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AMMONIA DEPOSITION NEAR HOT SPOTS: PROCESSES, MODELS AND MONITORING METHODS

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ABSTRACT. Atmospheric reduced nitrogen (NH_x) mainly originates from hot spots, which can be considered as intensive area or point sources. A large fraction of the emitted NH_x may be recaptured by the surrounding vegetation, hence reducing the contribution of these hot spots to long-range transport of NH_x. This paper reviews the processes leading to local recapture of NH_x near hot spots as well as existing models and monitoring methods. The existing models range from research models to more operational models that can be coupled with long-range transport model provided the necessary information on emissions is available. Local recapture of NH_3 ranges from 2% to 60% within 2 km of a hot-spot and it is sensitive to source height, atmospheric stability, wind speed, structure of the surrounding canopies, as well as stomatal absorption, which mainly depends on green leaf area index and stomatal NH_3 compensation point of vegetation, and finally, cuticular deposition, which depends primarily on vegetation wetness. The main uncertainties and limitations on NH_x recapture models and monitoring techniques are discussed.

KEYWORDS: NH_3, NH_4^+, reduced nitrogen, local scale, dispersion, trans-boundary pollution.

1 INTRODUCTION

Due to the decrease of sulphur and nitrogen oxides emissions under a series of UNECE protocols, reduced nitrogen (NH_x), has become the dominant pollutant in Western Europe contributing to acidification of ecosystems *(e.g.* Vestring and Storing, 2000). At the global scale NH_x and NO_x emissions are comparable, although large uncertainties exist on NH_x emissions (Dentener and Crutzen, 1994; Bouwman *et al.*, 1997). Moreover, NH_x deposition, with other nitrogen (N) deposition, leads to eutrophication and changes in the biodiversity of semi-natural ecosystems (Van Breemen and van Dijk 1988; Roelofs *et al.*, 1985; Fangmeier *et al.*, 1994, Krupa, 2003; EEA, 2003). Although atmospheric ammonia (NH_3) is not a greenhouse gas (GHG), deposition of NH_x may lead to increased GHG emissions (N_2O) (Melillo *et al.*, 1989) or reduced consumption of CH_4 (REF). Additionally, ammonium sulphate aerosols, $(NH_4)_2SO_4$, contribute to half of the negative radiative forcing of the atmosphere due to aerosols (Houghton *et al.*, 2001, Adams *et al.*, 2001), as well as contributing to impacts of secondary aerosol on human health.

As it is know since the end of the 19th century (Eriksson, 1952), ammonia mainly originates from livestock (Bouwman *et al.*, 1997; Oudendag *et al.*, 1998; Misselbrook *et al.*, 2000; Dämmgen and Erisman, 2005). The main NH_x sources are housing and waste storage (Jarvis and Pain, 1990; Bussink and Oenema, 1998; Pain *et al.*, 1998; Döhler *et al.*, 2002), and land spread manure (Génermont and Cellier, 1997; Asman *et al.*, 2004). Hence the main NH_x emissions are "hot spots" sources in the sense that they are intense and either spatially small (point sources, such as barns and manure storage) or temporally short (application of manure). The emitted NH_x is either (i) dry-deposited as gaseous NH_3 by stomatal absorption and non-stomatal adsorption to canopy surfaces (e.g. Sutton *et al.*, 1993a,b; Sutton *et al.*, 1995a), (ii) dry-deposited as particulate ammonium (NH_4^+) essentially by Brownian diffusion (particle size < 1 µm), (iii) wet-deposited as ion NH_4^+, or (iv) transformed by chemical reactions with other gases or aerosols (Dlugi *et al.*, 1997; Nemitz *et al.*, 2002; 2004ab, Nemitz and Sutton, 2004). But NH_3 can also be emitted by the plants themselves, which can either act as sinks or sources of NH_3 depending on their nitrogen (N) nutrition status and the atmospheric NH_3 concentration (Farquhar *et al.*, 1980; Sutton *et al.*, 1995a,b, 2001a; Schjoerring *et al.*, 1998; Andersen *et al.*, 1999; Milford *et al.*, 2001a; Hill *et al.*, 2001). Moreover, non-stomatal adsorption of NH_3 is influenced by the load of acidic pollutants to the surface (Erisman and Wyers, 1993; Sutton *et al.*, 1993c; Fléchard *et al.*, 1999).

The combination of hot spots sources and effective deposition processes leads to sources and sinks of NH_x being spatially heterogeneous at a scale of a square kilometre (Sutton *et al.*, 1998a; Dragosits *et al.*, 1998; Hutchings *et al.*, 2001a,b; Dragosits *et al.*, 2002). Direct measurement of NH_x deposition near hot spots is challenging due to intense local advection (Loubet *et al.*, 2001, 2003; Hensen *et al.*, 2006a). Indirect estimates using mass balance, ^{15}N labelling, SF_6 to NH_3 ratio methods, as well as modelling studies, have estimated that the fraction recaptured within 2 km downwind from the source of NH_3 emitted ranges between 2% and 60% (Asman, 1998; Loubet and Cellier, 2001; Sommer and Jensen, 1991; Theobald *et al.*, 2001; Loubet *et al.*, 2006). The large variability of NH_x deposition near sources is known to depend critically on the canopy structure surrounding the source (roughness, side fluxes) (Klaassen, 1991; Draaijers *et al.*, 1994; De Jong and Klaassen, 1997; Theobald *et al.*, 2001; Loubet *et al.*, 2006), the NH_3 emissions from the canopy (Schjoerring *et al.*, 1998; Riedo *et al.*, 2002), the litter (Nemitz *et al.*, 2000a, 2000b), or from the soil (Génermont and Cellier, 1997), as well as the non-stomatal NH_3 fluxes (van Hove *et al.*, 1989; Erisman and Wyers, 1993; Sutton *et al.*, 1995a; Fléchard *et al.*, 1999; Loubet and Cellier, 2001). Less known, are wet deposition fluxes and chemical transformations of NH_x near intensive sources, as well as direct emissions of particulate NH_4^+ (McCulloch *et al.*, 1998). Despite this knowledge on local deposition, its quantitative assessment within global models is still a challenge at European scale, and probably in all regions having large livestock populations. As a result, options related to spatial interactions in hot spots have until now been little considered within mitigation strategies to reduce trans-boundary NH_x pollution.

The complexity of the processes involved and the variability of the deposition fluxes near hot spots have led to the use of models and monitoring techniques to evaluate the fraction of NH_x re-deposited locally.

Models. There are few models for NH_3 deposition near hot spots that deal with the complexity of the processes noted above. Some existing models treat within-canopy vertical transfer and leaf-scale exchange (Baldocchi, 1988; Baldocchi, 1992; Harper *et al.*, 2000), other models that treat dispersion and deposition of NH_3 above the canopy, DEPO1 (Asman, 1998), LADD (Hill, 1998), and FIDES (Loubet *et al.*, 2001), or at larger scales (Asman and Janssen, 1987; Singles *et al.*, 1998; Fournier *et al.*, 2002, etc. See Van Pul *et al.*, 2006). There are also models for the dispersion of tracers within the canopy, although without exchange processes (e.g. Wilson and Sawford, 1996). However, there are few models addressing within- and above-canopy dispersion *together with* ammonia exchange within the canopy and at the ground, as done by MODDAS-2D (Loubet *et al.*, 2006). Existing overviews of modelling local deposition of NH_x have been provided by Asman (2002) and Hertel *et al.* (2006). The main limitations of current NH_3 short-range deposition models are:

(i) a good knowledge of the emission from the hot spot, in both time and space;

(ii) the parameterisation / modelling of the NH_3 emissions from the plants, which is known to depend on the plant, the N and water supply (and henceforth on N deposition if it is intensive), the variations in global radiation, and to physiological changes throughout the season (Schjoerring, 1997; Milford *et al.*, 2001a; Loubet *et al.*, 2002);

(iii) the non-stomatal NH_3 deposition, which depends on leaf surface wetness but also on the ionic composition of these water films, and hence on the NH_x load, but also on the interaction with other chemical compounds (Fléchard *et al.*, 1999);

(iv) the use of detailed turbulence model to precisely evaluate the sensitivity of modelled NH_3 deposition on turbulence in complex situation, such as downwind of buildings and within tree-belts;

(v) accurate estimates of the NH_3 emission dynamics at both the daily and the yearly time scale for a diversity of animal species, building types, and effluent management practices;

(vi) the wet deposition component near hot spots, which amount should be evaluated for a range of climatic conditions with contrasted precipitation frequency and temperatures;

(vii) the amount of other nitrogen compounds emissions from hot spots (aerosols, dusts, amines) and their subsequent nearby deposition;

(viii) the parameterisation of chemical reactions between NH_3 and acidic compounds or NO_x, especially in “rural-urban” zones.

Monitoring and effect assessment. As measuring deposition of NH_3 with strong local advection is still challenging (Hensen *et al.*, 2006a), alternative methods have been developed consisting in monitoring NH_3 concentration and nitrogen (N) enrichment in plants around hot spots (Pitcairn *et al.*, 1998; Sutton *et, 20*01b; Tang *et, 20*01; Pitcairn *et al.*, 2002; Dämmgen *et al.*, 2005). The monitoring methods are based on low cost techniques (acid coated denuders; filter packs; batch samples). Specific experiments have also been conducted to assess the deposition to tree belts (Theobald *et al.*; 2001). The main limitations of the NH_3 monitoring and effect assessment methods are:

(i) To accurately measure NH_3 concentrations over long periods under fluctuating conditions, in such a way that representative results are obtained for larger areas.

(ii) To relate measured NH_3 concentration with NH_x deposition or similarly N in plants to NH_x deposition, taking account of the tendency for deposition rates to saturate at very high concentrations;

(iii) To correctly sample in time and space;

(iv) To be able to estimate local NH3 deposition rates to sensitive receptors (e.g. nature areas) in the vicinity of hot spots with sufficient accuracy for regulatory screening and detailed assessment, where necessary accounting for corrections due to advection effects (e.g. Loubet *et al.*, 2001; Milford *et al.*, 2001b);

(v) The challenge to provide basic level screening assessments of the effects of NH_3 hot spots on adjacent nature areas on a routine basis at modest costs.

2 AMMONIA EMISSIONS FROM HOT SPOTS

Ammonia is mainly emitted from animal housings, manure storage, and land-spread manure, and to a smaller extent from mineral fertiliser application and grazing (Bouwman *et al.*, 1997; Misselbrook *et al.*, 2000). Hence, in western countries, most NH_3 sources are concentrated in small areas surrounding the farms, which may be defined as a hot spot. It is well known that NH_3 concentration above a solution containing NH_4^+ increases exponentially with temperature and pH of the solution (e.g. Génermont and Cellier, 1997). This feature, as well as turbulent exchange, is among most important processes involved in emissions of NH_3.

Emissions of NH_3 from housings depend mainly on the number of animals, and the feeding quantity, the construction of the floors, but also on the type of management (Sommer *et al.*, 2006), the pH of the litter. The ventilation rate (Seedorf *et al.*, 1998a) and the temperature inside the stables (Seedorf *et al.*, 1998b; Wathes *et al.*, 1998) are also essential factors regulating the emissions. In naturally ventilated stables, the rate of ventilation results from a combination of free and forced convection and hence depends on wind and outdoor and indoor temperatures (Hensen *et al.*, 2006b). However, the emission from animal housings does not only depend on the number of animals present, but also partly on the manure handling system (liquid manure/solid manure, slatted floor, partially slatted floor, deep litter etc.) and storage system (open tanks, tanks with a crust, tanks with a cover) (Hutchings *et al.*, 2001a) .

Emission of NH_3 after fertilisation depends on the nature of the fertiliser (animal manures are sometimes a more important source. Note: Spreading of solid manure may happen with no NH_3 emissions, as nothing is left after storage!), the application method and farming practices (Hutchings *et al.*, 2001b), the location and time where the application takes place, manure (solid/liquid etc.), soil properties (essentially pH), and the meteorological conditions; mainly temperature and wind speed, the time-span between application and incorporation, but also precipitations (Génermont and Cellier, 1997; Huijsmans *et al.*, 2003; Rosnoblet *et al.*, 2006). Emissions of NH_3 storage facilities mainly depend on pH and outdoor temperature (see e.g. Olesen and Sommer, 1993). Figure 1 illustrates the effect of soil pH on NH_3 volatilisation from land-spread manure.

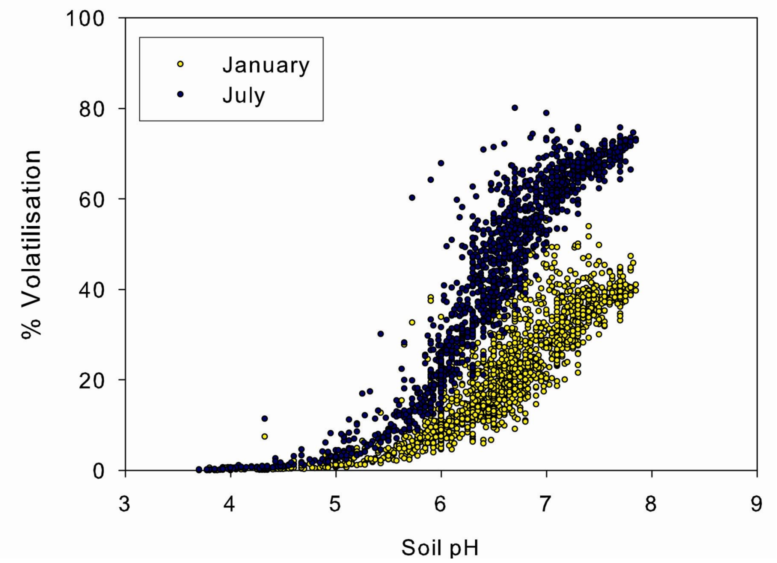

Figure 1. Percentage NH_3 volatilised from land-spread manure as a function of soil pH, as output from the VOLT'AIR model, for January and July 2000, over England and Wales (Theobald *et al.*, 2005).

Temporal variation of NH_3 emissions. Seasonal variability of NH_3 emissions is due to a combination of both management practices and meteorological conditions. The application of manure and fertilizers occurs predominantly during spring, but to a lesser extent in autumn. Similarly animals are grazing outdoor only part of the year. The temperature and wind speed dependence of NH_3 emissions also explains seasonal variations, but also induce daily variations (Asman, 1992; Battye *et al.*, 2003; Gilliland *et al.*, 2003; Anderson *et al.*, 2003, Aneja *et al.*, 2003). The daily variability of NH_3 emissions from a naturally ventilated stable is illustrated in Figure 2, while Figure 3 illustrates modelled seasonal variability of NH_3 at a national scale in Denmark.

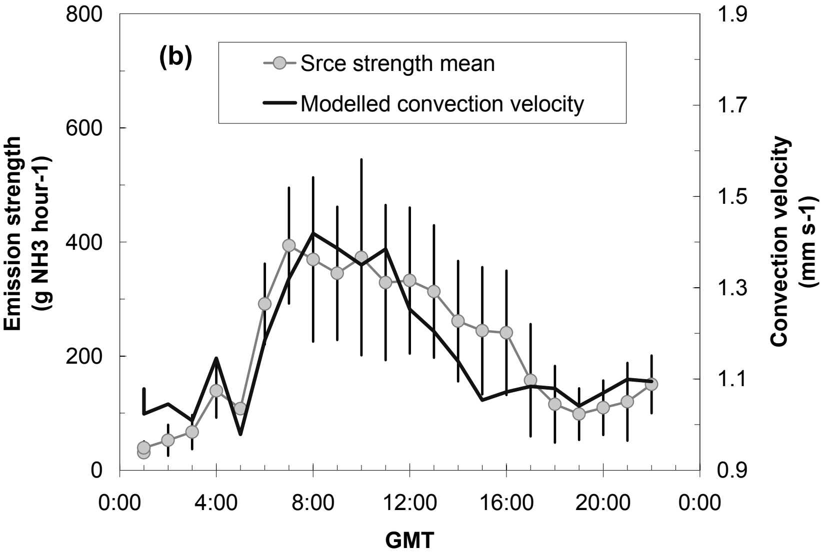

Figure 2. Daily variability of NH_3 emissions from naturally ventilated farm buildings containing 550 animals (2/3 cattle and 1/3 pigs) in Braunscheig, Germany. The estimate was obtained by an inversion method, using measured NH_3 concentration at 230 m and a local dispersion model (FIDES-2D, Loubet *et al.*, 2001). Also shown is an equivalent "convection velocity" representing the building ventilation rate, which was estimated as the sum of a free and forced convection term (Hensen *et al., 20*06b). The error-bars are ± standard deviation.

Modelling NH_3 emissions from hot spots. Many transport-chemistry models have so far not taken the seasonal or diurnal variations in NH_3 emissions into account. One reason is either the difficulty to get detailed information as input to model those variations (Hutchings *et al.*, 2001b). However, improvement has been made, from constant emission models (Singles *et al.*, 1998), and sine functions; which was first derived for TREND (Asman, 1992), and has also been applied in various of the early versions of the EMEP model (Hov *et al.*, 1994; Olendrzynski *et al.*, 2000), and the ACDEP model (Hertel *et al.*, 1995; Ambelas Skjøth *et al.*, 2002). Recently, with information on agricultural practices being more available, NH_3 emissions are more often modelled in a more dynamic way (Génermont and Cellier, 1997; Søgaard *et al.*, 2002; Van Jaarsveld, 2004; Pinder *et al.*, 2004; Sommer *et al.*, 2006; Pinder *et al.*, 2006). The current versions of TREND and OPS use detailed parameterizations of the diurnal and seasonal variations in the NH_3 emission rate that are based on dynamic models (Van Jaarsveld, 2004). If models are applied to smaller areas, where much more detailed information has been collected ,models take many more factors into account (Smits *et al.*, 2005).

Emission inventories with high spatial and temporal resolution have been implemented in a couple of studies. One example is the American study by Pinder *et al.* (2006). They combined a model for housing activity (Pinder *et al.*, 2004) with a redistribution method (Gilliland *et al.*, 2003) to obtain a high-resolution inventory for application in their model system. Another example is the Danish process based emission inventory (Ambelas Skjøth *et al.*, 2004; Gyldenkærne *et al.*, 2005), which accounts for climatic conditions, agricultural practice and meteorology. The emission inventories obtained for the site of one of the Danish monitoring stations Tange are shown in Figure 3 for the years 1989 and 2003. The differences between these two years are due to changes in Danish legislation that have been applied over this period. Danish farmers are now forced to store the manure, and make the application of manure on the fields only during growth season. Model calculations based on these inventories are performed on routine basis under the Danish Background Air Quality Monitoring Programme (Ellermann *et al.*, 2006). The model applied in this programme has been the Lagrangian long-range transport model ACDEP (Hertel *et al.*, 1995), which was also used for the first testing of the inventory. Recently ACDEP has been substituted with the Eulerian model DEHM-REGINA, which has been shown to make a better description of the transport processes.

