

Nitrogen processes in the atmosphere

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Executive summary

Nature of the problem

- The two main groups of atmospheric reactive nitrogen compounds (reduced and oxidized nitrogen) have different fates due to differences in governing processes.
- Abatement strategies need to take into account these differences when assessing the impact on the sensitive ecosystems.

Approaches

- The chapter outlines the governing physical and chemical processes for the two main groups of reactive nitrogen compounds.
- The chapter is divided into sections concerning: emissions, transformation, aerosol processes, dry deposition and wet deposition.

Key findings/state of knowledge

- Reactive nitrogen compounds consist of reduced nitrogen (ammonia and its reaction product ammonium), oxidized nitrogen (nitrogen oxides) and organic nitrogen compounds.
- Nitrogen oxides have little impact close to the sources since they are emitted as nitrogen monoxide and nitrogen dioxide with low dry deposition rates. These compounds need to be converted into nitric acid (about 5% per hour) before deposition is efficient.
- Ammonia has a high impact near the sources due to high dry deposition rates. Ammonia may therefore have significant impact on ecosystems in areas with intense agricultural activity leading to high emissions of ammonia.
- Both ammonia and gaseous nitrogen oxides lead to formation of aerosol phase compounds (ammonium and nitrate) which are transported over long distances (up to more than 1000 km).
- Very little is known either quantitatively or qualitatively about organic nitrogen compounds, other than that they can contribute a significant fraction of wet-deposited N, and are present in gaseous and particulate forms in the atmosphere.

Major uncertainties/challenges

- Ambient air concentrations of reactive nitrogen compounds are fairly well (often within $\pm 20\%$ – 30%) reproduced by state-of-the-art models, but estimates of deposition are most more uncertain (often more than $\pm 50\%$).
- Bidirectional fluxes of reactive nitrogen are still not well understood.
- Sources and forms of organic nitrogen deposition are largely unknown.

Recommendations

- There is a significant need for studies of fluxes of reactive nitrogen compounds over sensitive ecosystems. These studies need to include detailed field studies, parameterization, application and testing of chemistry-transport models.

9.1 Introduction

The N_r compounds take part in a series of chemical and physical processes in the atmosphere. Figure 9.1 outlines the main pathways of N_r compounds in the atmosphere. In this context N_2O is disregarded, as it is mainly of importance in the stratosphere, and this compound is therefore only scarcely treated in the following. The left side of the figure illustrates pathways of NH_x whereas pathways of NO_y are illustrated to the right. However, the full picture is more complex than shown in the simple sketch. The aim of this chapter is thus to outline state-of-the-art of what is known to govern turnover processes for N_r compounds in the troposphere. The chapter will therefore describe anthropogenic and biogenic N emissions (Section 9.2), transformations of gas phase N compounds in the atmosphere (Section 9.3), aerosol processes involving N compounds (Section 9.4), as well as dry (Section 9.5) and wet (Section 9.6) deposition to both terrestrial and marine ecosystems of both gas phase and aerosol phase N compounds. Atmospheric transport and dispersion of N_r compounds is handled in Simpson *et al.* 2011 (Chapter 14, this volume), which also deals with the assessment of atmospheric N deposition.

9.2 Emissions of N compounds to the atmosphere

The N_r released to the atmosphere consists of three parts: NH_3 , NO_x , and N_2O , respectively, with smaller (and poorly quantified) contributions from organic compounds such as amines.

9.2.1 Ammonia emission handling

Agricultural activities are the dominating sources of NH_3 emissions (Bouwman *et al.*, 1997). In western countries these activities contribute 85%–100% of the atmospheric releases (Anderson *et al.*, 2003; Sutton *et al.*, 2000), and e.g. in Denmark 98% of the anthropogenic NH_3 emissions are related to agricultural production with the remaining 2% being emitted from petrol cars with catalytic converters (Gyldenkærne *et al.*, 2005; Mikkelsen *et al.*, 2005).

NH_3 emission from animal waste is a physical process taking place from wet surfaces (Elzing and Monteny, 1997). The process is highly temperature dependent and varies significantly over day and season (Gyldenkærne *et al.*, 2005; Skjøth *et al.*, 2004). The regional variation is a function of production methods and agricultural practice, whereas temporal variations depend mainly on meteorology (but equally on agricultural practice). Organic bound N in the manure is not a direct source of NH_3 . The emission strength is therefore mainly related to the manure or fertilizers content of TAN (Total Ammoniacal N = $NH_3 + NH_4^+$), pH, temperature, and wind speed. The agricultural sources of NH_3 may be grouped as:

- point sources, i.e. animal houses and manure storages,
- application of manure and mineral fertilizer to the fields,
- grazing animals,
- other sources including plants.

These categories are in the following described in detail with focus on a parameterization of spatial and temporal variation developed for the Danish area (Gyldenkærne *et al.*, 2005), and

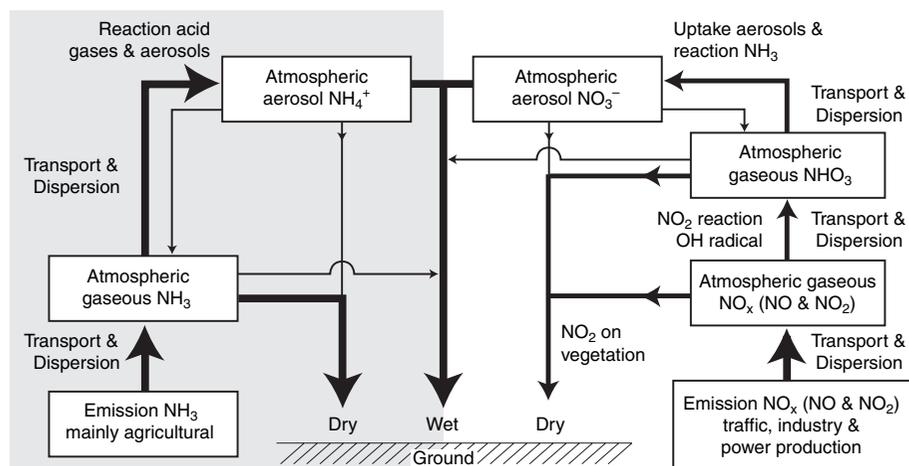


Figure 9.1 Illustration of the pathways of reactive nitrogen (N_r) in the atmosphere. The left side of the figure illustrates the atmospheric pathways of NH_x (gas phase ammonia (NH_3) and aerosol phase ammonium (NH_4^+)) compounds, and the right side of the figure illustrates pathways of the NO_y (NO_x and reaction products) compounds. NH_3 is emitted mainly from agricultural sources. In the atmosphere it is subject to transport and dispersion, but also scavenging by dry deposition and by transformation to aerosol bound NH_4^+ in reactions with acid gases and aerosols. Aerosol bound NH_4^+ has generally a long lifetime in the atmosphere and may therefore be transported over long distances (>1000 km). The NH_4^+ containing aerosols are mainly removed by wet deposition. Nitrogen oxides (NO_y) are emitted to the atmosphere as NO_x (the sum of nitrogen monoxide (NO) and nitrogen dioxide (NO_2)), where also these compounds are subject to transport and dispersion. NO_2 may be dry deposited to the vegetation, but it is mainly scavenged from the atmosphere by reaction with OH radical in the formation of nitric acid (HNO_3). HNO_3 has a very short lifetime in the atmosphere, since it is quickly scavenged by uptake in aerosols, reaction with NH_3 or by dry deposition (it sticks to any surface – aerosol as well as ground). Uptake in aerosols or formation of new aerosols by the reaction with NH_3 leads to aerosol bound nitrate (NO_3^-). Also NO_3^- containing aerosols (in some cases the same aerosols that contain NH_4^+) are mainly scavenged by wet deposition. Aerosol phase NH_4^+ and NO_3^- may under certain circumstances depending on humidity and temperature – be released back to gas phase NH_3 and HNO_3 . N_2O is excluded in the figure, as it does not play an important role in the atmospheric N deposition. For simplicity, reservoir compounds like HONO, HO_2NO_2 , PAN and PAN-like species have also been disregarded from the sketch. Source: Hertel *et al.* (2006).

currently considered as the best and most advanced (Pinder *et al.*, 2007). The parameterization has been implemented into the atmospheric transport models: the ACDEP model (Skjøth *et al.*, 2004), the Danish Eulerian Hemispheric Model (DEHM), the Unified EMEP model (Fagerli *et al.*, 2007), and the local scale model OML-DEP (Sommer *et al.*, 2009).

Animal houses and manure storages

Significant variations in NH_3 emissions are found for different types of animals and housings (Koerkamp *et al.*, 1998). The variations are related to amount of TAN in the manure, stable temperature, and ventilation rate. Highly complex surface models describe the NH_3 emissions from agricultural buildings (Muck and Steenhuis, 1982; Olesen and Sommer, 1993; Oudendag and Luesink, 1998; Zhang *et al.*, 1994), but are not applicable for large scale modelling (Gyldenkærne *et al.*, 2005; Pinder *et al.*, 2004). A simplified parameterization based on wind speed and ambient air temperature is in this case a more practical approach. Most inventories are using total N or TAN content in the manure together with fixed average emission factors (EF) for different types of animals, housing systems, and manure applications. The EF should be location specific and account for local conditions, and such data are currently being processed for the entire European area.

At large scales, it has been shown that the variation in emissions $E(t)$ from stables and storages may be described by a simple parameterization (Gyldenkærne *et al.*, 2005; Skjøth *et al.*, 2004):

$$E(t) = C \times T(t)^{0.89} \times V(t)^{0.26}, \quad (9.1)$$

where C is a constant which can be related to the amount of N or TAN in the manure at a given time and location, $T(t)$ is the temperature as function of time, and V is the wind speed or the rate of ventilation. This formula may help to distribute a known annual emission into smaller time step v .

Concerning the differences between animal types, pig and poultry have a critical temperature that is relatively high compared with cattle. This means that in Northern Europe stables with pigs and poultry are heated during winter. The magnitude of the overall annual emission from a given manure storage reflects the type of storage, whereas the temporal variation in the emission reflects variations in ambient air temperature (Gyldenkærne *et al.*, 2005). In warm areas and during warm periods of time, the emissions from all buildings will reflect outdoor temperatures. Buildings containing pigs and poultry thus have significant emissions also during cold periods, when cattle barns and storages have low emission rates.

Applying the parameterization in equation (9.1) and the simplified functions shown in Figure 9.2, the temporal variation in NH_3 emissions may be simulated. Figure 9.3 shows as an example of calculated temporal variation in NH_3 emission from a pig stable, cattle barn and manure storage.

Application of manure and mineral fertilizer

The emission of NH_3 from field application of manure and mineral fertilizer takes place at distinct times of year with

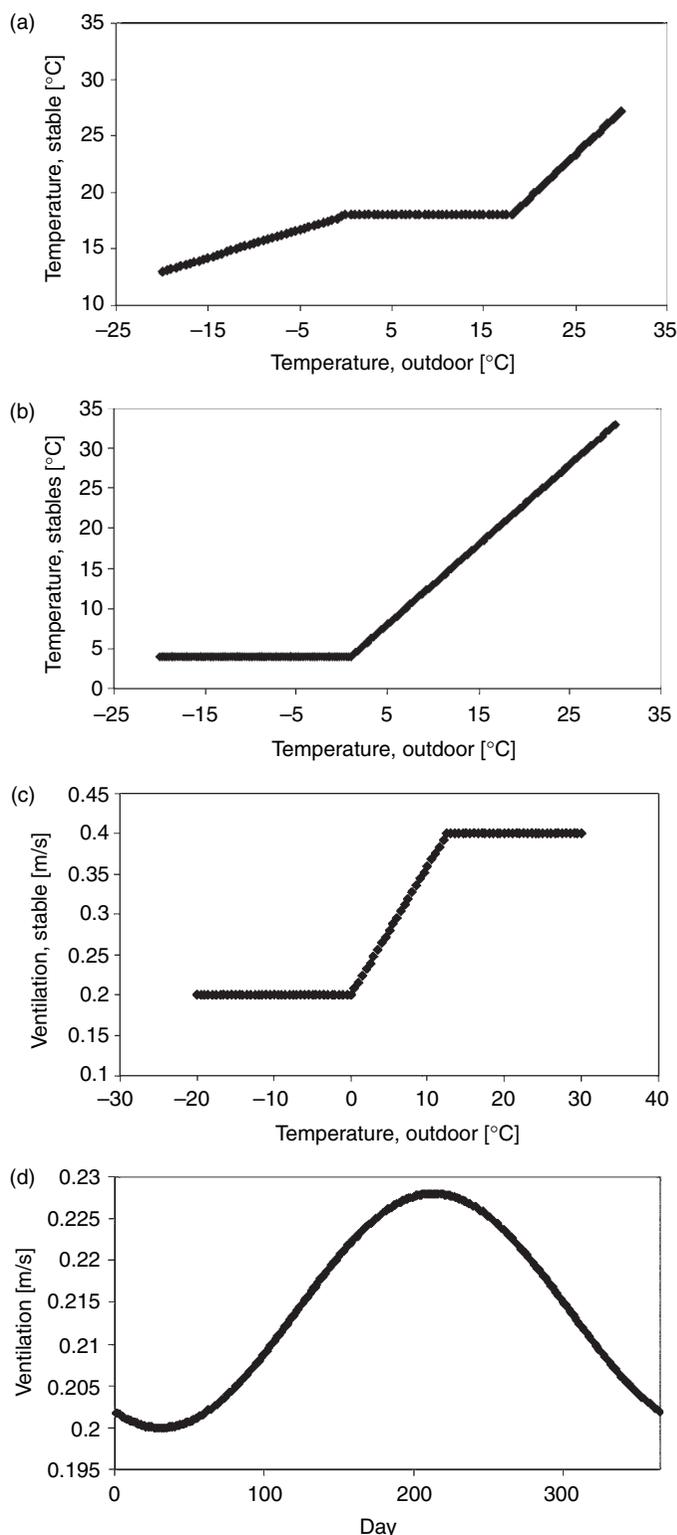


Figure 9.2 The indoor temperature as function of outdoor ambient air temperature for (a) isolated stables, (b) open barns. Ventilation rate for (c) isolated stables as function of ambient air temperatures, and (d) open barns as function of day of year.

relatively short duration compared with point source emissions. The application method is crucial for the magnitude of the emission. Very high emissions are related to the application

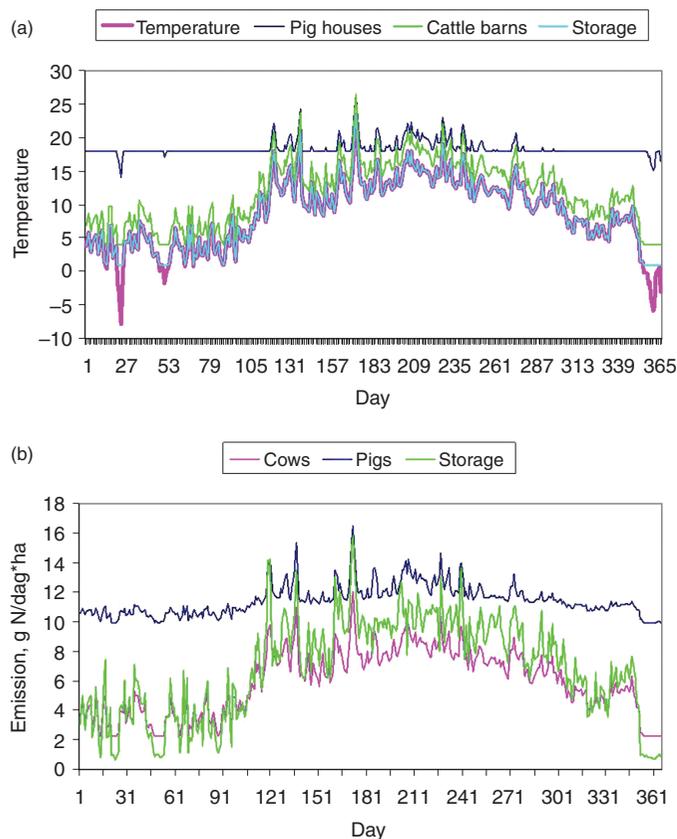


Figure 9.3 Simulations for open and isolated stables and manure storages. The top figure shows the calculated daily mean temperature, and the lower figure shows the calculated daily emission at Tange, Denmark in the year 2000. Source: Ellermann *et al.* (2004).

of broad spread methods, whereas soil injection methods lead to very low emissions. National regulations may in some cases play a significant role with regards to the seasonal variation. In some countries manure application is constrained with almost no regulation, whereas in many North European countries manure application is abandoned during winter time. To overcome a shortage in manure storage capacity farmers often empty their slurry tanks in the autumn. This may give high emissions in the autumn. The timing of mineral fertilizers and the related NH_3 differ also between regions giving different temporal emission patterns, where farmers in the Southern parts of Europe initiate application of fertilizer earlier than in Northern Europe. Figure 9.4 shows the temporal variation in NH_3 emission having four typical application times during the year 2000 at Tange in Denmark.

