at Xiamen.

Ammonium concentrations, which appeared to be correlated with the sulphate concentrations, ranged from 13.5 \textmu mol L\textsuperscript{-1} to 200 \textmu mol L\textsuperscript{-1} for polluted sites. Background sites showed significantly lower ammonia concentrations. The molar concentration ratio of ammonium:sulphate for all Chinese sites was nearly stoichiometric for ammonium sulphate, at about 1.7:1 (ranging from 0.2:1 to about 4:1). This indicated that, on average, the sulphuric acid in rainwater was almost completely neutralized by ammonia. Ammonium concentrations in rain were higher in northern China than in southern China, a pattern that was consistent with observations at most sites in southern China, where rainwater pH values were lower than at sites in northern China [Galloway et al., 1987]. This was especially evident in the southern Chinese cities of Chongqing and Guiyang, where low pH readings have been recorded [Zhao et al., 1988] and where the equivalence ratios of sulphate plus nitrate to ammonium plus calcium were about 1.3:1.

Calcium concentrations at the polluted sites ranged from about 4 \textmu mol L\textsuperscript{-1} at Yanji to about 380 \textmu mol L\textsuperscript{-1} at a Beijing urban site. Calcium concentrations were higher in rainwater in northern China than in southern China (Table 8.3). Calcium clearly plays an important role in neutralizing
rainwater acidity and, with ammonia, must have been responsible for the higher pH values in northern China. Calcium concentrations at background sites were much lower than at urban or rural areas. Wet deposition of calcium at individual sites ranged from 1.5 mmol m$^{-2}$ yr$^{-1}$ at Yanji to 230 mmol m$^{-2}$ yr$^{-1}$ at Dalian, both in northern China. The median values at the northern and southern sites, 93 and 65 mmol m$^{-2}$ yr$^{-1}$ respectively, showed that deposition of calcium was higher in northern China.

The concentration of the ions that primarily influence the acidity of the rainwater had a large range at background sites in China. Sulphate concentrations ranged from 1.4 μmol L$^{-1}$ at Hailuogou in western Sichuan to 60 μmol L$^{-1}$ at Coachai in Guizhou Province. In comparison, sulphate concentration is 4 μmol L$^{-1}$ at the remote site of Katherine, Australia [Galloway et al., 1987]. Concentrations of nitrate ion at background sites were normally about 1 μmol L$^{-1}$ or less, but Zhao and Zhang [1991] report an annual mean concentration of 10.4 μmol L$^{-1}$ at the Caohai site. Generally, background rainwater concentrations were low; however, at sites where concentrations, especially of sulphate and ammonium ions, were higher, composition was probably influenced by anthropogenic emissions.

8.3.3 Dry Deposition

The only published sulphur dioxide data available to estimate dry-deposition fluxes were from residential areas of several northern and southern Chinese cities and from cleaner rural or mountain sites in the same region [Zhao et al., 1988]. These limited data may not be regionally representative. Table 8.4 gives average July, December, and annual sulphur dioxide concentrations from selected sites during 1982 and 1983. In residential areas of China, annual average sulphur dioxide concentrations are high, ranging from 0.81 μmol m$^{-3}$ at Guangzhou to 6.1 μmol m$^{-3}$ at Guiyang and with an average of 2.6 μmol m$^{-3}$ in residential areas. Taking this mean of 2.6 μmol m$^{-3}$ and an estimated dry-deposition velocity of 0.003 m s$^{-1}$, the annual dry-deposition flux is 250 mmol m$^{-2}$ yr$^{-1}$ in residential areas, a very large flux by any standards. The annual dry-deposition flux of sulphur dioxide throughout China was obviously lower, since the mean for the cleaner areas in Table 8.4 is about 0.54 μmol m$^{-3}$, implying a sulphur dioxide dry-deposition flux of about 51 mmol m$^{-2}$ yr$^{-1}$.

Table 8.4: Sulphur dioxide concentrations in China: 1982 and 1983.

<table>
<thead>
<tr>
<th>Category*</th>
<th>July</th>
<th>December</th>
<th>Annual</th>
</tr>
</thead>
<tbody>
<tr>
<td>North China</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shenyang</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Residential</td>
<td>0.14</td>
<td>0.20</td>
<td>10.80</td>
</tr>
<tr>
<td>Clean</td>
<td>0.09</td>
<td>0.23</td>
<td>3.27</td>
</tr>
<tr>
<td>Beijing</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Residential</td>
<td>0.83</td>
<td>0.27</td>
<td>6.06</td>
</tr>
<tr>
<td>Clean</td>
<td>0.09</td>
<td>0.09</td>
<td>0.91</td>
</tr>
<tr>
<td>Xian</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Residential</td>
<td>0.39</td>
<td></td>
<td>4.55</td>
</tr>
<tr>
<td>Clean</td>
<td>0.16</td>
<td></td>
<td>1.34</td>
</tr>
<tr>
<td>South China</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shanghai</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Residential</td>
<td>0.83</td>
<td>0.22*</td>
<td>1.89</td>
</tr>
<tr>
<td>Clean</td>
<td>0.14*</td>
<td></td>
<td>0.19*</td>
</tr>
<tr>
<td>Guangzhou</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Residential</td>
<td>0.75</td>
<td>1.00</td>
<td>0.83</td>
</tr>
<tr>
<td>Clean</td>
<td>0.19</td>
<td>0.23</td>
<td>0.16</td>
</tr>
<tr>
<td>Chongqing</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Residential</td>
<td>2.66</td>
<td></td>
<td>5.94</td>
</tr>
<tr>
<td>Clean</td>
<td>0.31</td>
<td></td>
<td>0.62</td>
</tr>
<tr>
<td>Guiyang</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Residential</td>
<td>6.30</td>
<td></td>
<td>6.55</td>
</tr>
<tr>
<td>Clean</td>
<td>1.00</td>
<td></td>
<td>1.70</td>
</tr>
</tbody>
</table>

*Clean sites were either on a mountain or at a rural site far from any urban area.

