CHAPTER 1 GENERAL INTRODUCTION

Introduction

The deposition of potentially damaging chemicals from the atmosphere to ecosystems is an undesirable consequence of air pollution. In the Netherlands, as elsewhere in Europe and North America, there is great and growing concern about the effects of airborne pollution and the accelerating acidification and or eutrophication of the natural environment. The regional distribution of affected ecosystems provides strong empirical evidence for a causal link to acid deposition (Last and Watling, 1991). There are many hypotheses which attempt to relate air pollution, for example, to forest decline but it has proved difficult to demonstrate cause and effect between acid deposition and ecosystem damage or change due to the co-occurrence of natural stresses (e.g. drought, pathogenic insects and fungi) and anthropogenic stresses (e.g. air pollution, climatic change, management practices). Furthermore, exposure to other gases such as ozone and deposition of, for example, heavy metals might also be important. The mechanisms of damage are insufficiently understood; also, the actual exposure to wet and dry deposited pollutants have been found difficult to define. In this chapter some background information will be given on the issue of acidification, followed by a brief overview of the history of atmospheric deposition research. The chapter will be concluded with the objectives and an outline of this book.

1.1 INTRODUCTION TO THE ISSUE OF ACIDIFICATION

The term 'acid rain' or 'acid deposition', which covers the whole range of physical, chemical and biological processes involved in the issue of acidification, has evolved gradually. Strictly speaking, the term 'acid rain' refers to precipitation more acid than in remote areas. The term 'acid rain' was first encountered in 1858, when the effect of the atmosphere on stones, bricks and mortar was described (cf. Smith, 1872):

'It has often been observed that the stones and bricks of buildings, especially under projecting parts, crumble more readily in large towns, where much coal is burnt, than elsewhere. Although this is not sufficient to prove an evil of the highest magnitude, it is still

worthy of observation, first as a fact, and next as affecting the value of property. I was led to attribute this effect to the slow, but constant action of the acid rain. If it affects substances with so great an excess of silica, it will not be expected that calcareous substances will resist it long, and one of the greatest evils in old buildings in Manchester is the deterioration of the mortar.'

It has been shown from rainfall acidity measurements that precipitation more acid than in remote areas occurs in the industrialised regions of the world. pH values range from 4.0 in central Europe and North America to 6.3 in India and Australia (Figure 1.1). In remote areas of the world, the average pH in rain is about 5.6 (Sisteron *et al.*, 1989).

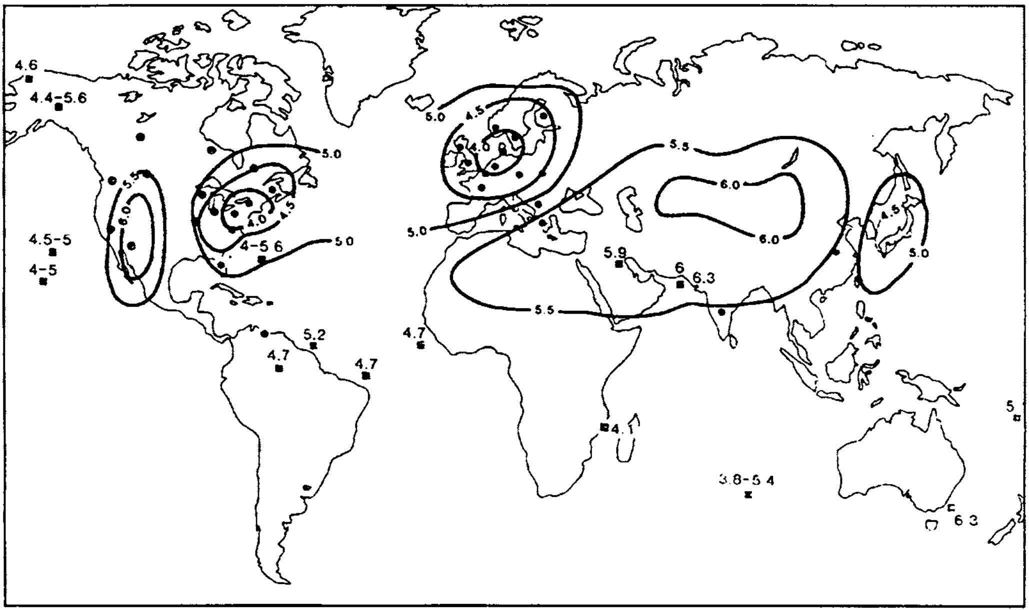

FIGURE 1.1 Pattern of rainfall acidity in the world (WMO, 1989)

The direct effects of ambient acids to plants were already recognised in 1854, as reported by a Belgium commission (Rapport à M. le Ministre de l'intérieur par la commission d'enquête, Bruxelles, 1856), which reported the influence of hydrochloric acid on trees and bushes. The negative effects to vegetation were found to be related to the size of the exposed area, but mostly to the wind direction. The relation of the sensitivity of species to hydrochloric acid was found for a list of species. In Germany, the direct effects of sulphur dioxide and sulphuric acid on vegetation was observed in and near the cities (Tiegs, 1927). Critical effect levels were defined for sulphuric acid concentrations. An ambient concentration limit of 1:1 000 000 (1 ppm) would be regarded as safe, whereas 1 : 100 000 would lead to mortality on clear days after several minutes and 1 : 25 000 to death of all vegetation within seconds. It was found that the sensitivity of different species depended on stand conditions and age. Coniferous trees were found more sensitive than deciduous trees (Tiegs, 1927) Acidification of soils was already recognised around 1900 when a German scientist Wieler postulated the theory that the sulphuric acid reaching the soil could dissolve and rinse soil constituents such as chalk, which thus could no longer be used for growth (Tiegs, 1927). Smith (1872) warns for the destruction of roots due to the acid exposures in Belgium, France and Germany.

Scientific research on acidification of rivers and lakes started in the 1920s (cf. Abrahamsen *et al.*, 1989). Experiments had indicated that the trout populations were declining as a result of low pH of the water (Dahl, 1926). The relation between the acidity of freshwater and precipitation was suggested in 1934 (Torgerson, 1934). The public interest in the subject was renewed in Scandinavia about 30 years ago (Odén, 1967). This interest arose from concern regarding freshwater acidification and reduction in fish populations in areas with a low capacity for neutralising acidic inputs. The acidification of the Scandinavian lakes was demonstrated to be the result of long-range transport of air pollution. Acidification of lakes was found to be the result of high inputs of sulphur and nitrogen compounds (Hauhs and Wright, 1988; Brydges and Wilson, 1991). The tall stacks built in the 1960s brought about a considerable reduction in the immediate vicinity of the sources but, in general, it can be stated that when pollutants are emitted at higher levels in the atmosphere, the atmospheric residence time and transport distance increases. The actual transport distance depends on wind, climate and meteorological conditions.

