Atmospheric transport and deposition of reactive nitrogen in Europe

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Executive summary

Nature of the problem

- Observations of atmospheric reactive nitrogen (N_r) deposition are severely restricted in spatial extent and type. The chain of processes leading to atmospheric deposition emissions, atmospheric dispersion, chemical transformation and eventual loss from the atmosphere is extremely complex and therefore currently, observations can only address part of this chain.

Approaches

- Modelling provides a way of estimating atmospheric transport and deposition of N_r at the European scale. A description of the different model types is provided.
- Current deposition estimates from models are compared with observations from European air chemistry monitoring networks.
- The main focus of the chapter is at the European scale; however, both local variability and and intercontinental N_r transfers are also addressed.

Key findings/state of knowledge

- Atmospheric deposition is a major input of N_r for European terrestrial and freshwater ecosystems as well as coastal sea areas.
- Models are key tools to integrate our understanding of atmospheric chemistry and transport, and are essential for estimating the spatial distribution of deposition, and to support the formulation of air pollution control strategies.
- Our knowledge of the reliability of models for deposition estimates is, however, limited, since we have so few observational constraints on many key parameters.
- Total N_r deposition estimates cannot be directly assessed because of a lack of measurements, especially of the N_r dry deposition component. Differences among European regional models can be significant, however, e.g. 30% in some areas, and substantially more than this for specific locations.

Major uncertainties/challenges

- There are very few measurements of many of the key compounds (e.g. gaseous HNO_3, coarse-nitrate, NH_3), which are needed to enable comprehensive model evaluation. Data on all compounds should be available at the same site if the mass-balance of N_r is to be assessed, pointing to the need for integrated site measurements in air monitoring networks.
- The main needs for oxidised N_r compounds are to evaluate how well the models capture the partitioning between gaseous HNO_3 and either fine or coarse nitrate aerosol. For reduced N_r compounds, better estimates of NH_3 emissions are needed, and how these are affected by meteorological factors as well as agricultural practices, coupled with an understanding of biosphere–atmosphere exchange.
- Dry deposition of particles, sub-grid fluxes of NH_x compounds, and effects of topography on wet deposition are especially difficult to parameterise properly.

Recommendations

- There is a significant need for studies to constrain uncertain model parameters. This includes measurements of both the gas and particle phases of N_r compounds, and of atmosphere–biosphere fluxes of N_r compounds over sensitive ecosystems.
- A balanced programme of observations and models is needed and is critical to future understanding of atmospheric transport and deposition of N_r containing pollutants at local to global scales.

14.1 Introduction

This chapter attempts to answer the overriding question: what are the atmospheric inputs of reactive nitrogen (N_r) in Europe, and how well can we estimate these?

This issue is of particular concern for semi-natural ecosystems and sea areas, where the atmospheric supply of nitrogen can form an appreciable part of the total nitrogen load.

As discussed elsewhere in this report, nitrogen measurements are of course essential for understanding the state of the atmosphere, and hence to help answer the first part of this question. However, as outlined by Hertel *et al.*, 2011 (Chapter 9, this volume), the chain of processes linking emissions, atmospheric dispersion, chemical transformation and loss from the atmosphere of N_r compounds is extremely complex. Observations can typically address only a small portion of this chain.

In particular for this chapter, observations of atmospheric deposition are severely restricted in spatial extent and type. Typically only the 'wet' deposition of atmospheric nitrogen can be observed, and even this issue is fraught with uncertainty when we try to measure deposition to canopies. Nitrogen in the form of both ammonium and nitrate, together with most other plant nutrients, is strongly affected by canopy exchange (mainly uptake on the surface of the foliage), which affects throughfall composition. Unlike for S-species, N-species can be retained by the forest canopy, and throughfall is not a reliable indicator of total deposition. Another emerging and difficult field is that of organic nitrogen and its contribution to especially wet deposition (Cape *et al.*, 2001; Gonzalez Benitez *et al.*, 2009, 2010). (This issue is discussed by Hertel *et al.*, 2011 (Chapter 9, this volume), but not in this chapter as the sources of much of the measured organic nitrogen are still unclear. Further, the models presented in this chapter only consider oxidised organics, such as PAN, rather than reduced compounds.)

The situation for dry deposition is even worse, with no routine method of measuring dry deposition. Some flux data are available from a limited number of sites employing micro-meteorological methods (Fowler *et al.*, 2001, 2009), but estimates of particle deposition rates are still very uncertain (Pryor *et al.*, 2008a,b,c). Measurements of the dry deposition of gaseous nitrogen species usually rely on the measurement of concentrations and estimates of deposition velocity (Zhang *et al.*, 2009).

Given the lack of an observed deposition field over Europe, models are thus an essential tool for our understanding of the nitrogen cycle. A wide variety of models is available, but most aim to provide some or all of the following benefits.

- To allow for spatially comprehensive estimates of pollutant concentrations, and for mapping of deposition patterns over large areas.
- To integrate our understanding of atmospheric chemistry and transport. Models address emissions, dispersion and transport over multiple scales, chemical transformation, and dry and wet removal of pollutants.
- To allow an exploration of the relative importance of different physical/chemical processes, in order to test hypotheses, and to focus attention on the most important mechanisms.

- To predict future pollution levels, including 'what-if' scenarios in which different policy options are explored.
- A comparison of model predictions against observed values is essential if scientists and policy makers are to have confidence that we understand the nitrogen cycle.

Models are of course necessarily approximations to the real world, and they have to be evaluated thoroughly against measurements if we are to have any confidence in their abilities. For these reasons this chapter will focus mostly on models (in particular chemical transport models, CTMs) and their results, although with strong coupling to measurements. Section 14.2 will briefly present the types of models typically used to assess atmospheric deposition, Section 14.3 will present deposition estimates from global to local scales. Model evaluation will be discussed in Section 14.4, and Section 14.5 will discuss the remaining uncertainty and challenges.

The main focus of the chapter is the European regional scale, and deposition issues, but we will also present results covering scales from global to local (~1 km scale) in order to place the results in context.

14.2 Types of models

A bewildering variety of models is available for air pollution studies, with applications ranging from near-source dispersion or process studies to global scale. For example, the European Topic Centre on Air and Climate Change model documentation system lists 123 different models, developed around the world (EIONET, 2010). The United States Environmental Protection Agency maintains a similar list (EPA, 2010). Recent reviews of different types of models and their applications can be found in Bleeker *et al.* (2009), Hertel *et al.* (2006), Holmes and Morawska (2006), Seinfeld and Pandis (1998), Sportisse (2007) and van Pul *et al.* (2009), for example.

The number of models partly reflects the difficulties of the task at hand, with models limited by basic theoretical principles as well as by practical problems. Difficulties arise from our limited understanding of many biological, meteorological and chemical processes, the difficulty of specifying many of the important inputs for modelling nitrogen exchange (e.g. NH_4^+ levels in vegetation, soil water, atmospheric emissions, surface properties), and the still-real problems of computer processing power.

Thus, all models are compromises in which all aspects of the problem are simplified to some extent. The goal, and art, of modelling is to capture the most important processes for the problem at hand, so that the model is useful for its purpose, and can be relied upon to a reasonable extent. In this chapter we will discuss the main types of models typically used for problems related to oxidised or reduced nitrogen in relation to air quality issues. The main focus is Europe, but we also discuss applications from local scale to global scale.

This section discusses the main types of models which are typically used to calculate nitrogen inputs to ecosystems or water surfaces, namely plume, Lagrangian or Eulerian models. For a discussion of other types of models (e.g.

computational fluid dynamics models, canyon models) see Hertel *et al.* (2006).

Plume models

Plume models are widely used in operational local-scale modelling of releases from industry and power plants. Examples of such models are the American AERMOD (Cimorelli *et al.*, 2005), the UKADMS (Carruthers *et al.*, 1994), the Dutch OPS (Duyzer *et al.*, 2001; van Pul *et al.*, 2004) and the Danish OML (Olesen *et al.*, 1992). An inter-comparison study of plume models has shown a reasonably good agreement for most conditions (Olesen, 1995) and this type of model is in general suited for application in local-scale air pollution regulation, or for emissions verification. An example of a plume model applied specifically for NH$_3$ deposition modelling is OML-DEP (Hertel *et al.*, 2006). Further discussion of these and other models can be found in Hertel *et al.* (2006) and Holmes and Morawska (2006).

Lagrangian models

In Lagrangian models, an air parcel is tracked along a trajectory computed from wind speed and wind direction. Lagrangian models may use just one, or many, vertical layers. Where more than one layer is used, the approximation is usually made that all layers are transported with the same velocity, e.g. for ACDEP (Hertel *et al.*, 1995) or FRAME (Singles *et al.*, 1998; Fournier *et al.*, 2005). Although global-scale models usually use the Eulerian framework, the UK STOCHEM model uses a Lagrangian formulation in which very many independent air parcels are followed and allowed to exchange material with each other (Collins *et al.*, 1997).

Lagrangian models are typically computationally fast since they are usually applied to a restricted number of receptor points or air parcels, and with simplified treatment of meteorology and dispersion. In some models, this allows for a more advanced treatment of other aspects, e.g. of chemistry – the UK Photochemical Trajectory Model makes use of the Master Chemical Mechanism (MCM), with MCM v3–1 treating about 13 500 reactions between 5900 species (Johnson *et al.*, 2006; Jenkin *et al.*, 2003), or of detailed aerosol dynamics, e.g. UHMA (Korhonen *et al.*, 2004). Figure 14.1 provides a relevant example of the type of detailed atmospheric processing which can be analysed with MCM.

Eulerian models

In Eulerian models, calculations are performed simultaneously for a grid of cells. For each of these grid-cells, advection, turbulent exchange, chemistry, and dry and wet deposition are computed. Examples of such models are the EMEP model (Berge and Jakobsen, 1998; Simpson *et al.*, 2003), CHIMERE (Bessagnet *et al.*, 2004), LOTOS (Schaap *et al.*, 2008), MATCH (Robertson *et al.*, 1999), RADM (Chang *et al.*, 1987), CMAQ (Binkowski and Roselle, 2003), STEM (Carmichael *et al.*, 1991), and DEHM-REGINA (Frohn *et al.*, 2001).