*1984 instead.

Source: Zhao et al. (1988).
The average sulphur dioxide concentrations at the cleaner sites were significantly lower than those at the residential sites, as the average concentration of 0.54 μmol m⁻³ indicated. Sulphur dioxide concentrations in southern China appear to be somewhat higher than those in northern China, as the 1982 respective averages of 3.0 μmol m⁻³ and 2.2 μmol m⁻³ suggest. Nevertheless, the total wet- plus dry-deposition fluxes of sulphur in parts of China are among the highest in the world. Our understanding of acid deposition cycles and effects in China clearly must be expanded.

8.4 HONG KONG

8.4.1 Overview

Air quality monitoring began in 1983 with five urban stations operated by the Hong Kong Government Environmental Protection Department (EPD). The network was subsequently expanded to 10 and then to 16 stations covering the whole territory. Measurements carried out included SO₂, NOₓ, O₃, TSP (total suspended particle mass concentration), RSP (respirable particle mass concentration), and wet deposition collected as wet-only weekly samples. The latter measurements started at two stations in October 1984, expanded to six stations by 1989, with the long-term aim of having a network of nine stations carrying out wet-only rainwater sampling.

In addition to the EPD sites a single rainwater sampling site had been operated by the Royal Observatory (RO) as part of the BAPMoN network since early in 1988. This site also used wet-only weekly sampling.

8.4.2 Wet Deposition

8.4.2.1 Sources of Information

The wet-only data discussed below were mainly from the RO site. However, we also refer to annual average wet-deposition data from five EPD sites. The SO₂ and NO₂ annual mean data are from EPD sites.

8.4.2.2 Quality of Information

Ion balance checks and multivariate statistical analysis of the RO rainwater composition data indicated that this data record was of very high quality. The only question about data quality concerned a trend towards lower pH at the end of the time series that correlated well with a trend towards an excess of cations in the ion balance, suggesting the development of a systematic analytical error towards low pH. This problem had disappeared in the more recent data.

The quality of the EPD data was unknown; however, our understanding is that the same Government Chemistry Laboratory performed the rainwater analysis for the Royal Observatory and Hong Kong sites, so at least in terms of analytical performance it may be assumed that all the data discussed are of high quality (with the noted exception of the most recent pH data).

8.4.2.3 Summary of Information

With only three full years of raw data available from the RO site, a detailed discussion of trends in annual mean concentrations and deposition for each species of interest was not warranted. Instead, Table 8.5 provides a summary of all annual mean data available from the RO site and Table 8.6 gives the EPD data.

Seasonal cycles in concentration and deposition for nss-SO₄²⁻ are in Figure 8.8. The wet deposition cycles were typical of those for nitrate, ammonium, and nss-Ca²⁺. They were driven by the seasonality in rainfall occasioned by the two monsoon seasons: the northeast monsoon from November to March and the southwest monsoon (that with the heaviest rain) from April to October (Fig. 8.9).
### Table 8.5: Annual volume-weighted mean concentrations and annual deposition for selected rainwater species at the Hong Kong BAPM/N station

<table>
<thead>
<tr>
<th>Rainfall Amount (mm)</th>
<th>nss-SO$_4^{2-}$</th>
<th>NO$_3^-$</th>
<th>NH$_4^+$</th>
<th>nss-Ca$^{2+}$</th>
<th>H$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1989</td>
<td>1331</td>
<td>20.4</td>
<td>20.3</td>
<td>23.0</td>
<td>4.4</td>
</tr>
<tr>
<td>1990</td>
<td>1843</td>
<td>13.7</td>
<td>11.7</td>
<td>14.7</td>
<td>1.8</td>
</tr>
<tr>
<td>1991</td>
<td>1524</td>
<td>10.6</td>
<td>8.9</td>
<td>10.3</td>
<td>1.9</td>
</tr>
</tbody>
</table>

**Concentrations (µmol L$^{-1}$)**

<table>
<thead>
<tr>
<th>Deposition (mmol m$^2$ yr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1989 1331</td>
</tr>
<tr>
<td>1990 1843</td>
</tr>
<tr>
<td>1991 1524</td>
</tr>
</tbody>
</table>

**Deposition (mmol m$^2$ yr$^{-1}$)**

Sources: WMO database; P. Sham, personal communication, 1992

### Table 8.6: Annual deposition of selected rainwater species at Environmental Protection Department wet-only sampling sites.

