CHAPTER 2 EMISSION, TRANSFORMATION AND TRANSPORT

Introduction

The atmosphere consists mainly of nitrogen (78%), oxygen (21%), argon (1%) and a highly variable amount of water vapour (ranging from less than 0.1% to ca. 4%). Besides these components, the atmosphere contains a large number of so-called trace gases, which play an essential role in preserving life on earth, despite their low concentrations in the order of parts per million (ppm) or less. These trace gases are either emitted into the atmosphere from natural sources (sometimes also as a result of human activities) or they are formed in the atmosphere by chemical processes. Among the air pollutants relevant for acidification and eutrophication are sulphur compounds, and oxidised and reduced nitrogen compounds. Once emitted, gases will be transported and dispersed, leading to long-range transport over several hundred kilometres. Almost all air pollution is emitted at or near the surface of the earth. Transport, transformation and removal are mainly confined to a thin layer of ca. 2-3 km, called the planetary boundary layer (PBL). The understanding of the physics and chemistry of the PBL is important for the development of atmospheric transport models and models for deposition as well as for the interpretation of measurements. In this chapter a comprehensive overview on emission, transformation and transport of gases and aerosols in the PBL and the resulting concentration patterns will be presented.

2.1 EMISSION OF NITROGEN AND SULPHUR COMPOUNDS

Sulphur dioxide was one of the first air pollutants recognised as being harmful to humans and ecosystems (see section 1.1 or 1.2). Therefore it is one of the most studied pollutants, with much research being carried out in the early seventies. In the eighties, interest in Europe moved from sulphur compounds to nitrogen compounds. One of the main reasons for that, next to recognising nitrogen as being harmful, is that abatement strategies for sulphur emissions during the last decade have been successful in western Europe, Canada and the USA.

2.1.1 ATMOSPHERIC SULPHUR AND NITROGEN COMPOUNDS

Compounds of sulphur found in the atmosphere include sulphur dioxide (SO_2), sulphur trioxide (SO_3), such aerosol constituents as sulphuric acid (H_2SO_4) and different forms of sulphate such as ammonium sulphate ($(NH_4)_2SO_4$), hydrogen sulphide (H_2S), dimethyl sulphide (DMS), and, finally, different other forms of sulphur (e.g. COS, CH_3SH, CH_3SCH_3 and CS_2). Sulphur is emitted mainly through human activities in the atmosphere in the form of SO_2 (~95%). The most important natural source of SO_2 is volcanoes. The oxidation reactions of SO_2 eventually all lead to the formation of sulphates in a time period in the order of days. SO_3 is emitted together with SO_2, however, in very small amounts compared to SO_2. H_2S is formed primarily from the natural decay of vegetation on land, marshlands and in the oceans (Welphdale, 1987). DMS is primarily emitted from oceans, whereas organic sulphur compounds might be emitted from oceans and vegetation.

Several nitrogen oxides are known, including nitrous oxide (N_2O), nitric oxide (NO), nitrogen dioxide (NO_2), nitrogen trioxide (NO_3), dinitrogen trioxide (N_2O_3), dinitrogen tetroxide (N_2O_4) and dinitrogen pentoxide (N_2O_5). At normal temperatures and small partial pressures N_2O_3 and N_2O_4 decompose rapidly to form NO_2. Oxidised nitrogen is emitted into the atmosphere mainly by combustion processes and from soils in the form of NO. In the presence of O_3, NO is converted rapidly into NO_2. As a result of photochemical reactions in the atmosphere or by hydrolyses of NO_2, HNO_3 and HNO_2 can be formed. Also peroxyacetylnitrate (PAN) can be formed from photochemical conversion of NO_2. N_2O is emitted from soils under conditions of denitrification (Meszaros, 1987). Nitrate aerosols are formed by the reaction of HNO_3 with sea salt or with NH_3.

Reduced nitrogen are present in the atmosphere almost entirely as NH_3 or particulate NH_4^+. NH_3 in Europe is primarily emitted from animal manure, whereas NH_4^+ is primarily formed in the atmosphere as a reaction of NH_3 with H_2SO_4, HNO_3 or HCl.

2.1.2 EMISSIONS

Table 2.1 lists global, European and North American emissions of sulphur dioxide, nitrogen oxides and ammonia separated into anthropogenic and natural sources (Whelpdale, 1987). Anthropogenic emission of SO_2 results from fossil fuel combustion. Most important sources are refineries, power plants, domestic heating and traffic (Table 2.2). In addition to these anthropogenic sources, emissions of reduced sulphur compounds have also been quantified. Estimates of the amount emitted by the biosphere from oceans, soils, terrestrial vegetation and from volcanoes and biomass burning range between 35 and 70 Tg S a^{-1} (see Table 2.3). After oxidation and including oxidised sulphur emissions from natural sources, total natural emissions are roughly equivalent to anthropogenic emissions of about 70 - 100 Tg S a^{-1} on a global scale. In Northern America and Europe, however, anthropogenic emissions dominate.

TABLE 2.1 Total SO_2, NOx and NH_3 emissions in 1987 in the world and on European and American scales separated into natural and anthropogenic emissions (Whelpdale, 1987; NAPAP, 1989)

Scale	SO_2 Tg S a^{-1}		NOx Tg N a^{-1}		NH_3 Tg N a^{-1}	
	Anthropogenic	Natural	Anthropogenic	Natural	Anthropogenic	Natural
Global	85	82	33	18	77-95	32-36
Europe	26	2	5.8	0.5	5.3	0.6
North America	15	1	6.9	1.1	1-10	unknown

Natural nitrogen emissions form only 10% of total nitrogen emissions in Europe. European emissions form 5 - 8% of the total global nitrogen emissions. Total emissions of nitrogen oxides in Europe from the main source categories are presented in Table 2.2. The most important sources are traffic, power stations and industry. Nitrogen oxides are also emitted from soils by denitrification and formed by conversion of NH_3 by OH in the atmosphere. Natural emissions of nitrogen comprise lightning and stratospheric destruction of N_2O.

TABLE 2.2 Source contribution of anthropogenic sulphur dioxide, nitrogen oxides, and ammonia to anthropogenic emissions in 1980 in Europe (Hov *et al.,* 1987; Asman, 1992)

Source contribution to total emissions in Europe	SO_2	NOx	NH_3
Power stations	36%	30%	
Refineries	3%	1%	
Chemical industries	2%	3%	2%
Other industries	42%	26%	
Non-industrial sources	16%	5%	
Traffic	1%	35%	
Livestock breeding			81%
Fertilisers			17%

Ammonia sources include livestock farming, fertilisers, coal combustion, human respiration, households, industry, sewage sludge and traffic (Table 2.2). The contribution of different sources is given by Asman (1992). The major sources for ammonia are agricultural activities, i.e. low level sources. More than 80% of ammonia emissions result from intensive pig, cattle and poultry breeding. Natural sources comprise wildlife and oceans. These emissions are, however, very small compared to anthropogenic emissions.

TABLE 2.3 Emissions of reduced sulphur compounds to the atmosphere in Tg S a^{-1}

Emission sources [a]	Emission
Emissions from the oceans, mainly dimethyl sulphide	16 - 38
Soils and plants	4.8 - 15
Volcanism	9 - 13
Coastal wetlands	2
Biomass burning	>2.4
Sum natural Emissions	32 - 68

[a] Natural emissions as H_2S, COS, CH_3SH, CH_3SCH_3 DMS. and CS_2

Data from: Andreae (1991); Andreae and Andreae (1988); Andreae and Jaeschke (1992); Andreae and Raemdonck (1983); Bates *et al.* (1987); Berresheim *et al.* (1989); Cullis and Hirschler (1980).

2.1.3 EVOLVEMENT OF ANTHROPOGENIC EMISSIONS SINCE 1900

Emissions between 1900 and 1990

Figure 2.1 shows total emissions of sulphur dioxide, nitrogen oxides and ammonia in Europe between 1900 and 1990 (De Leeuw, 1995). Since 1900 all emissions show a distinct upward trend. During the First and second World Wars total sulphur emissions in Europe decreased somewhat. Since 1950 all nitrogen emissions have shown an upward trend. Ammonia emissions doubled between 1950 and 1990, while emissions of nitrogen oxides increased by more than a factor of three. Sulphur dioxide emissions increased by more than a factor of two in these years. After 1985 emissions of both oxidised and reduced nitrogen showed a slight increase, whereas emissions of sulphur dioxide decreased in most countries. Abatement strategies for sulphur emissions during the last decade have been very successful in western Europe (Tuovinen *et al*, 1994), leading to an overall emission reduction of the order of 50%. A comparable trend in emissions has been observed in the USA (National Research Council, 1986; NAPAP, 1992). Figure 2.2 shows the evolvement of sulphur and nitrogen emissions in the USA between 1900 and 1988. Compared to the European estimates a similar evolution of emissions can be observed. Between 1900 and 1970, estimated SO_2 emissions increased by a factor of three, and NOx emissions increased almost ten fold (NAPAP, 1992). In the 1970 - 1987 period, US anthropogenic emissions of SO_2 decreased 28%. NOx emissions remained at the same level during this period.

