Modelling of the atmospheric transport and deposition of ammonia at a national and regional scale

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1 Introduction

1.1Background
Measurements of ammonia and ammonium concentrations and depositions from monitoring programmes are crucial for providing information about trends and actual loads of ammonia in the environment. Such data may together with data from field campaigns form the basis of our understanding of the physical and chemical processes governing the fate of ammonia. However, modelling of the concentrations and depositions of ammonia (in combination with measurements) extends our possibilities substantially. Measurements are usually carried out at a limited number of locations. Model calculations are therefore used to obtain information with higher geographical resolutions and for estimates of loads at locations not covered by the monitoring network. Well-tested and well-calibrated models are furthermore highly useful in the interpretation of measurements, and thereby also as a tool in the analysis of the governing processes for the fate of the pollutants in the environment.
With modelling the relation between source and receptor is established. This means that the contribution of specific sources, economic sectors or countries to the concentration and deposition can be estimated. Modelling is the only way to carry out scenario studies in environmental management. The scenario studies may answer questions like – what will happen when a source is added or a specific measure will be implemented or how will the future situation look e.g. in the year 2020, given that current emission ceilings are met, or further scenarios are followed?

Modelling the transport, transformation and deposition of atmospheric ammonia is a challenge due to the complexity of the governing processes (Asman et al., 1998; Hertel et al., 2006). Ammonia is generally speaking emitted from low source heights: the release takes place from the ventilation system of a stable or from volatilisation during the application of manure and from a vast amount of sources. This means that a) ammonia, along with the fact that it deposits quickly, is deposited in larger amounts close to the source than is the case for other air pollution components and b) the concentration and deposition patterns show large local gradients. In turn the deposited ammonia may re-emit and re-deposit. At the same time ammonia reacts (with a time scale of minutes to few hours) relatively fast with acid gases and particles in the atmosphere and forms aerosol-bound ammonium salts. The chemical transformation and the dispersion and deposition take place on similar time scales. Modelling the ammonia deposition upon ecosystems is less straightforward because of the possible re-emission of ammonia by ecosystems that have large nitrogen burden. Therefore specific parameterisations are needed for modelling the ammonia concentrations and depositions.

1.2 Why this document and goals for the Workshop?
A number of different model types are currently in use in research as well as in environmental management in the field of ammonia. The models differ in a number of modeling concepts such as the spatial scale, the description of the emission and deposition processes. Analyses of the model performances as well as analyses of the differences in calculation results may provide useful insight into what is currently the state-of-the-art in modelling ammonia in the

environment and how differences in parameterizations in models can explain observed differences between models. We will focus here on the models that calculate the ammonia concentration and deposition at a national or regional scale.

So in summary the goals of this document and this working group at the Workshop are:

1) Review the parameterizations used in the atmospheric dispersion and transport models of ammonia with the emphasis on the emission process, the vertical dispersion, the deposition process and the chemical conversion;

2) Discuss the performance and validation of the models and discuss observed differences between modelled and measured ammonia concentrations and explain these differences in terms of (shortcomings in) the used process parameterizations;

3) Compare the models results against a common reference; for this workshop we use the EMEP unified model results;

4) Define recommendations for improving the atmospheric dispersion and transport models of ammonia on a national and regional scale.

1.3 Scope of the document

First a brief overview of the processes that describe the dispersion, transport and deposition of ammonia will be given (Section 2). Focus in this part will be on the emission parameterisations, description of the deposition processes and the chemical transformation. Subsequently, an overview of current models on a national and regional scale and their most important concepts, their performance and validation will be presented (Section 3). In Section 4 we will tentatively indicate the reasons for the differences in performance in terms of the modeling concepts and define items for the discussion at the Workshop. Section 5 will on conclusions and recommendations and will be filled in at the workshop.

2 Overview modeling of the ammonia concentration and deposition

2.1 Brief overview of the most important atmospheric processes

Ammonia is emitted to the atmosphere mainly from agricultural sources. In essence the emission of ammonia is the evaporation from animal manure and is highly dependent on the specific agricultural activity and environmental circumstances. In the atmosphere ammonia is subject to dispersion and transport, removed by dry and wet deposition and transformed to aerosol-bound ammonium in reactions with acid gases and aerosols (Figure 1, Hertel et al., 2006; Asman et al., 1998). Due to the relatively fast deposition and conversion process and the low emission height the atmospheric lifetime of ammonia is typically a few hours. Aerosol-bound ammonium has generally a much long lifetime in the atmosphere and may, therefore, be transported over long distances (>1000km). The main removal path of the ammonium-containing aerosols is wet deposition.

2.2 Overview modelling concepts and parameterisations

Different approaches have been used in the modelling of the fate of ammonia in the atmosphere. The choice of the complexity of the parameterizations is often a function of among others a) the state of knowledge of the process, b) the availability of input parameters, c) the purpose of the model, d) the available computer power. In the following subsections we will elaborate the most important processes and the determining variables therein.

In the next subsections we will elaborate on these processes and the commonly used parameterizations for modelling these processes.
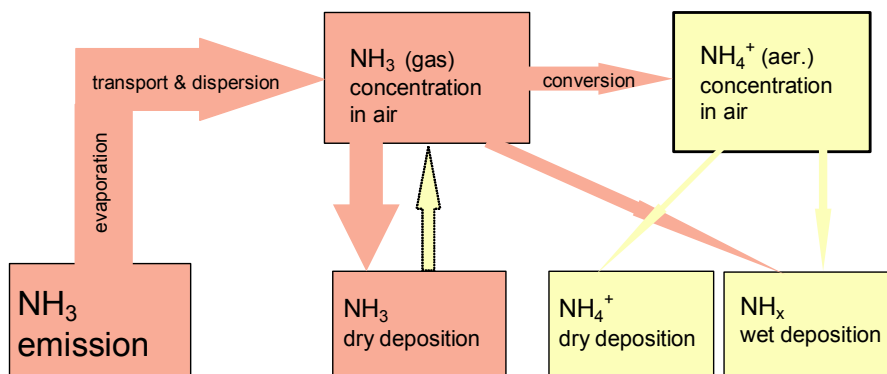
Figure 1. The most important atmospheric processes that determine the fate of ammonia in the atmosphere. The thickness of the arrows indicate the relative importance of the process.

2.2.1 Emissions

In modelling apart of the total emission amount from the sources also the variation in the emission factors and the spatial resolution of the data is very important. The emissions of ammonia mostly originate from animal housings and from the application of manure. The emission from aninmal housings depends mainly on the ventilation (Seedorf et al., 1998a) and the temperature inside the stables (Seedorf et al., 1998b; Wathes et al., 1998). The emission of ammonia from manure application are a function of the application method, the meteorological conditions and the soil type (Huijsmans et al., 2003). Other sources of ammonia are grassing animals, storage facilities and fertilized crops (see e.g. (Ambelas Skjøth et al., 2006) but common for all sources is that the emission of ammonia to a large degree depends on the ambient temperature and wind speed. Therefore, the total ammonia emission varies to a large degree during the day and during the season (Battye et al., 2003; Gilliland et al., 2003; Anderson et al., 2003).

Most transport-chemistry models deal with the seasonal or diurnal variations in a strongly simplified way. One reason is the lack of input data (Hutchings et al., 2001).

The emission amount is often calculated from a combination of the activity data and the emission factor corresponding to the activity.

Most national or local scale inventories for ammonia are compiled as annual mean values for grids of varying resolution (Sutton et al., 2000; Bouwman et al., 1997; Olivier et al., 1998; Dragosits et al., 1998). An exception is the European scale inventory (Gyldenkærne et al., 2005a) with 10km x 10km resolution which was presented at the ACCENT meeting in Urbino 2005. This inventory is divided into 16 main groups (Gyldenkærne et al., 2005b) and is prepared for implementation into air pollution models (Ambelas Skjøth et al., 2004e) using separate parameterizations for each group.

On national level various inventories with high spatial resolution may be found. Examples are the UK 5km x 5km inventory (Dragosits et al., 1998), and the similar Dutch inventory (Duyzer et al., 2001), which has also been compiled for resolutions of 500m x 500m (Pul et al., 2004) and even 250m x 250m (Duyzer et al., 2001) for 11 main source groups and a Danish inventory with either 1km x 1km (Ambelas Skjøth et al., 2006) or 100m x100m

(Geels et al., 2006; Ellermann et al., 2006), where the latter is divided in 16 main source groups.

At the European level, EMEP and CORINAIR collect inventories for the annual emissions on a grid with a spatial resolution of 50km x 50km. Within the EUROTRAC GENEMIS project more detailed inventories (16.67km x 16.67km) for the emissions from EU member countries were compiled (Schwarz et al., 2000; Wickert et al., 2001). This inventory has been used to subdivide the annual EMEP emission inventories to 16.67 km x 16.67 km (Hertel et al., 2002)

2.2.2 Transport and dispersion

In describing the dispersion of the emitted ammonia in the atmosphere we may split this process in a local part at a meter to kilometre scale and a further part at a scale typically tenth to thousand of kilometres. The latter is often referred to as the mean transport of air pollution. For ammonia, emitted at low sources, particularly the local scale dispersion is important when one wants to describe concentration and depositions at a (sub) kilometer scale (Asman, 2001). The dispersion at local scale can be calculated using K-theory models in a grid framework or analytical solutions to the advection diffusion equation which deliver continuous profiles with height (Gryning et al., 1987). At what vertical grid spacing the calculation should take place depends on the spatial and temporal scale of the ammonia problem under consideration.

Describing the transport of ammonia at larger spatial scales is not different from other air pollution components. We will only give here a brief overview of the commonly used concepts. In modelling the transport or advection of in air pollution there are basically two types of models: the Lagrangian and the Eulerian type. In the Lagrangian models, an air parcel is traced along a trajectory computed from wind speed and wind direction. The trajectories in the models are used in a backward mode describing pollutants arriving at a number of selected receptor points and in a forward mode describing transport of pollutants from a number of selected sources in the model domain. In Eulerian models, calculations are performed simultaneously for a grid of receptor points. For each of these receptor points transport in and out of the grid cell is computed. Besides the transport, all other physical and chemical processes included in the models may in principle be identical for the two types of models; Lagrangian and Eulerian. It has been shown that a 20% uncertainty in the calculation of 96h back-trajectories is quite common (Stohl, 1998; Stohl & Koffi, 1998), and it is generally considered that the transport description is more accurate in Eulerian models.

The Eulerian models are generally more computer resource demanding especially when a high geographical resolution is wanted which particularly is the case for ammonia related problems. However, with the increasing computer power becoming available, and with application of nested grid techniques solving the mathematical challenge of having a high resolution domain defined within a coarser resolution domain, this problem is becoming less significant.

It has been a general tendency over the last decade that Eulerian models have been replacing Lagrangian models where these previously were in use. However, the faster nature of Lagrangian models means that they are still in use for environmental problems which desire a relatively high spatial resolution such as for ammonia.

2.2.3. Dry deposition

The dry deposition is the most important removal process of ammonia from the atmosphere. The dry deposition process is a strong function of the transport rate from the ammonia in the air to the surface and the physical, chemical and biological characteristics of the surface.

NH_3 is able to stick to almost any surface, and the dry deposition is therefore often limited by the transportation rate to the surface (Asman, 1998). One of the important path ways for dry deposition of NH_3 is uptake through the stomata of plants. However, in addition there are two other major path ways for transport of NH_3 to plants: absorption of NH_3 to dew on the plants or to the thin water film on the leaves epidermis (Nemitz et al., 2004). Experimental data have shown that a co-deposition of SO_2 and NH_3 to the surface takes place. It has thus been shown that the SO_2/NH_3 concentration ratio together with relative humidity and temperature are

important factors for the deposition of both SO_2 (Fowler et al., 2001) and NH_3 (Neirynck et al., 2005) to natural surfaces.

In transport-chemistry models, the dry deposition of gases and particles is often described with a deposition velocity and the concentration of the substance at a reference height. In turn the deposition velocity is often parameterized with a so-called resistance model in which the transport to the surface and the surface uptake is described with resistances (Wesely, 1989). The dry deposition velocity for a gaseous compound is expressed as the reciprocal value of the total resistance to transport down to and removal on to the surface:

$$V_d = \frac{1}{R_t} = \frac{1}{R_a + R_b + R_c}$$

where R_t is the total resistance, R_a is the aerodynamic resistance, R_b is the quasi-laminar sub-layer resistance, and R_c is the surface resistance.

Generally speaking the resistances that describe the physical or meteorological part of the transport are well known under the assumption that the roughness characteristics are known. Using this resistance scheme it is assumed that the surface concentration of the air pollutant is zero. However, for ammonia this is not the case and formulations for the surface concentration are needed. So for ammonia the deposition process is in escence the net result of an exchange process which is bi-directional. The surface concentration of ammonia is often referred to as the compensation point, being the concentration where the exchange of ammonia changes from deposition to (re-) emission or visa versa. A number of experimental studies have demonstrated the bi-directional nature of NH_3 exchange for various types of vegetation: including conifer forest (Andersen et al., 1999; Duyzer et al., 1992; Wyers & Erisman, 1998), moorland (Sutton et al., 1993), grass (Phillips et al., 2004), heath land (Nemitz et al., 2004), cereal crops (Schjoerring et al., 1993) and (non fertilized) agricultural grassland (Milford et al., 2001, Wichink Kruit et al., 2006).

Specific dry deposition sub-models for the surface resistance that include the description of a compensation point for NH_3 have been derived and implemented in connection with the analysis of different plant surfaces e.g. for beans (Farquhar et al., 1980), Oilseed rape plants (Husted et al., 2000), and Calluna Vulgaris (Schjoerring et al., 1998b). It is common to apply a two or three pathway process description (Erisman et al., 1994, Loubet et al., 2001): a) a stomatal pathway, which is bi-directional and modelled using a stomatal compensation point, and b) a plant surface pathway, which denotes exchange with water surfaces or waxes on the plant surface and c) a soil surface pathway particularly important for sparse canopies or wet soil. The parameterization of the stomatal resistance is rather established and can be found in Baldocchi et al., 1987 or Wesely, 1989. The stomatal compensation point may be calculated from knowledge about the aqueous phase chemistry. The equilibrium NH_3 ambient air concentration for the stomatal compensation point has been expressed as (Sorteberg & Hov, 1996):

$$[NH_3(g)] = \chi_{cp} = 10^{(1.6035 - 4207.62/T)} \frac{[NH_4^+]}{[H^+]}$$

Where χ_{cp} is the compensation point concentration of NH_3, and $[NH_4^+]$ and $[H^+]$ are the concentrations of ammonium and hydrogen ion in stomatal cavity, respectively. The ratio $[NH_4^+]/[H^+]$ is often referred to as Γ. This Γ is vegetation dependent.

It has been shown that the leaf surface may work as a capacitance for NH_3 and SO_2 uptake, and that this capacitance increase with humidity (Van Hove et al., 1989). This transport is independent of solar radiation and contrary to the uptake through stomata, this uptake will also take place during the night. However, the uptake of ammonia by the leaf surface is often parameterized by fixed low values or descriptions as a function of relative humidity (Sutton et al., 1993, Erisman et al., 1994; Sutton et al., 1998).

A special issue is the dry deposition to marine waters. Experimental studies have shown that over sea the atmospheric fluxes of NH_3 may also be upward or downward (Sorensen et al., 2003; Quinn et al., 1988; Lee et al., 1998) depending on the meteorological conditions and the relationship between the pH and contents of NH_4^+ in the upper surface waters on the one side, and the NH_3 concentrations in ambient air just above the water surface on the other side. This bi-directional nature is similar to the just described fluxes for vegetation over land. An expression for the ammonia concentration close to the marine surface is given in Asman, 1998.