<table>
<thead>
<tr>
<th>Rainfall Amount (mm)</th>
<th>nss-SO$_4^{2-}$</th>
<th>NO$_3^-$</th>
<th>NH$_4^+$</th>
<th>nss-Ca$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Kwun Tong</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1985</td>
<td>1749</td>
<td>66.8</td>
<td>20.5</td>
<td>55.9</td>
</tr>
<tr>
<td>1986</td>
<td>1963</td>
<td>74.6</td>
<td>22.5</td>
<td>58.9</td>
</tr>
<tr>
<td>1987</td>
<td>2029</td>
<td>71.3</td>
<td>22.1</td>
<td>50.3</td>
</tr>
<tr>
<td>1988</td>
<td>621</td>
<td>38.1</td>
<td>11.8</td>
<td>34.9</td>
</tr>
<tr>
<td>1989</td>
<td>1711</td>
<td>54.5</td>
<td>14.9</td>
<td>37.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Central/Western</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1985</td>
<td>1789</td>
</tr>
<tr>
<td>1986</td>
<td>2121</td>
</tr>
<tr>
<td>1987</td>
<td>2109</td>
</tr>
<tr>
<td>1988</td>
<td>667</td>
</tr>
<tr>
<td>1989</td>
<td>1492</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Junk Bay</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1986</td>
<td>2316</td>
</tr>
<tr>
<td>1987</td>
<td>2200</td>
</tr>
<tr>
<td>1988</td>
<td>735</td>
</tr>
<tr>
<td>1989</td>
<td>1756</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Kwai Chung</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1989</td>
<td>1469</td>
</tr>
</tbody>
</table>

Source: Hong Kong Environmental Protection Department
Figure 8.8: Monthly mean nss-SO₄²⁻ (lower curve) and NO₃⁻ (upper curve) concentrations in rainwater at the Hong Kong BAPMoN site, 1989-1991.

Figure 8.9: Long-term mean rainfall pattern at Hong Kong.

8.4.3 Dry Deposition

In the absence of direct measurements of dry-deposition fluxes in Hong Kong, dry-deposition fluxes of SO₂ and NO₂ were estimated by combining EPD annual figures for gas concentrations (Table 8.7) and an assumed dry deposition velocity of 0.003 m s⁻¹ for both species. No estimates were possible for nitric acid because even indicative data were not available.
Taking typical \( \text{SO}_2 \) and \( \text{NO}_2 \) concentrations of 500 nmol m\(^{-3}\) and 1000 nmol m\(^{-3}\) respectively, plus the assumed deposition velocity of 0.003 m s\(^{-1}\), we estimated annual dry-deposition fluxes of 47 mmol m\(^{-2}\) yr\(^{-1}\) and 95 mmol m\(^{-2}\) yr\(^{-1}\) respectively.

**Table 8.7: Annual mean \( \text{SO}_2 \) and \( \text{NO}_2 \) concentrations in Hong Kong from Environment Protection Department data.**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{SO}_2 ) Concentrations (nmol m(^{-3}))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kwun Tong</td>
<td>1.58</td>
<td>1.04</td>
<td>0.89</td>
<td>0.42</td>
<td>1.11</td>
<td>0.87</td>
<td>0.56</td>
</tr>
<tr>
<td>Sham Shui Po</td>
<td>0</td>
<td>0.44</td>
<td>0.33</td>
<td>0.27</td>
<td>0.23</td>
<td>0.33</td>
<td>0.19</td>
</tr>
<tr>
<td>Causeway Bay</td>
<td>0.42</td>
<td>0.37</td>
<td>0.30</td>
<td>0.28</td>
<td>0.41</td>
<td>0.36</td>
<td>0.25</td>
</tr>
<tr>
<td>Tsim Sha Tsui</td>
<td>0.62</td>
<td>0.41</td>
<td>0.78</td>
<td>0.76</td>
<td>0.55</td>
<td>0.83</td>
<td>0.65</td>
</tr>
<tr>
<td>Central/Western</td>
<td>0.39</td>
<td>0.28</td>
<td>0.19</td>
<td>0.26</td>
<td>0.23</td>
<td>0.30</td>
<td>0.25</td>
</tr>
<tr>
<td>Junk Bay</td>
<td>0.23</td>
<td>0.20</td>
<td>0.41</td>
<td>0.30</td>
<td>0.23</td>
<td>0.14</td>
<td>0.11</td>
</tr>
<tr>
<td>Tsuen Wan</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.55</td>
<td>0.447</td>
</tr>
<tr>
<td>Kwai Chung</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.00</td>
<td>1.73</td>
</tr>
<tr>
<td>Hong Kong South</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.17</td>
</tr>
<tr>
<td>Averages</td>
<td>0.73</td>
<td>0.45</td>
<td>0.48</td>
<td>0.37</td>
<td>0.47</td>
<td>0.55</td>
<td>0.51</td>
</tr>
</tbody>
</table>

| \( \text{NO}_2 \) Concentrations (nmol m\(^{-3}\)) |
| Kwun Tong  | 1.19 | 2.56 | 2.54 | 1.61 | 2.02 | 1.30 |
| Sham Shui Po | 1.02 |      |      |      |      |      |
| Causeway Bay | 0.87 |      |      |      |      |      |
| Tsim Sha Tsui | 0.61 | 0.87 | 0.80 |      |      |      |
| Central/Western | 1.28 | 0.65 | 1.21 | 1.45 | 1.37 | 0.69 | 1.30 |
| Junk Bay    | 0.82 | 1.19 | 0.87 | 0.46 | 0.46 | 0.26 |
| Tsuen Wan   | 1.39 |      |      | 1.45 |      |      |
| Kwai Chung  | 0.89 |      |      |      | 0.78 |      |
| Averages    | 0.72 | 0.85 | 1.58 | 1.78 | 1.28 | 1.08 | 1.00 |

8.4.4 Summary

The wet- and estimated dry-deposition fluxes at Hong Kong confirmed the influence of anthropogenic emissions of sulphur and nitrogen on atmospheric acidity in this region. The total wet- plus dry-deposition fluxes for sulphur and nitrogen, approximately 90 and 110 mmol m\(^{-2}\) yr\(^{-1}\) respectively, are comparable to those in large parts of Europe and northeast North America and are lower only than those from the "hot spots" in these acid-impacted regions.

