Assessing Dry Deposition of Ammonia to Deciduous Forest

Measurements and Modelling in Environmental Planning using Critical Loads

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Department of Environmental, Social and Spatial Change

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Front page picture:  View from the meteorological mast in the field station, Lille Bøgeskov

Photo: Bjarne Jensen, 30 May 2011
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Preface

This study is an integrated experimental master thesis in geography and teksam at the Department of Environmental, Social, and Spatial Change (ENSPAC) at Roskilde University (RUC). The thesis corresponds to 60 ECTS (12 months) and is performed in the studying year of 2010/11. A collaboration with the Department of Atmospheric Environment at National Environmental Research Institute (NERI), Aarhus University, was arranged in order to perform a part of the experimental work confined to atmospheric measurements of NH$_3$ fluxes at the measuring site in Sorø and the work with the local-scale deposition model OML-DEP developed by NERI.

I would like to express my sincere gratitude to my supervisors; external supervisor Senior Scientist at NERI, Lise L. Sørensen and internal supervisors; Senior Scientist at NERI/Adjunct professor at ENSPAC, Ole Hertel, Associate Professor at ENSPAC, Eva Bøgh, for providing me the opportunity to perform this study in cooperation with NERI and for their supervision throughout this study. Furthermore, I would thank the staff at NERI that have performed great work and help confined to technical work at the field station, chemical analyzes of NH$_3$ samples in the laboratory, preparation of the OML-DEP model, and valuable discussions. Great thanks are particularly owed to Research Technicians Bjarne Jensen and Morten Hildan, Senior Scientists, Helle V. Andersen, Camilla Geels, Per Løfstrøm, and Jesper Christensen, and Post. Doc. Carsten A. Skjøth, and the department for letting me use the facilities in the house. Additionally, I would like to thank Senior Scientists: Ebba Dellwik and Andreas Ibrom, and Research Engineer, Søren W. Lund from RISØ DTU that have been very helpful providing me further data from the field station, guidance, and technical support at the field station. Finally, I wish to thank my friends and family for their patience and support during this work. Particularly, a great thanks to Kenneth Kleissl and Felipe Cvitanich for their help with MATLAB programming for the data analysis, and to Dario Pacino for giving me feedback on my writing.
Abstract

According to the European Habitats Directive, Denmark is committed to sustain and protect high biodiversity levels in selected sensitive ecosystems. Exceedances of critical loads of atmospheric nitrogen to particularly Danish forest have been demonstrated from model calculations. Modelling and measuring atmospheric ammonia concentrations and fluxes in forests are, however, challenging due to high reactivity of ammonia, complex forest-atmosphere interactions, and lacking knowledge of ammonia exchange between vegetative surfaces and the atmosphere. In this project, the atmospheric concentration, flux, and dry deposition velocity of ammonia above deciduous forest have been investigated for validating the performance of current assessment techniques in relation to environmental management. An experimental investigation has been carried out for the beech forest site, Lille Bøgeskov, assessing atmospheric NH$_3$ using two micrometeorological measurement techniques; relaxed eddy accumulation (REA) and Conditional time average gradient (COTAG), and the local-scale deposition model (OML-DEP). The leaf area index has been measured regularly to investigate the sensitivity of atmospheric ammonia to vegetative dynamics of forests. Measured and modelled ammonia concentrations were in good agreement varying in the range of 0.56-0.68 µg NH$_3$-N m$^{-3}$. The results were, however, inconsistent considering ammonia fluxes. Evident emission fluxes of up to about 0.8 µg NH$_3$-N m$^{-2}$ s$^{-1}$ after leaf fall contributing to the atmospheric concentration of ammonia were found with REA. This was shown neither with COTAG nor with OML-DEP. The inconsistency is related to large uncertainties in measurements due to sensitivity of REA, potential difficulties of using COTAG above forest, and missing process descriptions of vegetative ammonia emissions in OML-DEP. No significant sensitivity of LAI on calculations of the dry deposition velocity was observed. An area of improvement could be, to include LAI in the parameterization of $z_0$. Integrated approaches of combining measurements and modelling in CL assessment are valuable tools. Improved measurement techniques and improved process descriptions for local-scale exchange models are, however, still needed to obtain improved determinations and assessments of CLs.
Dansk Resume

Ifølge det europæiske habitatdirektiv, er Danmark forpligtet til at bevare og beskytte høj biodiversitet i udvalgte følsomme økosystemer. Overskridelser af tålegrenserne for atmosfærisk kvelstoff, til især danske skove, er påvist fra modelberegninger. Modellering og måling af atmosfærisk ammoniak for skove er dog stadig udfordrende, på grund af ammoniaks høje reaktivitet, komplekse skov-atmosfære interaktioner, og en stadig manglende viden om udveksling af ammoniak mellem vegetative overflader og atmosfæren. I dette projekt er koncentration, fluk, og tørdepositionsfastighed af atmosfærisk ammoniak over løvfældende skov blevet undersøgt, for at validere de aktuelle vurderings metoder i forbindelse med miljøplanlægning. Eksperimentelle undersøgelser af atmosfærisk NH₃ er blevet gennemført for bøgeskov, Lille Bøgeskov, ved to mikrometeorologiske målemetoder; Relaxed Eddy Accumulation (REA) og Conditional Time Average Gradient (COTAG), og lokal-skala modellen (OML-DEP). Bladarealindekset er blevet målt regelmæssigt for at undersøge følsomheden af atmosfærisk ammoniak overfor den vegetative dynamik i skove. Målte og modellerede ammoniak koncentrationer var i god overensstemmelse med hinanden og varierende mellem 0,56-0,68 µg NH₃-N m⁻³. Resultaterne var dog uoverensstemmende for fluksmålingerne. Tydelige emissions flukse, op til omkring 0,8 µg NH₃-N m⁻² s⁻¹ efter løvfald, som bidrager til den atmosfæriske koncentration af ammoniak, blev fundet med REA. Dette blev ikke vist, hverken med COTAG eller med OML-DEP. Uoverensstemmelserne i fluksmålingerne er relateret til store måleusikkerheder, som skyldes følsomheden af REA metoden, potentielle problemer ved anvendelse af COTAG metoden over skov, og manglende procesbeskrivelser af vegetative ammoniak emissioner i OML-DEP. Der blev ikke fundet nogen signifikant følsomhed overfor LAI på beregninger af tørdepositionsfastighed med OML-DEP. Et forbedringsområde i OML-DEP kunne derfor være, at inkludere LAI i parametreringen af z₀. En integreret tilgang ved kombinering af målinger og modelberegninger i vurderinger af tålegrenser er et værdifulde værktøj i miljøvurdering og -overvågning. Forbedrede måleteknikker og procesbeskrivelser for lokal-skala modeller for ammoniak udveksling er dog stadig nødvendigt for at opnå forbedrede fastsættelser og vurderinger af tålegrenser.
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<td>Atmospheric boundary layer</td>
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<td>( \beta )</td>
<td>Busingers value</td>
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<td>CL</td>
<td>Critical load ( [\text{kg ha}^{-1} \text{yr}^{-1}] )</td>
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<td>( \text{CO}_2 )</td>
<td>Carbon dioxide</td>
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<td>COTAG</td>
<td>Conditional Time Average Gradient</td>
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<td>Atmospheric concentration of ( \text{NH}_3 ) ( [\mu \text{g NH}_3-\text{N} \text{ m}^{-2} \text{ s}^{-1}] )</td>
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<td>d</td>
<td>Zero plane displacement height</td>
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<td>DALR</td>
<td>Dry Adiabatic Lapse Rate</td>
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<td>DAMOS</td>
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<td>EIA</td>
<td>Environmental impact assessment</td>
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<td>( \text{NH}_3 )</td>
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<tr>
<td>( \text{N}_r )</td>
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<td>OML-DEP</td>
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<td>Aerodynamic resistance ( [\text{s m}^{-1}] )</td>
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<tr>
<td>( r_t )</td>
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<tr>
<td>REA</td>
<td>Relaxed Eddy Accumulation</td>
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<tr>
<td>RH</td>
<td>Relative humidity</td>
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<tr>
<td>SLAI</td>
<td>Start date (day number) of LAI season</td>
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<td>Symbol</td>
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<tr>
<td>SLAI-len</td>
<td>Number of days of the foliation process</td>
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<td>Spd</td>
<td>Wind speed ([\text{m s}^{-1}])</td>
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<td>T</td>
<td>Temperature ([\text{°C}])</td>
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<td>(v_d)</td>
<td>Dry deposition velocity ([\text{cm s}^{-1}])</td>
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<td>(u_*)</td>
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1 Introduction

Atmospheric nitrogen (N) compounds are natural nutrients and provide an important, but limited, nutrient input for the growth of vegetation in natural ecosystems. However, they can also cause critical negative effects on nature, particularly in semi-natural ecosystems like forests. Consequences of enhanced N load in terrestrial ecosystems are for example eutrophication, which leads to a reduction in biodiversity due to favouring species better adapted to high N inputs. Particularly, forest ecosystems are exposed to large concentrations of atmospheric N compared to other vegetative surfaces. This is caused by the height, roughness, and large surface area of forests. Additionally, vegetative surfaces absorb N compounds both by adherence to the surface and by uptake through stomata (Erisman and Draaijers, 2003).

According to the European Habitats Directive1, Denmark is committed to sustain and protect high biodiversity levels in selected sensitive ecosystems. One criterion to achieve favourable preservation is that the supply of N to these ecosystems should not exceed the critical load (CL). CL is an estimate of a pollutant load which an ecosystem can be exposed to without changing its composition and dynamics. If the CL is exceeded, the changes to the ecosystem can be irreversible. CLs are used as indicators to determine environmental goals aiming at protecting natural ecosystems. CLs are usually experimentally determined by modelling and measurements. In order to take differences of different locations into account, CLs are often presented in intervals instead of single values. At the European scale, exceedances of CLs of N in natural and semi-natural ecosystems were estimated for half the area in 2004 (Schutyser and Condé, 2009). In the majority of vulnerable ecosystems in Denmark, the CLs of N are also exceeded (Normander et al., 2009). Calculations of atmospheric N deposition to Danish nature resorts, using the Danish Ammonia Modelling System (DAMOS), indicate that particular forests are exposed beyond the CLs (Frohn et al., 2008). An example from Aarhus vicinity is shown in Figure 1.1, displaying the total N load modelled at different nature resorts in Aarhus with the CL intervals. For all forests, the CL is exceeded, indicating clearly that, especially, forests are subjected to large violations of CLs. Further calculations have shown that in Denmark, even the atmospheric background of N depositions exceeds the CL (Hertel et al., 2003).

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Ammonia (NH\textsubscript{3}) is a part of the polluting reactive N (N\textsubscript{r}) and originates in the atmosphere primarily from agricultural activities (Hertel et al., 2006; Sutton et al., 2000). The gaseous NH\textsubscript{3} is a highly reactive pollutant and deposits fast. Model calculations have demonstrated that 20% of the atmospheric NH\textsubscript{3} deposits within 2 km from the source (Hertel et al., 2004). Thereby a significant part of the locally deposited NH\textsubscript{3} can be regulated by local and national regulation of NH\textsubscript{3} emission. According to models, and a few experimental studies, forests are among the most vulnerable ecosystems to atmospheric NH\textsubscript{3} deposition. A high input of NH\textsubscript{3} to forests may, over a long-term period, cause changes to the forest ecosystems, particularly of the forest undergrowth. This leads to threats to the growth of trees, but increases also the vulnerability to extreme weather and insect attacks (Xiankai et al., 2008). As an overall consequence biodiversity can be reduced and result in a more homogeneous nature in the landscapes (Frohn et al., 2010; Normander et al., 2009).

Only a few studies have determined dry deposition of NH\textsubscript{3} to forest canopies through field measurements, and highly varying fluxes are reported (Andersen et al., 1993; Duyzer et al., 1992; Duyzer et al., 1994; Wyers et al., 1992; Wyers and Erisman, 1998). A number of NH\textsubscript{3} flux studies for nature habitats, performed since the 1990ties, have furthermore indicated bi-directional flux patterns, which means that some nature habitats serve as both sink and source for NH\textsubscript{3}, and thus both receiving and emitting NH\textsubscript{3} (Andersen et al., 1999; Duyzer et al., 1994; Erisman and Wyers, 1993; Sutton et al., 1997; Wyers and Erisman, 1998). The potential of habitats acting as N-emission contributors complicates further the modelling of the atmospheric N and hence, the process is not yet included in the operational tools (Ellermann et al., 2006). Recent research is directed to the development of models that take the bi-directional fluxes into account (Massad et al., 2010b; Nemitz et al., 2001).
1.1 Project Objective

OML-DEP represents the state-of-the-art in local-scale modelling of NH\textsubscript{3} dry deposition, however, uncertainties are still significant and a target for improvement. Measurements of NH\textsubscript{3} dry deposition and further model development of NH\textsubscript{3} fluxes near the surfaces in vegetated terrestrial ecosystems could improve our understanding of these processes and the methods of calculation. Describing forest-atmosphere interactions in local-scale models is difficult due to the high complexity of forests. One important factor describing the surface properties of vegetated surfaces is the leaf area index (LAI\textsuperscript{2}). The LAI of a deciduous forest influences the dry deposition by 1) affecting the atmospheric motions of air above the canopy due to the roughness of the surface, and 2) influencing the leaves uptake of NH\textsubscript{3} through stomata. At present, LAI is only to a limited degree included in OML-DEP. Thus, a deeper investigation of the influence of LAI on NH\textsubscript{3} dry deposition processes could contribute to clarify areas of improvement in the current method of parametrizing dry deposition of NH\textsubscript{3}. To obtain a deeper knowledge of the processes of N pollution of Danish nature habitats along with the scientific tools used in environmental management, the aim of this thesis is: To investigate how advanced measurements of NH\textsubscript{3} dry deposition above a deciduous forest along with new observations of LAI can improve the current method of calculating dry deposition. This leads to the following research questions:

1. Are advanced measurements of dry deposition of NH\textsubscript{3} to deciduous forest in accordance with model calculations?

2. How is the influence of LAI on the dry deposition of NH\textsubscript{3} to deciduous forest, and to what extend is it reflected in the current method of calculation?

3. How can atmospheric measurements and modelling be related to the CL used for environmental management?

To answer these research questions, an experimental approach has been used. Concentration and vertical fluxes of NH\textsubscript{3} (hereafter referred to as c\textsubscript{NH\textsubscript{3}} and F\textsubscript{NH\textsubscript{3}}, respectively) were measured by two micrometeorological techniques; conditional time average gradient (COTAG) and relaxed eddy accumulation (REA), in the autumn 2010 for the deciduous forest, Lille Bøgeskov, in Denmark. The REA and COTAG system were installed in Ll. Bøgeskov, tested, and calibrated before measurements of atmospheric NH\textsubscript{3} began in August. LAI was measured regularly in Ll. Bøgeskov throughout the growth season 2010. The OML-DEP model was set up to calculate the atmospheric NH\textsubscript{3} concentration and deposition for the same site and period as measurements were performed in. Measured and calculated results of c\textsubscript{NH\textsubscript{3}} and F\textsubscript{NH\textsubscript{3}} are compared. Due to the vegetative dynamics of forests, the sensitivity of atmospheric NH\textsubscript{3} dynamics to LAI is investigated. The dry deposition velocity is calculated using the old and new values of LAI, respectively. COTAG and REA have different appli-

\textsuperscript{2} LAI is a dimensionless index of the amount of leaf material in an ecosystem, and is defined as the total one-sided area of photosynthetic tissue per unit ground surface area.
cation opportunities, advantages and challenges. COTAG is a new low-cost system aiming at providing NH$_3$ fluxes on monthly average values of $c_{\text{NH}_3}$ and $F_{\text{NH}_3}$. REA is a more demanding system that provides half-hourly mean values of $c_{\text{NH}_3}$ and $F_{\text{NH}_3}$. It is investigated whether the simple and cheaper technique of COTAG performs sufficiently to be included in environmental management related to CLs. Finally, it is discussed how these presented techniques can contribute to the use of CLs in environmental management.

1.2 International collaboration

The experimental work in this study, confined to the measurements of atmospheric NH$_3$, takes part in the European research project NitroEurope IP$^3$ which is just about to be completed. The main goal of NitroEurope IP was to address the effect of reactive nitrogen (N$_r$) supply on net greenhouse gas budgets for Europe. Danish participants to the project include among other research institutions ENSPAC, Roskilde University, and NERI, Aarhus University. The contribution of this M.Sc. study is related to one of 6 components in NitroEurope IP about observing N fluxes and pools. The newly developed COTAG system would be tested for different European sites of different ecosystems to investigate the systems potential to contribute to the establishment of robust datasets of NH$_3$ exchange between surfaces and the atmosphere. In Denmark, COTAG should be tested for forest in comparison with REA, which is the contribution from this thesis. A presentation of some of the results from this thesis was presented on a poster, by my attendance on the concluding conference of the NitroEurope IP held in Edinburgh, Scotland, in April 2011 (Appendix A).

1.3 Outline of the Thesis

A deeper understanding of the problems and present challenges associated with the ecological, scientific, and environmental management of N pollution load of Danish forest related is first presented (Chapter 2). Theoretical principles of atmospheric processes controlling the dry deposition of atmospheric NH$_3$ to deciduous forests and methods of measuring and modelling atmospheric NH$_3$ deposition are then explained (Chapter 3). The measurement site, Ll. Bøgeskov, experimental design, methods used, and data treatment is then described (Chapter 4). Results and interpretations of meteorological measurements and simulations, atmospheric $c_{\text{NH}_3}$ and $F_{\text{NH}_3}$, measured LAI, and calculated $\nu_d$ are presented and interpreted (Chapter 5 and 6). The overall results are discussed by intercomparisons and comparisons to other studies along with a discussion of the scientific tools used for environmental planning (Chapter 7). The overall conclusions are summarized (Chapter 8) and set into perspectives of potential for further research to improve assessment of atmospheric NH$_3$ (Chapter 9).

$^3$ NitroEurope is a project for integrated European research into the nitrogen cycle. NitroEurope will run for 5 years from February 2006 until 2011 (www.nitroeurope.eu).
2 Background

About 78% volume of the atmospheric N content consist of free nitrogen molecules ($N_2$). $N_2$ is harmless to human and nature, but chemical reactions in the atmosphere can transform $N_2$ into the polluting reactive N ($N_r$). An investigation of 68 acid grasslands across Great Britain demonstrated that long-term continuous atmospheric inorganic N deposition as well as chronic low-level stresses reduced species richness significantly (Stevens et al., 2004). The investigation shows a reduction rate of one species per 4 m$^2$ for every 2.5 kg N ha$^{-1}$ year$^{-1}$ of chronic inorganic N deposition. Terrestrial nature is originally exposed to low concentration of inorganic N, while species are adapted to such conditions. When ecosystems receive an excessive supply of nutrients, eutrophication can occur and the adapted species will be less competitive, whereby they can become extinct in the area.

2.1 Atmospheric ammonia dynamics

Ammonia ($NH_3$) is a part of the reactive reduced form of N, $NH_3$ originates in the atmosphere mainly due to agricultural activities (98%) such as evaporation from animal sheds along with spreading of manure on fields (Ellermann et al., 2007; Skjøth, 2010). Atmospheric $NH_3$ has a relatively short life cycle due to its high reactivity, stickiness, and solubility. Therefore, the main part of the emitted $NH_3$ is deposited to local surfaces and can cause crucial polluting damage on local environment. When $NH_3$ is emitted to the atmosphere, it takes part in a number of different atmospheric processes covering e.g. chemical transformations, transport, and dispersal, before deposition on the surface. The deposition of atmospheric N compounds is the scavenging of N from the atmosphere to a surface and is commonly defined as “the direct deposition of gases or aerosols at terrestrial or marine surfaces” (Hertel et al., 2006). Deposition appears dry or wet, which relates to the scavenging by turbulent transport and/or gravitational settling onto the surface or by pollutants uptake into precipitation, respectively. In this project, only dry deposition is considered.

2.1.1 $NH_3$ deposition to forests

The downward transport of $NH_3$ through the atmosphere to the surface is happening due to turbulent transport. Subsequently the specie is absorbed onto the surface due to diffusion or uptake through stomata (Ellermann et al., 2007). This makes the structure and dynamics of the atmosphere along with surface properties and physiological leaf characteristics important when considering dry deposition to forest canopies. A number of factors determines the dry deposition of $NH_3$ to receptor surface i.e. meteorological conditions, distance from the source, chemical and physical characteristics of the specie as well as physical, biological, and chemical properties of the receptor.
surface (Hertel and Frohn, 2009). A rough surface, like a forest, is commonly said to contribute to a fast deposition, due to more turbulence contrary to the smooth surfaces as e.g. marine surfaces. Marine surfaces, however, enhance the deposition process of NH$_3$ due to its high solubility (Ellermann et al., 2007). Dry deposition of NH$_3$ is also closely related to seasons changing due to meteorological variations, agricultural practices, and the season of growth in vegetative ecosystems.

Forests are very complex ecosystems due to their structure and dynamics. Forest canopies create more turbulence in the lower atmosphere compared to shorter vegetation. According to Andersen et al. (1999), this gives relatively higher deposition velocities to forests compared to other terrestrial ecosystems. Previous studies from the Netherlands (Duyzer et al., 1992; Duyzer et al., 1994; Wyers et al., 1992) and Denmark (Andersen et al., 1993) have shown that the dry deposition velocities of NH$_3$ to forests are relatively high and variable. Based on these studies, Wyers and Erisman (1998) calculated the mean dry deposition velocity to 22-36 mm s$^{-1}$. The highly variable results from measurements make it difficult to validate the deposition models. The OML-DEP model has been validated using measured data and showed overall good results; however, it also seemed to overestimate deposition rates (Ellermann et al., 2006; Hertel, 2009). An improved knowledge of the processes that controls $F_{\text{NH}_3}$ between surfaces and the atmosphere is therefore still needed in order to optimize calculations of NH$_3$ dry deposition to vegetative surfaces.

### 2.1.2 Critical load of nitrogen

CLs are generally defined as "quantitative estimates of exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge" (Nilsson J. and Grennfelt P., 1988). Values of the CLs are determined by scientists through field investigations or model calculations. CLs are used to determine ecosystems under pressure with potential risk of loosing biodiversity and are applied in national environmental impact assessments (EIA) and for determining emission strategies (e.g. the National Emissions Ceilinds Directive (NEC) from EU. In order to represent differences of European locations, CLs are often presented as intervals instead of single values. This is because the actual CL of an ecosystem is determined by a large number of specific conditions i.e. soil properties, surface cover, and climatic parameters that requires long experimental studies to investigate for each nature type. Therefore, no specific determinations of the CL for individually location exist, but the interval represents, however, the range that is found from empirical studies of the nature type.

A number of recent studies, carried out by NERI, have shown that current atmospheric N loads exceed CLs for the sensitive ecosystems in Denmark. Three studies in Denmark, at different locations, have mapped the load of total N, based on calculations using DAMOS (Frohn et al., 2008; Frohn et al., 2010; Geels et al., 2008). DAMOS includes two models to calculate the regional background level (DEHM) and
deposition of N components different from gaseous \( \text{NH}_3 \) and the local scale deposition of \( \text{NH}_3 \) (OML-DEP), respectively. All three studies indicate that the N deposition to a large amount of the investigated terrestrial ecosystems exceeds the CLs. Even not a total shut down of all local sources in the surrounding areas, would be able to comply with CLs. This is largely caused by airborne N from non local sources. A deeper knowledge of the local emission and deposition processes is needed if regulation shall succeed in decreasing the N load to below the CL.

### 2.2 Environmental management of atmospheric \( \text{NH}_3 \)

In Denmark, no precise goals for the load or reduction in N deposition are outlined. Denmark is, according to the Danish Act on Environmental Goals\(^4\), committed to preserve a high biodiversity in the selected sensitive ecosystems, known as the Natura 2000 areas. Natura 2000 is a European network of protected areas that originates from the European Habitats Directive as a part of the biodiversity policy of EU. In Denmark, the regional Environmental Centers are responsible for the monitoring of the nature habitats within Natura 2000. The practical management is, however, delegated to the municipalities. The municipalities need to follow the specific guidelines and goals outlined for Natura 2000 areas in the Natura 2000 action plans. In assessments of the biological state of nature in the Natura 2000 habitats, the municipalities are required to use objective sources. CLs are considered to be objective estimates. The municipalities must ensure that the environmental impacts of atmospheric N input to the Natura 2000 areas is below the CLs. NERI commonly performs the scientific consultancy to the regional Environmental Centers and the monitoring to support environmental policy decisions. In the National Monitoring and Assessment Programme for the Aquatic and Terrestrial Environment (NOVANA), NERI estimates the air quality and assesses the atmospheric deposition of N deposition every year using DAMOS.

In Denmark a rather strong regulation of the \( \text{NH}_3 \) emissions from livestock farms have been enforced, indicated by a decreasing trend in the atmospheric \( \text{NH}_3 \) concentration during 1989-2003 along with changed seasonal variations (Skjøth et al., 2008). Manure application has been restricted to the growth season of crops, and if farmers intend to extend their animal production, they need permission from Danish authorities, which are in this case are the municipalities. In such applications, the municipalities examine the possible environmental impacts of the action applied for. In relation to N pollution, the “Manual for assessment of local environmental impacts caused by airborne N through the expansion and establishment of larger livestock” from the Danish Ministry of the Environment, 2003, is used as a part of the environmental impact assessment (EIA). According to this manual, the assessment of the

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\( ^4 \) Danish Ministry of the Environment, Bekendtgørelse af lov om miljømål m.v. for vandforekomster og internationale naturbeskyttelsesområder LBK nr. 932 af 24/09/2009 (Miljømålsloven).
environmental impacts shall be based on the actual N load and the determined CL (Danish Ministry of the Environment, 2003). Furthermore, according to the Danish Environmental Protection Act, specific conditions of use of Best Available Technique (BAT) can be required of the farmer, concerning the emission of N.

The current calculated exceedances of CLs are in conflict with the European Natura 2000 targets and make it difficult for Denmark to meet the commitments (Jensen et al., 2004). A buffer zone project carried out for the earlier Forest and Nature Agency (now termed the Nature Agency) were therefore performed in 2003 using DAMOS. The results demonstrated a significant reduction of atmospheric N deposition to nature areas by establishing buffer zones of 200 m around nature areas where activities of NH₃ emissions was kept to minimum. Further economical investigations indicated that this way of regulating the N deposition to terrestrial ecosystem was also cost-efficient (Jensen et al., 2004). This potential tool was, however, not been implemented in the Danish environmental management and Hertel et al. (2009) concluded in 2009 that there did not seem to be any political will for such an action. Today, regulation of NH₃ deposition is based on nomograms and tables of calculations. Estimates of emissions before and after the action applied for along with calculations of the local deposition based on both local and non-local contributions are used. These results are then examined in relation to estimated CLs of the affected nature habitat. This method is one of the three steps from a suggested new procedure of EIA presented in 2006 (Geels et al., 2006).

