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Governing processes for reactive nitrogen compounds in the European atmosphere

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Abstract. Reactive nitrogen (N_r) compounds have different fates in the atmosphere due to differences in the governing processes of physical transport, deposition and chemical transformation. N_r compounds addressed here include reduced nitrogen (NH_x: ammonia (NH_3) and its reaction product ammonium (NH_4^+)), oxidized nitrogen (NO_y: nitrogen monoxide (NO) + nitrogen dioxide (NO_2) and their reaction products) as well as organic nitrogen compounds (organic N). Pollution abatement strategies need to take into account the differences in the governing processes of these compounds when assessing their impact on ecosystem services, biodiversity, human health and climate. NO_x ($NO + NO_2$) emitted from traffic affects human health in urban areas where the presence of buildings increases the residence time in streets. In urban areas this leads to enhanced exposure of the population to NO_x concentrations. NO_x emissions generally have little impact on nearby ecosystems because of the small dry deposition rates of NO_x. These compounds need to be converted into nitric acid (HNO_3) before removal through deposition is efficient. HNO_3 sticks quickly to any surface and is thereby either dry deposited or incorporated into aerosols as nitrate (NO_3^-). In contrast to NO_x compounds, NH_3 has potentially high impacts on ecosystems near the main agricultural sources of NH_3 because of its large ground-level concentrations along with large dry deposition rates. Aerosol phase NH_4^+ and NO_3^- contribute significantly to background $PM_{2.5}$ and PM_{10} (mass of aerosols with an aerodynamic diameter of less than 2.5 and 10 µm, respectively) with an impact on radiation balance as well as potentially on human health. Little is known quantitatively and

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qualitatively about organic N in the atmosphere, other than that it contributes a significant fraction of wet-deposited N, and is present in both gaseous and particulate forms. Further studies are needed to characterise the sources, air chemistry and removal rates of organic N emissions.

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1 Introduction

Reactive nitrogen compounds (N_r) affect ecosystem health (Sutton et al., 2011), human health (Aneja et al., 2009) and contribute to climate change (Butterbach-Bahl et al., 2011b; Erisman et al., 2011; Xu and Penner, 2012). However, the actual impact of specific emissions depends on a cascade of competing processes taking place simultaneously, which transforms pollutants along multiple paths, with multiple impacts (Galloway et al., 2003). One example is the release of ammonia (NH_3). Strong NH_3 sources contribute to high N loads to nearby ecosystems through a fast dry deposition rate (dry deposition velocities are typically 5–20 $mm\,s^{-1}$, Flechard et al., 2011, but may approach 40 $mm\,s^{-1}$, Phillips et al., 2004). This process competes with reactions that lead to the formation of aerosol phase ammonium (NH_4^+). The latter contributes to $PM_{2.5}$ and PM_{10} (mass of aerosols with an aerodynamic diameter less than 2.5 and 10 µm, respectively) with much longer transport distance and with potential health effects and impact on the radiation balance. The NH_4^+-containing aerosols are typically assigned low dry deposition velocities (in the order of 1 to 10 $mm\,s^{-1}$, Duyzer, 1994), but uncertainties are large (e.g. Flechard et al., 2011) and there is increasing recognition of the role of chemical divergence (dissociation of NH_4NO_3) in producing apparently high deposition velocities (Fowler et al., 2009). In some cases ammonium aerosols can be transported up to 1000 km away, since the aerosols are mainly wet scavenged. Figure 1 provides an overview of the N_r pathways, with an emphasis on atmospheric N deposition. NH_3 is emitted mainly from agricultural sources (Bouwman et al., 1997), and has a typical atmospheric residence time in Europe of about 24 h (according to model calculations with OPS, Johannes van Jaarsveld, personal communication). Both NH_3 and gaseous NO_x lead to formation of aerosol phase compounds (NH_4^+ and NO_3^-, respectively) which have atmospheric residence times of several days. Furthermore, NH_3 can take part in bi-directional surface fluxes (Sutton et al., 1995); in areas with large nitrogen (N) inputs, NH_3 may be released from plants and soil, and in areas with high gas-phase concentrations, deposition rates may be limited by surface saturation, and re-emission of absorbed NH_3 may occur (Flechard et al., 1999; Massad et al., 2010b; Nemitz et al., 2004a; Sutton et al., 2009a, b). By comparison, the primary form in which oxidized nitrogen (NO_y) is emitted is nitrogen monoxide (NO), which reacts to form nitrogen dioxide (NO_2) over minutes and hours depending on local oxidant chemistry (interactions are described well in various text books see, e.g. Seinfeld and Pandis, 2006). Both of these compounds (especially NO) are removed slowly by dry deposition to vegetation. The main scavenging process is therefore by chemical conversion. In the case of NO_2, chemical reaction with hydroxyl (OH) radical forms nitric acid (HNO_3) with a typical transformation rate of about 5 % per hour (Hertel, 1995). HNO_3 has a short atmospheric lifetime (on the order of seconds to hours), since it is quickly scavenged by uptake in aerosols, reaction with NH_3 or by dry deposition (it typically sticks to any surface – aerosol as well as vegetation and the ground) (Hertel et al., 2006). A US study (Day et al., 2008) found a lifetime of HNO_3 of 2.5 h for a mountain area in a sunny and warm climate, but the lifetime depends strongly on the environment, and another study has thus shown lifetimes of 7–20 min in air masses processed by clouds containing ice-crystals (von Kuhlmann and Lawrence, 2006). Another US study showed that HNO_3 and PAN concentrations in the urban areas of Houston, Texas were of similar magnitude and could be up to 1.5 ppbv during daytime (Luke et al., 2010). Uptake of HNO_3 into existing aerosols or formation of new aerosols by reaction with NH_3 leads to aerosol bound nitrate (NO_3^-) as does the reaction with sea salt (Pryor and Sorensen, 2000). Such NH_4^+ and NO_3^- containing aerosols are mainly scavenged by wet deposition, due to the relatively small dry deposition rate of submicron aerosols (Gallagher et al., 2002). 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. The greenhouse gas nitrous oxide (N_2O) is excluded in Fig. 1, as it has little impact on atmospheric N deposition. To maintain simplicity of the diagram, N_r reservoir compounds (e.g. HONO, HO_2NO_2, PAN and PAN-like species) are also disregarded in Fig. 1, although these are discussed in the subsequent sections. The actual split between various pathways depends on the precise location where local climate conditions, local emission densities and distance from high emission areas all determine the overall fate of N_r. Another example of atmospheric processes affecting the impact of N_r is the complex flow conditions in urban street canyons. The generally short residence time of air in urban streets means that only fast reactions of NO_x are relevant. However, the presence of buildings, especially in streets with close building facades on both sides of the street, increases the local residence time of traffic pollutants emitted in the street sufficiently to significantly increase also the exposure of the population (Hertel and Goodsite, 2009). These processes – the flow conditions and the chemical conversion – affect the ratio between NO which has little direct impact on human health and the airway irritant NO_2 that, for example, may enhance the impact of airborne allergens (Tunnicliffe et al., 1994). As can be seen from this short introduction, the atmospheric chemistry and governing processes removing N_r from the atmosphere are both complex and diverse, reflecting the many compounds involved and their different characteristics. To be

Table 1. Comparison of European emissions of N_r in Tg, using the nitrogen content of both NH_3 and NO_x to analyse the overall trend development of N_r release into the atmosphere. Emission figures based on the EDGAR* emission inventory, 4.2.

	1985		1990		1995		2000		2005	
	Tg	Share (%)	Tg	Share (%)	Tg	Share (%)	Tg	Share (%)	Tg(%)	Share
Agriculture	5.98	55.3 %	5.68	54.2 %	4.80	52.8 %	4.76	55.3 %	4.65	55.5 %
Road transport	1.73	16.0 %	2.09	20.0 %	1.85	20.3 %	1.51	17.6 %	1.34	15.9 %
Other mobile sources	0.36	3.3 %	0.26	2.5 %	0.24	2.6 %	0.24	2.8 %	0.26	3.1 %
Power generation	1.43	13.2 %	1.38	13.2 %	1.31	14.4 %	1.18	13.8 %	1.27	15.2 %
Industrial production	0.87	8.0 %	0.65	6.2 %	0.53	5.9 %	0.51	5.9 %	0.48	5.8 %
Other	0.44	4.1 %	0.41	3.9 %	0.36	4.0 %	0.40	4.6 %	0.38	4.5 %
Total	10.81		10.47		9.08		8.60		8.38	
			−3 %		−16 %		−20 %		−23 %	

* Source: European Commission, Joint Research Centre (JRC)/Netherlands Environmental Assessment Agency (PBL). Emission Database for Global Atmospheric Research (EDGAR), release version 4.2., http://edgar.jrc.ec.europa.eu, 2011.

able to relate these processes more effectively, the present paper provides an overview of the governing atmospheric processes of N_r in the atmosphere, with particular attention to the nature of the emissions and removal processes, including bi-directional exchange where this occurs. This review further develops an extensive analysis of this topic (Hertel et al., 2011), as originally conceived in the European Nitrogen Assessment (2011). While the paper focuses on Europe, the general principles are applicable globally. For the purpose of this review, we have disregarded N_2O as it has no health effects at ambient concentration levels and an insignificant role in atmospheric deposition of N. It should be noted though that it does play a role in the chemistry of the stratosphere and as a climate forcer (Pinder et al., 2012), as well as in leading to depletion of stratospheric ozone (Brink et al., 2011; Butterbach-Bahl et al., 2011b).

2 Emissions

N_r is mainly released to the atmosphere as NH_3, NO_x, and in poorly quantified amounts of other gases such as HONO or organic N (e.g. amines). By comparison, emission of N_2O accounts for a much smaller fraction, representing about 15 % of the total European N_r emission to the atmosphere (Leip et al., 2011). An overall distribution of the emission of reactive nitrogen compounds and how these have evolved during the period 1985 to 2005 is shown in Table 1.

2.1 Ammonia emissions

In western countries, agricultural activities contribute 85–98 % of the atmospheric NH_3 emissions (Anderson et al., 2003; Gyldenkærne et al., 2005; Sutton et al., 2000a). These emissions arise in some cases from the direct breakdown of mineral fertiliser, but more importantly from the breakdown of organic matter (such as urea) within animal wastes. The emission process is a chemical and physical process which is highly temperature dependent and varies significantly over day and season (Gyldenkærne et al., 2005; Skjøth et al., 2004). The agricultural sources may be grouped as

- point sources, i.e. animal houses, manure storage and “slurry lakes” (Sommer et al., 2009);
- application of manure and mineral fertiliser to fields (Smith et al., 2009);
- grazing animals (Petersen et al., 1998);
- other sources including releases from plants (Larsson et al., 1998) such as legumes (Gyldenkærne et al., 2005) and vegetation during management and senescence (Sutton et al., 2000b, 2009a, b).