Emission of NH_3 from grazing animals

The emission from grazing animals depends on time spent in the field and N content in the grass. The latter leads to excretion of large amounts of excessive N as TAN compared with more extensive grassland. However, the urine is easily entering the soil, which will lower the emission potential compared to surface applied slurry. In Southern Europe, animals are in the field most of the year. Sheep may remain in the field most of the time, whereas dairy cattle in many countries are inside

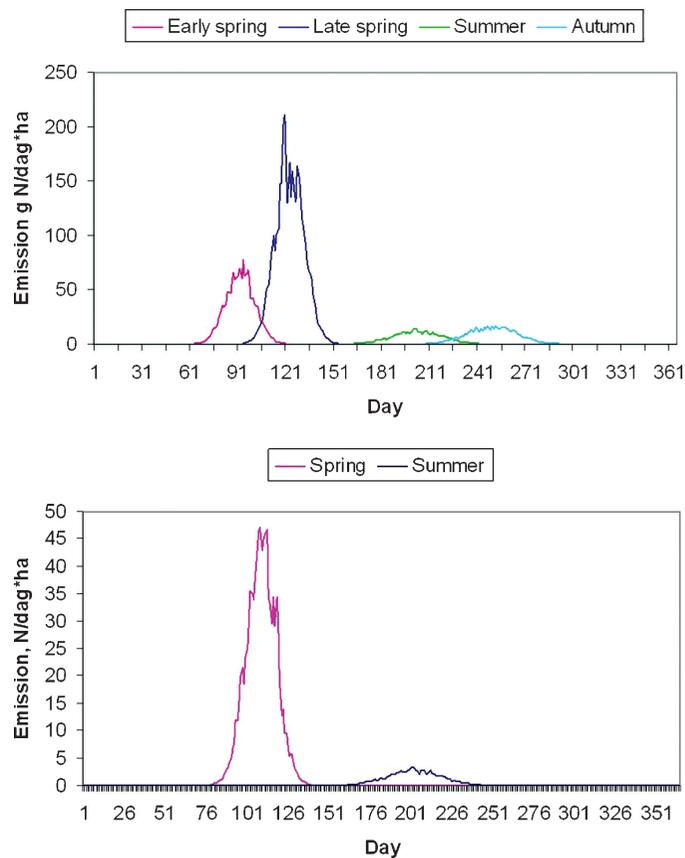


Figure 9.4 The emission strength and temporal variation in NH_3 emission in the Tange area in Denmark related to application of manure during spring, summer and autumn (top) and mineral fertilizer during spring and summer (bottom). Source: Ellermann *et al.* (2004).

the stables approximately half of the year (see e.g. *Regional Air Pollution Information and Simulation* model (RAINS) database (RAINS, 2010)). The number of grazing animals will in general follow the availability of grass, or the season of growth. There is little knowledge on the effect of temperature on the NH_3 emission.

Emission of NH_3 from other sources

Legumes and plants taking up excess fertilizer are emitting NH_3 (Larsson *et al.*, 1998). The emission depends on the enrichment of the apoplast with NH_4^+ , and the compensation point (Farquhar *et al.*, 1980) (see Section 9.5), which is a function of the plant status with respect to growth and stress, etc. The emission is still not well described with respect to magnitude, as well as temporal and spatial variation. Emissions from non-agricultural sources are in general not well described but include sweat from humans, exhaust from gasoline cars with catalytic converters, excreta from pets and wild animals, and evaporation from waste deposits (Sutton *et al.*, 2000). In Europe, the largest national non-agricultural NH_3 emission has been reported for the UK with a fraction of about 15% (Sutton *et al.*, 2000), compared with about 2% reported for Denmark (it has been disputed whether the Danish inventory accounts for natural NH_3 emissions).

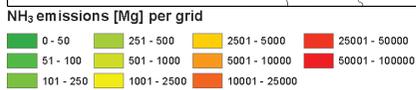
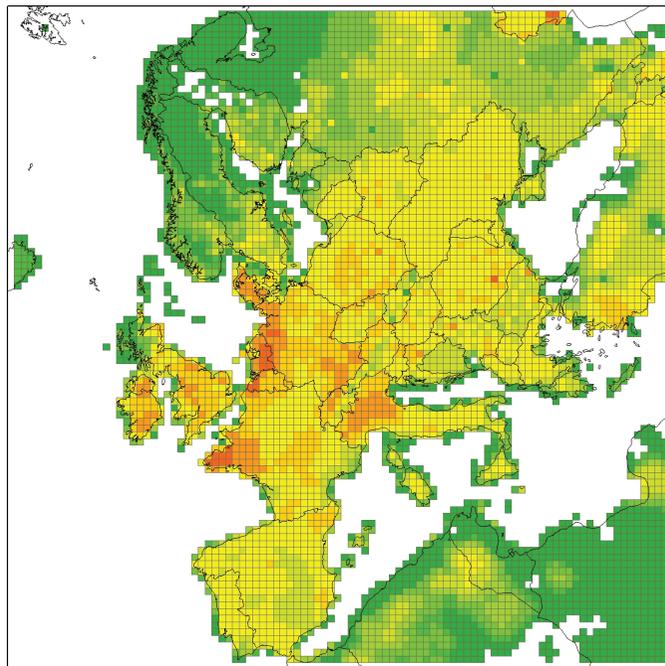
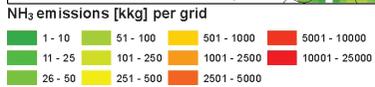
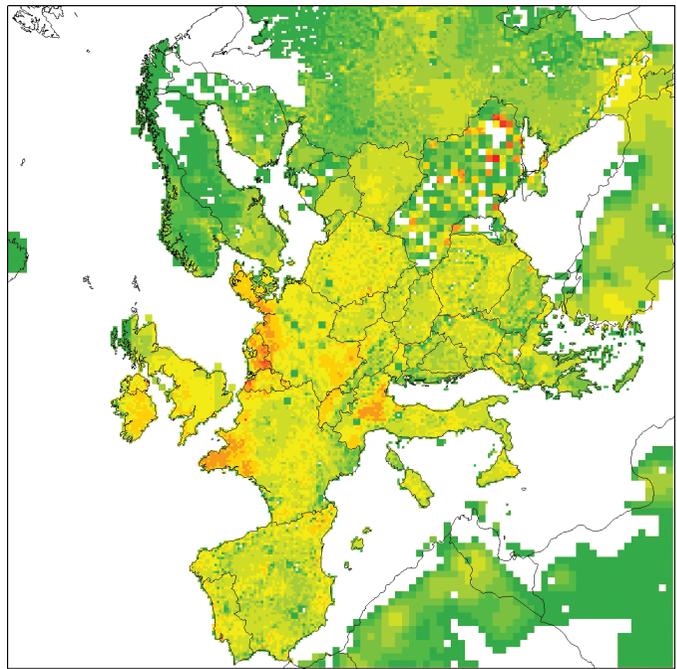
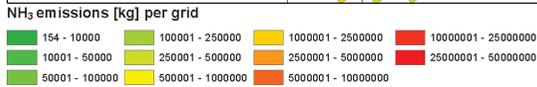
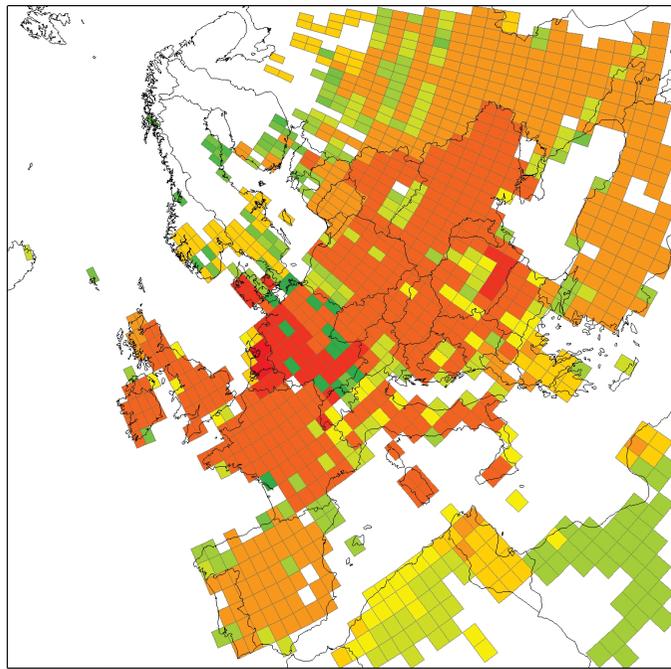


Figure 9.5 Annual NH₃ emissions in Europe based on: (top left) Edgar data from 1995 (1° × 1°) in kg NH₃/grid cell, (top right) EMEP data from 2000 (50 km × 50 km) in Mg NH₃/grid cell, and (bottom) NERI data based on EMEP and GENEMIS data (16.67 km × 16.67 km) in tonnes NH₃/grid cell.

Relative distribution of ammonia emissions between sectors

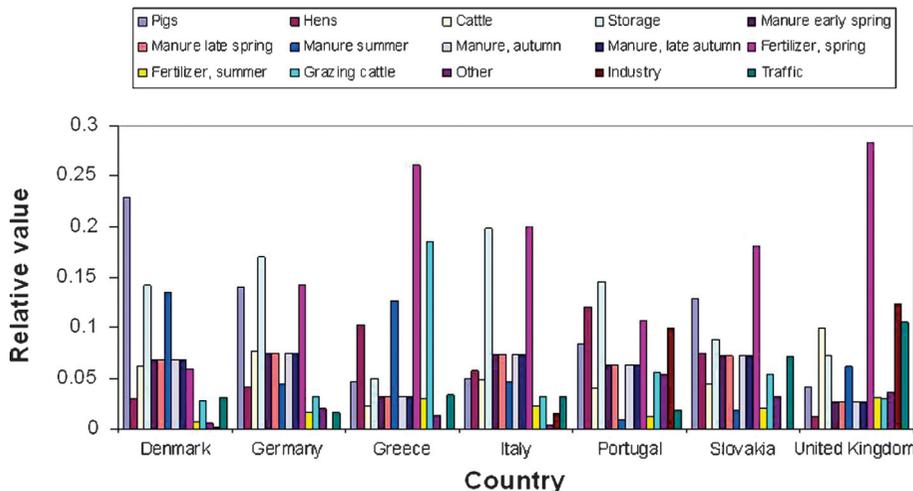


Figure 9.6 The relative distribution between different NH₃ sources in national emissions. Data derived for the year 2000 (Hertel *et al.*, 2006).

Spatial distribution in NH₃ emissions

At the European level, EMEP (Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP, 2010)) and CORINAIR (CORe INventory AIR emissions) compile inventories of the annual mean emissions on a grid with a spatial resolution of 50 km × 50 km. The EDGAR (Emissions Database for Global Atmospheric Research; EDGAR, 2010) and GEIA (Global Emissions Inventory Activity; GEIA, 2010) databases are available on 1° × 1° resolutions, and the EUROTRAC (EUREKA project on the transport and chemical transformation of trace constituents in the troposphere over Europe) GENEMIS (Generation and Evaluation of Emission Data) project (Eurotrac, 2010) compiled inventories with a grid resolution of 16.67 km × 16.67 km. The GENEMIS data was for the year 1994, but has in some studies been used to redistribute EMEP emission inventories for following years, assuming unchanged relative distribution over the years (Hertel *et al.*, 2002; Spokes *et al.*, 2006). NH₃ emission has evidently a non-uniform distribution throughout Europe (Figure 9.5).

Figure 9.6 shows the relative national distribution in NH₃ emission between the typical agricultural emission source categories.

Site specific long term trends in NH₃ emissions

In Denmark before 1989, the NH₃ emission was relatively low during winter time as a result of low activity and low temperatures. The accumulated manure during winter was applied to crops in the fields during spring, but also to grass fields during summer. Finally the manure storages were emptied in autumn (Figure 9.7). This pattern is typical in Northern Europe with moderate to large agricultural activity and limited legislative control.

In the 1990s Denmark implemented the until now strongest European regulation on local agricultural activities in order to reduce emissions to air, soil and water (Grant and Blicher-Mathiesen, 2004; Skjøth *et al.*, 2008). This included improving the entire production chain with respect to

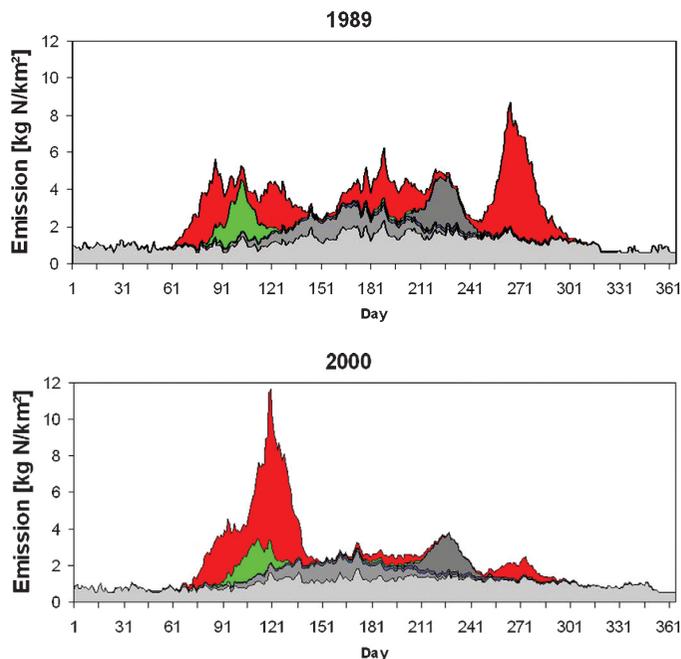
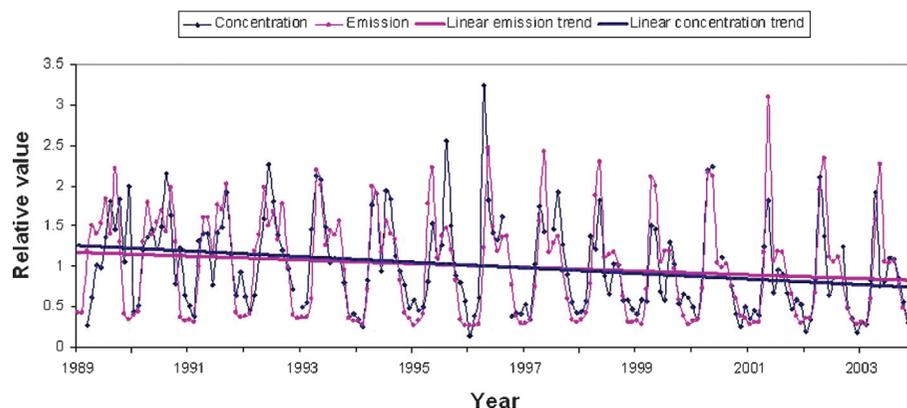


Figure 9.7 Temporal variation in daily NH₃ emission [g N/ha/day] from different sources in Tange, Denmark for the years 1989 (top) and 2000 (bottom). Source: Skjøth *et al.* (2008).