It is important to monitor and carefully follow the state of nature when managing the environmental impacts of air pollution on nature habitats. Monitoring programs are important in environmental management and assessment, and are i.e. used to provide information about trends in air pollution levels and to assess CLs. In monitoring programs, measurements can be used to provide crucial information of concentration of a pollutant at a specific site and additionally, contribute to improve our knowledge on air pollution processes. Measurement are often time demanding and expensive and limited to specific measuring sites. Therefore, air pollution models are important and very useful tool in monitoring programs. Models are able to extend information obtained from measurements fast and is often used for interpretation and extension of measurement results (Hertel, 2009). Models calculate atmospheric processes on the basis of mathematical expressions of different simplified processes (emission, dispersal, chemical transformation, transport, and deposition) that the pollutants go through from emission to deposition. The mathematical models make it possible to calculate deposition of i.e. NH₃ between different surfaces and the atmosphere, and investigate effects of certain parameters by manipulating them in the model.

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5 Danish Ministry of the Environment, Bekendtgørelse af lov om miljøbeskyttelse, LBK nr. 879 26/06/2010 (Miljøbeskyttelsesloven).
3 Atmospheric surface fluxes of NH$_3$

Short-range atmospheric pollution processes, like dry deposition of atmospheric NH$_3$, occur in the lowest part of the troposphere\(^6\), called the atmospheric boundary layer (ABL) (also known as the planetary boundary layer (PBL) or boundary layer (BL)). Atmospheric flows and processes are, in this layer, highly determined by surface-atmosphere interactions (Arya, 1999).

3.1 The Atmospheric Boundary Layer

Motions of air, heat, momentum and other substances in the atmosphere are caused by turbulent flows in the lower atmosphere. The dry deposition of NH$_3$ is therefore highly dependent on the dynamics in the atmosphere that are responsible for the turbulence. The superior source of energy driving these dynamic processes is radiant energy received from the Sun together with the primary forces acting on the air in the atmospheric system. The atmospheric system can be divided into three categories: macro-, meso- and microscale, where processes occur at different spatial and temporal scales. The transport of NH$_3$ is confined to the latter scale of micrometeorology and the ABL. Stull (1988) defines the ABL as “that part of the troposphere that is directly influenced by the presence of the earth’s surface, and responds to surface forcings with a timescale of about an hour or less”. The ABL is formed from continuous interactions between the surface and the atmosphere, thus the atmospheric motions are primarily turbulent in this part of the atmosphere. Turbulence is responsible for the major transport of substances in the atmosphere. The flow rate of a quantity of substances in the atmosphere is termed a turbulent flux density (\(F\) [g m$^{-2}$ s$^{-1}$]) and is mathematically expressed by the concentration gradient of the substance divided by the resistance to the flow as follows:

\[
F = \frac{c_2-c_1}{r} \text{[g m}^2\text{s}^{-1}] \tag{3.1}
\]

where \(c_2-c_1\) [g m$^{-3}$] is the difference in concentration of the substance in two heights and \(r\) [s m$^{-1}$] is the total resistance to the flow performed by the atmosphere and the surface (Oke, 1978).

Turbulence occurs as a result of continuous interactions between surface and atmosphere and exists in two different categories; the mechanical turbulence and the thermal (or convective) turbulence. Mechanical turbulence is generated by the influence of the physical parameters of the surface, such as topography and roughness, on the

\(^6\) The lowest 10-15 km of the atmosphere.
Atmospheric surface fluxes of NH$_3$ atmosphere. These parameters determine the frictional resistance that the surface exerts on the atmosphere when air is passing and thereby mechanical turbulence is generated. A parameter $z_0$ [m] termed roughness height is an expression for the roughness of a surface. $z_0$ is determined by surface characteristics upwind, such as the forest’s structure including height and density of the roughness elements. A rule of thumb asserts that $z_0 = 0.1h$ where $h$ [m] is the height of the roughness element. The roughness of a dense and tall forest is larger than of a sparse and lower forest due to the height and surface area. The turbulent flow above a forest is generally more turbulent due to the high roughness, and thereby is the transport of momentum and scalars more efficient than over a homogeneous flat surface. Thermal turbulence is a result of convection from the Sun’s heating of the surface, and is determined by thermodynamic properties of the atmosphere and the surface (such as albedo, emissivity, heat capacity, and moisture content). When the air just above the surface is heated, it is lifted due to buoyancy effects caused by the lower density of warm air compared to cold air (Oke, 1978).

The micrometeorological processes in ABL extends in a temporal scale from about an hour to a day due to the diurnal cycle of receiving solar energy and the structure and dynamic in the layer. The structure of the ABL is caused by different “surface forcings” on the atmosphere (i.e. absorption of solar radiation, evaporation, transpiration, frictional drag, and effects of the topography) along with the dynamic and thermodynamics of the troposphere (Arya, 1999). The depth of the ABL over land surfaces can extends up to app. 2 km in daytime on a sunny summer day due to convection and in night time it can decrease to less than 100 m or even non-exist. The top of the ABL is limited due to the atmospheric inversion$^7$ of temperature in the tropopause$^8$ (Oke, 1978).

The micrometeorology of forests induces particular influences on atmospheric flows in the ABL. A deciduous forest is organized in three zones; floor, trunk space, and canopy. The canopy zone is the most important zone considering forest-atmosphere interactions, and particular the presence of green leaves, described by LAI, is important. LAI is highly seasonal variable which may also appear in the seasonal dry deposition pattern. LAI vary typically in a range of 0-6 for a forest over a year and peaks in the summer while equals 0 for deciduous forest between defoliation and foliation (winter term). A high LAI entails a larger roughness and thus entail more turbulence above the forest. LAI have, besides affecting the roughness, crucial controlling effects in the interactions between terrestrial ecosystems and atmosphere e.g. the photosynthesis and the radiation balance. The canopy zone yields great effect when considering accumulating incoming radiation along with its capability to transmit and emit long wave radiation downwards to the forest floor and upwards to the atmos-

$^7$ A temperature inversion is an increase in temperature with height.

$^8$ The upper boundary of the troposphere.
Atmospheric surface fluxes of NH\textsubscript{3}.

The albedo of deciduous forests is relatively low (0.15 – 0.20) depending on the leaf orientation and location, which gives little reflection of incoming radiation. A canopy full of leaves will always have a lower albedo than a bare one. Additionally, the natural orientation of leaves along with the depth of the canopy also enhance absorption of radiation, due to multiple internal reflections from physical substances in forest stands which makes a canopy absorb large amount of incoming radiation (Oke, 1978). The net radiation\textsuperscript{9} is partitioned between sensible heat flux, latent heat flux, and a storage terms. Latent and sensible heat fluxes make up the largest amount of energy pathways in forests due to their good ability of accumulating radiation and evapotranspirating. Terrestrial ecosystems store energy physically and biochemically as important parameters in forests energy balance. The physical energy storage occurs by physical uptake within the plant material, while the chemical storage occurs due to photosynthesis. Even though the air above forests canopies is heated relatively slow, forests retain the heat very good and contribute to convective turbulence also in the late afternoon/evening when incoming radiation decreases (Oke, 1978).

3.1.1 Internal boundary layers
Obstacles on the surface are responsible for generating several internal boundary layers (IBL) within the ABL. In each of these IBLs transport of pollutants is governed by different processes. A typical structure of the ABL consists of a laminar sub-layer a roughness layer, and the turbulent surface layer (Figure 3.1).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure3.1.png}
\caption{The vertical structure of the troposphere, consisting of several internal boundary layers; Roughness layer, turbulent surface layer, and the planetary boundary layer (Oke, 1978).}
\end{figure}

The two layers closest to the surface depend on the surface elements such as the dimension of for example height, shape, plan density, flexibility and spacing. The first layer, laminar sub-layer, is a thin (few mm and sometimes even less thick) layer immediately above the surface, where transfer of a substance or momentum occurs

\textsuperscript{9} The net radiation is the available energy expressed as the sum of the incoming and outgoing long- and shortwave radiation: \( Q^* = K_{in} - K_{out} + L_{in} - L_{out} \)
only due to molecular diffusion and the flows are laminar. In the second layer, roughness layer, complex flows are generated due to individual roughness elements. The flow is highly turbulent because it is influenced by the characteristics of the surface. The extension of this layer depends therefore to a great extend on the size and density of the surface elements. The flow above and within a canopy is felt throughout the layer including the whole canopy height layer and extends considerably above the canopy layer. Usually this layer extends up to at least one to three times the height, or spacing, of the surface roughness elements. The third layer, turbulent surface layer (also called the constant flux layer), is characterized by small scale turbulence. The turbulent surface layer extends from the surface up to 50 meters and the turbulent fluxes can to a good approximation, be considered constant with height. Larger eddies of air and turbulent flows are generated in the upper app. 90 % of the ABL.

Impacts of mechanical turbulence decrease rapidly with height. Thermal convection does not follow similar tendency, whereas the daytime layer is primary dominated by free thermal convection. The mixing of airborne materials, such as pollutants and dust, is very efficient due to turbulence, and therefore this convective layer in the day time is often referred to as the mixing layer. At night time, when the flow above the roughness layer is confined to the forced convection of mechanical turbulence, a mixing layer is not present. Instead an inversion layer is created due to the stratification of the atmosphere caused by the stability (Section 3.1.3). Above the ABL comes the free atmosphere where motions primarily are laminar (Arya, 1999).

### 3.1.2 Vertical wind profile

The Monin-Obukhov Similarity Theory provides the general formulation for the vertical wind velocity profile in the surface layer, but is only valid for smooth surfaces. The vertical wind profile in neutral atmospheric conditions is commonly described as the logarithmic function:

$$
\bar{u}(z) = \frac{u_*}{k} \ln \left( \frac{z-d}{z_0} \right) \ [m \ s^{-1}]
$$

(3.2)

where \( \bar{u}(z) \) [m s\(^{-1}\)] is mean wind velocity as a function of height, \( u_* \) [m s\(^{-1}\)] is the friction velocity\(^{10}\), \( k \) is the von Karman constant equal to 0.4, \( z \) [m] is the height, and \( z_0 \) [m] is the roughness height. In forests, where the vegetation is very tall, the zero-displacement height \( d \) [m] is applied, which describes the level within the forest where most of the momentum is absorbed. More practically, it describes the height above the ground where the neutral logarithmic profile is valid. A commonly used rule asserts that \( d = 2/3 h \) [m] (Figure 3.2a). With increasing height, the wind direction tends to turn clockwise in the Northern Hemisphere and the wind speed increases. In the top of the ABL \( \bar{u} \) is app. constant with height (Oke 1978).

\(^{10}\) The friction velocity represents the stress performed by the surface ant the wind velocity on the atmospheric flow.
Figure 3.2: The vertical wind velocity profile a) above tall vegetation, where $d$ [m] is the displacement height, $h$ [m] is the vegetation height, and $z_0$ is the roughness height [m] and b) the wind speed above an open country and a forest where $z_g$ [m] is the top of ABL (Oke, 1978).

Figure 3.2 illustrates the wind speed increase with height and how roughness elements affect the top of the ABL.

### 3.1.3 Atmospheric stability

Atmospheric flows are affected by the thermal stratification of the atmosphere, called the atmospheric stability. The stability influences dispersal of pollutants in the ABL by suppressing or enhancing the dispersal. The stability can be determined by the vertical temperature gradient and is often divided into three categories: Stable, neutral, and unstable. The air pressure decreases by increasing height, and when a parcel of air is moving upwards, it is affected by buoyancy forces. This provokes an expansion of the air parcel and thereby a decreasing temperature within the parcel. This decrease in temperature is termed the *adiabatic temperature decrease* and means that no exchange of heat between the parcel and the ambient atmosphere occurs. If the air is dry, the adiabatic temperature decrease is termed the *Dry Adiabatic Lapse Rate* (DALR) and decreases by a rate of 9.8 °C km$^{-1}$ (Holden 2008). The difference between the actual vertical temperature profile, termed the *Environmental Lapse Rate* (ELR), and the DALR is used to characterize the atmospheric stability (Figure 3.3).

Figure 3.3: Stability classes; stable, neutral, and unstable. The green line illustrates DALR, the red line illustrates ELR, and the circle illustrates a dry air parcel.
**Unstable**

When ELR decreases more than DALR by increasing height the atmosphere is said to be unstable (Figure 3.3). In this atmospheric situation, a parcel of air that is displaced upwards will be affected by buoyancy forces. This is due to the temperature within the parcel that is higher than the temperature of the ambient air. In this case, when a parcel of air is displaced vertically, it tends to keep going in the same direction. Situations of unstable atmosphere often exists in the afternoon on sunny summer days when the solar energy heats up the Earth’s surface and makes ELR decrease more than DALR. These cases cause a very high rate of vertical mixing of the air, and contribute to diluting the concentration of any pollutants in the atmosphere locally and constitute to a greater dispersal.

**Stable**

In a stable atmosphere, air does not tend to move vertically. In this case, the ELR decreases less than DALR and makes a vertical displaced air parcel tend to return to the original levels. This is due to the colder temperature within the parcel than that of the ambient air (Figure 3.3). In a stable atmosphere, the vertical mixing of air is small which can give relatively high local concentrations of atmospheric pollutants. A stable atmosphere is often seen in night times when the Earth’s surface is cooled and ELR decreases or in any temperature inversion.

**Neutral**

When the atmosphere is not stable or unstable, it is neutral. In a neutral atmosphere, ELR equals DALR and an air parcel will not tend to move vertically on its own, unless influenced by external forces (Figure 3.3). In that situation, the temperature within the air parcel equals the temperature in the ambient air. This results in no buoyancy effects. The atmosphere is often neutral (or close to neutral) in cloudy and windy days, when overcast restricts heating and cooling of the surface. It must be noted that completely neutral atmospheric condition does almost never appear.

The Monin-Obukhov length $L$ [m] is used to assess the stability of the atmosphere. $L$ simply describes the height above ground level at which production of turbulence by mechanical and buoyancy forces (thermal turbulence) are equal. $L$ originates from the Monin-Obukhov Similarity Theory, and is introduced in order to describe the atmospheric turbulence (Foken, 2006). $L$ varies proportional with the thickness of the boundary layer. It is mathematically defined by:

$$L = \frac{u^3}{\kappa \left( \frac{q}{T_0} \right) \left( \frac{q}{c_p \rho} \right)} \text{[m]}$$  \hspace{1cm} (3.3)

where $\frac{g}{T_0}$ [m s$^{-2}$ K$^{-1}$] is the gravity acceleration divided by the surface temperature in Kelvin units, $q$ is the kinematic heat flux, $c_p$ [K m s$^{-1}$] the specific heat, and $\rho$ [kg}
Atmospheric surface fluxes of NH$_3$ is the air density (Foken, 2006). An important note of this theory is, that vertical fluxes of heat and momentum in the surface layer are assumed constant with height and that the flow considered takes place in a horizontal homogenous and quasistationary surface layer (Arya 1988). A dimensionless stability parameter $\zeta = (z - d)/L$ is often used to classify the atmospheric stability conditions where $z$ [m] is the height of considering the flow. If $\zeta = 0$, the atmosphere is neutral, $\zeta < 0$, the atmosphere is unstable, and $\zeta > 0$, the atmosphere is stable.

3.1.4 Atmospheric turbulence

Pollutants in the atmosphere are dispersed by turbulence mainly driven by small scale eddies in the mixing layer. Turbulent flows are extremely complex in spatial scale and vary largely on temporal scale. Since it is difficult to assess and predict turbulent flows, their statistical characteristics are used. One method is the Reynolds decomposition, which breaks down the turbulent flow into a time averaged mean value and fluctuating component (Garratt, 1992). Doing Reynolds decomposition, on i.e. the wind velocity, the turbulent flow is described as:

$$u = \bar{u} + u'$$  \hspace{1cm} (3.4)

where $u$ [m s$^{-1}$] is the resulting turbulent flow, $\bar{u}$ [m s$^{-1}$] is the mean component and $u'$[m s$^{-1}$] is the fluctuating component.

The turbulent flux of a given pollutant (vertical flux density) $F_c$ is mathematically described as the product of the wind speed $u$ and the concentration $c$ [g] of the pollutant:

$$F_c = u \cdot c$$  \hspace{1cm} (3.5)

By performing the Reynolds decomposition on $u$ and $c$, the flux may be described as the sum of the mean product of $u$ and $c$ plus the mean product of the fluctuation parts of $u$ and $c$:

$$F_c = \bar{u} \bar{c} + u'c'$$  \hspace{1cm} (3.6)

because $u' = 0$ and $c' = 0$. If the value of $F_c$ is positive the flux is upwards and if negative the flux is downwards.

3.2 NH$_3$ surface fluxes above vegetation

It has now been described, how the atmospheric flow is influenced by the surface, which defines some crucial factors controlling dry deposition of gasses to forest. $F_{NH3}$ are, however, also influenced by the physiology of the surfaces of the different elements comprised in vegetation. Particular does the biophysically active leaves take large part in controlling deposition of NH$_3$ due to the stomata uptake, while
other plant materials, such as twigs and bark does not have any significant influence (Asman et al., 1994). In Figure 3.4 a cross section of a leaf is illustrated.

![Figure 3.4: Resistance diagram of the pathways and processes for transfer between air and plant tissue (Hicks et al., 1987) The resistances are described in Section 3.3.2.](image)

A significant part of the uptake of NH$_3$ in vegetation occurs through the stomata. Thus it is of great influence when the stomata is open and this is determined by a number of factors i.e. the intensity of light, water potential of leaves, temperature, relative humidity, age of leaves, and seasonal variations.

In a larger spatial scale, the forest does also influences the deposition due to i.e. roughness changes at the forest edge and openings within the forest. Particular effects from the edge induce crucial influence on dry deposition processes by enhancing due to i.e. increased turbulence. This effect was seen up to five times the tree height distance into the forest from the edge dependent of LAI (Draaijers et al., 1994). Among other parameters, LAI determines the drag force that is created when air passes the edge and thereby influence the turbulent flows. Light and water level are also different in the edges, than over the interior of the forest, which affects the opening of the stomata and thereby the uptake of NH$_3$ through stomata (Draaijers et al., 1994). The relative humidity (RH) is a measure of the saturation of the atmosphere by water vapour and does also influences the atmospheric NH$_3$ deposition. This happens either by absorbing NH$_3$ into the water droplets and vapour (wet deposition) and thereby reducing c$_{NH3}$, or by enhancing adsorption due to the solubility of NH$_3$ (Andersen et al., 1999; Sutton et al., 1995; Wyers and Erisman, 1998).
3.2.1 Compensation point

The exchange of NH₃ between vegetative ecosystems and the atmosphere is bi-directional which means that the flux can be upward directed (emission) as well as downward directed (deposition). Agricultural cropland emits NH₃ due to evaporation associated to fertilizing events, but semi-natural and natural ecosystems are still regarded as a sink more than a source of NH₃. A number of studies indicate, however, the bi-directionality of FₙH₃ above forests (Andersen et al., 1999; Duyzer et al., 1994; Erisman and Wyers, 1993; Sutton et al., 1997; Wyers and Erisman, 1998). The NH₃ exchange between a mixed coniferous forest and the atmosphere was in one study found to be emission events in 14% of the net fluxes (Neirynck et al., 2005). Farquhar et al. (1980) was the first to calculate a NH₃ compensation point that could explain bi-directional fluxes. The NH₃ compensation point is the concentration for which, NH₃ is neither absorbed nor emitted by the leaf surface (Farquhar et al., 1979; Farquhar et al., 1980). The compensation point has been found to be a central parameter, controlling the direction of FₙH₃ above vegetative surfaces (Schjoerring et al., 1998). One deals with the compensation point at both leaf and canopy scale. The leaf NH₃ compensation point (also termed the stomata NH₃ compensation point) depends on the NH₄⁺ concentration and PH in the leaf apoplastic solution and the cₙH₃ in the atmosphere. The canopy compensation point is influenced further by potential cuticular NH₃ deposition and soil NH₃ emission (Kruit et al., 2007). If the atmospheric cₙH₃ is less than the compensation point, an emission flux can occur. The magnitude as well as the variability due to the influence of external factors such as meteorology and seasonal changes is, however, still only to a small extent investigated. Nevertheless, very recent results report a seasonal dependence of the NH₃ compensation of beech leaves whereby the compensation point is highest in the early and late season (Wang et al., 2010). This means that emissions occur mainly in the early and late growing season while deposition occurred during the mid-summer.

3.3 Local-scale modelling NH₃ dry deposition

The dry deposition of atmospheric NH₃ is determined particular by the distance from the source due to the high reactivity of NH₃. The meteorological situation and the local variations in the land use, however, make also up great influence. Studies have indicated that approximately up to 50% of the emitted NH₃ deposits within 50 km downwind from the source (Hertel et al. 2005, and references herein). The atmospheric NH₃ contribution originates, however, also from regional sources. When calculating local NH₃ deposition it is, thus, important to take both local and regional contribution into account. Mathematic models are used to represent real processes, but in order to make the calculations feasible with the available computer capacity, they are often roughly simplified. Atmospheric motions need to be described in air pollution dispersion models, but this description is very challenging. They are, as described, complex and varies greatly between different scales from the very small
eddy fluxes, driven by molecular diffusion, to the largest eddies, driven by larger turbulent systems.

Calculations in a high spatial resolution (local-scale) can be very computer demanding and in many cases not feasible. Models in different scales, are therefore often combined in a coupled modelling system, just as DAMOS. DAMOS is used in the current Danish monitoring program NOVANA to calculate the atmospheric concentration and deposition of NH$_3$. DAMOS includes the two atmospheric dispersion models, DEHM$^{11}$ and OML-DEP$^{12}$ to calculate the regional background level and deposition of atmospheric N components different from gaseous NH$_3$ and the local scale dry deposition of atmospheric NH$_3$, respectively.

**DEHM**

The regional-scale air pollution model, DEHM, provides calculations of regional background concentration level of NH$_3$ along with other dry deposited N compounds and the wet deposited N as inputs to the local-scale model OML-DEP. DEHM covers the northern hemisphere and zoom in to a high resolution for Denmark of app. 17 x 17 km (Christensen, 1997) (Figure 3.5).

![Figure 3.5: The full calculation area of DEHM. The outer area is calculated in a resolution of 150 x 150 km, the area within the red framed square is calculation for Europe with a 50 x 50 km resolution, and the area within the green square is calculation for Denmark in a resolution of 17 x 17 km (Ellermann et al., 2007).](image)

DEHM is a tree-dimensional model that uses the newest available information of emission, land use, and meteorology to describe the physical and chemical atmospheric processes influencing NH$_3$ in the atmosphere. A contribution to the atmospheric $c_{NH3}$ from regional sources is transported into the modelling area with atmospheric motions and thereby contributes to local NH$_3$ deposition. To include this contribution in the local-scale calculations, DEHM calculates the boundary conditions in the upwind boundaries of the local area and transmits this information continuously.

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$^{11}$ DEHM is an acronym for Danish Eulerean Hemispheric Model

$^{12}$ OML is an acronym for Operational Meteorological Air Quality Models, in Danish: Operationelle Meteorologiske Luftkvalitetsmodeller and DEP stands for Deposition
to OML-DEP. A deeper description of DEHM and the physical parameterizations can be found in the original references (Christensen, 1997).

3.3.1 OML-DEP
The local-scale model OML-DEP is the applied dispersion model particular designed to calculate the NH$_3$ dry deposition to different land surfaces (Berkowicz et al., 1986; Olesen et al., 1992; Olesen, 1995). On the basis of input information on background concentration, emission, location, land use, meteorology, and a receptor net, the hourly dry deposition to specific nature habitats, can be calculated. OML-DEP operates in a spatial resolution of 400 x 400 m, called a grid cell, with the considered point in center (Ellermann et al., 2007). The model consists of two main modules; one to calculate the dispersal of emitted NH$_3$ and one to calculate dry deposition.

OML-DEP is based on statistical descriptions of a Gaussian plume, where a normal distribution of an emission dispersal is assumed around its downwind center line both in horizontal and vertical direction (Figure 3.6).

![Figure 3.6](image)

Figure 3.6: A typical Gaussian dispersed plume of a pollutant emitted from a point source, where $x$, $y$, $z$ is the three directions in the coordinate system, $h$ is the stack height, $H$ is the effective stack height, and $\Delta h$ is the additional stack height due to plume rise (Oke, 1978).

The Gaussian distributed concentration $c$ is mathematically expressed as:

$$c(x, y, z, H) = \frac{Q}{2\pi u \sigma_x \sigma_y} \left( e^{-\frac{(x-H)^2}{2\sigma_x^2}} + e^{-\frac{(x-H)^2}{2\sigma_y^2}} \right) e^{-\frac{y^2}{2\sigma_z^2}} \text{ [g m}^{-3}] \quad (3.7)$$

where $x, y, z$ are the three directions in the coordinate system, $H$ [m] is the effective height of release above ground (in Figure 3.6 illustrated as $H_g = h_g + \Delta h$), $Q$ is the
source emission rate [g s\(^{-1}\)], \(\bar{u}\) is the mean horizontal wind speed through the plume [m s\(^{-1}\)], and \(\sigma_y\) [m] and \(\sigma_z\) [m] are the horizontal (y) and vertical (z) standard deviation of the pollutant distribution (Arya, 1999). The theoretical principles for the Gaussian plume model are limited to some assumptions. The model requires idealized uniform flows where turbulence is found homogenous and mean wind speed is larger than the standard deviation of the turbulent fluctuations (Arya, 1999). Lyons and Scott 1990 lists 7 important assumptions that are implied in the Gaussian plume model which can be found in Appendix B.

