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Investigating sources of measured forest-atmosphere ammonia fluxes using two-layer bi-directional modelling

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Abstract

Understanding and predicting the ammonia (NH₃) exchange between the biosphere and the atmosphere is important due to the environmental consequences of the presence of reactive nitrogen (Nᵣ) in the environment. The dynamics of the natural sources are, however, not well understood, especially not for forest ecosystems due to the complex nature of this soil-vegetation-atmosphere system. Furthermore, the high reactivity of NH₃ makes it technically complex and expensive to measure and understand the forest-atmospheric NH₃ exchange. The aim of this study is to investigate the NH₃ flux partitioning between the ground layer, cuticle and stomata compartments for two temperate deciduous forest ecosystems located in Midwestern, USA (MMSF) and in Denmark (DK-Sor). This study is based on measurements
and simulations of the surface energy balance, fluxes of CO2 and NH3 during two contrasted periods of the forest ecosystems, a period with full developed canopy (MMSF) and a senescent period for the DK-Sor site, with leaf fall and leaf litter build-up. Both datasets indicate emissions of NH3 from the forest to the atmosphere. The two-layer NH3 compensation point model SURFATM-NH3 was used in combination with a coupled photosynthesis-stomatal conductance model to represent seasonal variation in canopy physiological activity for simulating both net ecosystem CO2 exchange rates ($R^2 = 0.77$ for MMSF and $R^2 = 0.84$ for DK-Sor) and atmospheric NH3 fluxes ($R^2 = 0.43$ for MMSF and $R^2 = 0.60$ for DK-Sor). A scaling of the ground layer NH3 emission potential ($I'_g$) was successfully applied using the plant area index ($PAI$) to represent the build-up of a litter layer in the leaf fall period. For a closed green forest canopy (MMSF), unaffected by agricultural NH3 sources, NH3 was emitted with daytime fluxes up to 50 ng NH3-N m$^{-2}$ s$^{-1}$ and nighttime fluxes up to 30 ng NH3-N m$^{-2}$ s$^{-1}$. For a senescing forest (DK-Sor), located in an agricultural region, deposition rates of 250 ng NH3-N m$^{-2}$ s$^{-1}$ were measured prior to leaf fall, and emission rates up to 670 ng NH3-N m$^{-2}$ s$^{-1}$ were measured following leaf fall. For MMSF, simulated stomatal NH3 emissions explain the daytime flux observations well, and it is hypothesized that cuticular desorption is responsible for the observed NH3 emissions at night. During leaf fall in DK-Sor, ground fluxes dominate the NH3 flux with a mean emission rate of 150 ng NH3-N m$^{-2}$ s$^{-1}$. This study shows that forests potentially comprise a natural source of NH3 to the atmosphere, and that it is crucial to take into account the bi-directional exchange processes related to both the stomatal, cuticular and ground layer pathways in order to realistically simulate forest–atmosphere fluxes of NH3.

Keywords: ammonia; biosphere atmosphere exchanges; compensation point; deciduous forest; measurements; modelling

1 Introduction

Predicting the surface exchange of atmospheric ammonia (NH3) is important in order to assess the environmental consequences of the presence of reactive nitrogen (Nr) in the environment (Sutton et al. 2011). However, prediction of the NH3 exchange between the biosphere and the atmosphere with process-based models is challenging due to the complex nature of the soil-vegetation-atmosphere system (e.g., Sutton et al. 2013). These exchange
processes are controlled by a number of feedback mechanisms depending on climatic,
biological, chemical and physical conditions (Flechard et al. 2013).

Atmospheric chemistry and transport models (CTMs) are recognized tools for studying the
fate of nitrogen (N) in the coupled biosphere – atmosphere system (Bash et al. 2013; Pinder et
al. 2008; Rao et al. 2011; Tuccella et al. 2012; Wichink Kruit et al. 2012). In the past decade,
these models have been improved substantially to represent the governing processes that
determine atmospheric NH₃ fluxes (e.g., Hertel et al. 2012; Hamaoui-Laguel et al. 2014;
Hendriks et al. 2013). This includes the development of dynamic NH₃ emissions models
(Paulot et al. 2014; Skjøth et al. 2011), detailed NH₃ emission inventories (Paulot et al. 2014;
Pouliot et al. 2012; Kuenen et al. 2014; Vethof et al. 2012) and the parameterization of
processes for simulating canopy NH₃ compensation points (Bash et al. 2013; Wichink Kruit et
al. 2012), i.e., the atmospheric NH₃ concentrations at which the net atmospheric NH₃ flux is 0
ng m⁻² s⁻¹.