And the non-agricultural sources include

- wild animals (Anderson et al., 2003; Riddick et al., 2012; Simpson et al., 1999; Sutton et al., 2000a; Theobald et al., 2006);
- catalyst processes, mainly related to road traffic (Kean et al., 2009; van Vuuren et al., 2011);

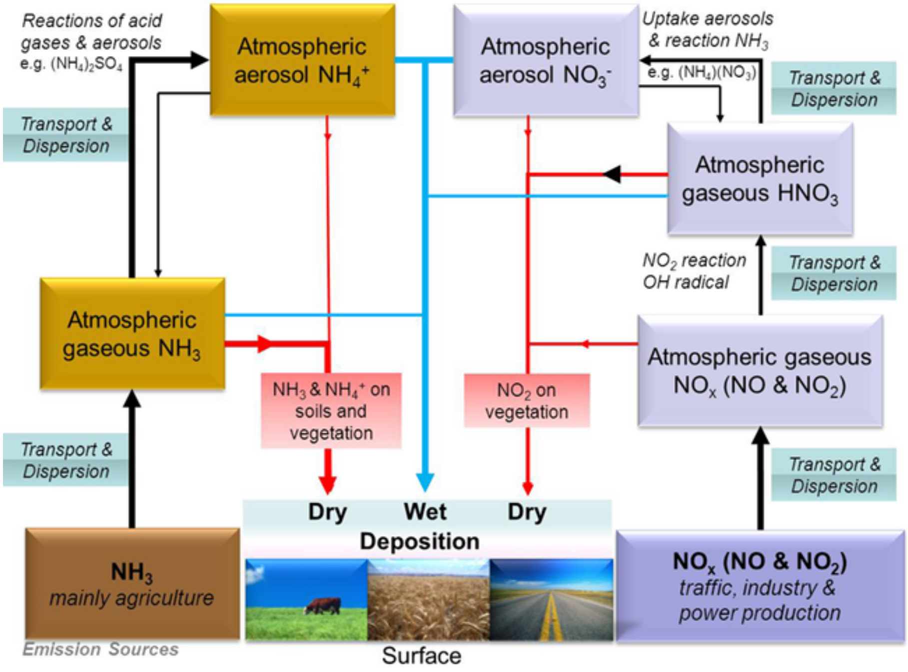

Fig. 1. A sketch which illustrates the various pathways of reactive nitrogen compounds in the atmosphere. The left side of the figure illustrates the atmospheric pathways of NH$_x$ (gas phase ammonia (NH$_3$) and aerosol phase ammonium (NH$_4^+$)), and the right side of the figure illustrates the pathway of nitrogen oxides (NO$_y$) compounds in the atmosphere (NO$_x$ = NO + NO$_2$ and reaction products). The sketch is a modified version of the figure in Hertel et al. (2006). Reservoir compounds nitrous acid (HONO), peroxy nitric acid (HO$_2$NO$_2$), PAN (CH$_3$C(O)OONO$_2$) and PAN-like species like isoprene nitrates as well as nitrate (NO$_3$) and dinitrogen pentoxide (N$_2$O$_5$) radicals have been disregarded in the sketch for simplicity.

- manufacturing processes such as production of fertiliser, glass wool, catalysts and cement (Reis et al., 2009) and http://edgar.jrc.ec.europa.eu/index.php;
- humans, pets, landfills, urban areas and sewage systems (Reche et al., 2012; Sutton et al., 2000a);
- non-anthropogenic sources including natural fires from ecosystems (Andreae and Merlet, 2001; Simpson et al., 1999; Yokelson et al., 2007);
- emission from plants due to compensation points (Farquhar et al., 1980; Husted et al., 2000; Massad et al., 2010a; Mattsson et al., 2009; Sutton et al., 1995);
- emission from sea surfaces (Barrett, 1998; Sørensen et al., 2003).

The above split of the agricultural sources is used in a parameterisation that for a number of years has been considered as the most advanced description of temporal and spatial variations in NH$_3$ emissions in Europe (Pinder et al., 2006; Zhang et al., 2008). This parameterisation was originally developed for Denmark (Gyldenkærne et al., 2005; Skjøth et al., 2004) for which detailed information about animal numbers, manure management and crop growth is available on farm and field level. Recent studies have shown that these methodologies can be used in large scale models over both USA (Bash et al., 2012; Cooter et al., 2012) and from Central to Northern Europe (Skjøth et al., 2011). Here it should be noted that the European situation is considerably more difficult than USA. USA provides access to agricultural census data such as animal numbers and crop assignments at the county level (e.g. Cotter et al., 2012), while the available information over the European continent varies (e.g. detailed farm-level information in the Netherlands/Denmark and almost no available information from Belerus/Ukraine). A flexible methodology which is based on both the idea of splitting agricultural sources into sectors and using an open source code is therefore developed within the EU FP7 project ECLAIRE (http://www.eclaire-fp7.eu). The methodology in ECLAIRE use the European approach as a starting point as this parameterisation and other more simple approaches have been successfully implemented in the atmospheric chemistry and deposition (ACDEP) model (Skjøth et al., 2004), the DEHM model (Brandt et al., 2012; Skjøth et al., 2011), the EMEP MSC-W model (Fagerli et al., 2007; Simpson et al., 2012), the local scale models OML-DEP (Geels et al., 2012; Sommer et al., 2009), the SCAIL (Theobald et al., 2009) screening method developed for the UK as well as most recently the local scale models AIRMOD and ADMS (Theobald, 2009). This approach therefore allows for gradual replacements of single elements in the existing simple European approach with more advanced methodologies such as process based calculations of mineral fertiliser (Hamaoui-Laguel et al., 2012). We here use split of agricultural emissions into several agricultural sectors as the basis for describing NH_3 emissions. Non-agricultural sources of NH_3 are generally poorly described, which is largely a consequence of the limited number of data on many different processes. These sources include human sweat, excreta from pets and wild animals, exhaust from gasoline vehicles with catalytic converters, stationary combustion sources and industry as well as evaporation from waste deposits (Sutton et al., 2000a).

2.1.1 Animal houses and manure storages

Highly complex surface models have been developed for describing NH_3 emissions from agricultural buildings (Muck and Steenhuis, 1982; Olesen and Sommer, 1993; Oudendag and Luesink, 1998; Zhang et al., 1994) in order to help better manage emissions. However, in chemistry-transport modelling (CTM) a simplified parameterisation based on wind speed and temperature has proven more practical (Skjøth et al., 2004):

$$E(t) = C \cdot T(t)^{0.89} \cdot V(t)^{0.26} \quad (1)$$

where C is a constant related to the amount of N or TAN (Total Ammoniacal Nitrogen = sum of NH_3 and NH_4^+) 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. Equation (1) is used to distribute a known annual emission into shorter time steps. In Northern Europe, pig and poultry sheds are heated in winter and have reduced ventilation (Fig. 2). The annual emissions from manure storage vary with type of storage, and temporal variation follows ambient temperature (Gyldenkærne et al., 2005; Skjøth et al., 2004). In warm areas and during warm periods, emissions from buildings reflect outdoor temperature (Seedorf et al., 1998). Buildings with pigs and poultry have significant emissions also in cold periods, due to their warmer indoor temperatures, when outdoor storage and naturally ventilated cattle barns have low emission rates. Based on these principles and ambient temperature, it is possible to simulate temporal variations in emissions from manure storage, pig, poultry and cattle sheds (Fig. 3).

2.1.2 Manure application and mineral fertiliser

NH_3 emissions from field application of manure and mineral fertiliser take place at distinct times of year and with relatively short duration compared with animal related point sources. Soil type (Loubet et al., 2010) and the application method are crucial for establishing the magnitude of the emission. Broad-spread application over the whole of the ground surface leads to very high emissions, whereas direct soil injection or band-spreading methods strongly reduce emissions (Skjøth et al., 2008). National regulations can significantly alter seasonality when these affect application methods (Skjøth et al., 2008) although these emissions have substantial uncertainties (Sintermann et al., 2012). In many countries manure application is constrained by almost no regulation, whereas in most Northern European countries, such application is banned during winter to limit nutrient wash out, especially under the EU Nitrate Directive. To overcome shortage in storage capacity, farmers in Northern Europe often empty their tanks in autumn to allow them to handle emissions from animals kept indoors throughout the winter. This practice leads to late autumn emission peaks in NH_3 emission. In many southern European countries animals are outdoor most of the year (see Fig. 2 in Skjøth et al., 2011), which means much less manure is collected in the barns. Also for mineral fertiliser there are regional differences, as farmers in Southern Europe start fertiliser application earlier than Northern European farmers.

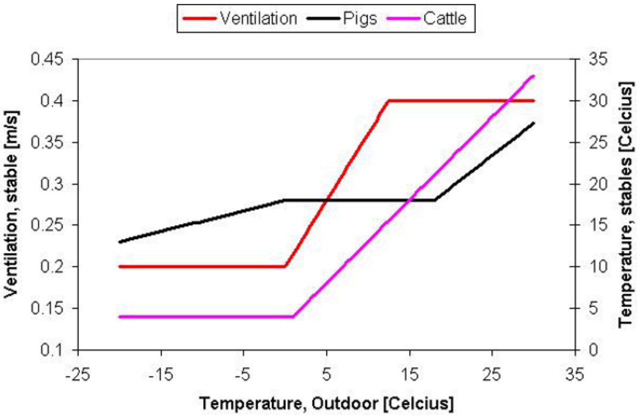

Fig. 2. The indoor temperature as function of outdoor ambient temperature for isolated stables (black) and open barns (pink). Isolated stables have a less steep increase in indoor temperatures because the ventilation rate (red) in these stable systems depends on outside temperatures.

2.1.3 Grazing animals

The time that animals are in the field, together with the N content in the grass, govern the emission from grazing animals. Animals that are feeding on grass with a high N content excrete large amounts of N (as TAN) compared with animals on grassland with less nitrogen-rich grass (Petersen et al., 1998). However, urine from grazing animals quickly enters the soil (Webb et al., 2005) which reduces the emission in comparison, e.g. to surface applied slurry. The larger dry matter content of slurries limits infiltration into the soil, which is the main reason for the larger emissions compared with urine from grazing animals. In Southern Europe, animals in general are in the field most of the year. In Northern

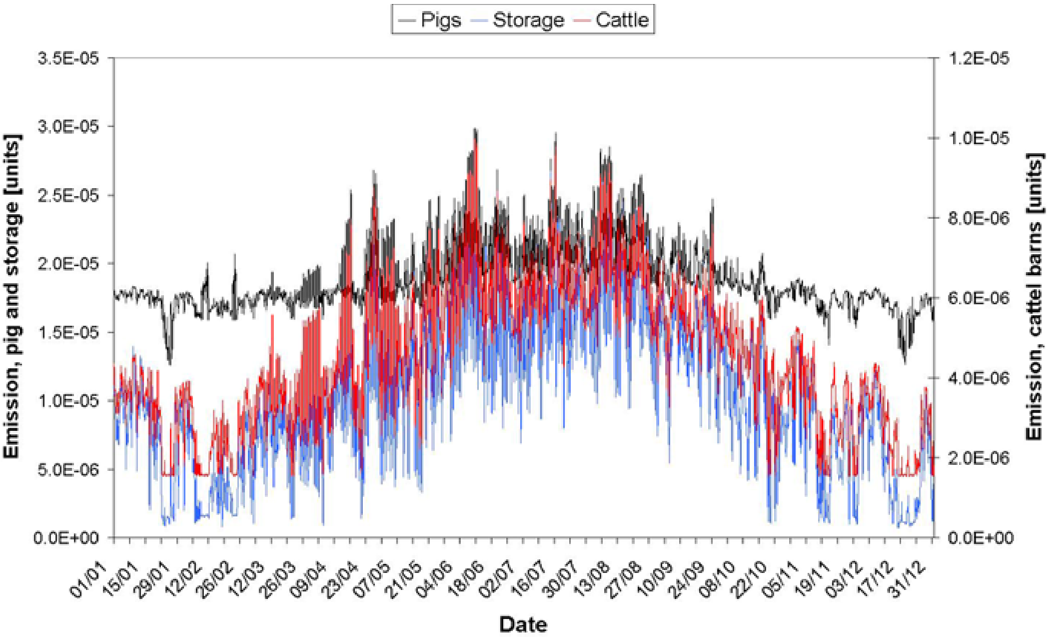

Fig. 3. Simulations of ammonia emission for open and isolated stables and manure storage using hourly meteorological input of temperature and wind speed. All times series were created by using meteorological data for the year the year 2007 and the emission model available at http://www.atmos-chem-phys.net/11/5221/2011/acp-11-5221-2011.html.

Europe, only sheep stay in the field most of the time. In most countries cattle are inside sheds approximately half of the year (Skjøth et al., 2011). In principle temperature should increase NH_3 emission related to grazing animals or outdoor yards used by livestock, however, clear temperature responses have not always been seen in practice (Misselbrook et al., 2001). However studies suggest that emissions from the urine fraction are larger during summer than during autumn (Ryden et al., 1987).