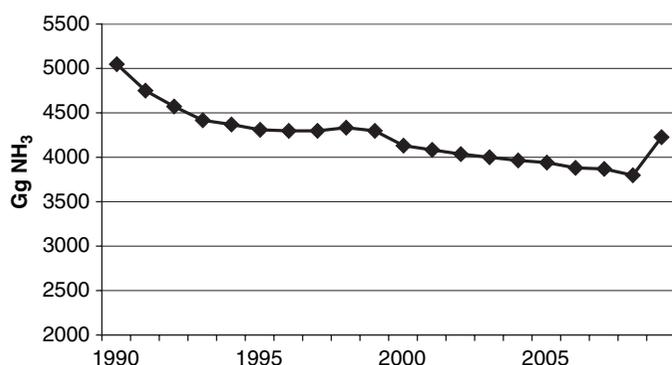
reducing NH₃ emissions. The farmers had to increase the fraction of manure applied during growth of the crops in spring, and similarly decrease the fraction applied in summer and autumn. This is seen in Figure 9.8, where the emission peak in spring is more pronounced and emissions in summer and autumn reduced when comparing 1989 to 2000. The overall Danish release of NH₃ was decreased significantly (Table 9.1) despite an increase in animal production over this period (Skjøth *et al.*, 2008).

Long term trends in NH₃ emissions on European scale

The NH₃ emissions have been reduced in countries like Denmark, Germany and the Netherlands, whereas for

Tange concentration and emission changes from 1989-2003**Figure 9.8** Comparison of the trends in computed monthly mean NH_3 emissions (pink) and observed monthly mean ambient air NH_3 concentrations (blue) for the Danish monitoring station Tange during the time period 1989 to 2003 (Skjøth *et al.*, 2008). All values are relative to the annual mean in 1989.**Table 9.1** Annual emission of ammonia (ktonnes N) from selected European countries during the period 1985 to 2000

	1985	1990	1995	2000
Denmark	113	109	92	83
Germany	706	630	523	514
Netherlands	204	187	153	126
France	642	628	624	649
Sweden	44	42	50	46
Norway	19	19	21	21
Finland	35	31	29	27

**Figure 9.9** Trend in NH_3 emissions on European scale for the period 1990 to 2005, and further projected to 2010. Source: EMEP (2010).

countries like France, Sweden and Norway only very small changes have occurred over the past 15 years (Table 9.1). Over the EMEP domain, emissions have decreased since 1990, and projections point at a further decrease in 2010 (Figure 9.9).

9.2.2 Nitrogen oxide emission handling

Nitrogen oxides (NO_x is the sum of nitrogen monoxide (NO) and nitrogen dioxide (NO_2)) are generated at high temperatures

in combustion processes mainly from oxidation of free atmospheric nitrogen (N_2).

European emission inventories

EMEP – For Europe various inventories on different scales and compiled with different objectives are available. National inventories are aimed at fulfilling the obligations due to international agreements and conventions, e.g. the European Commissions' National Emission Ceilings Directive (NECD) or the UNECE Convention on Long-range Transboundary Air Pollution (CLRTAP). NO_x emissions are subject to the NECD and the NO_x Protocol as well as the Gothenburg Protocol under CLRTAP. While the NECD covers only EU member states, the CLRTAP protocols cover the whole UNECE region (see Figure 9.10). However, not all countries have ratified all protocols and thus may not be obliged to report. These inventories focus on anthropogenic emissions and sources, but biogenic and natural emissions are reported by some countries. The officially reported emissions are often incomplete and subject to gaps, and a gap-filling procedure has thus to be applied when used, i.e. in modelling (see example in Figure 9.10).

EDGAR – In contrast to the officially reported compilations of national emissions, the EDGAR (EDGAR, 2010) is an example of an independent bottom-up inventory with global coverage for all main pollutants and greenhouse gases and compiled from expert estimates and available emission factors and activity data.

National inventories

European inventories provide spatial resolution of e.g. $50 \text{ km} \times 50 \text{ km}$ (Figure 9.10) or $0.5^\circ \times 0.5^\circ$. For many European countries, however, data are available at $10 \text{ km} \times 10 \text{ km}$, $5 \text{ km} \times 5 \text{ km}$ or even $1 \text{ km} \times 1 \text{ km}$ (see Figure 9.11). Vehicle emissions can be computed using an emission module in the Danish Operational Street Pollution Model (OSPM, 2010). This module uses COPERT IV (see COPERT, 2010) emission factors and a road and traffic database. A GIS script compiles kilometres travelled as function of road type and vehicle category (Jensen *et al.*, 2008) on a $1 \text{ km} \times 1 \text{ km}$ grid, and another programme (UrbEmi) calculates the road traffic emissions.

EMEP WEBDAB NO_x emissions for 2005

National Totals, including shipping

Unit: Gg

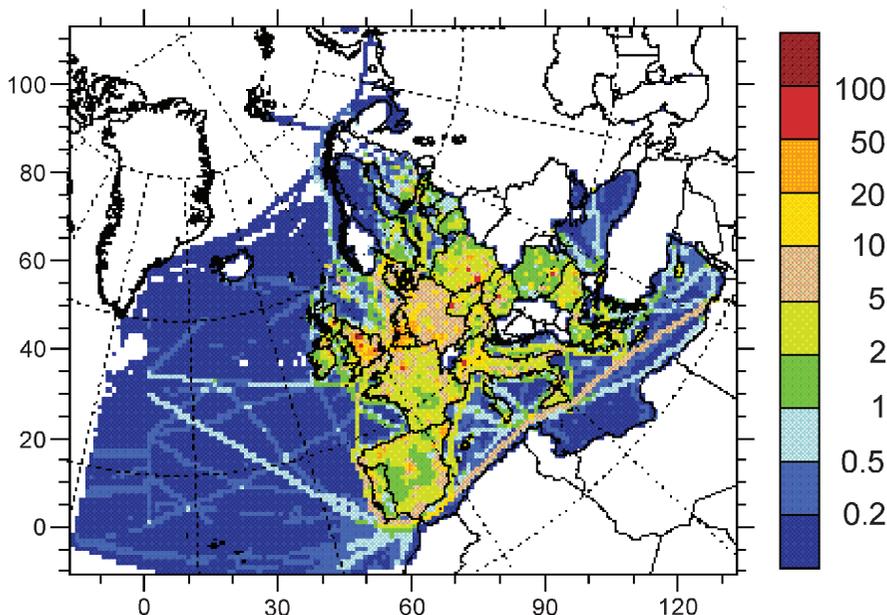


Figure 9.10 European NO_x emissions on the 50 km × 50 km EMEP grid for the year 2000 (EMEP, 2010).

Table 9.2 NO_x sectoral contribution based on EDGAR data for Europe in the year 2000, including 37 countries (source: FT32, EDGAR 2010)

Sector	Emissions in Gg	Share
Power generation	6721.75	25.2%
Industrial production	4092.07	15.4%
Residential & commercial combustion	1603.53	6.0%
Road transport	6085.19	22.9%
Other mobile sources	3646.38	13.7%
International shipping	3012.02	11.3%
Air transport	613.80	2.3%
Waste incineration	17.23	0.1%
Biomass & agricultural burning	829.81	3.1%
Total	26 621.79	

Data from: EU27, Croatia, FYR of Macedonia, Turkey, Switzerland, Norway, Albania, Russian Federation, Bosnia & Herzegovina, Ukraine, Federal Republic of Yugoslavia

Key source analysis

The source sectors are summarized in Table 9.2. The bulk of NO_x emissions in Europe stem from both stationary and mobile combustion sources. Road transport and public power generation are by far the largest contributors to NO_x emissions, followed by residential and commercial combustion and off-road sources.

The NatAir project (NatAir, 2010) compiled emissions of NO from forest and agricultural soils at about 98.22 Gg for

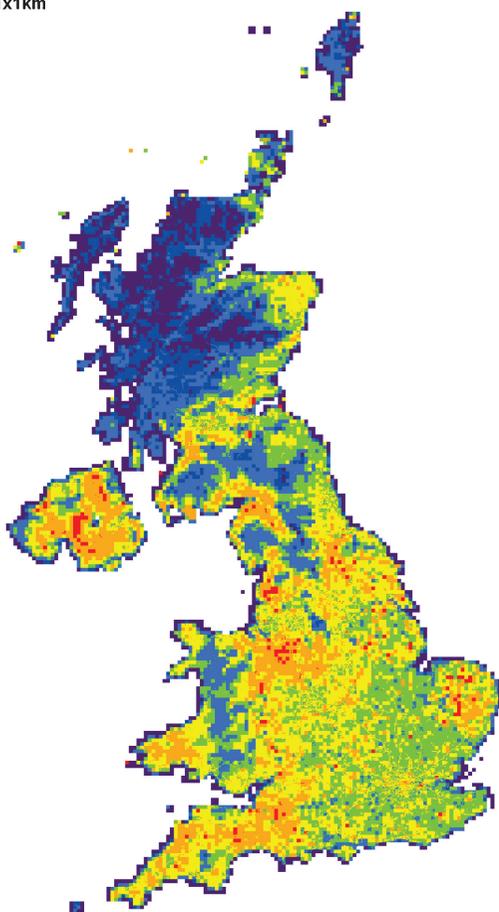
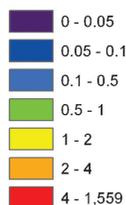
the EU15 (Friedrich, 2002). Up-scaled to the entire European area, this is pointing at forest and agricultural NO emissions in the order of 200 to 300 Gg NO yr⁻¹. Emissions from lightning activities calculated within NatAir show 325 Gg yr⁻¹ for the EU15 region, which according to the EDGAR inventory is in the same order as biomass and agricultural burning emissions.

Past and future trends

Trends for NO_x emissions in the period 1990 to 2005 have steadily pointed downwards (Figure 9.12) due to legislation to reduce emissions from stationary sources (e.g. the EC Large Combustion Plants Directive) and mobile sources (mainly the EURO emission standards for vehicles), amounting to approx. 34% reduction of EU27 emissions. Further reductions are anticipated with legislation for road transport sources over the next few years. A review on European NO_x emissions with emphasis on road transport is provided in Vestreng *et al.* (2008). Commitments for phasing out nuclear energy may, however, lead to a replacement of nuclear by biomass or coal burning plants and thereby increase emissions from this sector. International shipping emissions are rising steadily and this increase is projected to continue, although the reductions from regulating quality of marine fuels and other abatement strategies are not accounted for in these projections.

NO_x to NO₂ ratio – Ambient NO₂ concentrations do not decrease at the same rate as NO_x in European hotspots (Carslaw *et al.*, 2007; Lambrecht, 2007), mainly due to increasing NO_x/NO₂ ratio in late diesel technology vehicles. Hourly NO₂ limit values are mandatory in Europe from 2010 (EC Daughter Directive 99/30/EC, and primary NO₂ in vehicle

UK Emissions Map of Ammonia 2008 kg/1x1km



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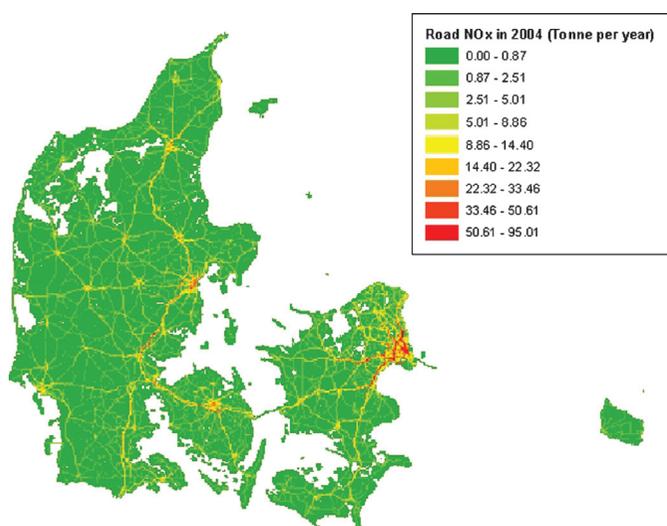


Figure 9.11 National high resolution maps of NO_x emissions, displaying (a) UK National Atmospheric Emission Inventory data (Source: UK NAEI: <http://www.naei.org.uk/mapping/mapping-2008.php>; Crown copyright) and (b) spatial distribution of NO_x road emissions in Denmark in 2004 on a 1 × 1 km² grid.

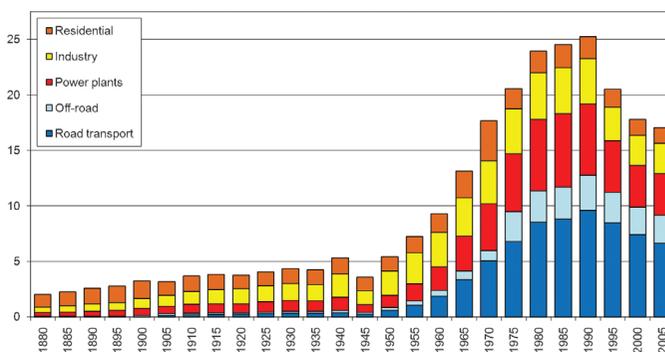


Figure 9.12 Sector trends in European NO_x emissions 1880–2005 (unit TgNO_x) (Vestreng *et al.*, 2008).

exhausts may thus need to be addressed in future emission inventories.

Secondary emission control options of especially large stationary combustion units include selective catalytic reduction (SCR). A common problem with SCR systems is the release of unreacted NH₃, referred to as *ammonia slip*. Slip can occur when catalyst temperatures are not in the optimal range for the reaction or when too much NH₃ is injected. SCR systems are increasingly used also for mobile sources, specifically heavy duty trucks, where ammonia slip is an issue more difficult to optimize than for stationary combustion units.

Ecosystems and soil NO and N₂O emissions

Globally, agricultural soils represent the largest soil source of N₂O (54%), followed by tropical wet forests (21%) and temperate forests, savannahs and natural grasslands contribution at almost equal parts to the remaining 25%. The impact of N fertilizer on N₂O emissions in temperate climates is well studied, whereas less is known about agricultural systems in tropical countries or tropical wet forest systems. Ongoing measurements in tropical forest and agricultural systems in Borneo suggest much larger emissions in wet tropical countries than in temperate regions (Nemitz and Skiba, personal communication). Of the agricultural soils intensively managed grasslands in the UK, Netherlands and other temperate climates are hotspots of N₂O emissions, because (a) grasslands receive larger rates of mineral fertilizer and manure, (b) grasslands occur in high rainfall regions, and (c) grazed grasslands have compacted soils. Such conditions all favour NO production.

NO_x emission from soils may represent >40% of the emissions at the global scale (Davidson and Kingerlee, 1997; IGAC, 2000), and >10% for some European countries (Butterbach-Bahl *et al.*, 2004; Skiba *et al.*, 1997; Stohl *et al.*, 1996). Emissions resulting from fertilizer use could represent 40% of soil emissions at global scale (IGAC, 2000) and up to 65% for the USA (Hall *et al.*, 1996). Rural agricultural areas receiving N fertilizers in countries with long dry periods are likely the largest sources of soil NO. The NitroEurope Integrated Project (NEU, 2010) and the NOFRETETE (*Nitrogen oxides emissions from European Forest Ecosystems*) project point at Europe forests as large sources of NO (Pilegaard *et al.*, 2006). The coniferous forest at Högwald,

DE, receiving high atmospheric N deposition is a large source of NO, whereas the boreal forest at Hyytiälä, FI, and moorland sites in FI and UK have very small emissions (Skiba *et al.*, 1997). In semi-natural/natural ecosystems that do not receive N from fertilization or grazing, atmospheric N deposition significantly affect NO and N₂O emissions. The NOFRETETE project showed correlation between N deposition rates and NO emissions from coniferous forest soils (Pilegaard *et al.*, 2006). Along a wet deposition gradient in Cumbria (17–40 kg N ha⁻¹ yr⁻¹), a linear relationship was observed between wet deposition of N, KCl extractable NH₄⁺ and NO₃⁻ and NO and N₂O emissions from semi-natural grassland on peat (Skiba *et al.*, 2007).

9.3 Transformation of N compounds in the atmosphere

The following section provides a description of atmospheric transformation processes of N_r and highlights where these processes play a significant role.