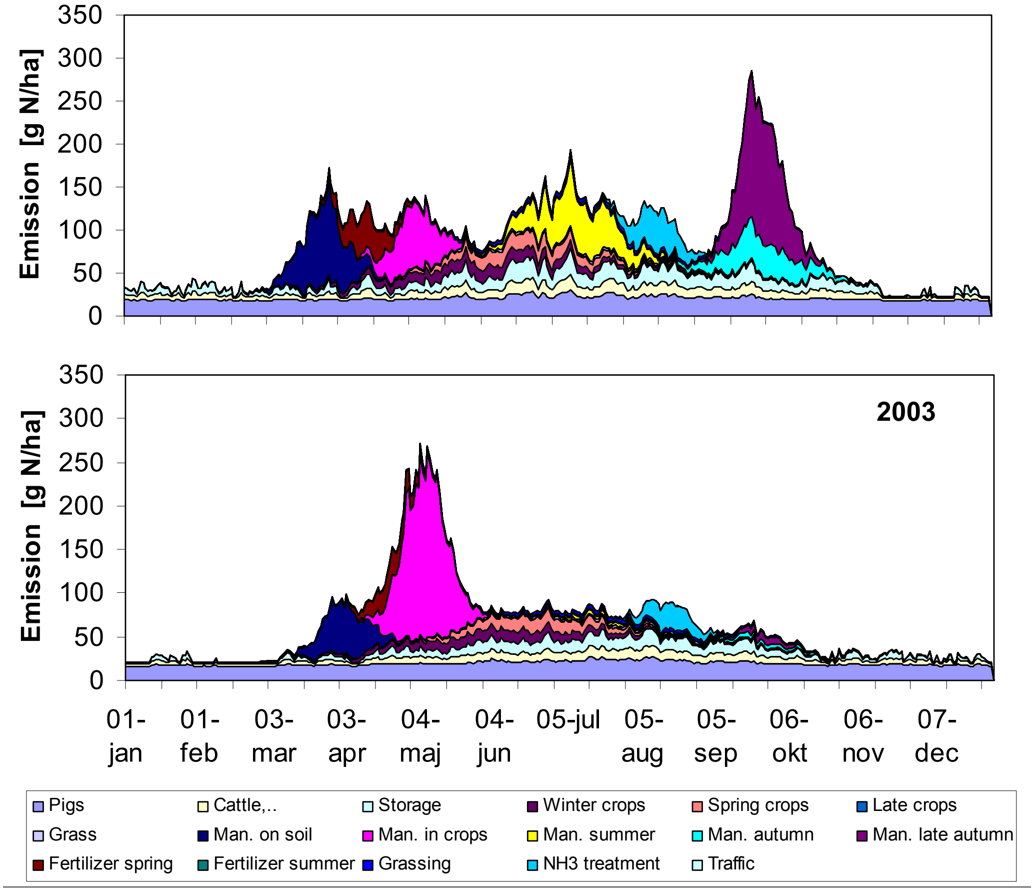

Figure 3. Seasonal variations in modelled Danish ammonia emissions in 1989 (upper plot) and 2003 (lower plot) simulated with a growth model combined with local meteorological data. Differences between the two years are due to changes in local legislation regarding application of manure on the fields in Denmark that have taken place over the period.

Uncertainties in NH_3 emissions estimates. When modelling the deposition around a single farm, there is usually rather detailed information available about the housing and manure handling system. This is usually not the case when the deposition is modelled for a larger area. The basic information that is usually available is the number of animals present at a certain date annually in the housings belonging to each farm (e.g. in a husbandry register). Estimates then have to be made about the housing system. The emission belonging for one animal category can e.g. vary by a factor of two, depending on the housing system (Hutchings *et al.*, 2001a,b). This means that emissions in transport models are rather sensitive to assumptions regarding the housing and manure handling system. Housing and manure handling systems may show variations over countries. There is also some uncertainty in the position of the emission sources, since in local databases the position of the farm is usually that of the house where the farmer lives, which is not necessary the same as the position of the animal housings and storage facilities. National emission factors are revised regularly, as in France, where a project started in 2006 whereby emissions of NH_3 and GHG will be measured for a diversity of animal species, farm buildings, effluent management practices and climates.

Emission of other nitrogen compounds. Although nitrogen emissions from farms are mainly in the form of gaseous NH_3, other forms may contribute as well: N_2O, NO and N_2 are emitted, in particular from solid systems (Dämmgen and Hutchings, 2007). Primary aerosols (skin and feather particles) also contain nitrogen, and some nitrogen containing volatile organic compounds may also be emitted (REF),. Schade and Crutzen (1995) found considerable emissions of methylamine, mainly in the form of trimethylamine-N, which possibly can react to N_2O and HCN. The deposition velocities of these species have however been hardly studied. Nitrous oxide (N_2O) and N_2 are also common in composting elements (Fukumoto *et al.*, 2003).

Emission of other reactive species. Other reactive species may interact with NH_x in the atmosphere surrounding the farm as well as modyfying deposition rate of NH_3 near the farm (Erisman *et al.*, 1993).

A first estimate of the emissions of volatile organic compounds from animal husbandry reveals a considerable emission of sulfur species, mainly as dimethyl sulfide (DMS) from mammals (two thirds of the total) and dimethyl disulfide (DMDS) from poultry (one third of the total) (Smith *et , 20*00a; Chavez *et al.*, 2004), as well as hydrogen sulfide (H_2S), from pig units (Lim *et al.*, 2003). The overall emissions of these species are so large that their chemical fate needs to be considered. In general, all S species apart from sulphur dioxide (SO_2) and sulphuric acid or sulfates (H_2SO_4, SO_4^{2-}) are unstable under atmospheric conditions. However, SO_2 concentrations in ambient air indicate that the bulk of the S emissions from animal husbandry is unlikely to produce SO_2.

Once released from the animal house, DMS and DMDS are likely to be oxidized (Möller, 2003; Sørensen *et al.*, 1996; Saltelli and Hjorth, 1995). However, their reaction pathways and products differ:

- Approximately two thirds of the DMS released react with OH radicals forming methane sulfonic acid (MSA) CH_3-S(O_2)-OH and dimethyl sulfone ($DMSO_2$) CH_3-S(O_2)-CH_3. These reactions do not result in the formation of SO_2. Nevertheless, the reaction products, MSA in particular, play a role in the formation of condensation nuclei and should be removed from the atmosphere primarily by wet deposition, thus exhibiting their acidifying properties.
- One third of the DMS reacts with OH radicals to form sulfur dioxide (SO_2) and sulfuric acid (H_2SO_4). Both species are deposited dry and wet. A considerable increase of SO_2 concentrations is not likely to occur (Shon *et al.*, 2005). However, both species will contribute to acidification. The mean atmospheric lifetime of DMS is in the order of magnitude of a day.

- Within the atmosphere, DMDS reacts much faster than DMS. Its mean lifetime is minutes. The reactions with OH radicals result in the formation of methane sulfenic acid (CH_3-S-OH) and methyl sulfide radicals (CH_3-S). Methane sulfenic acid should react to form MSA (Finlayson-Pitts and Pitts ,1986); the reaction products of the radical should be SO_2 and H_2SO_4.

Sulfur compounds emitted from hot spots may no interact with NH_3 in the gas phase, but they may increase the potential for NH_3 recapture downwind from hot spots (Durenkamp *et , 20*02) by modifying the pH of the receptors (vegetation surfaces, ground). There is however little information to get a clear view of potential interactions between NH_3 and sulfuric compounds deposition.

3 MODELLING NH_X LOCAL DEPOSITION

3.1Atmospheric diffusion

The rapidity with which substances released into the atmosphere are dispersed depends on the wind speed, the turbulence and atmospheric stability (e.g. Seinfeld and Pandis, 1998). Moreover, vertical mixing in the atmosphere can be limited above a certain height, called the mixing height. This mixing height shows diurnal and seasonal variations and depends on turbulence and the atmospheric stability. The existence of a mixing height is especially important for dispersion and transport at regional scales, but during nighttime the mixing height may be so low that it also influences local dispersion. The turbulence and the wind field do not only depend on meteorological conditions, but are influenced by the presence of buildings and by the surface roughness. The wind speed increases with height and this will have an influence on the dispersion away from sources.

Deflection and disturbance of the wind field by a structure (housing, storage tank etc.) has an influence on the dispersion of the pollutant released from this structure (see e.g. Bjerg et al, 2004). In the upwind displacement zone the approaching airflow is deflected around the structure. Immediately leeward of the structure there is a zone that is relatively isolated from the main flow, and further downstream there is a highly disturbed wake. If the pollutant emitted very close to the top of the structure and the exit velocity of any stack small, then the pollutant will be transported downward by “downwash” on the leeward side of the building. This will often be the case for animal houses with outlets on the roof. If an exit stack is relatively high, the pollutant will not be transported downward. The dimensions of the structure (height, width, orientation to the wind, inclination of the roof etc.) all have an influence on the airflow.

The influence of building on the wind field (and hence deposition) will be at minimum at 5-10 times the emission height and at least as large downwind, as the buildings reach upwind (Irvine *et al.*, 1997; Flesch *et al.*, 2005). This means in practice often of the order of 50-150 m downwind.

A description of the local scale transport with the option of simulating the complex flow around buildings may be provided with application of Computational Fluid Dynamics (CFD) models. These models provide a very high spatial resolution, but are in general very demanding with respect to computer resources. An inter-comparison of European CFD models has shown that they provide similar flows even for the more complex building configurations (Ketzel *et al.*, 2002). However, there may be discrepancies between the CFD models concerning where the peak-values appear. The description of the flow very close to buildings may have considerable impact on the calculated concentrations and thereby also on the obtained deposition values further away from the source. CFD models are usually only able to generate wind/turbulence fields and concentration fields, but not calculate deposition. Some atmospheric transport and deposition models, such as the Lagrangian stochastic dispersion models may use the output of the wind/turbulence fields of the CFD-models as an input (e.g. Bouvet *et al.*, 2006).

3.2 Chemical reactions

3.2.1 Photochemical reactions

NH_3 reacts with OH radicals ($NH_3 + OH \rightarrow NH_2 + H_2O$). The rate of this reaction has been estimated at $3.3 (\pm 1) \times 10^{-12} \exp(-933 (\pm 100) / T (K))$ $cm^3\ mol^{-1}\ s^{-1}$ (Diau *et al.*, 1990). Assuming [OH] = 5×10^5 mol cm^{-3} the lifetime of NH_3 is about 110 days, which is much longer than the actual lifetime of NH_3. This means that this reaction is not an important sink for NH_3 in the atmosphere.

3.2.2 Reactions with acids

Ammonia reacts with acids: H_2SO_4-containing aerosol (almost all H_2SO_4 is in the particulate form because it has a very low vapour pressure) and gaseous HNO_3 and HCl. $(NH_4)_2SO_4$ as a solid or in aqueous solution is the preferred form of SO_4^{2-}. Once formed it does not evaporate again. Two regimes can now be distinguished (Nenes *et al.*, 1998; Seinfeld and Pandis, 1998):

- An NH_3-poor atmosphere. In this case there not enough NH_3 to neutralize all H_2SO_4 and the aerosol will for that reason be acidic and the vapour pressure of NH_3 remain low.
- An NH_3-rich atmosphere. In this case all H_2SO_4 reacts with NH_3 and the remaining NH_3 can then react with HNO_3 or HCl to form particulate NH_4NO_3 or NH_4Cl. NH_4NO_3 and NH_4Cl may exist as a solid or as an aqueous solution of NH_4^+, NO_3^- and Cl^-, depending on the relative humidity, temperature as well as the presence of other inorganic salts (Stelson and Seinfeld, 1982). In an ammonia-rich atmosphere NH_4NO_3 or NH_4Cl in solid or dissolved form is generated if the concentration products in the gas phase, $[NH_3][HNO_3]$ or $[NH_3][HCl]$, exceed threshold values. These threshold values decrease with temperature and decrease with increasing humidity, i.e. at lower temperatures and higher humidities NH_4NO_3 formation is enhanced.

The time scales to achieve gas-aerosol equilibrium vary from 1 h to several hours for fine particles (0.1 μm < diameter < 1 μm). For coarse particles (diameter > 1 μm) the time scale is so long that NH_3 generally is not in equilibrium with these particles.

The reaction rate of NH_3 with acids k_{gpc} depends on the concentrations of the acid species present in the atmosphere and shows temporal and spatial variations and is also dependent on the height above ground level. In most regions of Europe ,more acid precursors in the form of SO_2 and NO_x are present than the emitted NH_3 can neutralise. Since NH_3 emissions occur at or near ground level, the quantity of acid neutralised by NH_3 diminishes with height (Erisman *et al.*, 1988). It is likely that often acids are fully neutralised at ground level in large parts of Europe, though not for the whole season. However, in some places with low NH_3 emissions, as in northern Scandinavia neutralisation of acids might not be reached even at ground-level (Hilde Fagerli, EMEP, Norway, personal communication, 2006).

In practice k_{gpc} can be determined from field experiments, based on many assumptions (Erisman *et al.*, 1988; Harrison and Kitto, 1992), or can be inferred from fitting transport models with measured concentrations of gases and aerosols. Using this technique Asman and Janssen (1987) found a pseudo-first order reaction rate of 8×10^{-5} s^{-1} (about 30% h^{-1}), a rate that might have been reduced since 1987 due to reduced emissions of SO_2 in Europe (van Jaarsveld *et al.*, 2000). The reaction rate is so low that it can be assumed that all released NH_3 has not reacted within a few km from sources, but at larger distances the reaction should be taken into account. This can either be done by having a separate chemistry model to parameterise the reaction rate as a function of the NH_3, SO_2 and NO_2 concentrations and then to apply this relation to find the reaction rate of NH_3 to particulate NH_4^+ in an atmospheric transport and deposition model (van Jaarsveld *et al.*, 2000) or by modelling the reaction rate within the atmospheric transport model. For the last option, emissions of participating compounds (NH_3, SO_2, NO_x) are needed, preferably on the same scale. Moreover, information is also needed on many reaction rates, which will slow down the calculations considerably.

The transformation of NH_3 to particulate NH_4^+ produces sub-micron aerosols, which have relatively small deposition velocities (they are too small to settle and too large to be subject to Brownian motion), hence favouring long-range transport of NH_x. As such, gas-to-particle conversion of NH_3 is of great importance for trans-boundary transport of NH_x, although remains an issue of secondary importance in detailed analysis of NH_3 hot spots.

3.3Dry deposition

3.3.1 General

Although this section focuses on ammonia, sometimes some information is given on particles or other gaseous compounds, so that the reader gets an impression of the difference in properties. Some general information can e.g. be found in Sutton *et al.* (1995a, 1998b, 2000).

Transport to and from the surface occurs by turbulent and molecular diffusion. In the atmosphere turbulent diffusion (transport by eddies of different sizes) is responsible for the transport, and can be considered the same for gases and particles smaller than ~10 µm in diameter (Wilson, 2000). For larger particles gravitational settling and cross-trajectory effects (due to gravitational forces and inertia, heavy particles do not follow the fluid trajectories exactly) cannot be neglected (Sawford and Guest, 1991). However, ammonium-containing particles are not that large, except maybe for dusts ejected from housings, which may contain nitrogen.

Close to the surface, in the so called “laminar boundary layer” ,transport takes place by molecular diffusion (gases) or Brownian motion (particles). For particles with a diameter > 0.4 µm interception plays also a role close to the surface especially if the surface has sharp edges or is covered with hair-like objects. For particles with a diameter > 1 µm, impaction increases deposition due to inertia (see e.g. Seinfeld and Pandis, 1998).

Gases are absorbed by diffusion through stomata, but can also be deposited onto the leaves/needles especially if the gases are soluble in water and the leaves are covered by a water-layer. Stomata are closed when it is dark (no photosynthesis occurs then),when the leaves are CO_2 saturated, and during water stress. Particles diffuse too slowly and can therefore not be transported through the stomata. For that reason deposition of particles occurs mainly onto leaves/needles. Once deposited to vegetation, particles are not easily released to the atmosphere again, apart from re-suspension for large particles.

3.3.2 Resistance analogue models for exchange of gases between the surface and the atmosphere

Models describing the exchange or gases between the atmosphere and the surface are usually based on the resistance analogy similar to that of Ohm’s law for electricity (Dämmgen *et al.*, 1997). This analogy relies on the assumption of constant flux layer, which is satisfied in a stationary surface layer with no local advection. Although this assumption would make these models not applicable to local dispersion, there always exists a layer near the ground where no advection occur and these models can be applied (Loubet *et al.*, 2001). Figure 4 shows different models for the dry deposition of gases that can either be used as model at the canopy scale, in which case the resistances are per unit surface of ground (noted with an uppercase R), or at the leaf scale, in which case the resistances are given per unit surface of leaf (noted with a lowercase r).