8.5 INDIA

8.5.1 Overview

According to the estimates of Kato and Akimoto [1992], India’s \( \text{SO}_2 \) and \( \text{NO}_x \) emissions were only about two-thirds those of Japan in 1975, but by 1987 they had surpassed Japan’s emissions by factors of about 2.5 and 1.5 respectively. In addition, Foell and Green [1991] predicted that, if energy production efficiency and emission regulations do not change, Indian emissions of \( \text{SO}_2 \) and \( \text{NO}_x \) will both be in the range of 5-6 Tg yr\(^{-1}\) (0.078-0.094 Tmol \( \text{SO}_2 \) yr\(^{-1}\) and 0.11-0.13 Tmol \( \text{NO}_x \) yr\(^{-1}\)) by the year 2000, or about four times the 1975 emission levels. Such a large potential increase in only 25 years underscores the possibility of greatly enhanced deposition of acidic sulphur and nitrogen species over India.

The considerable recent interest in acid deposition in India has been demonstrated by a number of short-term research studies (see references cited in Ayers [1991]). Long-term data on precipitation chemistry are available from the 10-site BAPMoN network established in the early
1970s. Unfortunately, because of the unknown quality of the Indian BAPMoN data and the lack of representative, long-term SO$_2$ or NO$_x$ data across the country, a detailed assessment of acid deposition across India is impossible at present.

### 8.5.2 Sources of Information

Rainwater composition data date back to July 1973 for the Pune site; the nine other Indian BAPMoN sites were established between then and July 1976. The WMO central data repository contains most available data. Mukhopadhyay et al. [1992] provide summary statistics derived from the data set. Site characteristics are given in Table 8.8.

Systematic data on SO$_2$ and NO$_x$ were available for 1990 from 10 cities in India under the re-established National Air Quality Monitoring (NAQM) Programme [NEERI, 1991].

#### Table 8.8: Characteristics of Indian BAPMoN sites.

<table>
<thead>
<tr>
<th>Description</th>
<th>Latitude (°N)</th>
<th>Longitude (°E)</th>
<th>Elevation (m)</th>
<th>Annual Rainfall (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allahabad</td>
<td>25.5</td>
<td>81.7</td>
<td>98</td>
<td>1027</td>
</tr>
<tr>
<td>Jodhpur</td>
<td>26.3</td>
<td>73.0</td>
<td>217</td>
<td>380</td>
</tr>
<tr>
<td>Kodakanal</td>
<td>10.2</td>
<td>77.5</td>
<td>2343</td>
<td>1672</td>
</tr>
<tr>
<td>Minicoy</td>
<td>8.3</td>
<td>73.0</td>
<td>2</td>
<td>1588</td>
</tr>
<tr>
<td>Mohanbari</td>
<td>27.5</td>
<td>95.0</td>
<td>111</td>
<td>2759</td>
</tr>
<tr>
<td>Nagpur</td>
<td>21.1</td>
<td>79.0</td>
<td>310</td>
<td>1127</td>
</tr>
<tr>
<td>Port Blair</td>
<td>11.7</td>
<td>92.7</td>
<td>79</td>
<td>3180</td>
</tr>
<tr>
<td>Pune</td>
<td>18.5</td>
<td>73.9</td>
<td>659</td>
<td>714</td>
</tr>
<tr>
<td>Srinagar</td>
<td>34.1</td>
<td>74.8</td>
<td>1587</td>
<td>664</td>
</tr>
<tr>
<td>Visakhapatnam</td>
<td>17.7</td>
<td>83.3</td>
<td>72</td>
<td>973</td>
</tr>
</tbody>
</table>

Sources: Indian Meteorological Service; Mukhopadhyay et al. (1992).

### 8.5.3 Quality of Information

The quality of the rainwater composition data from the Indian BAPMoN stations is impossible to assess. The samplers, although wet-only [Mukhopadhyay et al., 1992], use manual deployment and retrieval of open funnels rather than automatic sampling devices. No information is currently available as to the comparability of this method between sites or in comparison with the types of automatic samplers specified in the recommended WMO protocols and used routinely in the large European and North American acid deposition networks.

The Indian network used stainless steel (rather than polyethylene) rainwater collection funnels, filtered samples on site, and accumulated samples over monthly periods. There was no information available to assess the comparability of data produced using these protocols with data produced elsewhere within the global network.

There was also some question about the accuracy of the analytical procedures employed, especially the wet-chemical methods used for most of the anion determinations in the data record. In a review of the performance of the BAPMoN network, Miller [1992] noted that the Indian analytical laboratory ranked 18 in an overall estimate of analytical chemistry performance where a ranking greater than 10 indicated the need for improvement.