Since about 1975 the novel forest decline in the former Federal Republic of Germany has been observed as extensive and rapid (Brydges and Wilson, 1991). In the last few years interest in the effects of pollutants on crops and materials has grown and, in particular, effects on conservation areas like forests, moorland pools and heathlands. Other effects related to acidification are the result of exposure of humans to acidic gases and aerosols, and reduction in the visibility in the affected areas. Since 1986, most countries have co-ordinated their forest damage surveys on the basis of a system devised in the framework of the International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests, under the convention on Long Range Transboundary Air Pollution. Figure 1.2 shows the intensity of defoliation resulting from the 1988 inventory (UN ECE/ICP Forest (1989). The percentages show that ailing forests are to be found to a greater or lesser extent in all the countries of Europe.

Dutch Priority Programme on Acidification

A programme on the issue of acidification was started in 1985 in the Netherlands as a result of the awakening interest of policy-makers in the effects of air pollution on forests and other vegetation due to dry and wet deposition of sulphur and nitrogen species (Heij and Schneider, 1991). Gradually it became evident that the specific air pollution climate in the Netherlands

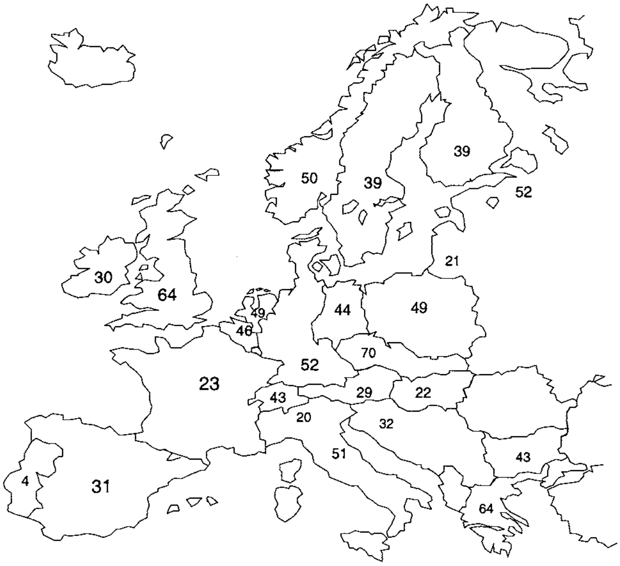

FIGURE 1.2 Intensity of defoliation for all species, or conifers only in 1988. Percentage of trees in classes 1-4 (>10% defoliation)

deviates from that of other European countries. Severe effects as a result of very high local nitrogen inputs were observed in the Netherlands (Schneider and Bresser, 1988), while in other parts of Europe, effects were attributed to high acid inputs by sulphur and nitrogen species (Scandinavian lakes) or by exposure to ozone (conifers in Germany) (Schlaepfer, 1992).

The causal chain related to these effects, studied in the Dutch Priority Programme on Acidification (DPA), is shown in Figure 1.3. Gases and aerosols can cause damage to vegetation through direct effects on the parts of the vegetation above ground and through indirect effects, via the soil solution, on the parts of the vegetation below the ground (Heij and Schneider, 1991). Effects on the soil solution can be expressed as changes in the concentrations and budgets of sulphur, nitrogen and aluminium in particular. With regard to nitrogen, the acidification problem is closely linked with the problem of N eutrophication. The critical loads and critical levels refer to thresholds, which can serve as a tool to assess the occurrence of effects in natural ecosystems due to acid deposition. A critical load is a quantitative estimate of an exposure to one or more pollutants *below* which significant harmful effects do not occur. A critical level is defined as the concentration of a pollutant in the atmosphere *above* which direct adverse effects on receptors may occur. International co-operation within the framework of the UN Economic Commission for Europe is taking place to produce maps of critical loads and levels in Europe to create a basis for policy measures (Hettelingh *et al.*, 1991). In this respect, accurate estimates of actual deposition to vegetation, soils and lakes became an important topic in the DPA.

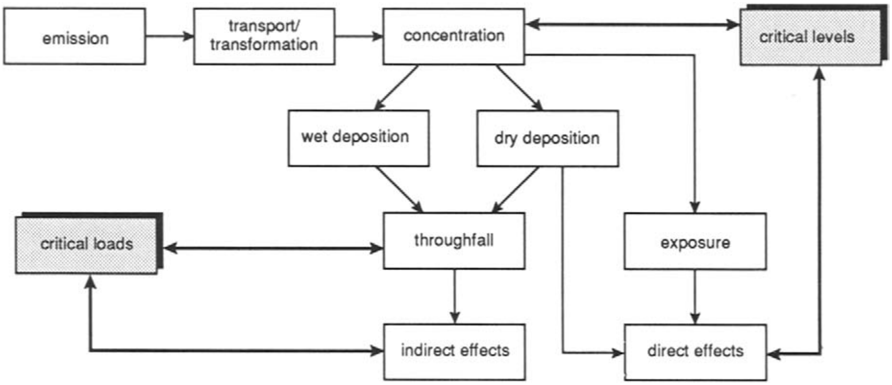

FIGURE 1.3 Cause and effect chain studied in the DPA (Heij and Schneider, 1991).

Acidification of soils and lakes can be the result of deposition of acidic or acid-forming gases and aerosols, and/or acidic precipitation. The processes of deposition are illustrated in Figure 1.4. Dry deposition is the process where gases and aerosols are deposited directly from the atmosphere onto vegetation, the soil or materials. Wet deposition is the result of rain-out or wash-out by precipitation. Deposition of pollutants by fog and dew is often called occult deposition. Total deposition is the sum of dry, wet and occult deposition. Throughfall and stemflow refer to the water dripping from tree canopies and trunks, respectively. The flux of an ion below the canopy in throughfall provides information on the deposition to the soil.

The acidifying components which play a role in the acidification are gaseous sulphur dioxide (SO_2), nitrogen oxides (NO and NO_2), nitric acid (HNO_3), nitrous acid (HNO_2), peroxyacetylnitrate (PAN), hydrochloric acid (HCl), Hydrofluoric acid (HF), organic acids, ammonia (NH_3) and ammonium (NH_4^+), nitrate (NO_3^-) and sulphate (SO_4^{2-}) aerosols. These components are emitted mainly by anthropogenic sources such as industry, refineries and power plants (SO_2), industry and traffic (NOx), livestock breeding (NH_3) and incinerators (HCl), or formed in the atmosphere from these gases (HNO_3, HNO_2, PAN and aerosol compounds). If HCl is formed by the reaction of acidic gases with sea salt, it is considered to be of quasi-natural origin (Lightowlers and Cape, 1988). On the global scale, acidifying components are to a large extent originating from natural sources (Welphdale, 1987) such as volcanoes, oceans, soil, burning processes, wildlife, meteorites and lightning.