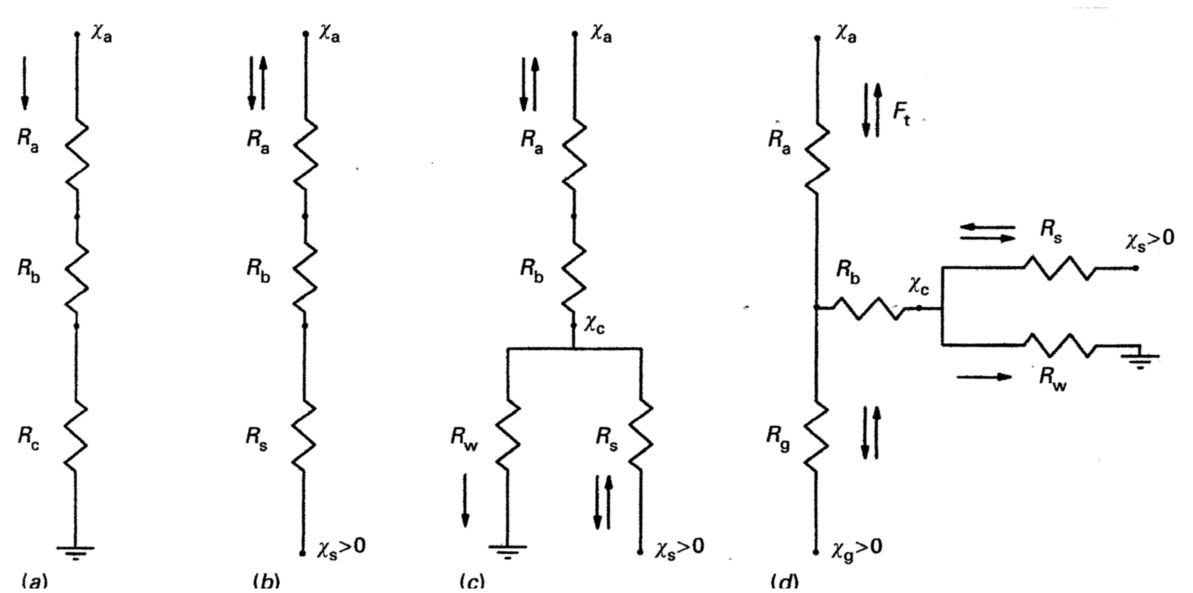

Figure 4. Different types of resistance models for describing exchange of gases between the surface and the atmosphere, with increasing complexity: **(a)** deposition velocity model, **(b)** bi-directional exchange model, **(c)** bi-directional exchange model with a cuticular pathway, and **(d)** two-layer bi-directional exchange model with a cuticular pathway and an emission potential at the ground. Here $\chi_a = c_{air}$; $\chi_c = c_{canopy}$; $\chi_s = c_{stomata}$, χ_c is the concentration outside the leaf, $R_a(z_{ref})$, R_b, R_s and R_w are the aerodynamic, the leaf boundary layer, the stomatal and the wet surfaces resistances for NH_3, respectively. (After Nemitz *et al.* , 2001)

Deposition velocity model. Figure 4a shows the simplest model of gaseous dry deposition, whereby the surface is assumed a perfect sink. The aerodynamic resistance $R_a(z_{ref})$ describes the transport by turbulent diffusion in the atmosphere from z to the laminar boundary layer. It is a function of the friction velocity and the atmospheric stability. The laminar boundary layer resistance R_b on molecular diffusion, while the surface resistance R_c (the canopy as a whole, or the water surface, etc…) depends on processes going on at the surface. In the model of Figure 4a, the flux F can be expressed as a function of the dry deposition velocity $V_d(z_{ref})$ or the resistances $R_a(z_{ref})$, R_b and R_c:

$$F = -v_d(z_{ref})\ c_{air}(z_{ref}) = -\frac{c_{air}(z_{ref})}{R_a + R_b + R_c} \qquad [1]$$

where $c_{air}(z_{ref})$ is the concentration in the air at reference height z_{ref}. The aerodynamic resistance $R_a(z_{ref})$ is given by :

$$R_a(z_{ref}) = \frac{1}{\kappa u_*}\left[\ln\left(\frac{z_{ref} - d}{z_{0m}}\right) - \Psi_h\left(\frac{z_{ref} - d}{L}\right) + \Psi_h\left(\frac{z_{0m}}{L}\right)\right] \qquad [2]$$

where $\kappa = 0.4$ is the von Karman's constant, u_* is the friction velocity (m s^{-1}), which is a measure for the turbulence and increases with wind speed for the same atmospheric stability, d is the displacement height (m), which is about 0.7 times the height of the vegetation -If individual vegetation elements are packed closely together, then the top of the surface begins to act as a displaced surface. The height of this displaced surface is called the displacement height -, z_{0m} the surface roughness length (m), which is a measure for the roughness of the surface, and is about 0.1 times the height of the vegetation. It is the height at which the wind speed is zero in an extrapolated logarithmic wind profile. Ψ_h is a correction function for atmospheric stability, L is the Monin-Obukhov length (m) and is a measure of the atmospheric stability. If L is very large (negative or positive) the atmosphere has a neutral stratification, whereas if L is relatively small and positive the atmosphere is stable, and if L is relatively small and negative the atmosphere is unstable. For neutral conditions: $\Psi_h = 0$. For stable conditions: $\Psi_h = -5(z_{ref} - d) / L$. For unstable conditions: $\Psi_h = 2 \ln((1 + x^2)/2)$, with $x = (1 - 15(z_{ref} - d)/L)^{1/4}$.

The laminar boundary layer resistance R_b for gases transfer through vegetation is often parameterized as follows (Hicks *et al.*, 1987):

$$R_b = \frac{2\left(\frac{Sc_g}{Pr}\right)^{\frac{2}{3}}}{\kappa\ u_*} \qquad \text{For } NH_3 : R_b = \frac{1.89}{\kappa\ u_*} \tag{3}$$

where Pr is the Prandtl number (dimensionless; value 0.72), Sc is the Schmidt number for gases (for NH_3: about 0.662). Sc decreases with the diffusivity of the gas and does not depend much on temperature.

From eqns. [2-3] it can be seen that $R_a(z_{ref})$ and R_b decreases with increasing u_*. Moreover, V_d cannot become higher than $V_{max} = 1/(R_a + R_b)$. The rather simple model of Figure 4a describes well the dry deposition of NH_3 to semi-natural and natural vegetation, which have a low nitrogen status.

Stomatal compensation point. NH_3 exchange with plants receiving large amount of nitrogen is however known to be bi-directional, due to the existence of a non-zero stomatal compensation point concentration C_s, which mainly varies with the nitrogen status and the temperature of the plant (Sutton *et al.*, 1995a; Schjoerring, 1997; Loubet *et al.*, 2002). Indeed, agricultural crops have NH_3 compensation points that vary from 0.1 to 20 ppb (0.07 – 14 µg m^{-3}) (Schjoerring *et al.*, 2000), and even temporarily up to 40 µg NH_3 m^{-3} (Figure 5), which may lead to large emissions from crops (Schjoerring, 1991; Husted and Schjoerring, 1996; Holtan-Hartwig and Bøckman, 199). The equations for Figure 4b hence should rather be used in such case. The flux between the surface and the atmosphere is then given by:

$$F = -\frac{c_{air}(z_{ref}) - c_s}{R_a + R_b + R_s} \tag{4}$$

where R_s is the stomatal resistance. The stomatal compensation point C_s results from the thermodynamic and chemical equilibrium between the ammonium concentration in the apoplast (NH_4^+), and the gaseous NH_3 concentration in the sub-stomatal cavity. This equilibrium is mainly dependent on temperature and pH of the apoplastic solution (Schjoerring, 1997; Smith *et al.*, 2000b). Following Schjoerring (1997), and Nemitz *et al.* (2000):

$$C_s = 4.79\ 10^{-12} \cdot \Gamma \cdot \exp\left(10396\ \frac{T_{leaf} - 25}{298 \times (T_{leaf} + 273)}\right) \tag{5}$$

where Γ is the ratio of the molar concentrations $[NH_4^+]/[H^+]$ in the apoplast (Nemitz *et al.*, 2000). Γ expresses a potential compensation point independent of temperature, which is representative of the plant and the ecosystem: small Γ (typically 20-100) for non-fertilised ecosystems and large Γ for fertilised ecosystems (typically 300-3000). Even fertilised ecosystems such as grazed grassland show a great variability in Γ (e.g. Schjoerring, 1997; Loubet *et al.*, 2002).

Getting into more details, the value of Γ for semi-natural grassland with short grass in Germany, which received fertilizer at a rate of 70 kg N ha^{-1} yr^{-1}, was about 1000 (REF). This is lower than observed for grassland in the UK, which received 300 kg N ha^{-1} yr^{-1} where values for Γ were observed of 3000 (long grass, 15 cm high) and 13000 (short grass, 5 cm high) (Sutton *et al.*, 1998b). For a Dutch heathland that was not fertilized, but is situated in an area with a high N deposition a value of Γ was observed of 1200, which is large for semi-natural vegetation (Nemitz *et al.*, 2004a). Husted *et al.* (2000) found for oilseed rape (Brassica napus ssp. napus) Γ values of 200-500. As an example, Figure 5 shows the effect of Nitrogen supply on C_s for maize (Loubet *et al.*, unpublished data):

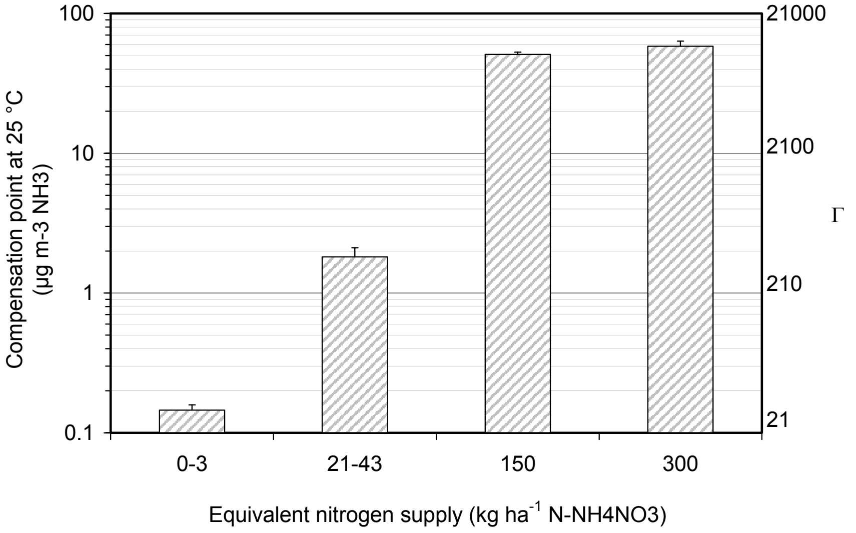

Figure 5. Compensation point concentration at 25°C and Γ values in maize leaves during the vegetative growth, as a function of an equivalent nitrogen supply, estimated using a plant density of 100 000 plants ha^{-1}. Averages are made over the period 5 leaves to flowering. Error-bars correspond to standard errors (stddev / nb).

The compensation point can either be determined from the NH_4^+ and H^+ concentration in the leaf apoplastic solution (e.g. Husted *et al.*, 2000), or inferred from flux measurements both over vegetation surfaces (Fléchard *et al.*, 1999) or within chambers (Hill *et al.*, 2001). The compensation varies with plant species, nitrogen status, and growth stage as well as leaf age. However, on an annual basis a net emission is observed from agricultural crops that will depend on the plant species, meteorological conditions and stress due to drought, diseases or pests. An annual average emission is of the order of 1-5 kg N ha^{-1} yr^{-1} during a growing season (Schjoerring and Mattsson, 2001), which is consistent with micrometeorological measurements (e.g. Milford *et al.*, 2001a).

In semi-natural areas like heathland and forest, the compensation point is generally so low that it does not play a role and only dry deposition occurs. In some cases, however, when air concentrations are very low, under very dry conditions or at high temperatures emission has been observed even from semi-natural ecosystems (e.g. Langford and Fehsenfeld, 1992; Erisman *et al.*, 1994a; Sutton *et al.*, 1995c; Fléchard and Fowler, 1998; Andersen *et al.*, 1999).

Cuticular pathway. As a very hydrophilic gas, NH_3 is readily adsorbed onto wet or humid surfaces, such as the cuticle of the leaves and the stems (Burkhardt and Eiden, 1994; van Hove *et al.*, 1989). The last process is often represented by a cuticular deposition pathway acting in parallel to the stomatal pathway (Sutton *et al.*, 1995a; Figure 4c; See **Appendix A** for detailed equations). The resistance to cuticular deposition of NH_3, R_w, is often modelled as a function of relative humidity RH, as follows (van Hove *et al.*, 1989; Sutton *et al.*, 1995a; Nemitz *et al.*,2000b):

$$R_w = R_{wmin} \exp\left(\frac{100 - RH}{\beta_{Rw}}\right) \qquad [6]$$

where R_{wmin} ranges between 2 and 20 and β_{Rw} is of the order of 6-12. It should be noted however, that cuticular deposition to "wet surfaces" may also occur without apparent dew (Duyzer *et al.*, 1992; Sutton *et al.*, 1992; Wyers and Erisman, 1998), which might be due to the presence of wet films at the leaf surface created by the conjunction of stomatal evaporation and the presence of hygroscopic aerosols deposited preferentially near the stomates (Burkhardt and Eiden, 1994). The empirical parametrization of Eq. [6] incorporates the effect of hygroscopy, but does not distinguish any dependence of R_w on R_s. Smith *et al.* (2000b) gives an alternative empirical expression of both temperature and relative humidity. Nemitz *et al.* (2001) included the dependence of R_w on the SO_2 / NH_3 concentration ratio.

It should be recognized that the parametrization of R_w is, however, a steady state simplification of a dynamic bi-directional exchange of NH_3 with leaf cuticles. An initial dynamic model of this effect was provided by Sutton *et al.* (1995a, 1998a). A simplification of that model was that the leaf surface pH needed to be specified. Fléchard *et al.* (1999) advanced this substantially, by developing a model that simulated leaf surface pH in response to wet and dry deposition processes and derived bi-directional cuticular exchange using a dynamical model that takes into account the uptake of different soluble pollutants their chemistry in the water layer on the leaf. In these models, the steady state value of R_w is effectively replaced by a capacitance of the leaf surface, a capacitance charge, with exchange limited by an adsorption /desorption resistance (R_d).

Near sources, cuticular deposition is likely to be very high in humid climate due to large NH_3 concentrations. Throughfall measurements near intensive source which are reported in the literature may be indicative of cuticular deposition, although they might be subject to uncertainties due to dry deposition onto collectors, flooding under high rain events, or biochemical transformations of NH_x deposited onto leaves (Theobald *et al.*, 2001; Dämmgen *et al.*, 2005; Erisman *et al.*, 2005). Theobald *et al.* (2001) report throughfall ranging 3% and 4% of the NH_3 emitted by a source releasing between 500 and 2800 kg N-NH_3 yr^{-1}. It should be noted that at very high concentrations the value of R_w tends to increase, due to a partial saturation of the leaf surface sink. This effect may be treated by consideration of the effect of the NH_3 / SO_2 ratio on R_w (cf. Nemitz *et al.*, 2001), as well as by empirical approaches based on observational data (Jones 2006; Pitcairn *et al.*, 2004).

Two layer exchange model. A two-layer resistance scheme (Figure 4d; Nemitz *et al.*, 2001; See **Appendix B** for detailed equations) may be considered to take account of a ground level source which can either be emissions from a fertilizer or from decomposing leaf litter (Denmead *et al.*, 1976; Sutton *et al.*, 1993c; Nemitz *et al.*, 2000a). The two-layer model shows a soil or litter compensation point, which may be very large, especially in nitrogen rich litter (Husted *et al.*, 2000; Nemitz *et al.*, 2001; Sutton *et al.*, 2001), where Γ can reach more than 100000 (Sutton *et al.*, 2006). The two-layer models have shown to be very useful in modelling the effect of the canopy structure one NH_3 exchange with the atmosphere (Personne *et al.*, 2006).

3.4Deposition of particulate ammonium

The dry deposition of particles to the ground can be represented by the scheme of Figure 4a, but with $R_c = 0$, and with a parallel pathway correspond to a resistance inverse to the settling velocity of the particle V_s. The computed deposition velocity for particles becomes simply (Slinn, 1982 ; Zhang *et al.*, 2001):

$$V_d = V_s + \frac{1}{R_a(z_{ref}) + R_{bpart}} \qquad [7]$$

where R_{bpart} is the boundary layer resistance for particle, which depends on Brownian diffusion. V_d depends strongly on the particle size, the characteristics of the surface (roughness) and u_*. The dry deposition velocity V_d of NH_4^+ containing particles for neutral atmospheric conditions was estimated by Erisman *et al.* (1994b) as:

$$V_d = \frac{u_*}{A} \qquad [8]$$

where: V_d and u_* are in m s^{-1}, A = 500 (dimensionless) for low vegetation and A = 100 for forests. Measurements show that the dry deposition velocity of NH_4^+ containing particles to moorland or grass is of the order of 0.2 cm s^{-1}, with a large uncertainty justifying the rough parameterisation of Eq. [8] (Sutton *et al.*, 1993c; Duyzer, 1994). The dry deposition velocity to forests is higher than to moorland.

The dry deposition velocity of NH_3 is potentially relatively high and is about a factor of ten higher than that of particulate NH_4^+. This means that NH_x after conversion from NH_3 to NH_4^+ is not dry deposited very well and is transported over long distances. The only efficient removal process for particulate NH_4^+ is wet deposition (Asman and Janssen, 1987). However, it should be noted that since agricultural areas are mainly ammonia sources, the overall areas that are strong sinks for ammonia (moorlands, forests etc) may be rather small. This points to an ongoing uncertainty on the relative atmospheric transport distance of ammonia and ammonium on regional scales (cf. van Pul *et al.*, 2006).

3.4.1 Measured dry deposition velocities of NH_3 to (semi-) natural vegetation

Measurement of NH_3 deposition velocity to semi-natural vegetation is reported in many studies (Table 1). Table 1 shows higher V_d for forest than for moorland and grassland, which reflects the higher u_* over forest. It also shows that V_d is often larger than what can be accounted for by stomatal uptake (Duyzer, 1994), as well as relatively high during nighttime, clearly indicating a non-stomatal uptake. The dry deposition velocity increases with surface wetness (Wyers and Erisman, 1998) and decreased with NH_3 concentration (Fléchard and Fowler, 1998). Due to the large non-stomatal dry deposition, dry deposition velocity of NH_3 is often larger than for SO_2 or O_3. It should be noted, however that there are many other studies such as these where deposition velocity values were not actually reported, but instead the studies reported net (bi-directional) fluxes together with parametrizations of Γ, R_w, etc.

Table 1. Example dry deposition velocity and canopy resistance data for NH_3 for semi-natural ecosystems (moorland, unfertilised grassland and forests), as found in the literature. The deposition velocity or R_c approaches correspond to the simpler model of Figure 4a.

Ecosystem type	v_d (cm s^{-1})	R_c (s m^{-1})	References
Moorland			
	1-4	<10[a)]	Sutton *et al.* (1992)
	1.9[b)]	0-150	Duyzer (1994)
	1.2	dry : 61 wet : 23 snow : 56 frozen : 50-100	Fléchard and Fowler (1998)[c)]
Unfertilised grassland			
	1.5-2.0	3-6	Sutton et al. (1993c)
	0.13-1.4	-	Hesterberg (1996)[d)]
	-	5-27	Sutton *et al.* (1997)[e)]
Forest			
Sitka Spruce, European Larch, Lodgepole Pine, Noble Fir	6.6	6	Sutton et al. (1993c)[f)]
Douglas Fir	2.5	20-25	Duyzer *et al.* (1994)[f)]
Douglas Fir	3.2	-	Wyers et al. (1992)[f)]
Norway Spruce	0.88 (stable atmosphere) 1.8-4.0 (other conditions)	-	Andersen *et al.* (1999)[f)]
Parameterisation			
Humid semi-natural ecosystems and forests		daytime wet : 500 night-time dry : 1000 night-time wet : 0	Erisman *et al.* (1994b)

[a)] During frozen conditions R_c = 50 – 200 s m^{-1}. [b)] Measurements made mainly during daytime. Estimated annual average 24-hour V_d = 1.4 cm s^{-1}. [c)] Emission observed during 6% of the time. [d)] A compensation point between 3 and 6 ppbv (2.1-4.2 μg m^{-3}) was observed. [e)] Sometimes emission occurs. [f)] Emission observed during some periods. It should be noted that, the number of experimental data as well as the experimental conditions may bias the interpretation (daytime over-represented, low wind speeds underrepresented). Moreover, since $V_d(z_{ref})$ depends on z_{ref}, the V_d may not be directly comparable. Evaporation of NH_3 from NH_4^+ containing aerosols deposited onto leaves may lead to slight underestimation of V_d (Nemitz et al, 2004a; Nemitz et al., 2004b, Nemitz and Sutton, 2004).

3.5Wet deposition

General. Cloud droplets and raindrops are usually acidic. If NH_3 is absorbed by cloud droplets or raindrops it reacts with H^+ to form NH_4^+. Both NH_3 and NH_4^+ containing particles can be removed by absorption in clouds droplets or scavenging below clouds. In general in-cloud scavenging of particulate NH_4^+ contributes most to the NH_4^+ concentration in rainwater. This holds, however, not for the contribution of a point source to the wet deposition close to this point source. There are two reasons for that:

- At short distances from the source the NH_3 plume has usually not reached the clouds and for that reason in-cloud scavenging of the NH_3 originating from the source will not occur.