2.2.4. Wet deposition

Wet deposition takes place by uptake of pollutants in precipitation (rain, snow, hail) as well as in cloud droplets – termed below-cloud and in cloud scavenging, respectively. Uptake in cloud droplets may not necessarily lead to deposition, since clouds often evaporate without producing precipitation; in average every tenth cloud encountered by an air parcel precipitates (Raes et al., 1993). A cloud droplet has a considerably longer atmospheric residence time compared with a rain droplet. In cloud scavenging is therefore generally a more efficient removal process for pollutants than the process of below-cloud scavenging. The wet deposition is a very important removal process for ammonia since ammonia is well soluble in water. For ammonia both in-cloud and below cloud scavenging are of importance. The uptake in rain and cloud droplets is limited by the diffusion into the droplet rather than the equilibrium concentration in the droplet.

In recent years many models include complex wet phase chemistry. However, in many transport-chemistry models, the overall principle behind the description of wet deposition is still considerably more simplified and based on a fixed relationship between the concentration in the droplet and the concentration in ambient air. Given this relationship is known, the rate of removal may be determined by a so-called scavenging coefficient:

$$\Lambda = \frac{S \times I}{H}$$

where Λ is the scavenging coefficient, S is the scavenging ratio (the ratio between the concentration in air and droplet), I is the precipitation intensity and H is the height at which the wet scavenging takes place.

In many cases the dependency of precipitation intensity is neglected and a constant scavenging rate is applied. The scavenging ratio for gases depends also on the solubility in water of the gas in question, the water content in the cloud and the ambient temperature. The scavenging ratio has been expressed in various ways, but one example is the one applied in the ACDEP model (Hertel et al., 1995):

$$S = \frac{1}{\dfrac{(1-cl)}{(H_{eff} \times R \times T)} + cl}$$

where cl is the cloud water content, H_{eff} is the effective Henry's law coefficient, R is the gas constant and T is the ambient temperature.

The accuracy of precipitation data is of course crucial for producing reliable wet deposition estimates. Precipitation amounts and intensity is highly heterogeneous and may vary strongly within short distances.(Badas et al., 2006)

The below-cloud scavenging of ammonia may be of importance in source regions. It has been shown from experimental results in America and South Korea that the wet deposition of NH_4^+ is correlated to the local NH_3 emission density.(Aneja et al., 2003; Park and Lee, 2002). Also van Jaarsveld et al. (2000) clearly show a correlation between spatial distribution of the wet deposition and the ammonia emissions over the Netherlands. When considering the contribution from a single farm, the wet deposition of NH_3 will, however, be very limited. This is due to the short periods with precipitation compared with the dry periods, and at the

same time a result of the short residence time of the pollutants in the nearby region of the farm. In the dutch OPS model a description of the below-cloud scavenging is incorporated (van Jaarsveld, 2004).


2.2.5. Chemical conversion

In the atmosphere NH_3 is quickly transformed into particulate NH_4^+ in the reaction with acid gases and aerosol particles (Seinfeld & Pandis, 1998). If sulphuric acid (H_2SO_4) is present in the atmosphere, gaseous NH_3 will practically always react with H_2SO_4 in gas or aerosol phase. The H_2SO_4 is formed from oxidation of SO_2 by OH radical or by ozone (O_3). The latter process is pH dependent, and may be catalyzed by NH_3 (Junge & Ryan, 1958; Apsimon et al., 1994); since NH3 increases the pH when it is taken up by the aerosols. Presence of nitric acid (HNO_3) and/or hydrochloric acid (HCl) together with NH3 will lead to an equilibrium between these gases and their aerosol phase reaction products – the ammonium salts: ammonium nitrate (NH_4NO_3) and ammonium chloride (NH_4Cl). In the reactions between gas phase NH_3 and gas phase acids, new aerosol particles are formed. However, NH_3 may also condense onto existing atmospheric particles.
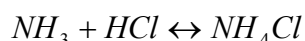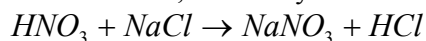
In transport-chemistry models, the reaction between NH_3 and H_2SO_4 forming ammonium bisulphate (NH_4HSO_4) and ammonium sulphate ($(NH_4)_2SO_4$) is considered as an irreversible process. For most atmospherically relevant conditions, the humidity is high enough so that most inorganic aerosol particles exist as highly concentrated salt solutions rather than solid crystals. Several field and model process studies of cloud processing have thus indicated that once ammonium sulphate is incorporated into a cloud, re-mixing with other ions in the aqueous phase can effectively achieve NH_3 degassing on subsequent evaporation of the cloud (Bower et al., 1995; Wells et al., 1997; Milford et al., 2000). The rate of the reaction between NH_3 and H_2SO_4 has been analysed in details in a number of laboratory studies (Baldwin & Golden, 1979; Huntzicker et al., 1980; McMurry et al., 1983). At high relative humidity the limiting factor for the transformation is the molecular diffusion of NH_3 to the acid particles, whereas at low humidity only 10 to 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 the large surface area makes the diffusion process more efficient. Organic material on the surface of the particles may, however, limit the uptake of NH_3 (Daumer et al., 1992). In the traditional model formulation the reaction takes place over two steps:

$$NH_3 + H_2SO_4 \rightarrow NH_4HSO_4$$

$$NH_3 + NH_4HSO_4 \rightarrow (NH_4)_2SO_4$$
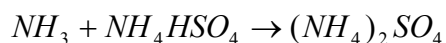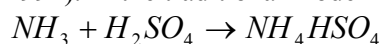
The reaction with HNO_3 is on the other hand a reversible process (Harrison & Pio, 1983; Seinfeld & Pandis, 1998). Experimental studies have shown that to a good approximation an equilibrium product of the gas phase concentrations of NH_3 and HNO_3 at saturation of the air, may be expressed by a function depending solely on temperature and humidity (Stelson et al., 1979; Stelson & Seinfeld, 1982):

$$NH_3 + HNO_3 \leftrightarrow NH_4NO_3$$
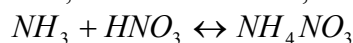
Besides the reactions with H_2SO_4 and HNO3, NH3 may also take part in a reaction with HCl and form NH_4Cl (Pio & Harrison, 1987). Usually HCl appear in very low ambient concentrations, but it may be released from sea spray particles when these take up HNO_3:

$$HNO_3 + NaCl \rightarrow NaNO_3 + HCl$$

$$NH_3 + HCl \leftrightarrow NH_4Cl$$

Similarly as for the reaction between NH_3 and HNO_3, experimental studies have determined an equilibrium product at saturation of the air with these two gases (Pio & Harrison, 1987).

In a number of transport models the conversion of ammonia to ammonium is parameterized in a simplified way using pseudo first order reaction rates of the conversion.

3 Overview current models

3.1 Overview current models
The models that took part are listed in Table 3.1.

Table 3.1. Overview of ammonia models at a national or regional scale

name	Owner/reference	type	Vertical structure; lowest troposhere	Emissions Spatial scale = horiz. Resolution Eulerian models	Emissions Sub Sector split	Emissions Temporal and meteorological variations
FRAME	CEH, Univ. Edin. Singles et al., 1998, Vieno 2005, Dore et al., 2006	Lagrangian	Variable; starting first layer from 1 m	5x5 km	Detailed agricultural activities	Annual
OPS	MNP/RIVM Van Jaarsveld, 2004	Lagrangian	Variable; calculation of profile	1x1 km (500x500 m)	Detailed agricultural activities	function of ambient temperature
MATCH	SMHI	Eulerian	Variable, usually first layer 60m, 6-11 layers below 1500m (1999-2003)	44x44 km (Europe) 11x11 km (Sweden)	(Agriculture) as one sector; minor emissions in other SNAP sectors	Simple schematic daily and seasonal variations
DAMOS	NERI (Christensen, 1997; Frohn, 2004; Frohn et al., 2001; Frohn et al., 2002)	Nested grid 3-D Eulerian	20 vertical layers with highest resolution in the PBL.	Europe on 50km x 50km, and for Denmark and nearby areas 16.67km x 16.67km.	The applied emission inventories are based on the snap coding of EMEP.	For the inner domain ammonia emission inventories are on hourly basis using local agricultural practice and meteorological conditions.
LOTOS/EUROS	TNO/MNP/RIVM	Eulerian	First layer 25 m		As one sector	Simple schematic daily and seasonal variations
EMEP-unified	UNECE/EMEP	Eulerian	First layer 90 m	50x50 km	(Agriculture) as one sector;minor emissions in other SNAP sectors	Simple schematic dialy and seasonal variations

name	Dry deposition description; All models use resistance model	Detail deposition Description; ammonia	Reference deposition description	Detail deposition; Ammonium aerosol	Wet deposition description	Chemical conversion description
FRAME	Applied to five land use classes	Two pathways; stomata and external leaf; Canopy comp. point optional	Vieno, 2005	Fixed deposition velocity	One coefficient for scavenging process	Pseudo first order reaction rate?
OPS	Applied to nine land use classes	Three pathways: stomata, external leaf surf. and soil; no stomatal/ canopy comp. point	DEPAC-routine; Erisman et al., 1994	Surface resistance; function of u_* and for forests also wind speed and rel. hum.	Scavenging coefficients for in-cloud, below cloud process	Pseudo first order reaction rate?
MATCH	Applied to ten land use classes (for Sweden)	Three pathways: stomata, external leaf surf. and soil; no stomatal/ canopy comp. point	Erisman et al., 1994	Usually a sim plified para metrised resistance used	One coefficient for scavenging process (vertical variation of scavenging coeff sometimes used)	reactions with sulphate and nitrate explicitly solved
DAMOS	Applied to nine land use classes	Two pathways: stomata and external leaf surface; no canopy comp. point. Co-deposition with sulphur dioxide.	(Frohn, 2004; Frohn et al., 2001; Frohn et al., 2002)	Assume size of ammonium containing aerosols of 0,8 μm.	Scavenging coefficient for in-cloud, below cloud scavenging	Explicit chemical mechanism with 63 compounds and 120 chemical reactions.
LOTOS/EUROS	Applied to nine land use classes	Three pathways: stomata, external leaf surf. and soil; no stomatal/ canopy comp. point	DEPAC-routine; Erisman et al., 1994	Surface resistance; function of u_* and for forests also wind speed and rel. hum.	One coefficient for scavenging process	reactions with sulphate and nitrate explicitly solved
EMEP	Applied to 16 land use classes	Two pathways: stomata and external leaf surface; no stomatal/ canopy comp. point	Simpson et al., 2003, Smith et al, 2003, Nemitz et al., 2001	Size dependent deposition velocity?	Scavenging coefficient for in-cloud, below cloud scavenging	reactions with sulphate and nitrate explicitly solved (EQSAM module)

3.2 Overview main features of each model

In this section the main features, validation and uncertainty sources of the models are presented.

3.2.1. FRAME

A summary of the model description is given below. More detailed descriptions and analysis of results are given in Singles *et al.* (1998), Fournier *et al.* (2004, 2005a, 2005b), Vieno (2005) and Dore *et al.* (2006).

3.2.1.1. Model description

- 5×5 km^2 resolution over the British Isles (incorporating the Republic of Ireland) grid dimensions: 244×172 with a 1° angular resolution in the trajectories.

- Input gas and aerosol concentrations at the edge of the model domain are calculated with FRAME-Europe, using European emissions and running on the EMEP 150 km scale grid.

- Air column divided into 33 layers moving along straight-line trajectories in a Lagrangian framework with a 1° angular resolution. The air column advection speed and frequency for a give wind direction is statistically derived from radio-sondes measurements. Variable layer thickness from 1 m at the surface to 100 m at the top of the mixing layer.

- Annual emissions of NH$_3$ are gridded separately for cattle, pigs, poultry, sheep, fertiliser and non-agricultural sources and mixed into the lowest surface layers with a source-dependent emissions height.

- Vertical diffusion in the air column is calculated using K-theory eddy diffusivity and solved with the Finite Volume Method.

- Wet deposition is calculated using a diurnally varying scavenging coefficient depending on mixing layer depth and a 'constant drizzle' approximation. A precipitation model is used to calculate wind-direction-dependent orographic enhancement of wet deposition. A single scavenging coefficient is used to represent in-could and below-cloud processes.

- Dry deposition for NH$_3$ is ecosystem specific and includes five land classes: forest, moorland, grassland, arable, urban & water. A canopy resistance parameterisation is employed including an optional canopy compensation point module for representation of bi-directional exchange of NH$_3$ (Vieno, 2005). A fixed deposition velocity is used for ammonium aerosol.

- The model chemistry includes gas phase and aqueous phase reactions of oxidised sulphur and oxidised nitrogen and conversion of NH$_3$ to ammonium sulphate and ammonium nitrate aerosol.

- The modelled chemical species treated include: NH$_3$, NH$_4^+$ aerosol, NO, NO$_2$, HNO$_3$, PAN, NO$_3^-$ aerosol, SO$_2$, H$_2$SO$_4$ and SO$_4^{2-}$ aerosol.

- Current model run time: 25 minutes on CEH Edinburgh Beowulf cluster using 100 processors.

3.2.1.2 Performance and validation of FRAME

The output from the model includes maps of annual average surface concentration of NH_3 (Figure -a) which may be used to assess exceedance of the critical level. Maps of annual wet deposition and vegetation-specific dry deposition of reduced nitrogen (Figure 3.1-a, Figure 3.1-b and Figure 3.1-c) are used for calculation of exceedance of critical loads for acid deposition and nitrogen deposition

Assessment of the accuracy of FRAME in estimating atmospheric concentrations and deposition rates of reduced nitrogen was made by comparison with measurements. For this purpose, data from the UK national ammonia monitoring network was employed comprising over 100 DELTA samplers and ALPHA samplers (http://www.cara.ceh.ac.uk/nh3network). The network uses monthly sampling from the CEH **DELTA** system, (**DE**nuder for **L**ong **T**erm **A**tmospheric sampling; Sutton *et al.*, 2001). ALPHA samplers are passive diffusion samplers, developed for long term monitoring and suitable for use in remote areas with low ammonia concentrations (Tang *et al.*, 2001). Wet deposition data were obtained from the secondary acid precipitation monitoring network, comprising fortnightly collections of precipitation from 38 sites with ion concentrations analysed by ion chromatography (NEGTAP, 2001).

Figure 3.1-a, Figure 3.1-b and Figure 3.1-c illustrates the correlation of the model with measurements. The correlation of modelled concentrations of NH_3 with measurements (Figure 3.1-a) shows considerable scatter. The principal reason for this is the highly localised nature of NH_3 emissions, such that the modelled average concentration from a 5 x 5 km^2 model grid cell may differ significantly from that measured at a specific location within the grid cell (Dragosits *et al.*, 2002). The graph shows evidence that, particularly at low concentrations, the model overestimates NH_3 surface concentrations. There is a need for finer scale national modelling of ammonia concentrations, preferably at a 1 km resolution, in order to perform a more accurate model-measurement comparison. A better correlation is observed between modelled and measured NH_4^+ concentrations (Figure 3.1-b) and wet deposition (Figure 3.1-c). This is due to the more slowly changing pattern in NH_4^+ aerosol concentrations, which are not expected to vary on a scale smaller than the 5 km model grid resolution. Figure 3.1-b shows that the model generally underestimates NH_4^+ aerosol concentrations which may indicate that the rate of production of NH_4^+ aerosol from NH_3 gas is underestimated in the model.

A sensitivity study was conducted to assess which model parameters were responsible for the greatest uncertainty in total dry and wet deposition of reduced nitrogen to the UK. For the dry deposition of NH_3, the two most significant model parameters in introducing uncertainty were the canopy resistance, R_c (for which a 100% increase resulted in a 23% reduction in dry deposition) and the emissions of NH_3 (for which a 30% increase resulted in a 32 % increase in dry deposition). For wet deposition of NH_x, the two most significant parameters were the washout coefficient (for which a 100% increase resulted in a 32% increase in wet deposition) and the vertical diffusivity (for which a 100% increase resulted in a 14% increase in wet deposition).