9.3.1 Reactions between NH₃ and acid gases and aerosols

In the reactions between gas phase NH₃ and gas phase acids, new aerosol particles are formed. However, NH₃ may also condense onto existing atmospheric particles. Gaseous NH₃ will practically always react with sulphuric acid (H₂SO₄) in gas or aerosol phase, if H₂SO₄ is present. H₂SO₄ is formed from gas phase oxidation of SO₂ by hydroxyl (OH) radical or from aerosol phase conversion by hydrogen peroxide (H₂O₂) and ozone (O₃). The later process is pH dependent, and may in fact be catalysed by NH₃, since uptake of NH₃ increases the pH of aerosols (Apsimon *et al.*, 1994; Junge and Ryan, 1958). The reaction between NH₃ and H₂SO₄ is usually considered irreversible. In traditional CTM, it is thus common to describe the reaction as irreversible and taking place in two steps forming ammonium bisulphate (NH₄)HSO₄ and ammonium sulphate (NH₄)₂SO₄ (Hov *et al.*, 1994), respectively:



The rate of reaction between NH₃ and H₂SO₄ has been analysed in detail in laboratory studies (Baldwin and Golden, 1979; Gupta *et al.*, 1995; Huntzicker *et al.*, 1980; McMurry *et al.*, 1983). At high RH, the limiting factor for the transformation is the molecular diffusion of NH₃ to the acid particles, whereas at low RH only between 10% and 40% of the collisions between NH₃ gas molecules and H₂SO₄-containing particles lead to reaction (Huntzicker *et al.*, 1980; McMurry *et al.*, 1983). For small particles, the relatively large surface area makes the diffusion process more efficient. Organic material on the surface of the particles may, however, limit the uptake of NH₃ (Daumer *et al.*, 1992).

Whereas the NH₃ reaction with H₂SO₄ may be considered irreversible, this is not the case for the reactions with other acid gaseous compounds. Presence of nitric acid (HNO₃) and/or hydrochloric acid (HCl) together with NH₃ lead to equilibrium between these gases and their aerosol phase reaction products – the ammonium salts: ammonium nitrate (NH₄NO₃) and ammonium chloride (NH₄Cl). For the reaction with HNO₃ this may be expressed as:



Experimental studies show that to a good approximation an equilibrium product, $k_{eq} = [\text{NH}_3][\text{HNO}_3]$, of the gas phase concentrations of NH₃ and HNO₃ at saturation of the air, may be expressed by a function depending solely on temperature and humidity (Stelson *et al.*, 1979; Stelson and Seinfeld, 1982). The RH at the point of deliquescence RH_d [%] = 856.23/T + 1.2306, and

$$\ln(K) = \ln(K_{eq}) = 0.78 - \frac{24,220}{T} - 6.1 \frac{\ln(T)}{298} \quad RH < RH_d \quad (9.5)$$

$$\ln(K) = \ln(K_{eq}) - \frac{20,75 + \ln(K_{eq})}{101 - RH} \left[\frac{RH - RH_d}{100 - RH_d} \right] \quad RH \geq RH_d \quad (9.6)$$

where T is in K. Besides the reactions with H₂SO₄ and HNO₃, NH₃ may also take part with HCl and form NH₄Cl (Pio and Harrison, 1987a):



Whereas HCl is a primary pollutant emitted by coal burning and incineration, HNO₃ is the main secondary pollutant from oxidation of NO_x emissions (see Section 9.3.3). New measurement data indicate that in NW Europe, HCl concentrations are similar to those of HNO₃ in summertime, in terms of mixing ratio. However, NH₄Cl concentrations are much lower than NH₄NO₃ concentrations. HCl is emitted from anthropogenic sources, but it is also released in displacement reaction in sea spray particles when these take up HNO₃ (Wall *et al.*, 1988):



In the first EMEP model this reaction was accounted for by a first order decay of HNO₃ of 10⁻⁵ s⁻¹, and a reverse reaction rate coefficient of half this size (Hov *et al.*, 1994). Measurements in California showed that NO₃⁻ in the coarse-particle mode is primarily associated with high Na⁺ levels in marine air (Wall *et al.*, 1988), and that NO₃⁻ in coarse fraction particles has a peak at 3 μm diameter, where the product of the Na and mass distribution also peaks. This displacement reaction is thus the most likely explanation for

HCl concentrations of up to 250 pptv (Harris *et al.*, 1992) observed in the marine boundary layer. Experimental studies have determined an equilibrium product at saturation of the air with the two gases NH_3 and HCl (Pio and Harrison, 1987b). See also Figure 9.13.

NH_4NO_3 and NH_4Cl are semi-volatile and the salts are deliquescent under most tropospheric conditions in northern Europe and may dissolve in pre-existing aerosol droplets or absorb onto the surface of any pre-existing aerosol particles. Thereby NO_3^- , Cl^- and NH_4^+ are incorporated in suspended particulate matter in the particle size range, mainly in the submicron accumulation mode size-range, and therefore contribute to $\text{PM}_{2.5}$ and PM_{10} , the metrics used for human health assessment (Moldanova *et al.*, 2011, Chapter 18 this volume). It may be reasonable to assume equilibrium of NH_3 and HNO_3 , and NH_3 and HCl. However, observations of particle size distribution of inorganic N, S, and Cl species in maritime air over the North Sea show products of partial pressures of $[\text{NH}_3][\text{HNO}_3]$ and $[\text{NH}_3][\text{HCl}]$ that often fall below the theoretical lines of equilibrium (Ottley and Harrison, 1992), and one should therefore be careful when applying the assumption of equilibrium. This is due to sources and sinks, but mainly because the theoretical lines are for pure salts, while the co-existence of sulphate in the aerosol can dramatically decrease the equilibrium vapour concentration product.

9.3.2 Changed NH_3 to NH_4^+ conversion rate due to changes in S emissions

Early experiments carried out by McKay (1971) showed that 50% of the available NH_3 is converted into ammonium sulphate in about 35 minutes, based on concentrations present in the atmosphere at that time ($20 \mu\text{g m}^{-3} \text{SO}_2$ and $2.7 \mu\text{g m}^{-3} \text{NH}_3$). Models like the EMEP Unified Model assume an instantaneous and irreversible formation of ammonium sulphate, only limited by the availability of the least abundant of NH_3 and SO_4^{2-} . Any excess NH_3 may then react with HNO_3 , forming NH_4NO_3 . Over the last decades, a dramatic decrease in SO_2 emissions occurred (Figure 9.14). Especially in the East European countries, the SO_2 emissions dropped by approximately 60% in the late 1980s/early 1990s.

This drop in SO_2 emissions and resulting ambient concentrations has affected the formation of $(\text{NH}_4)_2\text{SO}_4$. Measurements show that in the Netherlands in the early 1980s the $\text{NH}_3/\text{NH}_4^+$ conversion rate was 28.8% per hour, while at present it is about 5% per hour (Van Jaarsveld, 2004). Trends in observations and EMEP model results for wet deposited N are in compliance with trends in emissions (Fagerli and Aas, 2008). For air concentrations less information is available, since most of EMEP sites did not start measuring TIA (Total Inorganic NH_x = gas phase NH_3 + aerosol phase NH_4^+) and TIN (Total Inorganic NO_3^- = HNO_3 + aerosol phase NO_3^-) until the end of the 1980s and only a few

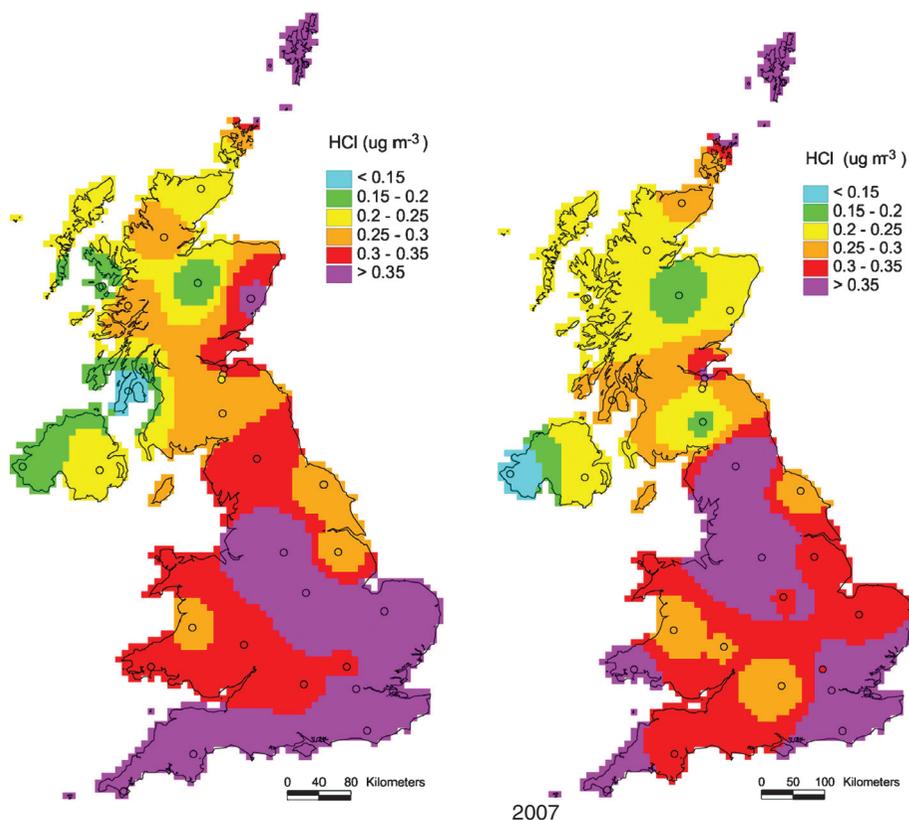


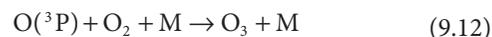
Figure 9.13 HCl concentrations 2006 (left) and 2007 (right) based on 30 sites with monthly monitoring. Source: Pollutant deposition (CEH, 2010).

sites (~20) have reported continuously. Moreover, the gas and particulate phases have very different chemical (e.g. their role in the $\text{NH}_4^+ - \text{NH}_3 - \text{HNO}_3 - \text{NO}_3 - \text{SO}_4^{2-}$ equilibria) and physical properties (e.g. the aerosols have a much longer residence time and are transported over longer distances), and the trend in the gas and particulate phase may thus be different.

In some Eastern European countries NH_3 emissions have declined by 30%–60%, but NH_x concentrations decreased only by 20%–30% (EMEP, 2010). In Germany, however, NH_x concentrations declined by 20%–30%, whilst emission reductions are reported to have been 10%–20%. The explanation is a combination of a less efficient formation of NH_4^+ aerosol (due to decreasing SO_x) and less efficient dry deposition of NH_3 due to less acidic surfaces; both effects leading to a shift towards gaseous NH_3 relative to particulate NH_4^+ .

9.3.3 NO_y chemistry in the troposphere

The emission of NO_x takes place mainly in the form of nitrogen monoxide (NO) and to a lesser extent (usually 5%–20%) as nitrogen dioxide (NO_2). The fraction of directly emitted NO_2 from road traffic in western countries has increased in recent years as a result of the use of catalytic converters. However, in the tropospheric boundary layer the distribution between NO and NO_2 is governed to a large degree by O_3 that reacts very fast with NO to form NO_2 . In sunlight NO_2 photo dissociates (wavelengths 200–420 nm) to form NO and the very short-lived oxygen ($\text{O}({}^3\text{P})$) radical. The latter will in most cases again form O_3 in a reaction with free oxygen (O_2).



In the above reactions M is a third body (either an N_2 or O_2 molecule) that absorbs excess vibrational energy and thereby stabilizes the formed O_3 molecule. These reactions all have time scales of seconds to minutes. The reaction rate of reaction (9.9) is temperature dependent, but has a typical value about $4 \times 10^{-4} \text{ ppbv}^{-1} \text{ s}^{-1}$. Under typical atmospheric boundary layer conditions, reaction (9.9) will either lead to the complete conversion of all the O_3 to NO_2 , or to the conversion of all NO to NO_2 (Clapp and Jenkin, 2001). In highly polluted atmosphere (e.g. an urban area) or close to pollution sources, the former behaviour is usually observed because although O_3 is widely distributed in the lower atmosphere, its concentration is not usually high compared with NO in the highly polluted atmosphere, and hence O_3 concentrations become rapidly depleted. During daylight, the main fate of NO_2 is to undergo photolysis (9.10), reforming O_3 (9.11) and NO (Dickerson *et al.*, 1982). This reaction has a typical rate coefficient under summer conditions in the mid afternoon at mid altitudes of about $7 \times 10^{-3} \text{ s}^{-1}$. Reaction (9.12) is the only production path for O_3 in the atmosphere.

Figure 9.15 illustrates the NO– NO_2 – O_3 chemistry in urban streets using a highly simplified module (Palmgren *et al.*, 1996) in the Operational Street Pollution Model (OSPM) (Berkowicz, 2000). This module includes the reactions (9.10) and (9.11) and an assumption of reaction (9.12) being instantaneous. In addition the model includes a ventilation rate between the street canyon and the surrounding air, and a distribution of the direct emission of NO and NO_2 from street traffic (Palmgren *et al.*, 1996).

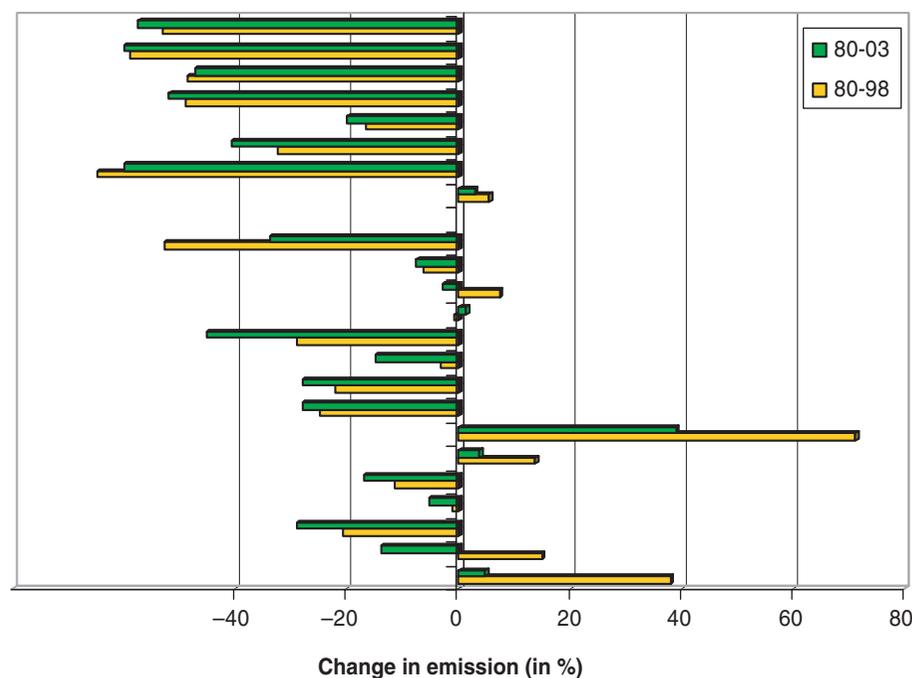


Figure 9.14 EMEP emission changes for different European countries for two periods: 1980–1998 and 1980–2003. Source: EMEP (2010).