- Most of the NH_3 will not yet have reacted with acid compounds (H_2SO_4 in aerosols or gaseous HNO_3 and HCl) so close to the source (see section 7) and for that reason most of the NH_x will be in the form of NH_3.

For that reason it can be expected that much of the NH_x from a nearby source is removed by below-cloud scavenging of NH_x, which is not as efficient as in-cloud scavenging of NH_x. In the following below-cloud scavenging of NH_3 will be discussed in more detail. A short description of in-cloud scavenging of NH_4^+ is discussed in **Appendix C**.

Wet deposition of NH_x is important as a background deposition (Hov and Hjollo, 1994). It originates partly from groups of sources within 50-100 km (wet deposition of scavenged NH_3) and partly from long-range transport (wet deposition of scavenged NH_4^+) (Asman and van Jaarsveld, 1992). It has been shown from experimental results that wet deposition of NH_x is correlated with the emission density on scales of 20-100 km (Asman and van Jaarsveld, 1992; Park and Lee, 2002; Aneja *et al.*, 2003). Within 0.5 – 1km from a source the contribution of the source to wet deposition of NH_x is much less than the contribution to dry deposition. This is caused by the fact that the plume has not been mixed up at this distance and the NH_3 concentration at ground level is relatively high. Wet deposition is determined by the average concentration over the whole plume height and not by the much higher ground-level concentration. Due to its limited importance at the very local scale wet deposition is not taken into account in most local models: Danish OML-DEP (Olesen, 1995), the UK LADD (Dragosits *et al.*, 2002), French FIDES (Loubet *et al.*, 2001) and MODDAAS (Loubet *et al.*, 2006). Conversely, wet deposition is included in DEPO1 (Asman, 1998).

Sometimes high NH_4^+ concentrations are measured with open precipitation collectors near sources. It is likely that a large fraction of these high concentrations are not caused by wet deposition, but by dry deposition of NH_3 to the (wet) surface of the rain collector.

Below-cloud scavenging of NH_3. Below clouds, NH_3 is taken up by falling raindrops (typical radius 0.1 – 1 mm). Falling raindrops have a relatively high speed (0.71 - 6.5 m s^{-1}). Moreover, they have a much smaller surface to volume ratio than cloud droplets. As a consequence, with the exception of small raindrops, it is unlikely that any droplet becomes NH_3-saturated in the plume. For convective conditions, a maximum scavenging coefficient can be derived following Asman (1995):

$$\lambda_b = 9.85 \times 10^{-5} I_{mm}^{0.616} \qquad [9]$$

where λ_b is the below-cloud scavenging coefficient for NH_3 (s^{-1}). This gives the fraction of the plume concentration that is removed per second; I_{mm} is the rainfall rate (mm h^{-1}, unit usually reported). Equation [9] shows that the removal rate of NH_3 by below-cloud scavenging increases with the rainfall rate. Although the uncertainty on λ_b is about a factor of 2, if we consider a low rain event (1 mm h^{-1}), and a shower (10 mm h^{-1}), and a plume moving 2 m s^{-1} downwind from a hot-spot (hence taking 500 s to travel a 1000 m), we found from Eq. [9] that between 5% and 20% of the NH_3 is removed from the plume during a rain event. If we combine this with the frequency of rain events (5-10% of the time in humid regions), we estimate that an order of magnitude of between 0.25%-2% of NH_3 scavenged by wet-deposition up to 1000 m downwind from sources. This amount is much smaller than typical near source removal by dry deposition.

It should be noted that if the assumption of NH_3-unsaturated droplets hold, below-cloud scavenging should not change the concentration gradients within the plume. Moreover, as scavenging affects the whole air column, it should only decrease with lateral dispersion and not vertical dispersion of NH_3.

Below-cloud scavenging of particulate NH_4^+. The efficiency of below-cloud scavenging of particles depends on the particle size (distribution) and the raindrop size distribution, which is a function of the rainfall rate. In the atmosphere NH_4^+ is predominately found in the fine particles (0.1 < diameter < 1 μm). For this size range the scavenging coefficient is very low: of the order of 1×10^{-7} s^{-1} for a rainfall rate of 0.5 mm h^{-1} and 1×10^{-6} s^{-1} for a rainfall rate of 25 mm h^{-1}. It is likely, however, that there are also larger particles (1 μm < diameter < 10 μm) emitted by housings that may have adsorbed NH_3 and therefore contain NH_4^+. These will be scavenged at a higher rate, but will also be dry deposited at a relatively high rate.

3.6Short description of existing models NH_x local deposition

There are many different types of local atmospheric transport models for ammonia and ammonium. The reason for that is that they are made for different purposes. One of the things that can vary is e.g. the scale. Some models are only suited to model the deposition up to 1 km from one source. Other models are able to give local depositions for a whole country. Some models are especially developed to study the results of one NH_3 field experiment, whereas others are models that describe the transport of and deposition of air pollutants in general. Which processes are incorporated into which detail in a model depends on the purpose of the model. If e.g. the recapture of NH_3 emitted from the soil by overlaying vegetation should be described it is necessary to have a multi-layer model that has the soil and vegetation in different layers. Sometimes a cascade of models is used, where the output of long-range transport models forms the background deposition onto which the results of a local deposition model are added as is the case with the combination DDR/LRTAP (Asman and Maas, 1986), DEPO1/TREND (Asman, 2004), FRAME/LADD (Theobald *et al.*, 2004) and DEHM-REGINA in combination with OML-DEP (see Table 2). An overview of dispersion models, which may be suitable for modelling local dispersion of NH_3 and be coupled with deposition of NH_3,is given in **Appendix D** and is therefore not detailed here.

Table 2. A non-exhaustive list of local atmospheric transport and deposition models for NH_x.

Mod.	Brief description	Parameters	Pluses	Minuses	Scale (km)	Big Leaf / Multi-layer	Refs.
DDR	3-D statistical Gaussian surface depletion model, first order reaction, mixing height	Frequency distribution wind speed, Pasquill classes, precipitation statistics and rate for each wind direction	Can cover a very large area with great detail, both point and area sources, can cover long periods	Meteorology, z_0, v_d everywhere the same, no detailed chemistry	0.01 – 500	Dry deposition velocities	1) 2)
TREND/ OPS	3-D statistical Gaussian dispersion model, first order reaction depending on actual concentrations, mixing height	Representative u_*, L, precipitation statistics and rate for each stability class for each wind direction	Can cover a very large are with great detail, both point and area sources, some possibilities for variation in z_0 and R_c, can cover long periods	Meteorology the same everywhere, no detailed chemistry	0.01 – 2000	Big leaf and two-layer model	3) 4) 5)
LADD	Hybrid model, with Lagrangian column following the mean flow and vertical diffusion law, coupled with surface exchange one version has been extended to include compensation point	u_*, zo, d, L_{MO} S_{srce}, source location r_s, r_w (mins and slopes) C_s	3D Fast Land use predefined C_s and R_s used	No inside canopy transfer	0.001 – 2000	Big-leaf	6)
DEPO1	Gaussian-3D model coupled with canopy compensation point resistance model, Includes reaction, dry deposition of NH_4^+ and wet deposition (below-cloud/in-cloud) of NH_3 and NH_4^+, and the existence of a mixing height.	u_*, zo, d, L_{MO} S_{srce}, source location r_s, r_w (mins and slopes) C_s, rainfall rate, scavenging ratios, pseudo-first order reaction rate	Can treat compensation points, point sources, areas sources, can cover a large area and long periods	Meteorology and z_0 constant understand	0.01 – 500	Big-leaf	7) 8)
FIDES	Analytical solution of the diffusion equation coupled with resistance analogue model at the canopy scale in 2D	z_0, d, u_*, L_{MO} S_{srce}, size source R_s, R_w C_s	Process based Fast Few parameters	Only in 2D z_0 constant no side flux	0.001 – 5000	Big-leaf	9)
MODDAAS	Lagrangian Stochastic dispersion model coupled with a leaf scale resistance analogue model in 2D	$U(z_{ref})$, $L_{MO}(z_{ref})$ S_{srce}, source location r_s, r_w (mins and slopes) C_s lad(z) and h(z)	Process based Multi-sources Multi-canopies Inside canopy transfer	Only 2D Slow Large no. of parameters turbulence parameterised	0.001 – 2000	Multi-layer	10)
DAMOS	The DAMOS (Danish Ammonia Modelling System) is a combination of the Eulerian long-range transport model DEHM-REGINA and the local scale plume model OML-DEP	u_*, z_0, L_{MO} S_{srce}, source location pseudo-first order reaction rate, land use	High temporal and geographical resolution in emissions – good description of transport	High demand for computer time	0.4 – 1000	Big-leaf	11) 12) 13) 14)

1) Asman and Maas, 1986; 2) Asman *et al.*, 1989; 3) Asman and van Jaarsveld, 1992; 4) van Jaarsveld, 1995; 5) van Jaarsveld, 2004; 6) Hill, 1998; 7) Asman, 1998; 8) Asman *et al.*, 2004; 9) Loubet *et al.*, 2001; 10) Loubet *et al.*, 2006; 11) Hertel *et al.*, 2006; 12) Frohn *et al.*, 2001; 13) Tilmes *et al.*, 2002; 14) Olesen, 1995.

DDR. DDR is a 3-D Gaussian surface depletion model (Asman and Maas, 1986; Asman *et al.*al., 1989). The way dry deposition is treated is derived from Horst (1977), but a pseudo first order reaction velocity (NH_3 to NH_4^+), dry and wet deposition and the existence of a mixing height are build into the model. A surface depletion model was chosen, because the dry deposition velocity of NH_3 is so large that dry deposition cannot be described adequately by The basic concept of a surface depletion model is that the deposition flux to the surface is represented by sources (or sinks) at the earth's surface with an equivalent negative source strength, The concentration distribution is then calculated as the sum of the non-depositing plume from the primary source plus the (negative plumes from all upwind surfaces that account for dry deposition. The dry deposition is then calculated as the near-surface concentration multiplied by the dry deposition velocity. This model is a statistical model in the sense that it uses frequency distributions of Pasquill stability classes and an average wind speed for each wind-direction for each class. The model has been used to model the NH_x deposition close to farms (0-500 m), as well as the background depositions on a 5x5 km^2 scale in the Netherlands including foreign contributions that were partly calculated with a long-range transport model that covers whole Europe (Asman and Janssen, 1987). The dry deposition was modelled using dry deposition velocities.

TREND/OPS model. TREND and the derived short-range model OPS is a Gaussian diffusion model that uses meteorological statistics and can cover whole Europe. (Asman and van Jaarsveld, 1992; van Jaarsveld, 1995; van Jaarsveld, 2004). It is used to calculate concentrations and depositions over longer time periods (month – 10 years). A meteorological pre-processor creates the meteorological input for the model from e.g. hourly meteorological observations. The meteorological input of the model consists of information on the frequency of occurrence of different stability classes for different wind directions. For each class for each wind direction there is a representative value of u_* and L, information on the mixing height and information on the precipitation (precipitation probability, precipitation intensity, length of rainfall period). The model takes into account diurnal and seasonal variations of the meteorological parameters. The wind speed and diffusivity in the model are height-dependent. Close to the source the model is based on a detailed description of the plume, whereas further away where the plume has reached the mixing height the process descriptions are simplified. Dry deposition of NH_3 and NH_4^+ are modelled using the big-leaf model or a two-layer model and wet deposition of both components is described with below-cloud and in-cloud scavenging coefficients. The model is a source depletion model that however, mimics the results of a surface depletion model. The model uses a pseudo-first order reaction rate to describe the reaction from NH_3 to NH_4^+. The reaction rate can be based on the results of detailed chemistry models taking into account actual concentrations of NH_3, SO_2 and NO_x. The model can treat both point sources and area sources.

DEPO1 and derived models. DEPO1 (Asman, 1998) is a steady state model, where vertical diffusion is treated with a K-model and cross-wind horizontal diffusion with friction and stability dependent. The model assumes the same surface roughness length everywhere. Wind speed and diffusivity in the model are height-dependent. The dry deposition velocities are modelled using the big leaf approach. The model can treat compensation points. Compensation points and surface resistances can vary over the model area. A pseudo-first order reaction rate of NH_3 to NH_4^+ is included in the model, but other components and more complicated reactions can be included as well. Below-cloud and in-cloud scavenging for NH_3 and NH_4^+ are calculated using scavenging coefficients. For below-cloud scavenging of NH_3 the scavenging coefficients of Asman (1995) are used. The model uses hourly meteorology (u_*, L, rainfall rate) as an input, but is also used to calculate deposition over long periods (10 years). DEPO1 was used to derive transfer matrices that were build into a GIS-system that was used to calculate the deposition on a $100x100m^2$ scale for an area of about 80x80 km2 size and which gives the user the opportunity to study the effects of emission reductions or different spatial distributions in an easy way (Asman *et al.*, 2004).

LADD. The LADD (Local Atmospheric Dispersion and Deposition) model is used to simulate atmospheric dispersion of NH_3 within domains of up to a few km. (Hill, 1998; Dragosits *et al.*, 2002). LADD is a Lagrangian model that simulates atmospheric dispersion and surface deposition by moving a vertical column of air along straight-line trajectories across a grid (Figure 6). This air column is divided into layers of increasing depth up to the height of the planetary boundary layer and moves across the grid at a rate equal to the mean wind speed for the trajectory direction. As the column moves across the grid, NH_3 is emitted into the layers containing sources and is mixed vertically within the column at a rate determined by the turbulent diffusion coefficient (K). This coefficient is calculated from the mean wind speed for the trajectory, the roughness length (z_0) assigned to the grid square, the height within the column, the boundary layer height and the atmospheric stability following the methods of Pasquill and Smith (1983) and Ayra (1988). Deposition from the lowest layer to the surface is calculated using z_0, the resistance of the surface to NH_3 deposition (R_c), atmospheric stability and mean wind speed. Within the model each grid square in the domain is assigned a value of z_0 and R_c, which are dependent on the land use. For each trajectory direction, parallel trajectories are modelled sequentially until the entire domain has been covered. The trajectory direction is then increased by a user-defined increment (e.g. 1°) and the process is repeated for all directions. Wind direction frequencies (for each 10° sector) are used to weight the contribution to NH_3 concentrations from each trajectory. The model input data are the emission strength and height for each grid square, the land cover for each grid square, the mean wind speed and the wind direction probability for each 10° sector, the height of the atmospheric boundary layer and the NH_3 concentrations at the domain boundaries. Once all trajectories have been modelled, the mean NH_3 deposition and the mean concentration (at various heights) for each grid square are output as well as the amount of NH_3 that is exported out of the domain.

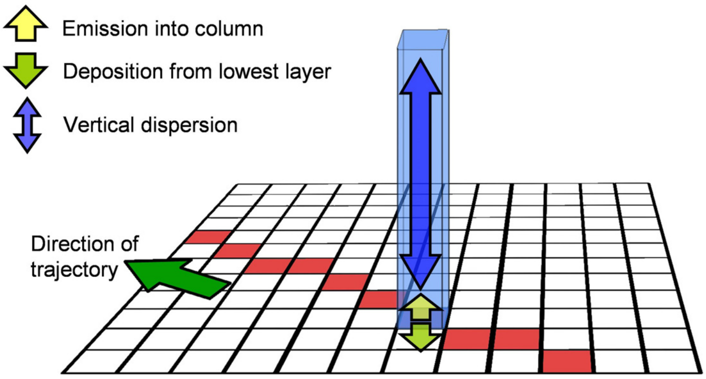

Figure 6. Diagram explaining the principles of the LADD model. The blue column of air moves along a trajectory indicated by the red grid squares. As the column moves across the grid three processes occur: NH_3 is emitted into the column; NH_3 is deposited from to the surface and the ammonia within the column is dispersed vertically.

FIDES-2D. The FIDES model (Flux Interpretation by Dispersion and Exchange over Short Range) is a steady state, two-dimensional model described in Loubet *et al.* (2001). No chemical reactions are considered in the atmosphere. The canopy height h and the roughness length z_0 are assumed constant, and wind speed and turbulence are assumed to be horizontally uniform. The big-leaf assumption is made, which considers the canopy as a unique layer at height z_s (larger than z_0), for heat, momentum, evaporation and NH_3. To assess the concentration $C_a(x,z)$ and the fluxes, the model (as does the MODDAAS-2D model) is based on the general superposition principle (Thomson, 1987), which relates the concentration at a location (x,z), $C_a(x,z)$, to the source strength at another location (x_s,z_s), $S(x_s,z_s)$, with the use of a dispersion function D(x,z/xs,zs) (in s m^{-3}) :

$$c_a(x,z) = c_{bgd} + \int_{\text{all } x_s} S(x_s,z_s)\, D(x,z / x_s,z_s)\, dx_s \qquad [10]$$

where C_{bgd} is the background concentration, assumed to be constant with height. A negative source strength (in µg NH_3 m^{-1} s^{-1}) denotes a sink. To estimate C_a using Eq. [10], $D(x,z/x_s,z_s)$ and $S(x_s,z_s)$ are first calculated using an exchange and a dispersion model, respectively. The dispersion model is taken from Huang (1979), which describes diffusion from a line source, based on the assumption that wind speed and diffusivity are power functions of height. The deposition model is the two-pathway resistance model of Figure 4c.

MODDAAS-2D. The MODAAS-2D model results from the coupling of a Lagrangian Stochastic Dispersion (LS) model with a leaf scale ammonia exchange model. MODDAAS-2D is similar to FIDES-2D in that it is a steady state and two-dimensional model, with no chemistry, which is also based on the superposition principle of Eq. [10]. However, the model is different in that it is a multi-layer model which considers explicitly the transfer through the canopy. The dispersion matrix approach (which is also used in FIDES) is used: the concentration in each grid cell is the sum of the contribution of all the sources weighed by the dispersion matrix element which has a unit of m s^{-1}. The LS model gives the dispersion matrix, using a parameterised or a given flow, following the approach of (Thomson, 1987).

The source terms S_i depending on the concentration in the grid cell C_i are resolved by solving the linear system corresponding to the discretisation of Eq. [10]. The radiation inside the canopy is estimated with an exponential attenuation. The exchange model follows in each grid cell is that of Figure 4c. The emission and deposition terms of the exchange flux are split as in FIDES in order to get a linear system for the concentration in each grid cell of the canopy. Details of the MODDAAS-2D can be found in (Loubet *et al.*, 2006).

DAMOS. The Danish Ammonia Modelling System (DAMOS; sketch in Figure 7) is a combination of the Eulerian long-range transport model DEHM (Christensen, 1997; Frohn *et al.*, 2002) and the Gaussian local scale transport-deposition model OML-DEP (Olesen, 1995) for the dry deposition making use of the surface depletion method from (Horst, 1977) with a pseudo first order reaction velocity (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 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 ammonia emissions are computed using the parameterisations with high spatial and temporal resolution (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).