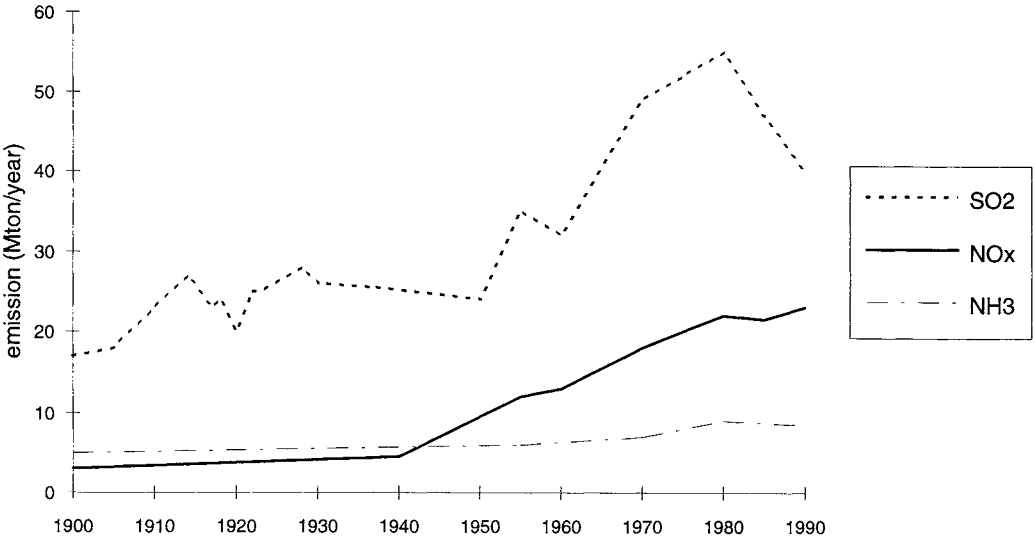


FIGURE 2.1 Emissions of sulphur dioxide, nitrogen oxides and ammonia in Europe from 1900 to 1990 (mton a^{-1}) compiled by De Leeuw (1995)

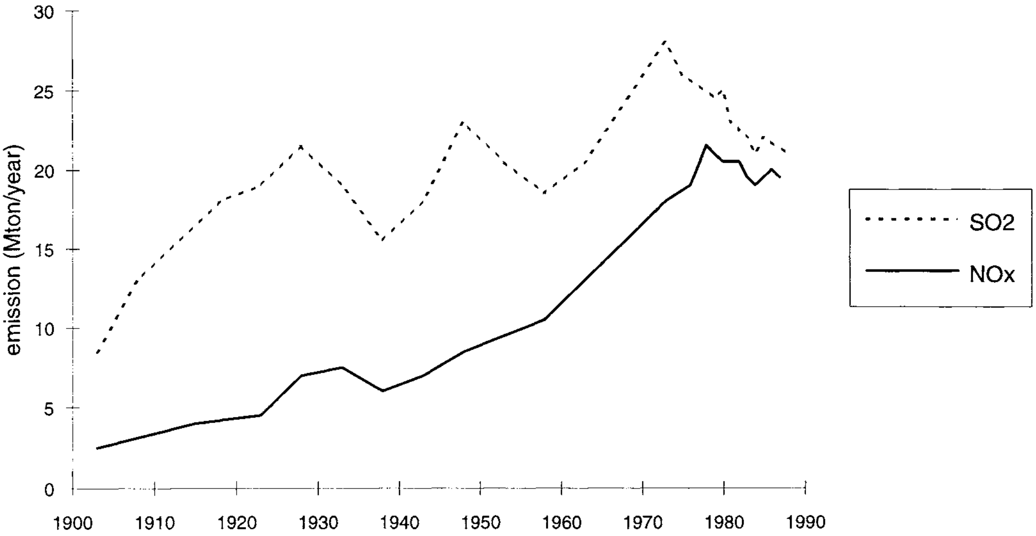


FIGURE 2.2 Emissions of sulphur dioxide, nitrogen oxides and ammonia in USA from 1900 to 1990 (mton a^{-1}) (NAPAP, 1992)

National emissions of sulphur and nitrogen for Europe are compiled by EMEP (Tuovinen *et al*, 1994) (See Appendix A). In most countries nitrogen oxide emissions in 1990 are similar to those in 1985 or a slight (<10%) increase is observed. In contrast to sulphur, a clearly decreasing trend for nitrogen oxides has not been observed in any country. For ammonia, there are few official emission estimates. Estimates have been made for Europe based on animal statistics and emission factors by Buijsman et al. (1984). These estimates were updated by Asman (1992).

Emissions in the Netherlands and Europe during recent years
Detailed emissions for different years are used for long-range transport model input to estimate the concentration and deposition distribution over the Netherlands or Europe (see section 2.3).

The Dutch total annual SO_2 and NOx emissions for the period 1980 - 1993 are given in Table 2.4 and plotted in Figure 2.3. The spatial distribution of SO_2 and NOx emissions in the Netherlands and in Europe shows that the highest emissions are from the industrial areas. For SO_2 emissions in the Netherlands this is the Rijnmond area at the west coast, and for NOx the 'Randstad' in the central-west part of the country. In Europe the so-called 'Black triangle', i.e. the border area between Germany, Poland and the Czech Republic, clearly displays the highest emissions of SO_2. Highest NOx emissions are found in Germany and the Netherlands. The annual average emissions for the countries in Europe are annually reported by EMEP (Tuovinen *et al.*, 1994).

TABLE 2.4 Dutch total annual emissions 1980 - 1993 expressed in kton SO_2, kton NO_2 for NOx

	1980	1981	1982	1983	1984	1985	1986	1987	1988	1989	1990	1991	1992	1993
SO_2	489	463	403	323	299	261	263	262	247	205	201	177	167	168
NOx	582	575	561	554	571	573	586	597	599	583	570	561	550	568

The TREND model was used with meteorological statistics obtained from measurements of the National Air Quality Monitoring Network to estimate the concentration and deposition distribution of NH_3 and NH_4^+ in the Netherlands (Van Jaarsveld, 1994 and Chapter 5). To model this distribution correctly, detailed knowledge on the emission of ammonia in the Netherlands is necessary. Ammonia emissions on a 5 x 5 km grid for 1987 and 1988 were estimated by Erisman (1989). The spatial distribution of the NH_3 emissions in 1980 to 1989 was obtained via scaling of the 1987/1988 distribution with the annual average NH_3 emission (Erisman, 1992; 1993a). Recently, Van der Hoek (1994) estimated 5 x 5 km grid emissions for more recent years (1990, 1991 and 1992). His method was also used to estimate emissions for 1993. The annual average emission in the Netherlands during 1980 to 1993 are listed in Table 2.5. The estimates in Table 2.5 are used here to show annual variations, as displayed in Figure 2.3. The highest emissions are found in three areas with intensive livestock breeding, i.e. the Peel area in the southeast, the province of Overijssel in the central-eastern part of the country and the Gelderse Vallei in the centre of the country.

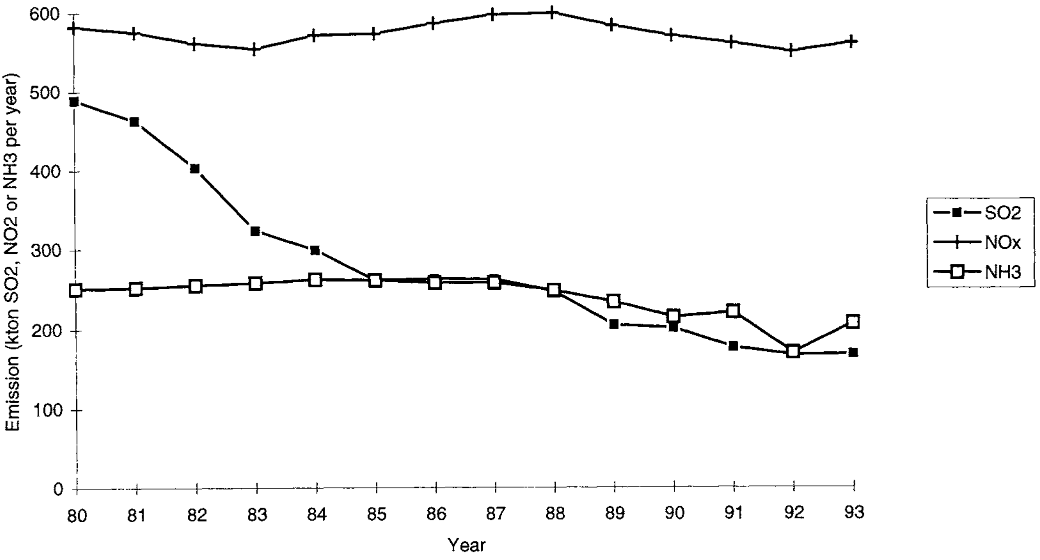


FIGURE 2.3 Total SO_2, NOx and NH_3 emissions in the Netherlands (kton a^{-1}).