2.1.4 Other agricultural sources including plants

Legumes and plants which take up excess fertiliser emit NH_3 (Larsson et al., 1998). This emission depends on the enrichment of the apoplast with NH_4^+, and the so-called compensation point (Farquhar et al., 1980), which is a function of the plant status with respect to growth, stress, etc. (this is described in more detail in Sect. 4.2 on bi-directional fluxes). This emission is still not well described with respect to magnitude, as well as temporal and spatial variation. Emissions from crops are often observed after fertilisation with either manure (Flechard et al., 2010) or mineral fertiliser (Milford et al., 2009). Grazing (Loubet et al., 2002) as well as cutting (Sutton et al., 2001) of grass is known to release NH_3. The management of the crops can heavily influence the loss of NH_3 to the atmosphere. However, little is known about these processes and only few studies of N-exchange between atmosphere and vegetation cover the entire season exploring the full cycle of growth and decay (Wang and Schjørring, 2012). Several mechanistic descriptions of the compensation point have been derived (Massad et al., 2010a; Wichink-Kruit et al., 2012) and these rely strongly on detailed information on agricultural production methods which for several decades have been difficult to obtain and generalise (Hutchings et al., 2001; Skjøth et al., 2011). A global inventory estimate a contribution to global NH_3 emissions from crops of $4.4\,\mathrm{Tg\,NH_3\,yr^{-1}}$ (Bouwman et al., 1997), but the magnitude of this emission is still subject to discussions and these emissions remain very uncertain.

2.1.5 Wild animals

According to a global inventory wild animals contribute $0.1\,\mathrm{T\,NH_3\,yr^{-1}}$ (Bouwman et al., 1997). Simpson et al. (1999) estimated a contribution from wild mammals in Europe of about $5\,\mathrm{Gg\,N\,yr^{-1}}$, much less than the estimated $27\,\mathrm{Gg\,yr^{-1}}$ from birds (of a total natural contribution of $65\,\mathrm{Gg\,N\,yr^{-1}}$). Generally, however, few studies have been carried out to quantify emissions from wild animals, and yet the perhaps best described non-agricultural sources of NH_3 are probably from colonies of wild seabirds (Blackall et al., 2007; Riddick et al., 2012) and seals (Theobald et al., 2006). Although these contribute to a small fraction of global emissions, they occur in otherwise clean remote environments, representing major point sources under purely climatic control for the given animal densities.

Table 2. Available emission inventories containing data on reactive nitrogen compounds.

	Resolution	Reference	link	Comments
EMEP/CORINAIR	50 km × 50 km	Tørseth et al. (2012)	http://www.emep.int	
EDGAR	0.1° × 0.1°		http://edgar.jrc.ec.europa.eu	
GEIA	0.1° × 0.1°		http://gaiacenter.org	
GENEMIS	16.67 km × 16.67 km	Schwartz et al. (2000), Wickert et al. (2001)	http://gsf.de/eurotrac	only 1994 data

2.1.6 Catalyst processes, mainly road traffic

Elevated NH_3 levels have been reported near roads and in urban areas as a consequence of NH_3 emissions from vehicles fitted with catalytic converters (Cape et al., 2004). An inventory from Denmark indicates that Danish road traffic contribute 2.8 % of the national NH_3 emissions (Gyldenkærne and Mikkelsen, 2007). For the UK the fraction in 2010 was 3.6 % (http://naei.defra.gov.uk/emissions/emissions_2010/summary_tables.php?action=unece&page_name=NH310.html). The relative importance of European road traffic as a source of NH_3 is generally increasing as other sources are going down, at the same time as European road traffic is still increasing.

2.1.7 Manufacturing processes

On a global scale, industrial processes have been estimated to contribute 0.2 Tg NH_3 yr^{-1} (Bouwman et al., 1997), meaning that this is a minor part of the overall NH_3 emission. This estimate fits well with a recent Danish inventory indicating a contribution of 0.8 % from manufacturing processes for Denmark (Gyldenkærne and Mikkelsen, 2007).

2.1.8 Humans, pets, landfill, urban sources and sewage systems

Evaporation from NH_4^+ containing salts is a possible source of NH_3 in Southern and Central European cities where strongly elevated levels have been found: Barcelona (Reche et al., 2012), Rome (Perrino et al., 2002) and Rijeka (Croatia) (Alebic-Juretic, 2008). Danish sewage systems have been estimated to emit NH_3 of the same magnitude as has been reported for manufacturing processes (0.8 % of the national NH_3 emission). In a global inventory NH_3 emissions from humans and pets have been estimated to be 3.2 Tg NH_3 yr^{-1} (Bouwman et al., 1997).

2.1.9 Other non-anthropogenic sources

Estimates of emissions from biomass burning in a global inventory indicate that this is a relatively important source of NH_3 and globally contributes 10.3 Tg NH_3 yr^{-1} (Andreae and Merlet, 2001). A slightly older estimate is about 30 % smaller (7.2 Tg NH_3 yr^{-1}) (Bouwman et al., 1997), indicating that these estimates also have significant uncertainties. Simpson et al. (1999) estimated about 5 Gg N yr^{-1} from European wildfires. Just as crops receiving excess N may emit NH_3 (see Sect. 2.1.4), the vegetation in natural and semi-natural ecosystems may also release NH_3 under certain conditions. This emission will mainly be important for ecosystems in the vicinity of intensive agricultural sources. Although poorly quantified, this is likely to be a minor source of emission.

2.1.10 Spatial distribution

Table 2 contains a listing of available emission inventories regarding reactive nitrogen compounds with information about resolution and references/links. EMEP (the Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe; http://www.emep.int; Tørseth et al., 2012) and CORINAIR (CORe Inventory AIR emissions) have compiled inventories of annual mean emissions at the European level with a spatial resolution of 50 km × 50 km. EDGAR (Emissions Database for Global Atmospheric Research, http://edgar.jrc.ec.europa.eu) and GEIA (Global Emissions Inventory Activity, http://geiacenter.org) databases are available on 0.1° × 0.1° resolution, and EUROTRAC (EUREKA project on the transport and chemical transformation of trace constituents in the troposphere over Europe) and GENEMIS (GENeration and Evaluation of eMISsion data; http://www.gsf.de/eurotrac) compiled emission inventories for the year 1994 with a grid resolution of 16.67 km × 16.67 km (Schwarz et al., 2000; Wickert et al., 2001). The GENEMIS data have in some cases been used to redistribute EMEP emission to higher resolution for subsequent years, assuming unchanged relative distributions (Hertel et al., 2002). The need for high resolution inventories has been recognised by the model groups within MACC and MACC-II research programmes (http://www.gmes-atmosphere.eu/). They have therefore adapted a high resolution inventory with 7 km resolution of annual emissions at SNAP level-1 (Pouliot et al., 2012). The TNO MACC-II inventory is a combination of the officially reported inventories, information on geographic location of point sources and a correction procedure for inconsistencies. Figure 4 shows the spatial distribution of the EMEP and EDGAR emission data sets. The EDGAR data set has

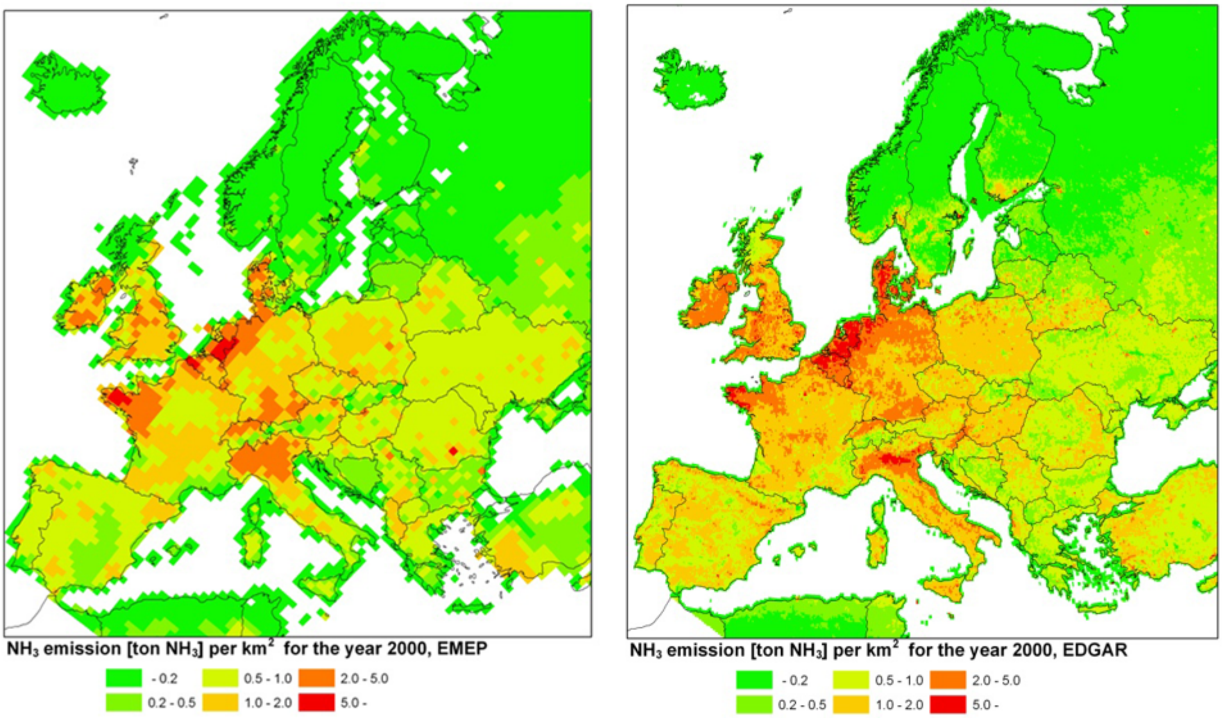

Fig. 4. Spatial distributions of annual NH_3 emissions in Europe for the year 2000 based on: (left) EMEP at 50 km × 50 km to the (right) EDGAR at 0.1° × 0.1°.

a considerably higher spatial resolution compared to the EMEP data set. The EDGAR data set is constructed centrally using a uniform methodology and uniform data set, while the EMEP data set is a compilation of national inventories that originates from national experts appointed by the single countries. One result is that the two inventories do not agree with respect to amounts of emissions within national boundaries. Such differences can be substantial (de Vries et al., 2011a, b). Here these differences are clearly seen in Fig. 4, with considerably higher emissions in central Europe in the EDGAR data set compared to the EMEP data set. Emissions are the most important input to all CTMs (Simpson et al., 2011), but for more than a decade have been considered to contribute some of the largest uncertainties in these models (Reis et al., 2009). Recently it has been shown that the existing methodology in the European emission inventory system that rely on national emission factors and neglecting climatic effects on ammonia emissions can be substantial (Skjøth and Geels, 2012). The differences between the different emission data sets and known uncertainties (e.g. impact on emissions from meteorology and climate) can therefore be expected to have a direct impact on model results for both process descriptions and impact assessments. Whereas emissions are usually reported as annual totals, there is considerable variation on hourly, daily and seasonal time scales which is represented poorly (if at all) in the data used for CTMs (Menut and Bessagnet, 2010; Pouliot et al., 2012).

2.1.11 Long-term trends

NH_3 emissions have been reduced in countries like Denmark, Germany and the Netherlands, whereas for France, Sweden and Norway only minor changes have occurred over the past 15 yr, and in countries like China and the US emissions have increased (Fig. 5). Over the next decade only very limited reductions in ammonia emissions are expected for both the European domain and for individual countries (Slentø et al., 2009). The uncertainties in these trends, including the small response of NH_3 concentrations to reduced animal numbers in central Europe (Horvath and Sutton, 1998) and to emission abatement policies in the Netherlands and Denmark (Bjerregaard, 2011; Bleeker and Sutton, 2006; Erisman et al., 1998; Skjøth et al., 2008; Sutton et al., 2003) have been a major topic of debate. The recent evidence (Bleeker et al., 2009; Horvath et al., 2009) indicates that increasing NH_3 concentrations in Eastern Europe were due to a reduction in SO_2 emissions (resulting in longer atmospheric lifetime of NH_3) a factor which also influenced the NH_3 trends in the Netherlands, Denmark and elsewhere. The observed trends in NH_3 concentrations are therefore a result of changes in atmospheric chemistry as well as changes in NH_3 emissions. Furthermore, due to the dependency on temperature, the climate change includes a climate penalty on ammonia emissions (Skjøth and Geels, 2012). This penalty and potential feedback mechanisms are currently not accounted for in neither CTMs nor climate models.