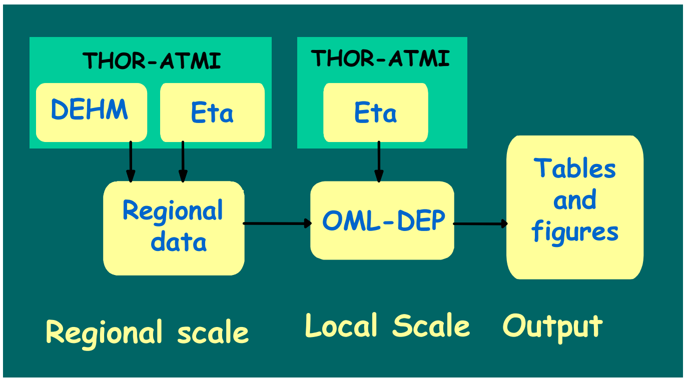

Figure 7. Sketch to illustrate the DAMOS (Danish Ammonia Modelling System) for assessment of atmospheric ammonia loads from livestock farms.

OTHER MODELS. An interesting approach has been used in Switzerland where mountains make modelling quite challenging. Spatially very detailed emission inventories were made for NH_3

(200x200m^2 or less), that formed the input for the calculations. In stead of using complicated atmospheric transport models they used a function of deposition vs. distance that was developed for The Netherlands (average for 10 years, averaged over all wind directions) (Rihm and Kurz, 2001). Although this should not be done in principle as the Swiss climates differ from the Dutch climate, a good correlation was obtained between modelled and measured values for 17 sites, Later Thöni *et al.*, (2004) refined the method adjusting the function distance vs. so that an optimum correlation was obtained for this function that then should be more representative of the Swiss situation. one of the reasons why the method is a bit questionable is that the dry deposition in Western Europe can show differences of a factors 2-5 between different wind directions, mainly because the difference in frequency. Nevertheless this type of approach, or a spatially very detailed model such as DEPO1 could then be used to redistribute the dry deposition of NH_3 calculated for 50x50 km^2 in such a way within the grid element that a reasonable inputs to nature areas can be estimated.

3.7 Available datasets for validating local scale deposition models

Validation of the NH_3 recapture model is a crucial point. Although NH_3 deposition should be used for validation, it is often not measured. Most datasets only contain concentration measurements at several distances downwind from a source, which is either controlled or measured. Table 3 gives an overview of the known datasets that could be used for validating local recapture models.

Table 3. Known datasets that could be used to validate short-range NH_x deposition models.

Dataset Name	Year	Brief description	References
Burrington Moor (Grassland)	1998	Slurry spread on a U shape 20 m width x 600 m long band. NH_3 emission measured with a 5 heights, denuder, mass balance . Concentration measured at 1 height down to 300 m downwind	Sutton *et al.*, 1997 Loubet *et al.*, 2006
Bretagne (Grassland)	1999	Slurry spread on a 30 m width x 90-150 m long band. NH_3 emission measured with a 3 heights, bubbler, mass balance . Concentration measured at 1 height down to 180 m downwind	Loubet *et al.*, 2006
Davron (maize)	1997	Controlled NH_3 line source of 200 m long. NH_3 emission controlled with a flow-meter and measured with a 7 heights Ferm denuder mass balance. Concentration measured at 7 heights within the maize canopy and above down to 160 m downwind	Loubet *et , 20*03
Woodland	2001	Controlled NH_3 line source of 30 m long. NH_3 emission controlled with a flow-meter Concentration measured at several heights within the forest down to 60 m downwind Turbulence measured Throughfall measurements	Theobald *et al.*, 2001

4 METHODS FOR EFFECT ASSESSMENT AND AIR MONITORING IN NH_3 HOT SPOTS

4.1 Key issues for effects assessment and NH_3 monitoring in hot-spots

Interest in the effects of NH_3 concentrations and deposition in hot-spot areas often arises when a semi-natural site (e.g. nature reserve) is considered to be at risk from exposure to atmospheric NH_3 or N deposition. Frequently in these cases, national- or regional-scale dispersion and deposition modelling is not sufficiently detailed to assess whether vulnerable semi-natural sites are at risk or not. For example, national-scale modelling with a spatial resolution of 5 km can provide an estimate of average concentration and deposition for the grid-square containing the site but due to the spatial variability of concentrations and deposition the actual values at the site may be very different. Local dispersion and deposition modelling can provide a better estimate of concentration or deposition at the site and can also take into account the location of sources relative to the site and detailed land cover and land use information. Modelled concentration and deposition data can be used to assess the potential impact on the site (e.g. by comparison with effect thresholds) and these analyses can be used by governments, local authorities or conservation organisations to determine the impact on the site in relation to conservation, human health and planning issues. The local-scale modelling is often done in conjunction with field measurements or long-term monitoring to provide an alternative method of impact assessment as well as data that can be used to verify the outputs of the modelling. The following paragraphs give an overview of existing measurement and monitoring techniques, the application of local-scale modelling and how these can be combined to estimate effects on semi-natural sites.

4.2 Review of methods for monitoring NH_3 concentrations and deposition in hot spots

NH_3 concentrations and deposition are generally variable over long time periods (e.g. > 1 year) and therefore monitoring needs to be carried out over at least this time period and at the shortest temporal resolution possible. Factors leading to this temporal variability are mainly due to the changing meteorological conditions, which affect the NH_3 source strengths, the atmospheric dispersion and dry deposition, the wet deposition and the canopy characteristics. Another important temporal factor is the agricultural activity and management throughout the year. Concentrations and deposition are also highly spatially variable and therefore it is often important to monitor these quantities at several locations to get information on the spatial variability, the potential effects on different ecosystems and the extent of these effects. Measurements should be placed at the locations that the effects need to be determined (e.g. edge of nature reserves closest to source or an ecosystem type of interest) as well as locations that would be useful for verifying any dispersion modelling (e.g. logarithmically spaced downwind of a source). The requirement for long-term monitoring at multiple locations means that it is normally only possible to use low-cost monitoring techniques.

Two complementary sampling strategies may be used for measuring ammonia in local hot-spot areas. Firstly, low temporal resolution monitoring (e.g. monthly resolution) provides information on spatial patterns and long-term trends. By using low-cost methods for such sampling, many sites can be compared, allowing assessments of local gradients and spatial representativity. The disadvantage of such methods is that they do not allow detailed diurnal interactions to be easily assessed. Therefore, a second, complementary approach, is to conduct detailed time resolved (e.g. half hourly) continuous measurements of NH3 concentration at 1 or 2 sites and relate the measured concentrations to wind direction, local meteorology and emissions. The second approach requires expensive continuous devices that generally require mains electricity supply, which can limit the flexibility where such measurements can be made.

Among the simpler methods for measuring NH_3 concentrations are passive diffusion samplers (e.g. Thijsse *et al.*, 1998, Tang *et al.*, 2001), acid-coated denuders (Ferm, 1979) and filter packs (Appel *et al.*, 1988; Sutton *et al.*, 1993a,b). Diffusion tubes rely on the process of atmospheric NH_3 diffusing along the inside of a tube towards an acid-coated filter. The NH_3 is captured by the filter as it reacts with the acid (e.g. citric acid or oxalic acid) to form an ammonium salt. The ammonium can then be extracted in the lab for analysis and the mean atmospheric NH_3 concentration over the exposure period can be calculated from the mass of ammonium present (Ferm, 1979). Acid-coated denuders are usually glass tubes coated on the inside with an acid. Atmospheric air is drawn through the denuder by a pump and the NH_3 in the air reacts with the acid to form an ammonium salt. This technique allows the selective removal of NH_3 on the denuders and subsequent collection of particulate NH_4^+on a downstream filter pack (e.g. Ferm 1979, Sutton *et al.*, 2001; Tang *et al.*, 2003). In a similar way to the diffusion tubes, after exposure, the ammonium is extracted and the mean atmospheric NH_3 concentration for the period that the pump was on can be calculated from the mass of ammonium present. The Ferm denuder method is tuned for hourly to daily measurement periods (e.g. Ferm, 1979). More recently, a modified system architecture has been used to allow simple denuders to measure monthly time-integrated samples, making them more suited to low cost, long term monitoring (Sutton *et al.*, 2001a).

Filter packs work on a similar principle to diffusion tubes except atmospheric air is drawn through the acid-coated filter using a pump, with a pre-filter used to collect particulate compounds (Appel *et al.*, 1988; Sutton *et al.*, 1993a). After exposure, the filters are analysed in a similar way to those in diffusion tubes. However, phase interactions in the collected samples give rise to uncertainty to the partitioning between gaseous NH_3 and aerosol NH_4^+. Therefore, the data are typically reported as the sum of the nitrogen species (TIA, Total Inorganic Ammonium). A developing method of monitoring NH_3 concentrations is the use of bio-monitors such as lichens (Van Dobben and Ter Braak, 1998; Wolseley *et al.*, 2006). Physiological measurements on the lichens (e.g. nitrogen content) can be linked to atmospheric concentrations of NH_3 and therefore provide a method of estimating long-term atmospheric concentrations of NH_3 (see posters, this workshop). Concentration measurements can be compared with threshold concentrations (such as critical levels; see Section 4.4) to estimate the effects of toxicity to ecosystems and humans. It is also important to assess effects by estimating the deposition (wet and dry) to the site in question. It is possible to estimate dry-deposition rates from concentration measurements but the estimates are often uncertain. Methods to do this will be explored later in this Section.

It is possible to measure rates of dry deposition directly using a range of techniques. The most accurate methods of dry deposition measurement are eddy-covariance (Famulari *et al.*, 2004), continuous gradient techniques (Sutton *et al.*, 2001b) and relaxed eddy accumulation (e.g. Fowler *et al.*, 2001; Nemitz *et al.*, 2001). However, these techniques tend to be the most expensive and, for the reasons given above about the need for multiple measurements over long time periods, will not be covered in this document. It is however possible to carry out low-cost gradient techniques. The COTAG (COnditional Time-Averaged Gradient) technique uses the low-cost denuders (Sutton *et al.*, 2001) to measure atmospheric NH_3 concentrations at several heights to derive time-integrated exchange rates (e.g. Fowler *et al.*, 2001). The equations needed to calculate a deposition (or emission) flux are only valid for a certain range of atmospheric stability conditions and to allow use of these equations, air is only sampled during periods with these atmospheric conditions. Provided this sampling time represents the vast majority of the measurement period, the sampled atmospheric concentrations can be used to calculate the flux (Fowler *et al.*, 2001; Erisman, 2001). Throughfall measurements can also be used to estimate deposition to a plant canopy (e.g. Draaijers *et al.*, 1994; Cape *et al.*, 1995). Throughfall is the precipitation that is collected on the ground below the canopy and represents the sum of dry and wet deposition to the leaves minus the NH_x that has entered the leaves either via the stomatal or cuticular routes (see Section 3) or has flowed down the plant stems/trunks (stemflow). In the AMBER experiment (Theobald *et al.*, 2004), throughfall measurements were made beneath a tree canopy to estimate the amount of dry deposition to the trees from an artificial NH_3 line source. It should be noted that throughfall measurements will underestimate deposition of NH_x since the component that has entered the leaves and the stemflow are not included. Dry deposition to leaves and branches can be estimated by washing the branches or leaves with deionised water after a measured period following the last precipitation event. In a similar way to the throughfall measurements, the NH_x washed off the leaves will represent the dry deposition to the plant minus the NH_x that has entered the plant either via the stomatal or cuticular routes (see Section 3.4) and stemflow since the last precipitation event.

Total deposition (wet plus dry) to short vegetation can also be estimated using the ammonium concentrations of pots of vegetation before and after being placed at the site of interest (Sommer and Jensen, 1991; Leith *et al.*, 2004). It is unadvisable to use bulk wet deposition measurements (i.e. wet and dry deposition to an open collector) as an estimate of total NH_x deposition, since the deposition characteristics of the collector will be different to that of vegetation the deposition rate will not be representative for the ecosystem in question.

As stated above, it is possible to relate concentration measurements to deposition estimates. Exchange of NH_3 with surface vegetation is a complex process (see Section 3). In some situations the exchange is bi-directional resulting in emissions from the vegetation to the atmosphere as well as deposition from the atmosphere to the vegetation. Models such as those detailed in Section 3 can be used to calculate a deposition flux from a measured concentration (Nemitz *et al.*, 2000b). However, these models require a lot of site specific input data (e.g. plant and soil physiological data, micro-meteorological data) and are often, therefore, too detailed to use for effects assessments. Deposition is the dominant exchange process close to sources of NH_3 since the atmospheric concentrations are generally higher than the compensation points of the vegetation. The deposition process can be simplified substantially by reducing the parameters down to just one; the deposition velocity. This avoids the complexity of having to parameterise many site-specific factors. In this simple scheme the deposition rate is calculated by multiplying the NH_3 concentration at the ground (or just above) by a dry deposition velocity specific to the ecosystem (Erisman *et al.*, 1994; Neirynck *et al.*, 2005). This approach needs to be used with knowledge of the uncertainties since it is not a very accurate method but is useful for screening purposes to calculate an approximate deposition rate.

4.3Dispersion modelling techniques for effects assessments

Dispersion modelling is often used in a effects assessments either on its own or in conjunction with monitoring. There is no substitute for accurate measurements for effects assessments but the use of modelling instead provides a faster and often cheaper way for these assessments. When done in conjunction with monitoring, the measurement data provide a method of model verification and also can be used for model improvement and development. It is important that the correct type of model is used for the task. Factors governing the type of model necessary depend on factors such as the process that you are trying to estimate (e.g. dry deposition, atmospheric concentration, advection, recapture), the input data available, the spatial/temporal scale necessary and the resources (time, equipment, money etc.) available. Once a suitable model has been selected, the input data necessary for the model must be collected (e.g. meteorological, soil, land cover, source data). The model is then run using these input data and the required output (concentrations, deposition etc.) is obtained. If monitoring data are available they can then be used to verify the model output. The output data are the used to estimate the potential impacts to the any vulnerable sites within the modelling domain. In addition to simulating real impacts, models can be used to investigate scenarios by varying the input data to look at the effects of source strengths, source locations, land cover changes, climate change etc.

4.4 Review of effects assessment of NH_3 in hot spots and experiments

After the completion of the modelling and/or monitoring the data can to be used to estimate the potential effects of the NH_3 concentrations and deposition on the receptor of interest: semi-natural ecosystems or humans. Most assessments take the form of comparing concentration and deposition estimates (measured or modelled) with relevant thresholds. For effects on semi-natural ecosystems ammonia concentrations are usually compared with ‘critical levels’, which are defined as “the concentration of a pollutant in the atmosphere, below which vegetation is unlikely to be damaged according to present knowledge” (Postumus, 1988). It should be noted that the critical level value for ammonia ($8\ \mu g\ NH_3\ m^{-3}$) is now considered by many scientists to be out-of-date and not sufficiently precautionary. In particular, it can be shown that exceedance of the critical loads occurs at much lower concentrations than the critical levels. (i.e. ammonia concentrations of >1-2 $\mu g\ m^{-3}$ are sufficient in most cases to lead to exceedance of the critical load). This indicates that the issue of most concern from ammonia is the indirect impact of nitrogen from ammonia deposition, rather than the direct toxic effect of ammonia concentrations. Deposition rates are usually compared with 'critical loads' which are defined as "the amount of pollutant deposited below which significant harmful effects on specified elements of the environment do not occur, according to present knowledge" (Nilsson and Grennfelt, 1988). Therefore if the deposition rate is less than the critical load (i.e. it is not exceeded), then it is usually assumed that significant harm to the ecosystem will not occur. Much recent work has gone into defining critical loads for different ecosystem types. The most recent culmination of this work was the Expert Workshop of 2002 in Switzerland (Bobbink *et al.*, 2003). This meeting agreed on many of the currently used empirical critical loads for nitrogen deposition for a range of ecosystem types. Many of these critical loads were based on data from experimental field studies. Following the effects assessment, information on potential exceedances of critical loads and levels can be used by government departments, planning committees or conservation bodies to conclude whether an impact on a semi-natural site will probably occur as a result of the process (ammonia source) being studied.

5 MAIN RESULTS FROM MODELLING AND MONITORING DEPOSITION NEAR HOT SPOTS

5.1 Example of NH_3 deposition modelling in a tree-belt downwind from a controlled source

The dispersion of NH_3 was modelled through a tree belt of 10 m height, located 15 m downwind of a line source placed at 2 m above ground. Figure 8 shows that the highest deposition and concentration occurs with the smallest wind-speed because with increasing wind speed the NH_3 is more diluted into air and also it passes under the crown of the trees, which lies roughly above 4 m. This illustrates the singularity of local deposition which depends on dilution / dispersion and deposition, as compared to deposition over homogeneous surface where deposition basically increases with decreasing aerodynamic resistance and hence increasing wind speed (see e.g., Seinfeld and Pandis, 1998).

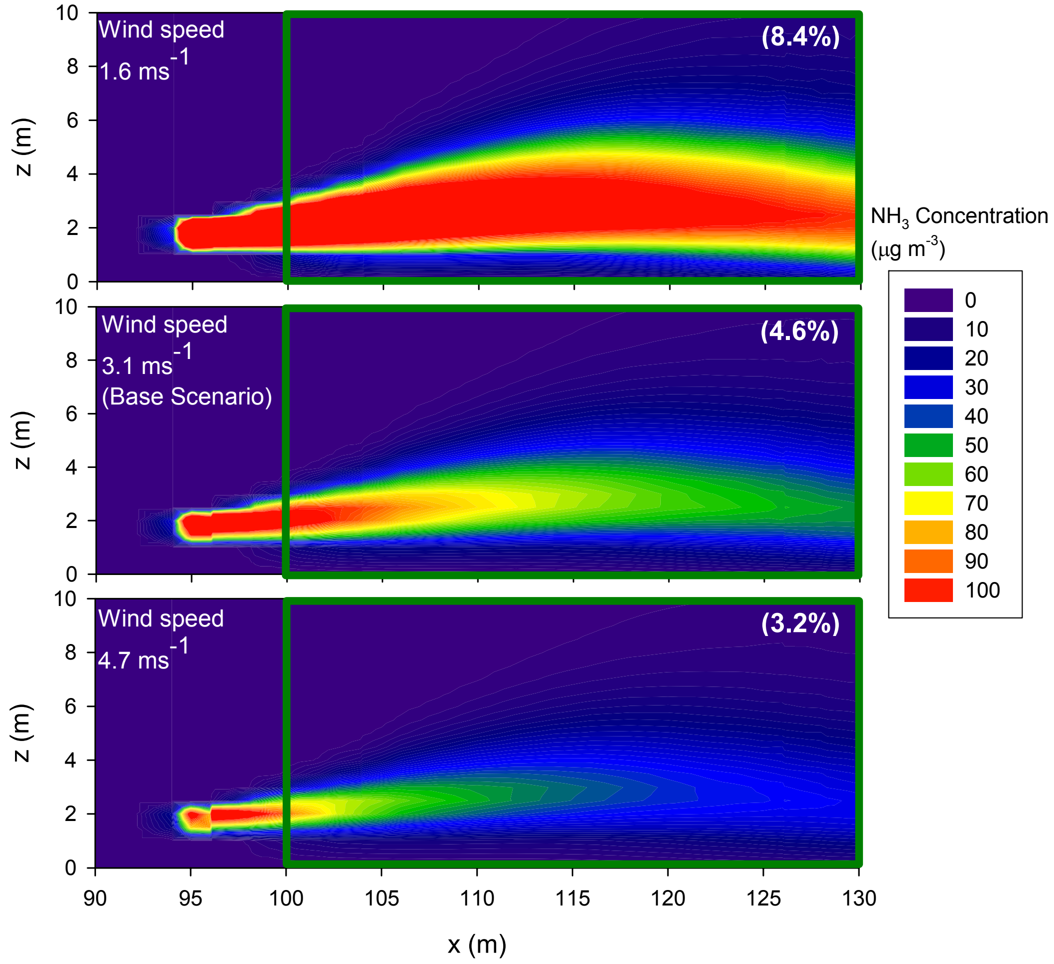

Figure 8. NH_3 concentration field in a tree-belt of 30 m long and 10 m height, 5 m downwind from an intensive line source placed at 2 m above grassland for different wind speeds, as modelled with the MODDAAS-2D model.