### 3.3.2 Parametrizing NH\(_3\) dry deposition

Dry deposition of NH\(_3\) is often parameterized by dividing the process into three steps going from the atmosphere to the surface. Each step yields a particular resistance to the dry deposition process and is governed by different factors introduced in previous paragraphs. This method is termed the resistance method. First, transport downwards through the atmosphere to the surface is forced by turbulence generated both due to buoyancy effects and mechanical turbulence. Subsequently, a transport through the quasi-laminar sub-layer occurs by molecular diffusion. Finally, the uptake or adsorption by the surface is controlled by the surface properties. The different resistances that these three steps yield influence the rate of the dry deposition that is called the deposition velocity \((v_d)\) [m s\(^{-1}\)]. When \(v_d\) is known, it can be used to estimate the vertical flux of specie by:

\[
F = -v_d C \quad [\text{g m}^{-2} \text{s}^{-1}]
\]

where \(C\) [g m\(^3\)] is the concentration of the specie in the air. If \(F\) is positive, the flux is upward directed and entails an emission from the surface to the atmosphere. If \(F\) is negative, the flux is downward directed and entails a deposition from the atmosphere to the surface. As the flux is assumed to be constant in the surface layer and the concentration depends on height, \(v_d\) also depends on the height. \(v_d\) can be estimated by an analogy to the resistance in electronics and is usually defined by:

\[
v_d = \frac{1}{\tau_t} = \frac{1}{\tau_a + \tau_b + \tau_c} \quad [\text{m s}^{-1}]
\]

where \(\tau_t\) [s m\(^{-1}\)] is the total resistances in the process, \(\tau_a\) [s m\(^{-1}\)] the aerodynamic resistance, \(\tau_b\) [s m\(^{-1}\)] the quasi-laminar resistance, and \(\tau_c\) [s m\(^{-1}\)] the surface resistance (Figure 3.7). Figure 3.7 illustrates the pathways of a gas depositing to vegetative receptor surfaces.
Atmospheric surface fluxes of NH$_3$

**Figure 3.7:** Resistance diagram of typical dry deposition pathways of atmospheric gasses to vegetative surfaces, consisting of three main resistances, $r_a$ [s m$^{-1}$] the aerodynamic resistance, $r_b$ [s m$^{-1}$] the quasi-laminar resistance, and $r_c$ [s m$^{-1}$] the surface resistance (Wesely and Hicks, 2000).

OML-DEP calculates the dry deposition of NH$_3$ on an hourly basis for each grid cell covered with one of 16 different land use classes based on the resistance method. The differences between the 16 land use classes are defined by i.e. LAI and $z_0$. The dry deposition processes have been expressed in different ways in the litterature. A parameterization of $v_d$ from Simpson et al. 2003 and Emberson et al. 2000 is used in OML-DEP.

**Aerodynamic resistance ($r_a$)**

The aerodynamic resistance is the resistance performed by the atmosphere on the species transport down to the surface. This resistance is governed by atmospheric stability conditions (buoyancy effects) and surface roughness and is the same value for all substances in the atmosphere (Wesely and Hicks, 1977). When the atmosphere is turbulent and well mixed the aerodynamic resistance is low and the concentration gradient of a pollutant is relatively small. Contrary, a stable atmosphere suppresses vertical motions and the concentration gradient is often found large (Erisman and Draaijers, 2003). The aerodynamic resistance $r_a$ is parameterized; on for unstable ($L < 0$) and one for stable ($L > 0$) atmospheric conditions:
Atmospheric surface fluxes of NH$_3$

Unstable:  
\[
 r_a = \frac{1}{\kappa \cdot u_*} \ln \left( \frac{z_{\text{ref}}}{z_0(lc)} \right) - \psi_H \left( \frac{z_{\text{ref}}}{L} \right) + \psi_H \left( \frac{z_0(lc)}{L} \right) \quad [m^2 \, s^{-1}] 
\]  
\[
 \psi_H = 2 \ln \left( \frac{1}{2} \left( 1 + (1 - 16)^{\frac{1}{2}} \right) \right) 
\]

Stable:  
\[
 r_a = \frac{1}{\kappa \cdot u_*} \ln \left( \frac{z_{\text{ref}}}{z_0(lc)} \right) - \psi_H \left( \frac{z_{\text{ref}} - z_0(lc)}{L} \right) \quad [m^2 \, s^{-1}] 
\]  
\[
 \psi_H = -5 
\]

where the functions $\psi$ is the stability similarity function for heat that is included when deviating from neutral conditions. $z_{\text{ref}}$ [m] refers to the reference height of the wind (equal to 2 m) and $lc$ refers to land use classes. The roughness length $z_0$ [m] is determined by the height of the vegetation $h_{\text{veg}}$[m] according to $z_0(lc) = 0.1 \, h_{\text{veg}}(lc)$. $h_{\text{veg}}$ is determined by general values depending on latitude. This gives values of $h_{\text{veg}} = 20$ m and $z_0 = 2$ m, respectively. As seen in Equation 3.10 and 3.11, $r_a$ is affected by the mechanical turbulence, expressed in $u_*$ in a logarithmic dependence, like it is described in the vertical wind profile (Equation 3.2).

**Quasi-laminar resistance ($r_b$)**

The quasi-laminar resistance is confined to the laminar sub-layer immediately above the surface (0.1-1 mm) which we can explain by a layer consisting of many viscous sub-layers in, where the transport happens through molecular diffusion. This diffusion is influenced by the surfaces ability to absorb a particular gas, which means that the chemical, physical, and biological properties of the surface and the gas determines $r_b$. The viscosity of air and a diffusion coefficient is used to estimate this resistance. Mathematically $r_b$ is expressed as:

\[
 r_b(i) = \frac{2}{\kappa u_*} \left( \frac{Sc(i)}{Pr} \right)^{\frac{2}{3}} \quad [s \, m^{-1}] 
\]  

where $i$ indicates the specific gas or particle considered, $Sc$ is the dimensionless Schmidt number that takes the diffusivity of the gas and the kinematic viscosity of the air:

\[
 Sc = \frac{v}{D} 
\]  

where $v$ [cm$^2$ s$^{-1}$] is the kinematic viscosity$^{13}$ for air and $D$ [m$^2$ s$^{-1}$] is the diffusivity of the gas (Hicks et al., 1987). For NH$_3$, this diffusivity is 23.4*10$^{-6}$ m$^2$ s$^{-1}$ (Seinfeld and Pandis, 2006). $Pr$ is the dimensionless Prandtl number$^{14}$ that describes the ratio between the kinematic viscosity and thermal diffusivity. Above a canopy, the LAI

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$^{13}$ For air at 20ºC $v = 0.15$ cm$^2$ s$^{-1}$

$^{14}$ For air $Pr = ~0.72$ (Wesley and Hicks 1977)
influence $r_b$. Larger leaves make $r_b$ increase as the laminar sub-layer grows with the distance the air passes the leaf and the diffusion is prevented. The wind velocity and the temperature difference between the leaf and the ambient air also influence $r_b$. The higher wind velocities and smaller temperature difference lead to decreased $r_b$.

**Surface resistance ($r_c$)**

The surface resistance is the resistance confined to the particular surface. This is often the most detailed and difficult resistance to evaluate, because it is affected by many different properties of the surface, i.e. chemical factors like pH, moisture and the solubility, biological factors as LAI, leaf-structure, and thermal properties. $r_c$ is in many cases, therefore, set as a fixed value but it can also be calculated from a number of additional influencing factors (Hertel et al., 2006). The $r_c$ above a forest and other vegetative surfaces has a very strong seasonal variation due to the season of growth that influences the biological activity. The biological activity is also influenced by the diurnal variations of temperature, radiation, humidity and so on which affects the stomata conductance. The surface resistance can be divided into three further resistances; the foliage resistance, that embraces stomata, cuticular and mesophyll resistances, the resistance performed by the lower canopy that is influenced by the height of the threes and the structure of the canopy, and the resistance performed by the ground (water, soil, and other surfaces).

In OML-DEP, $r_c$ is described by two components that describe the NH$_3$ uptake through stomata and the uptake that does not depend on stomata, respectively. For NH$_3$ dry deposition to surfaces with vegetated cover $r_c$ is calculated:

$$r_c(i) = \frac{1}{lai \cdot g_{sto}(i) + g_{ns}(i)} \text{ [s m}^{-1}]$$ (3.14)

where $lai$ is LAI, $g_{sto}$ is the stomata conductance, and $g_{ns}$ is the non stomata conductance related to the cuticular resistance.

In OML-DEP, $g_{sto}$ is calculated as a function of leaf phenology, available light, vapour pressure deficit, temperature, and soil water content that is calculated for each land use classes. $g_{ns}$ is determined from atmospheric acidity, which is calculated from the relationship between atmospheric concentrations of NH$_3$ and sulphur dioxide (SO$_2$), along with the surface temperature and relative humidity (Ellermann et al., 2005).

**Leaf area index**

It is, during previous paragraphs seen, that LAI is only included in the calculation of $r_c$, where it directly figures. LAI is also included in $g_{sto}$, where it is used to calculate

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$^{15}$ The rate a gas or water vapor passes through the stomata [mm s$^{-1}$]
the available light. LAI is applied in the model as a function of the growing season (Figure 3.8) (Emberson et al., 2000).

![Generic LAI function](image)

**Figure 3.8**: Generic function for LAI used in OML-DEP. LAI_min is the minimum value of LAI, LAI_max is the maximum value of LAI, SLAI is the day number of starting growing season, ELAI is the day number of ending growing season, SLAI_len is the number of the days from SLAI until LAI reaches LAI_max, and ELAI_len is the number of days with decreasing LAI from LAI_max to ELAI (Emberson et al., 2000).

In Figure 3.8, it is seen that the growing season is set to start on day 90 (31 Mar) and end on day 270 (27 Sep). The maximum value of LAI (LAI = 5) is valid between 26 May and 27 Jun and the minimum value of LAI (LAI = 3.5) is valid outside the growing season according to the script of the model.

### 3.4 Atmospheric NH₃ flux measurements

\( \text{F}_{\text{NH₃}} \) can be measured in several ways; i.e. micrometeorological methods as the eddy covariance (EC), relaxed eddy accumulation (REA), eddy accumulation (EA), or the aerodynamic gradient (AG) technique. \( \text{NH₃} \) is transported in the free atmosphere by turbulent diffusion basically by displacement of parcels (eddies) of air (Fowler and Duyzer, 1989). This makes a good reason to use micrometeorological measurement techniques. These methods have the advantage of not disturbing the soil-plant-atmosphere system. Additionally, they average the measurement over a large area, whereby problems related to enclosure methods, are avoided (Fowler and Duyzer, 1989). The physical and chemical properties of \( \text{NH₃} \) cause challenges to measurements of \( \text{NH₃} \). One is that \( \text{NH₃} \) is a very reactive specie, which often interferes with particulate ammonium (\( \text{NH₄}^+ \)) and second that \( \text{NH₃} \) deposits fast (Zhu et al., 2000). The vertical \( \text{F}_{\text{NH₃}} \) above forest canopies is in this project measured by two different micrometeorological techniques; Conditional Time Average Gradient (COTAG) and Relaxed Eddy Accumulation (REA). Both methods overcome the challenge of the high reactivity of \( \text{NH₃} \), by using the higher diffusion coefficient of \( \text{NH₃} \), than particles, in air to collect the \( \text{NH₃} \).
3.4.1 Conditional time averaged gradient (COTAG)

In attempt to create a low cost system to measure long-term fluxes of trace gases in the biosphere, COTAG has been developed (Famulari et al., 2010). COTAG is aimed to provide direct weekly to monthly average flux gradient measurements that is useful for measurements of long-term dry deposition of NH$_3$ (NitroEurope IP, 2009). Because atmospheric stability conditions varies greatly over relatively short time periods and thereby affects the concentration greatly, COTAG measures the averaged flux by a carefully defined range of stability and samples only concentration gradients when atmospheric stability is near neutral (Famulari et al., 2010).

The COTAG method is based on the AG method that originates from the K-theory on turbulent diffusion. The K-theory is based on small scale processes of molecules in molecular diffusion by the theory of Fick’s law of diffusion, which states that the turbulent flux ($F_x$) of a pollutant $x$ is inversely proportional to the product of the eddy diffusivity ($K_x$) and the vertical concentration gradient of the pollutant in the surface layer:

$$F_x = -K_x \frac{\partial C_x}{\partial z} [\text{g m}^{-2} \text{s}^{-1}]$$

(3.15)

Where $K_x$ is the diffusion coefficient (also called the eddy exchange coefficient) for the trace gas and $\partial C_x/\partial z$ is the vertical gradient of the air concentration in the constant flux layer (Arya, 1999; Fowler and Duyzer, 1989). The diffusion coefficient $K$ is derived from the vertical wind profile as the inverse function of the aerodynamic resistance $r_a$ (Section 3.3) (Seinfeld and Pandis, 2006):

$$K = \frac{1}{r_a} = \frac{1}{k \cdot u_*} \ln \left( \frac{z - d}{z_0} \right) - \psi_H \left( \frac{z - d}{L} \right) [\text{m}^2 \text{s}^{-1}]$$

(3.16)

COTAG uses a sonic anemometer$^{16}$ to get necessary turbulent parameters. Finally the COTAG method adds the particular conditional sampling criteria (NitroEurope IP, 2009). This near neutral stability criterions are defined by $(z - d)/L$ and is set, by NitroEurope IP, to $-0.02 < (z - d)/L < 0.02$ (referred to as neutral) and to $-1 < (z - d)/L < -0.02$ (referred to as unstable).

3.4.2 Relaxed Eddy Accumulation (REA)

REA is a method introduced by Businger and Oncley (1989) to measure vertical fluxes in the atmosphere through conditional sampling of air at a single height above canopy. The method is based on a modified version of the EC and EA method. The

$^{16}$ A sonic anemometer measures the wind speed in all three spatial dimensions and the virtual temperature, based on ultrasound pulses sent through the air between three upper and three lower transducers each pair of two containing a transmitter and a receiver. The speed of the ultrasound signal between the upper and lower transducers is affected by the wind and temperature why the signal provides meteorological data and can be used for deriving of turbulent fluctuations of wind, momentum and friction velocity (British Atmospheric Data Centre, 2006).
EC calculates vertical fluxes by direct measuring the covariance of vertical wind velocity fluctuations with gas concentrations fluctuations using a sonic anemometer and a fast responding chemical sensor (Fowler and Duyzer, 1989; Moncrieff et al., 1997). This method requires fast response sensors to measure vertical wind velocity and gas concentration. The EA technique overcomes this issue by sampling conditionally in proportion to the vertical wind velocity and analyses samples afterwards (Pattey et al., 1993). This method has a challenge by needing fast response sampling valves due to fast shifting between updrafts and downdrafts. REA simplifies those methods by a relaxation, meaning that REA still sampling continuous the upward and downward eddies separately, but with a constant flow rate and accumulates the measurements there after (Held et al., 2008). Additionally, REA includes a dynamic vertical velocity deadband around zero m s\(^{-1}\). This causes that air with a vertical wind velocity \(w'\) near zero is not sampled (Businger and Oncley, 1990). Thereby, only the most distinctly up- and downward eddies are sampled.

REA is based on the micrometeorological relationship between the vertical flux density \(F\) and the difference between the average trace gas concentration of upward \(\chi \uparrow\) [g m\(^{-3}\)] and downward \(\chi \downarrow\) [g m\(^{-3}\)] moving eddies (Hensen et al., 2009). The vertical flux is mathematical expressed by:

\[
F = \beta \sigma_w (\chi \uparrow - \chi \downarrow) \text{ [g m}^{-2} \text{s}^{-1}] \tag{3.17}
\]

where \(\chi \uparrow\) and \(\chi \downarrow\) are the average concentration in the up- and downdrafts respectively, \(\sigma_w\) is the standard deviation of \(w'\) [m s\(^{-1}\)], and \(\beta\) is an empirical dimensionless proportionality parameter (Businger and Oncley, 1990; Held et al., 2008; Hensen et al., 2009). A sonic anemometer measures the wind speed in all three spatial dimensions and the virtual temperature.

The REA method has been used for measurements of fluxes of different atmospheric species e.g. NH\(_3\), nitric acid (HNO\(_3\)), sulfur dioxide (SO\(_2\)), particulate sulfate (SO\(_4^{2-}\)) and carbon dioxide (CO\(_2\)) (Meyers et al., 2006; Myles et al., 2007; Pattey et al., 1993; Pryor et al., 2002; Zhu et al., 2000) and have been compared to other micrometeorological methods. Pattey et al. (1993) evaluated REA, comparing measurements of CO\(_2\) fluxes from REA with EC. The two techniques showed fine agreement. Pryor et al. (2002) found measurements of HNO\(_3\) fluxes to a deciduous forest similar between REA and the AG method. Finally an inter-comparison of 4 continuous REA systems has recently been conducted and compared to the AG method by Hensen et al. (2009). The investigation showed a reasonably good agreement between the 4 REA systems and the AG method in periods with low fluxes while the REA systems showed 20-70 % lower fluxes by higher concentrations (Hensen et al., 2009).
4 Methods and site

In order to achieve a comprehensive understanding of the scientific tools used in current processes of assessing loads of atmospheric NH\textsubscript{3} and to understand the dynamic of NH\textsubscript{3} fluxes near complex vegetative surfaces, this thesis illuminates the temporal distribution of dry deposition of atmospheric NH\textsubscript{3} to deciduous forest. In a combination of theoretical study and a long-term experimental field study, it is attempted to answer the three research questions of this thesis stated in Chapter 1. This chapter of methods and site presents a description of the experimental design and site, Ll. Bøgeskov. Furthermore, methodical descriptions of the measuring techniques applied and data processing are described. Finally, the setup of the model is described.

4.1 Experimental design and time line

The experimental work, in this thesis, consists of measuring concentration and vertical fluxes of NH\textsubscript{3} using COTAG and REA, calculation concentration and deposition of NH\textsubscript{3} using OML-DEP, and measuring LAI (Figure 4.1). The experimental work was performed for the deciduous beech forest site, Ll. Bøgeskov, due the year 2010.

![Experimental design](image)

**Figure 4.1:** Experimental design, consisting of measuring of concentration and vertical fluxes of NH\textsubscript{3} using COTAG and REA, local-scale modelling of concentration and deposition of NH\textsubscript{3} using OML-DEP, and measuring LAI.

Atmospheric NH\textsubscript{3} has most often been measured throughout spring and summer seasons due to highest atmospheric \( c_{NH3} \) related to the Danish agricultural practice, where emissions from manure application to the fields occurs mainly in the spring season. Heated animal stables, open barns, and manure storages, however, lead also to emissions. Variations in these emissions are particular controlled by temperature variations. Thereby, this emission peaks in the summer season similar to the temperature peak. Furthermore, emission from these sources are spread over a longer period and can, therefore, still be relatively high in the late summer and autumn (Skjøth, 2010). Additionally, physical properties of a deciduous forest are changing.
greatly during autumn due to defoliation and leaf fall along with changes in the meteorology are factors influencing the atmospheric $F_{NH3}$. $F_{NH3}$ was therefore investigated in the late summer and autumn along with investigations of LAI, while the spring and summer seasons were used to prepare, test, and install the measurement instruments at the experimental site (Figure 4.2).

$F_{NH3}$ measurements are performed at Ll. Bøgeskov in middle of Zealand in Denmark throughout the period 10 Aug 2010 – 11 Nov 2010. Some smaller breaks due to instrumental problems occurred due the measurement period. COTAG is, by this study, used for the first time in Denmark and the system went through a number of start-up problems associated to electricity and software among other things due a testing period from May to Aug 2010. Measurements of LAI were performed with an indirect technique using a LAI-2000 Plant Canopy Analyzer during the growing season of 2010 (May-Nov) (Figure 4.2).

4.2 Experimental site (Lille Bøgeskov)

The experimental work was performed at the beech forest (Fagus sylvatica) called Lille Bøgeskov (translated into Small Beech forest). The field station is located near Sorø in the middle of Zealand (55°29’13”N, 11°38’45”E) on an elevation of 40 m above mean sea level. Ll. Bøgeskov extends approximately 1 km east-west and 2.5 km north-south in a flat and relatively homogeneous terrain (Dellwik and Jensen, 2005; Pilegaard et al., 2003) (Figure 4.3).

Ll. Bøgeskov is mainly surrounded by a landscape characterized by agricultural activities of farm land, farms, and smaller villages. In the north north-western sector, in a distance of app. 1 km from the field station, a considerably larger forest, Store Bøgeskov (translated into Great Beech forest) is located bordering on a lake, Gyrstinge Sø of app. 263 ha. In Figure 4.4, the spatial distribution of the NH$_3$ emission point and area sources is illustrated.
**Figure 4.3:** Map of the field station in Ll. Bøgeskov, based on the Danish Topographic Map.

**Figure 4.4:** Ammonia emission sources around Ll. Bøgeskov. The circles indicate the point sources and the size of them indicate the quantity of emitted NH$_3$-N pr. year. The graduated colours indicate the emission from area sources in the same unit as point sources interpolated in between. Emission data are described in Section 0.
In Figure 4.4, it is seen that many point sources are located in the south-western sector from the field station. The largest NH$_3$ emissions from area sources come from the north-western sector, while the north north-eastern sector is related to relatively small emissions.

The forest consists predominantly of 82-year-old beech trees with an averagely height of 26 m and average tree diameter of 38 cm. Scattered stands of conifers constitute about 20 % of the forest area (Pilegaard et al., 2003). The mean summer peak of LAI, measured in Li. Bøgeskov since year 2000 is found to be 4.6 with the maximum value just above 5 LAI (Pilegaard et al., 2011).

Li. Bøgeskov is located in the northern temperate zone which determines the regional climate at the site. The climate is characterized by a maritime temperate climate with a mean wind speed of 3.9 m s$^{-1}$ coming predominantly from west south-west. Frontal systems are frequently passing (Pilegaard et al., 2003). The mean temperature extends from -0.1 °C in Jan to 16.3 °C in Aug and the main precipitation season is the summer and autumn from Jul to Dec, but precipitation occur all year round (DMI, 2010). Precipitation events during the measurement period at the site are illustrated in Figure 4.5.

![Figure 4.5: Precipitation measured by RISØ DTU in half-hourly resolution above Li. Bøgeskov.](image)

It is seen that precipitation occurred in a great extend throughout the autumn in 2010 only with few dry periods. Three rather intense rain events occurred throughout Aug, while 10 days in the middle of Sep were almost continuously influenced by rain, just as the 10 last days in Oct.

The beech blossoms in the spring, primo may, and last with green leaves until autumn, mid Oct. In the winter season, the beech loose most of its wither leaves (Nicolaisen, 1980). By webcam pictures taken by RISØ DTU app. every half hour in periods above the forest, the foliation date in 2010 was determined to 29 Apr. Defoliation was observed to begin on 23 Oct and on 8 Nov almost no leaves were present in the canopy.
A metrological mast of a height of 57 m and a cross section of \(30 \times 30\) cm and a scaffolding tower of 24 m height and a cross section of \(3 \times 3\) m is located at the field station in the middle of the forest (Figure 4.6). Thereby, fetches\(^{17}\) extend from 500 m in east-west directions to 1 km in north-south directions (Dellwik and Jensen, 2005; Pilegaard et al., 2003).

![Figure 4.6: Field station set up in Ll. Bøgeskov including a scaffolding tower (24 m) and a meteorological mast (57 m) and atmospheric measurement systems.](image)

**Roughness height and displacement height**

The roughness height \(z_0\) and the displacement height \(d\) for Ll. Bøgeskov were calculated in the year 2000 to 1.6 m and 19.0 m, respectively (Dellwik and Jensen, 2000). The result of \(z_0\) is considerably lower than the common rule where \(z_0 = 2.6\) m. The \(d\) is, however, in good agreement to the rule where \(d = 0.75 \times h = 19.5\) m. It is expected, that the forest has changed in the last 10 years, and estimates of the common rule, is therefore, assumed valid, and used in this thesis.

### 4.3 Micro meteorological measurements

During the measurement period, meteorological conditions have been measured and estimated using two sonic anemometers above the forest canopy (31 m and 34 m height). Besides that purpose, the two sonic anemometers were each controlling

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\(^{17}\) A fetch, also called fetch length, is the homogeneous straight distance between the measuring instruments at the mast to the upstream edge of the forest. Generally it is the distance to a roughness shift in terrain.
sampling by REA and COTAG. In this thesis, half-hourly averaged values of the wind velocity, $Spd$ [m s$^{-1}$], wind direction, $Dir$ [°], friction velocity $u_*$ [m s$^{-1}$], temperature, $T$ [°C], and Monin Obukhov Length $L$ [m] are used from the sonic anemometer in 34 m height. The sonic anemometer measures with a resolution of 10 Hz, but is averaged into half-hourly mean values. Additionally, measures of the wind velocity in all three directions $u, v$ and $w$ [m s$^{-1}$] are used in the calculations of $F_{NH3}$. Half-hourly data of the relative humidity, $RH$, and precipitation measured in Ll. Bøgeskov, are obtained from RISØ DTU. The precipitation is measured in 10 minutes resolution in 25 m height with 45° clear of trees above the sampler.

### 4.4 Leaf Area Index measurements

LAI is measured from an indirect and quantitative technique that calculates LAI from direct measurements of radiation with an optical sensor, using a LAI-2000 Plant Canopy Analyzer (LAI-2000 PCA). LAI-2000 is a hand-held instrument consisting of an optical sensor connected to a small computer that features the model algorithm. By this technique, the attenuation of the radiation from a diffuse sky is calculated as it passes through the canopy and deduces. Thereby, qualitative estimates of how much foliage is present in the canopy are conducted. The attenuation is measured at five angle intervals $^{18}$ (rings) from the zenith simultaneously above and below canopy to calculate the LAI, where each ring views a different portion of the sky. It is important to be aware that the LAI-2000 does not differ between “leaf” and “foliage”, which is the reason why it is more appropriate to say that the instrument calculates the foliage area index or plant area index (PAI). A 270° view cap was used heading away from the operator to restrict the view to mask out the operator and thereby remove any influence of the operators shade. A more detailed description of this technique can be found in Appendix C.

**Data collection**

The LAI-2000 was set up to calculate LAI from one above-canopy reading and ten below-canopy reading. In a transect of app. 18 m going from east (103°) to west (283°), ten points on the forest floor were marked out approximately equally distributed over the transect to constitute the measuring points for the below-canopy readings. The ten points were carefully selected to represent the spatial distribution of trees in Ll. Bøgeskov after getting an overview of the canopy from the top of the scaffolding tower. The above-canopy readings were performed in three different locations; from the top of the scaffolding tower, in an opening of the forest, or outside the forest edge, dependent of the different situations in the measuring days.

One measurement (7 May) is made from the top of the scaffolding tower, but due to risks of damages on the instrument from climbing up and down the tower the follow-

$^{18}$ 0-13°, 16-28°, 32-43°, 47-56° and 61-74°.
ing measurements were performed in an opening of the forest 50 m from the site. From the measurement on 20 Aug and onwards the above-canopy readings were relocated to outside the forest edge as the fully developed canopy field up a large part of the opening. The below-canopy readings were performed all the same way starting from east towards west in the height of one m above forest floor.