Observation sites of the UK national ammonia monitoring network can be grouped into three categories representative of: mixed agricultural, nature reserve and woodland. Figure 3.2.1.2 shows the correlation between the FRAME model predictions and the site observations for land-use specific sites. A strong difference in the gradient of the line of best fit is evident for the different groups of land categorisation. The model appears to be significantly over-estimating ammonia concentrations at low semi-natural sites. This occurs because nature sites tend to be 'havens' of low ammonia concentration within a model grid square which may have average emissions that are associated with intensive agricultural activity. On the other hand, it is noticeable that this division between different site types much improves the correlation between measurement and modelling for woodland and semi-natural areas (with R^2 of 0.84, 0.91) compared with all the sites combined (R^2=0.48). Sites in such woodland and semi natural areas will be less influenced by local sources than the sites in

mixed agricultural landscapes (R^2 0.58), demonstrating that natural spatial variability within each 5 x 5 km^2 grid square is a key reason for the modest R^2 values obtained between measured and modelled NH_3 concentrations.
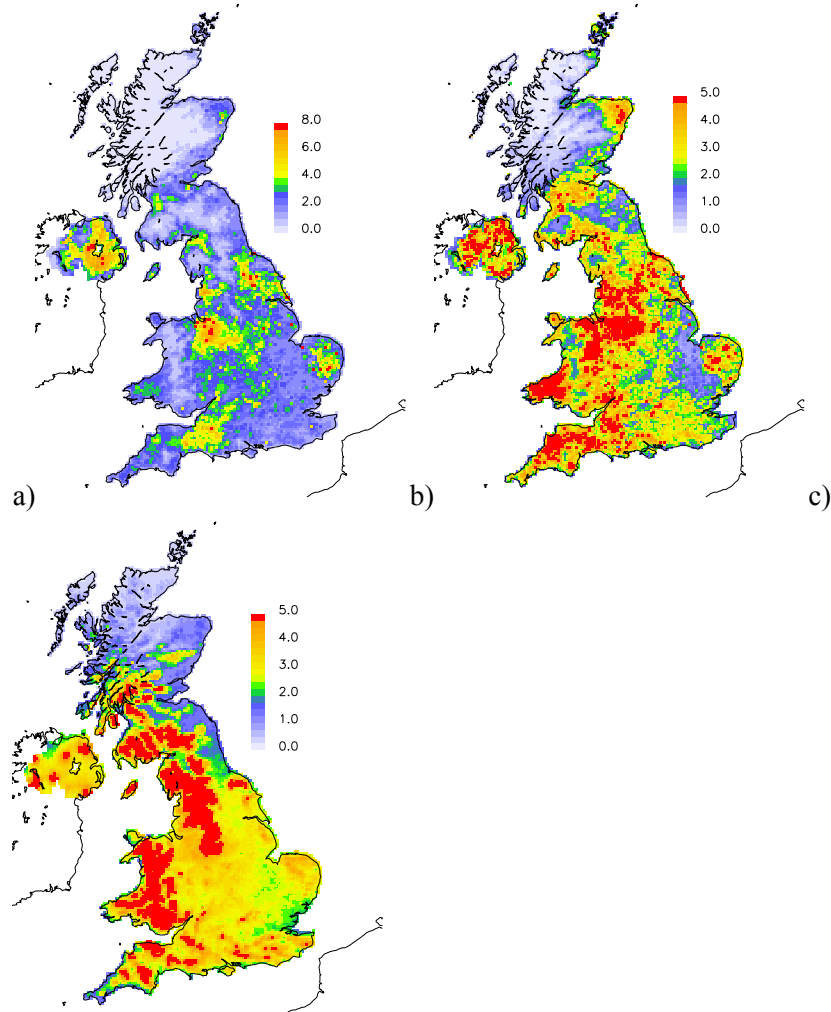

Figure 3.2.1.1: UK FRAME model prediction for 2002: a) NH3 surface concentration ($\mu g\ m^{-3}$), b) NHx dry deposition (kg N ha^{-1}) and c) NHx wet deposition (kg N ha^{-1}).
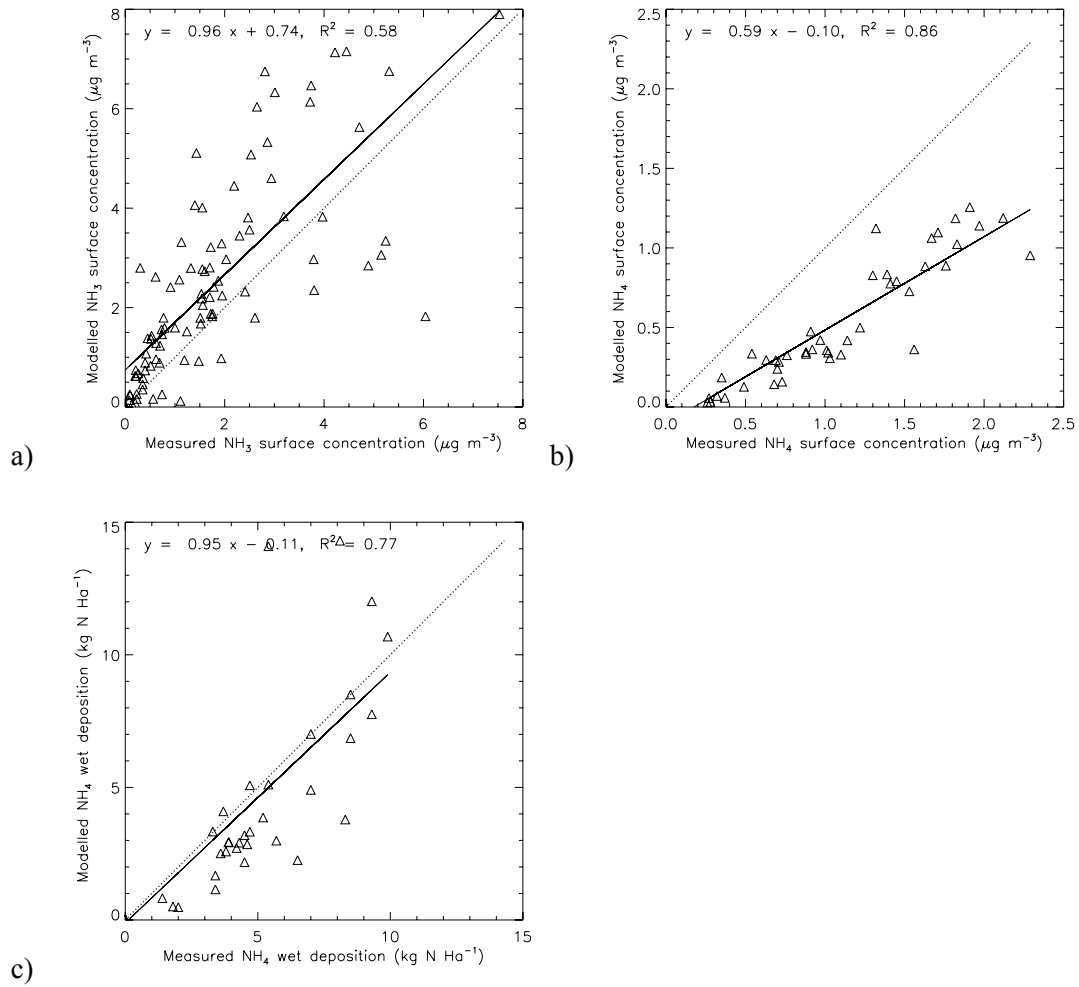
a)

b)

c)

Figure 3.1.1.2: Correlation of modelled: a) NH_3, b) NH_4^+ aerosol concentrations and c) NH_4^+ wet deposition with measurements from the national monitoring network for the year 2002 over the UK.
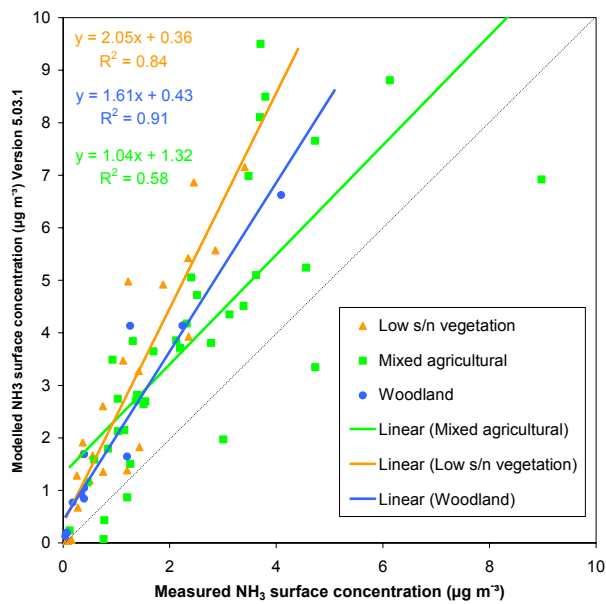

Figure 3.2.1.2: 1999 FRAME NH_3 predictions versus UK National ammonia monitoring network ($\mu g \ m^{-3}$).

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3.2.2 OPS

3.2.2.1 Model description
General
The OPS model represents a combination of a Gaussian plume model for local-scale application and a trajectory model for long-range transport (Van Jaarsveld, 1995; 2004). Especially in the case of ammonia the local scale plume model allows for a detailed approach of the low level release height in combination with near-source deposition. Dry and wet deposition for both NH_3 and the secondary product, NH_4^+ are calculated with a spatial resolution mainly dependent on the resolution of the emission data. The model is used for issues on acidification/eutrophication as well as in heavy metals and persistent organic pollutants. Asman and van Jaarsveld (1992) applied the model to the calculating the NH_x distribution in Europe. Furthermore, the model was successfully applied to deduce SO_2 and NO_x trends from measurements of ambient concentrations. An early version of the OPS model (called TREND model) has taken part in a number of model intercomparison studies (Derwent et al., 1989, Sofiev et al., 1999). More recently, results of the OPS model were compared with those of the EMEP unified model on the issue of, among others, ammonia and ammonium concentration and deposition in the Netherlands (Velders et al., 2003).
In the next three sections we describe the processes which are important particularly for ammonia.

Specific processes
Emission process
The emissions from land spreading of manure (EC_{spread}) is adjusted to the meteorological conditions. The factor relative to the average emission strength reads:

$$EC_{spread} = 1 + 1.55\ 10^{-5}\ [\ (100\ /\ Ra\ )^{0.8}\ (\ T + 23\ )^{2.3}\ ]^{1.25} \qquad (3.2.2.1)$$

in which T is the ambient temperature (in ^{o}C) and Ra the aerodynamic resistance over the lower 4m of the boundary layer. In the latter the effect of wind speed and atmospheric stability is taken into account. The relation between emission and meteorological conditions is a fit on the results of the numerical air-soil exchange model DEPASS (Van Jaarsveld, 1996). The factor determined in this way amounts to 1.8 on sunny days to 0.07 on very stable conditions. On average the factor varies from about 0.4 in January to 1.5 in July.

The emissions from animal housings (EC_{house}) are parameterized taking into account the outdoor temperature T:

$$EC_{house} = 1 + 0.04 * (\ T - T_{gem}\ ) \qquad (3.2.2.2)$$

Where T_{avg} is the long-term average outdoor temperature, for the Netherlands taken 10°C. The average factor for emissions from animal housings is about 0.7 in January and 1.3 in July. The factor 0.04 is based on relations with indoor temperatures and mechanically ventilated cattle-housings. It is assumed that the temperature variations for indoor and outdoor are similar. There is no distinction between the housing systems for cattle, pigs and poultry nor for natural and mechanically ventilated systems. Also there is no wind speed dependency included.

Vertical dispersion
The vertical dispersion is described for a number of regimes in the atmospheric boundary layer each characterised by distinct scaling parameters (Holtslag and Nieuwstadt, 1986). The parameterization of the vertical dispersion (main parameters σ_z) is modelled dependent on the height of the emission or centre of the plume and the atmospheric stability. In this way a

dedicated modelling of the local dispersion close to (low level) sources is obtained of which results are verified using data of the so called Prairie grass experiment (Van Ulden, 1978).

Chemical conversion

The formation of ammonium is simulated using a one-dimensional model, including the relevant chemical reactions as applied in the MPA model (De Leeuw *et al*., 1990) and also deposition processes. This model is used on the basis of actual meteorological data and supplied with background concentrations of SO_2, NO_x, NH_3, O_3 and OH radicals. The conversion rate follows from the production of ammonium sulphate and ammonium nitrate over a (long) period, divided by the mean ammonia concentration. The conversion rates are then translated into a parameterisation for this rate using regression analyses. This resulted in the following relation between the $NH_3 > NH_4$ conversion rate K_{NH3}:

$$K_{NH3} = 0.67 + 1.36\ C_1 + 10.7\ C_2 + 3.06\ (C_2)^4 - 0.29\ (C_2)^6 \qquad (3.2.2.3).$$

Where $C_1=NO_2/NH_3$ and $C_2=SO_2/NH_3$ both in ppb/ppb.
Background concentrations on a 10x10 km scale for the period 1980-2002 are available for calculating the conversion. Averaged over the Netherlands the conversion in 1980 was about 16%/h and in 1997 about 5%/h.

Deposition

Dry deposition of ammonia is parameterized following the well known resistance modelling. This is built in the module DEPAC and is described in detail by Erisman et al., 1994. The deposition to the surface is described for three pathways: stomata, external leaf surface and soil. The resistances are a function of the wetness of the surface indicated with a switch wet/dry and of the ratio between the NH_3 and SO_2 concentrations indicated with a switch high/low. The latter switch is always set to high for the Dutch situation.
Aerodynamic resistances are calculated as a function of atmospheric conditions and roughness length. The dry deposition of particles is also modelled with a resistance scheme. It consists of the aerodynamic resistance and a R_{part} in which all surface related processes are incorporated. The R_{part} is split in a resistance parameterization for surfaces with a roughness length below 0.5 m in which the description is a function of turbulence alone and above 0.5 m in which the description is a function of turbulence, wind speed at canopy height and a particle collection efficiency. The latter has a value for dry and wet conditions.

Wet deposition is described as a combination of in-cloud and below cloud scavenging. Near sources a clear relation between the ammonia concentrations in rain and air are found (Van Jaarsveld et al., 2000). This means that below cloud scavenging is an important process for ammonia. The process of wet scavenging is considered as a irreversible process for a well soluble component as ammonia. The scavenging coefficient is parameterized as a function of the molecular diffusion, rain intensity and the drop-size distribution.

3.2.2.2. *Performance and validation*

Ammonia concentrations were measured using passive samplers during one year at 159 locations equally distributed over the Netherlands. This dataset is used here as a reference for the capability of the model to describe spatial differences. Model calculations were carried out using 500 x 500-m resolution emission data as well as 5000 x 5000 m data. Results given in Fig. 3.2.2.1 show that the model simulates the spatial distribution nicely but that there is still an influence of the emission resolution. Of the 159 locations, 4 were situated within 50 m from animal housings. Yet, these locations do not pop up as outliers in the comparison indicating that the OPS model is capable of describing concentration gradients at a very local scale as long as the emissions are represented at the appropriate spatial scale.