Eulerian models are generally more computer-resource demanding than plume and Lagrangian models, especially when a high geographical resolution is desired. However, such
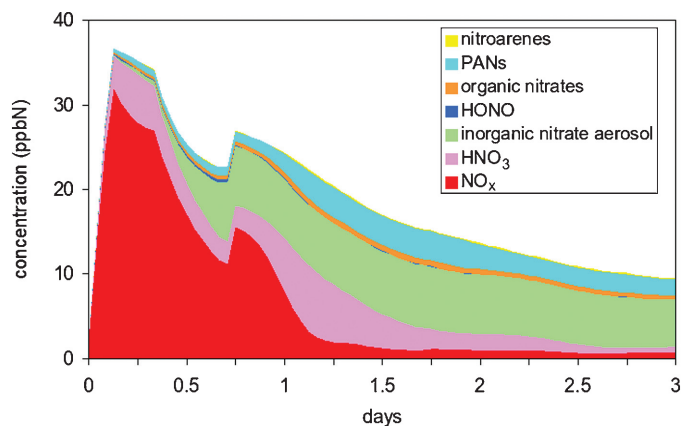

Figure 14.1 Example of the use of a Lagrangian box model for chemical simulation. These calculations used a pseudo-Lagrangian boundary layer box model to represent initial passage of an air mass over an urban area (three hours duration), during which time the box received enhanced emissions. Subsequently, the box received background emissions, which were based on the UK average. Discussed in more detail in Jenkin *et al.* (2006), these calculations demonstrated particularly important contributions from organic nitrates and PANs, a conclusion that is in broad agreement with observations.

models are generally recognised to provide the most comprehensive framework for chemical transport models (Sportisse, 2007; Seinfeld and Pandis, 1998). Unlike plume or Lagrangian models, Eulerian modelling involves calculations for the full spatial domain, and the structure allows for straightforward inclusion of complex meteorology and multiple, chemically interacting sources. Such models have been developed with simple one-way nesting (Kessler *et al.*, 2001; Vieno *et al.*, 2009, 2010) and more accurate and advanced models with two-way nesting also exist (Frohn *et al.*, 2001).

Inferential models

The last type of model mentioned here, inferential modelling, is very different, in that no chemical transport modelling is done at all. Where flux measurements are not available (i.e. at the vast majority of sites), an estimate of dry deposition fluxes may still be made by combining measured concentration data with relevant (micro)meteorological data and estimated deposition velocities.

Inferential modelling is important for its ability to provide a deposition estimate which is heavily observation-based, and as a framework for evaluating differences between model formulations for deposition velocity. This method has been applied within e.g. the US-CASTNET network (Clarke *et al.*, 1997) and the EU-NitroEurope network (Sutton *et al.*, 2007; Flechard *et al.*, 2010). See also Table 14.1.

14.3 Atmospheric deposition of reactive nitrogen

This section gives an overview of modelling results concerning the deposition of reactive nitrogen to land and sea areas. Scales ranging from global to local are covered, but most emphasis is given to the European scale. Unfortunately, observations cannot provide maps of total N$_r$ deposition, as typically only wet deposition can be measured, and then at spatially heterogeneous

Table 14.1 Advantages and disadvantages of common types of chemical transport models (adapted from Hertel *et al.*, 2006)

Advantages	Disadvantages	Scale T
Plume		
Fast, analytic solutions, easy to apply.	Highly simplified formulation. Difficulties with complex meteorology, chemistry. Cannot account for interactions between sources.	0–20 km
Lagrangian		
Fast for carrying out multiple model runs that concern a limited number of receptor points. Generally easy to apply for most purposes.	Short-falls in the description of transport and dispersion. The uncertainty increases with distance along the trajectory. Forward trajectory models can only handle simplified chemistry. Computationally demanding for a large number of receptor points.	1–500 km
Eulerian		
Allows comprehensive description of combined transport, dispersion and chemical modelling. Enables high-resolution three-dimensional simulations, treatment of complex terrain, and one or two-way nesting.	Generally computationally demanding – especially for three dimensional models with high resolution, e.g. including nesting techniques. Difficulties in handling plumes.	10 km–global

Notes: There are examples of all model types at essentially all scales, but we give here the main domain of application of the different types.

networks, so this section focuses on model results. However, Section 14.4 will present further data on observed wet deposition in the context of model evaluation studies, and discuss some of the uncertainties surrounding these estimates.

14.3.1 Atmospheric deposition: global scale

Global emissions of NO, NH_3 and SO_2 may have increased by more than a factor of three since the pre-industrial era. Regionally, these increases have been even more substantial, and emissions from large portions of North America, Europe and Asia increased by more than a factor of ten during the past century (van Aardenne *et al.*, 2001). Recent studies (Galloway *et al.*, 2004) indicate substantial further increases of emissions and deposition toward 2050. Other scenario studies suggest that increasing air pollution control will stabilise or reduce emissions by 2030 (Cofala *et al.*, 2007). The need to understand and predict such changes has led to a flurry of activity on global-scale modelling in recent years, further promoted by the establishment of the UNECE Task Force on Hemispheric Transport of Air Pollution (HTAP, 2010).

An extensive recent study of global N-deposition is that of Dentener *et al.* (2006). This study focused on global and regional deposition fluxes of both oxidised and reduced nitrogen compounds for the present day and near future (2030), using an ensemble of 23 models. This study showed reasonable agreement with observations in Europe and North America, where 60%–70% of the model-calculated wet deposition rates agree to within ±50% with quality-controlled measurements (Dentener *et al.*, 2006). The same models systematically overestimate NH_x deposition in South Asia, and underestimate NO_y deposition in East Asia (Figure 14.2).

These questions were addressed in several multi-model studies of nitrogen deposition. Recently the UNECE Task Force on Hemispheric Transport of Air Pollution evaluated the hemispheric transport of ozone, aerosol and precursors between four world regions. As discussed in Sanderson *et al.* (2008) (see also Erisman *et al.*, 2011, Chapter 2, Figure 2.10, this volume), Europe substantially impacts parts of Asia and North America, and, vice versa, Europe is mostly influenced by emissions from North America. A few percent of NO_y emissions from North America reach Europe. The TF HTAP interim report states that on average 75% of the NO_x emissions in Europe are deposited within Europe, with small fractions falling on North America (1%), South Asia (2%), East Asia (2.5%), and the remainder deposited in the oceans, and Russia.

14.3.2 Atmospheric deposition over Europe

In this section we focus on modelling results for the so-called regional scale models, those which are designed to run over large areas of Europe, with grid sizes of typically 30–50 km. One important model in this context is the EMEP model (Berge and Jakobsen, 1998; Simpson *et al.*, 2003, 2006a), as it is widely employed within the European air pollution abatement strategy and legislation work (Sliggers and Kakebeeke, 2004). This model is typically run with a 50×50 km^2 grid size, although first results for 10×10 km^2 are now available (Fagerli *et al.*, 2008). Other models typically applied at this scale include CHIMERE (Bessagnet *et al.*, 2004), LOTOS (Schaap *et al.*, 2008), MATCH (Robertson *et al.*, 1999), and DEHM-REGINA (Frohn *et al.*, 2001). Intercomparison of some or all of these models was presented in van Loon *et al.* (2004, 2007), Vautard *et al.* (2007) and Stern *et al.* (2008).

We will begin by illustrating the results from a so-called ensemble of chemistry transport models, which includes most of those mentioned above. Using an ensemble of models rather than a single model to simulate air quality for assessment or emission scenario evaluation purposes provides two new pieces of information. Firstly, the average (or the median) over this ensemble is a new result by itself, which is expected to have a smaller error because individual model errors cancel each
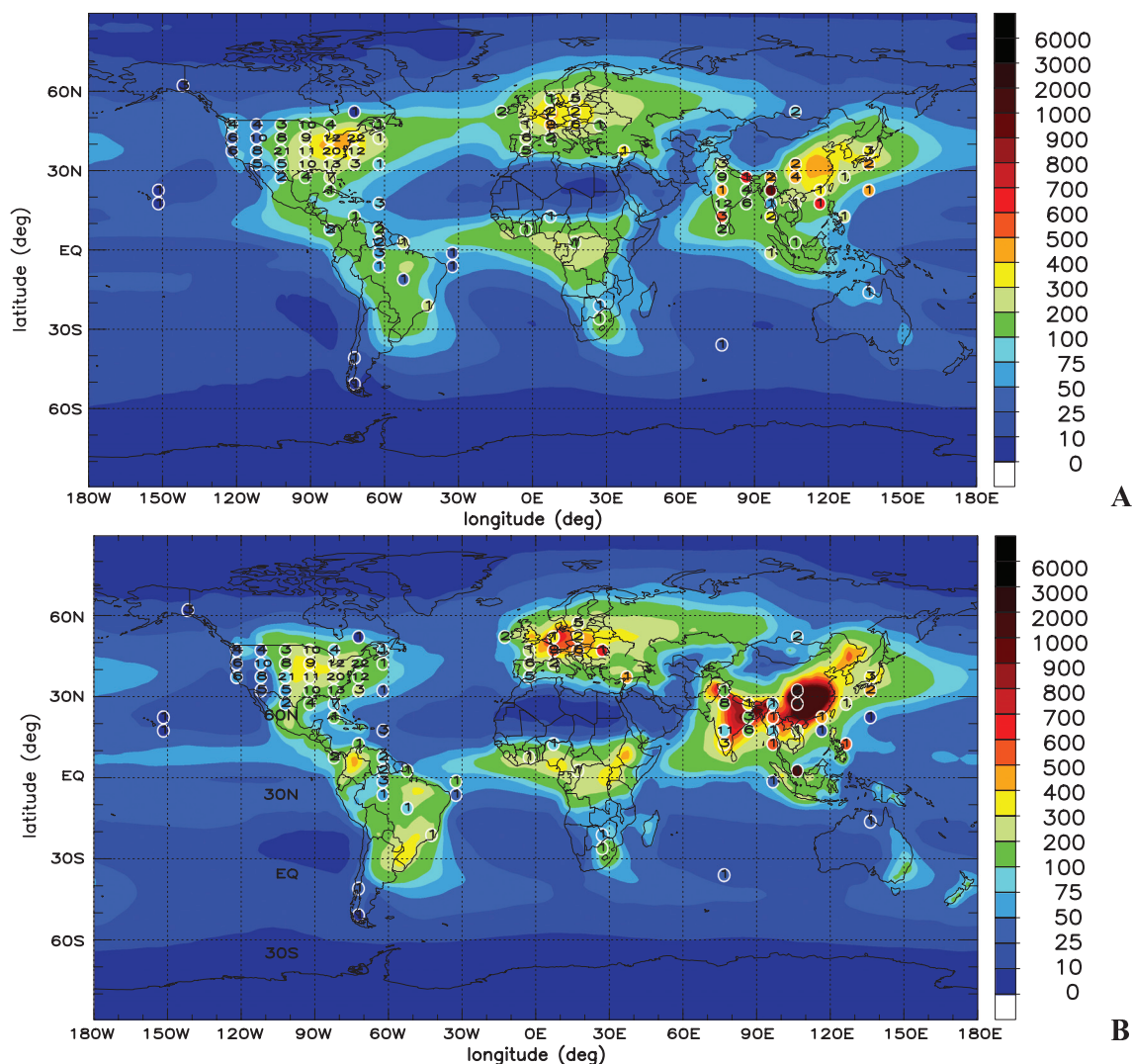
Figure 14.2 Annual wet deposition of (A) NO₃⁻ (HNO₃ and aerosol nitrate), (B) NHₓ (NH₃ and aerosol ammonium), for current-year (~ year 2000) simulation along with measurements grouped in 5° latitude and 10° longitude. The numbers within the circles indicate the number of stations in this latitude/longitude band. Units mg(N) m⁻² (100 mg(N) m⁻² = 1 kg(N) ha⁻²). From Dentener *et al.* (2006).