Through the growing season (May – Nov), LAI was measured continuous every approximately 14-30 days dependent of the measuring conditions. In the summer months, the measurements have only been performed once a month due to typically very constant PAR\textsuperscript{19} when the canopy is fully developed with leaves (RISOE DTU, 2011). Optimal meteorological conditions mean no precipitation and water droplets in the air or at the leaf surfaces and uniformly overcast sky. These conditions are difficult to meet each time of measuring. If these conditions aren’t met, uncertainties are related to the measurements. These situations are important to be aware of and are noted in the logbook (Appendix D).

**Data processing**

The software FV2000\textsuperscript{20} was used to view and manipulate (recalculate) the data. In order to remove effects of tree trunks, because the canopy zone is the primarily focus in this thesis, the first step was to sort out measurements of the outer (lower) ring (61-74°) of the raw data. Because LAI and PAI are both important to the NH\textsubscript{3} dry deposition process, it is chosen to derive both terms from the data. PAI and LAI are assumed equal at values above 4, which is a common value for a developed canopy where measurements can be assumed reasonable. The period of foliation and defoliation does, however, influence the indexes differently. LAI equals zero between defoliation and foliation, whereas PAI is influenced also by the presence of withered leaves, and will have a constant value above zero between leaf fall and foliation. The dates of foliation, defoliation, and leaf fall were therefore found. The foliation date in Ll. Bøgeskov in 2010 was observed from webcam photos taken app. every half hour by RISØ DTU to start on 30 Apr and defoliation were set to 23 Oct from personal observation. Leaf fall was found on 8 Nov also from webcam photos. Webcam photos from the foliation and leaf fall dates can be seen in Appendix E.

Beneath indexes of 4 LAI is estimated by linear interpolation to between 4 and zero in the foliation and defoliation periods. LAI wouldn’t, however, actually equal zero in the winter term due to the scattered stands of conifers in the forest, but this is neglected in here. The LAI measured on 16 Nov where no leaves were present in the canopy, is used for PAI between leaf fall and foliation.

\textsuperscript{19} Photosynthetically active radiation designates the spectral range of solar radiation from 400-700 nm.

\textsuperscript{20} LI-COR Biosciences, Environmental and Biotechnology Research Systems (http://www.licor.com).
The sky could easily have changed during each of the profile measurements that took app. 5 minutes. This leads to variations in the incoming light level, and influences the measurements. This possible error was investigated for one of the measurements (20 Aug) using measurements of incoming PAR in 57 m height from RISØ DTU to investigate the variations in the levels of light.

4.5 Ammonia flux measurements

Atmospheric NH$_3$ was measured above Li. Bøgeskov in the period of 10 Aug to 11 Nov 2010 using two different micrometeorological techniques; COTAG in 29.8 m and 34 m height and REA in 33 m height to comparison. Vertical $F_{\text{NH}_3}$ were derived from the concentration measurements.

4.5.1 Conditional Time Average Gradient (COTAG)

The COTAG system consists of one sonic anemometer and two inlet boxes installed in two different heights (Figure 4.6). The top boxes consist of six glass denuders (15 cm long) and the bottom box consists of seven glass denuders. COTAG samples only in near neutral atmospheric conditions, but in two pre defined intervals of near neutrality. Tree denuders in each box are sampling when $-0.02 < (z - d)/L < 0.02$, referred to as neutral and three in each box are sampling when $-1 < (z - d)/L < -0.02$, referred to as unstable. The seventh denuder in bottom box is sampling $c_{\text{NH}_3}$ when the atmospheric condition deviates from the defined stability intervals. The sonic anemometer measures the micrometeorological conditions related to wind and temperature to control the suction of air through the glass denuders that collects the NH$_3$. Air was pumped through the denuders by an air flow measured to 580 ml min$^{-1}$. The denuders were coated with a solution of citric acid in methanol that makes the NH$_3$ sticks to the denuders (Famulari et al., 2010). The sonic anemometer was located in the mast in a height of 31 m and the two inlet boxes in the heights of 29.8 m and 34 m respectively (Figure 4.6).

Data collection

The measurement period by COTAG were divided into 4 sampling periods with 4 different sets of denuders exposed;

- **Sample 1***: 10 Aug – 31 Aug
- **Sample 2**: 31 Aug – 11 Oct
- **Sample 3**: 11 Oct – 26 Oct
- **Sample 4**: 26 Oct – 11 Nov

* No measurements in 29.8 m height for neutral conditions

Meteorological data from the sonic anemometer were downloaded from the system using the appurtenant software LoggerNet and collected in data sets equal to the de-
nuder sampling periods. Chemical analyzes of denuders were performed by NERI whereby $c_{\text{NH}_3}$ were found.

**Data processing**

$c_{\text{NH}_3}$ were calculated from the measurements in 29.8 m height where the system is active at all moments (except for sample 1). In sample 1, the concentration from 34 m is used instead. The mean concentration have been weighted due to the air volume sampled in each conditions (Table 4.1).

<table>
<thead>
<tr>
<th></th>
<th>Neutral</th>
<th>Unstable</th>
<th>OFF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>70.74 %</td>
<td>8.25 %</td>
<td>21.01 %</td>
</tr>
<tr>
<td>Sample 2</td>
<td>91.03 %</td>
<td>3.90 %</td>
<td>5.06 %</td>
</tr>
<tr>
<td>Sample 3</td>
<td>78.12 %</td>
<td>2.47 %</td>
<td>19.41 %</td>
</tr>
<tr>
<td>Sample 4</td>
<td>79.99 %</td>
<td>5.28 %</td>
<td>14.73 %</td>
</tr>
</tbody>
</table>

*Table 4.1:* Air volume sampled in each of three sampling intervals neutral, unstable and OFF in each of 4 sampling periods.

In order to investigate the uncertainty of measurements the standard deviation between each set of three denuders from neutral and unstable measurements along with the detection limit\(^{21}\) was calculated. Mean values of $c_{\text{NH}_3}$ for each neutral and unstable sample is used to calculate the vertical $F_{\text{NH}_3}$ from Equation 3.15, the diffusion coefficient $K$ is derived according to Equation 3.16.

To correct for stability influences that affects the wind velocity profile and temperature profile to deviate from the logarithmic function, a similarity function for unstable atmospheric conditions is applied the calculation of $F_{\text{NH}_3}$ in unstable conditions. The stability function used by Andersen et al. (1993) is used here:

$$\psi_h = \frac{1}{\phi} - 1, \phi = \left(1 - 16 \left(\frac{z - d}{L}\right)\right)^\frac{1}{3}$$  (4.1)

Due to the conditionally sampling of neutral and unstable atmospheric conditions, mean values of $u_*$ and $L$ used to calculate $K$ and $\psi_h$ is calculated from extractions according to the atmospheric conditions. Calculations are performed in MATLAB (Appendix F).

\(^{21}\) Detection limits are used to identify the lowest quantity that can be detected. One common and simple method to estimate the detection limit (DL) is by $DL = 3*\text{stdv(blank)}$ and this is used here. Blank values are the concentration found on the unexposed denuders. In this case three blank denuders are used for each sampling.
To apply the uncertainty of measurements, the flux was calculated for each of the 9 potential gradients measured in each sample between the three denuders in the top box and the bottom box, from where, the standard deviation was calculated.

4.5.2 Relaxed Eddy Accumulation (REA)

The REA technique provided measurements of vertical fluxes in the atmosphere through conditional sampling of air at a single height above canopy. The REA technique was combined with a Wet Effluent Diffusion Denuder (WEDD) system in order to trap NH$_3$ from the upward and downward eddies separately by diffusion in an aqueous solution.

The REA system consists of three systems; a sonic anemometer to measure the micrometeorological conditions, an inlet system to collect NH$_3$ and an analytical detection system to calculate the concentration and fluxes. The diagram in Figure 4.7 illustrates the REA setup schematically.

![Schematic diagram of the REA system (Hensen et al., 2009).](image)

The sonic anemometer was located in the mast in a height of 34 m and the WEDD inlet system was located in the mast in 33 m (Figure 4.6). The dynamic deadband was set to $|w_o| < 0.5\sigma_w$ m s$^{-1}$.

The WEDD reacts by signal from the sonic with fast switching between air sampling the up- and downdrafts by 1 Hz, while the sampling of trace gas concentration is responding relatively slow within ~15 min to 2 h (Hensen et al., 2009). When air is pumped, with a constant flow of 10 l min$^{-1}$, into the diffusion scrubbers consisting of two mini-WEDD denuders$^{22}$, the NH$_3$ is separated from the particles in the flow.

---

$^{22}$ The diffusion scrubbers consist of tree tubes. An outer tube (70 cm long, 6 mm in outer diameter and 1 mm wall), made of PFA (perfluoralkoxy), an inner tube made of water saturated polypropylene membrane (0.4 mm inner diameter and 0.03 mm) and a glass jacket (60 cm long, 6 mm inner diameter
This happens by scrubbing with demineralised water, and thereby, due to NH$_3$’s higher diffusion coefficient than particles, the NH$_3$ is diffused to the saturated membrane of the inner tube (Sorensen et al., 1994). The sampling flow of air in the outer tube was sucked in constant by 1 l min$^{-1}$ in order to maintain a lamina undisturbed flow and prevent subsequent deposition of aerosols in the tube (Hensen et al., 2009; Sorensen et al., 1994). The aqueous NH$_3$ solution was then pumped directly to the analytic system by a peristaltic pump with a flow of 0.8 ml min$^{-1}$. The direct flow prevents subsequently contamination of the sample due to no personal handling. The two samples were mixed with two chemical reagents (OPA and sulfite) with a flow measured to app. 0.40 ml min$^{-1}$. The aqueous mixture were then heated to app. 60 degrees before entered the fluoroscencence detector in order to create the fluorescent compound signal, resulting in the data output of 10 Hz volt signals.

In order to keep the REA system running continuously during the measurement period, the system was checked out of an app. weekly visit, where the system was re-filled with H$_2$O, OPA and sulfite. To secure that the fluids in the system didn’t freeze when the air temperature was at or below the freezing point, ethanol was mixed in the water. Necessary adjustments on the system or setup were done as required. The peristaltic pump hoses were replaced one time in the middle of the measurement period to make sure no worn down or blocked hoses.

**Data collecting**

The REA system has been running almost continuously from 10 Aug 2010 until 11 Nov 2010. 10 Hz data output from the REA analytic system and sonic anemometer was collected in half-hourly data files. The dataset covers several micrometeorological and statistic quantities and volt signals of the two samples of the upward and downward c$_{NH3}$. Values of $u$, $v$, $w$, $T$, Spd, $\text{Dir}$, $u_*$, $L$, and the volt signals of $\chi$ ↑ and $\chi$ ↓ of NH$_3$ in the up and down denuder, was extracted from the data to describe the meteorology and to calculate c$_{NH3}$ and F$_{NH3}$ for Ll. Bøgeskov.

**Calibration**

The analytical system has been calibrated in order to convert volt signal to values of c$_{NH3}$ and to remove errors on data connected to the uncertainty of measurements related to the instrument. Standard calibration fluids of different known concentrations of NH$_3$ and clear water (c$_{NH3}$ of 0) were connected, respectively, to the REA system, and the calibration concentration was calculated from the reflected volt signals. Calibration fluids of 0, 10 and 25 ppb were used on both the upward system (WEDD Up) and the downward system (WEDD Down).

and 8 mm outer diameter) around the scrubber to keep it straight. The inner tube is centered inside and along the axis of the outer tube and have a mean pore size of 0.065 μm and a surface porosity of 40% (Sorensen et al., 1994).
As seen in Figure 4.8, the calibrations resulted in an apparent linear relation to the volt signals. Therefore, it is chosen to use the mean value of each system in the calculations (Table 4.2).

<table>
<thead>
<tr>
<th></th>
<th>0 ppb [V] (zero signal)</th>
<th>25 ppb [V] (calibration signal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WEDD up</td>
<td>0.1029025</td>
<td>1.803391</td>
</tr>
<tr>
<td>WEDD do</td>
<td>0.128391667</td>
<td>1.3866765</td>
</tr>
</tbody>
</table>

**Table 4.2:** Calibration signals [V] for the REA system. The zero signal indicate the signal measured of a 0 ppb NH$_3$ calibration liquid and the calibration signal indicate the signal measured of a NH$_3$ calibration liquid of 25 ppb.

**Data processing**

To calculate $F_{NH3}$ Equation 3.17 is used, but before that, a number of calculations have been done to prepare the data. The data processing was performed in MATLAB (Appendix G).

First, 10 Hz volt signals of $\chi \uparrow$ and $\chi \downarrow$ along with sonic data of meteorology were extracted from the data output format files. By critical examining the raw signals of $\chi \uparrow$ and $\chi \downarrow$, a rough sorting of data according to periods connected to instrumental problems and to suspicious and unrealistic signals was done, resulting in elimination of large amount of data. Very low and stable signals during Sep is suspected related to technical problems with the heating coiler and relatively large periods of instrumental problems in Aug and mid Oct were sorted out, leaving only the 4th sampling period (26 Oct – 11 Nov 2010) left. To remove wrong measures caused by air bubbles passing through the system, the maximum value for each minute of the 10 Hz data resulting in data set of 1 Hz was used in further calculations.

c$_{NH3}$ was calculated from the volt signals of WEDD Up and WEDD Down along with calibration signals and measured flows of air and liquids. An evaporation rate
on $0.55 \cdot \exp(0.12t)$\textsuperscript{23} where $t$ [°C] is the temperature set equal to 2 °C is applied to correct for evaporation of fluids in the system. The $\chi \uparrow$ and $\chi \downarrow$ along with the mean $c_{NH3}$ is calculated and averaged for every half hour. The half-hourly resolution are assumed to be a reasonable resolution to describe the vertical flux due to the time scale of the related meteorological phenomenon. The uncertainty of concentration measurements and detection limit was investigated from the calibration measurements of 25 ppb and 0 ppb respectively on both the WEDD up and WEDD down and is assumed constant through the measurement period.

Busingers value $\beta$ was calculated according to a formulation given by Businger and Oncley et al. (1990):

$$\beta = b_0 \exp\left(-0.75 \cdot \frac{w_0}{\sigma_w}\right)$$

(4.2)

where $w_0$ is the dynamic deadband, $\sigma_w$ is the standard deviation of the vertical wind velocity, and $b_0$ is the Busingers value when $w_0 = 0$. Busingers value is calculated in two ways, on the basis of the sensible heat flux $b_0(T)$ and the momentum flux $b_0(u)$ to examine the flux-profile relations of both momentum and sensible heat flux. The equation of calculating $b_0(T)$ is illustrated:

$$b_0(T) = \frac{T_{flux}}{\sigma_w \cdot (T_{up}-T_{down})}$$

(4.3)

where $T_{flux}$ is the vertical flux temperature calculated by the covariance of $Tw$ and $T_{up}$ and $T_{down}$ are the temperature when the fluctuating component of $w$ is upward and downward. According to the theoretical principles of the REA method, $\beta$ may be a value close to 0.4 - 0.6. If $\beta$ deviates too much from this, the flux does not follow the common Monin-Obukhov similarity theory, and errors may be associated to the flux measurements. Therefore a criterion that asserts that if $\beta$ is less that 0.2 or higher than 0.8 the $\beta = 0.6$ which is a reasonable value found by Businger and Oncley (1990) was applied. The potential maximum and minimum fluxes are calculated by applying the uncertainties found from the calibrations:

$$F = \beta \cdot \sigma_w ((\chi \uparrow + uncertainty) - (\chi \downarrow + uncertainty))$$

(4.4)

$$F = \beta \cdot \sigma_w ((\chi \uparrow - uncertainty) - (\chi \downarrow - uncertainty))$$

(4.5)

$$F = \beta \cdot \sigma_w ((\chi \uparrow + uncertainty) - (\chi \downarrow - uncertainty))$$

(4.6)

$$F = \beta \cdot \sigma_w ((\chi \uparrow - uncertainty) - (\chi \downarrow + uncertainty))$$

(4.7)

The two extremes (Equation 4.6 and 4.7) indicate the possible maximum and minimum fluxes that were found from visual judgement of the plots.

\textsuperscript{23} Experimental found by Sørensen and Jensen (not yet submitted) (Personal contact).
4.6 Local scale modelling

The OML-DEP model is used to calculate the atmospheric \( c_{\text{NH}_3} \) and deposition of \( \text{NH}_3 \) for Ll. Bøgeskov to compare calculated results with measured. Additionally, OML-DEP is used to investigate the influence of LAI in the parametrizing of \( v_d \). OML-DEP was set up to calculate the hourly concentration and deposition in a calculation grid of 40 x 40 calculation points in a modelling area of 400 x 400 m with Ll. Bøgeskov located in the centre. The model has been run for 2010 (exclusive Dec).

4.6.1 Model setup

The model setup includes following input data on land use, emission, meteorology, and boundary conditions (Ellermann et al., 2006)

Land use

OML-DEP operates with 16 different land use classes that are characterized by different surface covers, vegetation height, LAI, roughness among others, where each land use classes influences the deposition process in different ways. This thesis is concentrated on the land use class DF (Deciduous Forest). Information on land use in Denmark is collected in Area Information System (AIS) (Nielsen et al., 2000) in a nested grid of 100 x 100 m and is used to classify the 16 classes.

Emission

Input of emission data input is based on point and area sources of anthropogenic emissions of ammonia from the Danish agriculture in 2008. Information originates from the Central Husbandry Register, General Agricultural Register, reportings from the farmers themselves on accounting of fertilizing to the Danish Plant Directorate, and a map of fields. Point sources are shared among i.e. different stables and area sources are shared among fields in a spatial resolution of 100 x 100 m. Seasonal changes in the emission due to meteorological variations, particular the temperature and length of growing season, and the agricultural practice are also taken into account in the emission information used. Hobby agriculture and some animals i.e. horses are not included at present, and an uncertainty of 35-40 % is connected to the individual source (S. Gyldebkærne, 2006 in (Ellermann et al., 2006)).

Meteorology

The meteorological input of the year 2010 in OML-DEP comes from the weather forecast model MM5 version 3 which is a three dimensional numeric model. MM5 calculates the meteorological conditions in hourly resolution with the same spatial resolution as the regional scale model DEHM (17 x 17 km) for Denmark.

Boundary conditions

The atmospheric \( \text{NH}_3 \) in the calculation area consists of a contribution from local and non-local sources. Therefore, boundary conditions are also included in OML-DEP.
These conditions are calculated in DEHM on the basis of information of the location and size of the OML-DEP calculation area (Section 3.3).

**Output**

The output of running OML-DEP, results in hourly values of $c_{\text{NH}_3}$ 2 m above surface and deposition [kg NH$_3$-N ha$^{-1}$ yr$^{-1}$] in each 40 x 40 calculation points from 1 Jan 2010 to 30 Nov 2010. This thesis outlines the temporal perspectives, and therefore only the results from the centre point (Ll. Bøgeskov) are examined.

An estimate of the total deposition of atmospheric N [kg NH$_3$-N ha$^{-1}$ yr$^{-1}$] to Ll. Bøgeskov for the year of 2010 was calculated as the sum of dry deposition of NH$_3$, the dry deposition of other N compounds (NH$_4$ and NO$_3$), and the wet deposition of N (NH$_3$, NH$_4$, and NO$_3$). Estimates of the other parameters than dry deposition of NH$_3$ were extracted from DEHM.

4.6.2 **Dry deposition velocity, $v_d$**

As described earlier, $v_d$ is determined of the atmospheric concentration, the surface properties, and meteorological conditions (Section 3.3). Therefore, a program based on the dry deposition module extracted from OML-DEP, the meteorological output from MM5, and the concentrations was created to calculate $v_d$ for Ll. Bøgeskov throughout the year 2010. In Section 3.3 it was shown that LAI only figures in the parameterization of $r_c$ in the parameterization of the $v_d$ in OML-DEP. Therefore, the investigation of LAI is confined to this parameter.

The new measurements of LAI were converted to values that fit into function of determining LAI in OML-DEP (Figure 3.8). Table 4.3 lists the existing and new values:

<table>
<thead>
<tr>
<th></th>
<th>SLAI</th>
<th>ELAI</th>
<th>SLAI_len</th>
<th>ELAI_len</th>
<th>LAI_max</th>
<th>LAI_min</th>
</tr>
</thead>
<tbody>
<tr>
<td>OML-DEP old</td>
<td>90</td>
<td>270</td>
<td>56</td>
<td>92</td>
<td>5</td>
<td>3.5</td>
</tr>
<tr>
<td>OML-DEP new</td>
<td>120</td>
<td>296</td>
<td>77</td>
<td>40</td>
<td>6.25</td>
<td>0</td>
</tr>
</tbody>
</table>

*Table 4.3:* Existing (OML-DEP) and new (measured) values used to calculate the leaf area index (LAI) inputs in the calculation of $v_d$ in OML-DEP.

The program was run two times; first with the existing setup and thereafter with the new LAI inputs calculated from the LAI measurements resulting in two sets of parameters of $v_d$, $r_c$, $g_{sta}$, and $g_{ns}$. The two sets of data were compared and analyzed in relation to the effect of applying the new measures of LAI.
5 Results

In the following section, the results obtained throughout this study are presented. First, results of the measured and simulated meteorological conditions for Ll. Bøgeskov are presented. Then, the observed seasonally LAI measurements are presented along with the calculation of the dry deposition velocity \( (v_d) \) using OML-DEP with the original and new values of LAI is respectively, are presented. Subsequently, the measured atmospheric \( c_{\text{NH}_3} \) and \( F_{\text{NH}_3} \) are displayed.

Measurements of atmospheric \( \text{NH}_3 \) were performed for Ll. Bøgeskov in the period of 10 Aug to 11 Nov 2010, but due to instrument failure during large parts of the period on the REA system, only data from the 4th sampling period (26 Oct 2010 to 11 Nov 2010) was judged to be of reasonable quality. Therefore, it is chosen mainly to focus on results from the 4th sampling period. Results from the other three sampling periods of COTAG and OML-DEP will, however, also be presented shortly. Quantities of \( c_{\text{NH}_3} \) are given in units of \( \mu g \text{ NH}_3 \cdot \text{m}^{-3} \), fluxes are given in \( \mu g \text{ NH}_3 \cdot \text{m}^{-2} \cdot \text{s}^{-1} \), and deposition velocities in cm s\(^{-1}\).

5.1 MM5 meteorological simulations

The measurement period was generally characterized by typical Danish autumn weather with many days of precipitation, low temperature, and greatly varying wind speeds mainly coming from the southwest. The calculated meteorological conditions from the weather prediction model MM5 that goes as input to the OML-DEP model, are compared to the direct measured meteorological conditions above the forest canopy from the sonic anemometer in the meteorological mast in 33 m height. Figure 5.1 and Figure 5.2 shows the meteorological conditions of simultaneously measured and modelled wind direction (\( \text{Dir} \)), wind speed (\( \text{Spd} \)), friction velocity (\( u_\ast \)), temperature (\( T \)), stability (\( z/L \)), and relative humidity (\( \text{RH} \)). \( \text{Spd} \) is only assessed by measurements.
Figure 5.1: Meteorological conditions of wind direction (Dir), wind speed (Spd), friction velocity ($u_f$), temperature ($T$), stability ($z/L$), and relative humidity (RH) measured in 33 m height for L. Bøgeskov in 2010. Values are given in half hourly means.
Figure 5.2: Meteorological conditions of wind direction (Dir), friction velocity ($u_\tau$), temperature ($T$), stability ($z/L$), and relative humidity ($RH$) at standard height (2 m) for L. Bøgeskov in 2010. Values are given in hourly means.
5.1.1 Wind direction
Relative frequencies of the wind direction throughout the 4\textsuperscript{th} sampling period are shown in the two wind roses in Figure 5.3, illustrating the measured and the modelled wind direction respectively.

It is seen that in both cases the main wind direction is coming from the south-western sector. The measured Dir indicate the main wind direction coming directly from southwest (\sim 230\textdegree), while the calculated MM5 Dir indicate stronger components of south and west (\sim 190\textdegree and \sim 260\textdegree). In the north-eastern sector, the two wind roses deviate quite a lot from each other. This can be caused by i.e. disturbance on the measurements from the meteorological mast. The sonic anemometer is located in the south-western side of the mast. This means, when wind comes from the north-eastern direction, an uncertainty is associated with the results because the wind passes the mast before it meets the sonic anemometer. Thereby, mechanical turbulence is created around the mast which disturbs the measured flow by the sonic anemometer. Figure 5.1 and Figure 5.2 both indicate two periods of north-easterly coming wind; 31 Oct – 2 Nov and 8 - 11 Nov which might be due to frontal passages.

5.1.2 Wind speed
The wind speed was only measured and not modelled. Therefore, only measured results are presented. The wind speed varies between 0 and 9 m s\textsuperscript{-1} with a mean Spd calculated to be 3.06 m s\textsuperscript{-1}. The primary wind speeds is found between 0 and 5 m s\textsuperscript{-1}, which agrees with the common climatologically mean for Denmark on \sim 5 m s\textsuperscript{-1} (DMI, 2011). The large peaks seen in Figure 5.1 seem to occur in relation to the two frontal passages that were also seen in the wind directions. Diurnal variations are clearly seen in the data where, Spd decreases during night time and increases during day time. 4 dates indicate increasing Spd relative to the mean; 28 Oct, 3, 5, and 8
Nov. On these dates, $Spd$ reaches 6-9 m s$^{-1}$. A period from 31 Oct to 2 Nov is characterized by quite low $Spd$ of less than 2 m s$^{-1}$. This is also indicated by the diffuse wind direction in these periods, because the $Dir$ can be difficult to determine at low wind speeds.

**5.1.3 Friction velocity**

The friction velocity ($u_*$) is closely related to the wind speed and gives a measure of the turbulent flow above the canopy (Chapter 1). The modelled $u_*$ shown in Figure 5.2 is corrected in OML-DEP according to take the local roughness into account. This means, that $u_*$ is here given in the spatial resolution of 400 x 400 m from OML-DEP. Observing the measured $u_*$ by the sonic anemometer in Figure 5.1, it is seen that $u_*$ and $Spd$ is closely correlated. This means that a rather good mixing of the air can be expected for the days where the wind speed peaked. The simulated $u_*$ is in good agreement to the measured $u_*$. Only in few situations, $u_*$ seems to be a little overestimated as seen on 1 Nov, while it is underestimated in some few other situation (e.g. on 5 and 9 Nov). The measured $u_*$ varies between 0 - 1.8 m s$^{-1}$ with a calculated mean of 0.5 m s$^{-1}$ while the simulated $u_*$ varies between 0 - 1.2 m s$^{-1}$ with a mean calculated to 0.6 m s$^{-1}$.