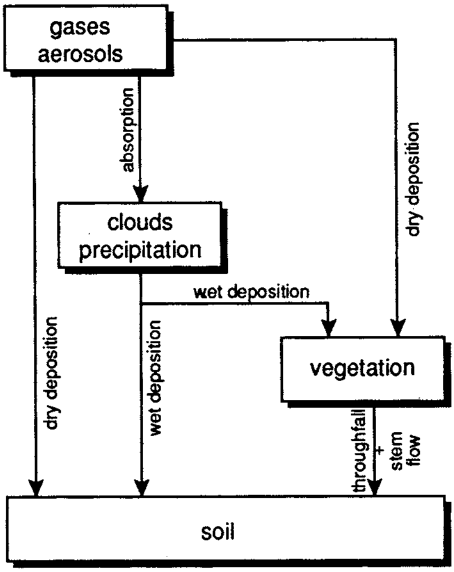

FIGURE 1.4 Schematic representation of deposition

In the causal chain, soil acidification and nitrogen cycling are the most important processes related to indirect effects (Heij and Schneider, 1991). The total nitrogen deposition can be estimated from the wet and dry deposition of the individual N-containing components. With respect to soil acidification, it is assumed that acid-forming oxides can be oxidised to strong acids in the soil. One mole of SO_2 can thus form two equivalents of acid, whereas one mole of NOx or HCl can form one equivalent of acid (Van Aalst, 1983). The soil processes leading to acidification are beyond the scope of this book (see for overviews, Hauhs and Wright, 1988; Van Breemen and Verstraten, 1991). The contribution of NH_3 to the acid deposition is related to the rate of soil nitrification. Under the influence of oxygen, nitrifying bacteria may transform ammonia into nitrate and acid according to (see e.g. Van Breemen *et al.*, 1982):

$$NH_4^+ + 2O_2 \longrightarrow NO_3^- + H_2O + 2H^+ \qquad [1.1]$$

Through this process, acids in gaseous form, in aerosols or in rain droplets initially neutralised by NH_3 can form two equivalents of acid when deposited: one can be considered as derived from NH_3 and one from the neutralised acid. Because of incomplete nitrification in the soil the contribution of NH_3 and/or NH_4^+ may be less than one equivalent H^+ per mole NH_3 deposited. This contribution is dependent on the type of soil and vegetation.

It has been estimated from intensive monitoring studies in forests distributed over the Netherlands (Heij and Schneider, 1991) that the actual acid load of sulphur compounds is generally equal to the potential acid load of sulphur. The actual acid load from nitrogen, however, was found to be only about half the potential load. The difference between potential acid load and actual acidification of the soil (in the sense of a reduced buffer capacity in the soil) is mainly the result of the removal or fixation of N through uptake by plants, denitrification, or immobilisation of N in the soil organic matter (Heij *et al.*, 1991). Furthermore, acids formed from gases in the atmosphere may be neutralised by basic substances before reaching the soil.

The maximum acid load to soils, or the amount of acidifying components removed from the atmosphere by deposition, hereafter referred to as total potential acid deposition, is estimated by:

$$\text{Total potential acid} = 2\text{SOx} + \text{NOy} + \text{NHx} \qquad [1.2]$$

where SOx is the total (dry + wet + occult) deposition of sulphur compounds (one mole of SOx forming two moles of acid), NOy the total deposition of oxidised nitrogen compounds and NHx the total deposition of reduced nitrogen compounds. Other acid or acid-forming species might be added to Eqn. 1.2, such as HCl, organic acids, PAN, H_2S and HF. However, the contribution of these gases to the total acid deposition is considered to be of minor importance relative to other acidifying components. The total potential acid deposition is expressed in mol H^+ ha^{-1} a^{-1}.

The studies related to atmospheric deposition within the Dutch Priority Programme on Acidification were focused mainly on quantification of the inputs and origin of sulphur and nitrogen compounds to heathland and forests in the Netherlands. The studies comprised experimental research as well as model development and application. The experimental and modelling research was to a large extent conducted within the framework of international programmes such as the EUROTRAC project (BIATEX) and some financed by the European Commission. The work was reviewed by an international review team. They concluded that the atmospheric deposition work conducted in the Netherlands so far was of world class quality (Heij and Schneider, 1995).
In the next section first a brief overview of the evolvement of atmospheric deposition research is given. After this historical overview, the studies conducted in DPA will be elucidated as an introduction to the contents of this book.

1. 2 HISTORY OF ATMOSPHERIC DEPOSITION RESEARCH

The study of sulphur and nitrogen deposition in the past had two different purposes. First, research was done in relation to plant nutrition. Both sulphur and nitrogen should be available to some extent for optimal growth of vegetation used in agriculture. That atmospheric nitrogen in the form of ammonia could be of benefit to plant growth was already recognised in 1804 by De Saussure. Ammonia was detected in rain by Von Liebig in samples collected by Zimmermann near Giessen in 1824 (Von Liebig, 1827). In 1825 Von Liebig demonstrated the presence of nitric acid in rain, but it was not until 1852 that Boussingault demonstrated that nitrogen in this form is also beneficial to plant growth. These observations have led to the development of ammonia observations in air and rain, and of nitric acid in precipitation.

Secondly, the relation to atmospheric pollution was studied, with emphasis on human health in relation to exposure of high concentrations of pollutants. In the period before the Second World War atmospheric pollution in the environmental sense was studied mainly because of impacts on human health problems. In the Middle Ages, the relation between human health and smoke from coal burning had already been established. During periods with low wind speeds and/or foggy conditions, the main industrialised cities in Europe experienced high concentrations of smoke, reducing the visibility and increasing the number of deaths each year caused by industrial activities. The most famous example in this respect is the London smog (Brimblecombe, 1987), but observations and statistics on pollution are also available for several cities in Germany (Wernicke, 1927) and in Budapest (Fodor, 1881). The relation between vegetation damage as a result of sulphuric acid and sulphur dioxide in the atmosphere was already studied the 1920s (Tiegs, 1927). The first results in approaching the problem of smoke in relation to human health yielded analyses of wet deposition in or near cities, or individual factories.