other to a certain extent. Secondly, the spread of the ensemble can be a measure of the uncertainty in model simulations.

In the EURODELTA study (van Loon *et al.*, 2007; Schaap *et al.*, 2010; Vautard *et al.*, 2008) seven modelling teams simulated the air quality over the European domain for the full year of 2001 using a harmonised emission database. Figure 14.3 illustrates the total Nitrogen deposition obtained from the ensemble-mean, along with the standard deviation of these results. Firstly, these results demonstrate the strong spatial variation in nitrogen deposition, with clear maxima over the Benelux area and Po Valley region of Northern Italy. The standard deviation of model results is large, however, e.g. representing about 30% of the mean value over the Netherlands.

Maps of just the wet-deposition component of one model, EMEP, will be presented and compared with observations in Section 14.4.3.

Deposition to ecosystems

Figure 14.3 presented total N deposition to model grids, but for assessing the vulnerability of ecosystems to deposition one needs to know the deposition rates to each type of land-cover within the grids. Importantly, deposition loads to forests are typically greater than to other ecosystems, enhanced by their greater aerodynamic roughness, and their ability to capture fine-particles (Ruijgrok *et al.*, 1997; Pryor *et al.*, 2008b). Here we present some examples calculated with the EMEP model, as this model utilises a so-called mosaic approach, in which deposition rates are calculated for up to 18 different landcover types per grid (Simpson *et al.*, 2001, 2003).

Calculated deposition to two important ecosystems are illustrated in Figure 14.4, with deposition given per unit area of ecosystem. This figure clearly illustrates the large gradients of N-deposition across Europe, and that areas in north-west Europe receive the highest loadings of N-deposition. Deposition to forests is significantly higher than to semi-natural areas. Similar calculations for croplands show even lower deposition rates than to semi-natural, partly due to the fact that crop lands are only vegetated for part of the year.

In order to further illustrate the sources of this nitrogen deposition, Figure 14.5 shows the calculated relative
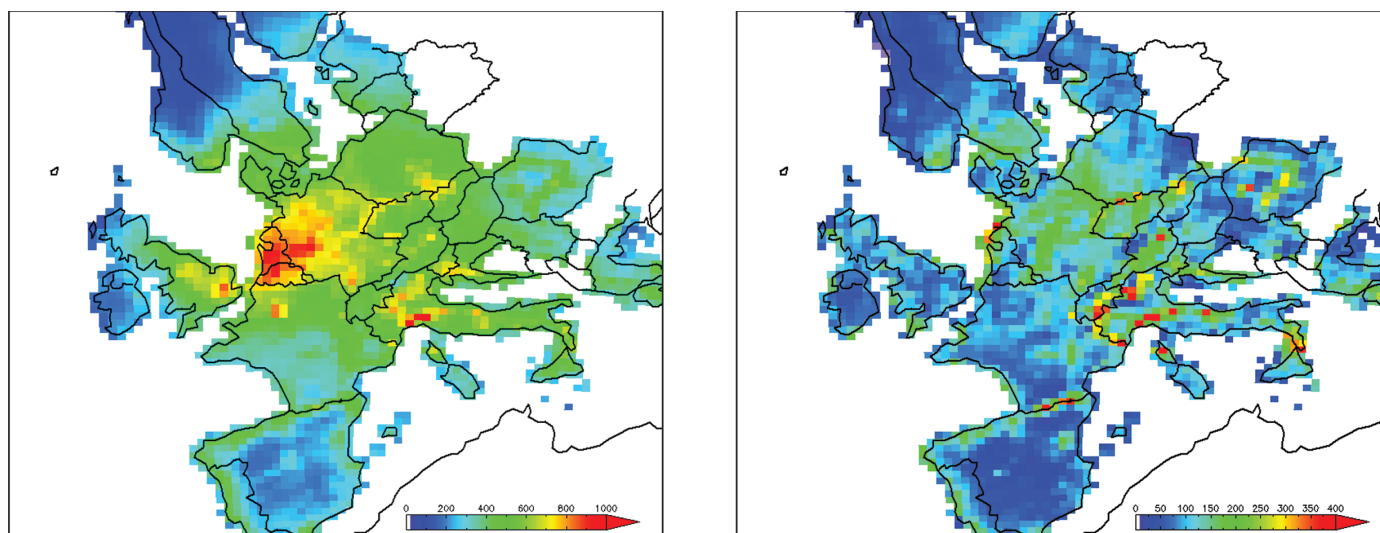
Figure 14.3 Calculated nitrogen deposition from an ensemble of seven models for 2001, together with the standard deviation (right) of the model estimates. Units: mg(N)m^{-2} (100mg(N)m^{-2} = 1 kg(N)ha^{-2}) (EURODELTA study, see text).
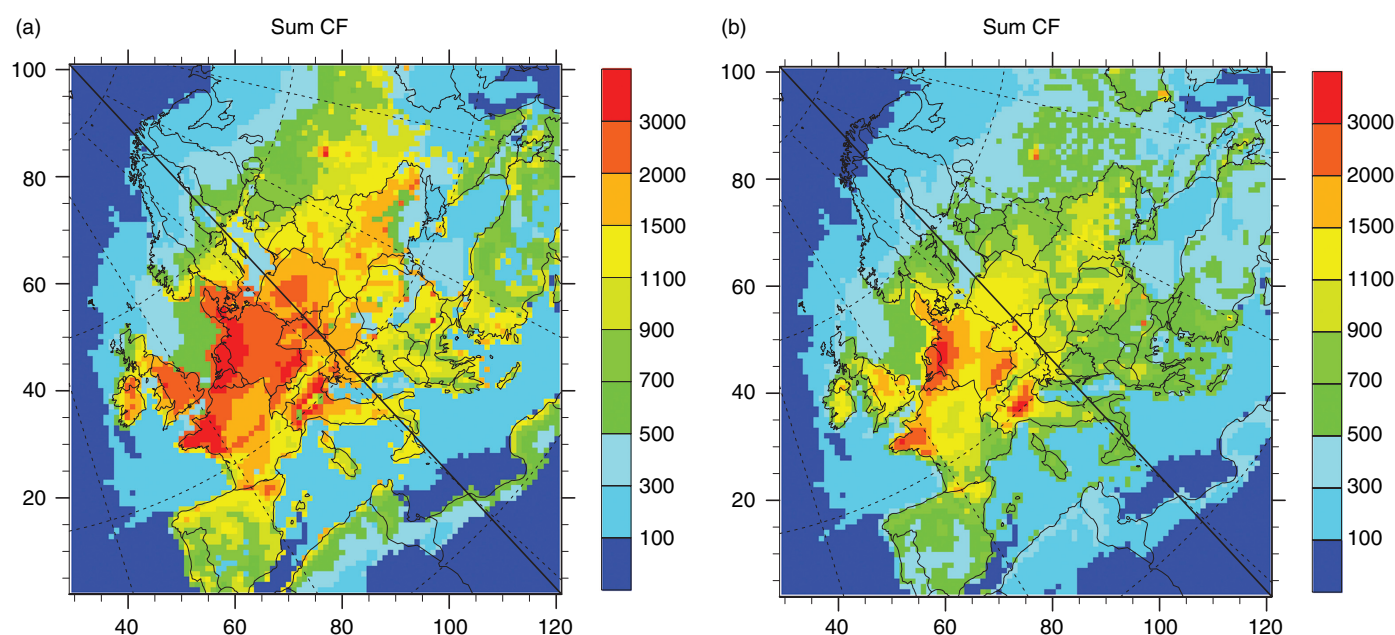

Figure 14.4 Calculated N-deposition densities (mg(N) per m^2 of ecosystem per year) to different ecosystems (year 2000): (a) coniferous forest, (b) semi-natural. Source: EMEP MSC-W.

contributions of dry and wet deposition, for oxidised and reduced nitrogen, to the total reactive nitrogen deposition to forests. In the Nordic countries, dry and wet deposition of oxidised nitrogen dominate, although wet deposition of reduced nitrogen accounts for around 20%–30% of the total in forest ecosystems, and somewhat more for non-forest ecosystems. Dry deposition of reduced-N is, however, the most significant contributor in many areas of central Europe, including parts of France, UK, Ireland and the Netherlands. Over southern Europe dry deposition tends to dominate over wet, as should be expected given the lower precipitation rates.