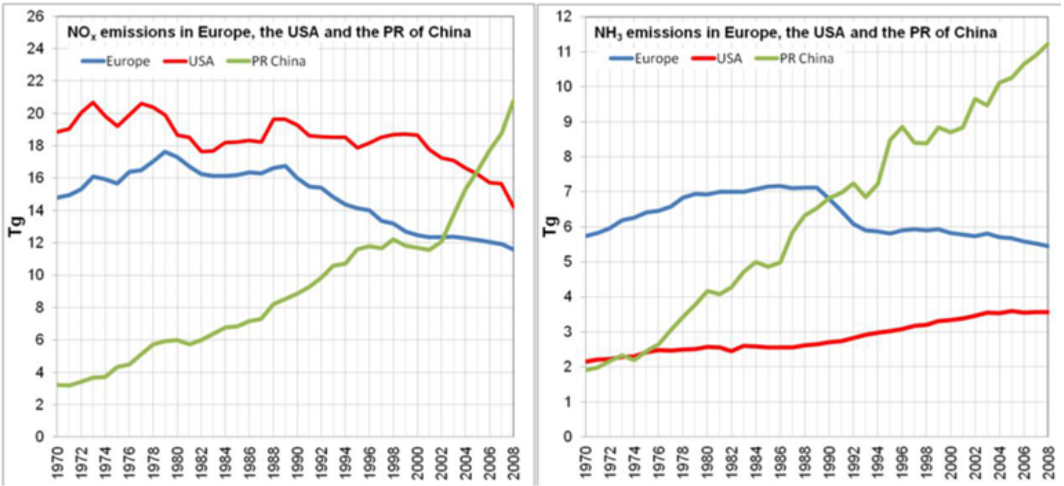

Fig. 5. Development of emissions of nitrogen oxides (left) and ammonia (right) in three world regions (Europe, USA, PR China) between 1970 and 2008 based on the Emissions Database for Global Atmospheric Research (EDGAR) version 4.2 (Unit: Tg). For a more detailed analysis of N_r emission trends, see Reis et al. (2009). Source: European Commission, Joint Research Centre (JRC)/Netherlands Environmental Assessment Agency (PBL). Emission Database for Global Atmospheric Research (EDGAR), release version 4.2. http://edgar.jrc.ec.europa.eu, 2011.

2.2 Nitrogen oxide emissions

NO_x is generated at high temperatures in combustion processes mainly from oxidation of free atmospheric nitrogen (N_2). The main source categories are

- road transport,
- other mobile sources including shipping,
- industrial production,
- energy production from fossil fuels,
- NO emissions from soils.

In addition to these categories smaller NO_x contributions are related to aviation, and biomass and agricultural burning (2 to 3 %), and other small contributions are related waste incineration and lightning (< 1 %) (Vestreng et al., 2009). These smaller contributions are not treated further in this paper.

2.2.1 Emissions of NO_x from road traffic

Road traffic is one of largest sources of NO_x emissions contributing 20 % to 25 % of total European NO_x emissions (Vestreng et al., 2008). The relative share of the NO_x emission from vehicles varies significantly from country to country; according to recent EMEP inventory from 4 % in Canada to 71 % for Russia (Mareckova et al., 2009). The most important sub-category for road transport is from heavy duty vehicles that (according to EMEP) contribute 9 % of the road traffic NO_x emission in Belarus but 41 % in Austria and Georgia (Mareckova et al., 2009). The NO_x emissions from European road traffic on individual roads can be calculated using the COPERT (COmputer Programme to calculate Emissions from Road Transport) model, which is available from: http://www.emisia.com/copert/General.html. The COPERT model contains emission factors for different vehicle categories with aging factors and driving conditions in different road types.

2.2.2 Other mobile sources including shipping

European NO_x emission from aircraft were generated within the EU Project QUANTIFY, and data are available from the homepage: www.pa.op.dlr.de/quantify. Shipping is one of the major sources of NO_x emissions in Europe contributing 10 to 15 % (Vestreng et al., 2008).

2.2.3 Industrial production

Industrial production is another important source category for NO_x emissions and contribute 10 to 15 % to European emissions (Vestreng et al., 2008).

2.2.4 Energy production using fossil fuels

Energy production is the other major source of NO_x emissions and contributes – just like road traffic – 20 to 25 % of total European NO_x emissions (Vestreng et al., 2008).

2.2.5 Emissions of NO from soils

In a global perspective, NO_x emissions from soil contribute > 40 % (Davidson and Kingerlee, 1997) (IGAC Newsletter, December 2000), and > 10 % for some European countries (Butterbach-Bahl et al., 2004; Simpson et al., 1999;

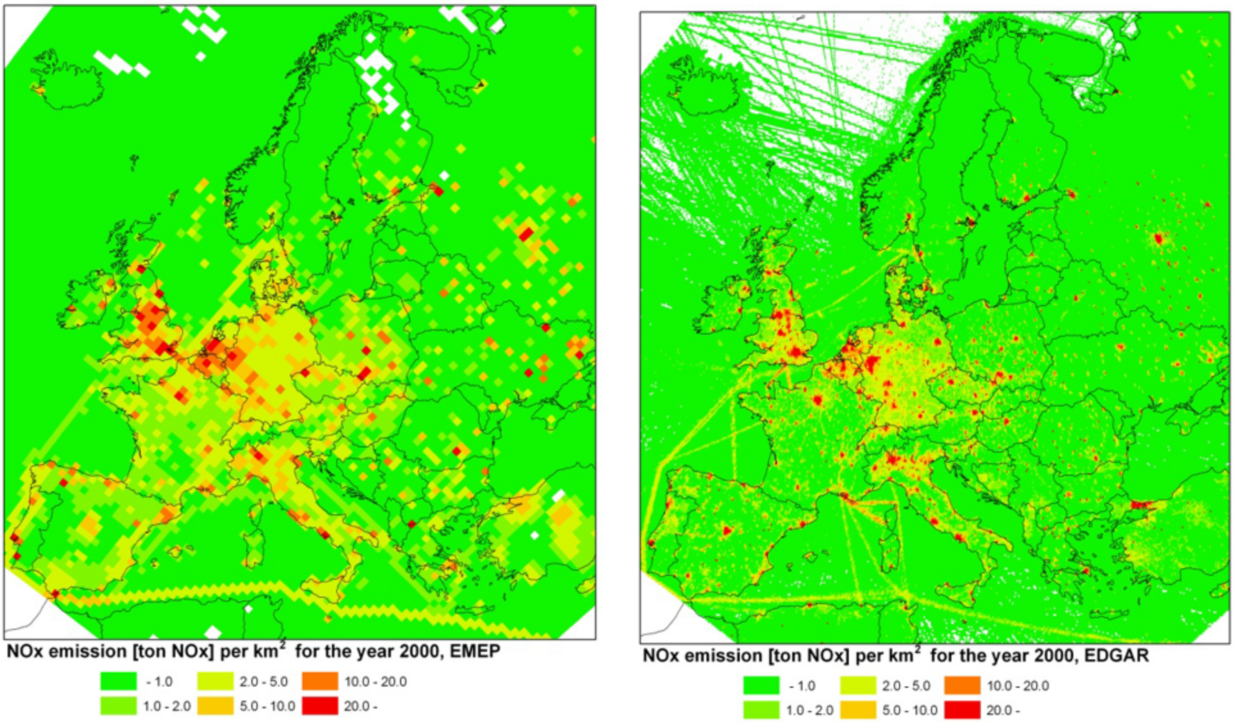

Fig. 6. Spatial distributions of annual NO_x emissions in Europe for the year 2000 based on: (left) EMEP at 50 km × 50 km to the (right) EDGAR at 0.1° × 0.1°.

Skiba et al., 1997; Stohl et al., 1996). The soil contribution to a countries NO budget is much smaller for industrialised country's with high fossil fuel combustion rates than in countries with small fossil fuel combustion rates. This is especially the case for countries in warm dry climate zones, as these conditions favour microbial NO production (Skiba et al., 1997). Estimates of emissions of NO_x from agricultural soil varies by more than a factor of two and are mainly related to mineral and organic fertiliser applications (de Vries et al., 2011c). Emissions that are related to application of fertiliser are estimated to account for 4 % of the soil emissions (IGAC Newsletter, 2000) and up to 65 % for the USA (Hall et al., 1996). Rural agricultural areas receiving N fertilisers in countries with long dry periods are probably the largest sources of soil NO where they can be of the same order of magnitude as N_2O fluxes (Loubet et al., 2011). The NitroEurope Integrated Project (Sutton et al., 2007; http://www.nitroeurope.eu) and the NOFRETETE (Nitrogen oxides emissions from European Forest Ecosystems) project both point to European forest soils being large sources of NO from soils (Pilegaard et al., 2006), presumably affected by enrichment with N from atmospheric deposition (Butterbach-Bahl et al., 2011a; Kesik et al., 2005).

2.2.6 Spatial distribution

Annual inventories of NO_x emissions are available from similar sources as for NH_3 (Sect. 2.1), which includes EMEP, EDGAR, EUROTRAC, GENEMIS and TNO-MACC. In the same way as for NH_3, the differences between the EDGAR and EMEP NO_x inventories can be seen in Fig. 6. The major road networks and urban areas are obvious hotspots and therefore easily visible. The same is true for shipping, where main transport routes are easily detectable and emissions may overall be higher than in urban areas. As a result of European regulation, power plants and large industry release pollutants at a height that leaves local urban areas almost unaffected by these emissions, although they naturally contribute to pollutant levels further downwind.

2.2.7 Temporal variation

Road traffic follows very regular temporal patterns. In Northern Europe the typical urban road traffic pattern include two rush hour periods – in the morning and afternoon. Often the morning rush hour is more pronounced than the afternoon rush hour, and this is reflected in emissions and resulting concentrations of NO_x (Hertel et al., 2008; Menut et al., 2012). In some parts of Southern Europe there may even be four rush hours or a generally elevated traffic flow throughout the daytime hours (Bigi et al., 2012; Vignati et al., 1996) as people are off work in the middle of the day.

Furthermore, different patterns are observed for weekday vs. weekend, and the pattern also differs for passenger cars and commercial vehicles (Berkowicz et al., 1996; Bigi et al., 2012; Vignati et al., 1996). Various studies have focussed on how to change transportation habits in urban areas, encouraging bicycle use, and discouraging rush-hour commuting (Murtagh et al., 2012; Su and Zhou, 2012; Zhao et al., 2012; Zhou, 2012). A UK study in this respect showed that car commuting is socio-economically structured in several ways and, for example, that high educational groups are more likely to adjust working hours to avoid rush hours (Goodman et al., 2012). Furthermore, highways are used for transport over longer distances and these have thus different diurnal traffic pattern compared with urban streets. Seasonal variations are less pronounced compared with diurnal variations, although increased power generation for heating, and increased direct fuel use, lead to increased NO_x emissions in winter in Northern Europe, whereas increased demand for air conditioning in summer is expected to lead to increased NO_x emissions in summer in Southern Europe. These differences in seasonal NO_x emissions have been shown to be reflected in the seasonal pattern of ozone concentrations in the urban areas in Europe (Pires, 2012).

2.2.8 Long-term trends and projections

European NO_x emissions have followed a steady downward trend over the time period 1990 to 2005. In total, a reduction of 34 % has been seen for the 27 Member States of the European Union (EU27) (Reis et al., 2009) as a result of regulation of emissions, e.g. the EC Large Combustion Plant Directive and the EURO regulations for road traffic vehicles (Fig. 5). Over the next decades further reductions will result from stricter regulation of road traffic despite increasing vehicle numbers and increasing distance travelled (Vestreng et al., 2008). Phasing out of nuclear energy may, however, lead to additional coal burning with the result of increasing NO_x emissions from electricity generation. Such factors make projections of future trends in NO_x emissions rather uncertain. International shipping has been steadily increasing, as have the associated emissions, but reductions will result from implementation of the HELCOM convention that includes NO_x Emission Control Areas (NECA) for the Baltic Sea and the North Sea (http://www.helcom.fi/Recommendations/en_GB/rec28E_13/). In urban streets, NO_2 has not followed the decreasing trend observed for NO_x (Carslaw et al., 2007; Lambrecht, 2007). The explanation is that the NO_2 to NO_x ratio in road traffic emissions has changed substantially in recent years as a result of late diesel technology vehicles and catalytic converters in gasoline driven vehicles that reduce the overall NO_x emission but with a higher NO_2 fraction in the remaining emission (Carslaw and Beevers, 2005). EU limit values for NO_2 are therefore currently exceeded in many European cities (Hertel and Goodsite, 2009), and this will persist until stricter EURO 6 norms are implemented from 2015 (http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:32007R0715:EN:NOT).