Nevertheless, the concentrations have been found to be underestimated (about 30%) by the model on the basis of these emissions. The underestimation found for the concentrations at the passive sampler sites is similar to the underestimation found for the LML network sites. This again indicates that the LML sites are representative for the range of ammonia concentrations in the Netherlands.
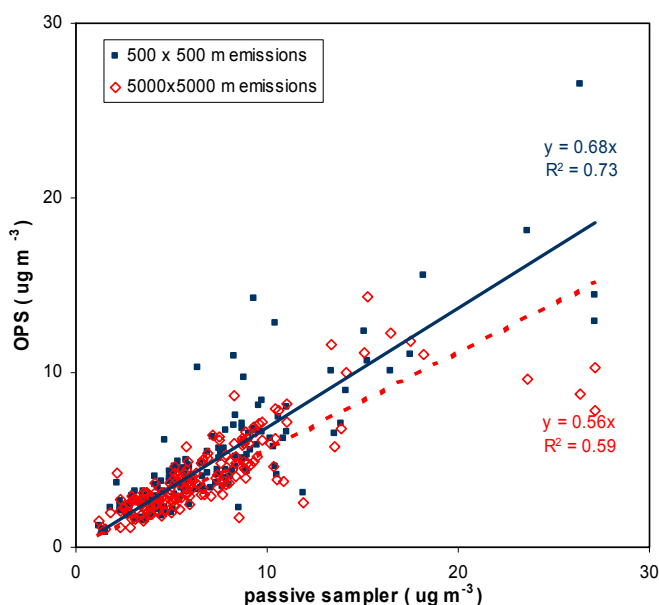

Figure 3.2.2.1: Ammonia concentrations for 159 locations in the Netherlands calculated with the OPS model based on emissions on a 500m resolution (black squares) and 5000m resolution (open diamonds) against ammonia concentrations measured with passive samplers (Van Pul et al., 2004)

A similar comparison was made on a much more local scale in the so called VELD project. In this project local emissions were inventoried with the help of local farmers. On the basis of these detailed emissions more than 75% of the (annual average) concentration differences (50 locations with passive samplers) within an area of 3x3 km could be explained by the model. Also this result indicates that simulations of atmospheric ammonia concentrations can be significantly improved when actual and detailed emission data is available.
In Fig. 3.2.2.2 similar results are given for ammonium concentrations and wet deposition. Here the model results are compared to observations of the LML network for the year 2000. This comparison shows that the model not only underestimates the ammonia concentration but also ammonium and wet deposition. Moreover, the underestimation appears to be systematic since the relative underestimation is nearly constant over the years (Fig. 3.2.2.3). Trends in atmospheric levels are well simulated by the model. This means that the change

over the years may be attributed to a general change (decrease) in emissions.
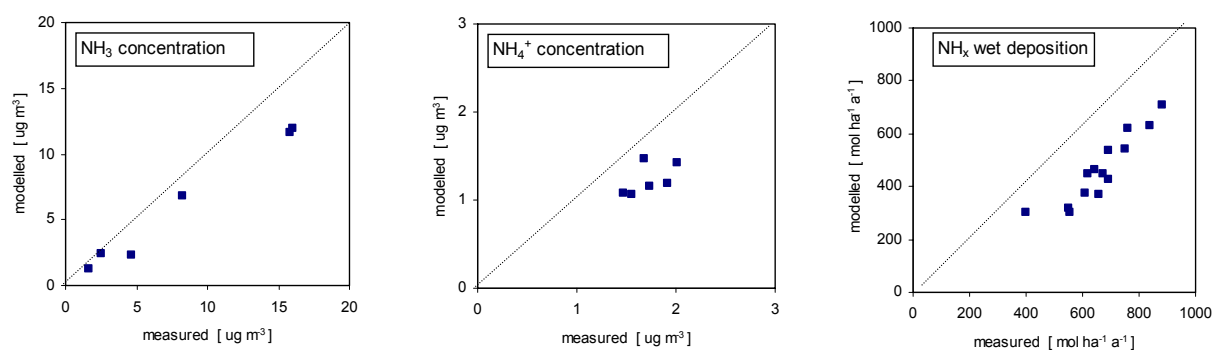

Figure 3.2.2.2: Comparison of the (2000) modelled spatial distributions of NH_3, NH_4 concentrations and NH_x wet deposition with observations of the Dutch Monitoring Network (LML).
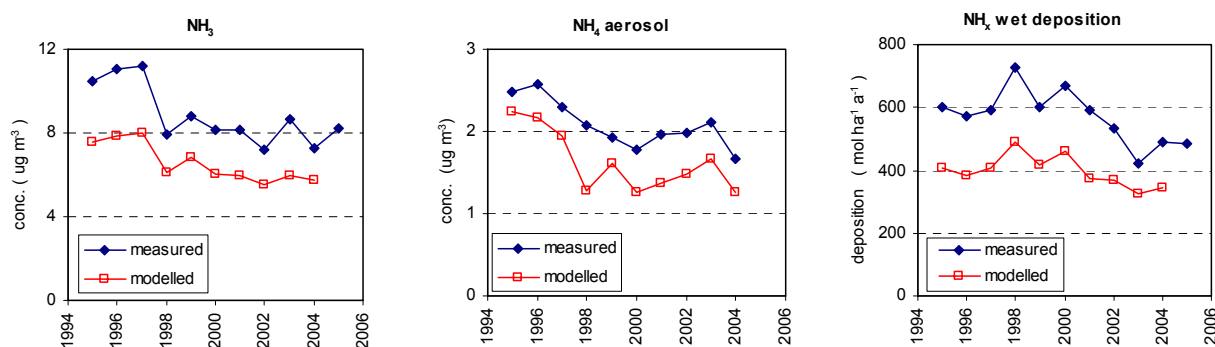

Figure 3.2.2.3: Trends in measured and modelled NH_3 and NH_4^+ concentrations and wet deposition

Uncertainties
Most sensitive (and uncertain) process in the model is the surface exchange process. Sensitivity analysis shows that the parameterization of the surface resistance is critical. Furthermore, the simulation of dispersion, transport and dry deposition in the lower part of the boundary layer during stable atmospheric conditions has a large impact on local concentrations. Also the emission term for land spreaded manure plays an important role. In terms of source categories it is shown that the contribution of land spreaded manure is significantly underestimated. This points most probably to too low emissions for this category.

Main conclusions
- A systematic difference of approx. 30% on a yearly basis is still found between measured and modelled NH_x species in the Netherlands. The underestimation is largest in the early spring situation.
- Trends in NH_x species in the Netherlands can be explained to a large extent by changes in anthropogenic NH_3 emissions
- Spatial variations in ammonia concentrations can be well simulated when actual emission data is available.

3.2.3. The MATCH model

3.2.3.1 Model description
The Multi-scale Atmospheric Transport and Chemistry (MATCH) model is a three-dimensional, Eulerian model developed at the Swedish Meteorological and Hydrological Institute (SMHI). It is used in a range of applications from urban scale studies (e.g., Gidhagen et al., 2005) on ca. 5km, or higher, resolution to regional/continental scale studies on acidifying/eutrophying deposition and photochemistry (e.g. Andersson et al., 2006, Langner et al., 2005; Siniarovina and Engardt, 2005). MATCH is also used for air pollution assessment in Sweden and the Baltic Sea region. The air pollution budgets of nitrogen and sulphur compounds for Sweden are calculated annually, using a system combining the MATCH model calculations and monitoring data from Sweden and the neighbouring countries. The model is also used operationally to provide forecasts of radioactivity in case of nuclear emergencies in Europe (Langner et al., 1998).

Emissions
Anthropogenic emissions of NH_3, NO_x, SO_x, NMVOC and CO (and natural emissions of SO_x) are taken from the UNECE/EMEP database (50km x 50km resolution; Vestreng et al., 2003) and regridded to the MATCH model grid (usually using a 0.4°x0.4° (ca. 44 km) resolution). For Sweden, higher resolution emission data (ca.1-5 km resolution) are available and these are used in national applications, e.g., the annual air pollution assessments, for the Swedish EPA, which are done at 11 km horizontal resolution. Emissions are handled in a simple way with emission heights (or profiles) and temporal variations specified for the different emission sectors used. Standard plume-rise calculations can be performed based on stack parameters (stack diameter, effluent temperature, volume flux). Individual point sources can be included but this is rarely done in the large scale studies with the photochemistry model.
For ammonia the agricultural emission sector dominates. For this sector all emissions are released in the lowest model level. Usually the same vertical resolution is used as for the meteorological data; this means that the surface emissions are spread in a ca 60m thick layer, when using the operational HIRLAM data from SMHI for Europe (for the years 1999-2003). Emissions of ammonia are not dependent on meteorological parameters. Only variations depending on month, weekday and hour are used. The standard temporal variation used in MATCH for the agricultural sector is as follows:

Month	J	F	M	A	M	J	J	A	S	O	N	D
Agric.	0.45	1.3	2.35	1.7	0.85	0.85	0.85	1.0	1.1	0.65	0.45	0.45

Day	MO	TU	WE	TH	FR	SA	SO
Agric.	1.0	1.0	1.0	1.0	1.0	1.0	1.0

Hour	1	2	3	4	5	6	7	8	9	10	11	12
Agric.	0.60	0.60	0.60	0.60	0.60	0.65	0.75	0.90	1.10	1.35	1.45	1.60
Hour	13	14	15	16	17	18	19	20	21	22	23	24
Agric.	1.80	1.75	1.70	1.55	1.35	1.10	0.90	0.75	0.65	0.60	0.60	0.60

In the EuroDelta-project more detailed temporal variations were used, based on data from IER/GENEMIS and TNO. In this case the monthly and weekly variations were different for different countries.

Transport

The basic transport model includes modules describing emissions, advection, turbulent diffusion and dry and wet deposition. Depending on the application specific modules describing, e.g., chemistry can be added to the basic transport model. MATCH is an "off-line" model. This means that atmospheric weather data are taken from some external source, usually a numerical weather prediction (NWP) model, and fed into the model at regular time intervals, currently every three or six hours. Such data are then interpolated in time to yield hourly data. Special attention is given to interpolation of the horizontal wind where vector increments are applied. The vertical wind is calculated internally to assure mass consistency of the atmospheric motion after the time interpolation of the horizontal winds. The model design is flexible with regard to the horizontal and vertical resolution, principally defined by the input weather data, and allows for an arbitrary number of chemical compounds. The advection scheme is Bott-type (Bott 1989), using fourth-order scheme in the horizontal and a second-order scheme in the vertical. A complete description of the transport model can be found in Robertson et al. (1999).

The vertical resolution of the model is usually based on the resolution of the meteorological data. Typically the lowest model level has a thickness of ca 60m when the operational HIRLAM NWP model of SMHI is used. For the years 1999-2001 the total number of model levels were 14 and for 2003 this was increased to 22 levels. In both cases the model vertical extent is ca 5500 m.

Deposition

The dry deposition of gaseous and particulate species is calculated using a resistance approach depending on land-use. For MATCH-Europe a simple scheme is used with only four different land-use classes (Water, Forest, Low vegetation and No vegetation). The dry deposition flux is proportional to the concentration of each component and the inverse of the sum of the aerodynamic resistance and a species specific surface resistance. For simplicity the same aerodynamic resistance is used for all surfaces within a grid square. For species with stomatal uptake as a major deposition route, surface resistance is calculated taking into account soil moisture, soil type, vegetation type, leaf area index, photosynthetic active radiation and temperature. For other species a simpler approach is used with only monthly varying surface resistances. For NH_3 and some other species lower deposition velocities are used for snow covered surfaces.

In the air pollution assessments for Sweden a more detailed dry deposition scheme is used with ten land use classes and a dry deposition parameterization based on Erisman et al. (1994) and Bartnicki et al. (2001).
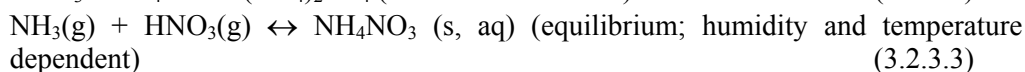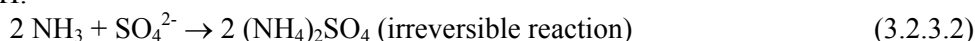
Wet scavenging of NH_3 is assumed to be proportional to the precipitation intensity and a species-specific scavenging coefficient:

$$\frac{dc_i}{dt} = -c_i \Lambda_i P \qquad\qquad (3.2.3.1)$$

where c_i is the concentration of species i, Λ_i is the scavenging coefficient (s^{-1} mm^{-1} hour) and P is the precipitation rate (in mm $hour^{-1}$). A vertical variation of the scavenging coefficient is often used. For example, the NH_3 the scavenging coefficient may be set to 0.000195 s^{-1} mm^{-1} hour in the lowest model level, increasing to 0.000389 s^{-1} mm^{-1} hour above the boundary layer zi. For particulate ammonium slightly lower values are used: 0.000028 s^{-1} mm^{-1} hour to 0.000195 s^{-1} mm^{-1} hour.

Chemical conversion

Only a few chemical reactions are considered for the ammonia-ammonium conversion in MATCH:

$2 NH_3 + SO_4^{2-} \rightarrow 2 (NH_4)_2SO_4$ (irreversible reaction) (3.2.3.2)

$NH_3(g) + HNO_3(g) \leftrightarrow NH_4NO_3$ (s, aq) (equilibrium; humidity and temperature dependent) (3.2.3.3)

The sulphate/sulphuric acid participating in the first reaction can be directly emitted or formed in the model by gas phase oxidation of SO_2, by OH or CH_3O_2, or aqueous phase oxidation, by H_2O_2 or O_3, in cloud droplets (a constant cloud water pH is used, usually set to 5).

As an alternative to the first reaction ammonium sulphate production can be considered as leading to an equal mixture of NH_4HSO_4 and $(NH_4)_2SO_4$:

$NH_3 + SO_4^{2-} \rightarrow \frac{1}{2}NH_4HSO_4 + \frac{1}{2}(NH_4)_2SO_4$ (3.2.3.4)

3.2.3.2. Performance/Validation

The MATCH-Europe model has, until recently, not been very thoroughly validated for ammonia or ammonium. The model has participated in some European model intercomparisons, e.g., within EuroTrac-2 (Hass et al. 2003) and, more recently, the EuroDelta project. Much of the focus has been on aerosols. Thus, ammonium has received much more attention than gaseous ammonia.

In the EuroDelta project five different regional scale models participate (Chimere, RCG, EMEP, MATCH and LOTOS/EUROS; in the validation/intercomparison part DEHM and the global TM5 models also took part). The models were run for two different meteorological years (1999 and 2001) using a number of different emission scenarios. A validation of the models performance for 2001 for aerosol components, including ammonium, will be published. The validation is mainly against EMEP measurement stations in the western/central/southern part of Europe (the domain common to all participating models).

For the measurement stations that measure total NHx (NH4 + NH3) MATCH, on the average, underestimates the concentrations by ca 15% and the average station correlation coefficient (for daily concentrations) is ca 0.57 (the ensemble of all the participating models had the correlation coefficient 0.54 and essentially zero average bias). The RRMSE was 50% both for the MATCH model and the ensemble of all models. The spatial correlation coefficient was 0.77 for the MATCH model, which was about equal to the EMEP model and slightly lower than the ensemble of models (0.80).

The MATCH results are of similar quality for stations that measure aerosol ammonia (NH4), average correlation coefficient 0.61, RRMSE 44%, spatial correlation coefficient 0.85. The average bias is small but MATCH shows a tendency to overestimate spring and late summer concentrations and underestimate winter concentrations.

Results for gas phase ammonia are in general poorer. The concentration is usually heavily underestimated and correlation coefficients are low, when comparing to daily measurements at EMEP stations. There are probably several reasons for this. It seems likely that some of the most important are the relatively coarse resolution of the model (both vertically and horizontally) and overestimated deposition of NH3 in the MATCH-Europe version used in the EuroDelta project.