5.2Sensitivity of local deposition of NH_x to environmental conditions

The modelled developed for NH_3 recapture near hot spots, have been used to assess the influence of environmental conditions on local dispersion. Asman (1998) has shown that NH_3 recapture at 2000 m downwind from a farm can represent up to 60% of the emissions, and that it increases with (i) increasing source height, (ii) increasing atmospheric stability, (iii) decreasing wind-speed, (iv) increasing surface roughness, and (v) decreasing compensation point of the surface. Asman (1998) has also shown, based on hourly meteorological data spanning over two years, that most frequently NH_3 recapture varies between 10% and 40% of the emission. Loubet *et al.* (2006) have confirmed, based on the within canopy transfer mode MODDAAS, that the predominant factors controlling short-range deposition are turbulent mixing at the source height, which is influenced by wind-speed, atmospheric stability, surface roughness and source height, as well as the stomatal compensation point C_s, the cuticular resistance R_w, and the stomatal resistance. In these studies information was given on the accumulated deposition as a function of the distance to the source, but not on the deposition as a function of the distance to the source.

Figures 9-11 illustrate the sensibility of local recapture of NH_x within 200 m downwind from hot spots to environmental conditions, based on simulations using the FIDES-2D model (Loubet *et al.*, 2001). The environmental factors looked at are those affecting the turbulent mixing (source height, wind speed (U), roughness length (z_0), stability of the surface boundary layer), as well as those affecting the transfer rate to the surface C_s, R_w and R_s. Aerosols deposition is also considered to discuss the issue of NH_4^+ from farm buildings, as either recently created aerosols or dust transporting a fraction of nitrogen. The base scenario considers (1) an area source emitting 500 µg NH_3 m^{-1} s^{-1} (roughly corresponding to 800 kg $year^{-1}$ for a 50 m x 5 m wide building) infinite in the crosswind direction (along-wind dispersion) of 5 m width, at h_s = 2 m height, (2) a wind speed of 3 m s^{-1} at the source height, (3) a roughness length (z_0) of 10 mm, (4) a zero displacement height (d), (5) thermal neutrality of the boundary layer, (6) a stomatal resistance $R_s = 80\ s^{m-1}$, (7) a cuticular resistance $R_w = 20\ s\ m^{-1}$, and (8) a compensation point $C_s = 0$ µg NH_3 m^{-3}. The model used for particles deposition is adapted from the FIDES model: the same dispersion model is assumed (which is a strong hypothesis for particles larger than 10-20µm), while the surface exchange scheme considers a resistance estimated following Seinfeld and Pandis (1998).

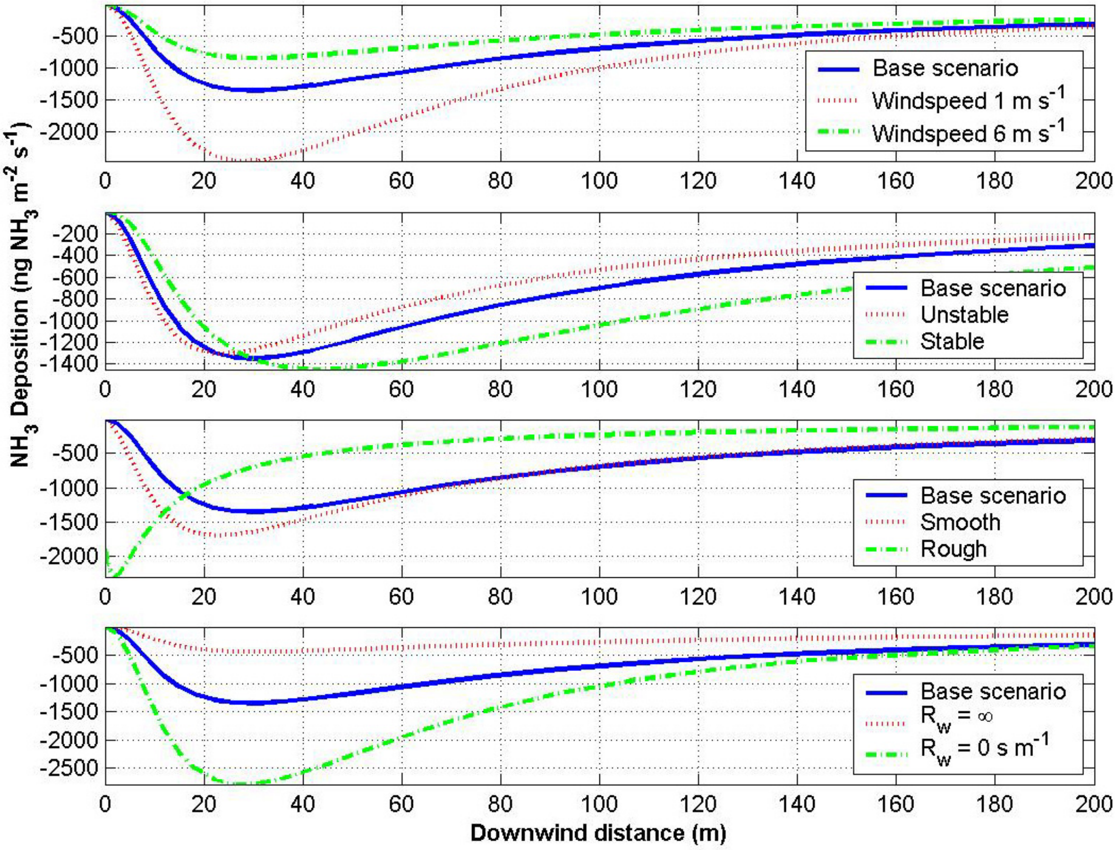

Figure 9. NH_3 deposition downwind from a 500 µg NH_3 m^{-1} s^{-1} source of 5 m width at 2 m height, as a function of downwind distance, as estimated with the FIDES-2D model. The base scenario is described in the text. Several effects are considered: wind speed at the source height (1 or 6 m s^{-1}); boundary layer thermal stratification (unstable L = -20 m, stable L = 20 m, where L is the Monin and Obukov length); surface roughness (Smooth z_0 = 1 mm, Rough z_0 = 1000 mm); surface resistance (only stomatal absorption $R_w = \infty$, surface completely absorbing $R_c = R_b$, where R_b is the boundary layer resistance of the canopy).

Figure 9, shows the qualitative effect of environmental conditions on local deposition:

- Increasing wind speed leads to decreased local deposition of NH_3, due to more dilution of the emitted NH_3, at the source and downwind;
- Surface layer stability favours local deposition of NH_3 due to decreased turbulence, and hence dilution, whereas instability decreases local deposition, due to increased turbulence. Note also that the distance of peak deposition increases in the order unstable < neutral < stable, due to the plume width increasing faster under unstable conditions;
- The rougher the surface is the larger deposition is very close toe the source, but also the faster it decreases with distance, hence in the end, rougher surface leads to smaller cumulated deposition (see Figure 11). This is due to rougher surfaces inducing larger turbulence rate and hence faster dilution of the plume (which also reaches more quickly the ground);
- Perfectly absorbing surfaces (which is represented by $R_w = 0$ s m^{-1}) leads to larger local deposition than surfaces with stomatal and cuticular absorption (base scenario), which itself is lower than stomatal absorption only ($R_w = \infty$). It should be noted however local NH_3 deposition is not linearly related to the "deposition velocity", because increasing deposition rate also leads to a faster depletion of the plume and hence decreases deposition further downwind;

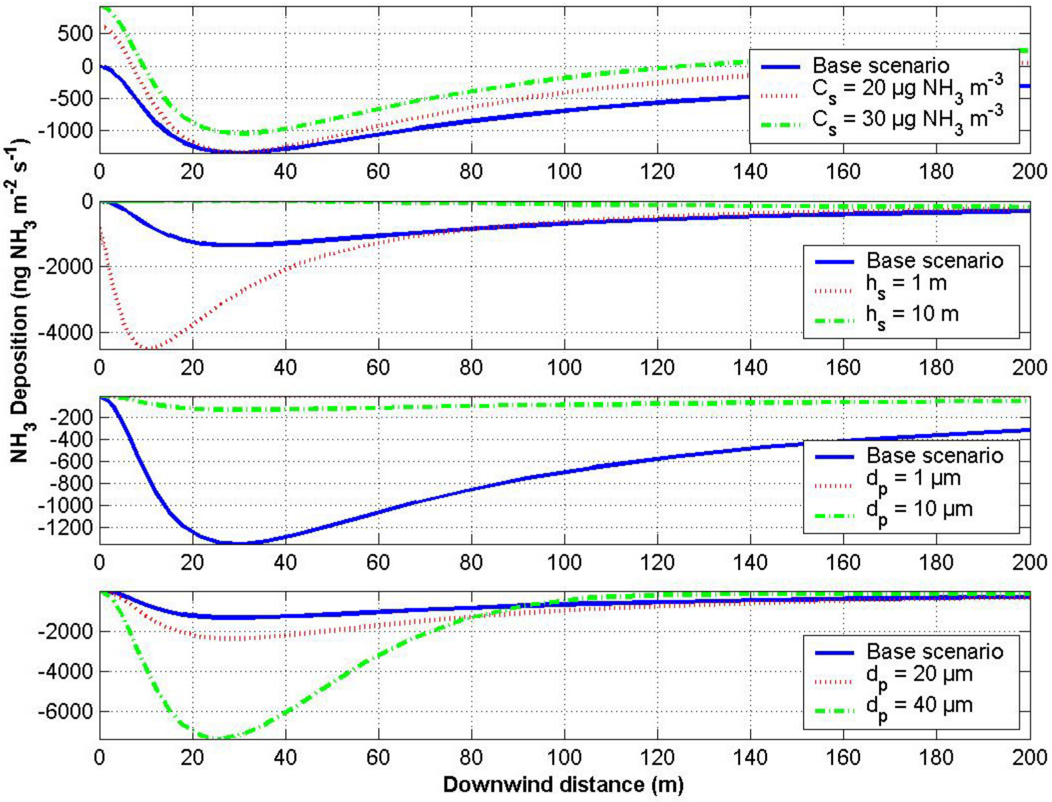

Figure 10. NH_3 deposition downwind from a 500 µg NH_3 m^{-1} s^{-1} source of 5 m width at 2 m height, as a function of downwind distance, as estimated with the FIDES-2D model. The base scenario is described in the text. Several effects are considered: canopy compensation point (canopy receiving large amount of nitrogen

C_p = 20 µg NH_3 m^{-3}, canopy saturated with nitrogen C_p = 30 µg NH_3 m^{-3}); source height (source very close to the ground h_s = 1 m, source at the roof of a building h_s = 10 m); particles of 1µm or 10µm and dust of 20 µm and 40 µm.

Similarly Figure 10 shows that:

- An increase of the stomatal compensation point C_s decreases local deposition of NH_3 and can even lead to emissions of NH_3 at distances larger than 100 m downwind from hot spots;
- Increase in source height decreases local deposition of NH_3 and inversely. However, similarly to effects of increased surface deposition, increased deposition with smaller height also decreases deposition at further distance, due to increased depletion of NH_3 from the plume. The peak distance also increases with increasing source height, as it then takes more distance for the plume to reach the ground;
- Particles of 1µm show almost no deposition, while 10 µm particles show deposit of about a tenth of the base scenario, whereas particles of 20 µm and 40 µm show larger deposit than the base scenario. It should however be noted that the FIDES-2D model for particles does not properly describes the dispersion of particles of 20-30 µm and that hence these results should be taken as qualitative.

Figure 11 synthesises the results of Figures 9-10, by displaying the fraction of NH_3 emitted that is recaptured at 200 m from the source for each scenario. The deposition at 2000 m is also shown to allow comparison with the work of Asman (1998). This allows to quantitatively compare the effect of each scenario. Figure 11 shows that up to 30% of NH_3 is recaptured at 200 m downwind from the source in the base scenario and that it varies between 12% and 55% depending on the environmental conditions (not considering particles). Apart from stability and wind speed, which are influential but can not be easily modified by abatement techniques (though wind-speed at the source height might be), the most influential parameters are (1) the source height, (2) the surface roughness, (3) the surface resistance, and (4) the stomatal compensation points. Hence, abatement techniques should preferentially focus on one of those parameters. In a simplified view, abatement techniques should try to maximise deposition very close to the source. Results of Figure 11 suggests that this could be achieved by shading the emission from wind (both by setting the source at the lowest possible height, or having trees around), and by ensuring an effective sink around it (well watered canopy, with well evaporating vegetation on the ground). One effective way might be to have tall trees with small LAI and an under-storey well watered arable crop.

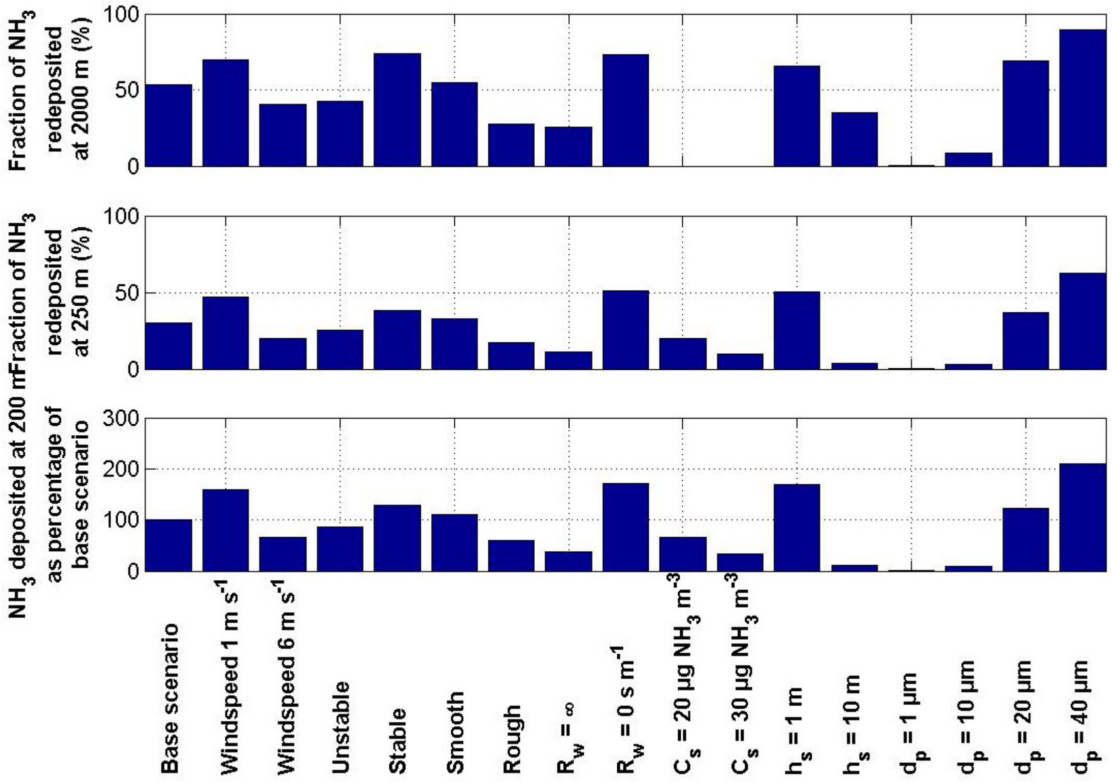

Figure 11. Fraction of NH_3 re-deposited at 2000 m and 200 m downwind from a 500 µg NH_3 m^{-1} s^{-1} source of 5 m width at 2 m height, as a function of downwind distance, as estimated with the FIDES-2D model. The base scenario is described in the text. Several effects are considered: wind speed at the source height (1 or 6 m s^{-1}); boundary layer thermal stratification (unstable L = -20 m, stable L = 20 m, where L is the Monin and Obukov length); surface roughness (Smooth z_0 = 1 mm, Rough z_0 = 1000 mm); surface resistance (only stomatal absorption $R_w = \infty$, surface completely absorbing $R_c = R_b$, where R_b is the boundary layer resistance of the canopy);canopy compensation point (canopy receiving large amount of nitrogen C_p = 20 µg NH_3 m^{-3}, canopy saturated with nitrogen C_p = 30 µg NH_3 m^{-3}); source height (source very close to the ground h_s = 1 m, source at the roof of a building h_s = 10 m); particles of 1µm or 10µm and dust of 20 µm and 40 µm. At 2000 m, the fraction re-deposited for the scenarios C_s = 20 and 30 µg NH_3 m^{-3} are not shown for clarity: the cumulated emission at 2000 m downwind amount 65% and 125% of the emission from the farm, respectively.

5.3Comparison of three approaches to model recapture of NH_3 to tree belt near hotspot

Figure 12 shows the recapture of NH_3 to a tree belt surrounding an intensive source of 11.9 kg N yr^{-1} for several scenarios (base scenario given in Table 101). The tree canopy presents a crown located in the upper part of the canopy, which allows a flow below the crown to take place. Three models are compared: the FIDES model (Loubet *et al.*, 2001), the LADD model (Hill, 1998), both models not taking account of within canopy horizontal transfer, and the MODDAAS model (Loubet *et al.*, 2006), which take account of within canopy transfer. Since the three models do not used similar inputs, the FIDES and the LADD models were adapted so as to give the same conditions as the MODDAAS model.

LADD. In LADD, the canopy height is not used and therefore a surrogate parameter was needed. The roughness length (z_0) was used since this scales approximately linearly with canopy height. Leaf area index (LAI) is also not used by LADD and instead, an adjustment to the canopy resistance was made, assuming that it is inversely proportional to LAI.

FIDES. The canopy is adjacent to the source making it difficult to simulate the effect of sources at different upwind distances. The best approximation was to spread the source further upwind to simulate moving the source in that direction e.g. to simulate a source 10 m upwind of the canopy, the source region covered 0-10 m upwind of the canopy edge and the emission strength reduced accordingly. In a similar way to LADD, z_0 was used as a surrogate for canopy height and the canopy resistances (stomatal and cuticular) were adjusted to simulate different LAIs.

Table 101. Parameters used in the base scenario of Figure 12 for modelling recapture of NH_3 emitted from a farm to a surrounding tree belt.