2.3 Emissions of organic nitrogen

Primary emissions of organic N are poorly understood, and much of what is measured as atmospheric organic N may have arisen from atmospheric reactions of VOCs with ammonia or oxidised N. The oceans, biomass burning and intensive animal production are a source of amines (Ge et al., 2011), but these are thought to make a small contribution ($0.3\,\mathrm{Tg\,N\,yr^{-1}}$) to overall organic N emissions on a global scale. A recent model has estimated global annual emissions of organic N as 27 Tg N, of which around half is attributed to human activities, but with very large uncertainty (range 2 to 95 Tg N) (Kanakidou et al., 2012)

3 Transformations

In the following a description of the most important chemical transformation processes for N_r is provided with highlights concerning where these processes play a significant role.

3.1 NH_x chemistry in the atmosphere

New aerosol particles are formed in gas phase reactions between NH_3 and gas phase acids. However, NH_3 may also deposit onto existing atmospheric particles. Whenever sulphuric acid (H_2SO_4) is present, NH_3 practically always reacts with this compound in an irreversible process forming aerosol phase ammonium bisulphate (NH_4HSO_4) and ammonium sulphate ($(NH_4)_2SO_4$). Naturally this reaction depends on the availability of H_2SO_4 which is currently decreasing in concentrations in Europe – this is, for example, illustrated in measured sulphate contents in precipitation in Estonia that has decreased up to a factor of four over the time period 1994 to 2005 (Treier et al., 2008). Early experiments (1960s) showed that 50 % of the available NH_3 was converted to NH_4^+ in about 35 min at concentration levels in those days ($20\,\mathrm{\mu g\,m^{-3}}$ SO_2 and $2.7\,\mathrm{\mu g\,m^{-3}}$ NH_3 in UK in the 1960s) (Mckay, 1971). H_2SO_4 is formed from gas phase oxidation of SO_2 by hydroxyl (OH) radical or from aerosol phase conversion by hydrogen peroxide (H_2O_2) and ozone (O_3). The latter process is pH dependent, and may be catalysed by NH_3, since uptake of NH_3 increases the pH of aerosols (ApSimon et al., 1994; Junge and Ryan, 1958).

The rate of conversion of gas phase SO_2 and NH_3 into aerosol phase ammonium sulphate has been studied in detail in laboratory experiments (Baldwin and Golden, 1979; Gupta et al., 1995; Huntzicker et al., 1980; McMurry et al., 1983). At high RH (RH – Relative Humidity), the limiting factor for the transformation is the molecular diffusion of NH_3 to the acid particles, whereas at low RH only between 10 and 40 % of the collisions between NH_3 gas molecules and H_2SO_4-containing particles lead to reaction (Huntzicker et al., 1980;

McMurry et al., 1983). For small particles, their relatively large surface area makes the diffusion process more efficient. It has, however, been shown that organic material on the surface of the particles may limit the uptake of NH_3 (Daumer et al., 1992). Whereas the NH_3 reaction with H_2SO_4 may generally be considered as irreversible, this is not always the case, and not the case for the reactions with other acid gases. While reaction to form ammonium sulphates is effectively not reversible when these exist in particulate form, the NH_3 can be returned back to the gas phase as a result of changes in atmospheric composition, e.g. during cloud processing (Bower et al., 1995, 1997; Wells et al., 1997), but gaseous NH_3 may also result from evaporation of cloud and rain droplets.

The presence of HNO_3 and/or hydrochloric acid (HCl) together with NH_3 leads to equilibrium between these gases and their aerosol phase reaction products – ammonium nitrate (NH_4NO_3) and ammonium chloride (NH_4Cl). For this reaction an equilibrium product, $k_{\mathrm{eq}} = [NH_3][HNO_3]$ of the gas phase concentrations of NH_3 and HNO_3 at saturation of the air is applied. Experimental studies show that this may be expressed as a function solely of temperature and humidity (Stelson et al., 1979; Stelson and Seinfeld, 1982). Besides the reactions with H_2SO_4 and HNO_3, NH_3 may also react with HCl and form NH_4Cl (Pio and Harrison, 1987; Raes et al., 2000). Whereas HCl is emitted as a primary pollutant from coal burning and waste incineration, HNO_3 is a major secondary pollutant from oxidation of NO_x. Measurements of fluxes over forests have indicated HNO_3 concentrations in the range of 600 to 700 pptv (Pryor and Klemm, 2004). Changes in temperature and/or humidity will lead to changes in the partitioning between gas phase NH_3/HNO_3/HCl and aerosol phase NH_4NO_3/NH_4Cl, with increasing humidity and decreasing temperature moving the partitioning towards the aerosol phase compounds.

Ice core data have indicated that the HCl input from sea salt de-chlorination has been enhanced by a factor of 2–3 during the second half of the 20th century similarly to the increase of atmospheric acidity in response to overall growth in NO_x and SO_2 anthropogenic emissions (Legrand et al., 2002); global NO_x and SO_x emissions are still increasing whereas European emissions are decreasing. New measurement data indicate that in NW Europe during summertime, HCl concentrations are similar (in terms of mixing ratio) to those of HNO_3 (Schaap et al., 2011). However, due to its higher volatility, NH_4Cl concentrations are generally much lower than NH_4NO_3 concentrations. HCl is emitted from anthropogenic sources including waste incineration and domestic coal burning in Europe which was historically also a significant source of NH_x in the atmosphere (Sutton et al., 2008), but is also released in displacement reaction in sea spray particles when these take up HNO_3 (Wall et al., 1988). HCl is not carried by most chemical transport models (CTMs). However, the assumption that the measured HCl is mainly produced by sea-salt reaction with HNO_3 needs to be reconciled with CTMs which tend already to underpredict NO_3^- levels. This displacement is still most likely the explanation for HCl concentrations of up to 250 pptv observed in the marine boundary layer (Harris et al., 1992). Measurements and model calculations for the Baltic Sea have indicated HNO_3 concentrations in the range around 300 to 600 pptv (de Leeuw et al., 2003). The displacement plays an important role in halogen and O_3 cycling (van Glasow and Crutzen, 2007). The resultant decline in HNO_3 due to the reactions with sea salt can promote the dissociation of NH_4NO_3, and this reaction has therefore been given considerable scientific attention as, for example in the EU projects ANICE(de Leeuw et al., 2001) and MEAD (Spokes et al., 2006). Model estimates suggest that equilibrium between HNO_3 and sea salt can take hours to days to reach steady state (Erickson et al., 1999; Keene et al., 2002), similar to time scales for transport across the coastal zone. Thus reactions may not be complete within the coastal zone and HNO_3 concentrations relative to NO_3^- can be highly variable depending on the history of the air mass and the history of the mixing between sea-salt aerosols and polluted continental air (Fischer et al., 2006).

NO_3^- is found in coarse as well as fine mode aerosol as a result of the displacement reaction, whereas NH_4^+ is present predominantly in the fine mode and only in very small amounts in the coarse mode (Yeatman et al., 2001) which affects the subsequent efficiency of deposition (coarse mode particles have higher deposition velocities).

3.2 NO_y chemistry in the atmosphere

The chemistry of NO_y and O_3 in the atmosphere has been discussed in numerous reviews (see, e.g. Crutzen et al., 1999; Jenkin and Clemitshaw, 2000), so only an outline is given here. A sketch showing the main chemical paths of NO_y is given in Fig. 7; only a short description including main research findings in this area is given in the following. The fraction of directly emitted NO_2 from road traffic in western countries has increased in recent years (Carslaw, 2005). However, in the tropospheric boundary layer the distribution between NO and NO_2 is governed to a large degree by O_3 that reacts quickly with NO to form NO_2. In sunlight NO_2 photo-dissociates (wavelengths 290 to 420 nm) to form NO and the very short-lived oxygen ($O(^3P)$) radical. The latter will in most cases again form O_3 in reaction with free oxygen (O_2), involving a third body (either an N_2 or O_2 molecule) that absorbs excess vibrational energy and thereby stabilises the formed O_3 molecule (Seinfeld and Pandis, 2006). These reactions all have time scales of seconds to minutes. The rate of reaction between NO and O_3 is temperature dependent, but has a typical value about $4 \times 10^{-4}\,\mathrm{ppbv^{-1}\,s^{-1}}$. Under typical atmospheric boundary layer conditions, this reaction will either lead to close to complete consumption of all the O_3 in the conversion of NO to NO_2, or to close the conversion of all NO to NO_2 (Clapp and Jenkin, 2001). In a 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 (Palmgren et al., 1996). During daylight, the main fate of NO_2 is to undergo photolysis, which remakes O_3 and NO (Dickerson et al., 1982). This photolysis reaction has a typical rate coefficient under summer conditions in the mid-afternoon at mid-latitudes of about $7 \times 10^{-3}\,s^{-1}$. The NO-NO_2-O_3 chemistry in urban streets may be simplified (Palmgren et al., 1996), assuming that O_3 is remade instantaneously, and thereby disregarding the formation of $O(^3P)$. This is done in one of the most commonly applied street pollution models – OSPM (Berkowicz, 2000; Kakosimos et al., 2010). An analysis of long-term O_3 trends at EMEP monitoring sites showed a mixed pattern (Torseth et al., 2012). A substantial year-to-year variability in O_3 concentrations is caused by varying meteorological conditions and this variability has made it difficult to separate trends related to emission change from other effects. For the Nordic countries the data indicated a reduction over the years in the occurrence of very low concentrations. The most pronounced change in the frequency distribution was seen for the UK sites and for the sites in the Netherlands, showing a reduction in the higher values. Smaller changes are seen in Germany, while in Switzerland and Austria, no change is seen in the frequency distribution of O_3.

The hydroxyl (OH) radical initiates the oxidation of a wide range of compounds in the atmospheric boundary layer (Finlayson-Pitts and Pitts, 1986). OH is formed in the daytime in the presence of sunlight (Jenkin and Clemitshaw, 2000). The photo-dissociation of O_3 leads to the formation of both $O(^3P)$ and $O(^1D)$ radicals; a fraction of the latter reacts with water vapour to form two OH radicals. This reaction is in competition with $O(^1D)$'s reaction with 3rd body O_2 or N_2 molecules to form $O(^3P)$, which in turn reforms O_3. The OH radicals initiate most of the degradation of hydrocarbons in the atmosphere, a chain of reactions that, for example, lead to the formation of high O_3 concentrations during summer. 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. In the reaction with OH radical CO is oxidized to CO_2, and at the same time a hydroperoxy radical (HO_2) is formed (Seinfeld and Pandis, 2006). Whenever NO is present, the most important atmospheric reaction of the hydroperoxy radical (HO_2) radical 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) are likewise important 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 to the CO oxidation, leading to formation of alkyl peroxy radicals (Jenkin and Clemitshaw, 2000) that subsequently convert NO to NO_2 in the same way as the HO_2 radical does. In combustion processes at high temperatures, e.g. inside the engine of a petrol or diesel-driven vehicle, NO is formed from ambient N_2. However, in very NO rich air (concentrations > 1 ppmv), e.g. inside the exhaust pipe of vehicles and inside emitting chimneys, a 3rd order reaction can take place between two NO molecules and O_2 with a reaction rate coefficient of $2.3 \times 10^{-38}\,cm^6\,molecules^{-2}\,s^{-1}$ (about $3{,}7 \times 0^{-59}\,ppbv^{-2}\,s^{-1}$) (Hampson and Gavin, 1978) to give off NO_2. The further transformation of NO_2 by reaction with OH to give HNO_3 takes place with a typical rate of about 5 % per hour in the troposphere.