The atmospheric measurements dating from around 1800 to early 1900 were mainly analyses of collected precipitation. Ambient concentration measurements of atmospheric components were to a large extent not made. The results of very old measurements are summarised in several reports and papers: Way (1855), Ludwig (1862), Smith (1872), Miller (1905), Liesegang (1927), Eriksson (1952), Brimblecombe and Stedman (1984), Brimblecombe (1987), and Ulrich and Williot (1993). This chapter will present a short overview of the research on atmospheric input measurements. The main focus will be on the old measurements, i.e. before the Second World War. After that time the research on atmospheric input increased gradually, with the main increase in the seventies and eighties.

1.2.1 NITROGEN COMPOUNDS

Evelyn, in his *Philosophical Discourse of Earth* (London, 1676), speaks of rains and dews as being *'impregnated .. with Celestial Nitre'*, and of *'nitrous spirits descending with their baulmy pearls'* (cf. Miller, 1905). The presence of ammonia in the atmosphere was noticed by De Saussure (1804) in Geneva. He came to the conclusion that the nitrogen of plants could only be derived from the vegetable and animal matters diffused through the soil, or existed in the form of ammonical vapours in air brought down by rain. That such ammonical vapours do exist in the air was considered by De Saussure to be proven by the change occurring to sulphate of alumina, which, when left exposed to the air, became converted by degrees into double sulphate of alumina and ammonia (cf. Way, 1855). Von Liebig (1827) believed that the nitrogen in soils was derived from the small amount of ammonia in air and rain. As a result, the necessity of applying manure for agricultural purposes was put to question (Lawes and Gilbert, 1851). Von Liebig's theory, therefore, has led to several investigations focused on the benefit of atmospheric nitrogen to plants. Greenhouse experiments were conducted by Ville and Boussingault in France to determine whether the nitrogen used by plants was from nitrogen (N_2) itself or occurring in the form of ammonia (cf. Way, 1855). Lawes and Gilbert (1851), and Boussingault (1886), eventually showed atmospheric N_2 to be of no benefit to plants.

Wet deposition

Precipitation sampling was already a well-known technique to determine the 'atmospheric composition'. Precipitation was sampled in the early days of the development of chemistry. The first analysis date was from 1749-50 when Andreas Sigmund Maggraf sampled with great care the cleanest rainwater and distilled it very carefully using new glass stills (cf Ludwig, 1862). He found hydrochloric acid and nitric acid as well as sodium chloride and lime. He recognised that it was very difficult to sample clean rainwater and snow: it should be sampled 'in the free sky', away from buildings. When he distilled his rainwater, he always found crystals that looked like sodium chloride, but were brown instead of white because they were covered with sticky oil particles. This was not strange because 'you could smell these oil particles after a spring or summer rain' (cf Ludwig, 1862). Later in 1788 in Leipzig Bergman determined the same substances in rain and snow (cf. Miller, 1905). Between 1820 and 1825 several analyses of rain water were made in Giessen and near the Baltic Sea (Germany) and in Utrecht (The Netherlands). Dalton analysed rain water in Manchester for chlorine. Brandes (1825) was probably the first to analyse several components in rain water in Salzuffeln, Germany. He evaporated the rain water and found the residue to contain organic substances, chlorine, sulphuric acid, soda, potash, magnesia, ammonia salts, carbonic acid, lime and oxide of iron (cf. Smith, 1872).

When it was discovered that NH_3 in precipitation was used by plants as fertiliser (Von Liebig, 1827), the interest in the ammonium content in precipitation increased. When Boussingault

(1886) showed the importance of nitrate in plant nutrition in 1856, also present in precipitation, this component was determined regularly too.

It was thought that the nitrogen in the form of nitrate in precipitation originated from lightning, because the highest concentrations were observed with measurements made during thunderstorms. Boussingault (1886) made measurements in a forest area under rural conditions during several types of precipitation events, and concluded that the atmosphere was the only source of nitrogen. Marggraf was the first who found nitric acid in rainwater. In several precipitation investigations nitric acid was determined, e.g. by Barral (1852) and Levy (1874) in Paris, Bineau (1855) in Lyon, Filhol (1855) in Toulouse, Gilbert and Lawes (1851) in Rothamsted and Smith (1872) in several sites in Great Britain. Boussingault was the first to sample rime, fog, snow and dew and analysed the samples for ammonium and nitrate concentrations. He was also the first who performed sequential sampling of precipitation (Way, 1855). Boussingault had been led to think, according to his experiments, that rain collected in rural fields contained notably less ammonia than that collected in towns. Most of the precipitation measurements were made in or near towns. Very high concentrations of ammonia in rain water were found by Barral (1852), Boussingault (1886) and Levy (1874) in Paris, by Bineau (1855) in Lyon, Filhol (1855) in Toulouse, Meyrac in Dax (cf Ludwig, 1862) and Pierre (1851) in Caen. Pierre (1851) gives the following explanation:
'Volcanoes in a state of activity throw out a notable quantity of ammonia salts. They are given off also in calcining organic matter, and in the combustion of coal (an explanation for the enormous concentrations of 130 and 138 mg/l observed by Boussingault, red.). Matters of organic origin, all more or less nitrogenised, decompose, either at the surface of the land or at a very small depth, and among the products of this decomposition we find carbonate of ammonia, a very volatile substance. A portion of this substance remains in the soil, and contributes to the prosperity of the plant; another part is dessiminated in the air. Carbonate of ammonia being very soluble in water, we can understand why it is found in rain.'

The oldest long-term measurements of wet deposition are those made at Rothamsted in England during 1880 - 1920 (see Brimblecombe and Stedman, 1984) and the measurement taken by Albert Levy in Montsouris near Paris during 1876 - 1907 (see Ulrich and Williot, 1993). These data are used in Chapter 5 to determine trends in atmospheric deposition in Europe. The problem in interpreting these data is that they are sampled near cities and/or in agricultural areas, but are not representative for background concentrations. Furthermore, measurement of nitrogen compounds is sensitive to many sources of errors, such as bird droppings, dry deposition of soil dust, particles and gases, microbial conversion or production and contamination in the laboratory (NH_3) (Eriksson, 1952, Galloway and Welphdale, 1980; Buijsman and Erisman, 1988).

Dry deposition

Ambient ammonia concentration measurements were made as early as 1840. Grager, a German scientist found 0.42 mg m^{-3}; Kemp, an Irishman, 4.78 mg m^{-3} and Fresenius, another German scientist, 0.17 mg m^{-3}. Pierre (1851) found during one year of observations in 1851 near Caen 'only' 0.65 mg m^{-3}. Smith (1872) analysed several samples for concentrations of NH_3 in London in 1870 and found concentrations in the range of 0.11 to 0.27 mg m^{-3}. Albert-Levy measured ambient concentrations of 21-29 µg m^{-3} NH_3-N during one year sampling in Paris in 1874. Fodor (1881) measured two years continuously in Budapest, Hungary and found an average of 39 µg m^{-3}.