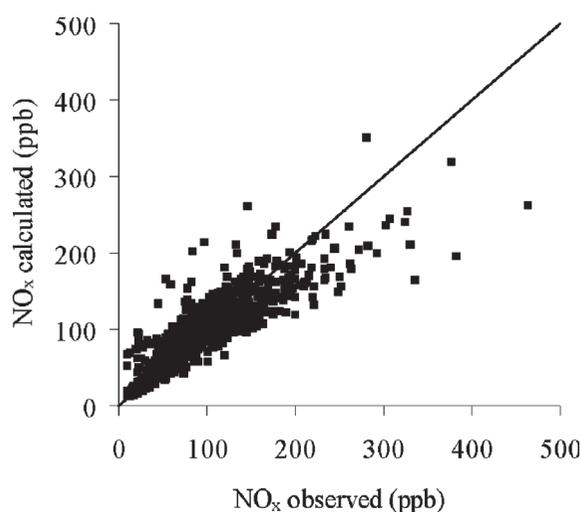
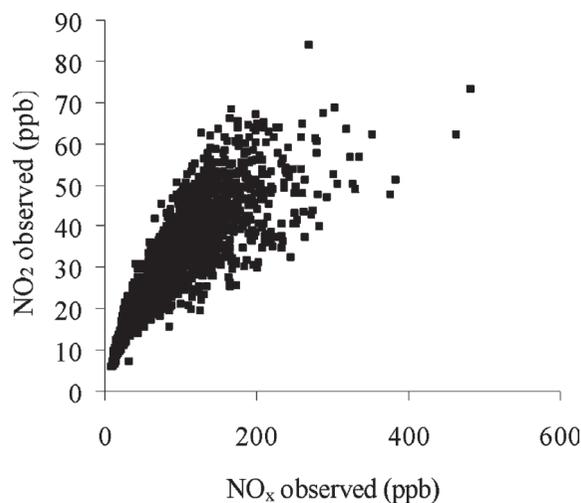
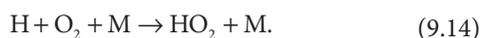
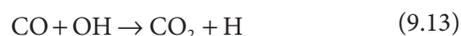
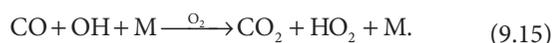


Figure 9.15 The chemistry of NO_x in urban streets. (Top) the observed relationship between NO_2 and NO_x . For NO_x concentrations below about 20 ppb, all NO_x is in the form of NO_2 , since the air contains sufficient O_3 for converting all NO to NO_2 . For higher NO_x concentrations, only the direct emission of NO_2 contributes to further increase in NO_2 concentrations. (Bottom) Comparison between observed and calculated hourly mean concentrations of NO_2 . All data are from Jagtvej in 2003, and calculations performed with OSPM. Only working days during daytime (800–1600) are included. Correlation coefficient (R^2) = 0.7 (Hertel and Brandt, 2009).

The OH radical initiates the oxidation of a wide range of compounds in the atmospheric boundary layer. OH interacts with peroxy radicals that are responsible for the formation of excess concentrations of photo oxidants like O_3 . In the background troposphere, carbon monoxide (CO) plays a role in this system:



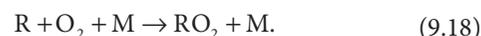
This conversion is so rapid that for all practical purposes reaction (9.13) may actually be written as:



Whenever NO is present, the most important atmospheric reaction of the hydroperoxy radical (HO_2) is the conversion of NO to NO_2 :



The hydroperoxy radical is one of many peroxy radicals that take part in the conversion of NO to NO_2 . Organic peroxy radicals (RO_2) play likewise an important role and are mainly formed by the attack of the OH radical on the organic compounds ubiquitously present in the polluted atmosphere. These reactions follow a similar path as the CO oxidation, and may in a simplified form be presented as:

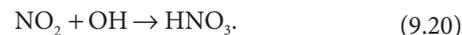


RXH represents the organic compound, whereas R is an organic radical such as the alkyl radical and RO_2 an alkyl peroxy radical. The only important atmospheric pathway of the alkyl radical is reaction (9.18) with O_2 to form alkyl peroxy radicals (Finlayson-Pitts and Pitts, 1986). The RO_2 radical may subsequently convert NO to NO_2 in the same way as the HO_2 radical (reaction (9.16)).

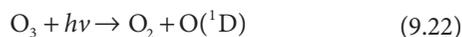
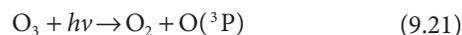
During combustion processes at high temperatures, e.g. inside the motor of a petrol or diesel-driven vehicle, NO is formed from ambient N_2 . However, in the very NO rich air inside the exhaust pipe of vehicles and inside emitting chimneys, another oxidation path than (9.11) takes place:



This reaction is a third order reaction with a second order dependence of the NO concentration, and has a reaction rate coefficient of $2.3 \times 10^{-38} \text{ cm}^6 \text{ molecules}^{-2} \text{ s}^{-1}$ (Hampson and Gavin, 1978). The further transformation of NO_2 to HNO_3 takes place with a typical rate of about 5% per hour in the troposphere:



The hydroxyl radical (OH) is formed in the daytime in the presence of sunlight (Finlayson-Pitts and Pitts, 1986). The photo dissociation of O_3 leads to the formation of both $\text{O}(^3\text{P})$ and $\text{O}(^1\text{D})$ radicals, a fraction of the latter reacts with water vapour to form two OH radicals:



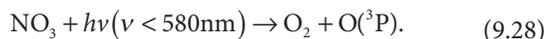
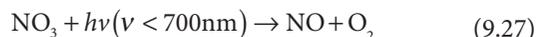
Reaction (9.17) takes place in competition with $\text{O}(^1\text{D})$'s reaction with third body O_2 or N_2 molecules to form $\text{O}(^3\text{P})$, that in turn reform O_3 in reaction (9.12). The OH radicals initiate

most of the degradation of hydrocarbons in the atmosphere, a chain of reactions that e.g. lead to the formation of high O₃ concentrations during summer.

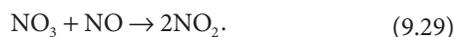
During night-time the nitrate (NO₃) radical has a less important but still somewhat similar role for the degradation of hydrocarbons in the atmosphere as the OH radical in daytime. Despite the considerably lower reactivity compared with OH, its higher peak concentrations in the night-time troposphere allow the NO₃ radical to play a major role in transformation of organic compounds. The NO₃ radical is formed during night-time in reaction with NO₂. The dinitrogen pentoxide (N₂O₅) is a reservoir compound for the NO₃ radical at low temperatures, but it is broken down to its precursors NO₂ and NO₃ at higher temperatures:



The typical night-time NO₃ radical concentrations in the atmospheric boundary layer are in the order 10⁷ to 10⁸ molecules m⁻³ (which is the pptv range). During daytime both NO₃ and N₂O₅ photo dissociate so fast that the concentrations of these compounds are insignificant. In the tropospheric boundary layer the photolysis of NO₃ radical (with a typical noon lifetime of about 5 s) follow two different paths (λ represents here the wavelength):



Close to pollution sources from combustion processes, e.g. road traffic or power plants, the NO₃ radical is quickly removed by reaction with NO:



During night-time the heterogeneous conversion of N₂O₅ to HNO₃ is an important process:



The lifetime of N₂O₅ with respect to this removal is on the order of minutes in the tropospheric boundary layer. This production of HNO₃ may in winter be equally important as daytime conversion of NO₂ by OH radical. As already described, particulate nitrate (NO₃⁻) is formed when HNO₃ reacts with NH₃ and form new aerosol particles, and when it sticks to existing particles in the atmosphere. In addition organic NO₃⁻ may be formed from gaseous NO₂ on the surfaces of aerosols in other heterogeneous reactions (see Section 9.3.4).

The NO₃ radical attacks alkanes by hydrogen abstraction in a similar way as the reactions of the OH radical:



Followed by formation of a peroxy radical (RO₂) that may oxidize an NO molecule to NO₂. Also for alkenes, the attack of the NO₃ radical is similar to the reactions of the OH radical; the NO₃ radical adds to the double bond. This reaction is followed by rapid O₂ addition which leads to the production of a peroxy radical.

Reaction of soil emissions of NO with atmospheric OH has been suggested to provide an in-canopy source of HNO₃ (Farmer *et al.*, 2006). HNO₃ concentrations usually peak during the day, regulated by the emissions of NO_x, photochemical activity and the gas/aerosol equilibrium of NH₄NO₃ shifting towards the gas phase with increasing temperature and decreasing relative humidity.

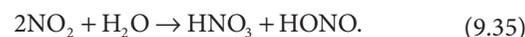
A reaction similar to reaction (9.22), but less important, is the reaction between NO and OH radical forming nitrous acid (HONO):



During daytime HONO photo dissociate ($\lambda < 400$ nm) rapidly back to the reactants:



Therefore, HONO formed in the late evening may serve as a night-time reservoir of OH and NO, which are subsequently liberated again the following morning, when sunlight starts up reaction (9.23) again. Studies in the highly polluted Po Valley in Northern Italy have shown an interrelation between simultaneous peaks in NO_x concentrations and aerosol surfaces and peak HONO concentrations during foggy periods (Notholt *et al.*, 1992). This was taken as evidence for heterogeneous conversion on aerosol surfaces through either of the reactions:



Probably this type of conversion plays an important role also in many urban areas over Europe, but so far only few studies have been carried out.

9.3.4 Organic N compounds in the atmosphere

The presence of atmospheric organic N compounds has been evident for years (Cornell *et al.*, 2003; Neff *et al.*, 2002), but direct measurements of individual species are rather sparse. The evidence of organic N comes from analysis of precipitation samples for total N and comparison with inorganic N content, to give 'dissolved organic N' (DON) by difference. This approach has been prone to several analytical artefacts (Cape *et al.*, 2001), but DON may in fact contribute up to half of total water-soluble N in precipitation. The fraction depends highly on location, and on whether air masses are of marine or terrestrial origin. DON has been ignored in estimating environmental consequences of N deposition, although there is reason to believe that many, if not all, components of DON are biologically available (Krab *et al.*, 2008; Lipson and Nasholm,

2001; Paerl and Whittall, 1999; Qualls and Haines, 1992). There appears to be a DON contribution from marine air masses (Cornell *et al.*, 1995, 2001), and DON proportions are consistently high in unpolluted air, especially in the tropics. For continental/terrestrial samples, annual average concentrations of DON in precipitation appear to correlate better spatially with NH_4^+ than with NO_3^- , suggesting an agricultural source, but the seasonal variation is not correlated with NH_4^+ concentrations, implying that different sources are involved (Cape *et al.*, 2004). There is limited evidence available from sampling of air directly using a nebulizing mist sampler that both gas phase and particle phase components contribute to water-soluble organic N (WSON) in the atmosphere, which leads to the occurrence of DON in precipitation. Organic N is measured in fog (Zhang and Anastasio, 2001) and cloud water (Hill *et al.*, 2007), but there is some concern that most analyses for DON are made on bulk rainfall samples (i.e. collected using an open funnel) and that a significant fraction of the measured DON might have been dry-deposited on the funnel surface. This presents problems of interpretation, but does not remove the problem of identifying the source, composition and fate of organic N compounds (see also Figure 9.16).

Evidence for reduced organic N in the atmosphere

Some measurements of individual components of reduced organic N in gas, particulate and aqueous phases have been reported and indicate potential sources and fates of these compounds (Table 9.3), but in most cases rather small concentrations are measured and these cannot account for the rather high proportions of DON in precipitation.

Formation of organic oxidized N compounds

When aldehydes are photo dissociated or react with OH, an alkyl radical is formed, which in turn may form peroxy alkyl

nitrates that serve as important reservoirs of NO_2 . The most abundant of these nitrates is the peroxy acetyl nitrate (PAN):



Reaction (9.38) is very fast, and reactions (9.38) and (9.39) may for many practical purposes be regarded as taking place in one step. PAN is thermally unstable and equilibrium between peroxy acetyl radical and NO_2 on one side and PAN on the other side is established in the boundary layer. High PAN and O_3 concentrations are often observed together during photochemical smog episodes. The thermal degradation gives PAN a lifetime of ~ 1.7 h at 273 K and 50 h at 263 K. The PAN formation is competing with NO degradation of peroxy acetyl radical:



This reaction is totally dominating at ppbv levels of NO meaning that PAN and other peroxy alkyl nitrates are formed only in the background atmosphere, and i.e. not inside urban areas. However, substantial PAN concentrations may still be observed in urban areas, especially at relatively low temperatures. The peroxy alkyl nitrates include compounds produced in a similar way as PAN, but generated from biogenic isoprene emissions that may be of importance in southern Europe, and have similar thermal degradation pathways as PAN.

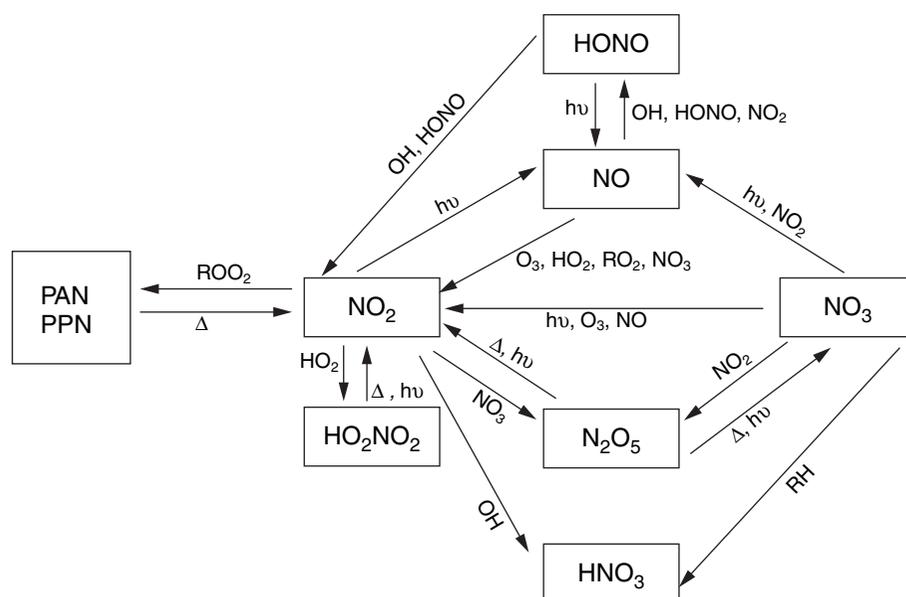


Figure 9.16 Illustration of the interaction between the various nitrogen oxide (NO_x) compounds in the tropospheric boundary layer. The symbol Δ represents energy leading to thermal degradation, $h\nu$ solar radiation leading to photo dissociation and RH a hydrocarbon reacting with the specie in question. PPN is a notation for peroxy propionyl nitrate, but also other peroxy nitrates than PPN and PAN play a role in this context (Derwent and Hertel, 1998).

Table 9.3 Reported data on reduced organic N compounds in the atmosphere

Species	Sources	Atmospheric reactions and fate	Other direct measurements
Amines and Urea	Direct emissions from some industrial processes and from agricultural activity such as slurry spreading (Kallinger and Niessner, 1999). Some data exist for the latter process relative to ammonia emissions, which may be helpful in modelling emissions, but release rates are c. 1% of NH ₃ . Ocean water may be source or sink (Hatton and Gibb, 1999).	Water soluble (Calderon <i>et al.</i> , 2007; Gibb <i>et al.</i> , 1999). Likely acid–base reactions and form particles (cf. NH ₄ ⁺) (Angelino <i>et al.</i> , 2001; Blando and Turpin, 2000). Photo degradation possible (McGregor and Anastasio, 2001). O ₃ reaction (Tuazon <i>et al.</i> , 1994). Likely high dry deposition rates (low surface resistance – ‘sticky’ molecules).	PTR-MS data on trimethylamine from slurry (Twigg, 2006). Published data (Beddows <i>et al.</i> , 2004; Gorzelska <i>et al.</i> , 1992; Gorzelska <i>et al.</i> , 1994; Gronberg <i>et al.</i> , 1992; Gundel <i>et al.</i> , 1993; Palmiotto <i>et al.</i> , 2001; Schade and Crutzen, 1995) (Cornell <i>et al.</i> , 1998; Mace <i>et al.</i> , 2003b; Mace <i>et al.</i> , 2003c; Mace <i>et al.</i> , 2003a; Mace and Duce, 2002).
Amino acids, proteins and peptides	Ocean surface (Milne and Zika, 1993), grassland (soil) (Scheller, 2001).	Photodestruction (Anastasio and McGregor, 2000; McGregor and Anastasio, 2001; Milne and Zika, 1993; Saxena and Hildemann, 1996).	Measurement data (Gorzelska <i>et al.</i> , 1992; Kieber <i>et al.</i> , 2005; Mace <i>et al.</i> , 2003b; Mace <i>et al.</i> , 2003c; Mace <i>et al.</i> , 2003a; Matsumoto and Uematsu, 2005; Scheller, 2001; Zhang and Anastasio, 2001; Zhang and Anastasio, 2003).
Hydrogen cyanide and methyl cyanide (Acetonitrile)	Biogenic emissions (terrestrial) (Shim <i>et al.</i> , 2007) and biomass burning (Bertschi <i>et al.</i> , 2003; Cicerone and Zellner, 1983; Holzinger <i>et al.</i> , 1999; Li and Tan, 2000); anthropogenic (Holzinger <i>et al.</i> , 2001).	(Bange and Williams, 2000; Cicerone and Zellner, 1983; Karl <i>et al.</i> , 2004). Other direct measurements: (Sprung <i>et al.</i> , 2001; Warneke <i>et al.</i> , 2001).	