Emissions of atmospheric NH₃ are mainly related to agriculture (Reis et al. 2009), generally
as a result of volatilizations from animal husbandry, the storages and spreading of manure and
mineral fertilizer (Skjøth and Geels 2013) that were found to be the dominant drivers of the
spatial and temporal atmospheric NH₃ concentrations (Hertel et al. 2012; Sutton et al. 2013).
However, NH₃ emissions also occur from natural sources such as from wild animals (e.g.,
Riddick et al. 2014; Theobald et al. 2006), forest fires (e.g., Andreea and Merlet 2001; Van
Damme et al. 2014b), sea surfaces (e.g., Sørensen et al. 2003), terrestrial ecosystems (e.g.,
Andersen et al. 1999; Hansen et al. 2013; Sutton et al. 1997), and from the chemical
partitioning of N compounds between the gas and aerosol phases (Pryor et al. 2001), but the
dynamics of these natural sources are not well understood, especially not for unmanaged
2011).

Atmospheric NH₃ exchange with the biosphere is bi-directional and it follows several
pathways; the soil, the leaves cuticles, and the stomata (e.g., Nemitz et al. 2001). Usually, it
has been assumed that NH₃ deposition occurs onto leaf surfaces and natural NH₃ emissions
occurs through the stomata depending on a stomatal NH₃ compensation point (Farquhar et al.
1980a). However, the fluxes can be bi-directional for all the compartments and depend on the
concentration difference between the atmosphere and the compartment. Each compartment
has a varying (unitless) NH₃ emission potential ($T$) which is defined as the ratio of ammonium
(NH$_4^+$) to hydrogen (H$^+$) ions in the water (Schjoerring et al. 1998). Usually the ground is the main source of NH$_3$, especially in agricultural ecosystems which receive large amount of nitrogen (Nemitz et al. 2000a; Sutton et al. 2009; Personne et al. 2015; Ferrara et al. 2014). These emissions may be due to direct emissions due to agricultural operations such as application of slurry (e.g., Ferrara et al. 2016) or may also be due to the microbiological breakdown of leaf litter (Nemitz et al. 2000a; David et al. 2009). Breakdown of litter also happens in non-agricultural systems such as forests where it was found to contribute to ecosystem fluxes of biogenic volatile organic compounds (BVOCs) (Greenberg et al. 2012) contributing to feed-back mechanisms within the Earth system (e.g., Carslaw et al. 2010). Forest NH$_3$ emissions have been observed in late summer/autumn periods that may be related to litter decomposition and soil evaporation (Hansen et al. 2013; Hansen et al. 2015) indicating that such sources could be relevant to include in CTM models.

In bi-directional NH$_3$ exchange models, the unitless NH$_3$ emission potentials of the ground layer ($\Gamma_g$) and stomata ($\Gamma_s$) are required to simulate the NH$_3$ compensation points of the ground layer and the stomata, respectively (Wichink Kruit et al. 2010). Typically, these models use constant $\Gamma$-values based on measurements, however, such measurements yet only exist to a very limited extent and are demanding to conduct. Furthermore, there is a substantial need to represent dynamic growing seasons in existing CTMs (Simpson et al. 2012) in order to represent realistic seasonal vegetation and ground layer emissions of nitrogen oxide (NO), NH$_3$, and BVOCs. During the growing season, physiological and biogeochemical processes cause seasonal variations in photosynthesis, stomatal conductance, leaf development as well as N mobilization and translocation (Wang et al. 2013). These processes are affecting the stomatal emission potential (Wang et al. 2011) and stomatal conductance being strongly correlated with both NH$_3$ emission and deposition fluxes of leaves (Gessler et al. 2000). Furthermore, seasonal variation includes the dynamic development of a leaf litter layer and decomposition influencing the ground layer emission potential (Callesen et al. 2013).