From Table 2.5 and Figure 2.3 it is obvious that after 1987 emissions gradually decreased. In 1992 several emission reduction measures were carried out for the first time on a large scale in the country, such as coverage of manure storage basins, change in nitrogen content of fodder and injection or ploughing of manure into the soil. Especially the injection of manure was expected to lead to large emission reductions (Heij *et al.*, 1991). The ammonia estimates for 1992 and 1993 are based on the assumption that measures implemented for emission reduction were 100% effective (Van der Hoek, 1994). This led to the estimation of 20% emission reduction in these years compared to 1991.

The NH_3 emissions for other countries for several years are listed Tuovinen *et al.* (1994). The NH_3 emissions reported by EMEP are based on estimates by Asman (1992). The spatial distribution of NH_3 emissions in Europe shows that the highest NH_3 emissions are found in central Europe with the highest values in the Netherlands, France, Belgium and Denmark.

TABLE 2.5 Overview of the ammonia emission in the Netherlands from 1980 to 1993

	1980[b]	1981[b]	1982[b]	1983[b]	1984[b]	1985[b]	1986[b]	1987[b]	1988[b]	1989[b]	1990[a]	1991[a]	1992[a]	1993[c]
Livestock breeding	235	234	236	240	243	242	242	239	227	211	223	232	174	183
Fertiliser	10	10	10	10	10	10	10	10	10	11	11	10	9	9
Industry	8	8	8	8	8	8	8	8	8	6	5	5	5	5
Households	1	1	1	1	1	1	1	1	1	9	10	11	11	11
Total	254	253	255	258	262	261	260	258	246	237	249	258	199	208

a Van der Hoek (1994)
b Erisman (1992)
[c] Assumed to be equal to 1992 (Van der Hoek, pers. comm.)

2.2 ATMOSPHERIC CHEMISTRY

Atmospheric chemistry is important in relation to atmospheric deposition in two ways. First, conversion of gases in the atmosphere might lead to cleaning the atmosphere of the pollutant gas, or to changes in the physical and chemical properties of the pollutant resulting in changes in deposition characteristics. Second, atmospheric chemistry is important because it might affect the gradient of a pollutant above the surface. This forms a problem when measuring the flux of the component above the surface and when determining its flux with deposition models, assuming a constant flux layer without sources or sinks between the level of determination of the concentration and the receptor surface.

The first case is especially important for all primary emitted gases: NH_3, SO_2 and NOx. NH_3 neutralises acidic gases forming aerosols. These aerosols have much lower deposition velocities, leading to longer transport distances. For SO_2 the same is true via the route of oxidisation to sulphuric acid, which in turn might be neutralised by NH_3. For NOx the coupling is somewhat more complicated because through formation of HNO_3 the deposition velocity of primarily emitted NOx is initially increased to a large extent. However, when neutralised by NH_3, the deposition velocity is lowered again by about a factor of about 4. The second case is especially important for equilibrium reactions between NH_3 and HNO_3, as well as between NOx and O_3.

Air pollution chemistry is often rather complicated in the sense that equilibria and higher-order reactions play an important role. Our knowledge of the chemical conversion processes stems in the first place from fundamental kinetic and mechanistic research. Chemical kinetic schemes are built from the kinetic parameters of the reactions that have been shown to be important. However, considerable uncertainty can remain in the results of kinetic parameters.

Therefore the schemes are tested as a whole against smog chamber experiments or in field studies. Validation of chemical schemes by field studies is only possible if an accurate and complete database for chemical and meteorological data is available. Although sophisticated air quality models incorporate updated detailed transport and transformation processes, many areas of uncertainty remain.

Air pollution models can be classified according to the treatment of chemical processes on the one hand and of dispersion and meteorological processes on the other. In most simple dispersion models like, for instance, the Gaussian plume model, chemical conversion can only be specified as a net first-order rate constant. Such an approximation allows for linear combination of the contributions of different sources to local concentrations, thus cutting down computational effort. On the other hand, simple models for chemical air pollution (e.g., box models) have a chemical reaction scheme as their main component, whereas dispersion and meteorology is dealt with in a rather limited way.

In this section the main chemical reactions for SO_2, NOx and NH_3 are described qualitatively and shown in Figure 2.4. Extensive overviews of chemical reactions can be found in Seinfeld (1986), Finlayson-Pitts and Pitts (1986), Meszaros (1987), and more recently in e.g. EUROTRAC reports (see e.g. Borrel *et al.*, 1995).

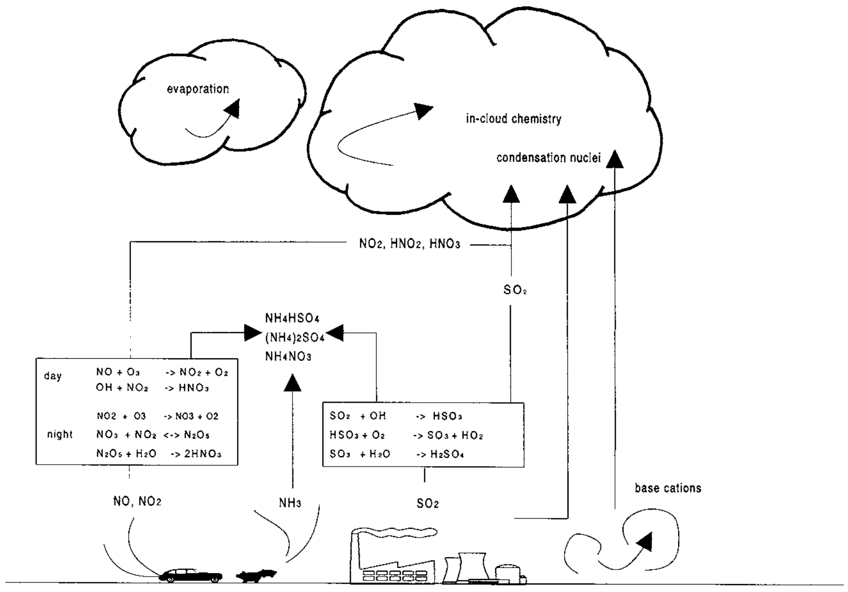


FIGURE 2.4 Atmospheric chemistry relevant for acidifying species.

SO_2

Once emitted, SO_2 may be oxidised to sulphuric acid aerosols or sulphates by reactions occurring in the gas phase, in the liquid phase, on the surfaces of solids, or combinations of these three. The main gas phase reaction is the reaction of SO_2 with OH radicals, first forming HSO_3 and subsequently H_2SO_4. The latter can be neutralised by NH_3 forming $(NH_4)_2SO_4$ or NH_4HSO_4. Rates of conversion generally seem to be higher during the day than at night, and in summer compared to winter (Meszaros, 1987). The presence of liquid water in aerosols, clouds and fog is found to be an important factor in determining the rate of conversion of SO_2 (Finlayson-Pitts and Pitts, 1986). Furthermore, the reaction rate in liquids is influenced by the pH, metallic catalysts and oxidising pollutants (O_2, O_3, H_2O_2) (Welphdale, 1987). Thus sunlight intensities, presence of oxidants and/or oxidant precursors, humidity and the presence of fog and clouds all appear to affect conversion rates. Because of the influence of these variable factors, a wide range of reaction rates is reported in the literature (see Finlayson-Pitts and Pitts, 1986, for a review). Typical summertime oxidation rates in rural areas cause 0.1 - 1.5% loss of SO_2 a^{-1}.

NOx

The atmospheric chemistry of oxidised nitrogen compounds is complicated because they may be converted into a number of different chemical forms. The main oxidised nitrogen compound emitted is nitrogen monoxide. It is oxidised in the atmosphere to nitrogen dioxide and further to nitrate. During the day, nitrogen dioxide is oxidised in the gas phase to nitric acid by the hydroxyl radical. Nitrogen dioxide reacts with water absorbed on a variety of surfaces to form nitric acid and nitrous acid. Nitrous acid is apparently released from the surface, while nitric acid stays absorbed. This provides a minor pathway for nitrate formation in aerosols (Hov *et al.*, 1987). Nitrous acid can also be formed by the reaction of nitrogen monoxide with OH (Pitts and Pitts, 1986). Although nitrous acid photolyses very rapidly, significant concentration levels can be detected in polluted areas in Europe in the middle of the day (Slanina *et al.*, 1990). PAN (peroxyacetyl nitrate) is formed from the reaction of peroxyacetyl radicals with nitrogen dioxide. Although PAN can be present in significant concentrations, its contribution to nitrogen deposition is expected to be low because of low deposition velocities (Dollard *et al.*, 1990).

During night-time, oxidation of nitrogen dioxide by ozone forming the nitrate radical may be an important source of nitric acid. The residence time in the atmosphere varies due to the different reaction processes involved. Of the gaseous nitrogen compounds, nitric acid has the highest deposition velocity and the shortest residence time in the air.

Particulate nitrate is formed by the reaction of gaseous nitric acid with sea salt, basic particles or gaseous ammonia (Seinfeld, 1986). Conversion of gaseous nitric acid and ammonia to particulate nitrate and ammonium is a process of importance for deposition, since easily deposited gaseous compounds are turned into fine particulate nitrate and ammonium, which are slowly deposited and transported over large distances. Ammonium nitrate and ammonium sulphate are hygroscopic, and the humidity in the air will to some extent determine the size of the particles in the air and thus influence the rate of deposition. Ammonium nitrate can be converted back to nitric acid at low ammonia concentrations (Stelson and Seinfeld, 1982a-c). The supply of ammonia is therefore an important factor in determining the residence time of nitrogen oxides.