At night, the nitrate (NO_3) radical has a similar but less important role in the degradation of hydrocarbons in the atmosphere to that of OH radical in daytime (for an extensive review of the chemistry, see Wayne et al. (1991). Despite the considerably lower reactivity compared with OH, its higher peak concentrations in the nighttime troposphere allow the NO_3 radical to play a major role in the transformation of organic compounds. The NO_3 radical is formed during nighttime from the reaction of O_3 with NO_2. Dinitrogen pentoxide (N_2O_5) formed in the reaction of NO_2 with NO_3 is a reservoir compound for the NO_3 radical at low temperatures, but it is broken down to its precursors NO_2 and NO_3 at higher temperatures in the dark. The typical nighttime NO_3 radical concentrations in the atmospheric boundary layer are of the order 10^7 to 10^8 molecules cm^{-3} (which is in the pptv range), although both measurements and modelling suggest that values away from the surface may reach 100s of ppt (e.g. Brown et al., 2006; Riemer et al., 2009). During the daytime both NO_3 radical and N_2O_5 radical photo-dissociate so fast that the concentrations of these compounds are insignificant. In the tropospheric boundary layer the photolysis of NO_3 radicals (with a typical noon lifetime of about 5 s) follows two different wavelength dependent paths forming NO and O_2 (wavelength < 700 nm) or NO_2 and $O(^3P)$ (wavelength < 580 nm). Close to pollution sources from combustion processes, e.g. road traffic or power plants, the NO_3 radical is quickly removed by reaction with NO leading to formation of two NO_2 molecules. In urban areas, emissions of NO rapidly destroy NO_3 close to ground level. However, above the surface at night NO_2 and O_3 can exist together in the absence of NO (as it has all been converted to NO_2), leading to NO_3 formation, as observed on a 160 m high tower in London (Benton et al., 2010). During the night, the heterogeneous conversion of N_2O_5 to HNO_3 is an important process. The lifetime of N_2O_5 with respect to this removal process is of the order of minutes in the tropospheric boundary layer. This production of HNO_3 may in winter be as important as daytime conversion of NO_2 by OH radical. As already described, particulate nitrate (NO_3^-) is formed when HNO_3 reacts with NH_3 and forms new aerosols, and when it sticks to existing particles in the atmosphere. In addition organic nitrate may be formed from gaseous NO_2 on the surfaces of aerosols in other heterogeneous reactions. The NO_3 radical attacks alkanes by hydrogen abstraction in a similar way to the reactions of the OH radical, and again leading to formation of a peroxy radical (RO_2) that may oxidise an NO molecule to NO_2. Also for alkenes, the attack of the NO_3 radical is similar to the reactions of the OH radical; the NO_3 radical adds to the double bond. This reaction is followed by rapid O_2 addition which leads to the production of a peroxy radical. Reaction of soil emissions of NO to give NO_2, which then reacts with atmospheric OH has been suggested to provide an in-canopy source of HNO_3 (Farmer et al., 2006). HNO_3 concentrations usually peak during the day, regulated by the emissions of NO_x, photochemical activity and the gas/aerosol equilibrium of NH_4NO_3 shifting towards the gas phase with increasing temperature and decreasing relative humidity (see, e.g. Andersen and Hovmand, 1994).

A reaction similar to that between NO_2 and OH, but less important, is the reaction between NO and OH that leads to formation of nitrous acid (HONO) (Finlayson-Pitts and Pitts, 1986). During daytime HONO photo dissociates ($\lambda < 400\,\text{nm}$) 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 in the sunlight (Schiller et al., 2001). 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, which has also been shown in UK studies (Harrison and Collins, 1998). Probably this type of conversion plays an important role also in many urban areas over Europe, but so far only a few studies have been carried out, and according to a recent review the mechanism are still poorly understood (Indarto, 2012). Similar heterogeneous reactions can also occur on land surfaces (Harrison et al., 1996), and daytime formation of HONO can take place due to photo-sensitised reduction of NO_2 on humid acid in soil (Stemmler et al., 2006). A recent study furthermore suggests that nitrate in agricultural soil may lead to emission of HONO (Su et al., 2011).

3.3 Organic nitrogen compounds in the atmosphere

The presence of atmospheric organic N compounds has been evident for years (Cape et al., 2011; Cornell et al., 2003; Neff et al., 2002), but direct measurements of individual species (except PAN, discussed below) are rather sparse. The recent evidence for 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 (Walker et al., 2012b). 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.

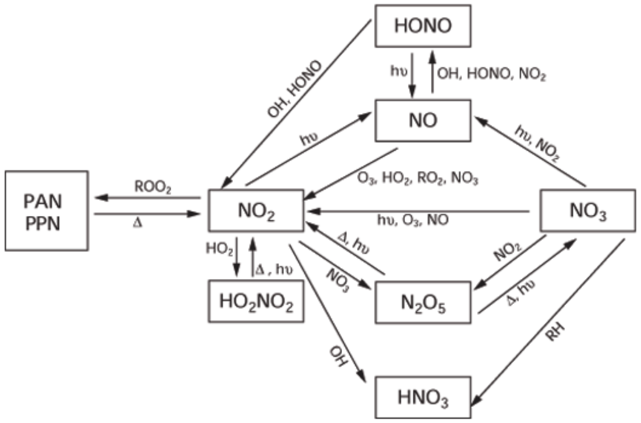

Fig. 7. Illustration of the interaction between the various nitrogen oxide (NO_y) compounds in the tropospheric boundary layer. The symbol Δ represents energy leading to thermal degradation, $h\nu$ solar radiation leading to photo dissociation and RH a hydrocarbon reacting with the species in question. PPN is a notation for other peroxy nitrates than PAN. Source (Derwent and Hertel, 1998).

The fraction of N in precipitation in organic form depends highly on location, and on whether air masses are of marine or terrestrial origin. DON has been large ignored in estimating environmental consequences of N deposition; such ecological impacts of DON depend on the bioavailability of the organic N, and 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 Whitall, 1999; Qualls and Haines, 1992).

DON appears to have multiple sources, including agricultural activities and many reduced N compounds are of biological origin, e.g. urea, amines, amino acids, etc. (Cape et al., 2011). There appears to be a DON contribution from marine air masses (Cornell et al., 1995, 2001, 2011), 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 with total N and are better correlated with NH_4^+ than with NO_3^- (Zhang et al., 2012). The overall correlation suggests a significant anthropogenic source of organic N either directly or via atmospheric reactions, and the better correlation with NH_4^+ than with NO_3^- support the suggestion of the importance of agricultural sources of DON emission to the atmosphere (Cape et al., 2011).

The seasonal variations in DON concentrations are not always 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 nebulising 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 (Benitez et al., 2010). Organic N has been 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 (Benitez et al., 2010). This presents problems of interpretation, but does not remove the problem of identifying the source, composition and fate of organic N compounds.

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 (Lin et al., 2010), but in most cases rather small concentrations are measured and these cannot account for the rather high proportions of DON in precipitation. Recent very sophisticated analyses of the composition of DON aimed at identifying functional groups are consistent with an important source involving reduced N, probably via reactions in the atmosphere (Altieri et al., 2012). Correlations between total N and DON in global databases and the remote atmosphere suggest DON represents on average about 25 % of atmospheric N deposition, although this proportion is highly variable in space and time.

Organic nitrogen compounds are also formed as secondary products in the atmosphere from the reaction of various organic compounds with oxidized nitrogen species (e.g. Jenkin and Clemitshaw, 2000). For example, when aldehydes are photo-dissociated or react with OH, an alkyl radical is formed, which in turn may form peroxy alkyl nitrates (Tanner et al., 1988) that serve as important reservoirs of NO_2 (Fig. 7). The most abundant of these nitrates is peroxyacetyl nitrate (PAN). 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 photo chemical smog episodes (Gaffney et al., 1999a). Thermal degradation gives PAN a lifetime of approximately 2 h at 273 K and 50 h at 263 K. The PAN formation competes with NO degradation of peroxy acetyl radical (Finlayson-Pitts and Pitts, 1986). This reaction is usually dominant at ppbv levels of NO, meaning that PAN and other peroxy alkyl nitrates are usually formed only in the background atmosphere (Gaffney et al., 1993), but substantial PAN concentrations may still be observed in urban areas at relatively low temperatures (Gaffney et al., 1999b). The peroxy alkyl nitrates include compounds produced in a similar way to PAN, but generated from biogenic isoprene emissions that may be of importance in Southern Europe, and have similar thermal degradation pathways to PAN. PAN is an important atmospheric N reservoir species, but it is probably not an important source of DON (Cornell et al., 2003).

4 Dry deposition and bi-directional fluxes

N_r is monitored in many regional networks across the world, such as the European EMEP programme (www.emep.int) that includes both long-term observations (Tørseth et al., 2012) and campaign studies (Aas et al., 2012), the former NitroEurope Integrated Project (NEU; www.nitroeurope.eu; Sutton et al., 2007) the US National Atmospheric Deposition Network (NADP; http://nadp.sws.uiuc.edu/) (Lamb and Bowersox, 2000), the Acid Deposition Monitoring Network in East Asia (EANET; www.eanet.cc) (Totsuka et al., 2005) and several others. However, these networks measure air concentrations rather than fluxes, and dry deposition is estimated using inferential modelling approaches (Erisman et al., 1994; Erisman and Draaijers, 1995; Meyers et al., 1998), such as using measured air concentrations and meteorology in combination with a dry deposition algorithm (e.g. Flechard et al., 2011; Skjøth et al., 2002) which are underpinned by often sparse databases of campaign based process studies or long-term monitoring in both cases with limited geographical coverage. This is partly due to the fact that instrumentation to measure fluxes of sticky compounds such as NH_3, HNO_3 or HONO are expensive and labour intensive to operate. The measurement of fluxes of each individual N_r compound is therefore technically more challenging than that of CO_2 fluxes. Robust low cost flux measurement approaches are lacking, although recent development of a conditional time-averaged gradient (COTAG) method (Famulari et al., 2010) shows promise for wide-scale deployment over long periods for short vegetation. A recent inter-comparison study on NH_3 fluxes deploying various techniques concluded that the major challenge is still obtaining consistently reliable NH_3 concentrations (Milford et al., 2009).

A first European flux measurement network for reactive nitrogen compounds was established within the NitroEurope IP (Skiba et al., 2009; Sutton et al., 2007; Tang et al., 2009). This network applied a three-tier approach, where selected N_r compounds were measured at a network of 13 supersites, using advanced micrometeorological flux measurement techniques. At a further nine regional sites the novel COTAG systems combined with a low-cost time-integrated approach for measuring soil gas fluxes (System for Inert Gas flux Monitoring by Accumulation, SIGMA, (Ambus et al., 2010) were deployed, while deposition was derived at a further 50+ "inferential sites" from concentration measurements, using inferential techniques (Flechard et al., 2011; Sutton et al., 2007; Tang et al., 2009).

A comprehensively detailed spatial coverage of N_r deposition can only presently be achieved through numerical modelling (e.g. Simpson et al., 2007, 2011). The gaseous N_r compounds usually making the biggest contribution to dry deposition are NH_3, HNO_3 and NO_2. Their relative contributions to N deposition depend on the pollution climate and meteorological conditions. In agricultural areas NH_3 may dominate the atmospheric N loading (e.g. Hertel et al., 2006), while in more industrial and urban areas HNO_3 and NO_2 may be more important. This pattern is seen even on the European scale; Simpson et al. (2007) showed that reduced nitrogen dominates dry deposition of N to forests close to the main agricultural areas, whereas oxidised nitrogen dry deposits over much larger transport distances. In addition, NH_3 deposition depends on the N status of the receiving surface, with fertilised vegetation and vegetation receiving high atmospheric N deposition inputs acting as a less efficient sink or even, in the case of fertilised vegetation, a net source of NH_3 (Loubet et al., 2009; Sutton et al., 1993; Walker et al., 2012a). In wet regions, leaf cuticles frequently provide an efficient sink for water soluble gases (NH_3 and HNO_3), although the cuticular sinks for both gases can become saturated under very dry conditions, increasing the importance of stomata as an uptake pathway (Nemitz et al., 2004b). Challenges in modelling NH_3 fluxes over vegetation have been addressed in a number of papers (Pleim et al., 2012; Wu et al., 2009). PAN deposition has been modelled in many studies (Wu et al., 2012); the dry deposition is much faster than expected on the basis of its solubility, with dry deposition velocities in daytime that may exceed 15 mm s^{-1} and nighttime values of half this magnitude (Doskey et al., 2004; Schrimpf et al., 1996), so much is still unknown about the mechanisms of its atmospheric removal (Turnipseed et al., 2006).

4.1 The dry deposition process

Dry deposition is the direct uptake 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 biological and chemical capability of the surface to capture or absorb the species (e.g. Fowler et al., 2009).

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) (see the Sketch in Fig. 8). 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)), representing the deposition flux (F) normalised by the air concentration at height z (x_z), i.e. $v_d(z) = -F/x_z$ and has units of m s^{-1} (Fowler et al., 2001a; Hicks et al., 1987).