**5.1.4 Temperature**

Two periods of different temperature is mainly characterizing the temperature ($T$) during the measurement period, in agreement between the measured and modelled results. The calculated $T$ is, however, to a little degree underestimated. The mean $T$ is measured to 8.5 °C and calculated relatively lower by MM5 to 7.5 °C. The 10 days between 27 Oct and 6 Nov shows that $T$ is lying around 10 °C with oscillations of a few degrees. On 6 – 7 Nov, $T$ decreases rapidly down to 5 °C, indicating a new air mass passing, also indicated in $Dir$. Following on 7 Nov, measured $T$ is quite constant around 5 °C. Both the hourly calculated $T$ and the half-hourly measured $T$ indicate a diurnal pattern with the highest temperatures in the daytime that decreases turning to night time.

**5.1.5 Stability**

The stability conditions of the atmosphere are here described by the dimensionless parameter $z/L$. In Figure 5.1 and Figure 5.2 it is seen that $z/L$ oscillates around zero, indicating mainly near neutral atmospheric conditions. It is clearly seen that the last half part of the measurement period is characterized by a more varying $z/L$ than the first part, likely to the pattern in $T$. The measured data show a diurnal pattern where stable conditions are met during night time, which indicate a very stratified atmosphere. During day time, the atmosphere turns to neutral or unstable which might be due to i.e. increasing wind speed and convection. Comparing $z/L$ to $Spd$, it is seen that in the periods with large $Spd$, the atmospheric stability is neutral or near neutral. The same diurnal pattern is to a less extent indicated in the modelled results.
The histograms (Figure 5.4) showing the distribution of the $z/L$ values, indicate that in both the measured and modelled case, there is an overweight of (near) neutral and stable conditions, while there only are relatively few unstable situations.

![Results](image)

**Figure 5.4:** Distribution of the a) measured and b) modelled $z/L$.

### 5.1.6 Relative humidity

Results of the relative humidity ($RH$) are shown in Figure 5.1. $RH$ is varying between 50 and 95 % with a diurnal pattern of lowest values in the night time and highest values in the daytime. It is to be expected that $RH$ is high, because precipitation occurred almost every day (Figure 4.5). The modelled $RH$ is a little higher than the measurements, and it does not show the same diurnal and systematic pattern as the measurements.

### 5.1.7 Summary

The meteorological simulations were generally seen to be in very good agreement to the measured meteorological conditions with only few exceptions. A more direct south-western wind direction was observed by the measurements than modelled, and the mean temperature seemed to be underestimated by 1 °C. Additionally, the MM5 model indicated a few more unstable atmospheric situations than measured.

### 5.2 LAI and dry deposition velocity

The measurements of LAI were performed in L1. Bøgeskov during the growing season in 2010, and are illustrated in Figure 5.5. Results are shown as the mean value of the two profiles measured on each measuring day, except for the 20 Aug, where one profile was neglected due to bad conditions (Appendix D). The filled circles indicate the raw measurements and the open circles indicate the data corrected for tree stems according to Section 4.4.
The LAI shows a nice curve of values starting in the beginning of May, reaching the highest in the months of Jul and Aug, and starts decreasing following the end of Aug. The raw data varies between 1.14 and 5.85 with the lowest value measured on 16 Nov where no leaves were present in the canopy due to leaf fall. The maximum value was measured on 20 Aug where the canopy was fully developed. LAI increases throughout May and Jun and stays quite constant between 4.82 and 5.85 in the following three month, Jul, Aug, and Sep. In the end of Sep, defoliation begins and LAI starts decreasing. The corrected data, that are corrected for tree stems around the measurement. The correction resulted in 8-30 % higher LAI values by which, the effect was larger at higher values of LAI. In the corrected data, the maximum value of LAI is 7.39.

It is clearly seen in the results, that the LAI-2000 PCA does not differ between green active leaves and other plant material in the canopy, because the LAI measured on 16 Nov, where no leaves were present in the canopy, equals 1.14 (raw data). Therefore these results are named plant area index (PAI) instead of LAI. The real LAI related to green active leaves is estimated by correcting according to the dates of foliation and defoliation (Section 4.4). In Figure 5.6, two graphs illustrate the PAI and LAI over the year 2010, respectively.
Due to the assumption that the values above 4 are the same for PAI and LAI, only the values less than 4 differs in between the two graphs. In this case, LAI equals zero between defoliation and foliation, in order to define the period of bio-physiological activity, while PAI keeps a values due to presence other plant material. The graph of PAI (left) indicate the measured data extrapolated to the full year and justified due to foliation (30 Apr 2010) and leaf fall (8 Nov). The LAI curve is justified due to dates of foliation and defoliation (23 Oct 2010). A steeper slope in the period of foliation and defoliation is seen in LAI compared to PAI.

5.2.1 Dry deposition velocity

The influence of applying a new input of LAI values in the method of calculating dry deposition velocity ($v_d$) in OML-DEP was investigated. LAI is only included in the estimation of the surface resistance (Equation 3.14) in order to estimate the stomata uptake of atmospheric NH$_3$ by vegetation. In Figure 5.7 the original and new values included in the LAI function in OML-DEP are illustrated in the graphs and listed beside the figure. The new values were derived from LAI measurements presented in previous section.

![Figure 5.7](image)

**Figure 5.7:** Original (OML-DEP old, red) and new (OML-DEP new, blue) values to calculate LAI in OML-DEP. The dashed line illustrates the measured LAI. LAI$_{min}$ is the minimum value of LAI, LAI$_{max}$ is the maximum value of LAI, SLAI is the day number of starting growing season, ELAI is the day number of ending growing season, SLAI$_{len}$ is the number of the days from SLAI until LAI reaches LAI$_{max}$, and ELAI$_{len}$ is the number of days with decreasing LAI from LAI$_{max}$ to ELAI.

<table>
<thead>
<tr>
<th>OML-DEP old</th>
<th>OML-DEP new</th>
</tr>
</thead>
<tbody>
<tr>
<td>SLAI</td>
<td>90</td>
</tr>
<tr>
<td>ELAI</td>
<td>270</td>
</tr>
<tr>
<td>SLAI$_{len}$</td>
<td>56</td>
</tr>
<tr>
<td>ELAI$_{len}$</td>
<td>92</td>
</tr>
<tr>
<td>LAI$_{max}$</td>
<td>5</td>
</tr>
<tr>
<td>LAI$_{min}$</td>
<td>3.5</td>
</tr>
</tbody>
</table>

It was found that the growing season was displaced forward by 30 days in the beginning of the season and by 26 days in the end. SLAI$_{len}$ and ELAI$_{len}$ were found significantly different than the original. The LAI$_{max}$ was calculated as the mean value of the measured LAI of values above 4. This gives a LAI$_{max}$ of 1.25 higher than the original setup. $v_d$, $r_c$, and $g_{sto}$ are the parameters that are affected by LAI in OML-DEP. Figure 5.8 illustrates the calculations of these parameters using OML-DEP by the original setup and by applying the new values.
Results

Figure 5.8: Daily values of dry deposition velocity ($v_d$), surface resistance ($r_s$), and stomata conductance ($g_{sto}$) calculated on L. Bøgeskov for the year 2010 using OML-DEP. The solid blue line (OML-DEP old) indicate the original setup of OML-DEP and the dashed green line (OML-DEP new), indicate the setup with new values of LAI. The figures at the right indicate the change in $v_d$, $r_s$, and $g_{sto}$ between the old and new setup of LAI values in OML-DEP.

Applying the new measurements of LAI does not result in any significant changes to the magnitude of $v_d$ other than displacing the curve according to the displacement of the LAI function (Figure 5.7), which is clearly indicated in the curve of $g_{sto}$. A decreased $v_d$ was seen in the start of the growing season. This is due to the increased $r_s$ explained by the decrease of LAI and thereby also the $g_{sto}$. The opposite was seen in the end of the season. The mean $v_d$ does only increase by 0.02 cm s$^{-1}$ applying the new LAI values, even though the LAI_max is 1.25 higher than the original input.

5.2.2 Summary
The measured LAI resulted in two curves; one indicating PAI and one indicating LAI that both peak in middle Aug. Foliation and defoliation begins on 30 Apr and 23 Oct, respectively. The correction performed to neglect stems of the trees, results in 8-30% higher values. A new input of LAI, created from the LAI curve, displaces the $v_d$ of NH$_3$ to the forest according to the displaced season. The magnitude changes in LAI between the original and new input does, however, not seem to have any significant influence when applying new LAI measures.
5.3 Atmospheric ammonia concentrations

The general picture of the \( c_{\text{NH}_3} \) measurements throughout the full measurement period indicate a decreasing trend shown both by the COTAG measurements and the OML-DEP calculations (Figure 5.9). In the 4\(^{th}\) sampling period, the REA system measures an interesting increasing concentration. This will be further described in the following section.

![Figure 5.9: The \( c_{\text{NH}_3} \) for L\( \text{i. Bøgeskov} \) in the measurement period of 10 Aug–11 Nov 2010 measured by COTAG denuder in 29.8 m height (red) and REA WEDD in 33 m height (blue) and calculated by OML-DEP (green). COTAG values plotted as weighted mean values for each of the 4 sampling periods, while REA values are plotted as half-hourly values. OML-DEP calculations are illustrated as diurnal mean values based on hourly estimates. The red square encompasses the 4\(^{th}\) sampling period.](image)

The \( c_{\text{NH}_3} \) calculated by OML-DEP varies between 0.2 and 2.4 µg NH\(_3\)-N m\(^{-3}\) and indicates a weekly pattern with the maximum concentration in the last part of the week. This weekly pattern was found to be caused by meteorological conditions (examples are given in Appendix H). The COTAG \( c_{\text{NH}_3} \) are calculated as weighted mean values of each sampling, weighted according to the air sampled in each of the three predefined stability conditions (Section 3.4.1). In Table 5.1, the concentration in the 4 sampling periods are listed separately for the three stability conditions, for each, height along with weighted mean values for the height of 29.8 m.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Neutral [µg NH(_3)-N m(^{-3})]</th>
<th>Unstable [µg NH(_3)-N m(^{-3})]</th>
<th>OFF [µg NH(_3)-N m(^{-3})]</th>
<th>Mean [µg NH(_3)-N m(^{-3})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.90</td>
<td>1.96</td>
<td>2.12</td>
<td>1.63</td>
</tr>
<tr>
<td>2</td>
<td>0.94</td>
<td>0.89</td>
<td>3.03</td>
<td>1.23</td>
</tr>
<tr>
<td>3</td>
<td>0.65</td>
<td>0.63</td>
<td>2.23</td>
<td>1.57</td>
</tr>
<tr>
<td>4</td>
<td>0.58</td>
<td>0.57</td>
<td>1.27</td>
<td>1.01</td>
</tr>
</tbody>
</table>

Table 5.1: Conditional \( c_{\text{NH}_3} \) measured for L\( \text{i. Bøgeskov} \) using COTAG in 4 sampling periods during autumn 2010. In sample 1, concentration in 29.8 m was not measured due to incomplete installation at that time.
It is seen that the mean $c_{\text{NH}_3}$ does not change significantly throughout the full measurement period but it decreases from 1.2 to 0.7 µg NH$_3$-N m$^{-3}$ during the measurement period. The highest $c_{\text{NH}_3}$ in all sampling periods is found for unstable atmospheric conditions of up to 3.0 µg NH$_3$-N m$^{-3}$ found in sample 2 at 34 m height. The neutral atmosphere gives lowest $c_{\text{NH}_3}$, even though the system has been activated over 70% of the time due to neutral conditions, compared to less than 9% due to unstable conditions. The detection limits (DL) are calculated for each of the 4 samplings (Section 4.5.1) to 0.02, 0, 0.003, and 0.003 µg NH$_3$-N m$^{-3}$, respectively. All measured concentrations are found to be higher than DL.

The uncertainties associated to the concentration gradients were investigated by standard deviations of each set of the two sets consisting of 2 x 3 denuders (neutral bottom and top and unstable bottom and top, the COTAG does not measure gradients during OFF conditions). Figure 5.10 shows the measured gradients including the standard deviations.

![Figure 5.10](image)

Figure 5.10: Temporally averaged $c_{\text{NH}_3}$ in neutral (left) and unstable (right) atmospheric conditions measured using COTAG in 4 sampling periods from 10 Aug-11 Nov 2010 for Ll. Bøgeskov. Filled circles indicate the mean concentration in 29.8 m and 34 m height and open circles indicate the concentration in all denuders. Error bars indicate the standard deviation.

No significant gradients were measured during the measurement period as indicated in Figure 5.10. Furthermore, many of the profiles are associated to large uncertainties, where the standard deviations in the two different heights overlap each other. This means that even the direction of the gradient is related to a large uncertainty. This is the case for sample 1 and 2 in the unstable conditions and in sample 4 for both neutral and unstable conditions. The measurement in sample 1 for unstable conditions indicate, as the only measurement, a negative mean gradient which means that $F_{\text{NH}_3}$ is directed upwards (emission) from the surface to the atmosphere. It is, however, associated to a large uncertainty which makes it difficult to determine.
Even though the gradients are small in both the neutral and unstable cases, the gradients are largest for the unstable conditions.

5.3.1 High resolution results of ammonia concentration

In the 4th sampling period the REA system were running almost continuously, only with two breaks; two hours on 1 Nov and three full days from 5 Nov to 8 Nov, due to technical work on the instruments. In these periods measurements are not usable. In Figure 5.11, the concentration assessed during the 4th sampling period by all three techniques is illustrated.

![Figure 5.11: cNH3 for Ll. Bøgeskov from 26 Oct –11 Nov 2010 measured by COTAG denuders (red) in 29.8 m and REA WEDD (blue) in 33m, and calculated by OML-DEP (green). REA WEDD values are given in half-hourly weighted mean values with the uncertainty of measurements (light blue shadow). COTAG denuders results are given in one weighted mean value. OML-DEP estimates are calculated in hourly mean values.](image)

REA measurements of cNH3 indicate a generally increasing concentration varying between 0 and 1.7 µg NH3-N m⁻³ while the modelled concentration indicates a slightly decreasing trend varying between 0 and 2.7 µg NH3-N m⁻³. The OML-DEP results show a diurnal pattern of highest concentrations in the afternoon, which can not be seen in the REA measurements. The concentration measured is rather low until the 30 Oct where after it starts increasing up to 1.3 µg NH3-N m⁻³ on 4 Nov. Following on the 8 Nov, cNH3 decreases to 0.7 µg NH3-N m⁻³ and increases thereafter to reach the maximum cNH3 measured of just above 2 µg NH3-N m⁻³ on 10 Nov. The OML-DEP concentration varies with 5-10 clearly peaks; most of them the same days were indications of frontal passages seem to occur. The uncertainty of the REA measurements is found from the calibrations to 0.35 NH3-N m⁻³ constantly throughout the measurement period. A large difference in the uncertainty of the two subsytems sampling the updrafts and downdrafts respectively were found. In Figure 5.12, cNH3 measurements of the two sub-systems, respectively, are illustrated, including the uncertainty associated to the two systems individually.
Figure 5.12: Half-hourly values of $c_{NH3}$ for LI. Bøgeskov from 26 Oct –11 Nov 2010 measured using REA WEDD in 33m. The figure indicates the concentration measured in the updrafts (light blue) and downdrafts (dark blue), separately. The dashed line indicates the delta concentration ($D_{NH3}$) which gives expectations to the direction of the flux; when $D_{NH3}$ is positive there is an upward flux (emission) and negative means a downward flux (deposition).

The $c_{NH3}$ measured in the updrafts and downdrafts eddies of air is approximate equal until the 30 Oct where after, the WEDD Up indicates higher $c_{NH3}$ values than the WEDD Down. In the period between 5 – 8 Nov, $c_{NH3}$ in the updrafts reaches 1.8 $\mu g$ NH$_3$-N m$^{-3}$, while the downdrafts indicate only the half concentration reaching only 0.9 $\mu g$ NH$_3$-N m$^{-3}$. Following on the 8 Nov, the downdraft $c_{NH3}$ decreases to 0.6 $\mu g$ NH$_3$-N m$^{-3}$, while the updrafts continue increasing and reaches a maximum $c_{NH3}$ throughout this sampling period of just above 3 $\mu g$ NH$_3$-N m$^{-3}$. As indicated in Figure 5.12, a relatively large uncertainty of measurement is related to the downdraft measurement of 0.09 $\mu g$ NH$_3$-N m$^{-3}$, while the uncertainty of the updraft measurements is 0.01 $\mu g$ NH$_3$-N m$^{-3}$. Due to the large uncertainty of the downdraft measurements, there is a risk that the concentration measured are lower than the actual limit of detection found to 0.0275 $\mu g$ NH$_3$-N m$^{-3}$.

The mean $c_{NH3}$ assessed by the three different techniques are all in good agreement with each other (Figure 5.13).

The mean $c_{NH3}$ during the 4th sampling period was found using OML-DEP to 0.56 $\mu g$ NH$_3$-N m$^{-3}$, REA to 0.68 $\mu g$ NH$_3$-N m$^{-3}$, and COTAG to 0.67 $\mu g$ NH$_3$-N m$^{-3}$. 
5.3.2 Summary
The atmospheric $c_{\text{NH}_3}$ assessed for the forest by all three techniques indicate very good agreement, particular when considering the mean value of a longer period. While the OML-DEP and COTAG indicates decreasing trends in $c_{\text{NH}_3}$ throughout the full measurement period, REA indicate increasing $c_{\text{NH}_3}$ in the 4th sampling period. Large uncertainties are, however, associated to especially the REA system.

5.4 Atmospheric ammonia fluxes
$F_{\text{NH}_3}$ is calculated from the measured $c_{\text{NH}_3}$ using the REA and COTAG technique and are calculated from the resistance method using OML-DEP. As for the previous section, first the full measurement period is considered and thereafter the 4th sampling period, where high-resolution measurements of REA were performed, is in focus. Figure 5.14 illustrates $F_{\text{NH}_3}$ measured and calculated using COTAG and OML-DEP.

![Figure 5.14: Diurnal averaged dry deposition of NH$_3$ for LL. Bøgeskov 10 Aug - 11 Nov 2010 calculated by OML-DEP (green) and weighted mean $F_{\text{NH}_3}$ measured using COTAG throughout 4 sampling periods (red). The dashed green line indicates the linear trend of the OML-DEP calculations.](image)

Both techniques show very small fluxes and indicate mainly deposition fluxes (Figure 5.14). OML-DEP is only intended to calculate concentration and deposition flux, wherefore the flux will always be negative (downward). In this case the deposition flux varies between 0 and -0.02 $\mu$g NH$_3$-N m$^{-2}$ s$^{-1}$ and shows a minor decreasing trend in the size of the flux towards zero. Small gradients were seen in the concentration measurements from COTAG. Therefore, also very small fluxes are estimated. COTAG fluxes are calculated as weighted mean values of the flux measures under neutral and unstable atmospheric conditions, and are weighted on the air volume of each of the conditions in each of the 4 samples. The results are plotted only when the two stability intervals are met wherefore the line seems dashed. The fluxes vary between 0.0083 and -0.0070 $\mu$g NH$_3$-N m$^{-2}$ s$^{-1}$ which is near the same interval as the model results, except from the first sampling period. The first sample indicates an emission flux apart from the following samples that indicate deposition fluxes. It must be noted that the meteorological output from the COTAG sonic ane-
Results

mometer indicates some kind of instrumental problems in a large part of the first sampling period (Appendix I), wherefore this sample are very uncertain. The uncertainty of COTAG gradient measurements (Figure 5.10) is used to calculate the uncertainties associated with the conditionally flux measurements (Figure 5.15).

![Figure 5.15](image1)

**Figure 5.15:** Temporally averaged $F_{\text{NH}_3}$ measured using COTAG in 4 sampling periods from 10 Aug–11 Nov 2010 for Ll. Bøgeskov separated in neural (left) and unstable (middle) conditions and the weighted mean flux (right). Filled circles indicate the mean flux of and open circles indicate the flux measured from the different potential gradients.

It is seen that the uncertainty is, by no doubt, largest for unstable conditions. In agreement with the $c_{\text{NH}_3}$ gradients, it is also seen here that the uncertainties associated to the calculated $F_{\text{NH}_3}$ are large. Even the direction is in many cases ambiguous.

5.4.1 High resolution results of ammonia fluxes and deposition
The $F_{\text{NH}_3}$ calculated from the REA technique was calculated using the temperature flux and the momentum flux to derive Busingers value $\beta_i$ and $\beta_u$ respectively. The two methods gave approximately equal $F_{\text{NH}_3}$; (Appendix J) but because atmospheric $\text{NH}_3$ is a scalar like the air temperature, it is chosen to use $\beta_i$ in the flux calculations. The REA flux from sample 4 shows a clearly increasing tendency, and shows mainly emission fluxes (Figure 5.16). The COTAG and OML-DEP fluxes are almost non-existent but downward directed.

![Figure 5.16](image2)

**Figure 5.16:** $F_{\text{NH}_3}$ for Ll. Bøgeskov from 26 Oct – 11 Nov 2010. Hourly mean values calculated using OML-DEP (green). Weighted mean values measured using COTAG (red) and half-hourly mean values measured using REA (blue). The dashed lines indicate the maximum and minimum flux that can be expected from the REA measurements.
In Figure 5.16 the REA flux indicates, in the beginning of the period, a small deposition flux of 0.05 µg NH$_3$-N m$^{-2}$ s$^{-1}$. The flux subsequently increases and reaches 0.2 µg NH$_3$-N m$^{-2}$ s$^{-1}$ on 30 Oct and decreases down to zero again. Subsequently, the flux increases and decreases again and peaks in 4 smaller periods of time by fluxes up to 0.75 µg NH$_3$-N m$^{-2}$ s$^{-1}$. The dashed blue lines around the REA flux indicate the uncertainty of measurements found from the calibrations (Section 4.5.2) and gives a picture of a relatively uncertain flux. There is, however, no doubt that the flux is directed upwards in a part of the sampling period. OML-DEP is only able to calculate a deposition flux oppositely to what the REA flux indicate wherefore no correlation between the calculated deposition flux and the measured REA flux is seen or could even be expected.

5.4.2 Summary

Quite inconsistent results of the F$_{NH3}$ above Ll. Bøgeskov are obtained, whereby COTAG and OML-DEP indicate very small deposition fluxes, while higher fluxes directed upwards are shown by REA. Large uncertainties influence the estimates.

5.5 OML-DEP calculations of total N deposition

The total deposition of atmospheric N to Ll. Bøgeskov was calculated for the year 2010 using OML-DEP. Results are illustrated in Table 5.2.

<table>
<thead>
<tr>
<th>N-load [kg N ha$^{-1}$ yr$^{-1}$]</th>
<th>Dry deposition of NH$_3$</th>
<th>Dry deposition of other N compounds*</th>
<th>Wet deposition of N compounds**</th>
<th>Total N***</th>
<th>Critical load interval</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.1</td>
<td>10.0</td>
<td>5.8</td>
<td>21.9</td>
<td>10 – 20</td>
<td></td>
</tr>
</tbody>
</table>

*NH$_4$ + NO$_3$  **NH$_3$ + NH$_4$ + NO$_3$  ***The sum of column 1, 2, and 3

Table 5.2: Total deposition of N to Ll. Bøgeskov calculated using OML-DEP along with the critical load interval based on recommendations from UN-ECE, 2004.

It is seen that the calculated total N load from the atmosphere equals 21.9 kg N ha$^{-1}$ yr$^{-1}$ and exceeds even the upper limit of the CL interval of 10–20 kg N ha$^{-1}$ yr$^{-1}$. The dry deposition of NH$_3$ makes up for app. one third (6.1 kg N ha$^{-1}$ yr$^{-1}$) and likely for the wet deposition (5.8 kg N ha$^{-1}$ yr$^{-1}$), while the dry deposition of other N compounds constitutes almost two thirds (10 kg N ha$^{-1}$ yr$^{-1}$).
6 Analysis

In order to understand the dynamic and quality of measured and modelled concentration and fluxes of NH$_3$ for Ll. Bøgeskov, an interpretation of results is presented in this chapter. First, the relation of $c_{\text{NH3}}$ and $F_{\text{NH3}}$ to meteorological conditions is investigated. Then, results of $c_{\text{NH3}}$ and $F_{\text{NH3}}$ are compared in between. Subsequently, the influence of LAI on $F_{\text{NH3}}$ is examined. Finally, the large difference between the results from the two measurement techniques (REA and COTAG) is investigated.

6.1 Relation of NH$_3$ concentrations to meteorological conditions

The calculated $c_{\text{NH3}}$ using OML-DEP is compared to the simulated meteorological conditions by MM5. To a minor degree, a relation between $c_{\text{NH3}}$ with the stability parameter $z/L$ ($r = 0.34$) and an inversely relation to the turbulent scaling parameter $u^* (r = -0.43)$ is indicated (Figure 6.1).

![Figure 6.1: Hourly stability ($z/L$) and friction velocity ($u^*$) values vs. the hourly calculated $c_{\text{NH3}}$ for Ll. Bøgeskov from 26 Oct –11 Nov 2010 using OML-DEP.](image)

$c_{\text{NH3}}$ increases due to stable atmosphere and to decreasing turbulent transport. This indicates that a stable atmosphere suppresses the mixing of air (Section 3.1.3). The low values of $u^*$ indicate small turbulent flows above the forest and thereby a little vertical transport, which can explain the high $c_{\text{NH3}}$ seen in these periods. The statistical 95 % confidence level equals 0.09, which means that the correlations is statistical significant at the 95 % confidence level. The coefficient of determination ($r^2$) indicates, however, that only 11 % of the variations in $c_{\text{NH3}}$ can be explained by the variations in $z/L$ and 18 % for $u^*$.

The $c_{\text{NH3}}$ measured using REA indicated closest relation (inversely) to the measured temperature ($r = -0.37$) and the relative humidity ($r = -0.22$) (Figure 6.2).
$c_{\text{NH3}}$ increases when $RH$ decreases, because a larger deposition will occur when vegetation is wet due to a reduced surface resistance. Similar to previously, the statistical 95 % confidence level equals 0.07, which means that also these the relations is statistical significant at the 95 % confidence level, but also with relatively low coefficients of determination (13 % and 4 % respectively). In the last part of the 4th measurement period, a coherent relation between $u^*$ and the REA $c_{\text{NH3}}$ can, however, be seen (Figure 6.3).