9.4 Dry deposition and bi-directional fluxes of N compounds

N_r compounds are being monitored in many regional networks across the world, such as the European EMEP programme (EMEP, 2010), the NitroEurope Integrated Project (NEU, 2010) the US National Atmospheric Deposition Network (NADP, 2010), the Acid Deposition Monitoring Network in East Asia (EANET, 2010) and several others. However, these networks measure air concentrations rather than fluxes, and deposition is estimated using inferential modelling approaches, which are underpinned by often sparse databases of campaign based process studies with limited geographical coverage. This is partly due to the fact that instrumentation to measure fluxes of sticky compounds such as NH₃, HNO₃ or HONO are expensive and labour intensive to operate. The measurement of each individual N_r compound is technically more challenging than that of CO₂ fluxes, for example. Robust low cost flux measurement approaches are lacking, although recent developments of a Conditional Time-Averaged Gradient (COTAG) method (Famulari *et al.*, 2010) show promise for wide-scale deployment over long periods for short vegetation. A first regional flux measurement network for N_r compounds is established within the European NitroEurope IP. This network takes a three-tier approach, where selected N_r compounds

are measured at a network of 13 supersites, using advanced micrometeorological flux measurement techniques. At a further nine regional sites the novel COTAG systems are being deployed, while deposition is derived at a further 50+ sites from concentration measurements, using inferential techniques (Tang *et al.*, 2009).

Spatial coverage of N_r deposition can only be achieved through numerical modelling. The gaseous N_r compounds most commonly considered for dry deposition are NH₃, HNO₃ and NO₂. Their relative contributions to N deposition depend on the pollution climate. In agricultural areas NH₃ may dominate the atmospheric N loading, while in more industrial and urban areas HNO₃ and NO₂ may be more important. In addition, NH₃ deposition depends on the N status of the receiving surface, with fertilized vegetation and vegetation receiving high atmospheric N deposition inputs acting as a less efficient sink or even net source of NH₃. In dry regions, stomatal deposition may make a larger relative contribution to net exchange than in wet regions, where leaf cuticles provide a very efficient sink for water soluble gases (NH₃ and HNO₃).

In the UK, dry deposition of NH₃, HNO₃ and NO₂ is estimated to have contributed 48 (14.5%), 57 (17.3%) and 9 (0.03%) Gg, respectively, to the total N deposition of 330 Gg N in 2004, with the rest originating from wet and cloud deposition (211 Gg, 63.9%) and aerosol deposition (16 Gg N, 0.05%) (Fowler

et al., 2009). The UK deposition model uses detailed knowledge of land use to estimate the vegetation-dependent deposition velocities and fluxes as a function of land use in each 5 km × 5 km grid square of the country, combined with long-term measurements of air concentrations which are unique in Europe in terms of spatial coverage.

9.4.1 The dry deposition process

Dry deposition is the direct deposition of gases or aerosols at terrestrial or marine surfaces. The dry deposition of gases and particles is a continuous process and governed by their air concentrations, turbulent transport processes in the boundary layer, the chemical and physical nature of the depositing species, and the capability of the surface to capture or absorb the species.

In relation to deposition transport, the boundary layer may be considered to consist of two layers: the fully turbulent layer and the quasi-laminar layer. The quasi-laminar layer is introduced to quantify the way in which pollutant transfer differs from momentum transfer in the immediate vicinity of the surface (Hicks *et al.*, 1987). In this layer, the transport is dominated by molecular diffusion. Once at the surface, the chemical, biological and physical nature of the surface determines the capture or absorption of the gases and particles. Deposition to water surfaces (oceans or fresh waters) may thus be very different from deposition to vegetated surfaces on land.

The deposition process may be considered as a series of resistances, by analogy with an electrical circuit (Monteith and Unsworth, 2008). The resistances refer to the transport processes through the various 'layers' defined above: turbulent transfer (usually denoted R_a), quasi-laminar (R_b) and surface (R_c). For a complex surface with several potential absorption sinks (e.g. vegetation) the resistance R_c may be viewed as a network of parallel resistances, representing transfer to the external leaf surface, through stomata, to water on the surface, or through the canopy to the underlying soil surface. The total resistance (R_T) is the sum of all the series and parallel resistances ($R_a + R_b + R_c$), and is usually expressed in units of s m^{-1} . The inverse of the total resistance ($1/R_T$) is known as the deposition velocity (v_d) and has units of m s^{-1} . The turbulent transfer resistance (R_a) depends upon the height at which the deposition flux is measured, so the total resistance (R_T) and deposition velocity (v_d) also vary with height above the surface. The transfer flux (F) is defined as the product of the air concentration of a gas or particles at height z , multiplied by the deposition velocity at height z , and (in the absence of competing chemical reactions (Sorensen *et al.*, 2005)) does not vary with height, provided that the air concentration is horizontally uniform. This formulation assumes that the surface concentration of the gas is zero – where this is not the case (see below) the effect can be described either as a decreased driving force for deposition (concentration difference between height z and the surface) or as an increased surface resistance.

The deposition velocity (v_d) is often reported as a constant even though it depends on a set of variables, e.g. wind

speed, surface roughness and atmospheric stratification. Joffre (1988) has suggested a parameterization which depends on the meteorological conditions, roughness length and the molecular diffusion coefficient for the compound of interest. The various components of the total transport resistance can be estimated from meteorological data if several assumptions are made concerning spatial and temporal homogeneity. The atmospheric turbulent resistance (R_a) can be calculated from:

$$R_a(z) = \frac{1}{\kappa u_*} \left[\ln \frac{z}{z_0} - \psi \left(\frac{z}{L}, \frac{z_0}{L} \right) \right], \quad (9.41)$$

where z is the reference height, z_0 is the roughness length, u_* is the friction velocity, κ is the von Karman constant (≈ 0.4) and L is the Monin–Obukhov length. For the diabatic surface layers (Businger, 1982) a stability function ϕ is introduced (Businger *et al.*, 1971). For neutral conditions $\phi = 1$ and ϕ is greater/less than unity for stable/unstable stratifications. In the above equation, ψ is the integrated stability function.

The resistance of the underlying thin molecular laminar sub-layer is given by (Kramm, 1989; Kramm *et al.*, 1991; Kramm and Dlugi, 1994):

$$R_b = \int_{z_0}^z \frac{D_i + K}{u} = - \left(\frac{u_z}{u} + B_i \right) \quad (9.42)$$

where u_{z_0} is a characteristic velocity for the layer $z, < z < z_0$, B_i is the sub-layer Stanton number, which is a function of the roughness Reynolds number $Re_*^* = u_* z/\nu$ and the Schmidt number, $Sc_i = \nu/D_i$. The Stanton number can be estimated as (Kramm and Dlugi, 1994):

$$B_i^{-1} = a Sc_i^b Re_*^c + \varepsilon, \quad (9.43)$$

where the following values are suggested for smooth surfaces $a = 13.6$, $b = 2/3$, $c = 0$ and $\varepsilon = -15.5$ and for rough surfaces, $a = 7.3$, $b = 0.5$, $c = 0.25$ and $\varepsilon = -5$.

The surface resistance term depends on the physical and chemical nature of the absorbing surface, and parameterizations should be adapted to the surface concerned. The value of v_d is often expressed as annual or seasonal averages, for the purpose of calculating deposition fluxes as the product of air concentrations and deposition velocities. Deposition velocities and concentrations should refer to the same height – usually the height at which the concentrations are measured. Tall vegetation causes increased atmospheric turbulence, so R_a values are smaller, and deposition velocities are larger, than for short vegetation. Consequently, estimating deposition of different components to the countryside requires knowledge about land use as well as the spatial pattern of air concentrations.

The air–sea gas exchange of the very soluble gases HNO_3 and NH_3 is rate limited by the vertical transport in the boundary layer, because the uptake at the water surface is very fast relative to other commonly studied gases. Of the two very soluble N-gases, HNO_3 exchange rates are larger than NH_3 due

to the higher solubility. The less soluble NO_2 and NO gases, deposit much slower to the marine surface. The surface resistance is the most important resistance for slightly soluble gases and relates to the transfer velocity K_c , which is also used for air-sea exchange of other gases like CO_2 , DMS and CH_4 . The surface resistance is a key parameter for the deposition of a gas to a water surface, and may be expressed as:

$$\frac{1}{R_c} = K_c = \frac{F_c}{\Delta c_w} \quad (9.44)$$

Here F_c is the flux across the surface and Δc_w is the concentration gradient across the laminar sub-layer in the water. The resistance across the water surface is controlled by the Henry's law coefficient (H), which describes the solubility of different gases, and is a strong function of temperature. The effective overall surface resistance is therefore:

$$R_{c,eff} = R_c / H^* \quad (9.45)$$

where H^* is the dimensionless Henry's law coefficient (Table 9.4).

The process of dry deposition of particles differs from that of gases in two respects.

- Deposition depends on particle size, since transfer to the surface involves Brownian diffusion, inertial impaction/interception and sedimentation (all of which are a strong function of particle size) (Slinn, 1982).
- It is assumed that the surface resistance for particles less than $10 \mu\text{m}$ diameter (Hicks and Garland, 1983) is negligibly small to all surfaces.

For submicron particles, the transport through the boundary layer is more or less the same as for gases. However, transport of particles through the quasi-laminar layer can differ. For particles with a diameter $< 0.1 \mu\text{m}$, deposition is controlled by diffusion, whereas deposition of particles with a diameter $> 10 \mu\text{m}$ is more controlled by sedimentation. Deposition of particles with a diameter between $0.1 \mu\text{m}$ and $1 \mu\text{m}$ is determined by the rates of impaction and interception and depends heavily on the turbulence intensity. Transfer through the quasi-laminar layer close to the surface presents a considerable restriction on the deposition of $0.1\text{--}1.0 \mu\text{m}$ diameter particles. Uptake of particles by surfaces is thus largely controlled by micro-structures and turbulence intensity.

Most of the theory and measurements of particle fluxes have focused on sulphate particles (SO_4^{2-}), which mostly occur in the submicron size range as $(\text{NH}_4)_2\text{SO}_4$. Other submicron aerosol particles are expected to behave similarly, although semi-volatile particles may form or evaporate depending on the local equilibrium with the constituent gases (e.g. NH_4NO_3 and NH_3/HNO_3). The most widely used model is an empirical parameterization (Wesely *et al.*, 1985), which is based upon flux measurements of SO_4^{2-} over grass. In this model, v_d is represented as a function of the friction velocity u^* and the Monin-Obukhov length L . Then for SO_4^{2-} particles and low vegetation, v_d can be calculated by using (Erisman and Draaijers, 1995):

$$v_d = \frac{u_*}{500} \cdot \left[1 + \left(\frac{300}{-L} \right)^{2/3} \right] \quad L < 0$$

$$v_d = \frac{u_*}{500} \quad L > 0 \quad (9.46)$$

Ruijgrok proposed another parameterization derived from measurements over coniferous forest (Ruijgrok *et al.*, 1997). In this approach, which is simplified from the Slinn model (Slinn, 1982), v_d is not only a function of u_* , but also of relative humidity (RH) and surface wetness. Inclusion of RH allows for particle growth under humid conditions and for reduced particle bounce when the canopy is wet. Dry deposition velocity is expressed as:

$$\frac{1}{v_d} = R_a + \frac{1}{v_{ds}} \quad (9.47)$$

where R_a is the aerodynamic resistance, which is the same as for gaseous species, and v_{ds} is the surface deposition velocity.

For tall canopies v_{ds} is parameterized by (Ruijgrok *et al.*, 1997) as

$$v_{ds} = E \cdot \frac{u_*^2}{u_h} \quad (9.48)$$

where u_h is the wind speed at the top of the canopy, which is obtained by extrapolating the logarithmic wind profile from Z_R to the canopy height h . Now u_h can be expressed as:

$$u_h = \frac{u_*}{k} \left(\ln \left(\frac{10 \cdot z_0 - d}{z_0} \right) - \psi_h \left(\frac{10 \cdot z_0 - d}{L} \right) + \psi_h \left(\frac{z_0}{L} \right) \right) \quad (9.49)$$

Note that E is the total efficiency for canopy capture of particles, parameterized for dry and wet surface separately (Erisman *et al.*, 1997). For dry surfaces, for SO_4^{2-} particles (Brook *et al.*, 1999):

$$E = \begin{cases} 0.005 u_*^{0.28} \\ 0.005 u_*^{0.28} \cdot \left[1 + 0.18 \cdot \exp \frac{RH - 80}{20} \right] \end{cases} \quad (9.50)$$

$$RH \leq 80\% \quad RH > 80\%.$$

For wet surfaces, for SO_4^{2-} particles (Brook *et al.*, 1999):

$$E = \begin{cases} 0.08 u_*^{0.45} \\ 0.08 u_*^{0.45} \cdot \left[1 + 0.37 \cdot \exp \frac{RH - 80}{20} \right] \end{cases} \quad (9.51)$$

$$RH \leq 80\% \quad RH > 80\%,$$

where RH is taken at the reference height.

Erisman and Draaijers used the following general form for the calculation of v_d (Erisman and Draaijers, 1995):

$$v_d = \frac{1}{R_a + \frac{1}{v_{ds}}} + v_s, \quad (9.52)$$

where v_s is the deposition velocity due to sedimentation, to represent deposition of large particles, and v_{ds} can be estimated from (9.48). Relations for E for different components and conditions may be derived from model calculations and multiple regression analysis (Erisman and Draaijers, 1995).

For larger supermicron particles (Na^+ , Ca^{2+} and Mg^{2+}), and therefore for some NO_3^- particles, and for low vegetation (for all particles), the sedimentation velocity has to be added:

$$v_s = 0.0067 \text{ m} \cdot \text{s}^{-1} \quad RH \leq 80$$

$$v_s = 0.0067 \cdot e^{\frac{0.0066 \cdot RH}{1.058 - RH}} \text{ m} \cdot \text{s}^{-1} \quad RH > 80\%. \quad (9.53)$$

For sulphate deposition velocity, observations suggest that there is a distinct upper limit which depends on land use type. As a result, it is required that

$$v_{ds} \leq v_m, \quad (9.54)$$

where v_m is the observed maximum deposition velocity (Walcek *et al.*, 1986).

9.4.2 Bi-directional fluxes of N-containing gases

Plant fixation of N_2 provides the single largest atmospheric N input to the biosphere worldwide. However, since it is not associated with acidifying effects, controlled by the plants themselves and its rate is not altered through human activity (other than through land-use change), it is not usually considered in atmospheric N deposition budgets. Direct measurement approaches of N_2 fixation are lacking as the flux to the biosphere is very small compared with ambient N_2 concentrations. Instead N_2 fixation is measured in laboratory, e.g. with isotope techniques.

Nitrous oxide (N_2O), an important greenhouse gas with a lifetime of 114 years, is usually assumed to be emitted by terrestrial surfaces (see Jarvis *et al.*, 2011, Chapter 10, this volume). Although reports of transient N_2O deposition fluxes in the literature are increasing in number, see, for example, Flechard *et al.* (2007), the magnitude of N_2O uptake is small and negligible compared with the main contributors to atmospheric N deposition.

For the other N containing gases there are several parallel pathways of pollutant exchange with vegetation, which include adsorption to the leaf cuticles, exchange through the stomata with the sub-stomatal cavity and exchange with the soil. All these processes are potentially bi-directional, depending on the relative magnitude of the air concentration and the gaseous concentrations in chemical equilibrium with the leaf surface, the apoplastic fluid and the soil solution, respectively. The likelihood for uptake increases with the water solubility

Table 9.4 Summary of Henry's law coefficients of various gaseous nitrogen compounds

Compound	Henry's law coefficient at 25 °C in water [$\text{mol kg}^{-1} \text{bar}^{-1}$]
NH_3	61
HNO_3	2.6×10^6
HONO	49
NO	0.0019
NO_2	0.012
N_2O	0.025
PAN	4.1

and Henry's law coefficient of the gas, which vary over several orders of magnitude (Table 9.4). A database of Henry's law coefficients is available (Mainz, 2010).