Deposition to European seas

The atmospheric input of N$_r$ to sea is significant. It has been estimated that approximately one quarter of the total nitrogen input to the Baltic Sea comes from airborne nitrogen deposited directly into the sea (HELCOM, 2005) and around 30% for the North Sea (Rendell et al., 1993).

A number of modelling studies have examined deposition to sea areas, with the Baltic and North Sea receiving most attention (Bartnicki and Fagerli, 2008; Hertel et al., 2002, 2003; Langner et al., 2009; de Leeuw et al., 2001, 2003; Schlunzen and Meyer, 2007). For example, Hertel et al. (2002) estimated around 40% of the nitrogen deposition over the North Sea to originate from agriculture activities and around 60% from emissions from combustion sources. As seen in Figure 14.6, wet deposition dominates over the dry deposition of nitrogen for three of the four sea areas. The dominance of wet deposition was also found by de Leeuw et al. (2003) and Hertel et al. (2002) for the North Sea (more than 80%). This dominance is expected
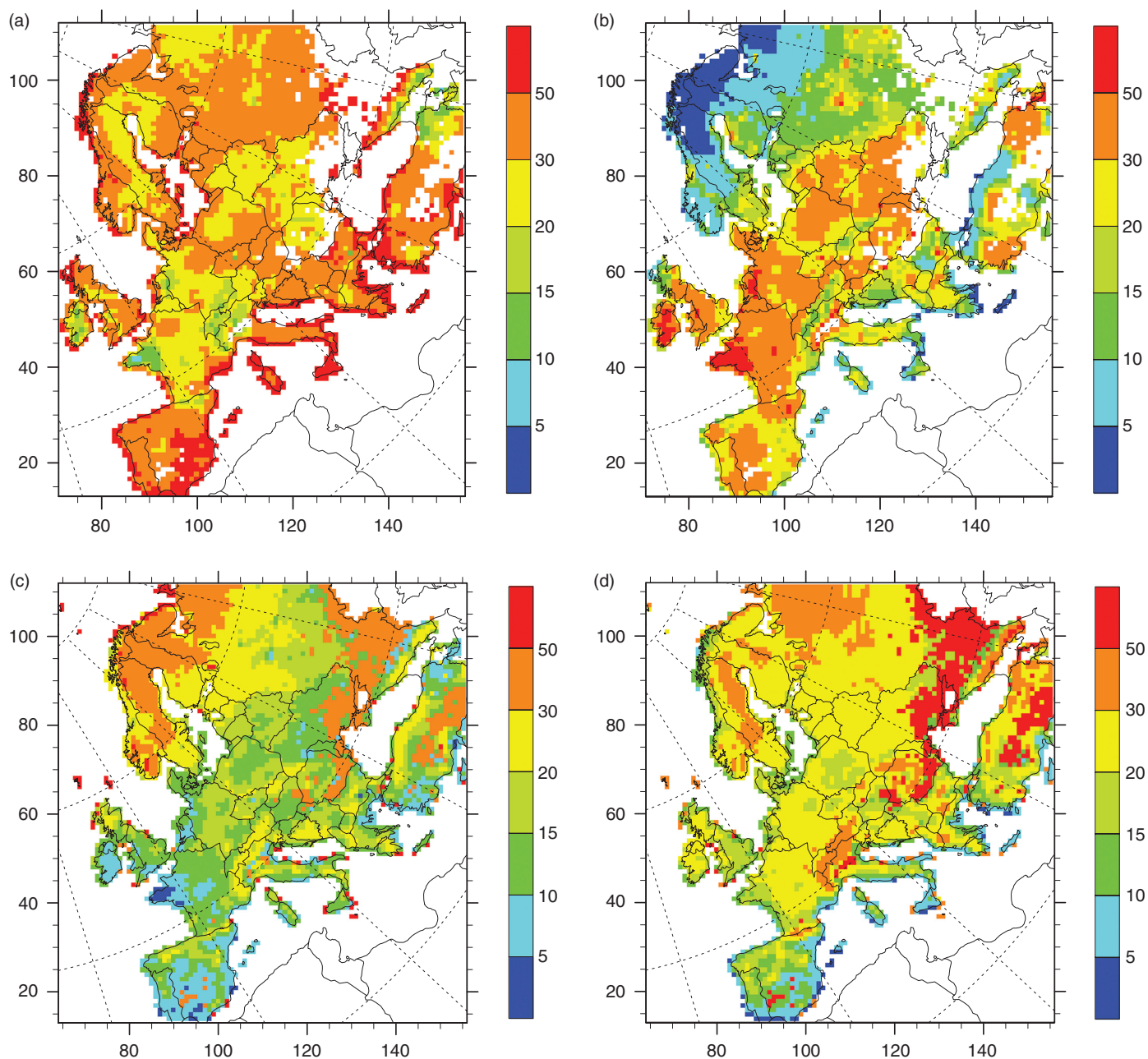
Figure 14.5 Calculated percentage contributions to total nitrogen deposition over coniferous forest: (a) dry deposition of oxidised N; (b) dry deposition of reduced N; (c) wet deposition of oxidised N; (d) wet deposition of reduced N. Calculations for the year 2000, from Simpson *et al.* (2006a).

since compounds such as NO_2 and PAN have low deposition rates to water surfaces. Further, the sea surface is usually aerodynamically smooth compared to land (especially forest), and so dry deposition of even soluble compounds is relatively less important over sea than land.

In general, nitrogen deposition originating from emissions on land have a strong gradient towards the sea. Ammonia is efficiently dry deposited close to the source areas and most of the reduced nitrogen that reaches the open sea comes in the form of ammonium particles which are efficiently wet deposited. NO_x deposition has a somewhat weaker gradient, reflecting a longer residence time in the atmosphere (NO and NO_2 do not deposit efficiently, but are transformed to HNO_3 which is efficiently dry deposited or forms nitrate aerosols.) Furthermore,

slower deposition processes of aerosols over water surfaces are assumed in the model.

The Mediterranean Sea is also different with respect to the share of agriculture related nitrogen deposition and deposition originating from emissions from combustion sources. Whilst the other seas have similar contributions of oxidised and reduced nitrogen deposition, the share of oxidised nitrogen deposition is more than 70% for the Mediterranean Sea, owing largely to the large contribution from ship traffic emissions.

In fact, for three of the four European seas discussed here, ship traffic emissions are among the most important contributor to oxidised nitrogen deposition to the sea area (Table 14.2). The exception is the Black Sea where emissions from Russia,
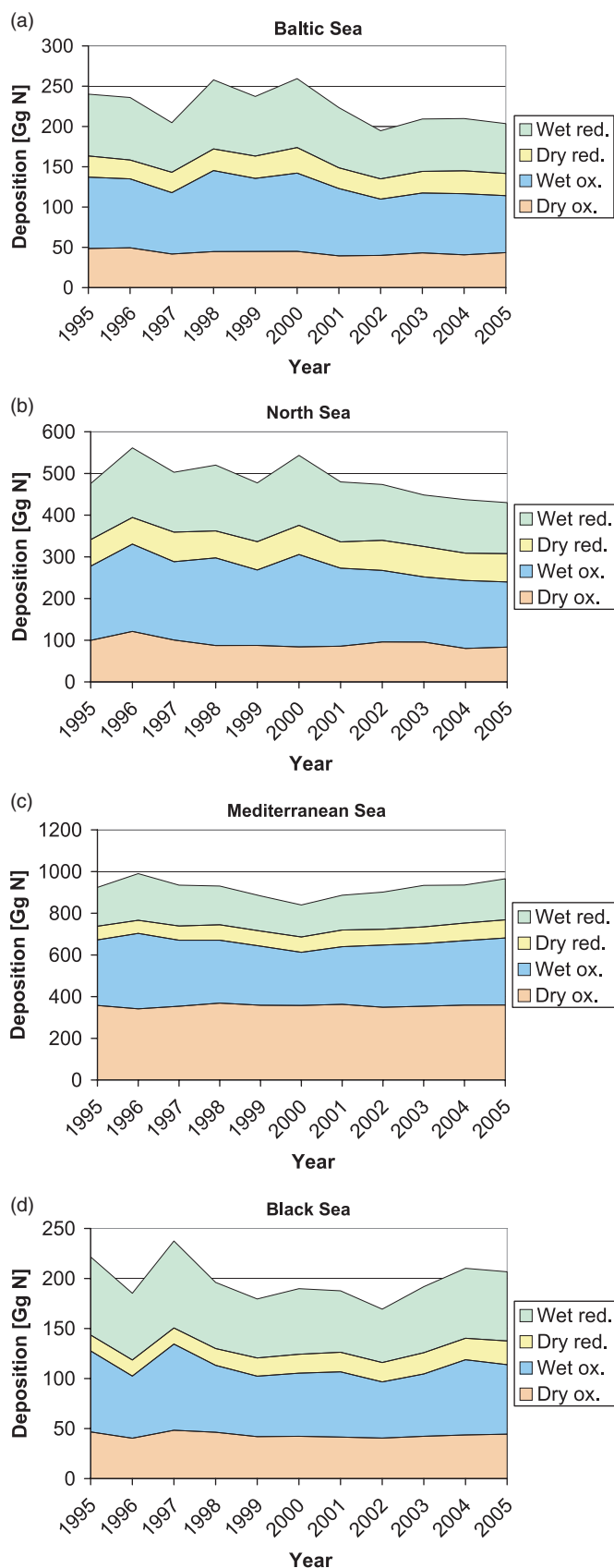
Figure 14.6 Time series of annual atmospheric load (Gg N/yr) of nitrogen to the European seas in the period 1995–2005. Oxidised and reduced dry and wet deposition and total nitrogen deposition are shown. From Bartnicki and Fagerli (2008).