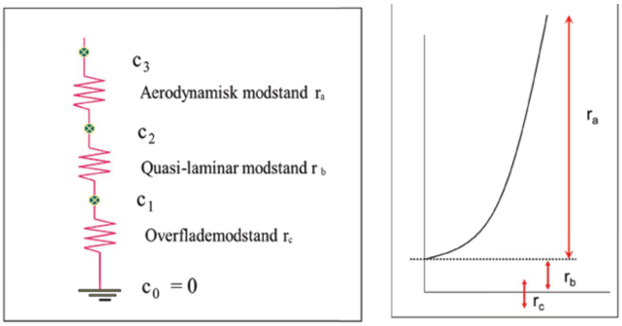

Fig. 8. Sketches illustrating the resistance method with the three resistances – the aerodynamic resistance, the quasi-laminar sub-layer resistance, and the surface resistance. The concentration at the surface is here assumed to be zero.

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 within the so-called surface layer (typically 10–100 m), provided that the air concentration is horizontally uniform.

The resistance formulation described above assumes that the concentration of the gas at the absorbing surface is zero (e.g. on the leaf cuticle or within plant stomata). Where this is not the case (see below), the effect can be described mathematically either as a decreased driving force for deposition (concentration difference between height z and the non-zero surface concentration) or as an increased surface resistance. The interpretation as a surface resistance in this context has the disadvantage that it is unable to simulate the bi-directional fluxes induced by non-zero surface concentrations.

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 parameterisation 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

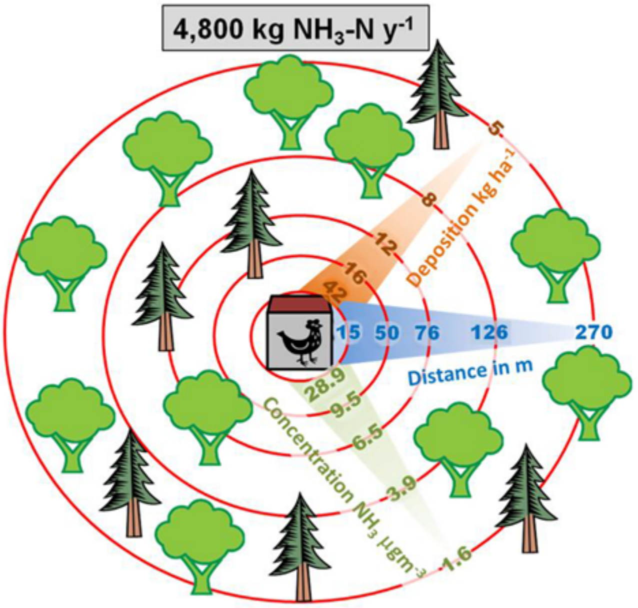

Fig. 9. Farm scale NH_3 emission and deposition, illustrating the rapid fall-off in deposition levels with distance from source (adapted from Fowler et al., 1998 and modified from version presented in Simpson et al., 2011).

can be estimated from meteorological data if several assumptions are made concerning spatial and temporal homogeneity (Erisman and Draaijers, 1995; Hicks et al., 1987; Nemitz and Sutton, 2004; Smith et al., 2000). The surface resistance (R_c) term depends on the physical and chemical nature of the absorbing surface, and parameterisations should be adapted to the surface concerned. 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.

When calculating fluxes, deposition velocities need to be used together with concentrations from the same height (z) – 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 to short vegetation (Cellier and Brunet, 1992). Consequently, estimating deposition of different components requires knowledge about land cover as well as the spatial pattern of air concentrations. Figure 8 illustrates farm-scale NH_3 emission and deposition. 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 (Spokes and Jickells, 2005). Of the two very soluble N-gases, HNO_3 exchange rates tend to be generally larger than NH_3 due to the higher solubility (i.e. smaller R_c), although NH_3 deposition can be faster to a perfect sink due to its smaller molecular weight than HNO_3 and correspondingly smaller boundary layer resistance (R_b). 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 (dimethyl sulphide) and CH_4.

The surface resistance (R_c) is a key parameter for the deposition of a gas and several parameterisation schemes have been derived from flux measurements. 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 governing R_b can differ. For particles with an aerodynamic diameter $< 0.1\,\mu m$, deposition is controlled by diffusion, whereas deposition of particles with an aerodynamic diameter $> 10\,\mu m$ is more controlled by sedimentation (Seinfeld and Pandis, 2006). Deposition of particles with an aerodynamic diameter between 0.1 and 1 µm is determined by the rates of impaction and interception and depends strongly on the turbulence intensity. Transfer through the quasi-laminar layer close to the surface presents a considerable restriction on the deposition of 0.1–1.0 µm aerodynamic diameter particles. Uptake of particles by surfaces is thus largely controlled by micro-structures and turbulence intensity. Although a range of theory-based models is available to describe aerosol deposition, they often predict features which conflict with measured deposition rates (Flechard et al., 2011; Petroff et al., 2008; Pryor et al., 2008a, b). For example, methods based on the well-known formulations of Slinn (1982) predict low deposition velocities to forest canopies. Alternative formulae of Zhang et al. (2001) predict higher deposition velocities, but no effect of canopy density. Several studies show that NH_4NO_3 has higher deposition velocities than sulphates, as a result of the partitioning of NH_4NO_3 to the more rapidly depositing HNO_3 and NH_3 gases (e.g. Fowler et al., 2009; Nemitz et al., 2004a; Wolff et al., 2010). 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, unlike 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. Erisman et al. (1997) found that deposition of aerosols to the Speulder forest contributed 20 and 40 % to the total dry deposition of S and N, respectively. Parameterisations of aerosol dry deposition velocities to all surfaces, and especially forests, differ greatly between models (Flechard et al., 2011).

4.2 Bi-directional fluxes of N-containing gases

Although reports of transient N_2O deposition fluxes are increasing in number, (e.g. Flechard et al., 2007), in terms of N inputs, the magnitude of N_2O uptake is small and negligible compared with the main contributors to atmospheric

N_r deposition. For other N_r containing gases there are several parallel pathways of pollutant exchange with vegetation, including adsorption to 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 of uptake increases with the water solubility and Henry's Law coefficient of the gas, which vary over several orders of magnitude (www.mpch-mainz.mpg.de/~sander/res/henry.html).

4.2.1 Nitric acid

Due to its high deposition rate, HNO_3 makes a significant contribution to N_r deposition in regions with high NO_x emissions. HNO_3 is highly water soluble and commonly assumed to deposit at the maximum rate permitted by turbulence, i.e. surface resistance is negligible. This is probably a reasonable approximation for most situations, but emission gradients or reduced uptake rates of HNO_3 have been observed, probably due to non-zero HNO_3 surface concentrations in equilibrium with NH_4NO_3 deposited to leaf surfaces (Neftel et al., 1996; Nemitz et al., 2004b; Zhang et al., 1994). For trace gases with negligible surface resistance, the deposition velocity is sensitive to the atmospheric resistances (R_a and R_b), which over rough surfaces are usually small (5–10 s m^{-1}). In such conditions, even a small surface resistance 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.

4.2.2 Ammonia

NH_3 is less water soluble than HNO_3, and NH_3 previously absorbed to wet leaf surfaces may more readily be desorbed (re-emitted) as leaf water layers dry out again provided that it has not yet been absorbed into the leaf tissues (Flechard et al., 1999; Sutton et al., 1998). 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 $NH^+_{4\text{apo}}$ concentration at the apoplastic pH (Farquhar et al., 1980; Massad et al., 2010b; Mattsson et al., 2009; Schjørring et al., 1998; Sutton et al., 1995).

Available evidence suggests that $NH^+_{4\text{apo}}$ increases with increasing N supply to the plant, either through fertilisation or high atmospheric N inputs (Massad et al., 2010b; Sutton et al., 1995). The system here is an exchange governed by the pH-dependent relation between NH_3 and NH_4^+. The compensation point χ_s is the product of a temperature function describing the Henry's Law equilibrium and the ratio of $\Gamma_s = [NH^+_{4\text{apo}}]/[H^+_{\text{apo}}]$. The Henry's law coefficient for NH_3 (mol atm^{-1}) may be expressed as $H_{NH_3} = 56\text{EXP}(4092(1/T - 1/298.15))$ (Dasgupta and Dong, 1986). Values of Γ_s range from < 100 for semi-natural vegetation in clean, remote environments to values around 1500 for semi-natural vegetation in environments with high N_r deposition, and to $> 10{,}000$ after fertilisation (Massad et al., 2010b). At 10 °C, this equates to values of χ_s of < 0.15, 2.3 and > 15 µg NH_3 m^{-3}, respectively. Emission potentials of fertilised soils and plant litter can be several orders of magnitude larger (Nemitz et al., 2000; Sutton et al., 2009a, b), allowing NH_3 emitted at the ground to be recaptured by an overlying plant canopy (Denmead et al., 1976). The decomposition of plant litter has been found to play an important role in agricultural canopies, such as oilseed rape and managed grassland (Denmead et al., 1976; Nemitz et al., 2000; Sutton et al., 2009b, c; Zhang et al., 2010) but it will often be less important for semi-natural vegetation, especially where litter has lower nitrogen content or is more acidic.

The large range of plant, litter and soil Γ values illustrates that the direction of NH_3 exchange is often difficult to estimate a priori. There are several reviews in the literature on bi-directional NH_3 exchange which have compiled data 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 this is the main driver of apoplast and bulk leaf NH_4^+ concentrations (Massad et al., 2010b; Sutton et al., 1993; Zhang et al., 2010), but the compensation point also varies between different plant species even when growing under the same conditions (Mattsson et al., 2009) and with growth stage and season (Milford et al., 2009; Riedo et al., 2002).

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. Maps of NH_3 net exchange 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.

The development of resistance models to describe bi-directional NH_3 exchange for eventual incorporation in atmosphere transport models has progressed through several clear stages in recent decades. Initially, atmospheric transport models only allowed the application of uni-directional dry deposition, using simple values of v_d (Asman and Janssen, 1987). Introduction of the idea of a stomatal compensation point by Farquahar et al. (1980) then led to incorporation of simple compensation point values in atmospheric models (see Fischer, 1987). The next stage of development was the introduction of the canopy compensation point approach, which offset bi-directional stomatal exchange with uptake onto leaf surfaces (Sutton et al., 1995; Sutton and Fowler, 1993). This approach was subsequently adopted in both small- and large-scale atmospheric transport models by Dentener and Crutzen (1994) (Sorteberg and Hov, 1996; Loubet et al., 2001). For example, Sorteberg and Hov (1996) found a reduction of 0–20 % in total sulphur deposition and a 0–25 % increase in NH_3 deposition when using a bidirectional scheme compared with a simple flux model allowing only NH_3 deposition. Lately Wichink-Kruit et al. (Wichink-Kruit et al., 2012) found that the inclusion of a compensation point model in the LOTUS-EUROS model redistributed N depositions on the regional scale and provided a considerable increase in NH_3 concentrations over sea areas, thus reflecting observed open sea concentrations (e.g. de Leeuw et al., 2003) to a much greater degree.

While the single layer canopy compensation point approach provided the foundation to simulate competing stomatal and cuticular processes within the plant canopy, it did not address the contribution of ammonia emissions from the ground surface or allow dynamics of bidirectional cuticular exchange. The latter process was subsequently addressed, allowing simulation of NH_3 release from drying leaf surfaces, initially using a fixed cuticular pH (Neirynck et al., 2005; Sutton et al., 1998), and subsequently extended to simulate full leaf surface chemistry, the model solving leaf surface pH according to comprehensive ion exchanges (Burkhardt et al., 2009; Flechard et al., 1999). Until now, this dynamic approach to treating leaf cuticle adsorption and desorption has been considered too complex for incorporation in atmospheric transport models.

By contrast to cuticular adsorption/desorption, the inclusion of a two-layer canopy compensation-point approach has been considered more tractable for general model application. The basis of this approach was introduced by (Nemitz et al., 2000, 2001), and has since formed the foundation for generalised empirical parameterisations estimated by Massad et al. (2010b) and Zhang et al. (2010) for use in atmospheric dispersion models, e.g. Gore et al. (2009).