	Source height (m)	**Distance from source (m)**	**Canopy length (m)**	**Canopy height (m)**	**Leaf Area Index**	**Wind Speed at 2 m ($m\ s^{-1}$)**	**Atmos. stability**
Base scenario	2	5	30	10	5	3.1	Neutral

In Figure 12 the units of the y-axes are the deposition to the canopy per unit width in the crosswind direction. The source used in the scenarios is assumed to be a line source running in the crosswind direction and therefore the deposition in these plots represents the modelled deposition from each metre of source. For example, the NH_3 release rate is 11.9 kg N yr^{-1} per unit crosswind distance. Therefore a deposition in the plot of 2 kg N yr^{-1} represents a recapture of 16.8% of the emitted NH_3. In general, FIDES gives a similar deposition rate to LADD, which is greater than that from MODDAAS.

The effect of moving the source upwind (Figure 12a) is to decrease the deposition in FIDES and LADD since the NH_3 is given more time to mix vertically before reaching the canopy. For MODDAAS, the effect is different with a peak in deposition when the source is 10 m upwind of the canopy. This is due to the canopy structure, since most of the recapture surfaces (leaves and branches) are above a height of about 4 m. If the source is too close to the canopy the NH_3 will pass underneath the densest part of the canopy in the MODDAAS model: an effect that cannot be simulated by the FIDES and the LADD models.

Figure 12b shows the effect of changing the source height. LADD gives greater recapture for lower sources and so does FIDES apart from when the source is at ground level. This is due to both a larger time for the plume to reach the ground while it is mixed, and a larger mixing efficiency of the plume due to increasing turbulent diffusivity with canopy height (and hence roughness). A ground level source was not modelled by MODDAAS but, for the heights modelled, the recapture increased with source height. This is also because of the canopy structure; the lower the source, the more NH_3 passes under the region of high canopy density in the MODDAAS model.

Increasing the wind speed (Figure 12c) decreases the recapture for all three models with LADD giving the largest gradient response. This is probably because the advection wind speed used in LADD is constant with height whereas FIDES and MODDAAS use a wind speed profile that changes with height.

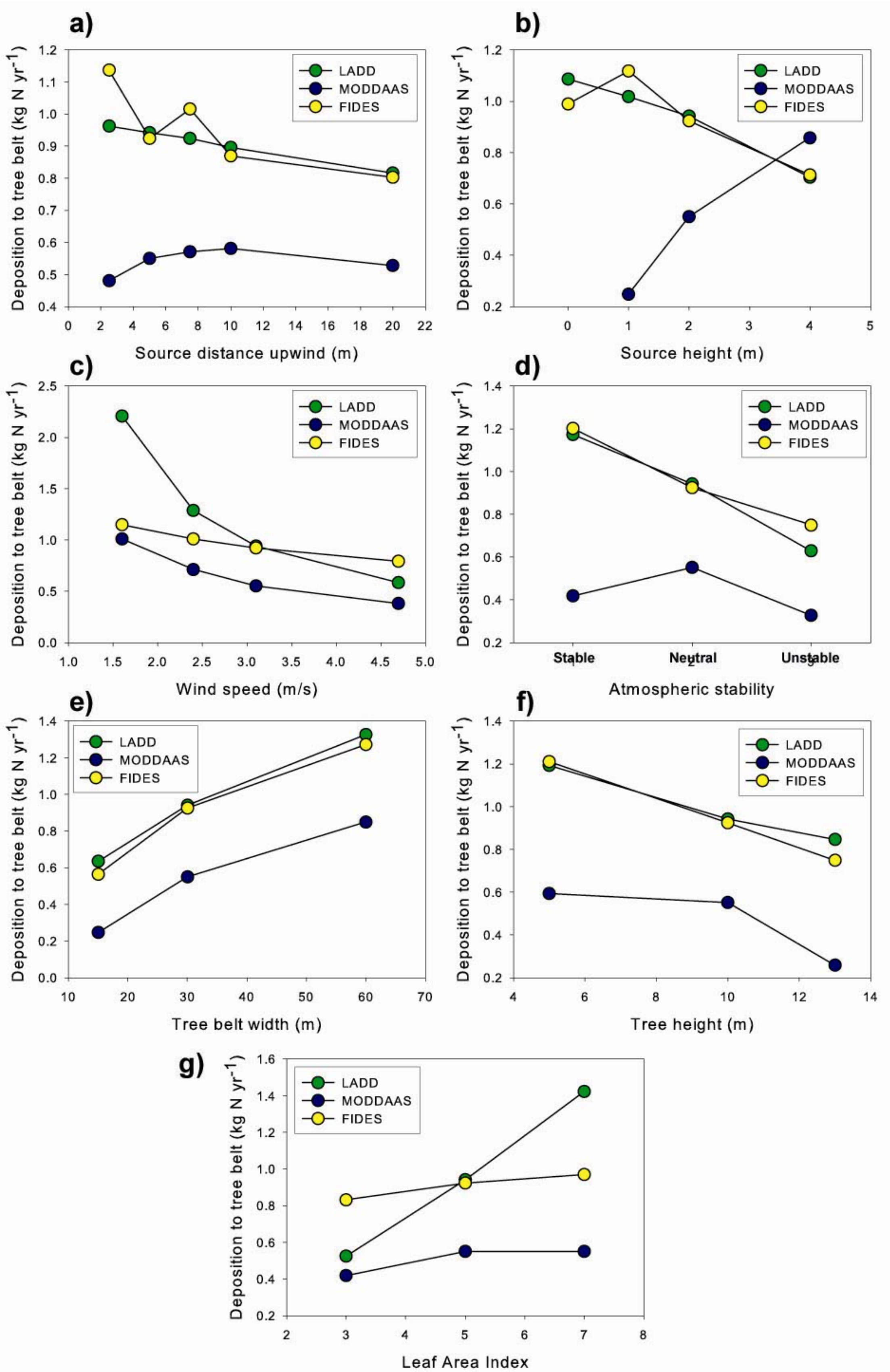

Figure 12. Ammonia dry deposition to a modelled tree belt (per crosswind unit length) for 7 scenarios using the FIDES, the LADD and the MODDAAS models. The units of the y-axes are deposition per m in the direction perpendicular to the wind, therefore (for a source strength of 11.9 kg N yr^{-1} per unit source length) a deposition of 2 kg N yr^{-1} represents a recapture of 16.8% of the emitted NH_3.

Both LADD and FIDES display a decrease in recapture as the atmospheric stability changes from stable through neutral to unstable (Figure 12d). This is due to the increased mixing of the atmosphere dispersing the NH_3 more vertically. The response of the MODDAAS model peaks at neutral stability. The low recapture during stable conditions is probably due to the NH_3 plume staying close to the ground and therefore not reaching the densest part of the canopy.

Increasing the tree belt width (i.e. the downwind extent of the canopy), increases the recapture in all three models in a very similar way (Figure 12e), whilst increasing the tree height has the effect of reducing the recapture (Figure 12f). This last effect may appear unexpected and requires interpretation of the different models. A taller tree canopy increases vertical mixing over the tree belt leading to more rapid dilution of NH_3 concentrations in the LADD and FIDES models, which has the effect of reducing the deposition. In the case of the MODDAAS model, increased tree height has the effect of ‘moving’ the densest part of the canopy upwards and away from the NH_3 plume, which for the base run was released at 2 m height, so that the plume passed under the model trees. Caution is therefore needed interpreting the results of this sensitivity test. Using MODDAAS as the most detailed of the models, it could also be shown a) that design of the woodland structure could increase the ammonia recapture of ammonia passing under the main canopy and b) that recapture of a plume the height of which was matched to the height of maximum canopy density, would increase with tree height.

Changing the LAI increases the deposition modelled by FIDES only slightly whereas for the LADD model the increase is proportional to the LAI (Figure 12g). This is because in FIDES it is the stomatal and cuticular resistances that are changed but in LADD it is the canopy resistance. For the MODDAAS model, increasing the LAI from 3 to 5 increases the recapture because there is a higher density of recapture surfaces but as the LAI is increased to 7, the canopy is getting too dense and the NH_3 plume is funnelled below the region of greatest density and therefore there is little change in the recapture.

The example simulations in Figure 12 shows that detailed models gives better insight than simplified models into the processes involved in local recapture by tree belt. The FIDES simulations in Figure 11 suggested that maximum recapture should be achieved by shading the emission from wind and ensuring an effective sink around it. Figure 12 confirms this statement but also gives precisions in what it means in terms of source location: the source should be located upwind of the densest part of the canopy in order for the plume not to pass below the crown of the canopy.

5.4 Simulation of NH_x deposition at landscape scales

The question of integrating local recapture of NH_x at regional and continental scale is a major concern in order to evaluate the weight of local to diffuse deposition. However, in order to integrate from the local scale to larger scales, there is the need to consider the intermediate “landscape scale”, at which the deposition to each individual hot spot can be aggregated to provide estimates of averaged NH_x deposition at larger scales. Other information on NH_x deposition can also be estimated at this scale, such as the percentage area, which exceeds nitrogen critical load. This intermediate “landscape scale” is also the scale at which the abatement techniques can be reasoned as a whole. Asman *et al.* (2004) have modelled both the background deposition of NH_x and NO_y with the TREND model on a 5×5 km^2 grid (van Jaarsveld, 1995), and the local NH_x deposition using the DEPO1 model on a much finer scale (100×100 m^2). Figure 13 shows the modelled sum of NH_x and NO_y, wet and dry deposition in this area. It can be seen that the background deposition is very large in this area (larger than 12.5 kg N ha^{-1} yr^{-1}), but also that deposition around hotspots can reach up values larger than 50 kg N ha^{-1} yr^{-1} over areas as large as 2 km, and even values larger than 100 kg N ha^{-1} yr^{-1} over smaller areas. Figure 13 also shows how patchy the NH_x deposition is, which illustrates the difficulty of measuring the concentration/deposiition in such an area from only a few measurements.

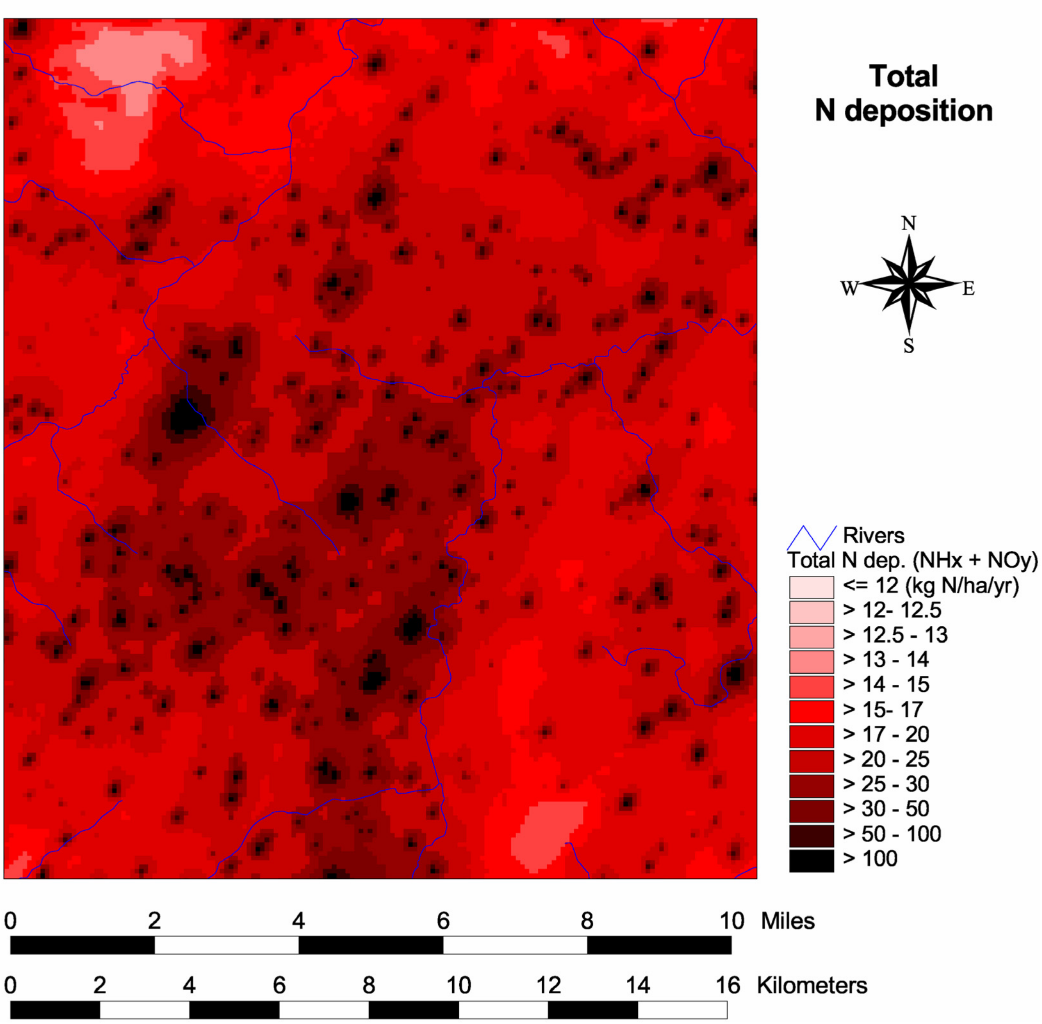

Figure 13. Sum of wet and dry deposition of NH_3 and NO_x and reaction products for Vejle County (domain 270 km^2) on a 100×100 m^2 scale (kg N ha^{-1} yr^{-1}), as modelled using the TREND model for background NH_x and NO_y deposition (all European sources) and the DEPO1 model for local NH_x deposition. From Asman *et al.* (2004).

In the UK, the LANAS (Landscape Analysis of Nitrogen and Abatement Scenarios) project carried out under the Global Nitrogen Enrichment (GaNE) programme of the NERC linked together four N flow models (farmyard, arable field, grazed field and atmospheric dispersion) to simulate the N flows and interactions within a study area in East Anglia (Theobald *et al.*, 2004). The study area consisted of arable land, rough grazing and intensive pig and poultry rearing. Figure 14 shows a map of the total N deposition flux for the study area highlighting the large predicted deposition fluxes near to the intensive pig and poultry rearing activities (in the east). These deposition rates were estimated by the LADD model. Since this model calculates NH_3 dry deposition velocities based on the land cover type (using the parameters z_0 and R_c), the deposition flux is influenced strongly by the land cover type. This is apparent in Figure 14 for a heathland (highlighted by the red oval) where the deposition flux is higher than that to the surrounding land cover types (arable and grassland).

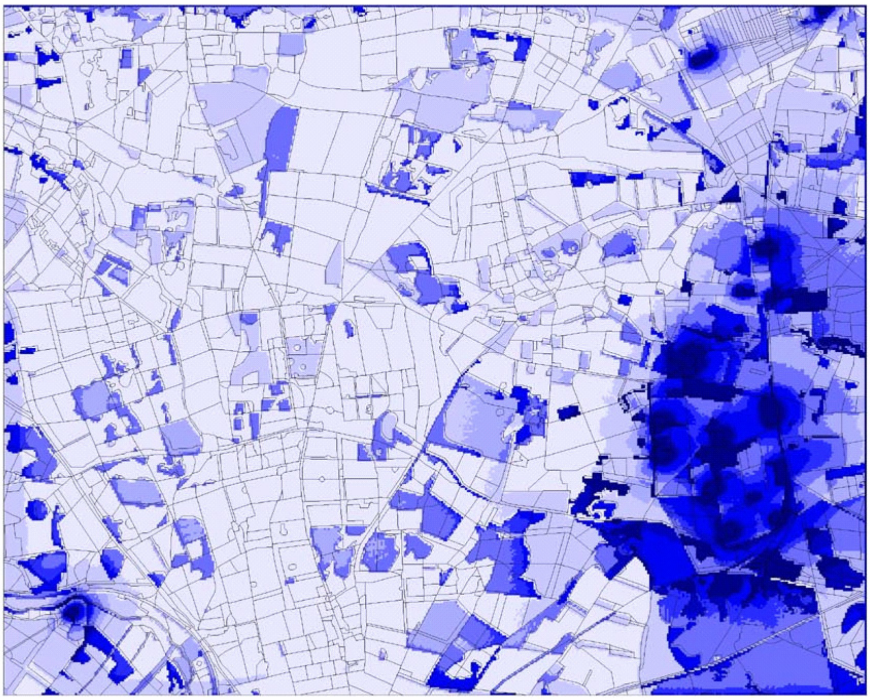

Figure 14: Map of NH_3 dry deposition for an area of East Anglia (8 km x 12 km, domain 96 km^2), England calculated by the LANAS model at a 25 m grid resolution (From Theobald *et al.*al., 2004).

5.5Main monitoring results.

Duyzer *et al.* (2001) conducted a study with many passive NH_3 samplers in four agricultural areas in The Netherlands. For this type of sampler continuous comparison with standard concentration measurement methods are needed. The standard deviation for the annually averaged concentration is 1%-5% at a typical concentration of 20 µg NH_3 m^3. The concentrations vary typically between 10 and 40 µg NH_3 m^{-3} within a few kilometres within these areas. It was shown that when 8 evenly distributed samplers were placed in a 5x5 km^2 area the accuracy in the average concentration for the whole area was better than 30%. This means that it is impossible to get an idea of the average NH_3 concentration within a country from measurements at a few sites only.

Velders *et al.* (2002) report on a project where the NH_3 concentration was measured during one year with passive samplers, where 1 sampler was placed in each of the 15x15 km^2 grid elements that were covering the whole Netherlands (159 sites). This project was started to obtain better information on the concentration patterns over the country. Kriging was used as a technique to interpolate the concentration between the sites. The average annual concentration over the country was 6.6 µg m^{-3}, whereas the average concentration of the stations that were continuously measuring with AMOR monitors was 7.8 µg m^{-3} for the same period. The error in duplo measurements at one site is about 1 µg m^{-3}. The error in the interpolation for The Netherlands as a whole is about 2.4 – 2.8 µg m^{-3}. This means that the relative error in the concentrations is about 50-80% in the areas with low concentrations and 15% in the areas with the highest concentrations (15 µg m^{-3}). The average NH_3 concentration in The Netherlands varied from 4.0 µg m^{-3} in autumn 2000 to 9.6 µg m^{-3} in May 2001. Locally there can be large influences of point sources leading to concentrations of between 20 and 70 µg m^{-3}.

Smits *et al.* (2005) conducted a study in an agricultural area in The Netherlands to investigate potential discrepancies between modelled and measured NH_3 concentrations and possible uncertainties in the emissions. In this study very detailed information farms and on activities on the farms as a function of time was collected during one year in a 3x3 km^2 are, and some less detailed information for a larger surrounding area. With this information and meteorological measurements in this area a very detailed emission inventory (place, time) was made, which was used as an input to the OPS atmospheric transport and deposition model. At the same time the NH_3 was measured continuously at two sites in this area using an AMOR ammonia monitor. During the same period the average NH_3 concentration was measured during 14-day period at 50 sites within the area. Figure 15 shows how the measured and modelled average NH_3 concentrations for the whole area compared with the modelled concentrations. One of the conclusions is that there is a large discrepancy in spring which probably could be caused by saturation of the vegetation with NH_3 (a high compensation point) and maybe also by an underestimation of emission during application of manure in periods with high solar radiation. Although the emissions are not measured and hence there is uncertainty in the emission rates it could be worthwhile for modellers to have access to this data set. This is maybe possible in the future if the farmers would agree to that, which would mean that the data would become available in an anonymous form.