Table 14.2 Contribution from international ship traffic emissions to oxidised nitrogen deposition in European seas (%). From Bartnicki and Fagerli (2008)

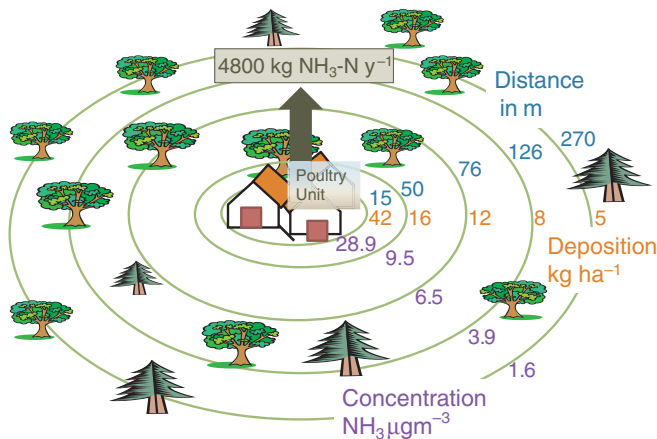| Receptor	Ship contribution
Baltic Sea	22%
North Sea	17%
Mediterrenean Sea	34%
Black Sea	7%

Turkey and Ukraine contribute around 20% each, with contribution from international ship traffic of around 7%. The main contributors to reduced nitrogen deposition are in general countries along the coast lines.

14.3.3 The local scale and scaling issues

As noted above, the grid resolution of models varies from typically less than 1 km in the most detailed local modelling to around 1° (*c.* 100 km) or larger for global scale models. Grid resolution affects not only the detail of model outputs, but has profound effects on the treatment of non-linear processes. Affected processes include for example the rate of oxidation of NO_x in plumes, and subsequent partitioning of NO_y into either rapidly depositing HNO_3 or longer-lived aerosol nitrate particles, or the bi-directional exchange of both oxidised and reduced nitrogen, where a mosaic of regions with high and low concentrations may well have a different net exchange to that found in a calculation where all concentrations are smeared out over a grid square. Many of the scaling problems associated with especially NH_3 modelling have been addressed in a series of recent reviews and so are not covered in detail here – the reader is referred to Bleeker *et al.* (2009), Hertel *et al.* (2006), Holmes and Morawska (2006), Loubet *et al.* (2009) and van Pul *et al.* (2009). Here we will concentrate on the comparability of regional and local scale models – and on the issues associated with bridging these scales.

It was noted in Loubet *et al.* (2009) (and refs cited therein) that the combination of hot-spot sources and effective deposition processes lead to sources and sinks of NH_x being spatially heterogeneous at a scale of a square kilometer or less. Direct measurement of NH_x deposition near hot spots is challenging due to intense local advection, and indirect estimates using mass balance, ^{15}N labelling, SF_6 to NH_3 ratio methods, as well as modelling studies, have estimated that the fraction recaptured within 2 km downwind from the source of NH_3 emitted ranges between 2% and 60% (Asman, 1998; Loubet and Cellier, 2001; Sommer and Jensen, 1991; Theobald *et al.*, 2001; Loubet *et al.*, 2006).

As another example, field studies in the Netherlands (Asman *et al.*, 1988) and the UK (Fowler *et al.*, 1998) show that individual sources lead to a large downwind gradient in concentration and deposition. Figure 14.7 shows an example of a farm scale emission and deposition gradient from 28 to 2 g m^{-3} and 40 to 5 kgN ha^{-1} yr^{-1}, respectively, within a distance of about 300 m.

4800 kg NH₃-N y⁻¹

Poultry Unit

Distance in m

270
126
76
50
15
42 16 12 8 5
28.9
9.5
6.5
3.9
1.6

Deposition kg ha⁻¹

Concentration NH₃µgm⁻³

Sum of deposition within 270m of farm woodland is:
155 kg N y⁻¹ (3.2% of emissions)

Figure 14.7 Farm scale NH₃ emission and deposition, illustrating the rapid fall-off in deposition levels with distance from source (adapted from Fowler *et al.*, 1998).
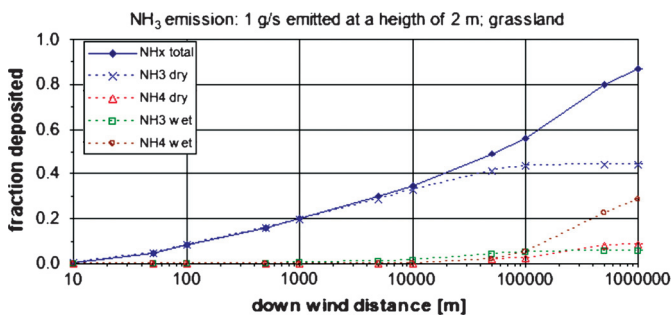

NH₃ emission: 1 g/s emitted at a heigth of 2 m; grassland

- NHx total
- NH3 dry
- NH4 dry
- NH3 wet
- NH4 wet

fraction deposited

down wind distance [m]

Figure 14.8 Annual mean cumulative deposition of NHₓ species as a function of downwind distance, calculated with the OPS model.

Figure 14.8 illustrates the cumulative deposition of ammonia and ammonium plotted against the distance downwind of a source (e.g. an animal house) as calculated by the OPS model (van Jaarsveld, 2004). Owing to the high dry deposition velocity of ammonia and the relatively low release height the loss

of material is substantial in the first kilometres. Almost 20% is already deposited after 1 km transport and 50% after 50 km. Indeed, an important aspect of ammonia is that local deposition is almost fully determined by dry deposition of NH₃. After approx. 50 km wet deposition of NH₄⁺ becomes the dominant deposition form. Modelling the transport and deposition of ammonia, therefore, requires relatively high resolutions, both in the horizontal and vertical dimension.

As of today, no single model is capable of reproducing a sufficiently wide range of length and time scales. Practical solutions include the (dynamical) nesting of small scale models into large-scale models or the use of output from large scale models to provide the boundary conditions for small scale models.

The development of Eulerian models with flexible resolution allows a systematic assessment of the effects of scale on model predictions. For example, Figure 14.9 illustrates the effect of increasing resolution on modelled deposition of reduced nitrogen using the same model (EMEP) at both 50 km resolution and 5 km resolution (see Vieno *et al.*, 2009). The increased resolution affects both the detail of the simulation, but also the location of the deposition. Deposition over hillsides more closely reflects the patterns of precipitation in the United Kingdom, and thus becomes more comparable to the results obtained by the UK CBED methodology (Smith *et al.*, 2000). This improvement partly reflects improved modelling of dispersion, but also partly improved meteorological modelling.

14.4 Comparison with observations

Although models are essential for mapping deposition, their trustworthiness can only be assessed by comparison with measurements. Unfortunately, as noted in Section 14.1, observations are lacking for many important aspects of the deposition process, so comprehensive evaluations are impossible. However, even routine measurements of parameters such as air concentrations, or concentrations in deposition, give valuable information.
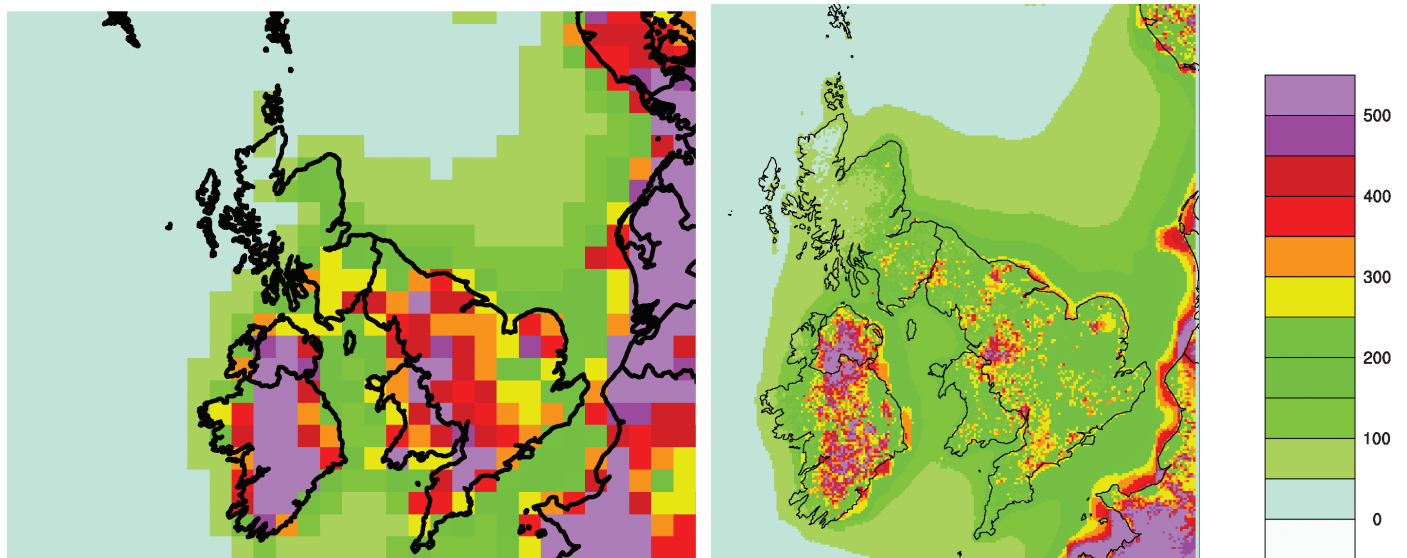

Figure 14.9 Calculated dry deposition of reduced nitrogen for UK, calculated from EMEP model runs at two resolutions: 50 km (left) and 5 km (right). Units mg(N) m⁻² (100 mg(N) m⁻² = lkg(N) ha⁻¹). Source: EMEP4UK model (Vieno *et al.*, 2009a,b).

It should also be noted that global and regional scale models cannot be expected to reproduce small-scale variations in deposition regimes, caused by such factors as local emissions (especially important for NH_3 close to agricultural sources, see Sutton *et al.*, 1998), topography (which has strong effects on rainfall amount and deposition, see Dore *et al.*, 1992; Fowler *et al.*, 1988; Hertel *et al.*, 2011, Chapter 9, this volume), or where processes not included in the model (e.g. occult deposition) are important. These problems are difficult to address, but by comparison with measurements we can make an assessment of the degree of agreement between the model and observed values.