When $u^*$ decreases during the 9 Nov, $c_{\text{NH3}}$ starts increasing. This can be explained by a larger transport of NH$_3$ into the measuring site, due to increased wind speeds. The increasing $c_{\text{NH3}}$ during the last 5 days of the period can also be caused by the dry period with no precipitation between 7 and 11 Nov, whereby wet deposition haven’t occurred. It can be expected that $c_{\text{NH3}}$ must be lower immediately after precipitation events and higher during dry periods, as is also indicated by some of the observations. It can be seen in for example on 28-29 Oct whereby precipitation occurs and $c_{\text{NH3}}$ decreases immediately after (Figure 6.4).
Considering the landscape around the measuring site, the north-easterly sector is dominated by the greater forest, Store Bøgeskov, and the lake Gyrstinge Sø (Figure 4.3). These landscape elements can be expected to influence the advective atmospheric flows around the meteorological mast due to creation of internal boundary layers. Additionally, it was seen from Figure 4.4 that only a few NH₃ emissions sources were located in this sector. Therefore lower levels of c_{NH₃} were expected under these conditions compared to other wind directions. Such evidence did, however, not appear in the results. Furthermore, a diurnal relationship between c_{NH₃} and low values of T at night time and higher T during day time could be expected. The decreasing T during night time cause a stabilization of the atmosphere that suppress the mixing of air and thereby reduce the mixing height or the atmospheric boundary layer (ABL). This will potentially lead to higher c_{NH₃} in the lower atmosphere. However, neither OML-DEP nor REA indicated such related pattern of c_{NH₃}.

The x-y plots in Figure 6.1 and Figure 6.2 show very wide scattered plots, indicating that many factors influence c_{NH₃}. Such factors could be the source strength, location, distance from the source, and varying wind direction. Scatter plots of the measured and modelled c_{NH₃} vs. the meteorological data can be found in Appendix K.

### 6.2 Relation of NH₃ fluxes to meteorological conditions

The REA F_{NH₃} was also investigated in relation to the measured meteorological conditions from the site. A rather good relation between \( u^* \) and the F_{NH₃} from the REA measurements is seen (\( r = 0.47 \)) (Figure 6.5), which can also easily be seen comparing the variations of F_{NH₃} (Figure 5.16) to the variations in \( u^* \) (Figure 5.1).
Similar to previously, the statistical 95% confidence level equals 0.07, which means that also these the correlations is statistical significant at the 95% confidence level. In this comparison, 22% ($r^2$) of the variations in $F_{NH3}$ are explained by the variations in $u'$. The relations of $F_{NH3}$ to $u'$ indicate that the turbulent flow above the forest canopy controls a large part of the flux (Section 2.1.1). A less well established relationship with other meteorological variables can be found. $Spd$, $u'$, $T$, and $RH$ indicated significant correlation according to the 95% confidence level, while $Dir$ and $z/L$ showed no significant correlation. The highest $F_{NH3}$ is found when wind is coming from the western sector, which is also the sector in where many point sources are located. $T$ seems to cause larger $F_{NH3}$ with increasing $T$ and $RH$ affects oppositely.

The modelled dry deposition of $NH_3$ using OML-DEP is found to be quite close related to $RH$ ($r = -0.52$) (Figure 6.6).

It is seen that $RH$ has the largest influence by a significant inverse correlation ($r = -0.52$). This indicates that variation in $RH$ in 27% ($r^2$) of the measurements explains the variations in $F_{NH3}$ by increasing dry deposition in humid conditions. Scatter plots of measured and modelled $F_{NH3}$ vs. the meteorological data is to find in Appendix L.

### 6.3 Concentrations vs. fluxes of $NH_3$

Comparing the REA $c_{NH3}$ to $F_{NH3}$, there is no doubt that the forest actually contributes to the atmospheric $c_{NH3}$ by the emission fluxes (Figure 6.7).
**Figure 6.7:** Half-hourly values of $c_{NH_3}$ to $F_{NH_3}$ measured for Ll. Bøgeskov in 2010 using REA.

It is clearly seen that $c_{NH_3}$ increases according to increasing $NH_3$ emission fluxes ($r = 0.67$). This is particular seen in the last part of the measurement period. Potential explanations for these emission fluxes are discussed in Chapter 1.

Comparing the OML-DEP $c_{NH_3}$ to $F_{NH_3}$, a quite close relationship is also seen ($r = -0.64$) (Figure 6.8).

**Figure 6.8:** Hourly values of $c_{NH_3}$ to $F_{NH_3}$ calculated for Ll. Bøgeskov in 2010 using the OML-DEP system.

It is seen that the deposition flux increases due to high concentrations, and in low concentration, almost no deposition occurs.

### 6.4 Impacts of LAI on $NH_3$ fluxes

The potential influence of LAI on $F_{NH_3}$ for Ll. Bøgeskov was investigated. Unfortunately, the high-resolution measurements from the REA system was not usable until after defoliation. Therefore, only the COTAG fluxes are compared with LAI. Neglecting the first sample of COTAG measurements, the COTAG flux indicated a decreasing deposition flux towards zero during the measurement period. Comparing this, with the measured LAI, it is seen that the deposition flux gets lower when LAI turns to zero (Figure 6.9).
Even though the flux is small, the deposition flux seems to decrease rapidly between sample 2 and 3 when LAI also decreases rapidly. This means that the deposition to the forest canopy is small when LAI is small. This can be explained by the stomata uptake of NH$_3$ that do not occur when leaves are not bio-physically active, and thereby reduces the surface resistance and the deposition.

The high-resolution measurements of F$_{NH3}$ using REA indicate a potential presence of a bidirectional flux. After defoliation (LAI = 0), F$_{NH3}$ begins changing direction from deposition to emission. This can be explained by the possibility that when leaves begin to wither and fall to the forest floor, they start decomposing. This process might cause a release of the NH$_3$ absorbed by the leaves (re-emission), likely to what Wang et al. 2010 found for Ll. Bøgeskov when investigating the compensation point. To investigate that, the results were compared to CO$_2$ fluxes measured by RISØ DTU, throughout the same time period for Ll. Bøgeskov. This gives an estimate of when bio-physical activity due to photosynthesis is occurring in the forest canopy. These measurements are also plotted in Figure 6.10, and it is seen that the direction of the CO$_2$ flux and F$_{NH3}$ follows same pattern, by being mainly downward directed before defoliation and starts changing to oppositely direction as LAI decreases and is upward directed as LAI equals zero.
6.5 COTAG fluxes vs. REA fluxes

In order to investigate the large difference between the fluxes measured by COTAG and REA, the fluxes were compared by separating REA data in neutral and unstable mean flux pools, likely to the COTAG. In Figure 6.11 the extracted data are illustrated and in Figure 6.12 the mean fluxes are given.

![Figure 6.11: $F_{\text{NH}_3}$ for L. Bøgeskov from 26 Oct – 11 Nov 2010 measured from COTAG (red) and REA (Blue) measurements. COTAG fluxes are given in mean values of the neutral and the unstable fluxes and the REA flux are given in half-hourly values. The dashed lines indicate the extracted REA measurements.](image)

It is seen that the COTAG system was sampling gradients in most of the time where the large emission fluxes were measured from REA. The COTAG did, however, not trap these fluxes. Thereby it can be eliminated that the large fluxes could have been present mostly due to stable atmospheric conditions where the COTAG does not measure gradients. The mean flux from COTAG of unstable conditions is based on very few samples of air compared to the neutral mean flux, which makes the flux during unstable conditions potentially more uncertain than the neutral.

![Figure 6.12: Comparison of COTAG and REA fluxes separated into neutral and unstable fluxes. Error bars indicate the uncertainty of measurements.](image)

Comparing the averagely flux pools for neutral and unstable conditions measured from REA and COTAG, it is seen that the fluxes during unstable conditions are closer to each other than in the neutral case (Figure 6.12 (left)). In Figure 6.12 (right), the COTAG fluxes are zoomed into and it is shown that the uncertainty on the estimated COTAG fluxes indicate that the flux could be oppositely directed due to the large uncertainty, even though, they are very small.
7 Discussion

In this study, the atmospheric concentration, flux, and dry deposition velocity of NH$_3$ along with the leaf area index have been assessed at the deciduous forest site Ll. Bøgeskov during the year 2010. Measuring and modelling techniques were used. In this chapter, the results obtained are discussed by inter-comparisons and comparisons with results obtained in other studies. Furthermore, sources of errors and uncertainties associated to the results are discussed. Finally, the use of the three techniques as tools in environmental management processes including critical loads is discussed.

Ammonia concentrations

Overall, the $c_{NH_3}$ assessed by the three different methods are in good agreement, particularly when comparing the mean values. The long-term gradient measuring system (COTAG) and the high-resolution local-scale model (OML-DEP) indicate both decreasing trends in $c_{NH_3}$ during the full measurement period (10 Aug – 11 Nov 2010). In contrast, the high-resolution measurement technique (REA) indicates increasing trend in the 4$^{th}$ sampling period (26 Oct – 11 Nov 2010). The mean $c_{NH_3}$ during the 4$^{th}$ sampling period were found to be nearly similar among the three techniques of 0.56, 0.68, and 0.67 µg NH$_3$-N m$^{-3}$ for OML-DEP, REA, and COTAG, respectively. The OML-DEP results varied in the range of 0-2.5 µg NH$_3$-N m$^{-3}$ and the REA results varied in the range of 0-2 µg NH$_3$-N m$^{-3}$. These results are in fairly good agreement with $c_{NH_3}$ for forests found in other studies. For a spruce forest in the western part of Denmark, $c_{NH_3}$ varied in the range of 0.25-1.6 µg NH$_3$-N m$^{-3}$ during Aug-Nov for the years 1991-1995 (Andersen et al. 1999). For a deciduous broad-leaved forest in Indiana (USA) $c_{NH_3}$ varied between 0.025-0.43 µg NH$_3$-N m$^{-3}$ during Feb and Mar 2000 (Pryor et al. 2001). These results indicate that the magnitudes of $c_{NH_3}$ measured during this study are in a reasonable range. For a coniferous forest in the Netherlands, the mean $c_{NH_3}$ of a two-year period (1992-1994) were measured to be about 5 µg NH$_3$-N m$^{-3}$ (Wyers et al. 1998). This is much higher than what has been measured in this study, but Wyers et al. (1998) performed measurements in all seasons, whereby higher concentrations in the spring and summer season may have occurred. These seasons are not represented in this current study. Many different results in the literature and from this study indicate that $c_{NH_3}$ is challenging to measure and is largely affected by site specific surface and meteorological conditions.

No clear relations of the OML-DEP $c_{NH_3}$ to the meteorological simulations were seen. It is, however, important to be aware that the meteorology input to OML-DEP has a coarse spatial resolution of app. 17 x 17 km whereas OML-DEP operates in a 400 x 400 m grid resolution. Thus, the MM5 model is not able to represent very local conditions, such as landscape around the forest. The relationship between the REA
c\textsubscript{NH3} and the meteorological data were quite inconsistent. Even if no significant relationship between c\textsubscript{NH3} and meteorological conditions can be found, it does not mean that no dependency exists. One possible explanation can be, that because many meteorological, emissions, and surface factors influences c\textsubscript{NH3} the picture gets diffused (Pryor et al., 2001). It was seen that the OML-DEP results comply with the measured REA results in few periods throughout the 4\textsuperscript{th} sampling period. In these periods, the results had the same temporal pattern, though sometimes displaced by a short time period. It can, however, not be expected that the high-resolution OML-DEP results compare directly to high-resolution measurements. OML-DEP is a static model that base calculations on assumptions calculated as new mean values for each grid cell every new hour of calculation. Therefore, it often gives more reasonable results when comparing mean values for longer period of time, which is also seen in this study.

**Vertical gradients of ammonia above forest**

Vertical gradients of c\textsubscript{NH3} above Ll. Bøgeskov were measured using COTAG in 29.8 m and 34 m height. It was seen that the COTAG c\textsubscript{NH3} differences between the two heights was close to zero in many of the samples, and in 4 of the 8 situations, the gradient was associated to such larges uncertainties that even the determination of the direction of the gradient was uncertain. Even though, the gradients were small in both neutral and unstable conditions, the gradients were largest for unstable conditions. The largest flux were found to be app. \(-1 \mu\text{g NH}_3\text{-N m}^{-3}\) compared to the largest gradient in neutral conditions of \(-0.05 \mu\text{g NH}_3\text{-N m}^{-3}\). This is inconsistent compared to the common theoretical comprehension, where unstable conditions lead to smallest gradients caused by enhanced mixing of air. Measurements from neutral and unstable conditions are, however, so small and non significant associated with very large uncertainties which make it difficult to conclude on these results. Additionally, it is by degrees experienced from other studies that the gradient method has difficulties detecting gradients when the air is well mixed (as it often is above rough surfaces), even though there might be potential fluxes (Andersen et al., 1993). Therefore a very stratified atmosphere from stable condition often leads to much more clear gradients, because the air mixes very slowly under these conditions. But even then, the stratification can bias the flux if the measurements in different heights are influenced by different masses of air. Nevertheless, this might not be the case in the Ll. Bøgeskov site, because the meteorological mast only reaches 57 m above surface, along with the relative small distance between the two COTAG sampling boxes (3 m). However, if the boxes are located to close to each other, they might sample almost uniform air with almost the same c\textsubscript{NH3}. This can be an issue of these COTAG measurements. According to Andersen et al (1993), the precision in gradient measurements also to some extent relates to the magnitude of the concentration, where low concentrations are associated with larger uncertainties than larger concentrations. This might also be a potential reason for the small gradients seen in this study. The REA system does also measure c\textsubscript{NH3} gradients, in terms of the concentration difference between the air mowing upward and downwards. The REA gradient from
the 4th sampling period indicated a more clear difference of $c_{\text{NH}_3}$ between the updrafts and downdrafts, which in most of the period were negative, opposite to the gradient from COTAG. It was seen that large uncertainties were associated in particular with the WEDD sampling downdrafts air samples, while the WEDD that sampling updrafts where significantly more certain. This illustrates the sensitivity of the REA system, which is discussed later.

Profile measurements can also be disturbed by other parameters from the forest effects (Chapter 1) that perturb the commonly applied profile theory not to be valid. A number of studies have found the classical logarithmic flux-gradient relationships derived from the surface layer similarity theory not to be valid over plant canopies and tall vegetation or very rough surfaces (Cellier and Brunet, 1992; Dellwik and Jensen, 2000; Dellwik and Jensen, 2005). Dellwik and Jensen (2005) and (2000) found difficulties of flux-profile relationship above the Ll. Bøgeskov site due to the creation of internal boundary layers caused by the roughness changes in the surrounding landscape, inhomogeneities within the forest composition, and short fetches. These parameters influence the micrometeorological conditions that are measured in the meteorological mast in Ll. Bøgeskov. Particularly, the relative small fetches that Ll. Bøgeskov comprises have the potential to cause the surface roughness layer to extend to above the height where measurements can be taken due to the height of the meteorological mast. This means that maybe the logarithmic profiles can’t be expected to be valid in the profile measurements taken throughout this present study. Furthermore, the fetch length is difficult to estimate due to many clearings and level variations in the canopy surface, whereby a longer fetch gives better measuring conditions than a shorter one (Dellwik and Jensen, 2005).

**Flux estimates of ammonia**

Overall, the $F_{\text{NH}_3}$ measured using the three techniques were inconsistent in the 4th sampling period. Due to the almost nonexistent gradients observed with the COTAG system, very small, mainly deposition, fluxes were obtained throughout the measurement period. Contrary, the REA system indicated comparative large mainly emission fluxes. The COTAG fluxes and the calculated deposition fluxes using OML-DEP were, however, rather comparable in magnitude and direction throughout the three last sampling periods.

The approximately linear relationship between $u^*$ and the REA $F_{\text{NH}_3}$ that was found, is similar to earlier observations (Andersen et al. 1993). Contrary, the wetness of the surface did not illustrate the influences of enhancing dry deposition (Section 3.2) that is reported in other studies. In this study decreasing $RH$ leads to emission fluxes. This might be related to emission fluxes due to drying surfaces, which is discussed later in this chapter. For the OML-DEP deposition fluxes, it was found that $RH$ had the crucial controlling influence, whereby other factors did only had little influence. Large difference in COTAG and REA $F_{\text{NH}_3}$ were seen throughout the 4th measurement pe-
period. It was seen that the majority of the eliminated measurements from COTAG due to stable conditions were characterized by very small fluxes observed by the REA. Thereby, it can be concluded that the conditional sampling method in COTAG is not the reason to the inconsistency between the two techniques according to this study. Furthermore, it was seen that the estimates did agree better for unstable conditions than for neutral conditions. However, in both situations a large difference was still found along with large uncertainties associated to particular the unstable measurements.

**Uncertainties of measurements**

The measurements performed with both systems are associated to the relatively large uncertainty of measurements related to both the techniques. The choice of stability correction function in the flux calculations from the gradient measurements can, however, also be a source of error. Many stability correction functions are suggested in literature, and in this study just one more or less coincidental function, that earlier also was used by Andersen et al (1993), is used. The proximity of the forest canopy can influence the values of the stability correction functions for the height where measurements are performed (Andersen et al., 1993) as discussed in previous paragraph. Additionally, compared to the COTAG system, the REA system is a very sensitive system that needs careful handling during measuring campaigns. Preferably more calibration measurements than performed during this measuring campaign could have improved the data and reduced the uncertainty of measurements. The inlet and analytical systems needs an app. weekly refill of H\textsubscript{2}O and chemical reagents, respectively. This means that personal handling due these sessions potentially can influence the samples by adding further NH\textsubscript{3} emitted from the persons themselves. This gives a risk of raising the uncertainty of the measurements. Additionally, the constant flows of air and liquid inside the system needs to sustained to prevent turbulence and subsequent pollution inside the system. For the chemical reagents, not even only a constant flow, but also an equal flow of the two fluids has to exist. This can be difficult to meet. Advantages of the REA technique are that the sample of air sampled by the REA system does not get in contact with humans before it is analyzed as the case for COTAG, which reduces risk of contamination by NH\textsubscript{3} emitted from the person handling the sample. Though, there is a difficulty of the system, for which, the NH\textsubscript{3} in the ambient air can penetrate into the fluid system that delivers H\textsubscript{2}O to the diffusion scrubbers and thereby raise the background $c_{\text{NH3}}$ in the air sample. Even though, large uncertainties are present to the REA system, there is no doubt that emission fluxes did occur. Therefore, it is obvious to conclude, that the agreement between the results obtained by COTAG and OML-DEP (Figure 5.16) can be assumed to be a coincidence more than an accurate representation of biophysical processes controlling the NH\textsubscript{3} flux. The OML-DEP can not be comparable to these measurements, because the model is not able to take any natural emission fluxes into account. Therefore, the large uncertainties of the COTAG method may be the reason why the COTAG system does not to trap these emission fluxes above the forest.
Compensation point

The results of the $F_{\text{NH}_3}$ for the beech forest site measured by REA indicated clearly an $\text{NH}_3$ emission flux in a large part of the measurement period. This indicates the potential existence of a bi-directional flux. $\text{NH}_3$ emission fluxes are in several studies explained by the existence of a $\text{NH}_3$ compensation point of different vegetative land covers which has over time widely been discussed (Andersen et al., 1999; Duyzer et al., 1994; Erism and Wyers, 1993; Sutton et al., 1997; Wyers and Erism, 1998). Many studies have reported that generally forest act as efficient sinks to atmospheric $\text{NH}_3$, whereas agricultural croplands in some cases, usually due to events of applying $\text{NH}_3$ to the fields as fertilizing, emits $\text{NH}_3$ due to evaporation of the applied $\text{NH}_3$. However, eventually it is known that not only agricultural crop lands act as sources of $\text{NH}_3$, but also natural and semi-natural vegetation do have the potential to emit $\text{NH}_3$ (Schjoerring et al., 1998). The compensation point was not measured during this study, but there might be a possibility that the emission of $\text{NH}_3$ from the beech leaves could be related to the presence of a $\text{NH}_3$ compensation point. In this study 13 days in the late autumn of measurements from the REA system was considered valid judged reasonable, and from these measurements, 82% of the estimated flux indicated emission fluxes against the 18% of deposition. Not forgetting the uncertainty associated to the estimates, the few deposition fluxes obtained was associated to very large uncertainties, while there is no doubt that emission fluxes did occur. Another study above a mixed coniferous forest indicated that 14% of the net fluxes were representing emission events (Neirynck et al., 2005). They found that the emission occurred mainly during day time where $c_{\text{NH}_3}$ was small, but in some situation emission did also occur at high concentration in days of dry weather and high temperatures. In this study, the same correlation is to a much less extend indicated, and can only be coupled to the emission fluxes seen until 8 Nov. Leaf fall did occur on approximately 8 Nov, and when the leaves are not present the stomata release will not occur. A potential compensation point inn canopy scale could, however, still exist.

The largest emission fluxes were found in the continuous dry period (8–11 Nov), though the temperature was down at approximately 5 °C these days which was the lowest temperature measured during the measurement period. Another explanation of the upward $F_{\text{NH}_3}$ that was found from the REA estimates, besides the one of the compensation point, where $\text{NH}_3$ is released from the stomata, could be emissions of $\text{NH}_3$ by evaporation from moist soil and wet leaves (Pryor et al. 2001). After a precipitation event with a following drying period evaporation can lead to subsequently emission fluxes of the deposited $\text{NH}_3$. It has been found that the soil temperature is a controlling parameter in this context (Roelle and Aneja, 2002).

The results indicating an emission flux and thereby pointing in the direction of the conclusion of a bi-directional exchange of $\text{NH}_3$ between the forest and the atmosphere could also indicate that the direction of $F_{\text{NH}_3}$ is related to variation in LAI. A couple of days after LAI meets zero, the REA flux seems to change direction and
increase (Figure 6.10). This can possibly be related to a release of NH$_3$ from the senescence and decomposing process of the leaves. Unfortunately, there were no REA measurements to compare with when biophysically active leaf were present in the canopy. A seasonal relation in the direction of $F_{\text{NH}_3}$ above the same beech forest, have, however, been found recently. The potential emission fluxes were found in the early and late growing season, while the forest acted as a sink during the mid-season (Wang et al., 2010). This might indicate that the withering and decomposition process of beech leaves result in a re-emission of the deposited NH$_3$ to the atmosphere. The couple of days between LAI equals zero and the emission begins could be due to a lag time for the leaves starting to wither till they release the NH$_3$.

The compensation point and other natural emission of NH$_3$ are not yet taken into account in OML-DEP whereby an important source of error is associated to the dry deposition calculation. This makes the reasonability of the results uncertain. At a newly held conference within the NitroEurope IP, it was experienced that, at present, many ongoing studies search methods to include these processes in local-scale models to calculate the NH$_3$ exchange between vegetative surfaces and the atmosphere (Massad et al., 2010a; Massad et al., 2010b).

**Deposition velocity and LAI**

No really significant changes were observed comparing results of $v_d$ calculated by the original OML-DEP setup and the setup including the new values of LAI. It was seen that, even though the new values of LAI were up to 25 % larger, it was not the magnitude of LAI that had any significant effect. An apparent difference between the old and new LAI input were the displacement of the growing season, but also the length of the slopes in the start and end of the growing season. In the original function of LAI proposed by Emberson et al. (2000) the increasing slope were about half the length (number of days) of the declining slope. The new input indicates more or less the opposite pattern and a more symmetrical annual pattern. According to the nature of how a deciduous canopy gains leaves and looses leaves, it usually takes longer time for the forest to loose leaves in the autumn, than develop leaves in the spring. The LAI obtained through this study does not indicate this pattern, which might be due to errors associated to the measurements. Uncertainties can be related to the deviations in the measuring conditions from the optimal conditions (Section 4.4) or changes in the level of incoming light when the sky weren’t uniform. The incoming PAR above the forest in 57 m was investigated and indicated a decreasing light level in the five minutes the LAI measurement was performed on 20 Aug. This causes, in this case, an overestimation of the reference measurements that was taken in the higher level of light, while the below-measurement were taken in lower levels of light. In other cases the oppositely, meaning an underestimation of LAI, could be possible and must be considered as an essential source of error to the measurements.
Furthermore, the LAI values observed by the measurements were found relatively large compared to LAI reported of the same site in other studies (Pilegaard et al., 2003; Pilegaard et al., 2011). The differences between the values obtained in this study and earlier reported values can be caused by either measuring LAI at different locations in the forest, or due to differences between the compared years. A method to investigate this further could be investigating the Enhanced Vegetation Index in for example MODIS satellite images. Nevertheless, the magnitude of LAI did not seem to have crucial influence in the dry deposition velocity in the current way of using LAI in the method of calculation \( v_d \) in OML-DEP. It could, however, be interesting to investigate the use of LAI in OML-DEP further. Currently, LAI and the definition of the season is only used to determine \( r_c \) and \( g_{sto} \) but LAI (or actually PAI) does also influence the aerodynamic resistance \( (r_a) \) and the quasi-laminar resistance \( (r_b) \) in terms of the roughness scaling parameters \( z_0 \) which also affects the turbulent scaling parameter \( u^* \) that figures in both \( r_a \) and \( r_b \). As described in the theoretical chapter, a larger LAI of a forest leads to larger roughness. Though, LAI is not included in the parameterization of these parameters yet, but this might be an area of improvement of the method of calculation.

**Critical loads**

Calculations of total N deposition using OML-DEP indicated that CL of N to deciduous forest was exceeded for Ll. Bøgeskov throughout the year of 2010, likely to the results from Aarhus (Chapter 1). The empirical determined CL for deciduous forest is in the range of 10-20 kg N ha\(^{-1}\) and the model calculation resulted in 21.9 kg N ha\(^{-1}\) to Ll. Bøgeskov. Of these 21.9 kg N ha\(^{-1}\), dry deposition of NH\(_3\) accounted for a little less than a third and similarly for wet deposition of N, whereby the additional N compounds\(^{24}\) accounted for 45 %. The results indicate that even if all sources of NH\(_3\) were reduced, the N load will still exceed the lower limit of CL. Nevertheless, a reduction in NH\(_3\) deposition could bring the load below the upper limit of CL.