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 NH_4^+ concentration 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 a simple compensation-point exchange with the water surface: $F = v_e$ $(C_{eq} - C_{air})$ 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. The ambient air NH_3 concentration at equilibrium was expressed by Asman et al. (1994) as a function of NH_x concentration in sea water, activity coefficients for NH_3 and NH_4^+ in sea water, Henry's law coefficient for NH_3 and pH in sea water (Asman et al., 1994). The formulation has since been applied into the Lagrangian ACDEP model (Sørensen et al., 2003) using a distribution of NH_x concentrations in sea water from Barret (1998), where the results showed a redistribution of N deposition in the coastal region off the coast of the Netherlands. On a global basis Johnson et al. (2008) emphasised the importance of temperature control on air–sea NH_3 exchange over the remote ocean and argued that NH_3 emissions were much more likely over warm waters than over cold (Johnson et al., 2008). Similarly, results with the ACDEP model suggested high sensitivity to both NH_4^+ concentration and pH of the sea water (Sørensen et al., 2003).

4.2.3 Nitrogen monoxide

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 are a source and sink 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.

4.2.4 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 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 ppbv 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).

4.2.5 Nitrous acid

The biosphere/atmosphere exchange of HONO is generally bi-directional, and day-time 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 et al., 1994) or NO_2 reduction on humic acid (Stemmler et al., 2006). In connection with an experimental study, a parameterisation of bi-directional fluxes of both NH_3 and HONO

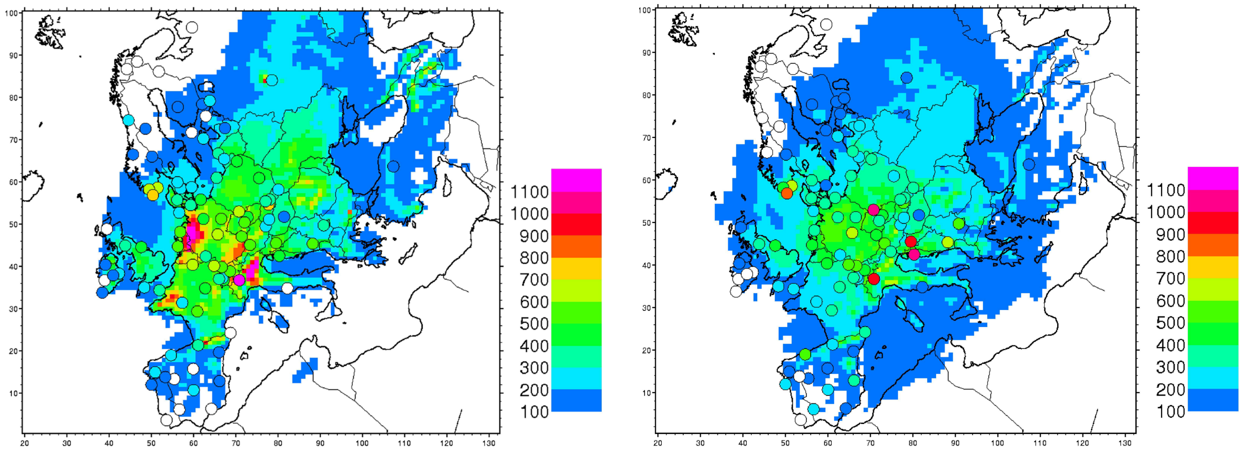

Fig. 10. Comparison of modelled and observed annual wet deposition of to the left NH_x and to the right NO_3^- (HNO_3 and aerosol phase NO_3^-). Modelled data are from the EMEP MSC-W model, observations from the EMEP network, both for the year 2001. The bullets depict observations with the same colour base as the modelled field. Measured annual deposition is calculated by using the measured precipitation amount and the NO_3^- and NH_4^+ concentration in precipitation (Simpson et al., 2011).

was applied for estimating dry deposition of N to the Amazon basin from measured ambient air concentrations (Trebs et al., 2006).

4.2.6 Organic nitrogen compounds

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., 2001b). 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 unusual. 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. Amines play a significant role in atmospheric new particle formation. Petäjä et al. (2011) showed that under atmospherically relevant conditions amines are needed to explain cluster formation (Petaja et al., 2011). Also several laboratory experiments have pointed out that amines have a marked enhancing impact on particle formation (Berndt et al., 2010; Murphy et al., 2007). Kurten et al. used quantum chemistry calculations and concluded that amines are far more efficient than ammonia in stabilizing small H_2SO_4-clusters in the atmosphere (Kurten et al., 2008).

5 Wet deposition

Unlike dry deposition, the wet deposition processes are indirect in that rain, hail and snow are vectors for conveying gaseous and aerosol compounds to the surface. The simple precipitation collectors applied in monitoring networks contrast 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 although this issue can be minimised in “wet only” collectors which are covered during dry periods. Wet deposition measurements are performed in the EMEP network (www.emep.int) (Tørseth et al., 2012).

5.1 Wet scavenging of aerosols

The bulk of the NH_4^+ and NO_3^- aerosol mass is present in the size range 0.1 to 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. Washout is responsible for 10 to 20 % of the N_r in wet deposition. The aerosol scavenging within cloud occurs through a number of physical and chemical pathways while the gases are incorporated through solution and oxidation processes. 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 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 to the droplet surface: 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. 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-cloud wet scavenging of the gaseous N_r depends on the solubility and reactivity of the specific gas. NH_3 and HNO_3 are highly soluble, and 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. 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 measurement of rainfall amounts, due to costs of chemical analysis. Furthermore, precipitation chemistry collectors are located at a height above ground to reduce contamination from ground based sources (Erisman et al., 2003), and the practice of locating collectors above the ground reduces the capture of small droplets due to aerodynamic screening by the collector Dammgen et al. (2005).

5.2 Distribution between dry and wet deposition

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 removes gas phase species which dry deposit quickly. Thus areas more than a few hundred km from sources receive most of their N_r deposition in precipitation (Bartnicki et al., 2011; de Leeuw et al., 2003; Hertel et al., 2003), except possibly for forests whose aerodynamic roughness maximises dry deposition. Simpson et al. (2006) presented calculations of the wet and dry fraction of both oxidised and reduced nitrogen over Europe, calculated with the EMEP MSC-W model for the year 2000. In these calculations, the dry deposition of Nr exceeded wet deposition in central and southern Europe, whereas wet deposition predominated in other areas. Figure 11 shows calculations with the latest version of the EMEP model (Simpson et al., 2012) for the year 2009, and for the grid-averaged deposition. These results (and similar for coniferous forest, not shown), reveal a different distribution for this later year. The wet deposition of oxidised N_r compared to reduced N_r is also apparent for these results. The dry deposition fraction is significantly lower in central Europe than shown in Simpson et al. (2006). Some of this difference is likely due to revisions in the model's dry deposition schemes (including land-cover characteristics) over the years, but some is also driven by reductions in the emissions of NO_x and SO_x. As discussed in (Fagerli and Aas, 2008), reduced SO_x emissions give a reduced formation of ammonium sulphate, hence allowing faster conversion of HNO_3 to longer-lived particulate-nitrate. This also implies a switch from dry deposition of HNO_3 to wet deposition of nitrate. In regions in which the amounts of precipitation are large, wet deposition dominates the N_r 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. Is should be noted however that CTMs typically cannot account for some of the more complex processes which affects N_r deposition, for example those of occult deposition or so-called orographic enhancement (both discussed below) can have a profound effect on the overall scavenging of pollutants from the atmosphere (Fowler et al., 2009).

5.3 Orographic effects

The meteorological process which enhances precipitation in much of maritime Northern Europe is the seeder-feeder mechanism, in which orographic cloud, formed over hills and mountains is washed out by precipitation falling from higher levels in the troposphere (Bergeron, 1965). Mountains are very effective in increasing rainfall and wet deposition by the seeder-feeder process in which low level hill cloud droplets are washed out by falling precipitation from higher levels. 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

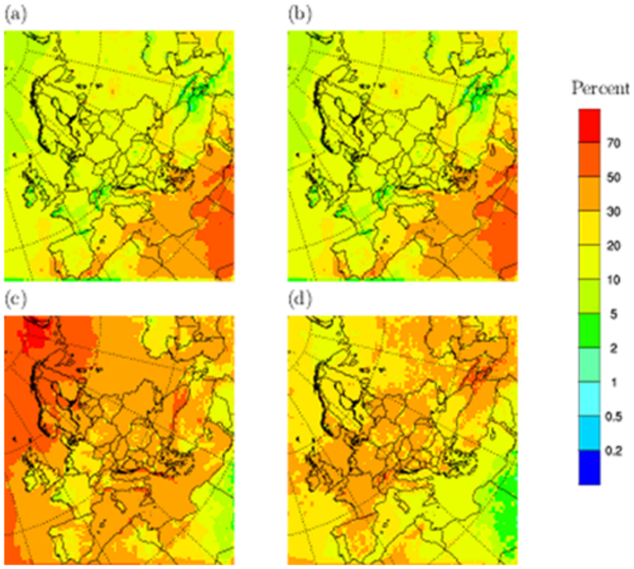

Fig. 11. Calculated percentage contributions to total nitrogen deposition for the year 2009: **(a)** dry deposition of oxidised N_r; **(b)** dry deposition of reduced N_r; **(c)** wet deposition of oxidised N_r; **(d)** wet deposition of reduced N_r. Calculations with EMEP MSC-W model (Simpson et al., 2012).

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 (http://www.rotap.ceh.ac.uk). The resulting wet, and total N deposition maps show a strong influence of altitude and require 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 (Fig. 10; Simpson et al., 2011). In principle the models are able to simulate the process, but the grid resolution of both the underpinning meteorological model and the model applied for deposition calculations needs to be able to capture the topographic scale of the variability and also take into account the spatial variation in the emissions (Dore et al., 2012), which for the UK area has been shown to be a spatial resolution of at least 1 km (Dore et al., 2012).

5.4 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 to 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. As the concentrations of major ions in hill cloud are enhanced, this deposition pathway leads to the exposure of vegetation to very high concentrations (SO_4^{2-}, NH_4^+, NO_3^-, 1–2 mM) (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.

6 Conclusions and perspectives

The emissions of N_r compounds are mainly related to releases of anthropogenic origin. These releases have typically strong diurnal and in some case also seasonal variations that relate to human activities (NO_x and NH_3) and climatic variables (mainly NH_3). N_r compounds are subject to rapid transformations in the atmosphere which profoundly affect their deposition rates. Thus NH_3 has a fast deposition rate but it also reacts with acids to form NH_4^+ salt aerosols which have low dry deposition velocities, but are liable to wet deposition. As a consequence, then NH_4^+ containing aerosols are readily capable of long-range transport. NO_x emissions are mainly in the form of NO, but the emissions from road traffic contain an important fraction of primary NO_2 which has increased in recent years. NO is rapidly converted to NO_2, which in turn is converted to HNO_3 either through daytime reaction with the OH radical, or by heterogeneous conversion processes at night. There is a strong need for further research on heterogeneous mechanisms of oxidation of nitrogen dioxide to nitric acid. While the general principles are known, the determinants of atmospheric conversion rates are very uncertain, despite the fact that these processes are the only ones operative at night, and can made a substantial contribution to nitrate formation. HNO_3 is subject to rapid deposition, but may also react to form NH_4NO_3 which is subject to long-range transport. NO_2 may also be converted by reaction on land and aerosol surfaces to HONO, which is photolysed to form OH radicals. Ambient air concentrations of N_r compounds are generally fairly well (often within ±20–30 %) reproduced by state-of-the-art models, while estimates of deposition are considerably more uncertain (often more than ±50 %). A significant part of the uncertainty in current CTMs is related to the fluxes with the surface, both emissions and deposition. There is therefore considerable need for studies of N_r fluxes, especially for sensitive ecosystems. These flux studies need to include detailed field studies, parameterisation, application and testing of models, such as CTMs, covering both the biosphere and the atmosphere such as CTMs. Furthermore, long-term trends show very different emission patterns for NH_3 and NO_x, where emissions in Europe and the US show marked declines for

NO_x and moderate reductions or stagnation for NH_3. In contrast, emissions from China, for instance, show a steep increase over the past decade and continue to grow rapidly (Reis et al., 2009). These variations will cause considerable changes in the atmosphere-biosphere system, where most N related feedback mechanisms remain to be studied (Arneth et al., 2010). Long-term studies of biosphere-atmosphere interactions in relation to N_r that take the full cascade of effects into account are therefore urgently needed.

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