The aim of this study was to investigate the contribution of the leaves and forest floor to the net NH$_3$ exchange at different development stages of the forest including fully developed and senescing periods. By using the two-layer bi-directional exchange model SURFATM-NH$_3$ (Personne et al. 2009) as a comparison and interpretation tool, the simulated fluxes are evaluated for two temperate deciduous forest reported by Hansen et al. (2013 and 2015). First,
the partitioning and the temporal pattern of the net flux of NH₃ measured above the two temperate deciduous forests are presented and then, the sources of NH₃ are interpreted and discussed in relation to the phonological state of the forest canopies.

2 Methods

2.1 Experimental data and sites

The atmospheric NH₃ concentration and fluxes of NH₃, carbon dioxide (CO₂) and heat were measured at two temperate deciduous forest sites, a beech forest study site in Denmark (DK-Sor) for 25 days during late fall in 2010 (Hansen et al. 2013), and the Morgan-Monroe State Forest (MMSF) site in the central Midwestern USA for 5 days during late summer in 2013 (Hansen et al. 2015) (Table 1). The atmospheric NH₃ measurements were conducted with half-hourly temporal resolution using the Relaxed Eddy Accumulation (REA) method (Businger and Oncley 1990) in combination with Wet Effluent Diffusion Denuders (WEDD) (Sørensen et al. 1994).

2.1.1 The DK-Sor site

The DK-Sor forest is located in the central part of Zealand (55°29’N, 11°38’E). The forest consists predominantly of beech trees (*Fagus sylvatica* L.) with an average canopy height of 26 m and covers 2.5 km². The mean summer peak plant area index (*PAI*) in the period 2000 to 2011 was 4.6 m² m⁻² with maximum *PAI* just above 5 m² m⁻² (Pilegaard et al. 2011). The surrounding landscape is dominated by agricultural land use. During the 25 day measurement campaign (21 October to 15 November 2010), the measured forest canopy *PAI* (LAI-2000, Li-Cor, USA) decreased from 3.7 m² m⁻² to 1.1 m² m⁻² and the mean temperature was 6.7°C. Leaf fall ended on 8 November (Hansen et al. 2013) where *PAI* equalizing 1.1 m² m⁻² representing trunks and branches only.

2.1.2 The MMSF site

Morgan-Monroe State Forest (MMSF) is located at 39°53’N, 86°25’W in Southern Indiana, USA. MMSF is a secondary successional broadleaf forest dominated by the deciduous tree species tulip poplar (*Liriodendron tulipifera*), white oak (*Quercus alba*), sassafras (*Sassafras albidum*), and sugar maple (*Acer saccharum*) and covers 97 km². The canopy height is 28-30
m and the summer peak PAI during 2013 was 4.6 m² m⁻² (Hansen et al. 2015). Beyond the limits of the forest, the surrounding land cover is dominated by cropland. During the 5-day measurement campaign (5 September to 10 September), PAI was 4.5 m² m⁻² and the mean temperature was 24.5°C.

2.1.3 CO₂ and energy fluxes

Carbon dioxide and energy flux observations and meteorological data used for input to the models or model validation were obtained from the European and American Fluxes Database Clusters; FluxNet (www.europe-fluxdata.eu) and AmeriFlux (http://ameriflux.ornl.gov). Eddy covariance data were gap-filled, flux-partitioned, and friction velocity (u*) corrections were applied according to the standard procedure in FluxNet (Papale et al. 2006; Reichstein et al. 2005).

The energy flux data for the DK-Sor site needed to be filtered due to a sensitivity of the sonic anemometer that made sonic temperature fluctuation measurements at high wind speeds unreliable. Data points during periods with high wind speeds (> 5 m s⁻¹) (DOY 294–300 and 307–310) were therefore removed.