Way (1855) was the first to hypothesise the existence of dry deposition. In his paper *The atmosphere as a source of Nitrogen to Plants*, he writes:

'We have seen then that the form of ammonia or nitric acid the soil receives annually a very large dose of nitrogen in a state to be made use of by plants. That the data yet obtained are not very precise ought not to surprise us, considering the difficulty of the subject. I think, too, that one point has been overlooked in all these inquiries: one experimenter devotes his attention to the ammonia in rain, another to that in air - both independently, at different times, and without concept. But in the meanwhile a cause, and, as I believe, a most active cause of abstraction of ammonia from the calculations of each of them, is at work; - I mean the absorption of ammonia and nitric acid from the air by the soil. Between each shower of rain this cause is continually - to an unknown, but perhaps, a large extent - robbing the air of these compounds; so that the rain when collected really represents that which this agency has not removed.'

The first dry deposition measurements are probably those made by Ville (1850) and Schlössing (1874) using nitrogen deficient plants in NH_3 rich chambers, and those by Bineau (1855) and Bretschneider (1872) using measurements of NHx absorption in dilute acid solutions or soil surfaces exposed to air. Furthermore, the sampling and analysis of snow after different exposure times by Boussingault (1886) might be labelled as dry deposition measurements. He found a 10-fold increase in NH_3 concentration in snow after a 36-hour exposure to the ambient air, although he reasoned that the source of ammonia was the soil and not the atmosphere. Similar observations were made by Müller (1888) in Braunsweig Germany. He also showed the dependence of NH_3 concentrations in snow on the emission of smoke by sampling outside the city (1 mg l^{-1} NH_3) in a sparsely populated area (1.5 mg l^{-1} NH_3), and in a densely polluted area (3 mg l^{-1} NH_3) of Braunsweig. Schlösing (1875) studied the absorption of ammonia by soil and estimated that about 40 kg NH_3-N ha^{-1} was absorbed from the air per year. Hall and Miller (1911) searched for information on whether ammonia was released by soil by exposing shallow dishes of sulphuric acid, some close to the ground and others four feet (1.2 m) above it. They found that the lower dishes generally contained less ammonia than the upper one, which they took as an indication of a steady absorption of ammonia by the soil.

Russell and Richard (1919) were the first to estimate the total flux of nitrogen by rain to Great Britain: the 56,000,000 acres of Great Britain would receive 65,000 tons of combined nitrogen. They found, however, that this was much less than their estimate of the emission from coal consumption.

1.2.2 SULPHUR COMPOUNDS

At the end of the seventeenth century Robert Boyle tried to devise sensitive techniques for the estimation of various components in air (cf. Brimblecombe, 1987). He advised the experimenter to hang up clothes or silks died with colours to use the fading or changes in colour as an indicator for the presence of particular nitrous or salino-sulphurous spirits. In 1744 the French chemist Rouelle found sulphur dioxide, or at least sulphate, in air by using a modified version of the technique outlined by Boyle. Van Driessen and Vanhof found in Amsterdam hydrogen sulphite and sulphuric acid (cf Ludwig, 1862). In Copenhagen the existence of hydrogen sulphite was demonstrated because the silver works in the houses near the coast were blackened to a large extent. Sulphuric acid was also determined in London by colouring Litmus paper red.

It took a long time before analytical methods were developed to determine ambient concentrations of trace gases. Smith (1872) measured sulphuric acid in Manchester and London at several places between 1868 and 1869. The sulphuric acid was formed from the burning of sulphur containing coal. He found four times higher concentrations in moist air than under dry conditions. He also reports concentrations measured in the Underground Railway (Metropolitan), which were about a factor of 4 higher than in the city. Witz (1885) identified sulphur in cities (Paris). He compared concentrations outside and inside apartments, in the cities and in the countryside. He was at that time the only one in France interested in sulphur arising from industrial emissions. The direct effects of H_2SO_4 and SO_2 to vegetation and indirect effects in relation to the loss of chalk as the result of SO_2 taken up by the soil (acidification) were recognised at the end of the 18th century (see Tiegs, 1927 for a review). Research was conducted near the main source areas (large cities) to determine acid concentrations, and by determining the sulphur concentrations in needles and leaves from trees grown at several distances from sources and where different wind directions prevailed. A strong relationship was found between sulphur content in needles and the distance from the source or prevailing wind direction.

Wet deposition

In 1819 Julia de Fontenelle found sulphates in dew water (cf. Smith, 1872). The first wet deposition measurements of sulphur were probably made in 1868 by Freytag in Essen,

Germany (Hasselhof and Lindau, 1903). Measurements in Manchester, England, were reported by Smith (1872). He describes the sampling and analysis of rain water as follows:
'A specimen taken in Greenheys field, half a mile from the extreme south-west of Manchester, wind blowing west, had a peculiar oily and bitter taste when freshly caught. A person to whom I gave some of it to taste supposed it had been put into a glass in which castor oil had been put. I had collected the water in a large meat-dish, which had been very carefully cleaned, and was then set on a stand about two feet from the ground during rain. .. Boiling removes all taste, and standing alone removes the taste of the oily matter and leaves only the taste of the smoke. The smoke here shows that it was not out of the range of chimneys, although the wind was west. The taste was that of the flattest and most insipid water, which could not be drunk with pleasure, independently of the nauseous taste.'

The first large-scale research on rain water composition was reported by R. A. Smith (1872) in his marvellous work: *Air and Rain: The beginnings of a chemical climatology.* Smith was more concerned with polluted air and rain in relation to public health, spreading of diseases and damage to buildings, than in the benefit to agriculture of the substances in it. In 1869 Smith sent glass bottles and funnels all over England for the collection of rain water '*in order to come to satisfactory conclusions, and such as would be useful to those who attended to the influence of air on health*'. The sites comprised several measuring points in 12 large towns (London, Manchester, Liverpool, St. Helen's, Runcorn, New-Castle, Glasgow, Aberdeen, Edinburgh, Dundee, Greenock and Perth), at 12 inland sites in England, 13 inland sites in Scotland and 8 coastal sites on the east coast and another 8 on the west coast. Most of the samples were taken during the winter months (December 1869 to February 1870); at only a few sites was one whole year sampled. Smith had made a list of instructions for the optimal collection and to ascertain the collection of the pure rain water. He advised, for example, not to touch the inside of the funnel after it was cleaned. Furthermore, he advised preventing solid matter, dust, falling leaves, snow and sea spray going into the bottle by using a stopper, or by putting the funnel and bottle inside. The funnel was to be placed somewhat above the ground to prevent splashing from the ground in the sample .