The interpretation of field measurements of the surface exchange of NO, NO_2 and O_3 are influenced by the photochemical equilibrium between these gases (Duyzer and Fowler, 1994). The reaction rates in this equilibrium system are fast enough to interfere with both measurements of and actual fluxes at the surface. Several methods have been described to correct for the equilibrium reactions to derive the 'real' surface exchange rates. Duyzer and Fowler concluded, however, that none of these methods are accurate enough.

NH_3

Ammonia has a relatively short residence time in the atmosphere. It is readily water soluble and rapidly converted to ammonium, thereby neutralising acid pollutants in the air as well as in the water phase. Particulate ammonium is formed by the reaction between gaseous ammonia and acid compounds in the air such as sulphur dioxide/sulphuric acid and hydrochloric acid droplets. NH_3 can also react with OH radicals, which forms only a minor loss process (Logan, 1982).

NH_3 will react irreversibly with H_2SO_4 -containing aerosol. A smaller part of atmospheric NH_3 will react with HNO_3 and HCl to form aerosol compounds such as NH_4NO_3 and NH_4Cl (Pio and Harrison, 1987) which can dissociate again. The net conversion rate of NH_3 into NH_4^+ in the atmosphere is thus the result of various reactions, diffusion to aerosols and vertical exchange processes in the atmosphere. The conversion rate was determined by Erisman *et al.* (1988) using vertical profiles of NH_3 and NH_4^+ measured at a 200-m meteorological tower in the centre of the Netherlands. For daytime periods a first-order reaction rate of $1 \times 10^{-4}\ s^{-1}$ and for night-time periods $5 \times 10^{-5}\ s^{-1}$ were determined. In fact, the reaction mechanism is much more complicated, because many components are involved and different types of reactions take place in both the gas phase and in solution.

The equilibrium between NH_3 and HNO_3 and HCl can be described using theoretical descriptions of the dissociation constant (Stelson and Seinfeld, 1982). Generally, the theoretical descriptions based on temperature and humidity compare reasonably well with dissociation constants derived from measurements of ambient concentrations of the gases and aerosols. However, at temperatures below 0 °C and at rh > 80% large deviations were found. This might have consequences when the theoretical descriptions are used to correct flux estimates or measurements influenced by the above-mentioned equilibrium reactions.

Because of the frequent predominance of sulphate, nitrate, ammonium and water by total mass, ambient atmospheric aerosol can often be characterised as consisting of a concentrated aqueous solution of ammonium nitrate, ammonium bisulphate and sulphate, nitric and sulphuric acids and two mixed salts of ammonium sulphate and nitrate. Which of these species predominates depends on ambient conditions. When these aerosols act as condensation nuclei or are incorporated into precipitation by rain-out processes, precipitation characteristics are determined by the chemical aerosol system. Thus the wet deposition flux is determined by the composition of the aerosols. To predict the quantity and composition of the aerosol, a prediction of the formation rate of nitric acid and sulphuric acid from NOx and SO_2 precursors, respectively, must be coupled to an equilibrium description of the aerosol. Furthermore, the neutralisation by NH_3, and with this its concentration, temperature and relative humidity play an important role. Therefore changes in precursor emissions play an important role in aerosol concentration and thus wet deposition (see also section 5.3).

2.3 FACTORS AFFECTING TRANSPORT

The maintenance of a tolerable environment depends very much on the ability of wind and turbulence to disperse pollutants rapidly as they are emitted. When these processes fail, the result is a quick build-up of concentrations. A good example of this is the situation in London in the fifties where people were exposed to enormous concentrations of sulphur in air and fog (Brimblecombe, 1987). There are some locations where natural ventilation is so poor that the emission of pollutants must, at all times, be carefully controlled. Factors affecting the dispersion of gases and particles include:

a) *Source characteristics.* Emissions of small sources usually have relatively little buoyancy, since temperature at the point of emission is not much higher than that of the surrounding air. Such sources are liable therefore to have their greatest impact in the immediate vicinity. Emissions from large-scale industrial installations, on the other hand, may be at higher temperatures, or may, by forced draught, compelled to rise more rapidly. Thus, any major impact in the immediate vicinity may be avoided but weaker effects over a wider area may be produced (Bosanquet, 1957).

Dilution and dispersion over a wide area is also aided by the use of tall stacks. Much is known of the relationship between source strength, stack heights and ground-level concentrations of pollutants through the application of mathematical modelling techniques, coupled with observations around selected sources (e.g. Pasquill, 1971). Introduction of tall stacks was thought to be the solution for problems caused by local build-up of concentrations in the sixties. Tall stacks are widely used for power stations and other major industrial sources. Pollutants emitted from these sources will be carried over great distances, often over national boundaries, and will eventually be deposited far away from their sources

b) *Topography and other landscape features.* The presence of hills and many other features of the landscape, have important effects on the dispersion of plumes from individual sources, or of the pollution from an area source as a whole. Many industrial cities have developed in river valleys, initially to take advantage of water transport. However, in general, the dispersion of pollutants in such a situation is poorer than it would be from a more exposed location.

c) *Climate and meteorology.* Meteorological factors are of fundamental importance in determining the whole spatial and temporal distribution of pollution. Apart from the general influence of the local climate, the great variability of the weather in any one locality is liable to lead to considerable changes in the concentrations of gases. In particular, temperature inversions can trap pollutants to produce concentrations of up to 100 times the usual concentration.

Large-scale meteorological factors affecting concentration distributions, and with these also deposition distributions, are dispersion, turbulence (transport), humidity and radiation (chemical conversion). Pollutants are mixed or dispersed through the lower atmosphere by turbulent diffusion, vertical wind shear and precipitation processes. Turbulence is generated both mechanically (e.g. wind shear and surface roughness) and thermally (e.g. convective motion from solar radiation heating the surface). The larger the scale and intensity of turbulence, the more efficient the mixing. Atmospheric motions are slowed down due to the surface drag in the boundary layer.

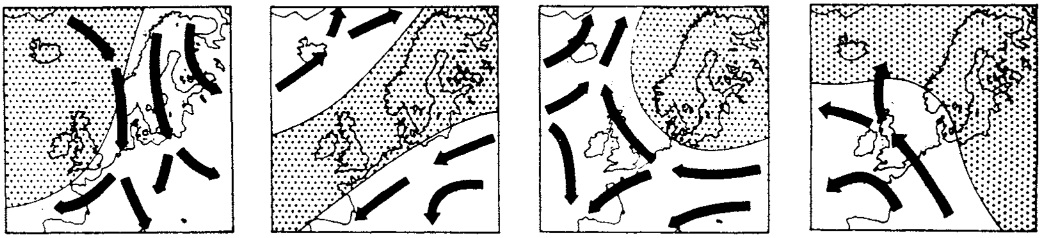
Principle features influencing European climate are the Icelandic low and the Azores high pressure system. They are present at all seasons, although their location and relative intensity can change considerably. The other major pressure system is the Siberian winter anticylone, the occurrence of which is intensified by the extensive winter snow cover and the marked continentality of Eurasia. Atlantic depressions frequently move towards the Norwegian or Mediterranean Seas in winter, but if they travel due east they occlude and fill long before they can penetrate into the heart of Siberia. Thus the Siberian high pressure is quasi-permanent at this season and when it extends westwards severe conditions affect much of Europe. In summer, pressure is low over all of Asia and depressions from the Atlantic tend to follow a more zonal path. Although the depression tracks over Europe do not shift poleward in summer (as a result of a local southwards displacement of the Atlantic Arctic front), the depressions at this season are rather less intense and the diminished airmass contrasts produce weaker fronts. The influence of maritime air masses can extend deep into Europe because there are few major topographic barriers to air flow and because of the presence of the Mediterranean Sea. Hence, the change to a more continental climate regime is relatively gradual except in Scandinavia where the mountain spine produces a sharp contrast between western Norway and Sweden (Barry and Chorley, 1977). Main circulation types above western and central Europe are presented in Figure 2.5.

A large part of western and central Europe is characterised by a relatively warm temperate rainy climate with average temperatures in the coldest month between -3° and 18°C and in the warmest month > 10°C. No distinct dry season can be studied in these areas. Southern Europe has the same temperate rainy climate but now with a clear dry period in summer. South-eastern Europe has a dry climate with mean temperatures in the warmest month > 18°C. Large parts of northern and eastern Europe have a cold boreal forest climate with mean temperatures in the coldest month < -3°C and in the warmest month > 10°C with no clear dry season. Some parts of Scandinavia have a tundra climate with temperatures in the warmest month < 0°C.