3.2.4. DAMOS

The Danish Ammonia Modelling System (DAMOS) is a combination of the Eulerian long-range transport model DEHM (Danish Eulerian Hemispheric Model, (Christensen, 1997; Frohn et al., 2002)) and the Gaussian local scale transport-deposition model OML-DEP (Olesen, 1995). OML-DEP makes use of the surface depletion method from (Horst, 1977) for the dry deposition and uses a pseudo first order reaction velocity for the conversion of NH3 to NH4+ (Asman et al., 1989). The DEHM calculations are performed for the entire Northern Hemisphere with 2-way nesting; the outer domain using a 150km x 150km resolution, for Europe a 50km x 50km resolution is applied, and for Denmark and nearby areas using a 16.67km x 16.67km resolution. These calculations are based on meteorological data generated by MM5 (Grell et al., 1994). The local scale model OML-DEP is applied for a 16km x 16km domain that covers the nature area for which detailed deposition mapping is needed. DEHM background concentrations of ammonia and sulphur dioxide are obtained for each hour by interpolation between up to three grid cells upwind from the OML-DEP domain. Meteorological data are from the MM5. OML-DEP calculations are performed for 40 x 40 receptor points evenly distributed over the domain each representing a 400m x 400m area.
The ammonia emissions are computed using the parameterisations with high spatial and temporal resolution based on local agricultural practice and meteorological conditions. These emissions are aggregated from an inventory on single farm and field level (Gyldenkaerne et al., 2005; Skjoth et al., 2004). The high resolution in the inventories has shown to be very important for the model performance (see the discussion in (Hertel et al., 2006)).
The dry deposition velocities are in both DEHM and OML-DEP performed with the same module which is based on the methodology in the EMEP model (Simpson et al., 2003). The deposition is calculated for nine land use categories.
An explicit chemical mechanism with 63 chemical compounds and 120 chemical reactions is used. The mechanism includes gas phase ammonia reactions with sulphuric and nitric acid forming aerosol phase ammonium compounds.

3.2.5. LOTOS/EUROS

3.2.5.1. Model description

LOTOS-EUROS is a three-dimensional (3D) chemistry transport model for Europe. The domain of LOTOS-EUROS is the area between 35° and 70° North and 10° West and 40° East. The projection is normal longitude-latitude and the standard grid resolution is 0.50° longitude x 0.25° latitude, approximately 25x25 km. In the vertical there are three dynamic layers and an optional surface layer. The model extends in vertical direction 3.5 km above sea level. The lowest dynamic layer is the mixing layer, followed by two reservoir layers. The height of the mixing layer is part of the diagnostic meteorological input data. The heights of the reservoir layers are determined by the difference between the mixing layer height and 3.5 km. Both reservoir layers are equally thick with a minimum of 50m. Simulations usually performed including the optional surface layer of a fixed depth of 25 m. Hence, this layer is always part of the dynamic mixing layer.

The transport consists of advection in 3 dimensions, horizontal and vertical diffusion, and entrainment/detrainment. The recently improved and highly-accurate, monotonic advection scheme developed by Walcek (2000) is used to solve the advection. Each hour the vertical structure of the model is adjusted to the new mixing layer depth. After the new structure is set the pollutant concentrations are redistributed using linear interpolation. Vertical diffusion is described using the standard Kz-theory. Vertical exchange is calculated employing the new integral scheme by Yamartino et al. (2004).

LOTOS-EUROS uses the TNO CBM-IV (Schaap et al., 2005) scheme which is a modified version of the original CBM-IV (Whitten et al., 1980). The scheme includes 28 species and 66 reactions, including 12 photolytic reactions. N_2O_5 hydrolysis is computed following Dentener and Crutzen (1993) and Jacob (2001). The formation of ammonium nitrate and ammonium sulphate is represented using ISORROPIA (Nenes et al., 1999). The dry deposition in LOTOS-EUROS is parameterised following a resistance approach (Erisman et al., 1994). No compensation point is taken into account for the deposition/emission of ammonia. Below cloud scavenging is described using simple scavenging coefficients for gases (Schaap et al., 2005) and following Simpson et al. (2003) for particles. In-cloud scavenging is neglected due to the limited information on clouds. Neglecting in-cloud scavenging results in too low wet deposition fluxes but has a very limited influence on ground level concentrations of ammonia and other components (see Schaap et al., 2004).

The standard meteorological data for Europe are produced at the Free University of Berlin employing a diagnostic meteorological analysis system based on an optimum interpolation procedure on isentropic surfaces (Kerschbaumer and Reimer, 2003). The anthropogenic emissions used here are a combination of the TNO emission database (Visschedijk and Denier van der Gon et al., 2005) and CAFÉ baseline emissions for 2000. For each source category and each country, we have scaled the country totals of the TNO emission database to those of the CAFÉ baseline emissions. Hence, we use the official emission totals as used within the LRTAP protocol but we benefit from the higher resolution of the TNO emission database (0.25x0.125 lon-lat). For a detailed description of the model and the input data we refer to Schaap et al. (2005)

Discussion on treatment ammonia emissions

The seasonal variation in ammonia emissions is uncertain and may differ regionally as function of farming procedures and climatic conditions. The seasonal variation in the ammonia emissions is modelled based on experimental data representative for the Netherlands (Bogaard and Duyzer, 1997). The seasonal variation shows a distinct maximum in March and a slight maximum in August due to the application of manure on top of a function that roughly scales with duration of daylight. Following Asman (2001) we assumed a diurnal cycle in the emission with half the average value at midnight and twice the average at noon. We recognize that these functions may only represent practices in nortwestern Europe.

Exchange, emission or deposition, of ammonia depends on the compensation point, which refers to the situation in which the ammonia concentration in air is in equilibrium with the vegetation. Assessing the compensation point of ammonia is not possible for many surfaces (Asman, 2001). Furthermore, the sub-grid variability in this parameter is expected to be very high. Hence, we do not take it into account.

Due to the emissions there is a large vertical gradient of ammonia concentrations in the source areas with highest concentrations near the ground. However, in our model the emissions are completely vertically mixed over the first mixing layer. We may therefore underestimate the effective dry deposition of ammonia close to the sources. To account for this effect Asman and Janssen (1987) and Dentener and Crutzen (1994) lowered the 'effective' emissions in their model by 25 %, assuming that this part of the emission was removed on sub-grid scales. Janssen and Asman (1988) argued that by uniformly lowering the ammonia emission, ammonium formation could be underestimated and more sophisticated correction factors were proposed. These correction factors would be highly variable depending on region, the surface roughness downwind of the sources, availability of acidic precursors, meteorological conditions and the history of the air parcel (e.g. Asman, 1998). Much of this information is not available in our model and therefore no correction factors are used in our model.

The deposition is treated following Erisman et al. (1994). The deposition velocity is calculated for 9 land use classes within a grid cell and then a weighted average (as function of area) is used to assess the average dry deposition velocity.
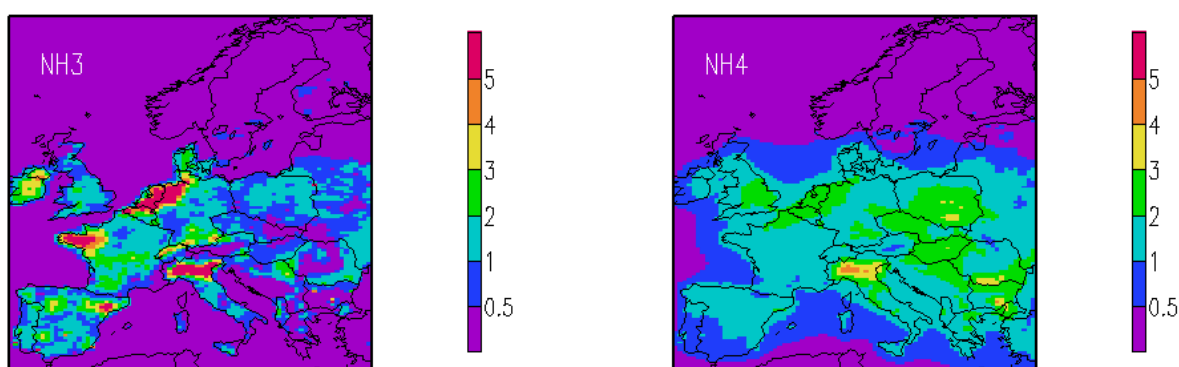
3.2.5.2. Performance and, validation

Figure. 3.2.5.1.. Annual modelled concentrations of ammonia and ammonium for 2001.

The LOTOS-EUROS model calculates the concentration in air and dry deposition fluxes on an hour by hour basis. As we operate a regional model we compare our results mainly to the EMEP network, which has only a few stations for NH3. However, a larger set of measurements is available for TNH4 (ammonium plus ammonia). In figure 3.2.5.3, we compare modelled and measured annual average concentrations for TNH4 for 2001. The nice spatial correlation shows that the model is able to capture the large scale variability in ammonia levels in Europe. The temporal correlation is on average 0.44 (-0.17 to 0.77), which is not very good.

In source areas the ammonia concentrations are underestimated significantly by the model. For example, At Vredepeel or Braunschweig we underestimate by a factor 3. Also, the temporal correlation is low. This is not a surprise given the resolution of the model and the siting of the stations. Simulations on a higher resolution are needed and planned for next year.
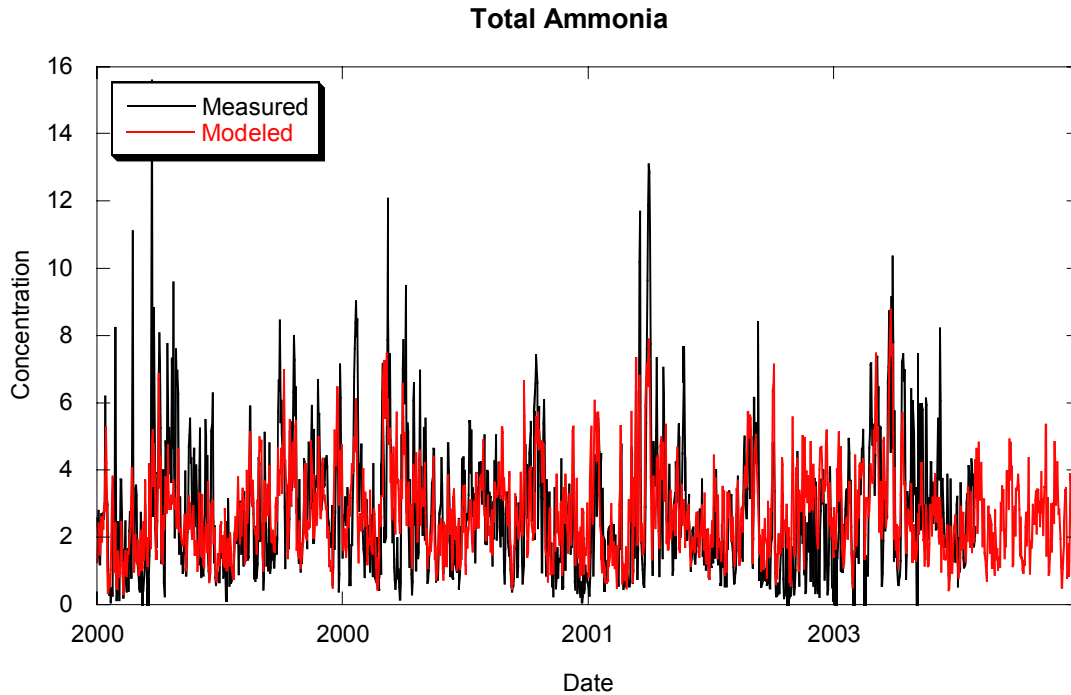
Total Ammonia

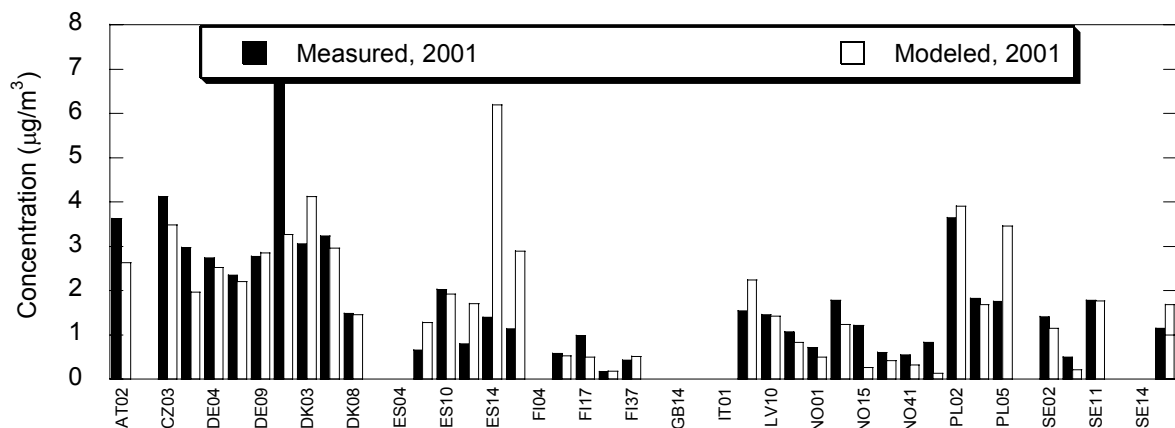Figure 3.5.2.2. Total ammonia concentrations at Zingst, Germany

Figure 3.5.2.3. Comparison of measured and modelled annual average TNH4 concentrations for 2001 in Europe

Table 2. Comparison between annual average concentrations of NH3 at a few sites in Europe.

Site	Code	Measured	Modelled
Braunschweig	DE97	5.4	1.4
K-puszta	HU02	1.6	1.0
Montelibretti	IT01	1.7	1.5
Vredepeel	NL10	19.0	8.6

The model is able to simulate the large scale variability and temporal variation at background sites. In source areas the levels are largely underestimated and the temporal correlation is not good. Reasons are the inherent fast mixing due to the Eulerian approach in combination with the averaging in the timing of the emissions which may in fact be highly variable.

3.2.6. EMEP Unified model

3.2.6.1. Model description

The Eulerian EMEP model is a multi-layer atmospheric dispersion model designed for simulating the long-range transport of air pollution over several years. The model domain is centered over Europe and also includes most of the North Atlantic and the polar region. The model has 20 vertical layers in σ-coordinates below 100hPa, with a surface layer of approximately 90 meters. It is primarily intended for use with a horizontal resolution of ca. 50x50km^2 (at 60 degrees N) in the EMEP polar stereographic grid. The EMEP Unified model use meteorological data from PARLAM (PARalell version of HIRLAM) [Benedictow, 1999], a dedicated version of the operational HIRLAM model (High Resolution Limited Area Model) maintained and verified at MET.NO. The numerical solution of the advection terms is based upon the scheme of Bott [Bott, 1989ab], as described in previous EMEP reports. The fourth order scheme is utilized in the horizontal directions. In the vertical direction a second order version applicable to variable grid distances is employed.

Chemical conversion

The scheme is based upon the ozone chemistry from the Lagrangian photo-oxidant model (Simpson et al. 1993, Simpson 1995, Andersson-Sk¨old and Simpson 1999, Kuhn et al. 1998), but with additional reactions introduced to extend the model's coverage to acidification and eutrophication issues. These additions include ammonium chemistry, gas and aqueous oxidation of SO2 to sulphate, and night-time production of nitrate. Additionally, a coarse particle nitrate species has been introduced. In total, the chemical scheme uses about 140 reactions between 70 species. The module EQSAM (Metzger et al. 2002b,a) is used to calculate the partitioning between gas and aerosol phase of HNO3 and NO3 aerosol and NH3 and NH+4 aerosol, respectively.

Dry Deposition

The dry deposition module is based on the resistance analogy and the dry deposition velocity depends on the aerodynamic resistance, the quasi-laminar resistance and the surface (canopy) resistance. The deposition velocity is calculated independently over each land-cover and applied as a net deposition rate (weighted by the fraction of each land-cover type within the grid) to the modeled concentration at the reference height.

R_c is divided into a stomatal (R_{sto}) and a nonstomatal component (R_{ns}), where the R_{sto} parameterization is described in Simpson et al.,2003.

Surface resistance, Rc

Surface (or canopy) resistance is the most complex variable in the deposition model, as it depends heavily on surface characteristics and the chemical characteristics of the depositing gas. Our approach makes use of bulk canopy resistances and conductances (R and G terms, where Gx = 1/Rx for any x), and of unit-leaf-area (one-sided) resistances and conductances, which we denote with lower-case letters r, g. The general formula for bulk canopy conductances, Gc, is:

$$G_c = LAI \cdot g_{sto} + G_{ns}$$

(3.2.6.1)

where LAI is the leaf-area index (m2 m−2, one sided), g_{sto} is the stomatal conductance, and G_{ns} is the bulk non-stomatal conductance. For non-vegetative surfaces only the last term is relevant.