2.2 The SURFATM-NH₃ model

The SURFATM-NH₃ model (Personne et al. 2009) is a one-dimensional model that uses a two-layer bi-directional NH₃ exchange scheme including a stomatal and ground layer NH₃ compensation point. By coupling a water and energy balance model with the two-layer NH₃ resistance scheme, SURFATM-NH₃ simulates the atmospheric NH₃ flux based on measured atmospheric NH₃ concentrations, and meteorological and vegetation input (net radiation, soil and air temperature, relative air humidity, wind speed, PAI and rain. The model furthermore, uses predefined NH₃ emission potentials for stomata and the ground layer of the site. The scheme is based on the traditional resistance analogue describing the bi-directional transport of NH₃ governed by a set of resistances controlled by the atmosphere, rₐ (s m⁻¹), the quasi-laminar boundary layer, rₚ (s m⁻¹), and the canopy, rₖ (s m⁻¹) respectively (e.g., Erisman and Wyers 1993). It expands the existing one-layer canopy NH₃ compensation point model (Sutton et al. 1998) with a ground layer compensation point, χₔ (mol l⁻¹), allowing emissions from the ground layer (Nemitz et al. 2001) (see Appendix A). In a similar way to the stomatal NH₃ compensation point, χₛ (mol l⁻¹), χₔ is estimated from the Henry’s law and dissociation
constants \((K_H = 10^{-1.76\text{ (unitless)}}\) and \(K_d = 10^{-9.25\text{ mol L}^{-1}}\) \text{ (Equation 1)}\) and the dimensionless emission potential of the ground layer \((\Gamma_g)\) \text{ (Equation 2)}.

\[
\chi_g = \Gamma_g \times K_d \times K_H \times \exp \left( \frac{\Delta H_{HH}^0 + \Delta H_d^0}{R} \times \left( \frac{1}{298.15} - \frac{1}{T_g} \right) \right) \quad (1)
\]

\[
\Gamma_g = \frac{[\text{NH}_4^+]}{[\text{H}^+]} \quad (2)
\]

with \(\Delta H_{HH}^0\) and \(H_d^0\) being free enthalpies of acid-base dissociation \(\text{NH}_4^+ / \text{NH}_3\) (kJ mol\(^{-1}\)) and for \(\text{NH}_3\) volatilization (kJ mol\(^{-1}\)) \text{ (Personne et al. 2009)}, \(R\) \(0.00831\text{ kJ K}^{-1}\text{ mol}^{-1}\) is the perfect gas constant, and \(T_g\) (K) is the temperature of the ground layer. The model simulates the total net atmospheric \(\text{NH}_3\) flux, \(F_T\) (\(\mu\text{g m}^{-2}\text{ s}^{-1}\) as a sum of each of the forest component fluxes; the stomatal, \(F_s\) (\(\mu\text{g m}^{-2}\text{ s}^{-1}\)), cuticular, \(F_w\) (\(\mu\text{g m}^{-2}\text{ s}^{-1}\)), and ground, \(F_g\) (\(\mu\text{g m}^{-2}\text{ s}^{-1}\)), flux which are all related to the \(\text{NH}_3\) canopy compensation point, \(\chi_c\) (\(\mu\text{g m}^{-3}\)) \text{ (see Appendix A)}.

2.3 Model setup

The SURFATM-NH3 model runs with a set of initialized state variables, physical parameters and constants (Table 2). As SURFATM-NH3 was formerly applied for agricultural sites \text{ (Personne et al. 2015; Loubet et al. 2012)}\, model parameters were adjusted to represent the two forest sites. When available, field measurements were used to set or calculate parameter values, or parameters were taken from published scientific work carried out at the sites \text{ (see references in Table 2)}\,. Otherwise, theoretical values were used \text{ (see references in Table 2)}\, or parameters were estimated by trial-error method within a range of realistic values found in the scientific literature \text{ (see Table 2)}.

2.3.1 Modelling the stomatal resistance

A physiologically based leaf photosynthesis-stomatal conductance model approach proposed by Collatz et al. \text{ (1991)}\, was used to simulate stomatal resistance \((r_s)\). Based on dynamic coupling between a stomatal conductance, \(g_s\) \text{ (m s}^{-1}\) \text{ model formulated by Ball et al. \text{ (1987)}\, (Equation 4)}\, and mechanistic simulations of photosynthesis \text{ (Equation 5)}\, the stomatal resistance \((r_s = 1/g_s)\) was simulated and included in SURFTAM-NH3

\[
g_s = m \frac{A_n h_s}{C_s} + b \quad (4)
\]