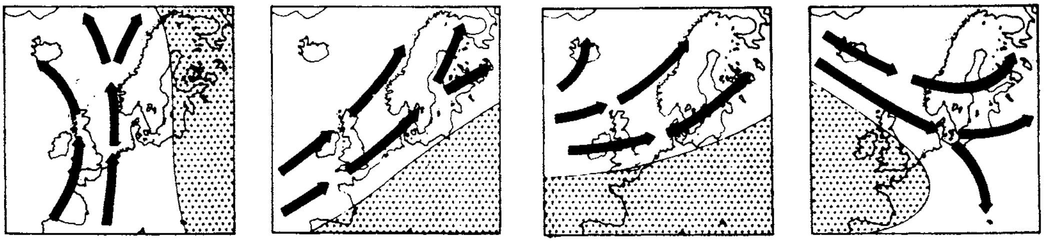
The Dutch climate can be characterised as a maritime climate. Although the wind directions are variable in the regions of the Netherlands, the long-term meteorology can be characterised by several features (KNMI, 1979). Low pressure areas usually move from west to east or from southwest to northeast. These air streams are usually accompanied by moist ocean air and moderate winds. Above the sea, the formation of showers, as a result of convection, is frequently observed. About 60% of the time, wind blows from the south to western directions. The remaining periods can be characterised as variable with regard to wind direction, wind speed and type of weather. One characteristic type of weather is observed during easterly winds, bringing dry air with a low wind speed from the east of the European continent. During such periods, a strong high pressure area is located near Scandinavia. This stable high pressure area persists for several days in a row, leading to episodes of high concentrations of air pollution in the Netherlands and in large other parts of Europe (KNMI, 1979; RIVM, 1990).

The influence of the sea on the climate is large. In summer, the sea brings cool air over the country, whereas in winter it brings warm air. The presence of such a large storage reservoir, not cooled or heated very fast, protects the Netherlands from temperature extremes. Extreme values are therefore nearly always observed in periods with easterly flows. Air coming from an easterly direction can be characterised as polluted because it passes over large industrial areas. Air coming from a (south)westerly direction can be characterised as relatively clean air. The annual amount of precipitation measured in the Netherlands is about 770 mm. The annual average wind speed, measured at a height of 10 m is 4.5 m s^{-1}. Average summer and winter temperatures are about 14 °C and 4 °C, respectively.

The deposition processes of interest constitute a complex sequence of atmospheric phenomena. The deposition fluxes, which are the result of these processes, can vary considerably with time and place. Variations in deposition are the result of large-scale and small-scale meteorological processes. In practice, processes in the boundary layer (height < 3 km) are of the most influence for the amount of deposition (Hov *et al.*, 1987; Hicks *et al.*, 1989).



N-circulation NE-circulation E-circulation SE-circulation



S-circulation SW-circulation W-circulation NW-circulation

BM-circulation HM-circulation TM-circulation Ww-circulation

FIGURE 2.5 Schematic representation of the main circulation types above western and central Europe. The location of the high pressure area is indicated by dots. The arrows give the tracking direction of depressions as well as the mean direction of the wind in the higher air layers. Generally, the characters represent the main direction of the circulation (e.g. SE = southeast); Ww = bending west circulation, BM = high pressure area above Atlantic ocean - central Europe, HM = high pressure area above central Europe, TM = low pressure area above central Europe (after Van der Ham, 1977).

During daytime, the atmospheric boundary layer is usually unstable as a consequence of isolation and convection. During night-time, usually a stable atmosphere is observed because of an upward energy flux due to radiation. The typical boundary-layer development during the day is shown in Figure 2.6. In the morning, during fumigation, the layer breaks open, transporting air from higher levels to ground level. Other meteorological features affecting the transport and deposition of air pollution are snow cover; radiation (influencing the reaction of components and regulating stomatal behaviour); temperature (affecting reaction rates and equilibria, and stomatal behaviour); amount and composition of precipitation; surface wetness by precipitation, dew and fog; wind speed and wind direction. More information on the impact of these features is presented in Chapter 3.

Particles play a crucial role in atmospheric chemistry and atmospheric transport. They can be considered as an important intermediate for gaseous deposition and transport. Furthermore, alkaline particles can increase the buffer capacity of sensitive ecosystems when deposited, thus reducing the effect of acidification due to deposition of acidifying components. The influence of particles in long-range transport, atmospheric chemistry, and wet, dry and fog deposition is gradually becoming clear but is not quantified to a satisfying extent.

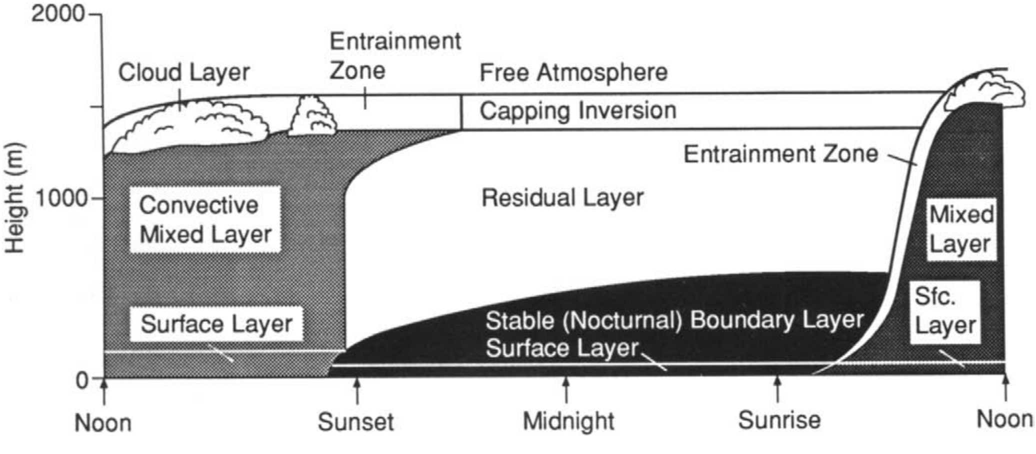


FIGURE 2.6 Daily variation of the boundary-layer development (Stull, 1988).

Natural sources of particles include 'seaspray', re-suspension, volcanoes, biomass burning and meteorites. The first of these two dominate the natural sources of particles. Seaspray is formed by the outburst of air bubbles in the foam on the sea. The aerosols brought into the atmosphere through this process are large particles of which the composition equals that of the ocean. The particles emitted into the atmosphere by re-suspension are composed as mineral dust. These are also mainly large particles in which significant concentrations of Ca^{2+}, Mg^{2+} and K^+ can be found. In the Netherlands deposited seaspray can be re-suspended, thus contributing to Na^+, Mg^{2+}, SO_4^{2-} and Cl^- concentrations in particles.

Acidifying particles are not directly emitted into the atmosphere but are formed by reactions between gases. Atmospheric transport of gases is influenced by particles by several means. Because the dry deposition velocity of particles is usually much lower than that of the gases, the formation of particles from gases leads to long-range transport of pollutants. Furthermore, deposition of gases is influenced through a shift in gaseous composition of the atmosphere, shifting equilibrium and thus the extent that gases are in gaseous or particle form. Gas deposition, especially of soluble gases, is influenced by the layers of water on top of the vegetation (see Chapter 4). Water layers are the result of direct water input from precipitation, or they are formed by deliquescence of particles deposited on the vegetation (Burkhardt and Eiden, 1994). This might be acidifying particles or base cations. Finally, particles serve as condensation nuclei, forming clouds. Gases and aerosols can be scavenged through precipitation.

2.4 LONG-RANGE TRANSPORT MODELLING

The way deposition is modelled depends on its purpose. It may be considered as a loss term in long-range transport modelling, or as an input term in determining the deposition to ecosystems. For the latter it is important to consider the scale on which the deposition is desired. If the scale is comparable to the scale considered in the long-range transport (LTRAP) model, the deposition estimates of this model can be used directly. But if the desirable scale is much smaller than that considered in the LTRAP model, sub-grid processes should be taken into account.

Modelling the dispersion of trace gases in the atmosphere, including their physical and chemical transformations, is an essential element of the general study of trace gas behaviour and in the determination of the functional relationships between emissions and concentration or deposition levels. Measurements and models are strongly intertwined. On the one hand, measurements are necessary for parametrisation and validation of models, while on the other model results may render support in the evaluation, generalisation or extrapolation of measurements. Dispersion models exist in all sizes and complexities. The choice for a model or model concept is determined by the spatial and temporal scale on which air quality and deposition estimates have to be made (cf. Van Dop, 1986). In general, the models can be divided into different categories according to their mathematical framework: Eulerian models with a fixed co-ordinate system, Lagrangian models, where the co-ordinate system moves with the representative parcel of air or hybrid models merging both concepts. Here we will focus on two Lagrangian-type LTRAP models that are used to determine the annual spatial distribution of pollution in Europe and in the Netherlands related to acidification. These are the EMEP (Eliassen and Salbones 1983, Iversen *et al.*, 1991) and TREND (Van Jaarsveld, 1994) models.