Finally we could not assess the quality of the data record by using standard procedures based on ion balance or conductivity. The data record for the decade before 1986 contains information
only on pH, conductivity, ammonium, chloride, nitrate, and sulphate and is therefore inadequate for testing purposes.

The SO₂ and NO₂ data were also of unspecified quality. The available monthly mean values were apparently from samples taken over 4 hours on 3 days per week using gas bubblers and "standard spectrophotometric methods for gaseous analysis" [NEERI, 1991]. We could find no details about measurement precision, accuracy, or interferences.

8.5.4 Summary

Because of the difficulties in assessing data quality, we have limited our discussion to the tabulation of the long-term mean data from the BAPMoN rainwater chemistry sites and the 1990 annual mean data on SO₂ and NO₂ from the 10 sites of the NAQM Programme (Tables 8.9 and 8.10). It was difficult to compare the two sets of data, since the BAPMoN network was specifically set up to sample regionally homogeneous samples, in other words, to avoid sharp gradients in concentrations caused by strong local sources such as cities and industrial areas. In contrast, the NAQM Programme sites were specifically chosen to sample the local effects of emissions at 10 large sites.

Table 8.9: Mean rainwater ion concentrations and deposition at Indian BAPMoN sites.

<table>
<thead>
<tr>
<th></th>
<th>Concentrations (μmol L⁻¹)</th>
<th>Deposition (mmol m⁻² yr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>nss-SO₄²⁻</td>
<td>NO₃⁻</td>
</tr>
<tr>
<td>Allahabad</td>
<td>4.9</td>
<td>48.2</td>
</tr>
<tr>
<td>Jodhpur</td>
<td>11.0</td>
<td>29.7</td>
</tr>
<tr>
<td>Kodaikanal</td>
<td>4.6</td>
<td>8.4</td>
</tr>
<tr>
<td>Minicoy</td>
<td>(-0.9)</td>
<td>9.8</td>
</tr>
<tr>
<td>Mohanbari</td>
<td>7.9</td>
<td>28.2</td>
</tr>
<tr>
<td>Nagpur</td>
<td>6.6</td>
<td>26.6</td>
</tr>
<tr>
<td>Port Blair</td>
<td>2.6</td>
<td>16.3</td>
</tr>
<tr>
<td>Pune</td>
<td>10.3</td>
<td>27.6</td>
</tr>
<tr>
<td>Srinagar</td>
<td>8.8</td>
<td>37.6</td>
</tr>
<tr>
<td>Visakhapatnam</td>
<td>53.5</td>
<td>34.7</td>
</tr>
</tbody>
</table>

Sources: Indian Meteorological Service; Mukhopadhyay et al. (1992).

Table 8.10: Gas concentration data from 10 Indian cities.

<table>
<thead>
<tr>
<th></th>
<th>SO₂ (μmol m⁻³)</th>
<th>NO₂ (μmol m⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Industrial</td>
<td>Residential</td>
</tr>
<tr>
<td>Ahemadabad</td>
<td>8.8</td>
<td>8.1</td>
</tr>
<tr>
<td>Bombay</td>
<td>22.3</td>
<td>15.8</td>
</tr>
<tr>
<td>Calcutta</td>
<td>18.1</td>
<td>22.7</td>
</tr>
<tr>
<td>Cochin</td>
<td>4.2</td>
<td>3.8</td>
</tr>
<tr>
<td>Delhi</td>
<td>13.5</td>
<td>13.1</td>
</tr>
<tr>
<td>Hyderabad</td>
<td>4.6</td>
<td>3.1</td>
</tr>
<tr>
<td>Jaipur</td>
<td>2.7</td>
<td>2.3</td>
</tr>
<tr>
<td>Kanpur</td>
<td>2.3</td>
<td>1.9</td>
</tr>
<tr>
<td>Madras</td>
<td>5.8</td>
<td>4.2</td>
</tr>
<tr>
<td>Nagpur</td>
<td>5.8</td>
<td>2.7</td>
</tr>
</tbody>
</table>

Source: NEERI [1991].

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With these differences in mind, one or two comments are possible. First, the rainwater deposition data suggested that nitrate deposition systematically dominated over sulphate deposition, even in equivalent terms, at the BAPMoN sites. Some tendency in this direction is also evident in the "cleaner" of the residential gas concentration data sets (Table 8.10). Second, the levels of nitrate deposition and the levels of dry deposition implied by the residential data in Table 8.10 (1 μmol m⁻³ of SO₂ or NO₃ with deposition velocity of 0.003 m s⁻¹ implies an annual deposition flux of 95 mmol m⁻² yr⁻¹) were certainly within the ranges found in acid-impacted regions of Europe and North America. Third, however, a singular characteristic of Indian rainwater and aerosol studies to date (Khemani et al., 1985, 1987; Varma, 1989) has been the high level of nss-Ca²⁺ apparent in the Indian atmosphere and wet deposition. The ability of the soil-dust-derived alkalinity associated with the nss-Ca²⁺ to neutralize atmospheric acidity derived from SO₂ and NO₃ has been noted in China (see section 8.3.2) as well as in India and may well substantially mitigate anthropogenic acidity over India.