\[
A_n = \min \{J_E, J_C, J_S\} - R_D \quad (5)
\]
The relative humidity at leaf surface, $h_s$ (unitless), and the CO₂ partial pressure at leaf surface, $C_s$ (Pa), determines $g_s$ along with leaf scale net carbon assimilation, $A_n$ (mol m⁻² s⁻¹), and two fixed constants ($m = 7$ and $b = 0.01$ mol m⁻² s⁻¹) representing the slope and intercept. $A_n$ is determined by the minimum of three potential capacities and the leaf dark respiration, $R_D$ (mol m⁻² s⁻¹) following Equation 5 (Collatz et al. 1991; Farquhar et al. 1980b). $J_C$ (mol m⁻² s⁻¹) is the light-limited assimilation rate, $J_S$ (mol m⁻² s⁻¹) is the rubisco-limited assimilation rate, and $J_S$ (mol m⁻² s⁻¹) is the assimilation rate due to the limitation of the export of assimilates inside the leaf. Measured $PAI$ is used as model input to upscale leaf simulations to canopy scale (Sellers et al. 1992). Details of the coupled photosynthesis-stomatal conductance model and the soil/ecosystem respiration parameterization are described in Appendix B. The results from using the $g_s$ model were evaluated using measured eddy covariance CO₂ fluxes (Pilegaard et al. 2011; Schmid et al. 2000) to verify NEE simulations. The simulated $r_s$ estimates were then utilized for modelling the atmospheric NH₃ exchange rate using SURFATM-NH₃. The simulations were performed for the full years 2010 (DK-Sor) and 2013 (MMSF) to examine the seasonal performance of the model.

### 2.3.2 Emission potential of the ground layer ($Γ_g$) and the stomata ($Γ_s$)

The NH₃ emission potentials of the ground layer and stomata, $Γ_g$ and $Γ_s$, were not measured at the two sites during the measurement campaigns. Therefore, measurements of $Γ_s$ from late fall period in 2008 and 2009 from the DK-Sor site, reported by Wang et al. (2011 and 2013), were used to set $Γ_s = 200$ for DK-Sor representative of senescing leaves, and a constant value for MMSF of 400 was used to represent $Γ_s$ of a green forest canopy with $PAI$ close to its maximum value. In this paper, we suggest a scaling of $Γ_g$ in the leaf fall period using $PAI$ to represent N enrichment of the ground layer (soil + litter) due to litter fall:

$$Γ_g = Γ_{g,\text{min}} + [(Γ_{g,\text{max}} - Γ_{g,\text{min}}) × ΔPAI]$$

where $ΔPAI = 1 - \left(\frac{PAI - PAI_{\text{min}}}{PAI_{\text{max}} - PAI_{\text{min}}}\right)$ represents the change in the litter layer derived from the measured $PAI$ using the LAI-2000 sensor (Figure 1). Considering the lag time from the beginning of leaf fall until decomposition is efficient, the scaling is applied for the period with $PAI$ decreasing from 3.5 (hence $PAI_{\text{max}} = 3.5$ m² m⁻²) until it reaches its minimum value ($PAI_{\text{min}} = 1.1$ m² m⁻²). Predefined minimum and maximum values of $Γ_g$ are used. We set $Γ_{g,\text{min}} = 300$ based on litter measurements from Wang et al. (2011 and 2013), and $Γ_{g,\text{max}} = 18000$ is
estimated by trial and error method to represent the higher ground layer N emission potential following the leaf fall period (Figure 1).

3 Results

3.1 Model testing for energy and CO₂ fluxes

Before SURFATM-NH₃ was applied to simulate the atmospheric NH₃ fluxes above the two forests, the model’s physical representation of the ecosystem dynamics was evaluated by 1) verifying the physiological representation of the canopy by comparing measured and modelled NEE, and 2) comparing simulated and measured energy fluxes.

SURFATM-NH₃ was run for all days with available NH₃ flux data for this study, i.e., 5 days in the late summer 2013 (DOY 248–253) for the MMSF forest site, and 25 days during the leaf fall period 2010 (DOY 294–319) for the DK-Sor site (Figure 2).

3.1.1 Net ecosystem exchange (NEE)

Model simulations of NEE are strongly correlated with measured CO₂ flux data (Figure 3) for both MMSF ($R^2 = 0.77$) and DK-Sor ($R^2 = 0.84$), and high concordance correlation coefficients (CCC) further signify good agreement between data and simulations of the two sites ($CCC = 0.72$ for MMSF and $CCC = 0.83$ for DK-Sor). For DK-Sor, the stomatal activity was less towards the end of the observation period due to leaf senescence and leaf fall. Hence the modelled atmospheric fluxes were less sensitive to leaf-scale $r_s$ variability in that period. The close agreement of the simulated CO₂ fluxes to the measured CO₂ fluxes ensures the consistent integration of the stomatal resistance $r_s$ in SURFTAM-NH₃ model.