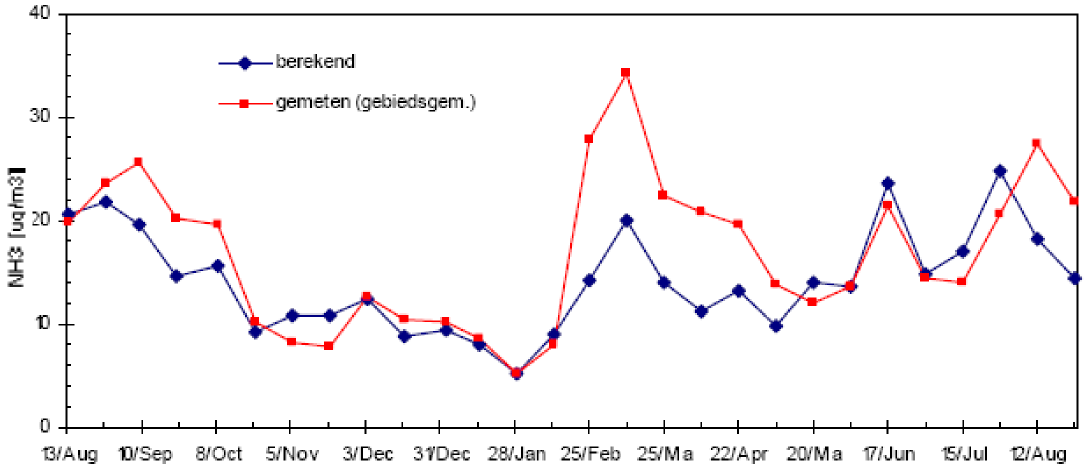

Figure 15. Modelled ("berekend") vs. measured ("gemeten") area averaged concentrations for a 3x3 km^2 area in The Netherlands, for the period July 2002 – September 2003 using the OPS model (Smits *et al.*, 2005).

6 CONCLUSIONS AND RECOMMENDATIONS

Hot spots may be defined as areas where intensive NH_3 emissions occur, which are mainly farms and their surroundings, where grazing and manure application take place, as well as slurry spread fields. The emissions from hot spots depend mainly on the number of animals in the farm but are also dependent upon environmental conditions, especially temperature and wind-speed, which are important parameters to consider for modelling deposition near hot spots. Other nitrogen components may be emitted by farms, such as NO_x, N_2O, N_2, VOC, or primary aerosols. Other reactive species (DMS, DMDS, H_2S), also emitted by farms may interact with NH_x deposition near hot spots.

Deposition of NH_X within one kilometre from hot spots ranges from 2% to 60% of emitted NH_x, and is mainly due to dry deposition of NH_3, since wet deposition, in a temperate climate, is evaluated as less than 5% recapture of the emitted NH_x. Moreover, photochemical reactions and chemical reactions with gaseous acids are unlikely to greatly affect local dispersion and deposition of NH_x near hot spots.

Dry deposition of NH_3 near hot spots results from a combination of turbulent dispersion, stomatal absorption, and non-stomatal deposition:

- Turbulent dispersion depends upon the topography of the site, the shape of the farm buildings, the structures of the surrounding canopies, the height at which NH_x is released into the atmosphere, the wind speed and atmospheric stability. Dry deposition is sensitive to all of these parameters. The height of release, or more generally the wind speed at the source height, is probably one of the most important parameter. However, little has been studied on the detailed turbulence surrounding the source and hence no definitive conclusions can be drawn onto which parameter is the most influential on dispersion in the case of farm buildings. In the case of emission from fields, there is less unknowns.
- Deposition due to stomatal absorption is large, and hence the “green” LAI of vegetation surrounding hot spots, as well as the vegetation water stress are major parameters influencing NH_x deposition.
- Deposition of NH_3 to external surfaces of plants is also a major influential process, which is also dependent upon the leaf surface and their wetness. Non-stomatal deposition can increase local NH_x deposition by a factor of two or three.

A range of models of local deposition of NH_x exist, either based on Lagrangian or Eulerian dispersion models of different complexity. The NH_3 deposition schemes range from deposition velocities to multi-layer approaches, big-leaf being the most common scheme. Some of the models take account of wet and aerosols deposition, as well as chemical reactions in the gas phase. Their spatial scales range from 1 m downwind from the source to several kilometres, with models being more adapted for very short range and others more adapted to “meso-range” NH_x deposition. Some of the models have been intensively validated against datasets that are available to the community. These models have proven their usefulness for studying the sensitivity of NH_x deposition to environmental conditions as well as the efficiency of abatement techniques. Some example of coupling of local scale NH_x deposition models with larger scale chemistry models and GIS emission databases also exist.

A range of method have been developed and proved adapted for long term monitoring of NH_x in the vicinity of hot spots. These methods are advantageous if used in conjunctions with dispersion models as they can be used both for estimating deposition of NH_x near hot spots and NH_x emissions from the farm with inverse modelling. There is however no available routine method to estimate NH_x dry deposition under local advection conditions.

It should be noted that there a lack of systematic studies of NH_x deposition near hot spots at the European scale, which could tell the magnitude of NH_x recaptured near hot spots at such a scale. The scale is important in that it means a range of farm managements, ecosystems, and climates that spans over the whole Europe.

From existing studies, it appears that the main uncertainties on estimating NH_x recapture near hot spots are linked with:

- Good estimates of hotspots sources and their seasonal and daily variability at larger scales.
- Measurements of NH_x dry deposition near hot spots to validate the local deposition models, which were, until now, mostly validated against monitored NH_3 concentrations.
- Modelling correctly night-time dispersion and deposition of NH_x near hot spots.
- Modelling the effects of farm buildings and tree belts of different shapes on the turbulent dispersion and the deposition of NH_x.
- Examining the potential saturation of the cuticular sink of NH_3 under strong NH_3 load and its subsequent de-saturation after rain events.
- Parametrizing the stomatal compensation point of the vegetation over the season, and its possible evolution due to deposited NH_x (and other compounds emitted from the farm).

Getting more information on the relative emissions of other N compounds from hot spots nd the potential impacts of other reactive species emissions on NH_x deposition near hot spots (sulphur compounds, acid compounds, …).

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APPENDIX A: A SINGLE-LAYER MODEL FOR EXCHANGE WITH STOMATA AND CUTICULE

This appendix gives the set of equations that describes the bi-directional exchange model of Figure 4c. The equation for the flux for model in Fig. 14c can be derived easily by assuming that a canopy compensation point exists (c_{canopy} in e.g. kg m^{-3}), which is linked to the stomatal resistance and the stomatal compensation point on the one hand and to the resistance for deposition to water layers r_w (m s^{-1}) on the other hand. The flux from the atmosphere to the canopy and including the soil is then:

$$F\left(z_{ref}\right) = -\frac{\left(c_{air}(z_{ref}) - c_{canopy}\right)}{r_a\left(z_{ref}\right) + r_b} \qquad \text{[A1]}$$

The flux can then be split up in a flux to the stomata and a flux to the canopy (including the soil). The flux to the stomata is:

$$F_s = -\frac{\left(c_{canopy} - c_{stomata}\right)}{r_s} \qquad \text{[A2]}$$

The flux to the canopy (including the soil is):

$$F_w = -\frac{c_{canopy}}{r_w} \qquad \text{[A3]}$$

Mass conservation implicates that:

$$F\left(z_{ref}\right) = F_s + F_w \qquad \text{[A4]}$$

In these equations c_{canopy} can now be eliminated:

$$F\left(z_{ref}\right) = -\frac{c_{air}\left(z_{ref}\right)}{r_a\left(z_{ref}\right) + r_b} + \frac{\dfrac{c_{air}\left(z_{ref}\right)}{\left(r_a\left(z_{ref}\right) + r_b\right)} + \left(\dfrac{c_{stomata}}{r_s}\right)}{1 + \left(r_a\left(z_{ref}\right) + r_b\right)\left(\dfrac{1}{r_s} + \dfrac{1}{r_w}\right)} \qquad \text{[A5]}$$

Note that this is the equation of Smith *et al.* (2000b) corrected for a typing error.

APPENDIX B: TWO-LAYER MODEL FOR EXCHANGE WITH THE STOMATA, CUTICULE AND THE GROUND

This appendix gives the set of equations that describes the two-layer bi-directional model of Figure 4d. As with the single-layer model with stomatal and cuticular resistances the canopy compensation point c_{canopy} has to be eleminated by expressing it in compensation points and resistances (Nemitz *et al.*, 2001). In this model also a concentration $c_{air}(z_{0m})$ is needed which is the concentration in the air just above the canopy (kg m^{-3}). The canopy compensation point can be found from (Nemitz *et al.*, 2001):

The total flux F_t (kg m^{-2} s^{-1}) is:

$$F_t = -\frac{\left(c_{air} - c_{air}\left(z_{0m}\right)\right)}{r_a} \qquad \text{[B1]}$$

The flux F_s from the canopy to the stomata is:

$$F_s = -\frac{\left(c_{canopy} - c_{stomata}\right)}{r_s} \qquad \text{[B2]}$$

The flux F_w from the canopy to the cuticula is:

$$F_w = -\frac{c_{canopy}}{r_w} \qquad \text{[B3]}$$

The flux F_f from the air just above the canopy to the canopy is:

$$F_f = -\frac{\left(c_{air}\left(z_{0m}\right) - c_{canopy}\right)}{r_b} \qquad \text{[B4]}$$

The flux F_g from the air just above the canopy and the ground is:

$$F_g = -\frac{\left(c_{air}\left(z_{0m}\right) - c_{ground}\right)}{r_{ac} + r_{bg}} \qquad \text{[B5]}$$

In this equation c_{ground} is the compensation point at ground level (kg m^{-3}), r_{ac} is the in-canopy aerodynamic resistance (s m^{-1}) and r_{bg} is the ground boundary layer resistance (s^{-1}). Mass conservation implicates that:

$$F_f = F_s + F_w \qquad \text{[B6]}$$

and

$$F_t = F_f + F_g \qquad \text{[B7]}$$

Which after little manipulation gives

$$c_{air}\left(z_{0m}\right)=\frac{\dfrac{c_{air}}{r_a}+\dfrac{c_{ground}}{r_g}+\dfrac{c_{canopy}}{r}}{\dfrac{1}{r_a}+\dfrac{1}{r_b}+\dfrac{1}{r_g}} \qquad \text{[B8]}$$

In this equation $r_g = r_{ac} + r_{bg}$.

An alternative expression for $c_{air}(z_{0m})$ can be obtained:

$$c_{air}\left(z_{0m}\right)=c_{canopy}\left(1+\frac{r_b}{r_s}+\frac{r_b}{r_w}\right)-\frac{c_{stomata}r_b}{r_s} \qquad \text{[B9]}$$

An equation for c_{canopy} can be simplified to yield:

$$\begin{aligned} c_{canopy} &= \left[\frac{c_{air}}{r_a r_b}+c_{stomata}\left(\frac{1}{r_a r_s}+\frac{1}{r_b r_s}+\frac{1}{r_g r_s}\right)+\frac{c_{ground}}{r_b r_g}\right]\times \\ &\left[\frac{1}{r_a r_b}+\frac{1}{r_a r_s}+\frac{1}{r_a r_w}+\frac{1}{r_b r_g}+\frac{1}{r_b r_s}+\frac{1}{r_b r_w}+\frac{1}{r_g r_s}+\frac{1}{r_g r_w}\right] \end{aligned} \qquad \text{[B10]}$$

Once c_{canopy} is known F_s and F_w can be found and then also the sum of them: F_f. From F_f then $c_{air}(z_{0m})$ can be found and then F_t and F_g can be calculated. The in-canopy resistance r_{ac} (s m^{-1}) at height (d + z_{0m}) (sum of the roughness length and the displacement height) is (Nemitz *et al.*, 2000b):

$$r_{ac}\left(d+z_{0m}\right)=\int_0^{d+z0m}\frac{1}{K_H(z)}dz \qquad \text{[B11]}$$

where K_H is the eddy diffusivity for heat (m^2 s^{-1}), which is also often taken to describe exchange of gases and particles.

$$r_{ac}=\frac{\alpha\left(d+z_{0m}\right)}{u_*} \qquad \text{[B12]}$$

where α (z) is a dimensionless height dependent constant (Nemitz *et al.*, 2000b).

For neutral conditions, Nemitz *et al.* (2000b) mention that Shuttleworth and Wallace (1985) provide the following equation, which only holds for neutral atmospheric conditions:

$$\alpha\left(d+z_{0m}\right)=\frac{h_c}{kn\left(h_c-d\right)}\left[\exp(n)-\exp\left(n\left(1-\frac{d+z_{0m}}{h_c}\right)\right)\right] \qquad \text{[B13]}$$

where h_c is the height of the canopy, k is the von Karman's constant (dimensionless; value: 0.4) and n an exponential-decay constant (see e.g. Monteith and Unsworth, 1990). No information is apparently available on a parameterization for stable or unstable conditions. Nemitz *et al.* (2001) note that for unstable conditions (free convection) it is likely that scaling with w_* would be more appropriate.

The boundary layer resistance at ground surface r_{bg} (s m^{-1}) can be parameterized as (Shuepp, 1977):

$$r_{bg} = \frac{Sc - \ln\left(\frac{\delta_0}{z_1}\right)}{ku_{*g}} \qquad [B14]$$

where Sc is the Schmidt number (dimensionless), δ_0 is the distance above ground (m) were the molecular diffusivity equals the eddy diffusivity, and z_1 is the upper height of the logarithmic wind profile that forms above the ground of which u_{*g}/k is the slope. Nemitz *et al.* (2001) note that there are no comprehensive datasets for h_c, $\alpha(z)$, u_{*g}, δ_0 and z_1 for a wide range of plant species and vegetation stages.

APPENDIX C: IN-CLOUD SCAVENGING OF NH_3 AND NH_4^+

Although in-cloud scavenging of NH_3 and NH_4^+ is probably not a process that might be highly important for deposition of NH_x near hot spots, a short description of its magnitude is given in this appendix.

Due to the high solubility of NH_3 in the acidic cloud droplets and the large surface to volume ratio, most NH_3 in clouds will be taken up into cloud droplets within a few seconds. Aerosols of the size that contains most NH_4^+ act as condensation nuclei, so most NH_4^+ in clouds will also be found in cloud droplets. For these compounds the scavenging rate is determined by the removal rate of cloud water by precipitation. The in-cloud scavenging coefficient $\lambda_{i,NH3,NH4}$ for NH_3 and NH_4^+ is:

$$\lambda_{i,NH_3,NH_4} = 3.5 \times 10^{-4} I_{mm}^{\;0.78} \qquad \text{(for clouds with a temperature} \geq 0°\text{C)} \qquad [C1]$$

$$\lambda_{i,NH_3,NH_4} = 2.4 \times 10^{-4} I_{mm} \qquad \text{(for clouds with a temperature} < 0°\text{C)} \qquad [C2]$$

The rainfall rate decreases with the cloud height. From the equations it can be seen that both NH_3 and NH_4^+ are removed at a somewhat higher rate by in-cloud scavenging in the lower part of the cloud than by below-cloud scavenging.

APPENDIX D: SHORT DESCRIPTION OF DISPERSION MODELS THAT ARE BE USED IN LOCAL DEPOSITION MODELS FOR NH_3

Two classes of dispersion models are often considered: the Eulerian models, which solve the time variation of a concentration field, and Lagrangian models, which follows the plume or the air column in space. Both Eulerian and Lagrangian approaches lead to a range of models from very simple (Gaussian-like models) to fairly complex models (CFD, Lagrangian Stochastic models). As NH_3 deposition near hot spots is large and evolves quickly with distance, it may be necessary to consider both dispersion within the canopy and the flow distortion due to the farm buildings and elements of vegetation, which may be treated with specific CFD codes. This section gives an overview of the existing dispersion models used or applicable to NH_3 dispersion and deposition near hot spots.

Gaussian-like models. Gaussian models (Gash, 1985), are a solution of the Advection-Diffusion Equation (ADE) with the assumption of constant wind speed (u) and diffusivity (K_z). Analytical solutions of the ADE that include variation of u and K_z with height are numerous e.g. (Smith, 1957; Philip, 1959; Huang, 1979; Wilson, 1982). There is existing analytical models including a deposition velocity (Chrysikopoulos *et al.*, 1992; Lin and Hildemann, 1997), though these models are not well adapted for NH_3 exchange, which is bi-directional. Other analytical models based on Lagrangian similarity, such as the (Horst and Slinn, 1984) model, are also well suited for modelling NH_3 deposition over the short-range (Asman, 1998). However, some ill-defined parameters that need to be adjusted for different stability class make them less attractive. The approach proposed by (Raupach, 1989) is very interesting for within-canopy dispersion, but its use is less justified for above-canopy transfer. Other approaches, which gives similar results but are more flexible, consist in solving numerically the above-canopy advection-diffusion equation (Asman, 1998). The main limitation of the previous models is that they only consider above-canopy dispersion and hence cannot deal with side fluxes (De Jong and Klaassen, 1997),

Air column models. Air column models are hybrid models that follow the air column as Lagrangian models, and solve the diffusion vertically in the column in an Eulerian framework. They are also based on constant wind speed (the column velocity), but consider a diffusivity that evolves with height. The LADD model (Hill, 1998), the FRAME model (Singles *et al.*, 1998), the TREND model (Asman, 1992) are all air column models. The main limitations of these models are as Gaussian-like models that they cannot deal with within side fluxes, but also that they poorly deal with lateral dispersion.

Within canopy dispersion models and CFDs. There is a great number of dispersion models that could potentially be used for modelling dispersion within the canopy and henceforth dispersion in a woodland near a farm building. These are first order Eulerian models e.g. (Zeng and Takahashi, 2000) which limits are that they are based on flux-gradient relationships, which may be broken due to intermittency of the turbulence within the canopy e.g. (Aylor *et al.*, 1993). Second or higher order Eulerian models are used to overcome this problem e.g. (Poggi *et al.*, 2004), though these introduce new parameters which are uneasy to set for within canopy transfer. CFD models are among these models, and they can be used to model the flow distortion around buildings. Large Eddy Simulation models are probably the most adapted for within canopy transfer modelling, though they also need a parameterisation of the sub-grid-scale variances e.g. (Su *et al.*, 1998). One main interest of Eulerian dispersion models is that they can predict both turbulence and concentration, as affected by canopy structure.

The Lagrangian Stochastic (LS) are another class of models (Rodean, 1996) that can be used for modelling within canopy dispersion. They are well adapted to simulate non-diffusive fluxes such as encountered in a canopy (Wilson and Sawford, 1996). Their main weakness is that they need the turbulence field as input ; Hence a turbulence model is needed as input of LS dispersion models to simulate dispersion.