Smith (1872) reported that all the rain was found to contain sulphuric acids in proportion to the distance to the town; the increase in acid also meant an increase in organic matter. Furthermore, he states:
'In the fields the amount of acid is not sufficient to neutralise the bases which are in union with the organic matter, and the residue is therefore alkaline; but in the town the amount of acid is equal or in excess; what is in excess is driven-off (during heating, ed.), and enough remains to saturate the bases, which become then neutral salts' and 'we may therefore find three kinds of air - that with carbonate of ammonia in the fields at a distance; that with sulphate of ammonia in the suburbs; and that with sulphuric acid, or acid sulphate, in the town'.

Precipitation was only sporadically analysed for sulphur compounds. Liesegang (1927) and Eriksson (1952b) report some analyses made in Germany, France and Russia between 1860 and 1920. These data are used in Chapter 5 to show the variation over several years. Long-term measurements of sulphur in precipitation are not available in the period before 1930. Since the 1950s interest and research on atmospheric pollution has increased rapidly. This resulted in a strong increase in the number of ambient concentration and precipitation measurements and the formation of monitoring networks. Rodhe and Granat (1984) provide an historical overview of European wet deposition monitoring and an evaluation of SO_4 in European precipitation for the period 1955 - 1982, based on data from the European Air Chemistry Network (EACN). EACN was established in the early 1950s by Scandinavian scientists to establish the wet deposition of nutrients to agricultural and forest soils. Later, the emphasis was placed on understanding chemical and meteorological processes and establishing long-term changes in precipitation chemistry associated with human activities. Continuous data on precipitation chemistry became available in 1955. Based on the EACN network data, the first maps of sulphur deposition in Europe were made by Enger and Eriksson (1955) and Bary and Junge (1963). Nowadays, the European network on precipitation chemistry and air concentrations is run by the co-operative programme for monitoring and evaluating the long-range transport of air pollutants in Europe EMEP. Further to this, there are several national networks.

Dry deposition

The interest in quantification of sulphur in the atmosphere and its deposition increased in the 1940s when it was recognised that sulphur fertilisation could lead to increased agricultural production. It was suggested by Alway (1940) that part of the sulphur requirements of plants might be supplied by direct adsorption of SO_2 by leaves (Chamberlain, 1980). He noted regions where sulphur was deficient due to winds carrying sulphur from sources seldom blowing their way. The first fumigation measurements of alfalfa were reported by Thomas *et al.* (1943) and Chamberlain (1980). The average rate of uptake derived from these experiments was about 1 cm s^{-1}. It was found to depend on pH and fumigation time, and SO_2 concentration. The work of Thomas *et al.* (1943) is considered one of the starting points of the study of SO_2 dry deposition (Chamberlain, 1980). The work of Thomas *et al.* was further extended by, for example, Olsen (1957) and Spedding (1969) for different receptors to determine the rate of uptake. The first gradient measurements of SO_2 concentrations over vegetation are probably those by Gilbert (1968). Many experiments determining SO_2 dry deposition velocities and resistances in the 1970s are reported (see Chapter 3).

1.2.3 THROUGHFALL MEASUREMENTS

Nutrient transfer in throughfall and stemflow is usually substantially larger than that in incident precipitation. The alteration of the composition of water in contact with plant tissues may be attributed to both canopy exchange and atmospheric dry deposition. Hales had already alluded nutrient losses by leaching in his *Vegetable Staticks* in 1727, but De Saussure (1804) remained the first to show experimentally that washed leaves contained less of certain materials than did unwashed leaves (cf. Tukey, 1970). Gaudichaud (1841) and Sachs (1892) observed that water droplets on leaves became alkaline and Garreau (1849) found small amounts of carbonates in washings from leaves (cf. Tukey, 1970). LeClerc and Breazeale (1908) exposed crop plants to artificial rainfall and noted a considerable reduction in cation content within the plants brought about by this treatment. Durant (1932) postulated that throughfall may also contain exudates from the canopy in dry periods. Arens (1934) reviewed papers on particular aspects of canopy exchange published prior to 1930.

That material added to incident precipitation may also originate from dry deposition is a comparatively recent idea postulated by Ingham in 1950. Will (1955) first showed the importance of throughfall relative to the nutrient flux in litterfall for Na, K and Mg. Madgewick and Ovington (1959) were the first to report that different forest types have unique effects in changing the concentration of precipitation (cf. Parker, 1983). Throughfall and stemflow measurements were originally used for the quantification of soil loads. During the last few decades, however, these measurements have been used for studies on atmospheric deposition as well (e.g. Johnson and Lindberg, 1992; Draaijers, 1993).

1.2.4 LONG-RANGE TRANSPORT

The first hypotheses of long-range transport of atmospheric components were related to the sea as a source of chloride in rain and at the surface. Maggraf already hypothesised in 1750 that the chloride he found in a precipitation sample must have come from the ocean. Meyrac (1852) in France showed that NaCl could be transported over long distances, with the ocean as the source. Smith (1872) stated: *'One of the uses of storms seems to be to supply the world with salt'*. That components could travel over long distances was also known because Sahara dust and components emitted by volcanoes, which must have been transported over at least 2500 km through the air were identified in several places in Europe. Ehrenberg demonstrated that material which he investigated by his microscope must have been originating from the eruption of the volcano St. Vincent in 1812. Ehrenberg hypothesised in 1850 that material not originating from volcanoes, originates from dust transported from south America by south-westerly winds to Europe (cf. Ludwig, 1862). Freysing analysed material deposited on the snow on the 12th of March 1847 in Tyrol and found similar characteristics as those described by Ehrenberg. Similar observations were made by Ehrenberg in 1850 in the Gotthard-Alpen, in 1851 in Graubundten and in 1855 in Zurich (cf. Ludwig, 1862).

Brogger (1881) suggested dirt on snow observed in Norway was the result of emissions from Great Britain (Last, 1991). In the Belgium Commission report on damage to vegetation (Rapport à M. le Ministre de l'intérieur par la commission d'enquête, Bruxelles, 1856), so-called 'safe distances' were given for the relation between damage and factories, suggesting transport of pollutants. Smith discussed these distances and hypothesised that they should be a function of wind direction and wind speed, and should not only be related to hydrochloric acid production, but also to smoke stacks producing sulphuric acid.