3.1.2 Energy fluxes

During the measurement period of MMSF, the forest PAI was 4.5 m² m⁻², the mean temperature was 24.3 °C, and it rained 12.8 mm (Table 1). The rain fell within a 3-4 hour period during the night on DOY 251 (Figure 2). Over the five days, the energy fluxes showed a typical pattern for vegetated ecosystems of peak fluxes during daytime with sensible heat fluxes ($H$) of up to 200 W m⁻² and latent heat fluxes ($LE$) of up to 400 W m⁻². Ignoring in-canopy heat storage and metabolic terms, the average instantaneous energy balance closure fraction $(H+LE)/(R_{n}-G)$ was 0.50 (Figure 4a), however accounting for the storage terms is
important for the energy balance closure (Stoy et al. 2013). The model simulates the diel patterns and ranges of the energy fluxes in strong agreement with observations, i.e., \( R^2 = 0.78 \) and \( CCC = 0.69 \) for \( H \), and \( R^2 = 0.87 \) and \( CCC = 0.78 \) for \( LE \) (Table 3).

The measurement period of DK-Sor was characterized by decreasing temperatures, leaf senescence and leaf fall. The canopy \( PAI \) decreased from 3.7 m\(^2\) m\(^{-2}\) to 1.1 m\(^2\) m\(^{-2}\) between DOY 294 and 312, and the mean temperature throughout the period was 6.7 ± 2.6°C (Table 1). \( LE \) was continuously lower than 200 W m\(^{-2}\), and \( H \) reached a daytime maximum of 100 W m\(^{-2}\) only twice for the 25 days of observed period. The simulated reference evaporation (Allen et al. 1998) confirmed low atmospheric evaporative demand (between -50 and 100 W m\(^{-2}\)) during the rainy and overcast measurement period (Figure 2). Even though the energy balance closure (Figure 4b) and the statistical synthesis for the comparison between simulations and measurements for the DK-Sor site (Table 3) are very weak during this overcast and rainy period (i.e., \( R^2 = 0.17 \) and \( R^2 = 0.07 \) for \( H \) and \( LE \), respectively), the typical diel pattern of the fluxes \( (H \) and \( LE \)) is clearly recognized (Figure 2).

### 3.2 Ammonia fluxes

At MMSF, the fluxes were positive during both day and night, indicating a release of NH\(_3\) from the forest ecosystem to the atmosphere. The measured NH\(_3\) fluxes showed a clear daytime pattern with maximum emissions during midday of up to 51.6 ng NH\(_3\)-N m\(^{-2}\) s\(^{-1}\) (Figure 5a), and the model represented the same day-time pattern with peak emissions during midday. The simulated range of daytime NH\(_3\) emissions is also in good agreement with measurements during most of the period (between 36 and 46 ng NH\(_3\) m\(^{-2}\) s\(^{-1}\)), however, the NH\(_3\) fluxes are overestimated during midday on the last two days. During nighttime, the model simulated zero or negative net NH\(_3\) exchange, while emissions of up to 30 ± 70 ng NH\(_3\)-N m\(^{-2}\) s\(^{-1}\) were measured.

The measured NH\(_3\) fluxes for DK-Sor show deposition fluxes of −250 ± 300 ng NH\(_3\)-N m\(^{-2}\) s\(^{-1}\) in the beginning of the period that gradually change to emission fluxes of up to 670 ± 280 ng NH\(_3\)-N m\(^{-2}\) s\(^{-1}\) towards the end of the measurement period (Figure 5b). This change occurred due to leaf senescence and leaf fall causing a smaller canopy surface area for NH\(_3\) depositions and possibly NH\(_3\) emissions related to N translocation and soil emissions (Hansen et al. 2013). Contrary to NH\(_3\) flux measurements at MMSF, no clear diurnal variation was observed in NH\(_3\) fluxes during the leaf-fall period in DK-Sor. Fluxes turned from negative
(deposition) to positive (emission) on DOY 303 at which time PAI had decreased from 4 m$^2$ m$^{-2}$ to less than 3 m$^2$ m$^{-2}$. The mean emission rate was 150 ± 138 ng NH$_3$-N m$^{-2}$ s$^{-1}$ during the rest of the measurement period (until DOY 319). The model simulated well the measured NH$_3$ emissions following leaf fall, however, during DOY 314–316, a NH$_3$ emission event with fluxes up to 500 ± 131 ng NH$_3$-N m$^{-2}$ s$^{-1}$ was measured which was not captured by the model.