The deterministic Lagrangian EMEP model is a receptor-oriented one-layer trajectory model originally developed at the Norwegian Meteorological Institute (Eliassen and Saltbones, 1983) and operationally applied in the framework of the 'Co-operative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe'. The European Monitoring and Evaluation Programme (EMEP) under the UN ECE Convention on Long Range Transboundary Air Pollution, consists of a monitoring programme and modelling of atmospheric transport, conversion and deposition. The aim of EMEP is to provide basic information about emissions, levels of concentrations and deposition. The model calculates 96-h trajectories in reverse time on the basis of the 850 hPa wind field from the arrival of an air parcel at a receptor. Receptor points are the grid points of a 150 x 150 km grid system covering Europe. The trajectories arrive at the receptor points four times a day. During the air parcel's travel along the trajectory, the gridded sulphur and nitrogen emissions are immediately mixed in the vertical up to the top of the constant mixed layer. The model is used every year to estimate sulphur and nitrogen pollution in Europe and to determine the country-to-country receptor matrices and country budgets (e.g. Tuovinen *et al*, 1994).

The statistical transport model TREND is able to describe both short- and long-distance transport, and average concentrations and depositions can be computed for time scales from 1 day to more than 10 years (Van Jaarsveld, 1994). It can account for both point sources of various heights and area sources of various shapes and heights. The sources need not be distributed on a regular grid system. It yields realistic results both within area sources and near point sources, as well as at long distances from sources. The receptor system is therefore determined by the resolution of the emissions. The concentrations and depositions in Europe are described on a 50 x 50 km grid system, whereas those in the Netherlands are estimated on a 5 x 5 km grid system. Computations are made for a limited number of meteorological situations (classes) with a representative meteorology for each class. Among the discretisations, a total of 12 wind-direction sectors and 6 atmospheric stability classes are distinguished. The basis for the model is formed by the Gaussian plume formulation for a point source. It is assumed that the plume is reflected only once at the surface and at the top of the boundary layer. Moreover, it is assumed that at larger distances from the source the plume is vertically distributed homogeneously over the whole boundary layer, apart from an attenuation near the surface due to dry deposition (Van Jaarsveld, 1994; Asman and Van Jaarsveld, 1992).

2.5 SPATIAL VARIATION IN CONCENTRATION

There is a large difference in residence times for the different constituents of the atmosphere. Residence times range from 5000 years and 1,000,000 years for oxygen and nitrogen, respectively, to less than a day for SO_2 and NH_3. Gases such as carbon dioxide, methane and nitrous oxide reside 4 to 10 years in the atmosphere, whereas nitrogen dioxide, water and aerosols can stay in the atmosphere for several days before they are lost to the surface. The longer the residence time of a constituent in the atmosphere, the smaller the spatial and temporal variations (Junge, 1974). The spatial and temporal variations of concentrations of constituents also result from the spatial and temporal variations in emission, and from the variation in rates of conversion or deposition to the surface. The concentration of trace constituents in the atmosphere would rise quickly if sink mechanisms did not assure the cleaning of the atmosphere. Oxidised nitrogen compounds are transported over larger distances than reduced. Typical transport distances for oxidised nitrogen and submicron particles may be 750 - 1000 km; for ammonia in the gaseous phase, distances are only 20 - 100 km, for SO_2, 50 - 200 km.

2.5.1 THE NETHERLANDS

Hourly averaged concentrations of SO_2, NO, and NO_2 are measured within the framework of the Dutch Air Quality Monitoring Network (LML) on a routine basis. From these measurements an accurate spatial distribution of concentrations over the Netherlands during the period 1980 - 1993 can be obtained. NH_3 is introduced in LML in August 1992. Since then continuous hourly averaged NH_3 data at eight locations have also become available (Van Elzakker *et al.*, 1994). Daily concentrations of SO_4^{2-}, NO_3^- and NH_4^+ aerosol are measured at a limited set of stations. In 1989 to 1992 filterpack measurements of total NO_3^- (gaseous HNO_3 and particulate NO_3^-) and total NHx (gaseous NH_3 and particulate NH_4^+) were made as daily averages for 1 out of 8 days at six sites. Measurements with the Annual Denuder System (ADS) were made with the same frequency at 4-5 sites by *RIVM* and *University of Wageningen,* yielding concentrations of SO_2, HNO_2, HNO_3, HCl, NH_3 and particulate NH_4^+, NO_3^-, and SO_4^{2-} (Mennen *et al.*, 1993). Current annual average concentrations of acidifying components in the Netherlands are given in Table 2.6. Maps of the SO_2 and NO_2 concentration distribution derived from LML data over the Netherlands in 1993 are given in Figure 2.7 A and B and of NH_3 calculated using the TREND model (Van Jaarsveld, 1995) in Figure 2.8.

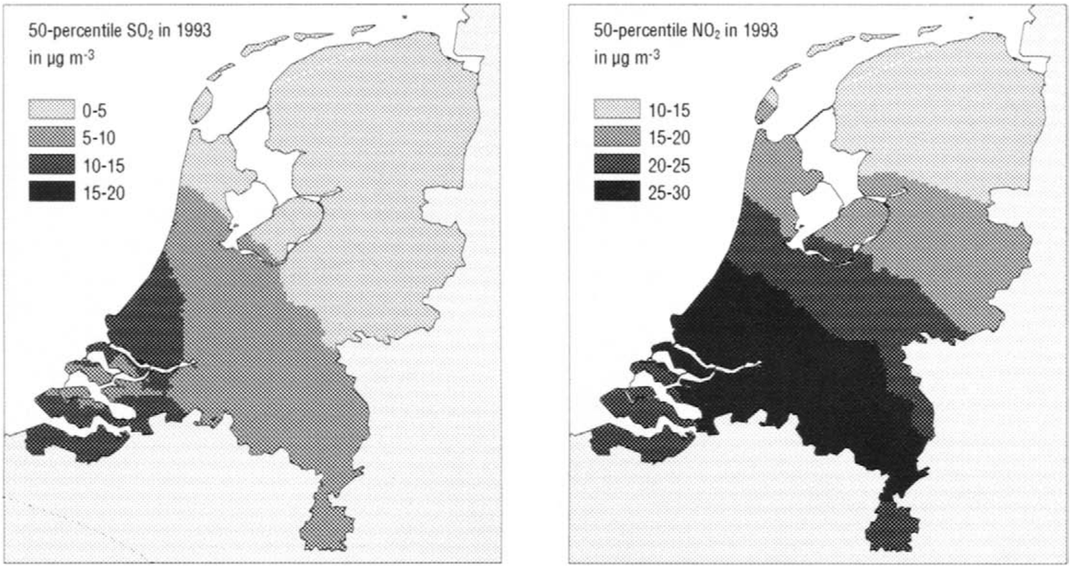


FIGURE 2.7 Distribution of annual median SO_2 and NO_2 concentrations in the Netherlands in 1993 (µg m^{-3}).

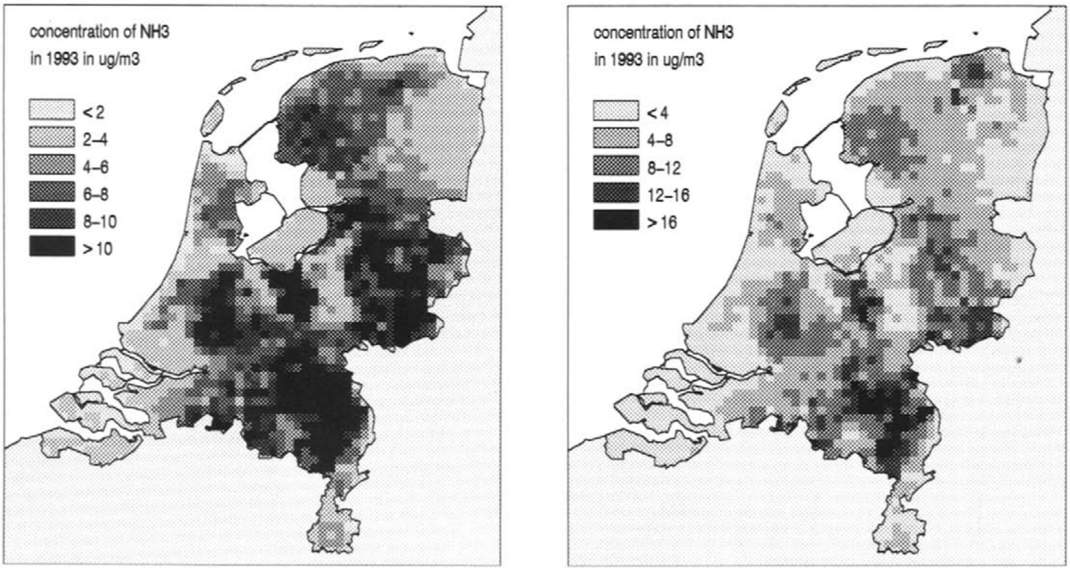


FIGURE 2.8 Distribution of annual average NH_3 concentrations in the Netherlands in 1993 (µg m^{-3}).