The first maps of sulphur deposition over large regions, the UK in this case, were made by Meetham (1950). He estimated sulphur and chloride deposition in the UK as the result of smoke emission. The first maps of deposition in Europe were made by Enger and Eriksson (1955). Acidification as a result of deposition of sulphur became of interest in the early sixties (Odén, 1960). In the eighties the concern about the excess nitrogen deposition and its contribution to acidification was recognised as an environmental threat (e.g. Van Breemen *et al.*, 1982). It was only 15 to 20 years ago that air pollution was assumed capable of causing effects not only close to sources. The most feared effects were those to humans because they were exposed to the highest concentrations of pollutants near to source areas (industry, cities). It was thought that the atmosphere was large enough to deal with the relatively low concentrations of pollutants emitted by anthropogenic activity. Furthermore, it was believed that the cleaning capacity of the atmosphere was thus that pollutants would be degraded fast and effectively. The only concern was therefore to keep the concentrations near sources as low as possible. Therefore, high chimneys were built to overcome local pollution. Unfortunately it was not foreseen that long-range transport of pollutants could lead, for instance, to acidification of Scandinavian lakes and destruction of the ozone layer.

The Scandinavian countries hypothesised that the acidification of their lakes was due to acid rain mainly caused by emissions other than their own. To determine whether this was possible, a long-range transport model was developed. This has led to the development of the EMEP (European Monitoring and Evaluation Programme) langrangian long-range transport model which is used under the UN ECE Convention on Long Range Transboundary Air Pollution to determine the concentration and deposition distribution over Europe, to determine the budgets for countries and the so-called blame matrices (Eliassen and Saltbones, 1983; Iversen *et al.*, 1991; Tuovinen *et al.*, 1994). Deposition was treated in this model only as a loss-term. It was thought that the atmospheric deposition had to be known only for large regions as long-term averages. It became clear recently that deposition variation in time and space is very large, and that for determining the relation between effects and deposition, receptor specific estimates are needed (this book).

1.2.5 SYNTHESIS

The historical overview of atmospheric deposition research shows that most emphasis has been on wet deposition measurements. The first measurements are a few hundred years old, but only since the beginning of the 20th century measurements of wet deposition were made on a large scale. There are, unfortunately, large uncertainties associated with these measurements (see e.g. Hansen and Hidy, 1982; Cogbill *et al.*, 1984; Ridder, 1978; Buijsman, 1989; and the discussion in section 5.4). This regards the sampling and analytical techniques, handling of samples, but also the representativity of measuring sites, the influence of local sources, etc.. Despite the uncertainties associated with the data, they can still be very useful in the evaluation of the evolvement of emissions and deposition in time (see section 5.4)
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Techniques for measuring dry deposition have only become available in the seventies. The dry deposition measuring techniques were less suitable for monitoring application than the wet deposition techniques, resulting in a lack of large-scale, long-term dry deposition measurements. Large scale ambient concentration measurements of gases and aerosols were only made since the fifties and sixties. It is therefore not possible to determine the evolvement of dry deposition based on measurements. Although some early studies report measurements of fog composition, these are not accurate and extensive enough to determine the fog deposition.

The long-range transport modelling is well developed during the past twenty years. The emphasis of the studies was on determining the large scale transport and deposition of pollutants. The local scale estimation of deposition was not addressed.

1.3 ATMOSPHERIC DEPOSITION RESEARCH IN THE NETHERLANDS

For assessing the wide range of potential effects of air pollution on ecosystems, it is essential to know the actual atmospheric deposition load. Moreover, it is necessary to know where threshold deposition loads are exceeded and which compounds contribute most to the loads. In this way abatement measures on emission controls can be optimised. Critical loads and target loads for ecosystems have been proposed, both internationally (Hettelingh *et al.*, 1991; 1993) and in the Netherlands (Schneider and Bresser 1988; Verzuringsnota, 1990; Heij and Schneider, 1991). These critical loads are defined on a spatial scale that presently does not allow adequate comparison with mapped deposition fields. The spatial resolution for which critical loads are developed is on ecosystem level, whereas deposition fluxes of acidifying components so far have been estimated on a much larger scale (Van Aalst, 1983; Asman *et al.*, 1986; Iversen *et al.*, 1991; Tuovinen *et al.*, 1994).

There are two ways of determining the ecosystem specific critical load exceedances: i.e. by measurement or by modelling. Total deposition at a site can be estimated using wet, dry and fog deposition measurements or surface accumulation measurements. However, because of the limitations of these techniques and because of the large spatial variability in deposition and type and size of receptors, it is impossible to base the deposition to regions or countries merely on measurements. The development of models for generalisation is therefore inevitable. In order to evaluate and increase the accuracy of modelled depositions, experimental work is needed. The focus of the current atmospheric deposition research in the Netherlands is therefore on both experimental and modelling programs. The experimental research deals with determination of the processes involved in deposition and to derive component and receptor specific deposition parameters which can be used in models. Furthermore, monitoring programs were initialised to determine time series for trend detection and to evaluate the changes in deposition parameters. The modelling is focused on understanding the deposition processes and on generalisation of the experimental results. Furthermore, the evolvement of deposition in the past, present and future, and the origin and source contribution is assessed using models. These models therefore form the basis for developing abatement strategies.

To date, critical load exceedance maps of Europe have been made using deposition estimates from large-scale dispersion models, such as the EMEP model (Iversen *et al.,* 1991) and the TREND model (Van Jaarsveld and Onderdelinden, 1991). These models are very useful for linking emission to deposition on a country to country basis. However, for effect-related studies, the grid squares used in these models (150 x 150 km and 50 x 50 km, respectively) are much too large in comparison with local variations in deposition. Within one grid cell, amounts of atmospheric deposition differ considerably between the various ecosystems or receptors. To cope with this receptor dependency, Erisman (1992) has developed an empirical deposition model in which dry deposition of sulphur and nitrogen compounds in the

Netherlands is inferred on a relatively small scale (5 x 5 km) from measured air concentrations, meteorological parameters, surface resistances and surface roughness. Surface roughness is estimated using detailed geographical information on land use. This inferential technique is also used to estimate atmospheric deposition in Europe on a 10 x 20 km scale (Van Pul *et al.*, 1994).

However, to assess the ecological impact of atmospheric pollutants on ecosystems, it is necessary to quantify the input of atmospheric pollutants in even more detail. Within individual land-use categories a considerable deposition variability may exist. For example, assuming an extensive, uniform forest stand, turbulent exchange between atmosphere and vegetation will be controlled to a large extent by the aerodynamic characteristics of the canopy which, in turn, will be determined by tree height and canopy density. Gases and particles transported to the canopy by this kind of turbulence can deposit on needles/leaves, branches and trunks. Actual deposition amounts will depend, for instance, on the local collecting surface area of the canopy elements, and their efficiency and capacity to capture or absorb gases and particles (Wiman *et al.,* 1990; Erisman, 1992; Draaijers, 1993). Because the above-mentioned parameters vary widely, one can expect a large deposition variability between forest stands.