Nitric acid

Because of its high deposition rate, HNO_3 makes a significant contribution to N_f deposition in areas exposed to air containing emitted NO_x . HNO_3 is highly water soluble and commonly assumed to deposit at the maximum rate permitted by turbulence, i.e. surface resistance is negligible. While this is probably a reasonable approximation for most situations, several authors have observed emission gradients or reduced uptake rates of HNO_3 , probably owing to non-zero HNO_3 surface concentrations in equilibrium with NH_4NO_3 aerosol deposited to leaf surfaces (Nefel *et al.*, 1996; Nemitz *et al.*, 2004; Zhang *et al.*, 1995). In the case of trace gases with negligible surface resistance, the deposition velocity is very sensitive to the atmospheric resistances (R_a and R_b), which over aerodynamically rough surfaces are small ($5\text{--}10 \text{ s m}^{-1}$). In such conditions, even a very small surface resistance for HNO_3 would strongly influence deposition rates. Currently there are insufficient field data to show whether HNO_3 deposition is subject to a surface resistance, and this remains a research priority.

Ammonia

NH_3 dominates atmospheric N deposition to semi-natural vegetation in agricultural areas, especially in Northern Europe where NH_3 deposition is favoured at high humidity and cold temperatures, although, these conditions also favour conversion to ammonium aerosol. NH_3 is less water soluble than HNO_3 . Thus, NH_3 previously absorbed to wet leaf surfaces may more readily be desorbed (re-emitted) as leaf water layers dry out again (Flechard *et al.*, 1999). Another complication is that plants under certain conditions may release NH_3 .

Generally plants contain inorganic N in the form of NH_4^+ and NO_3^- . These nutrients are mainly present in the liquid part (apoplast) between the cells of the plant. NH_4^+ is an important by-product of plant biochemical pathways resulting in non-zero NH_4^+ concentrations in the leaf apoplast, which results in non-zero gas-phase concentrations (stomatal compensation points, χ_s) in equilibrium with this NH_4^+ _{apo}

concentration at the apoplastic pH, for example. Current evidence suggests that $\text{NH}_4^+_{\text{apo}}$ increases with increasing N supply to the plant, either through fertilization or high atmospheric N inputs. The compensation point χ_s is the product of a temperature function describing the Henry's Law equilibrium and the ratio of $\Gamma_s = [\text{NH}_4^+_{\text{apo}}]/[\text{H}^+_{\text{apo}}]$. Values of Γ_s range from <100 for semi-natural vegetation in clean, remote environments over values around 1500 for semi-natural vegetation in environments with high N deposition to >10 000 after fertilization. At 10 °C, this equates to values of χ_s of < 0.15, 2.3 and > 15 $\mu\text{g m}^{-3}$, respectively. Emission potentials of fertilized soils can be even larger. This large range illustrates that the direction of NH_3 exchange is often difficult to estimate *a priori*.

Several papers have recently reviewed the literature on bi-directional NH_3 exchange and compiled extensive database on compensation points (Massad *et al.*, 2010b; Zhang *et al.*, 2010) in order to provide the necessary input for application in atmospheric transport models. The compensation points increase with N input as it is the main driver of apoplast and bulk leaf NH_4^+ concentrations (Massad *et al.*, 2010a), but the compensation point also vary between different plant species and with growth stage and season (Riedo *et al.*, 2002). The decomposition of litter has been found to play a dominant role (Zhang *et al.*, 2010). The stomatal pathway for NH_3 exchange is only available when stomata are open during daytime, and thus deposition to (often wet) leaf surfaces is the dominant pathway during the night, unless soil surfaces provide a major source and are well exposed to the atmosphere. Deposition fields of NH_3 are particularly uncertain, due to (i) uncertainties in the overall magnitude as well as spatial and temporal patterns of agricultural NH_3 emissions and (ii) the large variability of NH_3 deposition rates to different surfaces.

Specific dry deposition sub-models for the surface resistance that include the description of a canopy compensation point for NH_3 have been derived and implemented in connection with the analysis of different plant surfaces, e.g. for beans (Farquhar *et al.*, 1980), oilseed rape plants (Husted *et al.*, 2000), and heather (*Calluna vulgaris*) (Schjørring *et al.*, 1998). It is common to apply a two-pathway process description (Fowler *et al.*, 2009; Loubet *et al.*, 2001): (a) a stomatal pathway, which is bi-directional and modelled using a stomatal compensation point, and (b) a plant surface pathway, which denotes exchange with water surfaces or waxes on the plant surface. The stomatal compensation point may be calculated from knowledge of the aqueous phase chemistry. The equilibrium NH_3 ambient air concentration for the stomatal compensation point has been expressed as (Sorteberg and Hov, 1996):

$$[\text{NH}_3(\text{g})] = \chi_{cp} = 10^{(1.6035 - 4207.62/T)} \frac{[\text{NH}_4^+]}{[\text{H}^+]}, \quad (9.55)$$

where χ_{cp} is the compensation point concentration of NH_3 , and $[\text{NH}_4^+]$ and $[\text{H}^+]$ are the concentrations of ammonium and hydrogen ion in stomatal cavity, respectively.

The leaf surface may work as a capacitance for NH_3 and SO_2 uptake, and this capacitance increases with humidity (Van hove *et al.*, 1989). This transport is independent of solar radiation and contrary to the uptake through stomata, it also takes place during night. Sutton *et al.* (1998) defined the canopy compensation point as:

$$\chi'_{z0} = \chi(z-d) + F_g (R_a(z-d) + R_b), \quad (9.56)$$

where χ'_{z0} is the canopy compensation point, χ is the NH_3 ambient air concentration, z is the height above ground, d is the displacement height, and F_g is the vertical flux.

The vertical flux F_g may be divided into a flux towards the leaf surface F_w and a flux through stomata F_s :

$$F_g = F_w + F_s. \quad (9.57)$$

And these fluxes may be written as:

$$F_w = -\frac{\chi'_{z0}}{R_w}, \text{ and } F_s = \frac{\chi_{cp} - \chi'_{z0}}{R_s},$$

where R_w and R_s are leaf surface and stomatal resistances, and expressions for these may be found in the work by Sutton *et al.* (1993, 1998).

From the above two equations the total flux F_g may be expressed as:

$$F_g = \frac{\chi_{cp} - \chi'_{z0}}{R_s} - \frac{\chi'_{z0}}{R_w}. \quad (9.58)$$

Similarly the total flux may be derived from the expression of the canopy compensation point:

$$F_g = \frac{\chi'_{z0} - \chi(z)}{R_a(z) + R_b}. \quad (9.59)$$

Combining these two equations and eliminating the total flux F_g provides a general expression for the canopy compensation point:

$$\chi'_{z0} = \frac{\left(\frac{\chi(z)}{R_a(z) + R_b} \right) + \frac{\chi_{cp}}{R_s}}{\left(R_a(z) + R_b \right)^{-1} + R_s^{-1} + R_w^{-1}}. \quad (9.60)$$

Several generalized parameterizations of bi-directional NH_3 exchange have recently been developed for inclusion in regional CTMs (Gore *et al.*, 2009; Massad *et al.*, 2010b; Zhang *et al.*, 2010), but these have not yet been tested in the spatial modelling environments. In an earlier study, Sorteberg and Hov implemented a simpler parameterization of bi-directional fluxes of NH_3 into a Lagrangian long-range transport model, assuming pH to be a constant value of 6.8 (Sorteberg and Hov, 1996). Concerning the concentration of $\text{NH}_4^+(\text{aq})$, they assumed this to be 150 and 50 $\mu\text{mol l}^{-1}$ for crop and grassland, respectively. The model with these relatively crude assumptions was applied for the European area for the year 1993, and compared with basic scenario without bi-directional flux

parameterization. The results indicated a reduction of 0%–20% in total sulphur deposition and a 0%–25% increase in NH_3 deposition compared with a simple flux model. The emission through stomata was found to account approximately 0.1% of the total NH_3 emission.

Loubet *et al.* applied a 2D local scale model with the above parameterization of bi-directional fluxes of NH_3 based on the canopy compensation point approach to a moorland area (Loubet *et al.*, 2001). With the FIDES (Flux Interpretation by Dispersion and Exchange over Short Range) model they simulated transport and dispersion to a moorland placed 260 m downwind from a pasture grazed with sheep.

Experimental studies have shown that over the sea the atmospheric fluxes of NH_3 may also be upward or downward (Lee *et al.*, 1998; Quinn *et al.*, 1988; Sørensen *et al.*, 2003) depending on the meteorological conditions and the relationship between the pH and contents of NH_4^+ in the upper surface waters on the one side, and the NH_3 concentrations in ambient air just above the water surface on the other side. The bi-directional NH_3 flux over sea is expressed as an exchange with the water surface:

$$F = V_e (C_{eq} - C_{air}), \quad (9.61)$$

where V_e is the exchange velocity between air and sea (that equals $1/(R_a + R_b)$), C_{eq} is the NH_3 concentration in the air at equilibrium with the NH_x in the water, and C_{air} is the actual ambient air concentration of NH_3 . F is the flux of NH_3 ; the flux is positive when the sea emits NH_3 and negative when deposition takes place.

The ambient air NH_3 concentration at equilibrium is expressed as (Asman *et al.*, 1994):

$$C_{eq} = \frac{M_{\text{NH}_3} [\text{NH}_{xs}]}{R \times T \times H_{\text{NH}_3} \left[\frac{1}{\gamma_{\text{NH}_3}} + \frac{10^{-pHs}}{\gamma_{\text{NH}_4} \times K_{\text{NH}_4}} \right]}, \quad (9.62)$$

where C_{eq} is in $[\mu\text{g m}^{-3}]$, $[\text{NH}_{xs}]$ is the NH_x concentration in the sea $[\mu\text{M}]$, M_{NH_3} is the molecular mass of NH_3 $[\text{g mol}^{-1}]$, γ_{NH_3} is the activity coefficient of $\text{NH}_3 \times \text{H}_2\text{O}$, γ_{NH_4} is the activity coefficient of NH_4^+ in sea water, R is the gas constant ($8.2075 \times 10^{-5} \text{ atm. m}^3 \text{ mol}^{-1} \text{ K}^{-1}$) and H_{NH_3} is the Henry's law coefficient for NH_3 $[\text{M atm}^{-1}]$, pHs is the pH in sea water, which is a measure of the activity of H^+ in sea water, and K_{NH_4} is the dissociation constant for NH_4^+ $[\text{M}]$. The values for H_{NH_3} and K_{NH_4} are expressed as:

$$H_{\text{NH}_3} = 56 \text{ EXP} \left(4092 \left(\frac{1}{T} - \frac{1}{298.15} \right) \right), \quad (9.63)$$

$$K_{\text{NH}_4} = 5.67 \times 10^{-10} \text{ EXP} \left(-6286 \left(\frac{1}{T} - \frac{1}{298.15} \right) \right). \quad (9.64)$$

The above formulation was developed for computing the impact of bi-directional fluxes over the North Sea and applied to measured data (Asman *et al.*, 1994). The formulation has since been applied in the Lagrangian ACDEP model (Sørensen *et al.*, 2003), where the results showed a redistribution of N deposition in the coastal region off the coast of the Netherlands.

Nitric oxide

NO is rather water-insoluble and there is no efficient mechanism for NO to react on the surface or inside leaves, so its deposition rate is rather slow. By contrast, soils commonly act as a source for NO. Some of these soil emissions of NO are oxidized to NO_2 (and possibly HNO_3) within plant canopies, and taken up more efficiently than NO and thus the behaviour of NO still needs to be taken into account in surface-atmosphere exchange.

Nitrogen dioxide

Plant uptake of NO_2 is slower than that of the more water soluble gases (HNO_3 , NH_3), but it is a significant contributor to N deposition. The NO_2 deposition to vegetation is primarily regulated by stomata, and for most plants the internal resistance is negligible, and NO_2 deposition velocities may thus be computed from a knowledge of stomatal resistance or conductance (Thoene *et al.*, 1991). Studies indicate a small effective stomatal compensation point for NO_2 for some plant species, in the range of > 0 to 2 ppb; e.g. an American experimental study found a value of $1.5 \text{ nmol mol}^{-1}$ for the canopy compensation point for NO_2 over deciduous forest (Horii *et al.*, 2004). However, the underlying process is not currently understood, and some laboratory work has failed to reproduce the field observations. Because of its low water solubility, deposition to (and reaction with) surface water, including sea water, is also slow (Cape *et al.*, 1993).

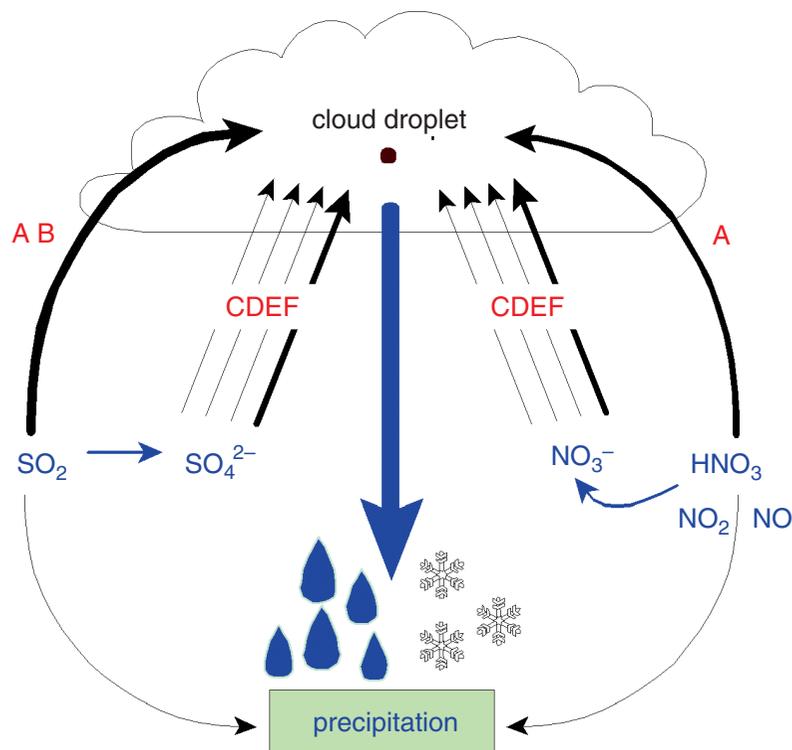
Nitrous acid

The biosphere/atmosphere exchange of HONO is generally bi-directional, and daytime concentrations of HONO are low, as it is rapidly photolysed in sunlight. With solubility similar to NH_3 , HONO is deposited to vegetation under most conditions. Observations of HONO emission have been attributed to production of HONO at surfaces, e.g. through the reaction of NO_2 with NO on wet surfaces (Harrison and Kitto, 1994) or NO_2 reduction on humic acid (Stemmler *et al.*, 2006). In connection with an experimental study, a parameterization of bi-directional fluxes of both NH_3 and HONO was applied for estimating dry deposition of N compounds to the Amazon Basin from measured ambient air concentrations (Trebs *et al.*, 2006).

Organic nitrogen compounds

Organic N compounds account for approximately 20%–30% of the total N deposition in precipitation (Cape *et al.*, 2001; Cornell *et al.*, 2003; Holland *et al.*, 1999) although this is often not included in N deposition estimates. Much of this organic contribution is presumably due to scavenging of organic N

Figure 9.17 The processes of capture of pollutants by cloud and rain.



A - dissolution B - oxidation C - diffusiophoresis D - Brownian diffusion
E - impaction F - cloud condensation nuclei pathway

compounds in the aerosol phase and cloud water. However, the contribution of gaseous organic N compounds to N deposition is even less studied. PAN is considered an important N reservoir species, responsible for much of the N transport in remote regions. PAN is thought to deposit slowly and remains stable at cold temperatures. At warmer tropospheric temperatures PAN decomposes quickly. Newly developed instruments have resulted in new measurements indicating deposition rates of PAN (and other PAN-like compounds) that are significantly larger than classical predictions (Turnipseed *et al.*, 2006; Wolfe *et al.*, 2009), especially to wet vegetation. Thus the lifetime of PAN with respect to deposition may be shorter than previously thought. In addition, PAN is water insoluble and the comparably large deposition fluxes to wet surfaces indicate that the current mechanistic understanding of the deposition process is incomplete. There are parallels to the deposition of O_3 , which also appears to exhibit larger deposition rates to wet surfaces than can be explained by its solubility (Fowler *et al.*, 2001). The importance of alkyl nitrates has recently been demonstrated for Blodgett Forest, Sierra Nevada, USA (Farmer *et al.*, 2006), although it appears that the pollution climate of their site is quite unique. Nevertheless, information is lacking to form a robust picture of the importance of these compounds across the full range of European conditions. Although amines have been measured as emitted from agricultural activities (Schade and Crutzen, 1995), there is currently no information on their dry deposition.