Here we focus on the evaluation of European-scale deposition estimates, but start with a brief introduction to the EMEP measurement network (Section 14.4.1) and an evaluation of the air concentrations (Section 14.4.2). Reliable modelling of gas and aerosol air concentrations is a necessary (but not sufficient) prerequisite for reliable modelling of atmospheric inputs to ecosystems and seas.

14.4.1 The EMEP network

The main measurement network providing European-scale data on reactive nitrogen concentrations and deposition is the EMEP network (EMEP, 2010). As discussed in detail in Fagerli and Aas (2008), 24 EMEP sites have reported nitrate and ammonium in precipitation from around 1980, with a good coverage of North and Central Europe and partly Eastern Europe. The measurements of these compounds in air did not start until the end of the 1980s. Nineteen sites reported long-term data series, but the majority of these sites were located in Nordic countries. In general, few long-term measurements are available from the south-east of Europe.

Nearly all of the air measurements conducted within the EMEP network are made using the filter pack method. It is well known that this method is biased for separate gas and particulate nitrogen compounds (EMEP, 1996). Ammonium nitrate on the aerosol filter may dissociate into gaseous nitric acid and ammonia that will be captured by the impregnated filters in the filter pack sampler. This causes a negative interference on the particle filter and positive interferences on the impregnated filters. The opposite may happen if ammonia or nitric acid is captured on the front aerosol filter. An artifact free separation of these gases and particles can be achieved using denuders, but only two EMEP sites had used this method at the time of the Fagerli and Aas (2008) study.

EMEP has an extensive quality control of the data that are included in the database. Laboratories that fail badly in field- and lab inter-comparisons (Aas and Hjellbrekke, 2005) are flagged. The data sets are graded according to their quality, and for model evaluation it is clearly best to use the data with the best quality (Fagerli and Aas, 2008).

14.4.2 Air concentrations

In this section we illustrate the performance of chemistry transport models for reactive nitrogen using the ensemble of models introduced in Section 14.3.2. Figure 14.10 compares the
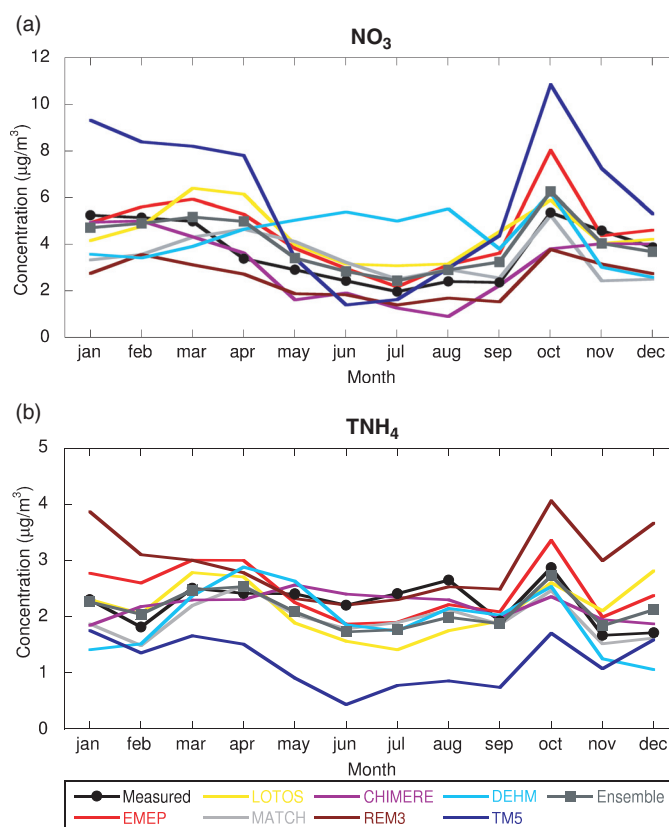
Figure 14.10 Modelled and measured seasonal variation of particulate nitrate and ammonium for 2001. The data represent the average monthly mean values for N_s stations over Europe. Number of stations (N_s) is indicated in Table 14.3. Units: µg m^{-3}. From Schaap *et al.* (2010).

mean seasonal variation of the ensemble mean model and its members to the observed variation for particulate nitrate and ammonium from the EMEP network. The spread of the models is a measure of gaps and uncertainty in our knowledge. For example, Figure 14.10 indicates a higher uncertainty for nitrate than for ammonium. These EURODELTA results indicate that in general, the models are able to capture the seasonal variation of the single components, but with significant uncertainty.

Table 14.3 shows the relative root mean square error (RRMSE) and mean correlation of concentrations found from this comparison. RRMSE values are higher for the nitrogen components than for sulphate, with largest values seen for total nitrate (TNO_3). This latter finding is partly an artefact though, related to the number and distribution of the measurement sites over Europe for different compounds. Nitrate (only six sites here) is measured in north-western and central Europe, at sites characterised by flat-terrain, continental meteorology and high pollution levels. By contrast, total nitrate (21 sites here) is mostly measured in less polluted areas near the sea and/or in areas with complex terrain. Low pollution levels and complex terrain are generally associated with lower model skills. All models show this characteristic for all species. Indeed, in north western and central Europe RMSE values for TNO_3 tend to be lower than for NO_3, reflecting the sensitivity of the nitrate partitioning to ambient conditions and precursor gas concentrations.

Table 14.3 Comparison of modelled and observed inorganic species for seven CTMs and their ensemble mean. Tables gives RRMSE value (%) and (in parentheses) temporal correlation coefficients between daily modelled and measured values, averaged over a number of stations (N_s) in Europe

Model	SO$_4$	SO$_2$	NO$_3$	TNO$_3$	NH$_4$	NH$_x$
N$_s$	36	27	6	21	8	19
EMEPv3.1	54 (0.61)	101 (0.52)	69 (0.59)	106 (0.50)	50 (0.61)	62 (0.49)
LOTOS-EUROS	51 (0.54)	85 (0.51)	62 (0.55)	87 (0.44)	52 (0.53)	56 (0.35)
MATCH	62 (0.62)	99 (0.57)	52 (0.56)	88 (0.51)	44 (0.61)	50 (0.57)
CHIMERE	59 (0.45)	139 (0.52)	62 (0.53)	84 (0.37)	46 (0.54)	62 (0.41)
RCG	57 (0.55)	107 (0.43)	53 (0.62)	75 (0.43)	48 (0.55)	74 (0.38)
DEHM	68 (0.55)	83 (0.51)	71 (0.38)	160 (0.43)	49 (0.54)	54 (0.49)
TM5	59 (0.50)	n.a	97 (0.59)	143 (0.50)	62 (0.57)	67 (0.43)
Ensemble	44 (0.68)	91 (0.58)	46 (0.66)	92 (0.56)	40 (0.66)	50 (0.54)

Notes: RRMSE is the relative root-mean square error, i.e. RMSE divided by the observations and in %; N_s is the number of stations; SO$_4$ is particulate sulphate; NO$_3$ and NH$_4$ are particulate NO$_3^-$ and NH$_4^+$; TNO$_3$ is the sum of HNO$_3$+NO$_3^-$; NH$_x$ is the sum of NH$_3$+ particulate NH$_4^+$.

The lower RRMSE values for NH$_3$ and NH$_x$ compared to the oxidised compounds reflect the fact that the majority of the ammonium is bound to sulphate.

The skill of the ensemble average is generally higher than the skill of the individual models. The better skill of the ensemble average or median has been shown earlier in several recent studies for air quality (Delle Monache and Stull, 2003; Pagowski *et al.*, 2005; McKeen *et al.*, 2007; van Loon *et al.*, 2007; Vautard *et al.*, 2008; Schaap *et al.*, 2010) as well as for transport of passive tracers (Galmarini *et al.*, 2004; Riccio *et al.*, 2007). In climate assessments (IPCC, 2007) for example, model ensembles has become essential to evaluate the state of the knowledge of the scientific community and the spread of its uncertainty.

14.4.3 Wet deposition

Comparison of model results for wet deposition or concentrations in precipitation is in many ways trickier than comparing gas concentrations. Hertel *et al.*, 2011 (Chapter 9, this volume) discusses the physical/chemical processes controlling wet-deposition of N$_r$ compounds, and the important role that topography can play in enhancing deposition rates. As noted in van Loon *et al.* (2004), the most important issue concerning the wet removal of species in CTM models is probably the meteorological input; model performance for wet deposition fluxes or concentrations in precipitation is strongly limited by the quality of the NWP models providing meteorological data. For example, models generally have problems with sub-grid precipitation, simulating precipitation more often, but in lower amounts, than reality. As precipitation scavenging is a complex and non-linear process (Barrie, 1992), such issues will cause errors in modelled wet deposition that are difficult to evaluate. There are also many uncertainties inherent in the deposition monitoring methods themselves (Draaijers and Erisman, 1993; Erisman *et al.*, 2005).

The precipitation amount may vary quite a lot over short distances, especially in mountain areas, and the sites are not always representative for the average gridded precipitation amount. For the EMEP network, the agreement between precipitation measured at EMEP sites and the EMEP model is within 30% at almost all sites. Some of this discrepancy is of course due to uncertainties with the NWP model, but some is also due to precipitation sampling problems.

In an early intercomparison of six different CTMs used in Europe, van Loon *et al.* (2004) found very poor model performance for the wet deposited components, despite fair to good performance for airborne components. A clear result of this study was that no model achieved good correlation coefficients (the best was just $r = 0.35$) for wet components, and bias and RMSE values could be very substantial (up to 60%–70% for wet deposition fluxes) relative to observed values. These results were much worse than equivalent results for concentrations in air. The models used in this study have been improved to some extent since this intercomparison, but it seems likely that a study using today's models would still show discrepancies of up to 50%.

The relatively poor agreement between modelled and observed wet deposition fluxes is not a specific feature of this inter-comparison or these models. Large differences between models were also found in the global models participating in the COSAM study, in which the wet deposition efficiency ranged over a factor of 4 (Roelofs *et al.*, 2001). A similar spread was also found for global models by Dentener *et al.* (2006) and Textor *et al.* (2006).