At sub-zero temperatures many of the following formulas use a low-temperature resistance. We use the formulation of Wesely (1989), where Ts is here in ◦C:

$$R_{low} = 1000 \, e^{-(T_s+4)}$$

(3.2.6.2)

Non-stomatal resistances

G_{ns} is calculated specifically for O3, SO2, and NH3. Values for other gases are obtained by interpolation of the O3 and SO2 values.

The non-stomatal resistance R_{ns} for NH3 is assumed to depend upon surface (2 m) temperature, Ts (◦C), humidity levels, RH (%), and on the molar 'acidity ratio':

$$a_{SN} = 0.6 \times [SO_2]/[NH_3]$$

(3.2.6.3.)

This acidity ratio is a first attempt to account for the observed changes in resistance in areas with different pollution climates (Erisman et al. 2001, Fowler and Erisman 2003). Other possible ratios include $[NH_3+NH_4^+]/[SO_2 + SO_4^{2-}]$, but there is insufficient data upon which to chose between these ratios for modelling purposes at this time. The factor 0.6 is used to allow for the fact that the ratio of these gases at the surface should be higher than predicted by the EMEP model, due to the large vertical gradients of NH3 above source areas.

The parameterisation of Smith et al. (2000) has been modified in order to take into account the effects of a_{SN}, based upon discussions with the Centre for Ecology and Hydrology (Smith et al. 2003). The resulting scheme can be expressed as:

$$R_{ns} = \begin{array}{ll} \beta F_1(T_s, RH)\, F_2(a_{SN}) & (T_s > 0) \\ 200 & (-5 < T_s \leq 0) \\ 1000 & (T_s \leq -5) \end{array}$$

(3.2.6.4)

Where β is a normalising factor (0.0455), $F_1 = 10\log(T_s + 2)e^{((100-RH)/7)}$ and $F_2 = 10^{(-1.1099a_{SN}+1.6769)}$.

The F_1 term is identical to that of Smith et al. (2000) and provides a relationship of R_{ns} with temperature and relative humidity. The second function, F_2, is an equation derived from observations presented in Nemitz et al. (2001), and relates the value at 95% relative humidity and 10◦C to the molar ratio of SO2/NH3. The two terms are equal for molar SO2/NH3 ratio 0.3. The factor β is introduced in order to normalize one equation to the other, i.e. to ensure that the combined parameterisation is equal to the two separate terms for 95% relative humidity, 10◦C and molar ratio 0.3. For above-zero temperatures R_{ns} is constrained to lie between 10 and 200 s/m. Finally, we do not distinguish wet or dry surfaces in this formulation (they are included in the RH dependency used above), so the conductances are:

$$G_{ns,dry} = G_{ns,wet} = 1/R_{ns}$$

(3.2.6.5)

Aerosol dry deposition

Aerosol dry deposition velocity at height z_{ref} is calculated as:

$$Vg = \frac{1}{Ra + Rb + RaRbvs} + vs$$

where vs is the gravitational settling velocity. Other terms are as for gases. An assumption is made that all particles stick to the surface, so that the surface resistance Rc is set to zero.

Wet Deposition

Parameterisation of the wet deposition processes in the Unified EMEP model includes both in-cloud and sub-cloud scavenging of gases and particles.

In-cloud scavenging

The in-cloud scavenging of a soluble component C is given by the expression:

$$\Delta C_{wet} = -C \frac{W_{in} \cdot P}{\Delta z \cdot \rho_w}$$

(3.2.6.6)

where Win is the in-cloud scavenging ratio, P (kg m−2s−1) is the precipitation rate, Δz is the scavenging depth (assumed to be 1000 m) and ρ_w is the water density (1000 kg m−3). We do not account for the effect that dissolved material may be released if clouds or rain water evaporate.

Below-cloud scavenging
For below cloud scavenging a distinction is made between scavenging of particulate matter and gas phase components. The sub-cloud scavenging of the gases is calculated as:

$$\Delta C_{wet} = -C \frac{W_{sub} \cdot P}{\Delta z \cdot \rho_w}$$

(3.2.6.7)

where W_{sub} is the sub-cloud scavenging ratio.
Wet deposition rates for particles are calculated, based on Scott (1979), as:

$$\Delta C_{wet} = -C \frac{A \cdot P}{V_{dr}} \cdot \bar{E}$$

(3.2.6.8)

where V_{dr} is the the the raindrop fall speed (V_{dr}=5 m s−1), A = 5.2 m3 kg−1 s−1 is the empirical coefficient (a Marshall-Palmer size distribution is assumed for rain drops), and E is the size-dependent collection efficiency of aerosols by the raindrops.

The emissions input required by the EMEP model consists of gridded annual national emissions. These emissions are provided for 10 anthropogenic source-sectors denoted by so-called SNAP codes (Selected Nomenclature for Air Pollution Sectors, Vestreng et al., 2002). In addition, an eleventh source-sector consisting almost entirely of emissions from natural and biogenic sources exists.
The emissions are distributed vertically according to a default distribution based upon the SNAP codes. Emissions are distributed temporally according to monthly (Jan.-Dec.) and daily (Sun.-Sat.) factors derived from data provided by the University
of Stuttgart (IER). These factors are specific to each pollutant, emission sector, and country. Simple day-night factors are also applied.

The model is fully documented in Simpson et al., 2003 and Fagerli et al., 2004 and applications of the model can be found in e.g. Fagerli et al., 2003, Simpson et al., 2006ab, Jonson et al., 2006, Fagerli et al., submitted.

3.2.6.2 Performance, validation and uncertainties of each model
The results from the EMEP Unified model have been compared to ammonia measurements available in the EMEP network between 1995 and 2004. 17 sites have reported data for at least 1 year during this period. Of these sites, 8 sites are situated in Norway, 1 in Denmark, 1 in Austria, 1 in the Netherlands, 1 in Italy, 1 in Turkey, 2 in Czech Republic, 1 in Lithuania and 2 in Latvia. These sites, although few in number, represent very different pollution climates with respect to ammonia, with yearly average concentrations ranging from about 0.05 $\mu g(N)m^{-3}$ at the remote site Jergul in northern Norway to ~15 $\mu g(N)m^{-3}$ at the Dutch site Vredepeel. It should be noted that only 3 of these sites use denuders, whilst at the other sites the gas-particle separation is achieved using filter packs, thus the measurements may be biased. The large gradient in ammonia concentrations over Europe is well captured by the model (spatial correlation coefficient of 0.99-1.0), reflecting that the spatial distribution of the ammonia emissions is reasonable.

The EMEP model systematically underestimates the ammonia concentrations by a factor of 2. This is probably related to the large height of the lowest layer (90 meters), which makes it difficult to simulate the large vertical gradient of ammonia above sources.

The modeled seasonal cycle in ammonia concentrations are in reasonable agreement with the measurements, with most correlation coefficients (based on monthly averages) of 0.5 or larger, reflecting that the factors used for disaggregating the ammonia emissions from yearly to monthly emissions are reasonable. Correlation coefficients between model results and measurements for day-to-day variations range between 0 (most of the Norwegian sites except NO01, NO08 and NO42) and 0.5 (NO01,DK08, HU02, CZ03, NL10). At present, ammonia emissions in the EMEP model are not coupled to meteorological conditions, and even if they were, many of the local scale processes (e.g. soil moisture, leaf wetness, pH) which control ammonia emissions are difficult to parameterize even on a field-scale and cannot be captured within large scale models. Moreover, ammonia measurements are seldom characteristic for a $50x50 \text{ km}^2$ grid square. Thus, it is difficult for a large scale model to capture short term variations in ammonia concentrations.

The model results of ammonium aerosol concentrations are in better agreement with measurements both with respect to absolute levels and short term variations. This secondary component dry deposits only slowly and is more determined by long range transport and therefore easier to model on a large scale. There are approximately 20 EMEP sites that report ammonium aerosol measurements. In general, the absolute levels of ammonium aerosol is captured within 30% at the different sites, most of the sites being overestimated. The model has a tendency to overestimate ammonium aerosol concentrations in winter time (30-40%) and slightly underestimate summer concentrations (~20%), with temporal (daily) correlation coefficients of r~0.6-0.8. For the sum of ammonia and ammonium (NHx), almost 50 sites report measurements to EMEP. A comparison of model results and measurements of the seasonal cycle of reveals a similar pattern as for ammonium aerosol, confirming the systematic underestimation of ammonia at all seasons.

For aerosol nitrate in air (measured at ~20 EMEP sites), there is a similar seasonal performance as for aerosol ammonium, indicating that the somewhat different seasonal pattern in the model results compared to the measurements are caused by a too efficient formation of ammonium nitrate in the cold periods (the seasonal cycle of sulfate agree well with the measurements). However, from a comparison with the few HNO3 measurements available, no systematic underestimation of HNO3 in the cold season is found. Thus, it is not clear whether or not the overestimation of NH4NO3 is related to the equilibrium chemistry between the NH3, HNO3 and NH4NO3.

For wet deposition of reduced nitrogen, more than 40 EMEP sites report measurements regularly. On average, modeled reduced nitrogen depositions and concentrations in precipitation are around 10% lower than the measurements. The gradient in reduced nitrogen wet deposition over Europe is rather well represented (r~0.7). The underestimation is largest during the early summer months June and July, whilst depositions in March are often overestimated. This systematic pattern might indicate that 1) the seasonal variation imposed on the ammonia emissions needs improvement or 2) the low modeled ammonium concentrations in summer leads to a too short residence time of reduced nitrogen in air and thereby too little wet deposition of reduced nitrogen. Above we discussed that ammonia concentrations were underestimated with approximately the same amount throughout the whole year, which oppose 1). Ammonium concentrations in the cold months January and February are overestimated, but wet deposition of ammonium in the same months are frequently underestimated. Thus, it is not clear why the model underestimate wet deposition of reduced nitrogen.

No attempt has been made towards simulating trends of ammonia as not enough measurements have been available suitable for validating ammonia trends on a European scale.

In Fagerli and Aas, submitted, modeled trends of the sum of ammonia and ammonium in air (1990-2003) and trends of reduced nitrogen depositions (1980-2003) were compared to measurements at EMEP sites in Europe. In areas with high ammonia emissions, the decrease

in the concentrations was similar to the decrease in ammonia emissions, whilst the decrease in the background areas (e.g. Norway, Sweden, Finland) was larger than expected based on the changes in emissions. In general, the model results were found to give similar trends as the measurements.

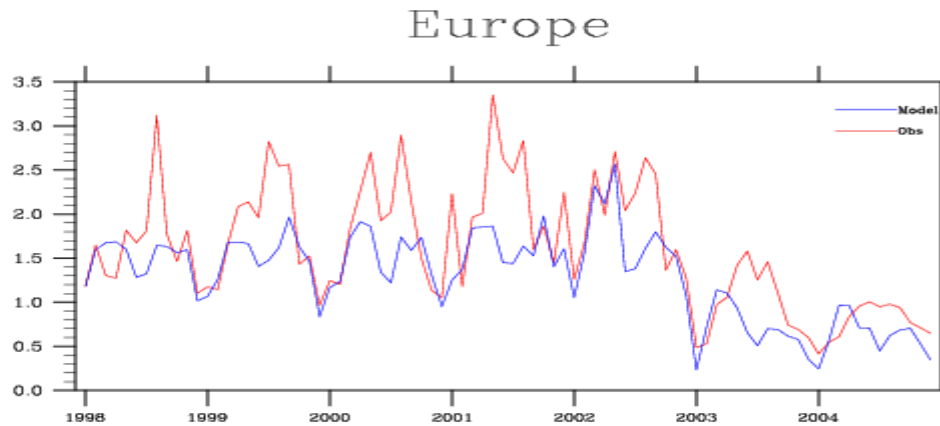Figures of the comparison between measured and modelled concentrations for EMEP stations.

Fig. 1 Monthly concentrations of ammonia (ug(N)m-3) in air (averaged over all EMEP sites with measurements), EMEP model results(scaled with 1.67) and EMEP measurements 1998-2004. Note that the number of measurement sites are not the same for every year.
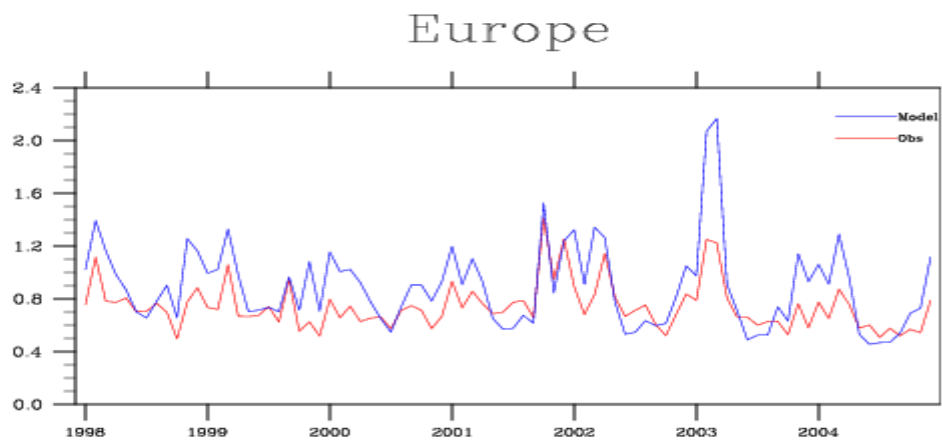
Fig. 2 Monthly concentrations of ammonium (ug(N)m-3) in air (averaged over all EMEP sites with measurements), EMEP model results and EMEP measurements 1998-2004. Note that the number of measurement sites are not the same for every year.
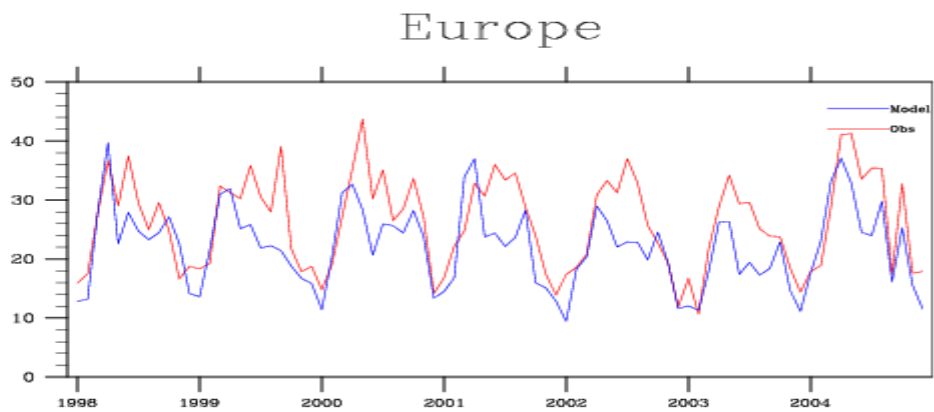

Fig. 3 Monthly concentrations of ammonium wet deposition (mg(N)/m-2)(averaged over all EMEP sites with measurements), EMEP model results and EMEP measurements 1998-2004. Note that the number of measurement sites are not the same for every year.
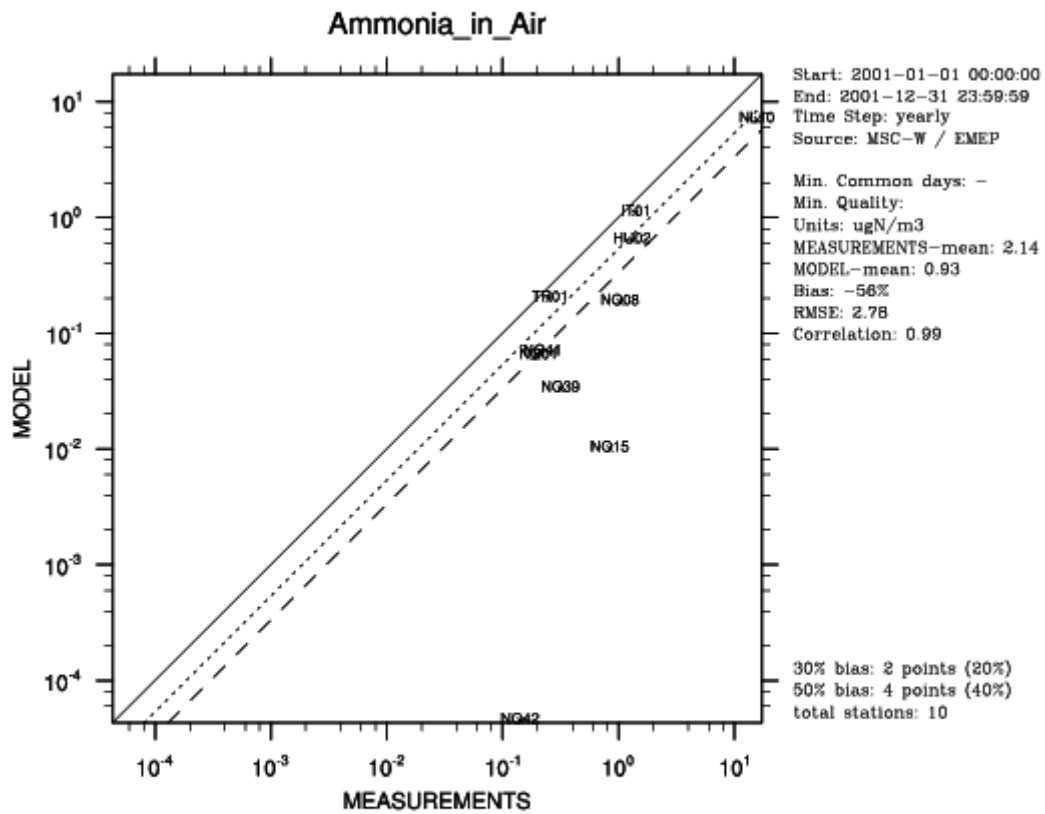
Fig. 4 Scatter plot of EMEP model results versus EMEP measurements of ammonia in air for 2001.