9.4.3 Deposition of N containing aerosols

Deposition of particles containing SO_4^{2-} , NO_3^- , Cl^- and NH_4^+ contributes to the potential acidification and eutrophication (N components) of ecosystems. Compared to gaseous deposition of acidifying compounds onto low vegetation, particle deposition fluxes are usually found to be small. However, in difference from wet deposition it takes place all the time and furthermore it is believed that the fluxes of small particles are currently underestimated for very rough surfaces like forests. Erismann *et al.* (1997) found that deposition of aerosols to the Spelder forest contributed 20% and 40% to the total dry deposition of S and N, respectively. Parameterizations of aerosol dry deposition velocities to forests differ greatly between models (Tang *et al.*, 2009).

9.5 Wet scavenging of N compounds from the atmosphere

Wet deposition or scavenging is defined as the removal of gases and aerosol from the atmosphere by precipitation snow, rain. Unlike dry deposition, the wet deposition processes are indirect; rain, hail and snow are the vectors for transport of the pollutant to the surface. The apparent simplicity of the measurement approach for wet deposition, a simple precipitation collector placed on the ground contrasts appreciably with the underlying physical and chemical pathways of solutes into the collected precipitation

sample. There is also significant uncertainty in the relative magnitudes of dry deposition of trace chemical species as gases and aerosols onto the collecting equipment.

The incorporation of pollutants in clouds and precipitation include many different processes, which will be considered in turn. The N_r compounds are present in aerosols or as gases. Regarding aerosols, the N is mainly present as NH_4^+ or NO_3^- (although some organic N is also present). The bulk of the aerosol mass is present in the size range 0.1–1.0 μm (diameter). These aerosols are removed through interception by falling rain or snow, a process known as *washout* or by incorporation of the aerosol into cloud droplets within clouds, a process known as *rainout* (Figure 9.17).

Washout is responsible for 10%–20% of the N in wet deposition on average, but depends naturally on the relative amounts of N present in cloud water and in the air through which the precipitation falls. The aerosol scavenging within cloud occurs through a number of physical and chemical pathways (Figure 9.17) as C, D, E and F while the gases are incorporated through solution and oxidation processes (A and B). The phoretic process includes diffusiophoresis, in which aerosol particles are transported in the direction of a mean flux of vapour molecules. In the case of a cloud droplet growing by vapour

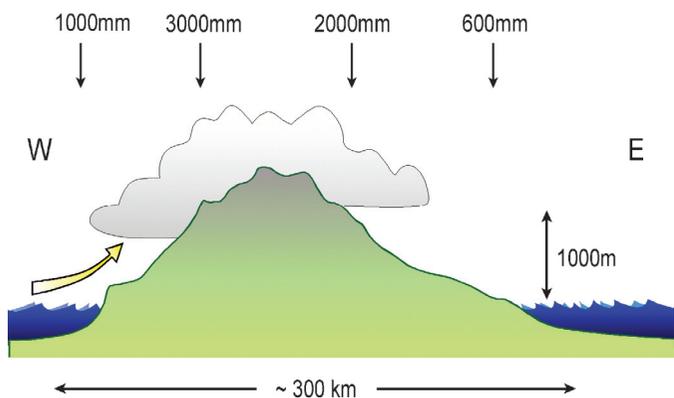


Figure 9.18 Orographic enhancement of precipitation in the UK; an East–West transect.

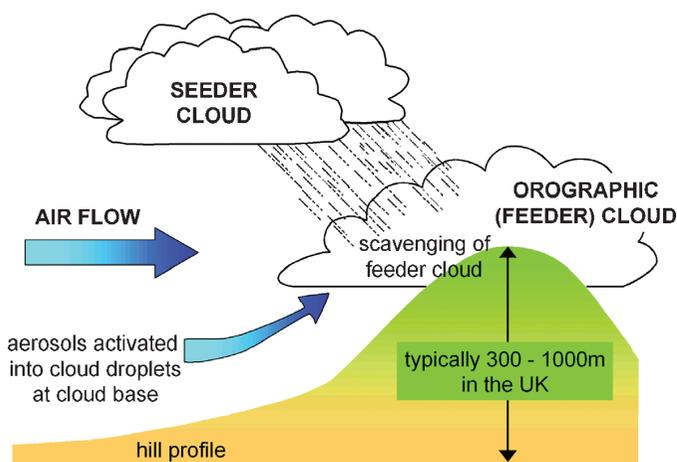


Figure 9.19 The seeder–feeder process of orographic enhancement of precipitation. Source: Fowler and Battarbee, 2005.

diffusion of water molecules towards the droplet surface, aerosols would move along the vapour flux towards the growing droplet. Additional phoretic mechanisms are presented by electrical and thermal gradients (electrophoresis and thermophoresis respectively). The phoretic processes contribute relatively small amounts of the solute in cloud water (Goldsmith *et al.*, 1963). Aerosols may also be captured by cloud droplets following Brownian diffusion (D) to the droplet surface and rates of Brownian diffusion vary strongly with particle size, being significant for particles smaller than 100 nm in diameter. However, diffusion rates are very small relative to molecular diffusion and diffusional mechanisms make only minor contributions to the wet removal pathway. The remaining minor process leading to capture of aerosols by cloud droplets is impaction and interception (E). As implied in the name these processes lead to the capture of aerosols by droplets when one is unable to follow the streamlines of airflow around the other and the aerosol and droplet collide. The bulk of the aerosol N in cloud water is incorporated through the activation of aerosols containing NO_3^- or NH_4^+ into cloud droplets. The N containing aerosols are effective cloud condensation nuclei and are readily incorporated into cloud droplets through the nucleation scavenging pathway. Thus the main route is nucleation scavenging for aerosol NO_3^- , and NH_4^+ (Pruppacher and Jaenicke, 1995). The pathway for below wet scavenging of the gaseous N compounds depends on the solubility and reactivity of the specific gas. In the case of NH_3 and HNO_3 , which are highly soluble, clouds and rain remove these gases effectively from the air. The contribution of NO and NO_2 to dissolved N in precipitation is very small as these gases are not very soluble (relative to NH_3 or HNO_3).

Wet deposition is monitored by simple methods (precipitation collectors) analysed for major anthropogenic ions SO_4^{2-} , NO_3^- , NH_4^+ , H^+ and marine ions Cl^- , Na^+ , Mg^{2+} . The networks of collectors for precipitation chemistry are much less dense than precipitation collectors for the national meteorological services, mainly because of the costs of chemical analysis. Furthermore, precipitation chemistry collectors are located a height above ground to reduce contamination from ground based sources, and the practice of locating collectors above the ground reduces the capture of small droplets due to aerodynamic screening by the collector. The relative contributions to deposition from dry and wet deposition change with distance from source as primary pollutant concentrations decline and oxidation from gas to particle remove gas phase species which dry deposit quickly. Thus the areas more than a few hundred km from sources receive most of their N deposition in precipitation.

In regions in which the amounts of precipitation are large, wet deposition dominates the N loads, as in most of the uplands of Europe. However, it is not simply the precipitation amount that needs to be considered in assessing the relative contributions of wet and dry deposition. The processes leading to orographic enhancement of rainfall amount have a profound effect on the overall scavenging of pollutants from the atmosphere. The meteorological process which enhances precipitation in much of maritime northern Europe is the seeder–feeder

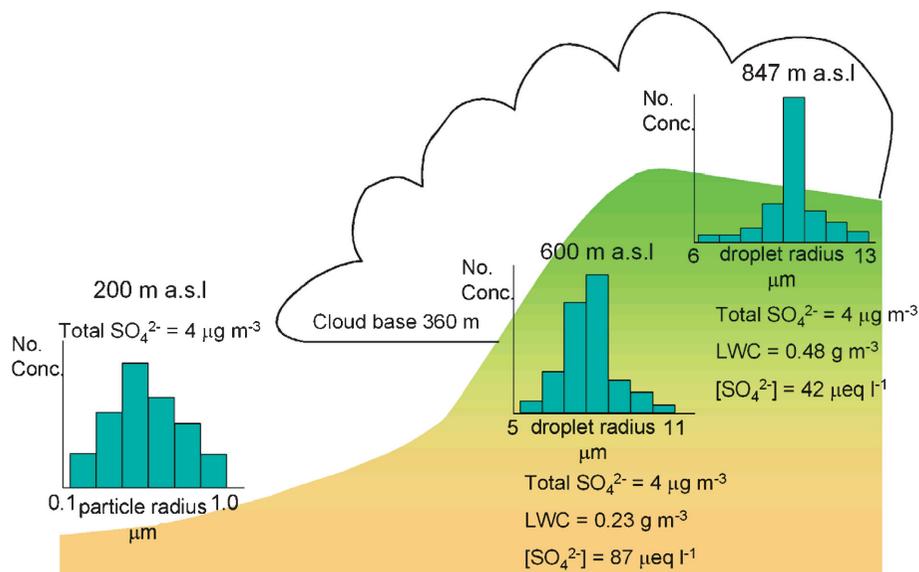


Figure 9.20 The incorporation of pollutant aerosols into orographic cloud. Source: Fowler *et al.*, (1991).

mechanism, in which orographic cloud, formed over hills and mountains is washed out by precipitation falling from higher levels in the troposphere, as shown in Figure 9.18 and first described by Bergeron (1965). The process occurs widely and is responsible for most of the enhancement of precipitation over uplands in the UK and Scandinavia. The process has been extensively studied in the UK, where, especially in the West of the country, annual rainfall is in the range 1000–3000 mm with the amounts in excess of 100 mm being mainly generated through seeder-feeder scavenging.

The mountains are very effective in increasing rainfall (Figure 9.18) and wet deposition by the seeder–feeder process (Figure 9.19) in which low level hill cloud droplets are washed out by falling precipitation from higher level. The hill cloud is more polluted than higher level cloud because boundary layer aerosols are effectively activated into cloud droplets as they are forced to rise and cool over the hills and mountains.

The seeder–feeder effects on precipitation amount have been simulated in process-based models and are able to simulate observed spatial patterns in precipitation (Carruthers and Choularton, 1983). Models have also been used to simulate the wet deposition of pollutants over mountains (Dore *et al.*, 1990) and compared with detailed campaign measurements in an upland area. Extending the modelling of orographic enhancement of wet deposition to the country scale has enabled detailed spatially resolved wet deposition maps to be generated (Dore *et al.*, 1990). As orographic enhancement of wet deposition has been shown to be a major contributor to the total deposition in upland Britain the explicit inclusion of the process in deposition maps has been regarded as a routine component of wet deposition mapping (NEGTA, 2001). The resulting wet, and total N deposition maps show a strong influence of altitude and requires a grid resolution on the same scale as the complex topography to reproduce (<10 km). Thus deposition modelling and mapping at a 50 km × 50 km scale fails to capture the spatial structure in wet

deposition, as described in Simpson *et al.* (2011, Chapter 14, this volume). In principle the models are able to simulate the process as the literature shows, but the grid resolution of both the underpinning meteorological model and the model applied for deposition calculations need to be able to capture the topographic scale of the variability.

Cloud droplet deposition

Unlike aerosols in the size range 0.1–1.0 μm, which are not deposited efficiently on vegetation, the hill cloud droplets are large enough (3–10 μm in diameter), to impact efficiently on vegetation (Fowler *et al.*, 1990); this deposition pathway is termed cloud deposition or *occult* deposition. For the UK it provides a very small contribution to the total but it is important for hills which are frequently shrouded in cloud (see Figure 9.20). As the concentrations of major ions in hill cloud are enhanced, this deposition pathway leads to the exposure of vegetation to very large concentrations (SO_4^{2-} , NH_4^+ , NO_3^- , 1000 μeq l⁻¹–2000 μeq l⁻¹) (Fowler *et al.*, 1990).

The orographic enhancement of wet deposition is not included in the assessments of wet deposition in all countries, and for regions with only small areas of upland, this will not lead to significant underestimates in wet deposition. However, for areas of Europe in which seeder–feeder scavenging of pollutant represents a substantial contribution to total deposition, it is important to simulate the process in mapping regional wet deposition, to avoid underestimating wet deposition and exceedances of critical loads.

9.6 Summary of emerging issues and unanswered questions

There are many uncertainties and unanswered questions regarding the fate of N_r species in the atmosphere. These uncertainties and unanswered questions relate to various aspects of the governing atmospheric processes: emission, transformation,

transport (see Simpson *et al.*, 2011, Chapter 14, this volume) and deposition.

Most of the N studies are concentrated on few mainly northern European countries. This applies for studies on agricultural NH₃ emissions. There is therefore a strong need for more field and monitoring studies of atmospheric N compounds in other parts of Europe, i.e. southern European countries.

9.6.1 Emissions

There is a need for emission inventories of higher spatial and temporal resolution than what is currently applied in atmospheric transport models, i.e. going from the traditional 50 km horizontal grid resolution towards inventories of 1–5 km and applying source specific seasonal and diurnal variations that account for actual meteorological conditions, local praxis, etc. The need for higher resolution inventories applies especially for NH₃ for which the near-source deposition plays a significant role, and current deposition mappings therefore face significant uncertainties due to insufficient resolution in the inventories. Detailed information about agricultural practice is necessary in order to derive these inventories that need to account for meteorological conditions and how these affect the emissions from different agricultural source categories.

9.6.2 Transformation

In relation to obtaining a better understanding of the transformation processes, there is a strong need for speciated field measurements and source apportionment studies of gas phase and particulate N_r compounds in the atmosphere. This applies especially to the organic N compounds for which the processes are not fully explored and the impact on the overall atmospheric N budget therefore still is fairly unknown.

Aerosol processes are in general subject for further development in atmospheric transport models as they still cannot fully explain observed PM_{2.5} and PM₁₀ mass, and this applies naturally also for the N_r compounds.

9.6.3 Deposition

New parameterizations are needed to describe bi-directional NH₃ exchange in atmospheric transport models, which currently tend to overestimate dry deposition to fertilized vegetation or semi-natural vegetation subject to large atmospheric N inputs. To put these parameterizations onto robust footings it is necessary to (i) compile databases of stomatal compensation points for the major biomes, (ii) derive operational, mechanistic parameterizations for cuticular uptake resistances (e.g. in response to local pollution climates), and (iii) compile European agricultural management profiles of fertilizer application.

Litter decomposition is emerging as a potentially important source of atmospheric NH₃, which is not well quantified, understood or parameterized.

Improved mechanisms are required to deal with sub-grid variability in NH₃ deposition. Due to limitation of the spatial

resolution, operational atmospheric transport models are usually not able to predict deposition to patch-work landscapes correctly. Because they average over rather large areas, the models underestimate the hotspots of dry deposition, which commonly results in the under prediction of critical loads exceedances. The large spatial variability in NH₃ concentrations across the typical European landscape also makes it hard to validate the models.

Direct micrometeorological measurement of dry deposition of reactive N compounds is limited to small-scale measurement campaigns, due to the costs of maintaining expensive instrumentation. Therefore dry deposition estimates usually rely on inferential modelling where deposition is derived from air concentrations which may either be measured or modelled, and (often uncertain) estimates of deposition velocities. Low-cost approaches are urgently required to provide robust direct measurements of N_r deposition across an extensive flux measurement network.

The contribution of organic N compounds to total gaseous and particulate dry deposition is largely unknown. Evidence from the western USA suggests that alkyl nitrates can make a significant contribution to the total N flux (Farmer *et al.*, 2006), but for European conditions, this question remains largely unanswered. No fluxes have been measured for gaseous amines. New evidence suggests that PAN dry deposition rates may be much larger than assumed in classical modelling approaches (Turnipseed *et al.*, 2006). The contribution of PAN to dry deposition of N may therefore have been underestimated. This also highlights the fact that our current understanding of the dry deposition mechanism is incomplete as PAN appears to deposit faster than can be explained by its solubility alone.

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