The EMEP model seems to have been subject to most evaluation against observed wet deposition estimates. Standard scatter plots showing the performance of the model against observed concentrations of NO$_3^-$ and NH$_4^+$ can be found in the yearly EMEP status reports; see Fagerli and Hjellbrekke (2008) and Berge and Hjellbrekke (2010). The model has also been compared to observed wet deposition for nitrogen from the ICP-forest network (Simpson *et al.*, 2006b). Differences in mean values between modelled and observed (ICP-forest) SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ total and wet deposition were within 20% in 1997 and 30% in 2000, with the EMEP model showing slightly lower values than the observations (Simpson *et al.*, 2006b). Modelled and observed concentrations of SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ in precipitation were very similar on average (differences of 0%–14%),
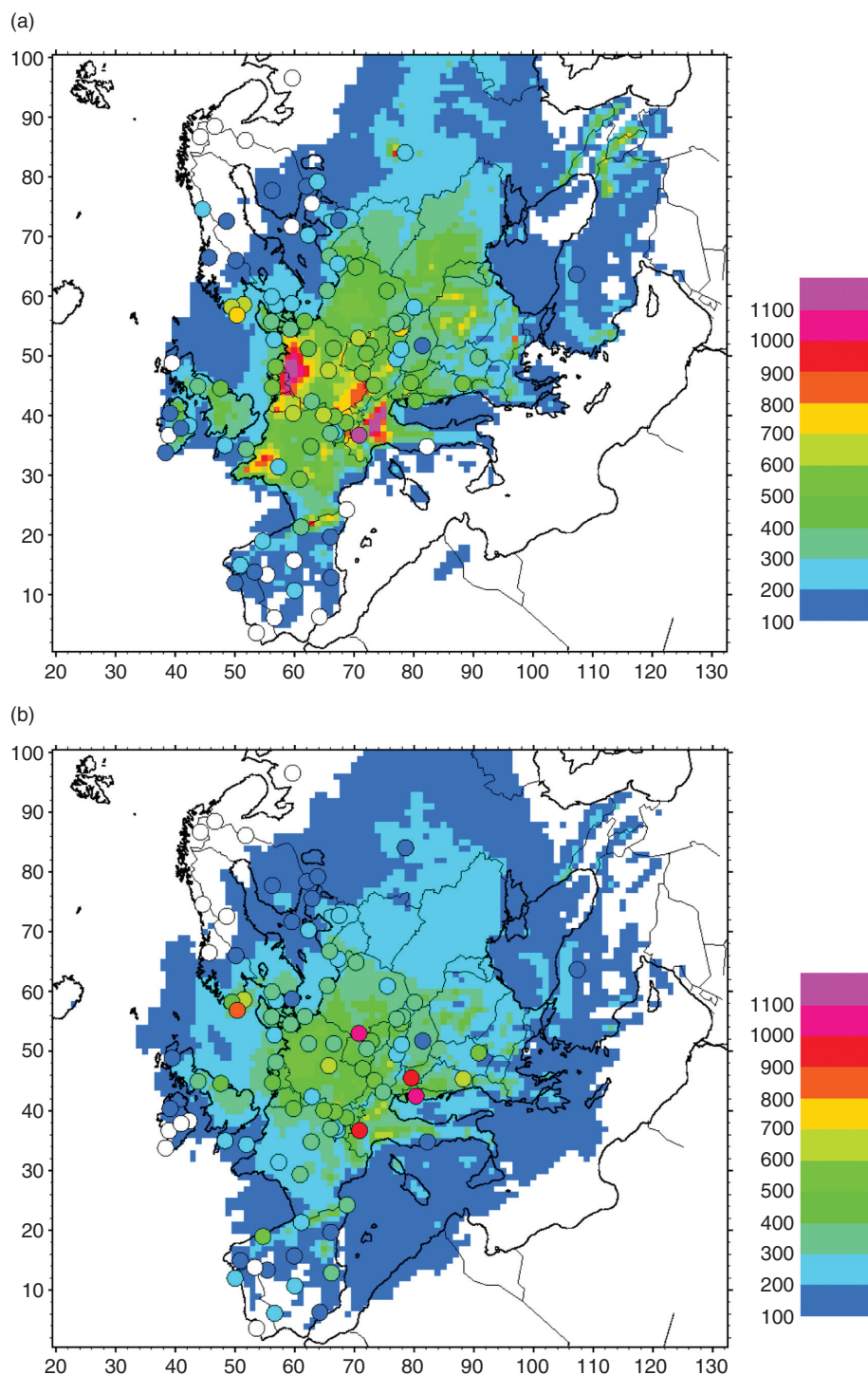
(a)

Figure 14.11 Comparison of modelled and observed annual wet deposition of (a) NH_x and (b) NO_3^- (HNO_3 and aerosol nitrate). Data are for 2001 in the EMEP model with observations. The bullets depict observations with the same colour bar as the modelled field. Measured annual deposition is calculated by using the measured precipitation amount and the nitrate and ammonium concentration in precipitation.

(b)

and the correlation between modelled and observed data is rather high for this type of comparison (between $r^2 = 0.4$–0.8 for most components and years).

Figure 14.11 compares measured wet deposition of oxidised and reduced nitrogen against results from the EMEP model. In these plots the measured deposition is calculated using the measured precipitation amount and the nitrate and ammonium concentration in precipitation. For reduced nitrogen, Figure 14.11 a reveals good agreement between modelled and

measured values, across almost all of Europe. The high modelled values near northern Italy are reflected in the measurements. Unfortunately, other regions with high predicted wet deposition have only a limited number of measurement sites (e.g. Netherlands, Belgium), and so it is difficult to evaluate model performance here. The EMEP model has a tendency to under-predict wet deposition in Nordic sites.

For oxidised nitrogen (Figure 14.11b), five sites stand out with much higher measured wet deposition than modelled.

Table 14.4 Comparison of observed and modelled (EMEP) contributions (%) of dry and wet deposition of oxidised (OXN) and reduced nitrogen (RDN) to total N-deposition (OXN+RDN) at Speulderbos forest, Netherlands, 1995. From Simpson *et al.* (2006a)

	Observed Dry+Wet			Modelled Dry+Wet		
	Dry	Wet	Dry+Wet	Dry	Wet	Dry+Wet
OXN	18	11	29	22	9	31
RDN	47	24	71	54	15	69

The reason for this seems to be that the observed precipitation at the sites far exceeds the modelled precipitation (e.g. by a factor of two for the Norwegian site). However, there is a very good agreement between model results and measurements at almost all other sites, which gives some confidence that the modelled budget of wet-deposition is within the uncertainty of the measured value.

14.4.4 Dry deposition

Although wet deposition represents an important fraction of N-deposition over Europe, dry deposition is also important. Hertel *et al.* (2011), (Chapter 9 this volume) discusses the physical/chemical processes controlling dry-deposition of N_r compounds. Unfortunately, the EMEP network has no specific measurements of dry deposition, so we cannot present maps of modelled versus observed dry deposition.

However, dry deposition monitoring has been performed over many years at Speulderbos forest in the Netherlands (Erisman *et al.*, 1997, 2001), the site with by far the highest deposition loads within the EU NOFRETETE project (Pilegaard *et al.*, 2005). Erisman *et al.* (2001) presented estimates of wet and dry deposition of oxidised and reduced nitrogen for Speulderbos, over the period 1995–1998, and Simpson *et al.* (2006a) compared EMEP model estimates against these. The modelled total deposition for the Speulderbos grid square in 1995 was 5200 mg(N) m^{-2}, within 10% of that found in the measurements (4798 mg(N)/m^{-2}). Table 14.4 illustrates the percentage breakdowns of this total deposition between wet/dry/OXN/RDN components. These relative contributions are remarkably similar, with reduced nitrogen accounting for about 2/3 of total deposition, and dry deposition dominating both the oxidised and reduced-N contributions.

Ongoing studies within NitroEurope (Sutton *et al.*, 2007) suggest problems with dry-deposition estimates, however. As part of the EU Nitro-Europe project, inferential modelling is being conducted with deposition codes from three European dry deposition models at selected sites of the NitroEurope (NEU) inferential network (Flechard *et al.*, 2010). The deposition modules are from the UK-CBED model (Smith *et al.*, 2000), the Dutch IDEM model (Bleeker *et al.*, 2004) and the EMEP scheme (Simpson *et al.*, 2001, 2003). This study has suggested that NH_3 is the single highest atmospheric N_r dry input in many parts of Europe. At sub-urban sites of the NEU network, HNO_3 and particulate NO_3^- and NH_4^+ could also contribute significant fractions of total dry deposition. There were, however, substantial discrepancies between models, with annual deposition rates varying as much as two-fold between models at given monitoring sites. This highlights the variability in model parameterisations, stemming from the variability in measured deposition rates and canopy resistances.

For NH_3, the stomatal compensation point and the external leaf-surface (or non-stomatal) resistance are the largest sources of divergence between models. The effective annual mean deposition velocity (V_d) predicted by the CBED model is negative for the cropland and grassland sites, as a result of a non-zero compensation point for these land-use classes, but otherwise the lowest V_d for NH_3 is always that predicted by the EMEP scheme. The discrepancies can be ascribed to different parameterisations for the non-stomatal resistances.

Model estimates of aerosol V_d differ greatly among the various modelling approaches and parameterisations (see Ruijgrok *et al.*, 1997, for a review), but it is in the size range 0.1–1.0 μm that the variability and uncertainty are greatest. Whereas mechanistic models predict very low deposition velocities for fine aerosols, typically of the order of 0.1 mm s^{-1}, field measurements suggest that V_d is 1–3 orders of magnitude higher (Gallagher *et al.*, 2002; Zhang *et al.*, 2001). Still, such field measurements are also subject to great uncertainty (Pryor *et al.*, 2008b,c; Rannik *et al.*, 2003). This is especially relevant for reactive nitrogen in the aerosol phase, as NH_4^+ and NO_3^- are mostly (>90%) present as sub-micron particles.

14.4.5 Evaluation of emissions

Emissions are the most important input to all CTM models, essential to both good model performance against observations and to the reliability of any emission control scenarios. Sources of reactive nitrogen to the atmosphere have been discussed for instance in Hertel *et al.* (2011) (Chapter 9 this volume), and uncertainties in inventories will be discussed in Section 14.5.