NH4+_in_Air

Start: 2001-01-01 00:00:00
End: 2001-12-31 23:59:59
Time Step: yearly
Source: MSC-W / EMEP

Min. Common days: –
Min. Quality:
Units: ugN/m3
MEASUREMENTS–mean: 0.79
MODEL–mean: 0.82
Bias: 3%
RMSE: 0.28
Correlation: 0.90

30% bias: 16 points (80%)
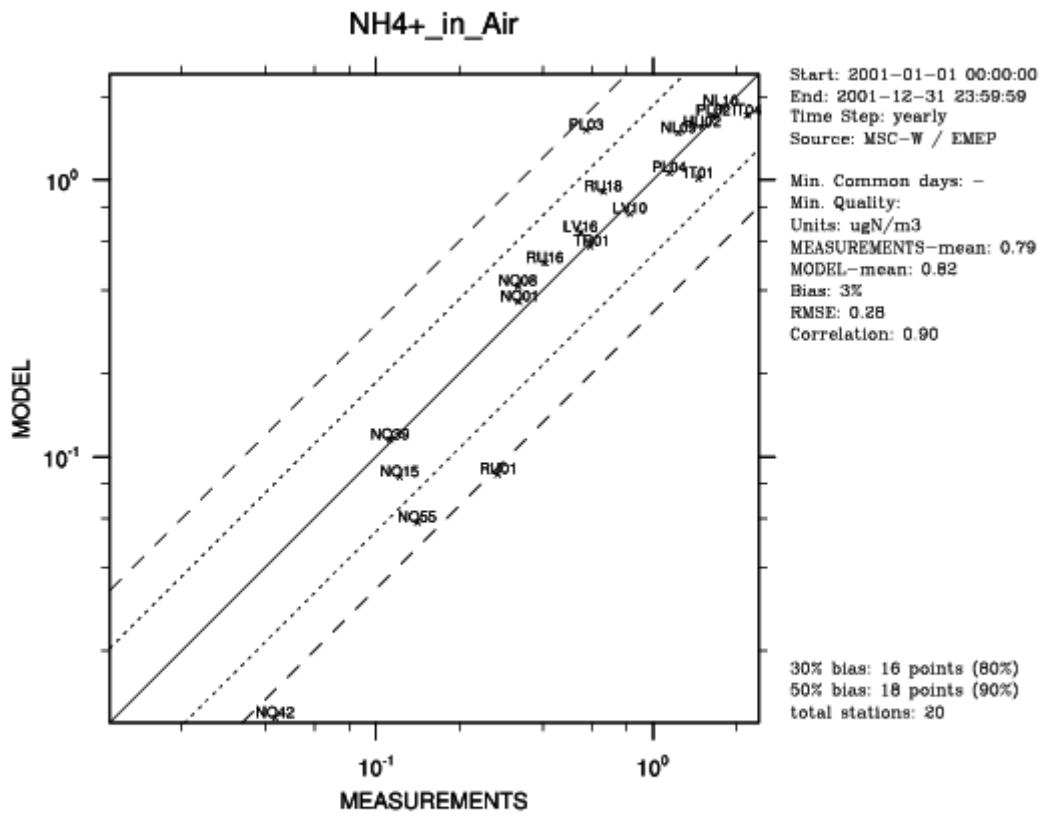50% bias: 18 points (90%)
total stations: 20

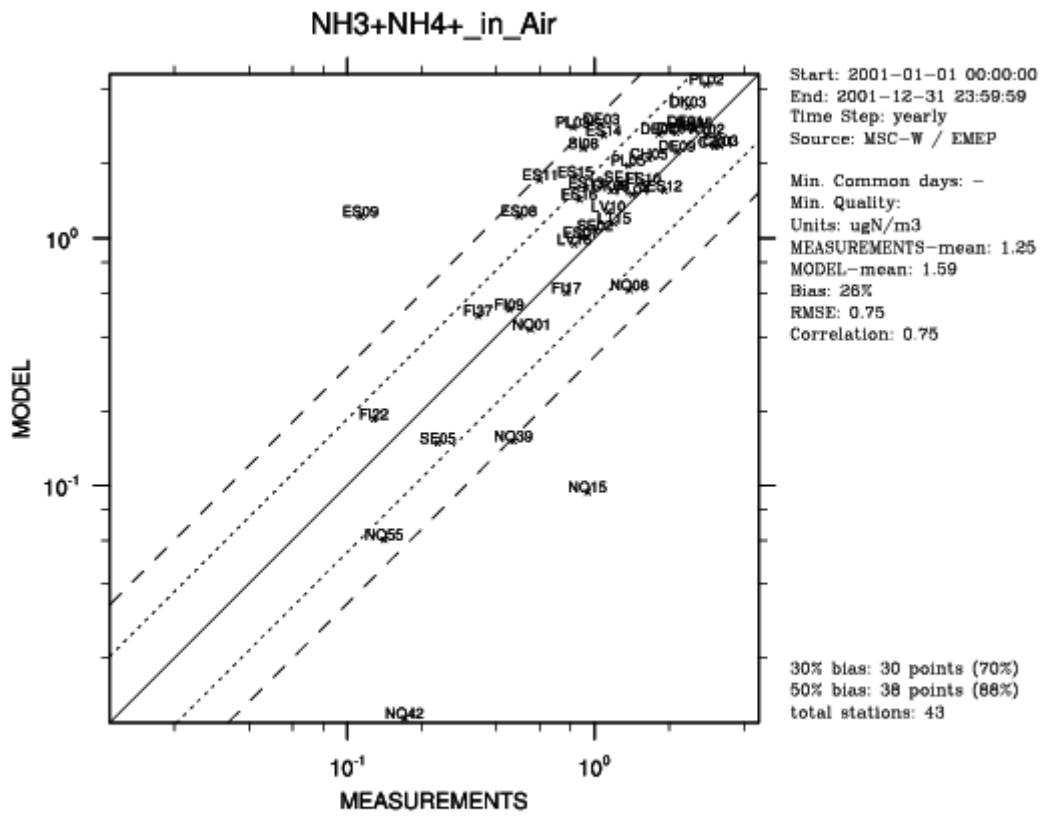Fig. 5 Scatter plot of EMEP model results versus EMEP measurements of ammonium in air for 2001.

Fig. 6 Scatter plot of EMEP model results versus EMEP measurements of
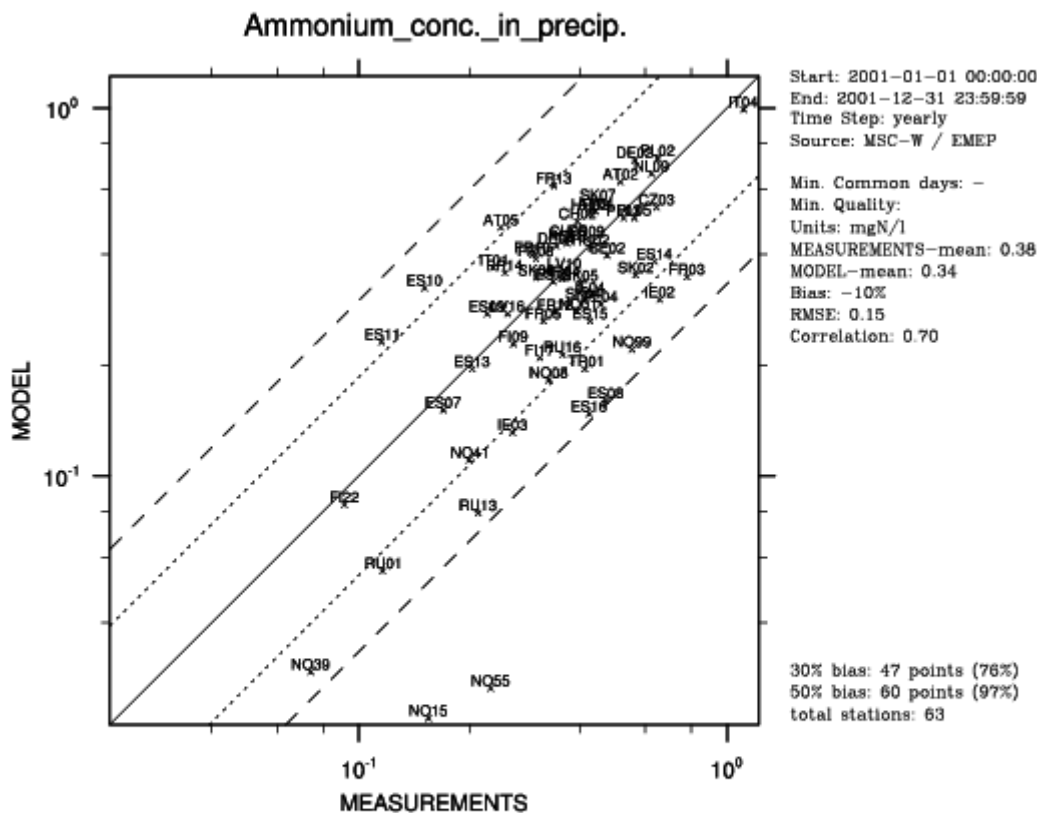ammonia+ammonium in air for 2001.

Fig. 7 Scatter plot of EMEP model results versus EMEP measurements of ammonium in precipitation for 2001.

3.2.6 bis EMEP4UK

- The Unified EMEP model (Tarrasón et al., 2003) is currently applied with increased spatial resolution over the United Kingdom. The new application is intended to allow mesoscale atmospheric transport model calculations over the British Isles.

- The new EMEP Unified model application is called EMEP4UK (Vieno et al., 2006) and is the Unified EMEP model implemented at the much finer horizontal resolution of 5 x 5 km^2. Pollutants such as reactive nitrogen and sulphur have a high spatial variability in the emissions and a short life time; therefore the associated dry deposition also has a high spatial variability (Vieno, 2006). This is very important when critical loads of nitrogen are calculated for specific ecosystems. To address these issues in the UK, the EMEP Unified model is being developed, using a nested approach, to run at high resolution over the UK.

- The 1 x 1 km^2 National Atmospheric Emissions Inventory (NAEI) is used to create the emission input for EMEP4UK. The NAEI emissions use the British National Grid

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(Transverse Mercator) coordinate system therefore an Arc info script is used to convert the emissions from 1 x 1 km^2 Transverse Mercator into the 5 x 5 km^2 polar stereographic projection used by both EMEP Unified and EMEP4UK models. The horizontal resolution can be freely chosen, but, in the current version of EMEP4UK is set to be 5 x 5 km^2.

- The emission input required by the EMEP4UK model consists of gridded annual national emissions of sulphur dioxide (SO_2), nitrogen oxides (NOx=NO+NO), ammonia (NH_3), non-methane volatile organic compounds (NMVOC), carbon monoxide (CO), and particulates ($PM_{2.5}$, PM_{10}).

- EMEP4UK can in principle use meteorological data from various sources using a pre-processor which converts and re-grids the required meteorological data. At the present time two datasets are been used to drive the EMEP4UK model: interpolated ERA40 and the Weather Research Forecast (WRF) model outputs (http://www.wrf-model.org/) The WRF model is state of the art in weather forecast modelling and is widely used by the academic community for research and weather forecast purposes. WRF uses a nesting domain approach to provide metrological data at the required horizontal and vertical resolution. Initial and boundary conditions (chemistry) are obtained from the EMEP Unified model.

4 Discussion

In the discussion the following questions will be addressed: What is the general picture of the performances of the models?; is there a systematic bias in the results and for specific areas or surfaces?; Can the differences be explained in terms of the model characteristics or even better a specific parameterization?

The models that are presented in Section 3 differ from a number of aspects. The differences in modeling concepts lead to a difference in model performance. The modelers have already indicated shortcomings in the models and possible reasons for observed differences between measured and modelled concentrations. We, tentatively, will give some of the issues here. However, this list will be complemented and discussed at the Workshop.

Issues that emerge from the model presentations and the validation against measurements:

1) Spatial scale of the model; particularly the models that calculate the concentrations at a relatively large scale (several tens of kilometers) underestimate the ammonia concentrations in air. The reason is twofold: a) these models do often have a large depth of the first (surface) layer which leads to a too rapid mixing of the emitted ammonia over this first layer and b) the local sub grid gradients in the emissions are not caught by the models. So sub grid concentration gradients cannot be calculated and often leads to an underestimation of the concentration for a site. However, this is also strongly dependent on the vicinity of the measurement site.

2) Dry deposition parameterization; a number of models use dry depositon parameterizations that do not include the compensation point of ammonia. In such cases the ammonia concentration in air may be underestimated caused by a too large dry deposition.

3) Chemical conversion of ammonia to ammonium; it is found by some of the models that a too high conversion may be the reason for the underestimation of ammonia concentrations.

4) Emissions; the lack or errors in the spatial and temporal representation of the ammonia emissions may lead to over- and underestimations of the ammonia concentrations. It is shown by models that using more spatial detailed emissions improved the correlation between measured and modelled concentrations considerably.

5 Conclusions and recommendations

The working group may end up with suggestions/advice on how certain processes should be dealt with in modeling the ammonia concentrations and depositions. This depends of course on temporal and spatial scale of the ammonia problem under consideration..
Employ initiative in setting up a real intercomparison, i.e. running the models with similar input.
Further recommendations.

6 References

Ambelas Skjøth, C., Ellermann, T., Gyldenkærne, S., Hertel, O., Geels, C., Frohn, L., Frydendall, J., and Løfstrøm, P. (2006). Footprints on Ammonia Concentrations from Emission Regulations. Presented at Bolger Conference Center, Potomac, Maryland, USA, 5 to 8 June 2006.

Ambelas Skjøth, C., Hertel, O., Gyldenkærne, S., and Ellermann, T. (2004a). Implementing a dynamical ammonia emission parameterization in the large-scale air pollution model ACDEP. Journal of Geophysical Research-Atmospheres, 109.