TABLE 2.6 Annual average concentrations of acidifying components measured for the Netherlands in 1993 (μg m^{-3})

Component	Concentration (4 m)
SO_2	9
NH_3 [a]	6.4
NO	12
NO_2	25
HNO_2	1.1
HNO_3	0.9
HCl	0.5
NH_4^+	5.1
NO_3^-	5.0
SO_4^{2-}	5.1
Cl^-	4.0
O_3	37

[a] Calculated with the TREND model

Figure 2.9 shows the country average of 50 percentile values of SO_2, NO_2, NOx and O_3 measured in the LML (RIVM, 1994), and the calculated annual average concentrations of NH_3. Ozone concentrations reach their highest levels in spring and summer, when photochemical production is highest. During episodic conditions in spring or summer, peak levels of O_3 above 240 μg m^{-3} can be reached; examples of this occurred in 1982, 1989 and 1990. O_3 concentrations do not show a trend, whereas SO_2 concentrations decreased during 1977 to 1993. NO_2 concentrations show a slight decrease, whereas NOx concentrations remained the same between 1978 and 1993. NH_3 concentrations decreased after 1987, with a strong decrease (20%) after 1991. These estimates are based on emission estimates and TREND model calculations.

2.5.2 EUROPE

Concentration measurements of sulphur dioxide, sulphate, nitrogen (di)oxide, total nitrate and total ammonium in the air are available from several locations in Europe within the EMEP programme. In addition to EMEP there are national networks, providing data on nitrogen oxides representative for a smaller scale. Local networks exist, for instance, in the Netherlands, UK, Germany, Belgium, Luxembourg, France, Denmark and Norway. Few or no routine measurements of ammonia, nitrous acid or nitric acid are available in Europe. Measurements of PAN are made at a number of stations within the EUROTRAC project 'Tropospheric Ozone Research' (TOR). Ammonia has been measured using passive samplers at several locations in the UK during the course of one year (Sutton, 1990), denuders at six locations in the Netherlands for 2 years (Erisman et al., 1986) and wet rotating denuders at eight locations in the Netherlands (Elzakker *et al*, 1994).

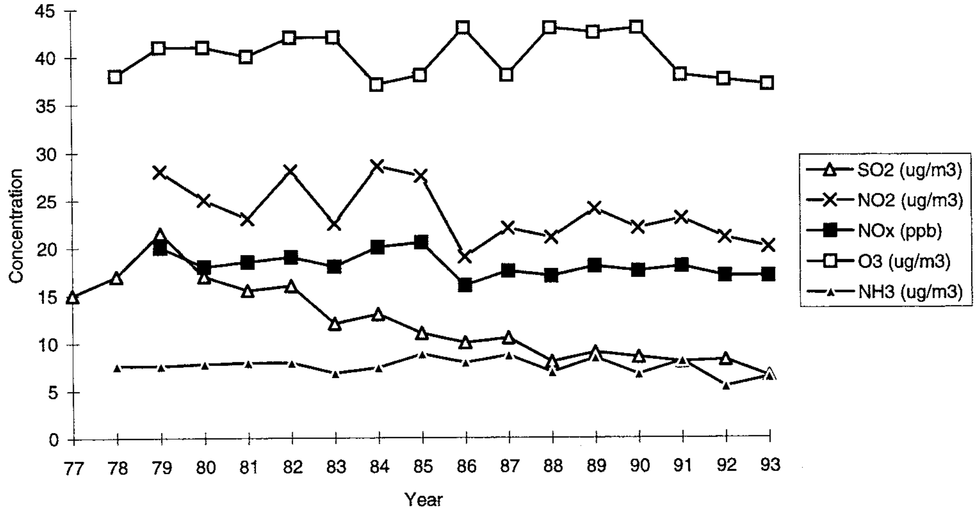
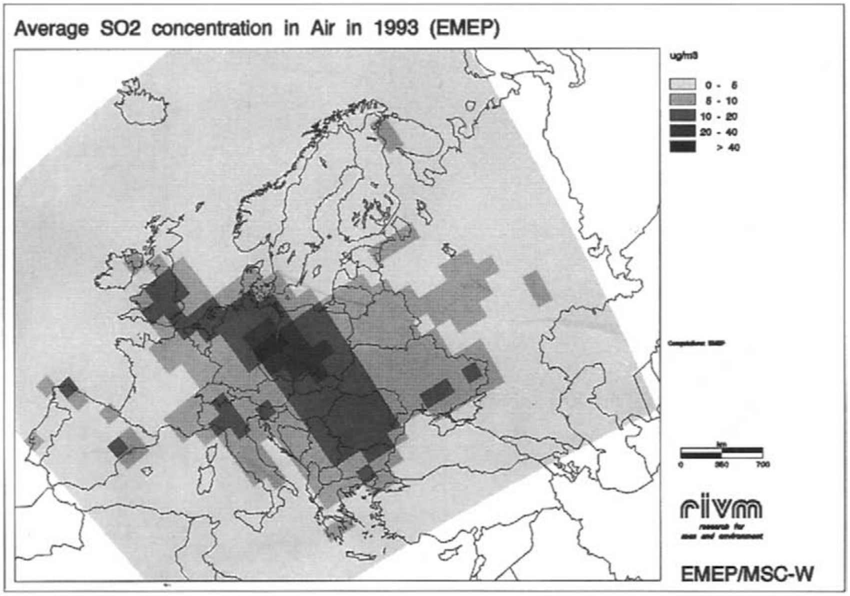


FIGURE 2.9 Annual country average of 50-percentile SO_2, NO_2, NOx and O_3 concentrations, and annual average NH_3 (μg m^{-3}) in 1977 - 1993 based on LML measurements (RIVM, 1994) and TREND model calculations (Van Jaarsveld, 1995).

When local maps are aggregated to a European map, problems may arise due to inconsistency in monitoring methods, quality, time coverage, etc. For this reason, model estimates based on emission inventories and meteorological data have been used to provide concentration maps for SO_2, SO_4^{2-}, NOx, HNO_3 , NO_3^-, NH_3 and NH_4^+ (Iversen *et al.*, 1991; Derwent *et al.*, 1989; van Jaarsveld and Onderdelinden, 1992; Tuovinen *et al.*, 1994). The spatial distribution of the concentrations of these components are given in Figures 2.10 (A - H) (Tuovinen *et al.*, 1994).

The annual mean concentrations of SO_2 and SO_4^{2-} are especially high in the border area between Germany, Poland and the Czech Republic (the ‘Black Triangle’). The highest concentrations of nitrogen oxides particulate nitrate are calculated for the United Kingdom, the Netherlands, Belgium, Germany and the Czech Republic, whereas nitric acid concentrations are relatively high in the Black Triangle. The highest ammonia concentrations are calculated for the Netherlands. Particulate ammonium concentrations are especially high in the Netherlands, Belgium, parts of Germany and France, Switzerland, Austria and northern Italy.



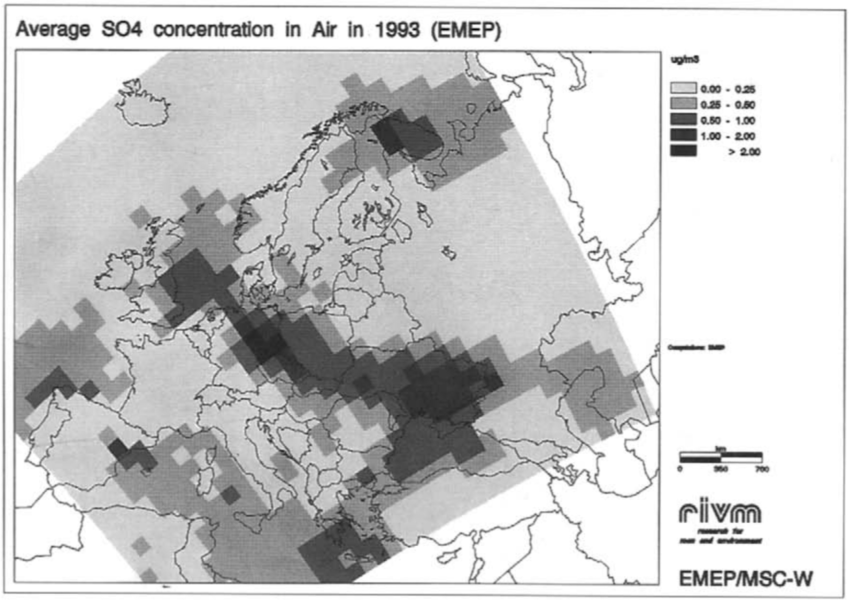


FIGURE 2.10 Annual mean concentration of SO_2 (above) and SO_4^{2-} aerosol (below) in 1993 in Europe as calculated by Tuovinen *et al.* (1994) using the EMEP-LTRAP model