CLs are simple, easy to understand, and quantitative estimates of the sensitivity of different ecosystems. Therefore they figures very fine as an environmental tool in nature habitats assessment in relation to EIA of livestock farms. Additionally, they figures in the Natura 2000 plans which are easy to understand and handle for the municipalities. However, even though the CLs relates to the biological condition of the nature by giving a maximum load of N an ecosystem can be exposed to without taking damage, the severity of a potential exceedance is not stated. CLs does not relate to any time scale and different ecosystems reacts different of too high N input in different time scales. This means that when the effect of a too high input of N to an ecosystem becomes visible, it might already be too late to take action to regulate the load. Therefore, the CL may in many cases be estimated too high. Additionally, the use of CLs are not specified precise, which means, that the different municipalities

\(^{24}\) NH\(_4\) and NO\(_3\)
do not have to be consistent in their management using CLs (Frederiksen, 2011). Therefore, the municipalities are free to decide when the CL is met or exceeded because they can choose how to operate with the interval. That means that some municipalities use the precautionary principle and aim at stay below the lower limit, while some can operate with the upper limit as the boundary (Frederiksen, 2011). Today, CL intervals based on recommendations from UNECE from 2004 and updated in 2005 are used in the management processes. These intervals must be assumed much generalized in order to make them widely applicable, but in reality, the CL of even the same nature type will differ between the individual habitats. However, the nature is dynamic and the natural CL can potentially also change. This is especially of very relevance for habitats that require much preservation which if the optimal preservation is ignored. New and more precise estimates of CL are needed to improve the management using CLs, which means that more measurements of the atmospheric input are also needed.

**Tools for environmental management**

Using model calculations to evaluate the biological conditions of nature resorts is a very useful and easy applicable method for which reason it is a widely used method. Deposition models include, however, very simplified descriptions of the many processes representing processes from emission to deposition. This is partly due to the finite resources to run such models but also related to lacked knowledge of some processes. As discussed until now, several uncertainties associated to the model calculation makes the calculation less reliable. Such calculation can have crucial effect in environmental management processes, especially if the nature habitat is designated as a Natura 2000 area, whereby particular restrictions according to CL are determined. This is particularly important for forests that are very difficult to calculate on due to many and complex forest-atmosphere interactions (Chapter 1 and 1).

Atmospheric measurements have the advantage of determining the actual input to a specific location or the surface-atmosphere exchange of a pollutant. Thereby, it is possible to assess seasonal changes, long-term trends, and process studies. Measurements are, however, closely related to the actual measuring site, where local parameters can cause the measurements to show very local events, which isn’t comparable to many other localities. Furthermore, measurements can with advantage be used to validate and parameterize models calculating atmospheric processes, because model calculations are nevertheless an easily applicable (contrary to measurements) and very efficient tool in planning processes. Most models calculations have, however, generally difficulties accounting for very local conditions unless they are semi-empirical and adapted to the site. Therefore, assessment methods of measurement and modelling can by advantage be integrated in monitoring programs (Hertel, 2009). The COTAG is a cheap and easily handling system. This gives the potential to be established in a large network of measurements to monitor the atmospheric surface exchange of NH3 in relation to CL studies and assessments. The COTAG did,
however, not show good results, when comparing to REA in this present study. CO-TAG is yet a brand new developed system and has not been through many validation studies. This makes it difficult say whether the system in general is problematic, or whether problems are confined to forests measurements. A COTAG system was tested above a blanket bog in the UK with the same predefined stability intervals as used here and showed good results (Famulari et al., 2010). Therefore, more measurements using COTAG are needed. Contrary, the REA system is very demanding and needs substantial resources for maintenance and carefully handling. Therefore, it does not have the potential to be established in a large network of monitoring stations, but do definitely can be used on shorter measuring campaigns and to validate long term measurement and model calculations as well as to process studies.

Atmospheric models are good tools in providing information of a larger geographical scale and at localities where performing measurements aren’t possible. Models are, however, very simplified descriptions of the reality in order to make them as comprehensive as possible and still make them able to be used by the finite resources available of for example computer resources. This makes generalizing of the processes described in models necessary to make the models useable at different scales and at a wide extent of localities. There are, however, also some inherent difficulties when comparing measurements and model calculations due to the scale the two techniques are performed in. Measurements are performed in a point scale confined to specific and very local environments, whereas models like OML-DEP operate within a grid. Thereby, very local conditions (i.e. forest edge effects and compensation points) are reflected in measurements, while such model estimates the results from mean values of a larger area. This is especially interesting in Denmark, because the landscape includes many small forests as well as other small nature habitats and emission sources. Therefore the discussion of scales is very interesting. Finally, the measurements indicated the potential of forests acting as a source due to a NH₃ release. This is a part of the exchange process that could be valid for all vegetative surfaces, but that is not described in OML-DEP. This discussion points out the importance of the input to a model to obtain a realistic output if considering a small area.

Beyond the need of more measurements and better measuring techniques to improve our knowledge on atmospheric NH₃ processes, there is a need for further investigations to quantify the NH₃ budget where natural sources as NH₃ re-emission from vegetative surfaces and soils are also taken into account. Such improvements could be included for deposition modelling using local-scale models and thereby improve estimates of the total N load in CL assessments. Despite the large uncertainties associated with the results obtained in this study due to the highly variable assessment techniques, the results must be considered as a good start for quantifying the NH₃ emission flux and the total net $F_{NH3}$ between vegetative surfaces and the atmosphere.
8 Conclusion

Throughout the experimental investigations it was found that measured and modelled results of $c_{\text{NH}_3}$ were in good agreement, however inconsistent, considering $F_{\text{NH}_3}$. The good agreements of $c_{\text{NH}_3}$ were seen in particular when comparing mean values for a longer period whereby $c_{\text{NH}_3}$ assessed from the three techniques (OML-DEP, REA, and COTAG) varied in the range of 0.56-0.68 µg NH$_3$-N m$^{-3}$. The inconsistency of $F_{\text{NH}_3}$ observed was related to large uncertainties of measurements due to sensitivity of REA and potential difficulties of using COTAG above forest. COTAG and OML-DEP indicated no significant $F_{\text{NH}_3}$, whereas REA showed evident and comparatively large emission fluxes indicating a contribution to $c_{\text{NH}_3}$ and the potential presence of bi-directional exchange of NH$_3$ between the forest and the atmosphere. This re-emission process is not yet taken into account in OML-DEP which biases the calculations.

The NH$_3$ emission fluxes could be related to seasonal variations of LAI, by an NH$_3$ release caused by decomposing leaves after leaf fall. Unfortunately, reasonable measures of $F_{\text{NH}_3}$ from REA were related to the period after defoliation. Therefore it is difficult to conclude on the influence on the dry deposition of NH$_3$ of LAI. No significant changes were, however, observed comparing calculations of $v_d$ using OML-DEP including the original LAI input and the measured values of LAI. Thereby, it can be concluded that the input of LAI to calculate $r_c$ is reasonable. The $r_c$ (and thereby indirectly also LAI) is, however, also of importance for calculating the NH$_3$ emission, which is not included in OML-DEP. Therefore, the influence of $r_c$ on the emission is not known from this thesis. However, the roughness which is represented by $z_0$ in the parameterization of $r_a$ and $r_b$ is, in OML-DEP, described only due to the height of the trees. An area of improvement could be, to include LAI in the parameterization of $z_0$ and thereby include influences of LAI also in $r_a$ and $r_b$.

Integrated approaches of combining measurements and modelling in CL assessment are valuable tools, due to the different opportunities and aims of the techniques. Large uncertainties are, however, still associated to the assessment techniques of atmospheric NH$_3$. The COTAG system is yet not reasonable to be included in an establishment of a large measuring network due to the incomparable results shown, and REA is way too demanding for a permanent network. Furthermore, the use of CLs in environmental management is not precisely specified in the authorities’ use of them, which cause very different and individual interpretations. Therefore better measuring techniques and improved process descriptions for local-scale exchange models are still needed to obtain improved determinations and assessments of CLs.
9 Perspectives

Throughout this thesis, many perspectives of assessing atmospheric \( \text{NH}_3 \) have been mentioned, and many questions relating to this topic are still left unanswered. More research was found to be needed in order to improve measurement and modelling techniques of assessing \( \text{NH}_3 \), particular for forest ecosystems, and to improve the use of the techniques as tools in environmental planning concerning CLs.

The results and methods used in this thesis can easily be set into perspective of relating research topics. One topic related is confined to the greenhouse gas budgets and climate change. The atmospheric N load influences the conditions of the ecosystems and also the greenhouse gas exchange. In Figure 6.10, indications of a relation between vertical fluxes of CO\(_2\) and \( \text{NH}_3 \) were seen. The CO\(_2\) fluxes were mainly downward directed before defoliation; however, as LAI turns to zero, the flux changed direction becoming upward, likely to the \( \text{NH}_3 \) flux measured using the REA system. From the NitroEurope IP conference (Section 1.2), it was experienced that the N load in vegetative surfaces influences the photosynthesis both at leaf scale, however, also by stimulating forest growth. Additionally, climate changes are predicted to extend the season of growth, which will influence the vegetative dynamics of forest ecosystems and other vegetative ecosystems. The influence of N deposition and climatic changes do, however, still represent uncertainties in ecosystem modelling when describing greenhouse gas exchange between vegetation and the atmosphere. Particularly, more research confined to the \( \text{NH}_3 \) compensation point would be needed to investigate the bi-directionality of \( \text{NH}_3 \) exchange between land-surfaces and the atmosphere. An improved knowledge of the influence of N deposition on vegetative terrestrial ecosystems could improve the prediction of the vegetation response to N fertilisation and other global change in the future. A quantification of the effect of N deposition on the greenhouse gas balance of particular CO\(_2\) would, therefore, be an essential step forward in the research and model development.

Future publication

I hope to publish an article related to this thesis. However, a large part of the planned measurement period went to test the measurement instruments along with instrumental failure after the measurements were started up. This resulted in only one sampling period to compare the two measurements systems (COTAG and REA), and in this period, the assessed \( \text{NH}_3 \) flux did not agree. Therefore, there is not yet formed basis for such article. However, the COTAG and REA system is started up again, at is planned to run for a couple of month in during the spring and summer 2011. Based on these additional and new measurements, I hope to be able to publish some of the main points from this thesis and the new results.
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APPENDIX
A NitroEurope poster
Measuring and modelling dry deposition of ammonia to deciduous forest using high temporal and spatial resolution techniques

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Aim
- To compare vertical NH3 concentrations and fluxes measured above deciduous forest using Conditional Time Average Gradient (COTAG) and Relaxed Eddy Accumulation (REA).
- To examine the performance of the Danish applied local-scale deposition model CML-DEP on calculating dry deposition of NH3 to deciduous forest by comparing calculations with new flux measurements.

Conclusion
- Measurements and model calculations are in good agreement on estimating atmospheric NH3 concentration.
- REA indicates a clearly bi-directional NH3 flux, while fluxes determined using COTAG are non-significant and associated with high uncertainty.
- There is a further need for improving the description of dry deposition in local-scale models whereby the NH3 vegetative emission and its contribution to the atmospheric NH3 flux is considered.

Introduction
Calculations of ammonia (NH3) deposition to Danish nature reserves indicate exceedance of critical load for N deposition particular to forests (ref.1). A continuous high N load in terrestrial ecosystems can cause critical effects to the biodiversity (ref. 3).

Modeling dry deposition processes of NH3 above forest is challenging due to the complex forest-atmosphere interactions along with a lacking knowledge of vertical NH3 fluxes between vegetation surfaces and the atmosphere. Therefore further measurements of fluxes are still needed to improve the current knowledge of NH3 fluxes and to verify the local-scale deposition models.

Method
Vertical fluxes of NH3 was measured above a beech forest (Fagus sylvatica) in Denmark from 10 August to 11 November 2010 using the long-term COTAG technique (28.8 m and 34 m) and the high time resolution technique REA (33 s). Calculations of concentration and dry deposition are performed using the local-scale deposition model (CML-DEP) applied in DAMOS (ref. 2). The DAMOS calculations are based on state-of-the-art emission inventories with hourly time resolution and a spatial resolution down to single farm level (ref. 4).

Concentrations
NH3 concentration above Liis Bagerslev measured using COTAG Banner (28.8 m) in four sampling periods and REA WEDD(33 m) only in the fourth sampling period and calculated by CML-DEP through the full measuring period.

OML-DEP calculations indicate an overall decreasing trend in the measuring period. These results are in good agreement with the concentration measured using COTAG that indicates mean concentrations decreasing from 1.1 to 0.7 μg NH3-N m⁻².

Fluxes
NH3 fluxes above Liis Bagerslev for 10 August – 11 November 2010 along with leaf area index (LAI) and CO2 fluxes.

High temporal resolution measurements of NH3 flux using REA indicate a bidirectional flux that could be related to LAI. After defoliation the NH3 flux begins changing direction from deposition to emission equally to the pattern of CO2 fluxes.

OML-DEP doesn’t take natural contributions as the NH3 vegetative emission into account in calculating NH3 deposition fluxes. Furthermore, the calculated flux seems underestimated due to an underestimation of the turbulent transport to the canopy.

Reference

Acknowledgement
The Danish Research Council (11-086731) has funded the project.
B Assumptions for Gaussian Plume Models

1. Continuous emission from the source at a constant rate, at least for a time equal to or greater than the time of travel to the location (receptor) of interest. The plume diffusion formulae assume that release and sampling times are long compared with the travel time to receptor, so that the material is spread out in the form of a steady plume between the source and the farthest receptor. A shorter release will result in an elongated puff with a time-dependent concentration field.

2. Steady-state flow and constant meteorological conditions, at least over the time of transport (travel) from the source to the farthest receptor. This assumption may not be valid during rapidly changing meteorological conditions, such as during the passage of a front or a storm and also during the morning and evening transition periods.

3. Conservation of mass in the plume. The continuity equation satisfied by the Gaussian plume formula is a mathematical expression of the condition that the mass flow rate through any plume cross section is equal to the source emission rate. This implies that none of the material is removed through chemical reaction, gravitational settling, or deposition at the surface. All the material reaching the surface through turbulent diffusion is reflected back and none is absorbed there.

4. Gaussian or reflected Gaussian distribution of mean concentration in the lateral (cross-wind) and vertical directions at any downwind location in the plume. The assumption of Gaussian distribution in the vertical direction is somewhat questionable, but does not appear to affect adversely the model predicted ground-level concentrations.

5. A constant mean transport wind in the horizontal (x-y) plane. This implies horizontal homogeneity of flow and the underlying surface and becomes invalid over a complex terrain.

6. No wind shear in the vertical. This assumption is implicit in the constant mean transport velocity $u$ in the Gaussian plume formulae. In practice, $u$ is often taken as the wind speed at 10 m height for near-surface sources (H < 10 m) and the wind speed at the effective release height for elevated sources. The variation of wind speed with height can also be considered in more accurately estimating the effective transport velocity, but this requires the knowl-
edge of vertical concentration distribution in the plume at each receptor location. The variation of wind direction with height is ignored, although its effect on the lateral plume spread and concentration field can be considered superficially through an appropriate parameterization of $\sigma_y$.

7. Strong enough winds to make turbulent diffusion in the direction of flow negligible in comparison with mean transport. This assumption, also known as the slender-plume approximation, which is implicit in the Gaussian plume model, generally becomes invalid very close to the source where material diffuses up-wind of the source due to longitudinal velocity fluctuations. The assumption becomes invalid farther and farther away from the source as mean wind becomes weaker and vanishes entirely (e.g., under extremely stable and free convection conditions).

(Lyons and Scott, 1990)
C LAI-2000 PCA technique

The LAI-2000 instrument provides measurements of the structure of the canopy related to the foliage amount and the foliage orientation. For calculating the LAI only information of the foliage amount is necessary. By this technique the attenuation of the radiation from a diffuse sky is calculated as it passes through the canopy and deduces and thereby results in qualitative estimates of how much foliage is present. The attenuation is measured at five angle intervals\(^{25}\) (rings) from the zenith simultaneously above and below canopy to calculate the LAI, where each ring views a different portion of the sky. This means that ring 1 measures the radiation straightly overhead 0-13º while ring 5 measures in the interval of 61-74º from zenith. To calculate LAI, measurements above canopy (referred as above-canopy readings) and below canopy (referred as below-canopy readings) are needed, to measure the total incoming diffuse radiation and the intercepted radiation respectively. The instruments calculates the LAI in all below-canopy readings on the basis of the above-canopy reading and results in an average value of LAI. The method of computing LAI for the LAI-2000 PCA is based on following formula:

\[
LAI = 2 \sum_{i=1}^{5} K_i W_i \ [m^2 m^{-2}]
\]

Where \(i\) relates to the ring number (1 to 5), \(K\) is the contact number, that express the number of contacts with foliage elements the light have had passing through the canopy, and \(W\) is a weighting factor that accounts for the weighting of each ring measurement (LI-COR, 1992).

Four major assumptions of foliage amount and orientation must in theory be met for the method of calculation LAI with the LAI-2000 (LI-COR, 1992). First of all the foliage is assumed to be black which means that the calculations do not include any transmitted radiation by foliage (radiation below 490 nm). Secondly the foliage is assumed to be randomly distributed within the beech forest canopy. Thirdly the foliage elements are assumed to be small in comparison to the area of view of each angle (ring). For that reason the approximate guideline from the instruction manual of letting the distance from the sensor to the nearest leaf over is be at least 4 times the leaf width. The 4\(^{th}\) assumption states that the foliage is azimuthally randomly oriented which means that the inclination of the foliage do not affects the calculations as long as the leaves do not faces the same compass direction. Ll. Bøgeskov nor other real canopies do conforms exactly to these assumptions, but it is sufficient to consider that the canopy of Ll. Bøgeskov is randomly, and that living foliage do have a relatively low transmittance and reflection below 490 nm.

\(^{25}\) 0-13º, 16-28º, 32-43º, 47-56º and 61-74º.
### D Logbook of LAI measurements

**Site:** Ll. Bøgeskov, Sorø, Denmark  
**Period:** May - Nov 2010  
**Instrument:** Licor LAI-2000 Plant Canopy Analyzer (PCA)

<table>
<thead>
<tr>
<th>No.</th>
<th>Date</th>
<th>Time</th>
<th>LAI</th>
<th>SEL</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7-May</td>
<td>12:00</td>
<td>2.50</td>
<td>0.00</td>
<td>~10 minutes between A and B measurements because the A measurement was taken from the top of the scaffolding tower. Small light green leaves in the beginning of foliation</td>
</tr>
<tr>
<td>2</td>
<td>15-May</td>
<td>11:50</td>
<td>2.41</td>
<td>0.10</td>
<td>Rain droplets on the lens. The A measurement taken in and opening in the forest.</td>
</tr>
<tr>
<td></td>
<td>12:15</td>
<td></td>
<td>2.43</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>18-May</td>
<td>13:45</td>
<td>2.55</td>
<td>0.17</td>
<td>Varying cloud cover with gaps of sunshine. The A measurement taken in and opening in the forest.</td>
</tr>
<tr>
<td></td>
<td>14:00</td>
<td></td>
<td>3.36</td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>30-May</td>
<td>11:10</td>
<td>3.83</td>
<td>0.16</td>
<td>Ref. measurement taken in and opening in the forest.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.83</td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>30-Jun</td>
<td>09:10</td>
<td>5.13</td>
<td>0.16</td>
<td>Overcast. The A measurement taken in and opening in the forest.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5.12</td>
<td>0.17</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>9-Jul</td>
<td>11:00</td>
<td>4.96</td>
<td>0.18</td>
<td>Thin layer of clouds and little rain. The A measurement taken in and opening in the forest.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4.92</td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>20-Aug</td>
<td>10:35</td>
<td>5.84</td>
<td>0.13</td>
<td>Varying overcast sky. The A measurement taken outside the forest.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5.68</td>
<td>0.17</td>
<td>The A measurement was taken in sunshine. Sorted out. The A measurement taken outside the forest.</td>
</tr>
<tr>
<td>8</td>
<td>26-Sep</td>
<td>12:10</td>
<td>4.67</td>
<td>0.15</td>
<td>Good uniform overcast sky. The A measurement taken outside the forest.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4.94</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>18-okt</td>
<td>14:00</td>
<td>4.13</td>
<td>0.12</td>
<td>Good uniform overcast sky. Leaves start to become yellow. The A measurement taken outside the forest.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.90</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>01-nov</td>
<td>12:50</td>
<td>2.65</td>
<td>0.11</td>
<td>Good uniform overcast sky, but very misty and humid. The A measurement taken outside the forest.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.34</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>16-nov</td>
<td>14:30</td>
<td>1.08</td>
<td>0.06</td>
<td>Thin layer of clouds with gaps of sunshine. No leaves. The A measurement taken outside the forest.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.20</td>
<td>0.05</td>
<td></td>
</tr>
</tbody>
</table>
E Webcam photographs above Lille Bøgeskov

**Figure E.1:** 30 Apr 2010 06:30 above Ll. Bøgeskov viewing northerly direction.

**Figure E.2:** 8 Nov 2010 12:30 above Ll. Bøgeskov viewing northerly direction.
F  MATLAB scripts for COTAG calculations

To estimate $F_{\text{NH}_3}$ by the COTAG method a number of calculations have been done. Calculations are performed in the technical computing language MATLAB and the scripts are found in the following sub-appendixes.

Calculating the ammonia flux

```matlab
%COTAG_NH3flux

%Programme to calculate NH3 conc. and flux from COTAG data
clear all; clc; close all;

%initialising counters
i=0;
sample=0;

%Loading data
DenuderData = xlsread('G:\Speciale\Data\COTAG2010\COTAG_Chemistry\Denuderdata.xls');

%Setting constants
h=26.; %Canopy height [m]
d=0.75*h; %Displacement height [m]
z=31.; %Sonic height [m]
z1=29.8; %Bottom box height [m]
z2=34.; %Bottom box height [m]
k=0.40; %Von Karmans constant
z0=0.1*h; %Roughness length [m]

for sample=1:4 %loop over samples
    clear SonicData;
    SonicData = xlsread(['G:\Speciale\Data\COTAG2010\CR1000_Results_2010_sample',num2str(sample),'.xls']);

    %Function to calculate $u^*$ and $L$ average values sorted by stability
    [Ustar_A(sample) Ustar_B(sample) L_A(sample) L_B(sample)] = Us-
    tar_MO(SonicData);

    %NH3 concentrations from 'COTAG_chemistry_DK_Sor.xls'
    Ctop_A=DenuderData(sample,1); %Mean NH3 conc in top box (neutral)
    Cbot_A=DenuderData(sample,3); %Mean NH3 conc in bottom box (neutral)
    Ctop_B=DenuderData(sample,5); %Mean NH3 conc in top box (unstable)
    Cbot_B=DenuderData(sample,7); %Mean NH3 conc in bottom box (unstable)
    C_OFF=DenuderData(sample,9); %Mean NH3 conc in OFF

    %Stability correction (heat) unstable (Andersen et al. 1992)
```

101
yb(sample) = \( \frac{1}{(1 - 16 \times (z - d) / L_B(sample)))^{(1/4)}} - 1; \)

% Calculation of the eddy diffusivity (K)
ra_B(sample) = \( \frac{1}{(k \times Ustar_B(sample)))^{(log(z-d/z0)-yb(sample))}} \)
%%%% Aerodynamic resistance (unstable)
ra_A(sample) = \( \frac{1}{(k \times Ustar_A(sample)))^{(log(z-d/z0))}} \)

% Eddy Diffusivity (neutral)
K_A(sample) = \( \frac{1}{ra_A(sample)} \)
K_B(sample) = \( \frac{1}{ra_B(sample)} \)

% Calculation of the NH3 flux (F)
Flux_A(sample) = \( -K_A(sample) \times (Ctop_A-Cbot_A) \)
Flux_B(sample) = \( -K_B(sample) \times (Ctop_B-Cbot_B) \)

% Write to file
sti1 = 'G:\Speciale\Results\COTAG\NH3Flux.dat';
NH3data = [Flux_A' Ustar_A' L_A' ra_A' K_A' Flux_B' Ustar_B' L_B' yb' ra_B' K_B'];
dlmwrite(sti1,NH3data);

% Function to calculate conditional u* and L
function [Ustar_A,Ustar_B,L_A,L_B] = Ustar_MO(SonicData)
% initialising counters
j=0;
k=0;
l=0;
m=0;
o=0;
t=0;
UA=0;
UB=0;
LA=0;
LB=0;

NoRows = size(SonicData,1);

stability=SonicData(:,2); % Stability (-1 (Unstable), 0 (stable), 1 (OFF), or 2 (OFF))
Ustar=SonicData(:,31); % Friction velocity [m/s]
L=SonicData(:,33); % Monin-Obukhov length [m]

for i=1:NoRows
if not(isnan(Ustar(i))) && not(isnan(stability(i))) &&
not(isnan(L(i)));
if stability(i)==0;
j=j+1;
k=k+Ustar(i);
o=o+L(i);
elseif stability(i)==-1;
l=l+1;
m=m+Ustar(i);
t=t+L(i);
end
if j>0;
MATLAB scripts for COTAG calculations

Ustar_A=k/j; % avg. Ustar for stability = 0 (neutral)
L_A=o/j; % avg. Monin-Obukhov length (neutral)
end
if l>0;
Ustar_B=m/l; % avg. Ustar for stability = -1 (unstable)
L_B=t/l; % avg. Monin-Obukhov length (unstable)
end
end
end

Sorting the flux according to stability intervals

%stability_sort
clear all; clc;

%initialising counters
i=0;
j=0;
k=0;
l=0;

stability = load('E:\Speciale\Data\COTAG2010\stability3.dat');

for i=1:length(stability)
if stability(i) == 0; % Flux A
C(i) = 0.6314; % COTAG conc A (stable) 29.8 m
F(i) = -0.0016272; % Calculated by myself
j=j+1;
else
if stability(i) == -1; % Flux B
C(i) = 2.0973; % COTAG conc B (unstable) 29.8 m
F(i) = -0.0054888; % Calculated by myself
k=k+1;
else
C(i) = 1.5729; % COTAG conc OFF 29.8 m
F(i)=nan;
l=l+1;
end
end
end

sti=['E:\Speciale\Data\COTAG2010\stability_cotag3.dat'];
dlmwrite(sti,[C',F']);
MATLAB scripts for REA calculations

To calculate the $c_{\text{NH}_3}$ from the REA measurements and to estimate $F_{\text{NH}_3}$ a number of calculations have been done. Calculations are performed in the technical computing language MATLAB and the scripts are found in the following sub-appendixes.