Satellite-borne instruments, e.g. GOME (Burrows *et al.*, 1999), SCIAMACHY (Bovensmann *et al.*, 1999), aboard the ENVISAT satellite, or OMI (Boersma *et al.*, 2007), represent an interesting possibility to assess emissions, or at least CTM results which can relate to emissions. Such satellites provide global coverage of some compounds at a spatial resolution of a few tens of kilometres. One of the first outstanding pictures provided by the use of such data was the decreasing NO_2 column trends over North America and Europe, and the increasing trend over China (Richter *et al.*, 2005; van der A *et al.*, 2006). However, the extent to which tropospheric columns can be used for characterising air quality, namely surface concentrations, is not

obvious, due to measurements uncertainty and column vs. surface representativeness. Blond *et al.* (2007) showed in particular that spatial variability of surface concentrations in and near European cities are not captured by satellite measurements.

Satellite measurements have also been used to constrain (Martin *et al.*, 2003) or estimate NO_x emissions (Leue *et al.*, 2001). Konovalov *et al.* (2005) and Blond *et al.* (2007) show that the spatial distribution of tropospheric NO_2 is generally well simulated by chemistry-transport models. However, sub-regional model underestimations, especially in Southern Europe, are present, which suggests an underestimate of NO_x emissions. Other models have been tested against satellite measurements, especially over China (Ma *et al.*, 2006).

Konovalov *et al.* (2006) attempted to invert measurements in order to obtain emissions at regional scale over Europe, using relations fitted to a chemistry-transport model. This method was also applied to the estimation of NO_x emission decadal trends (Konovalov *et al.*, 2008). It showed marked differences between trends in 'bottom-up' and satellite derived NO_x emission trend estimates in Southern European regions, while trends are consistent in Northern areas.

Satellites show also some potential for the evaluation of modelled fields of NH_3 and hence of their emissions (Beer *et al.*, 2008; Clarisse *et al.*, 2009). Current retrieval methods require improvement, however, before this potential can be realised.

14.5 Uncertainties and challenges

Estimation of the atmospheric inputs to N_r deposition is challenging because of uncertainties in the whole chain of processes – emissions, dispersion, chemistry and deposition. Monks *et al.* (2009) have discussed many of the issues with regard to oxidised nitrogen, and reviews such as those by Bleeker *et al.* (2009) or van Pul *et al.* (2009) provide much information on reduced nitrogen. Emissions and processes have been discussed in Hertel *et al.*, 2011 (Chapter 9 this volume). Here we highlight those issues specific to modelling and measurements rather than processes. As noted in Hertel *et al.* (2006), there is a substantial discrepancy in the relative importance of various physical and chemical processes that need to be taken into account in local and regional scale models for N deposition, due to the differences in time scale. On the local scale the dispersion of pollutants is the most important process with regards to the concentration levels, whereas beyond about 5 km it is increasingly necessary to have good descriptions of wet and dry deposition processes, and atmospheric chemistry.

Measurements

Generally, there are a variety of issues related to the measurements of N compounds in the atmosphere, due to their large number, low concentrations, reactivity and gas/aerosol interactions (Laj *et al.*, 2009). Highly reactive gases such as NH_3 or HNO_3 are very challenging to detect because of their interaction with parts of the instruments, resulting in slow sensor response times. Their very short lifetime in the atmosphere means that they are highly variable, spatially and temporally. HONO is notoriously difficult to measure, usually with

positive bias caused by photolysis (it is thought) of nitrate on sampling lines and inlets. The measurement of aerosol compounds such as ammonium and nitrate also requires sophisticated instrumentation. Indeed, one of the critical limitations for model evaluation is the lack of good measurement data on the partitioning of oxidised nitrogen between HNO_3, and fine and coarse particulate nitrate. Of the EMEP sites discussed by Fagerli and Hjellbrekke (2008), only a few sites reported results for the gaseous compounds, 15 for HNO_3 and 11 for NH_3, and of these only two use denuders whilst the others use filter-pack methods – results from the latter are very uncertain.

Organic N in the atmosphere is in general not measured as gas/particles with the exception of occasional measurements of PAN, amines and organic nitrates (but except for PAN not routinely monitored). The recent paper by Gonzalez Benitez *et al.* (2010) shows the potential scale of the problem. Measurement technology is available to measure organic N compounds such as amines and PANs, but the technology is still quite expensive, especially when it comes to continuous measurements.

Another basic problem is that the surface measurements which are typically available give only a partial picture of some important chemical components. For example, gaseous NO_3 is often discussed as a potentially important loss mechanism for hydrocarbons, providing a night-time alternative to OH radicals in driving chemistry (see Wayne *et al.*, 1991; Brown *et al.*, 2006). Unfortunately, this compound is extremely difficult to measure, and has very large vertical gradients – surface concentrations are both modelled (Fish *et al.*, 1999) and measured to be very small, even when boundary layer values are significant.

Over sea areas, evaluation of models is further complicated as validation is usually against measurements at coastal sites; observations in the open sea rarely exists. Furthermore, for the Black Sea and the Mediterranean Sea, very few observations exist for any location.

Meteorology

Uncertainties in the meteorological data used by models are often difficult to quantify, because many of the parameters that are critical for air pollution modelling are not measured, or only available through a series of assumptions. As well as precipitation (Section 14.4.3), an important example is the height of the boundary layer, or mixing height (H_{mix}), which controls the dispersion of all pollutants in the boundary layer but which is difficult to define even when radiosonde data are available (Seibert *et al.*, 2000; Stern *et al.*, 2008). Other important parameters include friction velocity and stability, both of which are crucial for deposition estimates. It can be noted that the uncertainties of meteorological inputs to CTMs receives relatively little attention, and these uncertainties are probably significant.

Emissions

As noted above, emissions are the most important input to all CTM models, but they often receive little attention despite being subject to substantial uncertainties (Reis *et al.*, 2009). As an example, looking at two recent emission inventories EDGAR

v.4 (EDGAR, 2010), and the UK National Emission Inventory (UKNAEI, 2010) for the year 2005, emission figures for NO_x and NH_3 for the UK both differ by about 30%. Such uncertainties are likely ubiquitous in European inventories, and indeed greater in countries with few emission measurement activities and where emission inventory development receives little funding.

Deposition modelling

There are very many uncertainties regarding the magnitude (and even direction) of surface–atmosphere exchange, especially concerning dry deposition, occult deposition and emissions from soils. Particle deposition rates are one obvious source of uncertainty (Pryor *et al.*, 2008a, c). As another example, the non-stomatal resistance term for NH_3 is not only a function of ambient NH_3 but also of the concentrations of acid gases (HNO_3, SO_2, HCl) which neutralise NH_3 in water films on vegetation (Flechard *et al.*, 1999; Fowler *et al.*, 2009). To quantify this effect mechanistically requires dynamic chemical modelling with very short time steps, which precludes the implementation of such schemes in regional models, and some models (EMEP, IDEM) use the NH_3/SO_2 ratio as a proxy in empirical parameterisations.

Flux networks such as Nitro-Europe will hopefully help reduce uncertainties in some parts of the N_r deposition budget, but there is a clear need for both improved instrumentation and analysis techniques before reliable estimates of N_r deposition can be made.

14.6 Conclusions

This chapter has attempted to answer the overriding question: *what are the atmospheric inputs of reactive nitrogen (N_r) in Europe, and how well can we estimate these?* We have focused mainly on presenting results from models, partly because of the limitations of measurements, but also because models allow for spatially comprehensive estimates of pollutant concentrations, and for mapping of deposition patterns over large areas. Models are also key tools to integrate our understanding of atmospheric chemistry and transport. Models address emissions, dispersion and transport over multiple scales, chemical transformation, and dry and wet removal of pollutants.

This chapter, along with Hertel *et al.*, 2011 (Chapter 9 this volume), has also discussed many of the uncertainties associated with deposition estimates of N_r. For specific locations, and especially at fine scales, such estimates can be very uncertain, with considerable variations on spatial scales of less than a kilometre. Differences between modelled and observed wet deposition of more than a factor of two are not uncommon for specific sites, especially in regions of complex topography. However, it should be remembered that mass considerations provide a strong constraint on the uncertainties in N_r deposition. Globally, all emissions of N_r will deposit somewhere, so that uncertainties in the deposition are equal to uncertainties in the emissions. Over Europe this equivalency still holds to a large extent, as the lifetime of emitted N_r is usually less than a few days. Such considerations probably explain why the current generation of chemical transport models perform quite

well (within 30%–50% say) when compared to the available (albeit very limited) observational data for wet deposition.

Estimation of deposition at fine scales remains however a formidable task, and this poses challenges for estimating exceedances of critical levels for sensitive ecosystems. Improvements in models, emissions, measurements and understanding of physical/chemical processes will be needed before we can map fine-scale N_r deposition with confidence.

Ideally, model evaluation and improvement of deposition estimates should be guided by direct measurements of fluxes of N_r, but such data are extremely expensive. In any case, observations of airborne components can also play a strong role in improving models, as there are many aspects of atmospheric chemistry which are still not properly evaluated.

The main needs for oxidised compounds are probably to evaluate how well the models capture the partitioning of N_r between gaseous HNO_3 and either fine or coarse nitrate. For reduced compounds, better estimates of emissions are needed, and how these are affected by meteorological factors as well as agricultural practices, coupled with an understanding of biosphere-atmosphere exchange.

Such work should benefit from detailed studies from research networks such as NitroEurope, EUCAARI and EUSAAR, and from field campaigns (Laj *et al.*, 2009; Kulmala *et al.*, 2009; Sutton *et al.*, 2007; Tang *et al.*, 2009). Long-term monitoring, and a balanced hierarchy of a limited number of so-called super-sites (level 3 in EMEP terminology) and larger numbers of simpler level 1 and 2 sites (UNECE, 2009) would still be a crucial requirement, however, in order to assess (among other things) emission inventories, atmospheric processes, and long-term model performance.

Acknowledgements

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