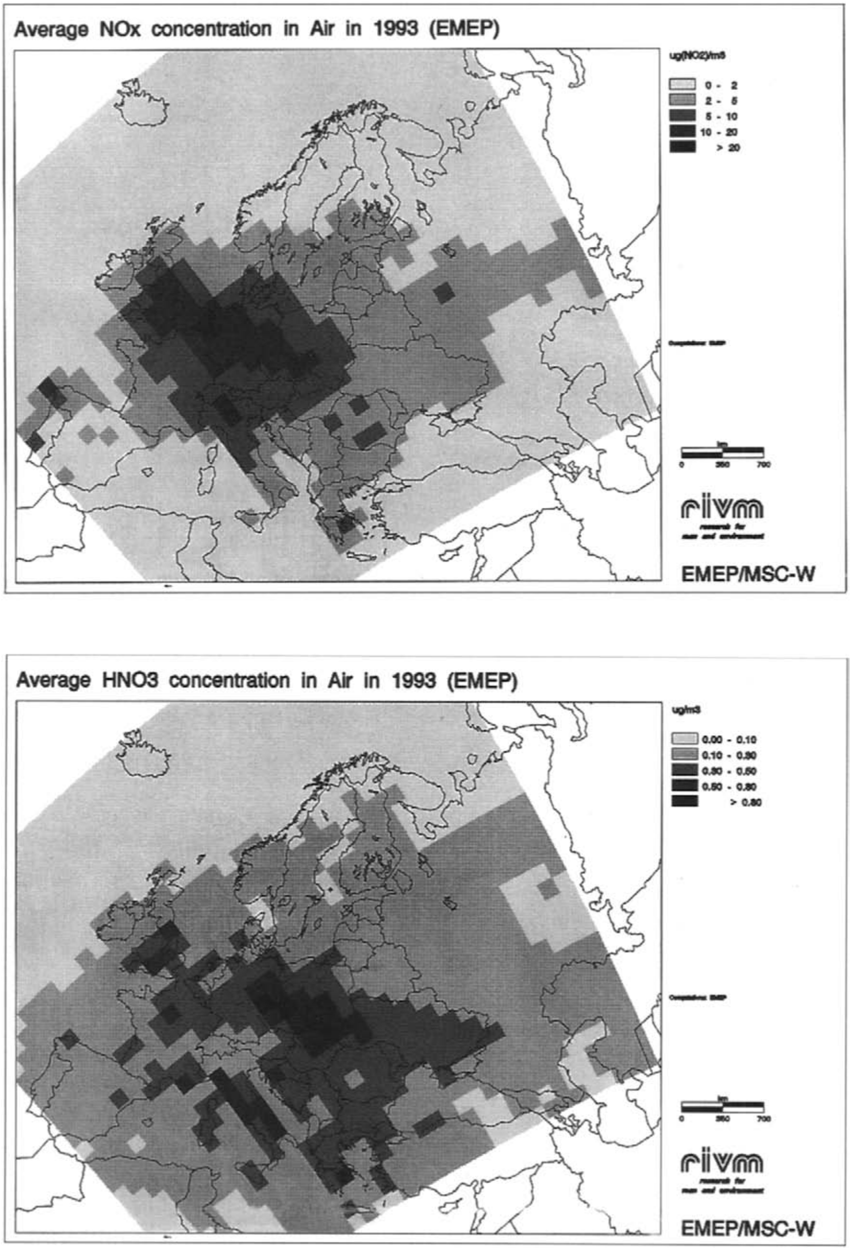


FIGURE 2.10 (*continued*) Annual mean concentration of NOx (above) and HNO_3 (below) in 1993 in Europe as calculated by Tuovinen *et al.* (1994) using the EMEP-LTRAP model

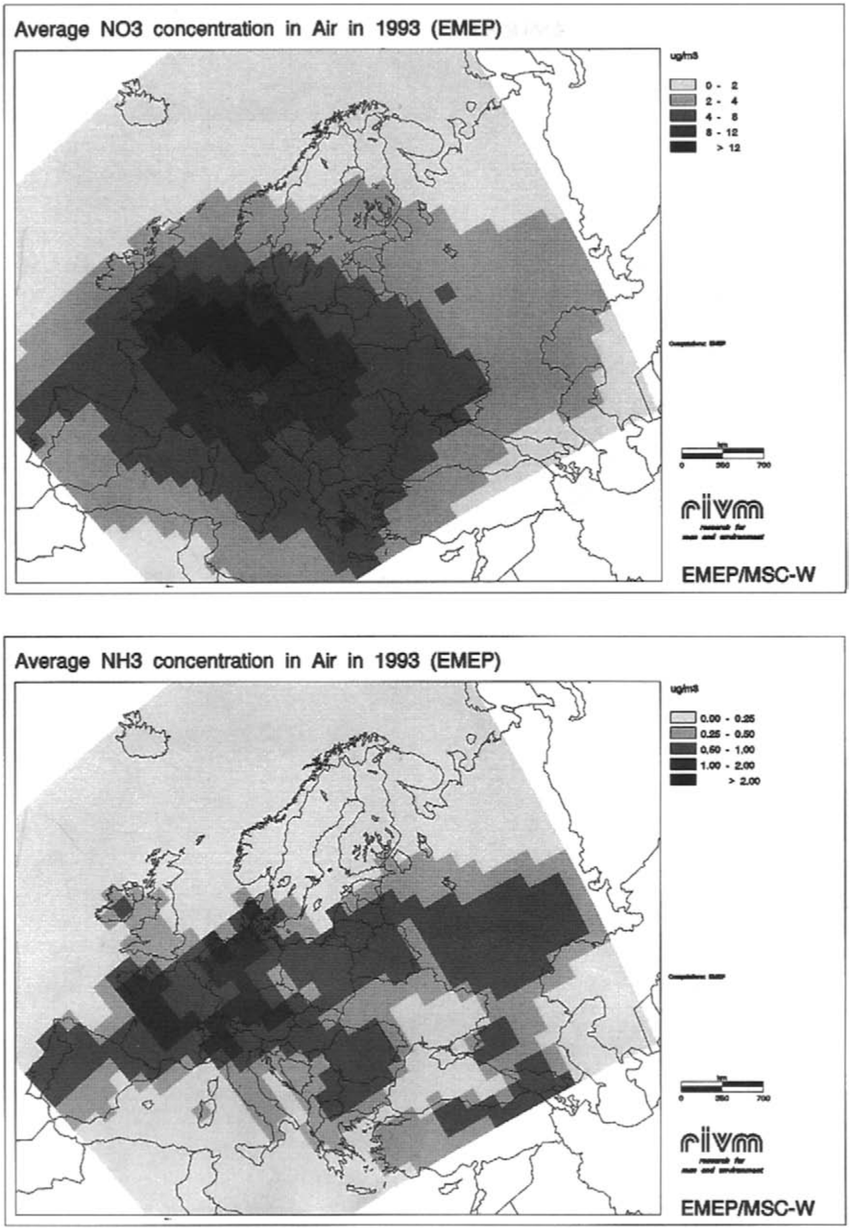


FIGURE 2.10 *(continued)* Annual mean concentration of NO_3^- aerosol (above) and NH_3 (below) in 1993 in Europe as calculated by Tuovinen *et al.* (1994) using the EMEP-LTRAP model

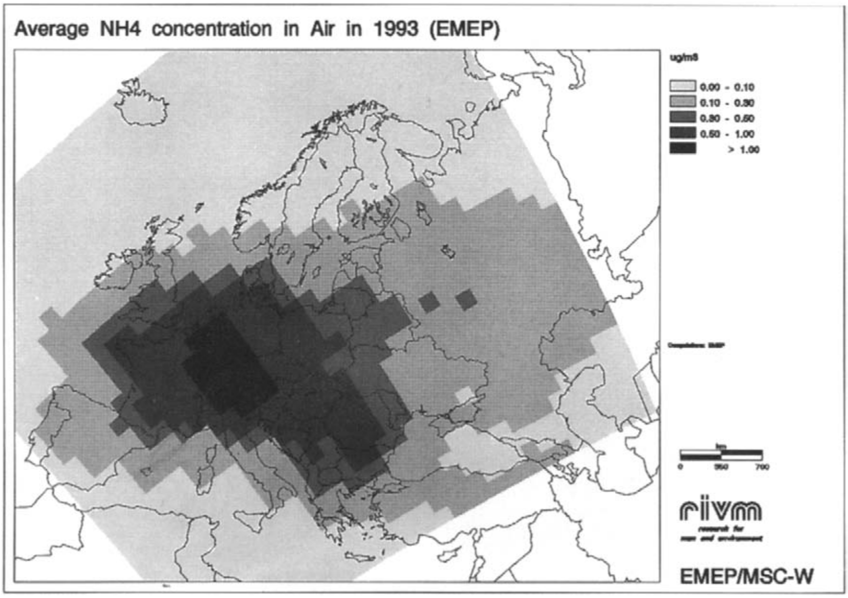


FIGURE 2.10 (*continued*) Annual mean concentration of NH_4^+ aerosol in 1993 in Europe as calculated by Tuovinen *et al.* (1994) using the EMEP-LTRAP model

In addition to the large-scale pollution gradients, there are small-scale concentration variations due to local source impacts. The highest concentrations are expected in or near source regions. As reduced nitrogen compounds are mostly emitted by low-level sources, very steep horizontal gradients in concentration and deposition flux can be observed (Asman *et al.*, 1989). These gradients can lead to serious underestimates in concentrations if large grid averages are used (Asman and Van Jaarsveld, 1992).

Beside the spatial variations in deposition, there is also variation in time. Due to differences in activities leading to variation in emissions and to differences in weather conditions, winds, precipitation, temperature, etc., large temporal variations in concentrations can be observed. There are seasonal variations in the presence of pollutants in air and in precipitation. Concentrations of nitrogen dioxide in the air (with the exception of heavily polluted urban air) is greater during winter than during summer. Concentrations of total ammonium show maxima during spring and autumn. Concentrations in precipitation of reduced as well as oxidised nitrogen are highest in the late spring and lowest in the late autumn.