Ambelas Skjøth, C., Hertel, O., Gyldenkærne, S., and Ellermann, T. (2004e). Implementing a dynamical ammonia emission parameterization in the large-scale air pollution model ACDEP. Journal of Geophysical Research-Atmospheres, 109.

Anderson, N., Strader, R., and Davidson, C. (2003). Airborne reduced nitrogen: ammonia emissions from agriculture and other sources. Environment International, 29, 277-286.

Andersen, H. V., Hovmand, M. F., Hummelshoj, P., and Jensen, N. O. (1999). Measurements of ammonia concentrations, fluxes and dry deposition velocities to a spruce forest 1991-1995. Atmospheric Environment, 33, 1367-1383.

Aneja, V. P., Nelson, D. R., Roelle, P. A., Walker, J. T., and Battye, W. (2003). Agricultural ammonia emissions and ammonium concentrations associated with aerosols and precipitation in the southeast United States. Journal of Geophysical Research-Atmospheres, 108.

Apsimon, H. M., Barker, B. M., and Kayin, S. (1994). Modeling Studies of the Atmospheric Release and Transport of Ammonia in Anticyclonic Episodes. Atmospheric Environment, 28, 665-678.

Asman, W. A. H. (2001). Modelling the atmospheric transport and deposition of ammonia and ammonium: an overview with special reference to Denmark. Atmospheric Environment, 35, 1969-1983.

Asman, W. A. H. (1998). Factors influencing local dry deposition of gases with special reference to ammonia. *Atmospheric Environment*, 32, 415-421.

Baldwin, A. C. and Golden, D. M. (1979). Heterogeneous Atmospheric Reactions - Sulfuric-Acid Aerosols As Tropospheric Sinks. Science, 206, 562-563.

Battye, W., Aneja, V. P., and Roelle, P. A. (2003). Evaluation and improvement of ammonia emissions inventories. Atmospheric Environment, 37, 3873-3883.

Bouwman, A. F., Lee, D. S., Asman, W. A. H., Dentener, F. J., VanderHoek, K. W., and Olivier, J. G. J. (1997). A global high-resolution emission inventory for ammonia. Global Biogeochemical Cycles, 11, 561-587.

Bower, K. N., Wells, M., Choularton, T. W., and Sutton, M. A. (1995). A Model of Ammonia/Ammonium Conversion and Deposition in A Hill Cap Cloud. Quarterly Journal of the Royal Meteorological Society, 121, 569-591.

Daumer, B., Niessner, R., and Klockow, D. (1992). Laboratory Studies of the Influence of Thin Organic Films on the Neutralization Reaction of H2So4 Aerosol with Ammonia. Journal of Aerosol Science, 23, 315-325.

Dragosits, U., Sutton, M. A., Place, C. J., and Bayley, A. A. (1998). Modelling the spatial distribution of agricultural ammonia emissions in the UK. Environmental Pollution, 102,

Duyzer, J., Nijenhuis, B., and Weststrate, H. (2001). Monitoring and Modelling of Ammonia Concentrations and Deposition in Agricultural Areas of The Netherlands. Water, Air, & Soil Pollution: Focus, 1, 131-144.

Duyzer, J. H., Verhagen, H. L. M., Weststrate, J. H., and Bosveld, F. C. (1992). Measurement of the Dry Deposition Flux of Nh3 on to Coniferous Forest. Environmental Pollution, 75, 3-13.

Ellermann, T. Andersen H. V., Bossi, R., Brandt, J., Christensen, J., Frohn, L. M., Geels, C., Kemp, K., Løfstrøm, P., Mogensen B., and Monies, C. Atmospheric Deposition. NOVANA (In Danish: Atmosfærisk deposition. NOVANA). 595, 1-66. 2006. National Environmental Research Institute. Technical Report.

Farquhar, G. D., Firth, P. M., Wetselaar, R., and Weir, B. (1980). On the Gaseous Exchange of Ammonia Between Leaves and the Environment - Determination of the Ammonia Compensation Point. Plant Physiology, 66, 710-714.

Fowler, D., Sutton, M., Flechard, C., Cape, J. N., Storeton-West, R. L., Coyle, M., and Smith, R. I. (2001). The Control of SO2 Dry Deposition on to Natural Surfaces by NH3 and its Effects on Regional Deposition. Water, Air, & Soil Pollution: Focus, Volume 1, 39-48.

Geels, C., Bak, J, Callesen, T., Frohn, L., Frydendall, J., Gyldenkaerne, S., Hansen, A. G., Hutchings, N., Jacobsen, A. S., Pedersen, P., Schneekloth, M., Winther, S., Hertel, O., and Moseholm, L. Guideline for approval of livestock farms (In Danish: Vejledning om godkendelse af husdyrbrug). 568, -83 p. 2006. Roskilde, Denmark, National Environmental Research Institute.

Gilliland, A. B., Dennis, R. L., Roselle, S. J., and Pierce, T. E. (2003). Seasonal NH3 emission estimates for the eastern United States based on ammonium wet concentrations and an inverse modeling method. Journal of Geophysical Research-Atmospheres, 108.

Gyldenkærne, S., Ambelas Skjøth, C., Christensen, J., Ellermann, T., Frohn, L. M., Brandt, J., and Hertel, O. (2005a). A high resolution ammonia emission inventory for regional scale air pollution models.

Gyldenkærne, S., Ambelas Skjøth, C., Hertel, O., and Ellermann, T. (2005b). A dynamical ammonia emission parameterization for use in air pollution models. Journal of Geophysical Research-Atmospheres, 110.

Harrison, R. M. and Pio, C. A. (1983). An Investigation of the Atmospheric Hno3-Nh3-Nh4No3 Equilibrium Relationship in A Cool, Humid Climate. Tellus Series B-Chemical and Physical Meteorology, 35, 155-159.

Hertel, O., Skjoth, C. A., Lofstrom, P., Geels, C., Frohn, L. M., Ellermann, T., and Madsen, P. V. (2006). Modelling nitrogen deposition on a local scale - A review of the current state of the art. Environmental Chemistry, 3, 317-337.

Hertel, O., Skjoth, C. A., Frohn, L. M., Vignati, E., Frydendall, J., de Leeuw, G., Schwarz, U., and Reis, S. (2002). Assessment of the atmospheric nitrogen and sulphur inputs into the North Sea using a Lagrangian model. Physics and Chemistry of the Earth, 27, 1507-1515.

Hertel, O., Christensen, J., Runge, E. H., Asman, W. A. H., Berkowicz, R., Hovmand, M. F., and Hov, O. (1995). Development and Testing of A New Variable Scale Air-Pollution Model - Acdep. Atmospheric Environment, 29, 1267-1290.

Huijsmans, J. F. M., Hol, J. M. G., and Vermeulen, G. D. (2003). Effect of application method, manure characteristics, weather and field conditions on ammonia volatilization from manure applied to arable land. *Atmospheric Environment*, 37, 3669-3680.

Huntzicker, J. J., Cary, R. A., and Ling, C. S. (1980). Neutralization of Sulfuric-Acid Aerosol by Ammonia. Environmental Science & Technology, 14, 819-824.

Husted, S., Schjoerring, J. K., Nielsen, K. H., Nemitz, E., and Sutton, M. A. (2000). Stomatal compensation points for ammonia in oilseed rape plants under field conditions. Agricultural and Forest Meteorology, 105, 371-383.

Hutchings, N. J., Sommer, S. G., Andersen, J. M., and Asman, W. A. H. (2001). A detailed ammonia emission inventory for Denmark. Atmospheric Environment, 35, 1959-1968.

Junge, E. and Ryan, T. G. (1958). Study of the So2 Oxidation in Solution and Its Role in Atmospheric Chemistry. Quarterly Journal of the Royal Meteorological Society, 84, 46-55.

Lee, D. S., Halliwell, C., Garland, J. A., Dollard, G. J., and Kingdon, R. D. (1998). Exchange of ammonia at the sea surface - A preliminary study. Atmospheric Environment, 32, 431-439.

Loubet, B., Milford, C., Sutton, M. A., and Cellier, P. (2001). Investigation of the interaction between sources and sinks of atmospheric ammonia in an upland landscape using a simplified dispersion-exchange model. Journal of Geophysical Research-Atmospheres, 106, 24183-24195.

McMurry, P. H., Takano, H., and Anderson, G. R. (1983). Study of the Ammonia (Gas) Sulfuric-Acid (Aerosol) Reaction-Rate. Environmental Science & Technology, 17, 347-352.

Milford, C., Theobald, M. R., Nemitz, E., and Sutton, M. A. (2001). Dynamics of Ammonia Exchange in Response to Cutting and Fertilising in an Intensively-Managed Grassland. Water, Air, & Soil Pollution: Focus, 1, 167-176.

Milford, C., Sutton, M. A., Allen, A. G., Karlsson, A., Davison, B. M., James, J. D., Rosman, K., Harrison, R. M., and Cape, J. N. (2000). Marine and land-based influences on atmospheric ammonia and ammonium over Tenerife. Tellus Series B-Chemical and Physical Meteorology, 52, 273-289.

Nemitz, E., Sutton, M. A., Wyers, G. P., and Jongejan, P. A. C. (2004). Gas-particle interactions above a Dutch heathland: I. Surface exchange fluxes of NH3, SO2, HNO3 and HCl. Atmospheric Chemistry and Physics, 4, 989-1005.

Neirynck, J., Kowalski, A. S., Carrara, A., and Ceulemans, R. (2005). Driving forces for ammonia fluxes over mixed forest subjected to high deposition loads. Atmospheric Environment, 39, 5013-5024.

Olivier, J. G. J., Berdowski, J. J. M., Peters, J. A. H. W., Bakker, A. J. H, Visschedijken, A. J. H, Bloos, and J.-P.J. Applications of EDGAR. Including a description of EDGAR 3.0: reference database with trend data for 1970-1995. RIVM report no. 773301 001/ NOP report no. 410200 051. 2001. Bilthoven, The Netherlands, RIVM.

Phillips, S. B., Arya, S. P., and Aneja, V. P. (2004). Ammonia flux and dry deposition velocity from near-surface concentration gradient measurements over a grass surface in North Carolina. Atmospheric Environment, 38, 3469-3480.

Pio, C. A. and Harrison, R. M. (1987). The Equilibrium of Ammonium-Chloride Aerosol with Gaseous Hydrochloric-Acid and Ammonia Under Tropospheric Conditions. Atmospheric Environment, 21, 1243-1246.

Pul, A. v., Jaarsveld, H. V., Meulen, T. v. d., and Velders, G. (2004). Ammonia concentrations in the Netherlands: spatially detailed measurements and model calculations. Atmospheric Environment, 38, 4045-4055.

Quinn, P. K., Charlson, R. J., and Bates, T. S. (1988). Simultaneous Observations of Ammonia in the Atmosphere and Ocean. Nature, 335, 336-338.

Schjoerring, J. K., Husted, S., and Poulsen, M. M. (1998b). Soil-plant-atmosphere ammonia exchange associated with Calluna vulgaris and Deschampsia flexuosa. Atmospheric Environment, 32, 507-512.

Schjoerring, J. K., Kyllingsbaek, A., Mortensen, J. V., and Byskovnielsen, S. (1993). Field Investigations of Ammonia Exchange Between Barley Plants and the Atmosphere .1. Concentration Profiles and Flux Densities of Ammonia. Plant Cell and Environment, 16, 161-167.

Seedorf, J., Hartung, J., Schroder, M., Linkert, K. H., Pedersen, S., Takai, H., Johnsen, J. O., Metz, J. H. M., Groot Koerkamp, P. W. G., and Uenk, G. H. (1998a). A Survey of Ventilation Rates in Livestock Buildings in Northern Europe. *Journal of Agricultural Engineering Research*, 70, 39-47.

Seedorf, J., Hartung, J., Schroder, M., Linkert, K. H., Pedersen, S., Takai, H., Johnsen, J. O., Metz, J. H. M., Groot Koerkamp, P. W. G., and Uenk, G. H. (1998b). Temperature and Moisture Conditions in Livestock Buildings in Northern Europe. Journal of Agricultural Engineering Research, 70, 49-57.

Sorensen, L. L., Hertel, O., Skjoth, C. A., Lund, M., and Pedersen, B. (2003). Fluxes of ammonia in the coastal marine boundary layer. Atmospheric Environment, 37, S167-S177.

Sorteberg, A. and Hov, O. (1996). Two parametrizations of the dry deposition exchange for SO2 and NH3 in a numerical model. Atmospheric Environment, 30, 1823-1840.

Stelson, A. W., Friedlander, S. K., and Seinfeld, J. H. (1979). Note on the Equilibrium Relationship Between Ammonia and Nitric-Acid and Particulate Ammonium-Nitrate. Atmospheric Environment, 13, 369-371.

Stelson, A. W. and Seinfeld, J. H. (1982). Relative-Humidity and Temperature-Dependence of the Ammonium-Nitrate Dissociation-Constant. Atmospheric Environment, 16, 983-992.

Stohl, A. (1998). Computation, accuracy and applications of trajectories - A review and bibliography. Atmospheric Environment, 32, 947-966.

Stohl, A. and Koffi, N. E. (1998). Evaluation of trajectories calculated from ECMWF data against constant volume balloon flights during ETEX. Atmospheric Environment, 32, 4151-4156.

Sutton, M. A., Dragosits, U., Tang, Y. S., and Fowler, D. (2000). Ammonia emissions from non-agricultural sources in the UK. Atmospheric Environment, 34, 855-869.

Sutton, M. A., Burkhardt, J. K., Guerin, D., Nemitz, E., and Fowler, D. (1998). Development of resistance models to describe measurements of bi-directional ammonia surface-atmosphere exchange. Atmospheric Environment, 32, 473-480.

Sutton, M. A., Fowler, D., and Moncrieff, J. B. (1993). The Exchange of Atmospheric Ammonia with Vegetated Surfaces .1. Unfertilized Vegetation. Quarterly Journal of the Royal Meteorological Society, 119, 1023-1045.

Schwarz, U., Wickert, B., Obermeier, A., and Friedrich, R. (2000). Generation of Atmospheric Emission Inventories in Europe with High Spatial and Temporal Resolution. Southampton SO40 7AA, UK: WITpress, Southampton.

Seinfeld, J. H. and Pandis, S. N. (1998). Atmospheric Chemistry and Physics : From Air Pollution to Climate Change. New York: John Wiley & Sons Inc.

Vanhove, L. W. A., Adema, E. H., Vredenberg, W. J., and Pieters, G. A. (1989). A Study of the Adsorption of Nh3 and So2 on Leaf Surfaces. Atmospheric Environment, 23, 1479-1486.

Van Jaarsveld, J,A, 2004. The Operational Priority Substances model. RIVM 500045001.

Van Jaarsveld, J.A., A. Bleeker and N.J.P. Hoogervorst, 2000. Evaluation of ammonia emission reductions using measurements and modeling. RIVM 722108025. In Dutch.

Wells, M., Bower, K. N., Choularton, T. W., Cape, J. N., Sutton, M. A., Storetonwest, R. L., Fowler, D., Wiedensohler, A., Hansson, H. C., Svenningsson, B., Swietlicki, E., Wendisch, M., Jones, B., Dollard, G., Acker, K., Wieprecht, W., Preiss, M., Arends, B. G., Pahl, S., Berner, A., Kruisz, C., Laj, P., Facchini, M. C., and Fuzzi, S. (1997). The reduced nitrogen budget of an orographic cloud. Atmospheric Environment, 31, 2599-2614.

Wesely, M. L. (1989). Parameterization of Surface Resistances to Gaseous Dry Deposition in Regional-Scale Numerical-Models. Atmospheric Environment, 23, 1293-1304.

Wickert, B., Heidekker, A., Friedrich, and R (2001). Calculations of emissions in Europe with CAREAIR. Berlin Heidelberg New York 2001: Springer-Verlag.

Wyers, G. P. and Erisman, J. W. (1998). Ammonia exchange over coniferous forest. Atmospheric Environment, 32, 441-451.