Furthermore, extensive uniform forested areas are not common in northern and western Europe. In Scandinavia forest landscapes consist of a spatial mosaic of several subsystems: forest stands of different composition, height and canopy structure, logging areas, peat bog areas, lakes etc. In the Netherlands, Denmark, Germany, France, the United Kingdom and several other parts of Europe, forests are usually relatively small and surrounded by vast agricultural areas (Bleuten *et al.,* 1989). Consequently, many forest edges and other transitional zones exist as important attributes affecting surface roughness. Compared to deposition of pollutants in forest interiors, this deposition in forest edges may be greater due to local advection and enhanced turbulent exchange. Especially forest edges exposed to prevailing winds and/or high pollutant doses will be subject to enhanced deposition (Draaijers *et al.*, 1994). Up to now, the deposition of air pollutants to forests has been modelled assuming an infinite horizontal shape. There is no technique available to adequately compensate for 'edge effects' as the underlying processes have still scarcely been studied.

As critical loads directly refer to soil loads, atmospheric deposition and forest soil loads must be linked. Furthermore, since most measures to decrease the effects of acidification presently considered are emission abatement measures, it is essential that the relation can be made between emission of various pollutants and the exposure and deposition, as well as the related effects. This relation is formally described in models. Models of the various compartments (air, soil, [ground]water, vegetation) are interconnected, for instance, in the Dutch Acidification System model DAS (Heij and Schneider, 1991) or the RAINS model (Alcamo *et al.,* 1989). In these models, there is, to date, no well-defined sub-model relating the deposition and the input into the soils below the vegetation. Experimentally, the input to the forest floors and soils below the vegetation has been characterised by measurement of throughfall and stemflow. Due to the interaction with vegetation (e.g. stomatal uptake and leaching), this flux may differ from the deposition flux. Several practical studies have shown that there may be large discrepancies between modelled deposition estimates and forest soil loads measured by throughfall and stemflow (Ivens *et al.,* 1990; Lovett *et al.,* 1992; Erisman, 1992; Cape *et al.,* 1992; Draaijers and Erisman, 1993). Model estimates as well as throughfall deposition estimates are found to be subject to relatively large uncertainties. For components such as Ca^{2+}, K^+, Mg^{2+} and nitrogen compounds (NO_3^- and NH_4^+), canopy exchange processes influence the throughfall composition in such a way that the relation between throughfall and model deposition estimates cannot easily be established. These exchange processes depend on many parameters, e.g. tree vitality, tree age, nutrient status of the soil and pollution climate (Parker, 1983), of which the impact cannot always be quantified adequately with present knowledge. Generally, SO_4^{2-}, Na^+ and Cl^- in throughfall have been found uninfluenced, to a large extent, by canopy exchange processes relative to the atmospheric input (Garten *et al.,* 1988; Ivens, 1990; Johnson and Lindberg, 1992). For this reason, throughfall measurements of these components may be very useful in establishing a relationship between soil loads and modelled deposition estimates.

1.4 OBJECTIVES AND OUTLINE OF THE BOOK

The aim of this book is to describe the current state of knowledge on atmospheric input of acidifying components to ecosystems in Europe. Several issues discussed in the previous section will be addressed; i.e. how to obtain ecosystem-scale deposition estimates using models and measurements, locally but also for Europe as a whole; what is the influence of complex terrain and/or local roughness variation on deposition fluxes; and what is the link between atmospheric deposition estimates and soil loads? The results of these studies provide a quantitative assessment of the actual atmospheric input of acidifying compounds to ecosystems in Europe.

To understand the effects of air pollution to ecosystems, detailed knowledge of concentration and deposition to various parts of the system (e.g. leaves, branches, stems, soil) and the subsequent fate of the pollutants are needed. However, these aspects will not be dealt with in this book. Rather, we will consider deposition as a total input into the system, focusing on deposition on the main target areas, forests, heather and other semi-natural ecosystems in the Netherlands and Europe, although deposition to crops and agricultural areas, and to materials and buildings will also be addressed.

The outline of the book is related to the main lines of atmospheric deposition research conducted in the Netherlands, i.e. first the problems are defined and an overview of the development and application of methods to tackle the problems is given. Then the methods to determine deposition are explained and results are presented. Finally, the uncertainty in results is assessed.

Following this general introduction, emissions, transport and atmospheric chemistry will be addressed in brief in Chapter 2. The aim of this chapter is to give some background information on the evolvement of emissions in Europe and on factors influencing atmospheric chemistry and transport of pollutants. The long-range transport modelling and spatial variations in concentrations are described. Chapter 3 will elucidate the different deposition processes. Measuring methods for deposition and their use in field campaigns and monitoring programs are described, along with a comparison of results of different methods applied simultaneously, resulting in a synthesis on the applicability of the different methods. An literature review of dry deposition measurement results is given in Chapter 4. The experimental results and knowledge on surface exchange mechanisms are translated into surface exchange parametrisations. The deposition parameters, obtained from the literature and from the studies described in Chapter 4, are used directly as input for the deposition models for generalisation of fluxes over the Netherlands and Europe (Chapter 5). In this chapter, the inferential method for dry deposition is described, and the procedures used to obtain local-scale deposition maps are elucidated. Maps of wet, dry and total deposition of SOx, NOy, NHx and potential acid are presented, along with an overview of the deposition evolvement for several years. Estimates of the natural background deposition are also presented for the sake of comparison. Chapter 6 assesses the uncertainty in deposition estimates by *i)* comparing modelled and measured deposition parameters of SO_2 at different sites, *ii)* comparing modelled deposition estimates with throughfall fluxes, and *iii)* by applying an extensive uncertainty analysis of deposition estimates in the Netherlands and Europe. At the end of Chapter 6 the methods and results described in Chapters 1 to 6 will be evaluated in a general synthesis. Three case studies are presented in the last chapter of this book. The first describes a long-term experiment using micrometeorological measurements and throughfall measurements over the heathland called ‘Elspeetsche Veld’. The second is a case study on the influence of canopy structure and forest edges on forest deposition using throughfall measurements. The third case study describes the Speulder forest experiment, where micrometeorological measurements, throughfall measurements and measurements of effect parameters have been made to assess the relation between exposure and deposition of pollutants on the one hand and effects on the other.