In summary, the currently available data were far too limited to permit any conclusions about the present state of atmospheric acidification over India or its likely future direction. The data presented above were only adequate to indicate the types of questions that new, high quality, geographically representative measurement programmes must address.

8.6 MALAYSIA

8.6.1 Overview

Malaysia had the most extensive rainwater composition network operating in southeast Asia. Operated by the Malaysian Meteorological Service (MMS), the network started up in 1977 and at the time of writing had 23 stations spread across both parts of the country. Eight of the stations accumulated wet-only weekly samples; the remainder had 24-hour bulk collections, which were accumulated to provide weekly bulk samples.

SO₂ and NO₃ monitoring in Malaysia had primarily been the responsibility of the Department of Environment (DE). A few urban and industrial gas monitoring sites were established in the late 1970s under the GEMS programme. However, measurements continued for only a relatively short time because of problems with instrument calibration and maintenance in the hot, humid equatorial environment. That situation has persisted despite attempts to continue and to upgrade the measurements; thus, only sporadic data from a few sites were available. By 1991 no DE gas sampling sites were operational.

Recently the Malaysian electricity authority, Tenaga National Berhad (TNB), established several SO₂ and NO₃ monitoring stations near its major fossil-fuel-fired plant. However data from these few additional sites were not routinely available.

8.6.2 Data Quality

Data quality at the MMS bulk sampling sites were difficult to assess, since only sulphate, nitrate, pH, and conductivity were routinely determined in these samples. Based on the complete chemical analyses reported for the eight wet-only sites, we had significant reservations about the quality of the data from the network as a whole. As noted in Miller (1992), ion balances were not achieved in the Malaysian data sets, and significant deficiencies were evident in the network’s sample collection and handling procedures. Accordingly, we felt a detailed assessment of the whole data base was not justified. In the following analysis, we discuss data from two sites, one an urban, industrial site and one a rural mountain site, to give an indication of the range in rainwater properties in Malaysia.

For the SO₂ and NO₃ data, the acknowledged difficulties with calibration and instrument maintenance and the lack of any independent check on data quality made these data even more
suspect than the rainwater composition data. Thus, although we mention indicative values below, the analysis and interpretation of all the Malaysian data should be considered only qualitative.

8.6.2.1 Wet deposition

The Petaling Jaya MMS site, an urban industrial location in the Klang Valley near Kuala Lumpur, showed dramatic changes in deposition fluxes in the data record, especially between 1981 and 1984. A several-fold increase in $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ deposition in these years that was not seen later could not have been real and was almost certainly the result of systematic errors in analytical performance that periodically take the ion balance from an excessive cation sum to an excessive anion sum and back again. Clearly these data should be interpreted with considerable caution.

Because the data record from 1985 onwards exhibits some degree of consistency it was scrutinized for evidence of any seasonal cycles in concentration or deposition. We found no large cycles for either nss-$\text{SO}_4^{2-}$ or $\text{NO}_3^-$, which exhibited mean deposition fluxes of about 50 and 40 mmol m$^{-2}$ yr$^{-1}$ respectively. An additional problem with the data set was that, on many occasions, individual data elements were missing, apparently because the ion concentrations were below the sensitivity range of the wet-chemical analytical methods used. The incompleteness of the record made it difficult to assess the representativeness of any interpretations made from these more recent data.

The other Malaysian site considered was the BAPMoN station at Tanah Rata, located at 1500 m altitude in the Cameron Highlands approximately 300 km north of Kuala Lumpur and the Klang Valley site mentioned above. The Cameron Highlands site was in a rural area where regional activities were confined to market gardening and tourism (guest houses and some hotels). The character of this site contrasted with the definitively urban industrial character of the Klang Valley site.

The Tanah Rata data record implied levels of annual $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ wet-deposition that were lower than those for the Klang Valley site by factors of 5-10. However, the data record from Tanah Rata suffered from both of the systematic analytical biases found for the other site. More $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ data elements were missing for Tanah Rata, presumably because lower ion concentrations caused more samples to be below the analytical detection limits.

Because of these problems, we decided not to do any further comparisons. One point to be made from the comparison was that, to the (unquantified) extent the data were reliable, the expected enhancement in the wet deposition fluxes of nss-$\text{SO}_4^{2-}$ and $\text{NO}_3^-$ at the urban industrial Klang Valley site in comparison with the rural Cameron Highlands site was apparent in the data.

8.6.3 Summary

The Klang Valley site appeared to reflect potentially significant acidic wet deposition by world standards. Without any direct measurements of $\text{SO}_2$ or $\text{NO}_2$/HNO$_3$ dry deposition for this region, we could only provide an indicative figure for dry-deposition fluxes. We assumed a deposition velocity of 0.003 m s$^{-1}$ and combined it with broadly averaged $\text{SO}_2$ and $\text{NO}_2$ concentrations taken from several sites over different years (mostly in the early 1980s) by DE. These indicative values of 200 nmol m$^{-3}$ and 250 nmol m$^{-3}$ respectively for $\text{SO}_2$ and $\text{NO}_2$ led to dry-deposition estimates of approximately 20 mmol m$^{-2}$ yr$^{-1}$ and 25 mmol m$^{-2}$ yr$^{-1}$ respectively. Adding these values to "typical" wet-deposition fluxes of approximately 50 mmol m$^{-2}$ yr$^{-1}$ for nss-$\text{SO}_4^{2-}$ and approximately 40 mmol m$^{-2}$ yr$^{-1}$ for $\text{NO}_3^-$ yielded a total S plus N (wet plus dry) deposition figure in acid equivalents of about 200 meq m$^{-2}$ yr$^{-1}$, a value within the range found in acid-impacted areas of Europe and northeastern North America.
8.7 INDONESIA

8.7.1 Summary

Long-term records of rainwater composition were available for Indonesia only from the network of BAPMoN Regional Stations, with the earliest data available from 1984. The stations were at Jakarta, Puncak, and Bandung in West Java; Kenten in South Sumatara; and Sampali in North Sumatra. Although four of the five sites operated wet-only samplers, the data quality was problematic to the point where no assessment was warranted.