Extracting volt signals and meteorology from raw data

```matlab
%NH3File
%Programme to create NH3 files
clear all; clc;

%initialising counters
i=0;
j=0;
k=0;
l=0;

%SETTINGS:
%set date and week
Maindir='E:/Speciale/Data/REA2010/Data/DataFiles';

weeks = dir((Maindir,'/*.'));
for k = 1:length(weeks)
    week = weeks(k).name;
    %spring over '.' og '..'
    if (~strcmp(week,'.') && ~strcmp(week,'..'))

weekdir=[Maindir,'/','week);

% hvor mange dage er der data for denne uge
dates = dir([weekdir,'/*.'));
for j = 1:length(dates)
    date = dates(j).name;
    %spring over '.' og '..'
    if (~strcmp(date,'.') && ~strcmp(date,'..'))

%set working directory
wdir=[weekdir,'/','date];
cd(wdir);

%set path to program files
path='E:/Speciale/Data/REA2010/Analyse/MatLab/';

%read list of available data files (.LST format)
LSTfiles = dir([wdir,'/*.LST']);
for i = 1:length(LSTfiles)

%extract date and time from filename
[versn, name, ext] = fileparts(LSTfiles(i).name);

timestamp=str2num(name);
```
d(i,:) = timestamp;

%DAQSYS files are de muxed ( ONLY if CAL files NOT exists)
dos([path,'de_mux ',name,' /S=(1,2,3,5,6,27,28) ']); %demux data
dos([path,'de_sux ',name,' /F=binary /M=0/S=(9,15,17,18,20,21,22,23,25,26) ']); %desux data

filename1=[name,'01.CAL'];
sid=fopen(filename1,'rb');
SX=fread(sid,'single');

filename2=[name,'02.CAL'];
cid=fopen(filename2,'rb');
SY=fread(cid,'single');

filename3=[name,'03.CAL'];
did=fopen(filename3,'rb');
SZ=fread(did,'single');

filename4=[name,'05.CAL'];
fid=fopen(filename4,'rb');
ST=fread(fid,'single');

filename5=[name,'06.CAL'];
gid=fopen(filename5,'rb');
Sspd=fread(gid,'single');

filename6=[name,'09.AVE'];
hid=fopen(filename6,'rb');
Sdir=fread(hid,'single');

filename7=[name,'17.AVE'];
jid=fopen(filename7,'rb');
Ustar=fread(jid,'single');

filename8=[name,'18.AVE'];
kid=fopen(filename8,'rb');
L=fread(kid,'single');

filename9=[name,'20.AVE'];
lid=fopen(filename9,'rb');
z_tresh=fread(lid,'single');

filename10=[name,'25.AVE'];
mid=fopen(filename10,'rb');
bt=fread(mid,'single');

filename11=[name,'26.AVE'];
nid=fopen(filename11,'rb');
bw=fread(nid,'single');

filename12=[name,'27.CAL'];
pid=fopen(filename12,'rb');
NH3_Up=fread(pid,'single');

filename13=[name,'28.CAL'];
qid=fopen(filename13,'rb');
MATLAB scripts for REA calculations

NH3_Do=fread(qid,'single');

filename14={[name,'15.AVE']};
rid=fopen(filename14,'rb');
wT=fread(rid,'single');

filename15={[name,'21.AVE']};
tid=fopen(filename15,'rb');
cnts_do=fread(tid,'single');

filename16={[name,'22.AVE']};
vid=fopen(filename16,'rb');
cnts_mid=fread(vid,'single');

filename17={[name,'23.AVE']};
bid=fopen(filename17,'rb');
cnts_up=fread(bid,'single');

fclose(sid);
fclose(cid);
fclose(did);
fclose(fid);
fclose(gid);
fclose(hid);
fclose(jid);
fclose(kid);
fclose(lid);
fclose(mid);
fclose(nid);
fclose(pid);
fclose(qid);
fclose(tid);
fclose(vid);
fclose(bid);

% Plot volt signals
figure(i)

subplot(2,1,1);
plot(NH3_Up,'r--','LineWidth',1);
axis([0 18000 0 2])
set(gca,'YGrid','on')
set(gca,'XGrid','on')
xlabel('[10 Hz]')
ylabel('[Volt]')
title(([int2str(d(i))], ' NH3_Up'),'FontSize',10)

subplot(2,1,2);
plot(NH3_Do,'g--','LineWidth',1);
axis([0 18000 0 2])
set(gca,'YGrid','on')
set(gca,'XGrid','on')
xlabel('[10 Hz]')
ylabel('[Volt]')
title(([int2str(d(i))], ' NH3_Do'),'FontSize',10)

sti2 = [wdir ' \ int2str(d(i)) ' NH3_Volt.jpg'];
print(sti2,'-djpeg');
MATLAB scripts for REA calculations

Closing files:

close(i);

Writing to files:

Data20Hz_ny=[SX SY SZ ST Sspd NH3_Up NH3_Do];
st1 = [wdir '/' name '.dat'];
dlmwrite(st1,Data20Hz_ny);

Data_sux=[Sdir wT Ustar L z_tresh bt bw cnts_do cnts_mid snts_up];
st2 = [wdir '/' name '.dut'];
dlmwrite(st2,Data_sux);

cnts=[cnts_do cnts_mid cnts_up];
st3 = [wdir '/' name '.cnt'];
dlmwrite(st3,cnts);

Correcting volt signals for bubbles of air:

% Volt_sort

clear all; clc;

% Initialising counters
i=0;
j=0;
k=0;
m=0;

% SETTINGS:
% set date and week
Maindir='E:/Speciale/Data/REA2010/Data/DataFiles1';

weeks = dir([Maindir,'/*.']);
for k = 1:length(weeks)
    week = weeks(k).name;
    % spring over '.' og '..'
    if (~strcmp(week,'.') && ~strcmp(week,'..'))
        weekdir=[Maindir,'/',week];

        dates = dir([weekdir,'/*.']);
        for j = 1:length(dates)
            date = dates(j).name;
            % spring over '.' og '..'
            if (~strcmp(date,'.') && ~strcmp(date,'..'))
                wdir=[weekdir,'/',date];
cd(wdir);

                % set path to program files
                path='E:/Speciale/Data/REA2010/Analyse/MatLab/';

                % read list of available data files (.LST format)
                LSTfiles = dir([wdir,'/*.LST']);

                for i = 1:length(LSTfiles)
% extract date and time from filename
[versn, name, ext] = fileparts(LSTfiles(i).name);

timestamp = str2num(name);
d(i,:) = timestamp;

DatFil1 = [name, '.dat'];
DatMat = dlmread(DatFil1);

NHup = DatMat(:,6);
NHdo = DatMat(:,7);

% Calculate maximum value of every minute (max_minute)
n=0;
for m = 1:600:length(NHup)
n=n+1;
max_up(n) = max(NHup(m:(m+599)));
max_do(n) = max(NHdo(m:(m+599)));
end

% Plot volt signals
figure(i)

subplot(2,1,1);
plot(max_up,'r--','LineWidth',1);
axis([0 30 0 2])
set(gca,'YGrid','on')
set(gca,'XGrid','on')
xlabel('['[min]')
ylabel('Volt [V]')
title(int2str(d(i)),'max_up','FontSize',10)

subplot(2,1,2);
plot(max_do,'g--','LineWidth',1);
axis([0 30 0 2])
set(gca,'YGrid','on')
set(gca,'XGrid','on')
xlabel('['[min]')
ylabel('Volt [V]')
title(int2str(d(i)),'max_do','FontSize',10)

sti2 = [wdir '\int2str(d(i))' 'volt_sort.jpg'];
print(sti2,'-djpeg');
close(i);

% write to files (.vol files)
maxdata = [max_up' max_do'];
sti = [wdir '/' name_'.vol'];
dlmwrite(sti,maxdata);
end
end
end
end
Calculating the ammonia concentration

```matlab
% nh3_conc
clear all; clc;

% initialising counters
i=0;
j=0;
k=0;
l=0;

% settings
maindir='g:/speciale/data/rea2010/data/sample4';

weeks = dir([maindir,'/*.']);
for k = 1:length(weeks)
    week = weeks(k).name;
    % spring over '.' og '..'
    if (~strcmp(week,'.')) && ~strcmp(week,'..'))
        weekdir=[maindir,'/',week];
        % hvor mange dage er der data for denne uge
        dates = dir([weekdir,'/*.']);
        for j = 1:length(dates)
            date = dates(j).name;
            % spring over '.' og '..'
            if (~strcmp(date,'.')) && ~strcmp(date,'..'))
                % set working directory
                wdir=[weekdir,'/',date];
                cd(wdir)
                % set path to program files
                path='g:/speciale/data/rea2010/analyse/matlab/';

                % read list of available data files (.lst format)
                lstfiles = dir([wdir,'/*.lst']);
                for i2 = 1:length(lstfiles)
                    % extract date and time from filename
                    [versn, name, ext] = fileparts(lstfiles(i2).name);
                    timestamp=str2num(name);
                    d(i2,:)=timestamp;

                    datfil1 = [name, '.vol'];
                    datmat=dlmread(datfil1);
                    nhup=datmat(:,1);
                    nhdo=datmat(:,2);

                    t=2;
                    cal_conc=25; % calibration liquid in ng/ml (1ng/ml is about 1ppb)
                    zero_sig_up=0.1029025;
                    cal_sig_up=(1.803391-zero_sig_up);
                    zero_sig_do=0.12839167;
```
cal_sig_do=(1.3866765-zero_sig_do);

liq_flow=0.08; %ml/min
air_flow=580; %ml/min

v_up=(nhup-zero_sig_up);

liqdo_conc=(v_up)/(cal_sig_up)*cal_conc; % is calculated as ngn/ml

v_std_up=std(nhup-zero_sig_up);

vplus_up=v_up+v_std_up;

vplus_do=v_do+v_std_do;

v_std_do=std(nhdo-zero_sig_do);
vminus_up=v_up-v_std_up;

vminus_do=v_do-v_std_do;

%calculate mean values of nh3_up, nh3_do, and d_nh3

evapo=0.55*exp(0.12*t);
cor_flow=liq_flow-(evapo*liq_flow)/100);
liqup_conc=(v_up)/(cal_sig_up)*cal_conc; % is calculated as ngn/ml

liqdo_conc=(v_do)/(cal_sig_do)*cal_conc; % is calculated as ngn/ml

nh3_up=((liqup_conc*1000)/(air_flow./cor_flow))*(100/99); % is calculated as ugn/m3

nh3_do=((liqdo_conc*1000)/(air_flow./cor_flow))*(100/99); % is calculated as ugn/m3

nh3_up_max=((liqup_conc_max*1000)/(air_flow./cor_flow))*(100/99);
nh3_do_max=((liqdo_conc_max*1000)/(air_flow./cor_flow))*(100/99);

%minimum

evapo=0.55*exp(0.12*t);
cor_flow=liq_flow-(evapo*liq_flow)/100);
liqup_conc_min=((vminus_up)/(cal_sig_up)*cal_conc;

liqdo_conc_min=((vminus_do)/(cal_sig_do)*cal_conc;
nh3_up_min=((liqup_conc_min*1000)/(air_flow./cor_flow))*(100/99);
nh3_do_min=((liqdo_conc_min*1000)/(air_flow./cor_flow))*(100/99);

%plot 'nh3_up','nh3 do','d_nh3'

figure(i2)
l=[1:30]';
plot(l,nh3_up,'r-',l,nh3_do,'g-',l,d_nh3,'b-');

% axis([0 2400 -5 2])
xlabel('time')
ylabel('nh3 [ug/m3]')
title([int2str(d(i2)),' delta nh3'],['fontsize',10])
legend('nh3_up','nh3_do','d_nh3')

%print to jpg file (d_nh3.jpg)
sti3 = ['e:/speciale/data/rea2010/data/sample4/d_nh3/'
int2str(d(i2)) ' d_nh3.jpg'];
Calculating half-hourly mean concentration

%MeanConc
clear all; clc;

%initialising counters
i=0;
j=0;
k=0;
l=0;
n=0;

%Settings
Maindir='G:/Speciale/Data/REA2010/Data/Sample4';

weeks = dir([Maindir,'/*.']);
for k = 1:length(weeks)
    week = weeks(k).name;
    %spring over '. ' og '..'
    if (~strcmp(week,'.') && ~strcmp(week,'..'))
        weekdir=[Maindir,'/',week];
        cd(weekdir)
        % set working directory
        wdir=[weekdir,'/',date];
        cd(wdir)
        %set path to program files
        path='G:/Speciale/Data/REA2010/Analyse/MatLab/';
        clear filelist;
        clear sorted_filelist;
        LSTfiles = dir([wdir,'/*.dyt']);
        for i2 = 1:length(LSTfiles)
            %write to file (.dyt file)
            data_d_nh3=[d_nh3 nh3_up nh3_do nh3_up_max nh3_do_max nh3_up_min nh3_do_min];
            sti4 = [wdir '/' name '.dyt'];
            dlmwrite(sti4,data_d_nh3);
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MATLAB scripts for REA calculations

% Extract date and time from filename
[versn, name, ext] = fileparts(LSTfiles(i2).name);
filelist(i2) = cellstr(name);
end

sorted_filelist = sort(filelist);

for i2 = 1:length(sorted_filelist)
    filename = strcat(wdir,'/',char(sorted_filelist(i2)),'.dyt');
    
    % Load data files
dytfiles = load(filename);
    NH3up=dytfiles(:,2);
    NH3do=dytfiles(:,3);
    
    % Calculate half hour mean, stdv, min, and max values
    NH3up_mean(i2) = mean(NH3up);
    NH3do_mean(i2) = mean(NH3do);

    stdv_up(i2) = std(NH3up);
    stdv_do(i2) = std(NH3do);

    min_up(i2) = min(NH3up);
    min_do(i2) = min(NH3do);

    max_up(i2) = max(NH3up);
    max_do(i2) = max(NH3do);

    DNH3(i2) = NH3up_mean(i2) - NH3do_mean(i2);
    Mean(i2) = mean(NH3up_mean(i2) + NH3do_mean(i2)); % WRONG. The right is calculated in excel!!!
end

% Write to file
sdate = [date(3:4),date(1:2)];
sti1=['G:/Speciale/Data/REA2010/Data/ConcFiles/' sdate '.cnc'];
dlmwrite(sti1,[NH3up_mean',NH3do_mean',stdv_up',stdv_do',min_up',min_do',max_up',max_up','DNH3','Mean']);
end
end
end
end

Calculating the vertical ammonia flux
% ReaFlux
clear all; clc;

% Initialising counters
i=0;
j=0;
k=0;
l=0;
n=0;

% Settings
Maindir='E:/Speciale/Data/REA2010/Data/Sample4';
weeks = dir([Maindir,'/*.']);
for k = 1:length(weeks)
    week = weeks(k).name;
    % spring over '.' og '..'
    if (~strcmp(week,'.') & & ~strcmp(week,'..'))
        weekdir=[Maindir,'/',week];
        % hvor mange dage er der data for denne uge
        dates = dir([weekdir,'/*.']);
        for j = 1:length(dates)
            date = dates(j).name;
            % spring over '.' og '..'
            if (~strcmp(date,'.') & & ~strcmp(date,'..'))
                % set working directory
                wdir=[weekdir,'/',date];
                cd(wdir)
                % set path to program files
                path='E:/Speciale/Data/REA2010/Analyse/MatLab/';
                LSTfiles = dir([wdir,'/*.LST']);
                for i2 = 1:length(LSTfiles)
                    % extract date and time from filename
                    [versn, name, ext] = fileparts(LSTfiles(i2).name);
                    timestamp=str2num(name);
                    d(i2,:) = timestamp;
                    % Load data files
                    datfiles = load([wdir,'/',name,'.dat']);
                    dytfiles = load([wdir,'/',name,'.dyt']);
                    % Define vectors
                    u = datfiles(:,1); % (18000x7 matrix)
                    v = datfiles(:,2); % (18000x7 matrix)
                    w = datfiles(:,3); % (18000x7 matrix)
                    t = datfiles(:,4); % (18000x7 matrix)
                    NH3up = dytfiles(:,2); % (30x2 matrix)
                    NH3down = dytfiles(:,3); % (30x2 matrix)
                    %%% OBS, hvis usikkerheder skal med
                    usik_up_add = (NH3up+0.0085);
                    usik_do_add = (NH3down+0.6916);
                    usik_up_sub = (NH3up-0.0085);
                    usik_do_sub = (NH3down-0.6916);
                    % Create new vectors
                    A=[u,v];
                    % Initialize new variables
                    uuup=0;
tup=0;
udown=0;
tdown=0;

%Calculate Tup, Tdown, Uup, and Udown
u_ny=sqrt(sum(A.^2,2));
U=mean(u_ny);
W=mean(w);
wf=w-W;

clear uup;
clear udown;

for n=1:length(wf);
    if wf(n)>0;
        uup(n)=u(n);
    else
        udown(n)=u(n);
    end
    if wf(n)>0;
        tup(n)=t(n);
    else
        tdown(n)=t(n);
    end
    n=n+1;
end

Uup=mean(uup);
Udown=mean(udown);
Tup=mean(tup);
Tdown=mean(tdown);

%Create new vectors
B=[t,w];
C=[u_ny,w];

%Calculate Tflux and Uflux
tflux=cov(B);
Tflux=tflux(1,2); %upper right corner
uflux=cov(C);
Uflux=uflux(1,2); %upper right corner

%Calculate stdw
stdw=std(w);

%Dynamic deadband set by Risoe
D=0.5*stdw; %Deadband set by Risoe

%Calculate Busingers constant (BetaU and BetaT) by Uflux and Tflux
BetaU=Uflux/(stdw*(Uup-Udown));
BetaT=Tflux/(stdw*(Tup-Tdown));

% Criterium for Beta values 0.2<B<0.8
if ((BetaT < 0.2) || (BetaT > 0.8))
    BetaT = 0.6; %Value set by Oncley et al. 1993
end
if ((BetaU < 0.2) || (BetaU > 0.8))
    BetaU = 0.6; % Value set by Oncley et al. 1993
end

% Calculate Businger's constant including deadband
BT = BetaT * exp(-0.75*D/stdw);
BU = BetaU * exp(-0.75*D/stdw);

Calculate the vertical NH3 flux
NH3flux_BT = BT * stdw * (NH3up - NH3down);
NH3flux_BU = BU * stdw * (NH3up - NH3down);

flux_1 = BT * stdw * (usik_up_add - usik_do_add);
flux_2 = BT * stdw * (usik_up_sub - usik_do_sub);
flux_3 = BT * stdw * (usik_up_add - usik_do_sub);
flux_4 = BT * stdw * (usik_up_sub - usik_do_add);

% Write to file
% NH3 flux
D = [NH3flux_BT, NH3flux_BU];
sti1 = [wdir '/ name ' .flx'];
dlmwrite(sti1, D);

% NH3 flux for stdv
D = [flux_1, flux_2, flux_3, flux_4];
sti1 = [wdir '/ name ' .sta'];
dlmwrite(sti1, D);

% Tflux, BetaT, Uflux, BetaU, and stdw
E = [Tflux, BetaT, BT, Uflux, BetaU, BU, stdw];
sti2 = [wdir '/ name ' .cov'];
dlmwrite(sti2, E);

figure(i2)
subplot(5,1,1);
plot(NH3flux_BT, 'b--', 'LineWidth', 1);
set(gca, 'YGrid', 'on')
set(gca, 'XGrid', 'on')
xlabel('[10 Hz]')
ylabel('[degree]')
title([int2str(d(i2)), ' NH3flux_BT', 'FontSize', 10])

subplot(5,1,2);
plot(NH3flux_BU, 'b--', 'LineWidth', 1);
set(gca, 'YGrid', 'on')
set(gca, 'XGrid', 'on')
xlabel('[10 Hz]')
ylabel('[m/s]')
title([int2str(d(i2)), ' NH3flux_BU', 'FontSize', 10])

sti2 = [wdir ' \ int2str(d(i2)) ' flux.jpg'];
print(sti2, '-djpeg');
close(i2);
end
end

Calculating half-hourly mean flux

% Mean Flux
clear all; clc;

% Initialising counters
i2=0;
j=0;
k=0;

% Settings
Maindir='G:/Speciale/Data/REA2010/Data/Sample4';

weeks = dir(fullfile(Maindir,'/*.'));
for k = 1:length(weeks)
    week = weeks(k).name;
    if (~strcmp(week,'.') && ~strcmp(week,'..'))
        weekdir(fullfile(Maindir, '/'), week);
        dates = dir(fullfile(weekdir,'/*.'));
        for j = 1:length(dates)
            date = dates(j).name;
            if (~strcmp(date,'.') && ~strcmp(date,'..'))
                wdir(fullfile(weekdir, '/'), date);

                % set path to program files
                path='G:/Speciale/Data/REA2010/Analyse/MatLab/';

                clear filelist;
                clear sorted_filelist;

                LSTfiles = dir(fullfile(wdir,'/*.flx'));
                for i2 = 1:length(LSTfiles)
                    [versn, name, ext] = fileparts(LSTfiles(i2).name);
                    filelist(i2) = cellstr(name);
                end

                sorted_filelist = sort(filelist);

                for i2 = 1:length(sorted_filelist)
                    filename1 = fullfile(wdir, './', char(sorted_filelist(i2)), '.flx');
                    filename2 = fullfile(wdir, './', char(sorted_filelist(i2)), '.cov');

                    % Load data files
                    flxfiles = load(filename1);
MATLAB scripts for REA calculations

covfiles = load(filename2);

NH3flux_BT=flxfiles(:,1);
NH3flux_BU=flxfiles(:,2);

Tflux(i2)=covfiles(:,1);
BetaT(i2)=covfiles(:,2);
BT(i2)=covfiles(:,3);
Uflux(i2)=covfiles(:,4);
BetaU(i2)=covfiles(:,5);
BU(i2)=covfiles(:,6);
stdw(i2)=covfiles(:,7);

%Calculate half hour mean values
fluxBT_mean(i2) = mean(NH3flux_BT);
stdv_fluxBT(i2) = std(NH3flux_BT);
min_fluxBT(i2) = min(NH3flux_BT);
max_fluxBT(i2) = max(NH3flux_BT);

fluxBU_mean(i2) = mean(NH3flux_BU);
stdv_fluxBU(i2) = std(NH3flux_BU);
min_fluxBU(i2) = min(NH3flux_BU);
max_fluxBU(i2) = max(NH3flux_BU);
end

%Write to file
sdate = [date(3:4),date(1:2)];
sti1=['G:/Speciale/Data/REA2010/Data/FImFiles/' sdate '.flm'];
dlmwrite(sti1,[fluxBT_mean',stdv_fluxBT',min_fluxBT',max_fluxBT',fluxBU_mean',stdv_fluxBU',min_fluxBU',max_fluxBU']);

sti2=['G:/Speciale/Data/REA2010/Data/CovFiles/' sdate '.cvm'];
dlmwrite(sti2,[Tflux',BetaT',BT',Uflux',BetaU',BU',stdw']);
end
end
end
H  OML-DEP $c_{NH3}$ and MM5 meteorological simulations

The $c_{NH3}$ calculated by OML-DEP of the full measuring period is indicating a weekly pattern that is found due to the meteorological variations. Examples are given here of the wind direction ($Dir$) and wind speed ($Spd$).

![Graph showing diurnal values of OML-DEP $c_{NH3}$ and MM5 simulations of wind direction and wind speed.]

**Figure H.1:** Diurnal values of OML-DEP $c_{NH3}$ and MM5 simulations of wind direction and wind speed.
I COTAG sonic anemometer meteorology

Some examples of the meteorological variables measured from the COTAG system during the full measuring period indicating instrumental failure in the first sampling period (10 Aug – 31 Aug 2010).

Figure I.1: Half-hourly values of meteorological variables measured from the COTAG system.
**J  $F_{NH3}$ calculated on two different Busingers values**

$F_{NH3}$ was calculated on two different derives of Busingers value. One from the temperature flux ($\beta t$) and one of the momentum flux ($\beta u$).

**Figure J.1:** $F_{NH3}$ calculated on Busingers values determined from momentum flux (BU) and heat flux (BT).
K  Relation between $c_{\text{NH}_3}$ and meteorology

The correlations between $c_{\text{NH}_3}$ and meteorology are investigated for the measured and the modelled parameters and meteorology respectively.

Figure K.1: Measured $c_{\text{NH}_3}$ vs. meteorology

Figure K.2: Modelled $c_{\text{NH}_3}$ vs meteorology
L  Relation between $F_{\text{NH}_3}$ and meteorology

The correlations between the estimated flux and meteorology are investigated for the measured and the modelled flux and meteorology respectively.

![Graphs showing correlation between flux and meteorology](image1)

**Figure L.1:** Measured $F_{\text{NH}_3}$ vs. meteorology

![Graphs showing correlation between flux and meteorology](image2)

**Figure L.2:** Modelled $F_{\text{NH}_3}$ vs. meteorology
According to the European Habitats Directive, Denmark is committed to sustain and protect high biodiversity levels in selected sensitive ecosystems. Exceedances of critical loads of atmospheric nitrogen to particularly Danish forest have been demonstrated from model calculations. Modelling and measuring atmospheric ammonia concentrations and fluxes in forests are, however, challenging due to high reactivity of ammonia, complex forest-atmosphere interactions, and lacking knowledge of ammonia exchange between vegetative surfaces and the atmosphere. In this project, the atmospheric concentration, flux, and dry deposition velocity of ammonia above deciduous forest have been investigated for validating the performance of current assessment techniques in relation to environmental management. An experimental investigation has been carried out for the beech forest site, Lille Bøgeskov, assessing atmospheric NH$_3$ using two micrometeorological measurement techniques; relaxed eddy accumulation (REA) and Conditional time average gradient (COTAG), and the local-scale deposition model (OML-DEP). The leaf area index has been measured regularly to investigate the sensitivity of atmospheric ammonia to vegetative dynamics of forests. Measured and modelled ammonia concentrations were in good agreement varying in the range of 0.56-0.68 µg NH$_3$-N m$^{-3}$. The results were, however, inconsistent considering ammonia fluxes. Evident emission fluxes of up to about 0.8 µg NH$_3$-N m$^{-2}$ s$^{-1}$ after leaf fall contributing to the atmospheric concentration of ammonia were found with REA. This was shown neither with COTAG nor with OML-DEP. The inconsistency is related to large uncertainties in measurements due to sensitivity of REA, potential difficulties of using COTAG above forest, and missing process descriptions of vegetative ammonia emissions in OML-DEP. No significant sensitivity of LAI on calculations of the dry deposition velocity was observed. An area of improvement could be, to include LAI in the parameterization of $z_0$. Integrated approaches of combining measurements and modelling in CL assessment are valuable tools. Improved measurement techniques and improved process descriptions for local-scale exchange models are, however, still needed to obtain improved determinations and assessments of CLs.