A central data quality problem that must be overcome in Indonesia related to analytical performance. First, concentrations of sodium and potassium had not been determined in rainwater samples, making it impossible to carry out the ion balance and conductivity checks routinely used in data quality assurance assessment. The lack of sodium data also compromised the ability to estimate nss-SO\textsubscript{4}\textsuperscript{2-} from total SO\textsubscript{4}\textsuperscript{2-} data. Second, the analytical methods employed in the past were mostly based on colorimetric or titrimetric wet-chemical methods with detection limits and precision inadequate for use at the lower end of the concentration ranges expected for rainwater ionic species. This was clearly demonstrated by inexplicable outliers and systematic shifts within many individual ion concentration records in the data set and by the fact that, in the BAPMoN laboratory intercomparisons, the Indonesian laboratory ranked very poorly [Miller, 1992]. This data quality issue must be addressed and the problems rectified as soon as possible.

8.8 AUSTRALIA

8.8.1 Overview

Bridgman [1988] summarized work on rainwater composition carried out in Australia before 1988 and referenced 16 separate data sets covering clean marine, clean continental, and polluted continental regions. Other works on Australian measurements published since 1988 include Ayers and Gillett [1988a, b], Bridgman [1988], Noller et al. [1990], Gillett et al. [1990], Post et al. [1990], and Ayers and Manton [1991].

The large land area and small population (about 18 million) concentrated in six widely separated cities of between 1 and 3 million inhabitants ensure that there is essentially no overlap or reinforcement of emissions or subsequent deposition from the separate urban/industrial areas. This fact, coupled with indigenous fossil fuels relatively low in sulphur content, also ensures that levels are systematically lower than those of the acid-impacted areas of Europe and northeastern North America, although acidic deposition from anthropogenic sources can be found in industrialized regions [Bridgman, 1988].

Indeed the Australian continental regions far removed from the major population centres offer a rare opportunity to investigate the characteristics of continental air masses in a relatively pristine state. Likens et al. [1987], for example, chose central northern Australia (Katherine) as the site for a remote, continental rainwater sampling site for the Global Precipitation Chemistry Project. Results from this site convincingly showed that annual mean nss-SO\textsubscript{4}\textsuperscript{2-} and NO\textsubscript{3}\textsuperscript{-} concentrations of less than about 5 $\mu$mol L\textsuperscript{-1} are to be expected in “unpolluted” regions. In contrast, in the more populated regions, such as the urban area of Sydney and the industrial Hunter Valley region, mean nss-SO\textsubscript{4}\textsuperscript{2-} concentrations ranged from 10 to 15 $\mu$mol L\textsuperscript{-1} and mean NO\textsubscript{3}\textsuperscript{-} concentrations were in the order of 10 $\mu$mol L\textsuperscript{-1} [Avery, 1984; Ayers et al., 1986b; Bridgman, 1988]. This contrast showed that the processes of atmospheric acidification by sulphuric and nitric acids could be clearly discerned in Australia. However, the overall levels of pH and sulphate and nitrate concentrations in these regions still fell well short of those causing concern in North America and Europe.
8.8.2 Sources of Information

Despite the many published research reports on various topics relevant to acid deposition, few relevant long-term data series were available in Australia. For wet-only rainwater composition data, there were only the series from Katherine [Likens et al., 1987] and the two regional BAPMoN stations at Coffs Harbour and Wagga Wagga [Ayers and Manton, 1991]. Data quality has been adequately reviewed in both sets of published results and can be considered good [Likens et al., 1987; Ayers and Manton, 1991].

There were no long-term data on dry deposition fluxes over Australia. There were some data on SO$_2$ and NO$_x$ concentrations from networks operated for local air quality purposes in most capital cities and in near-field regions around major industrial plants such as coal-fired power stations and metal-smelting complexes. Data quality was unknown but presumed to be adequate, given that most networks followed calibration and maintenance schedules routinely employed by the large European and North American networks.

8.8.3 Summary

Mean annual concentrations and deposition of nss-SO$_4^{2-}$ and NO$_3^-$ for the only three Australian sites with multiyear, wet-only rainwater composition data are given in Table 8.11. Comparable data for SO$_2$ and NO$_2$ were not available but, at locations such as those in Table 8.11, equally low values (by European and North American standards) could be anticipated. Data from the Latrobe Valley region, approximately 100 km east of Melbourne at 38°S were illustrative. Despite the presence of a 4000-MW coal-fired electricity generation plant, the annual mean NO$_2$ and SO$_2$ concentrations, averaged across 13 air quality stations in the valley between September 1986 and August 1987, were only 160 nmol m$^{-3}$ and 40 nmol m$^{-3}$ respectively. For assumed dry deposition velocities of 0.003 m s$^{-1}$, these concentrations suggested annual dry deposition fluxes for NO$_2$ and SO$_2$ of only 8 mmol m$^{-2}$ yr$^{-1}$ and 15 mmol m$^{-2}$ yr$^{-1}$ respectively. Adding these estimates to those for wet deposition in Table 8.11 confirmed an overall impression that, at regional-to-continental scales, acidic deposition in Australia is only mildly enhanced by anthropogenic emissions.

Table 8.11: Wet-deposition data from three unpolluted Australian sites.

<table>
<thead>
<tr>
<th></th>
<th>nss-SO$_4^{2-}$</th>
<th>NO$_3^-$</th>
<th>NH$_4^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Katherine</td>
<td>2.4</td>
<td>4.3</td>
<td>3.0</td>
</tr>
<tr>
<td>Coffs Harbour</td>
<td>7.0</td>
<td>6.8</td>
<td>5.0</td>
</tr>
<tr>
<td>Wagga Wagga</td>
<td>3.5</td>
<td>5.6</td>
<td>7.4</td>
</tr>
</tbody>
</table>

Sources: Likens et al. [1987]; Ayers and Manton [1991].

8.9 NEW ZEALAND

8.9.1 Overview

New Zealand has a small population (about 3.5 million) with a relatively low population density and is located well away from any major sources of transboundary air pollution. Accordingly, high levels of acidic deposition are not to be expected. Consequently, there has been relatively little interest in the study of rainwater acidity in New Zealand. The only multiyear rainwater composition data sets published from New Zealand consisted of five years (1983-1987) of monthly, wet-only data reported by Harvey and Clarkson [1988] for the site of Kelburn on the south coast of the North Island and for Lauder, an inland site on the South Island. Ayers et al. [1986a] reported a single year’s event-sampled data from New Plymouth, a second coastal site on the west coast of the North Island.
8.9.2 Summary

Annual mean concentration and deposition data are presented in Table 8.12. Both were low by the standards of the acid-impacted areas of the northern hemisphere and in comparison with the more polluted urban and industrial regions of Asia (e.g., parts of Japan, China, Hong Kong, Malaysia, etc.). The 12 months of data reported by Ayers et al. [1986a] for New Plymouth were completely consistent with the Kelburn and Lauder data. Thus, the New Zealand data clearly reflected the character of these sites as non-urban and non-industrial sites within an isolated country lacking significant local sources. These results, like those from comparable Australian sites, probably represent a regional "baseline" for continental sites experiencing a relatively small influence from anthropogenic emissions.

Table 8.12: Annual mean concentration and wet deposition at two New Zealand sites.

<table>
<thead>
<tr>
<th></th>
<th>nss-SO$_4^{2-}$</th>
<th>NO$_3^-$</th>
<th>NH$_4^+$</th>
<th>nss-Ca$^{2+}$</th>
<th>H$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kelburn</td>
<td>9.5</td>
<td>2.0</td>
<td>3.4</td>
<td>1.1</td>
<td>5.0</td>
</tr>
<tr>
<td>Lauder</td>
<td>12.1</td>
<td>3.0</td>
<td>17.2</td>
<td>1.9</td>
<td>2.5</td>
</tr>
<tr>
<td>Kelburn</td>
<td>12.3</td>
<td>2.9</td>
<td>4.3</td>
<td>1.3</td>
<td>6.3</td>
</tr>
<tr>
<td>Lauder</td>
<td>6.2</td>
<td>1.6</td>
<td>9.3</td>
<td>1.0</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Concentrations (µmol L$^{-1}$)

Deposition (mmol m$^{-2}$ yr$^{-1}$)

Source: Harvey and Clarkson [1988].

8.10 FUTURE PROSPECTS FOR DEVELOPING A REGIONAL UNDERSTANDING OF ACID DEPOSITION

We expect the availability of data from Asia and Oceania on the atmospheric aspects of acid deposition to improve rapidly. Underpinned by the current international emphasis on "global change" issues, a very significant "consciousness raising" has occurred throughout the Asia/Oceania region concerning atmospheric pollution in general and its many potential deleterious environmental effects. As a consequence, the period from 1990 has seen a growing regional/international effort to initiate new work to define and understand the current and likely future dimensions of the acid deposition problem in Asia. New measurement and modelling initiatives at the national level are occurring in some countries, and broadly based international programmes are underway under the auspices of the WMO and through GAW, IGAC, the DEBITS Activity with its CAAP (Composition and Acidity of Asian Precipitation) Experiment, and the RAINS-Asia project sponsored by the World Bank and Asia Development Bank. Others are being planned. Thus, there are good prospects that the current paucity of regional data will be substantially reduced during the 1990s.

Acknowledgements: The authors acknowledge considerable assistance with provision of data from many sources, including the Japanese Environment Agency, Toyama Prefecture, the Japanese Central Research Institute for the Electric Power Industry, the WMO Data Centre, the meteorological services of India, Malaysia, Indonesia, Australia, and New Zealand, The Royal Observatory and Environmental Protection Department in Hong Kong, the Korean Ministry of Environment, Jim Galloway, Zhao Dianwu, B. Mukhopadhyay, and Patrick Sham.
8.11 REFERENCES


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