3.3 Ammonia flux contributions

The SURFATM-NH$_3$ model was used to analyze the contribution of the individual sources to the total flux. It was found that for MMSF (Figure 6a), the stomatal exchange was the main contributor (up to 50 ng NH$_3$-N m$^{-2}$ s$^{-1}$) to the simulated forest NH$_3$ emissions during daytime. The strong stomatal control of NH$_3$ emissions is in turn controlled by environmental factors with a strong diel signal (radiation, temperature, humidity, CO$_2$). The modelled deposition to the leaf cuticles was small (up to 4.5 ng NH$_3$-N m$^{-2}$ s$^{-1}$) and predominant during the night when the other components were less active, and relative air humidity was high. The modelled ground layer only contributed with small emissions during day time (up to 1.5 ng NH$_3$-N m$^{-2}$ s$^{-1}$). The observed nighttime emissions were not simulated by the model.

For DK-Sor, during leaf fall (Figure 6b), the diurnal pattern differed substantially from that of the green canopy of MMSF. Here, the ground layer, or more specifically the fresh decomposing litter layer, was by far the largest contributor (up to 150 ng NH$_3$-N m$^{-2}$ s$^{-1}$) to the total simulated NH$_3$ emissions from the forest to the atmosphere. Depositions (up to 30 ng NH$_3$-N m$^{-2}$ s$^{-1}$) to the cuticular surfaces were simulated for DK-Sor whereas stomata were inactive during most of the measurement period due to advanced leaf senescence, and hence did not contribute significantly to the regulation of the NH$_3$ flux. The NH$_3$ fluxes thus showed a less pronounced diel pattern (Figure 6b) with slightly higher emissions during daytime (average of 91 ng NH$_3$-N m$^{-2}$ s$^{-1}$) as compared to nighttime (average of 70 ng NH$_3$-N m$^{-2}$ s$^{-1}$).

3.4 Model sensitivity to the emission potentials

The sensitivity of the simulated mean diel NH$_3$ flux to the emission potentials for leaves ($I_s$) and the ground layer ($I_g$), respectively, was examined for the different phenological stages represented by the two studied forests. For this purpose, a range of 0-1000 was chosen for $I_s$
and 0-30000 for $I_g$ as inputs for SURFATM-NH$_3$ modelling. The modelled NH$_3$ fluxes of the green forest canopy were sensitive to $I_g$ (Figure 7a), but this was not the case for the senescing forest canopy (Figure 7b) with PAI decreasing from 3.7 $m^2 m^{-2}$ to 1 $m^2 m^{-2}$ (Figure 1). During and after leaf fall, the modelled NH$_3$ fluxes of DK-Sor were very sensitive to $I_g$, while the sensitivity of NH$_3$ fluxes to the large range of $I_g$ input values is less for MMSF (Figure 7c and 7d). Due to the use of PAI for scaling $I_g$ in this study (Equation 6), $I_g$ will however remain low (close to $I_{g,min}$) for a green closed canopy such as MMSF, and this causes also the simulated soil NH$_3$ fluxes to remain low (Figure 6a) irrespective of the parameter value set for $I_{g,max}$. In contrast, the simulated NH$_3$ fluxes of senescent forests (e.g., DK-Sor) will remain very sensitive to the chosen parameter value for $I_{g,max}$, and the soil NH$_3$ emission contributes significantly to the canopy NH$_3$ fluxes in this case (Figure 6b).

4 Discussion

This study aimed to analyze contributions of measured NH$_3$ fluxes from individual forest compartments (ground layer, cuticle and stomata) and to quantify these individual contributions to the net forest - atmosphere NH$_3$ flux for two deciduous forests showing distinct diurnal (MMSF) and non-diurnal (DK-Sor) NH$_3$ flux patterns indicative of forest NH$_3$ emissions. The distinct diurnal and non-diurnal flux patterns may be related to dominant processes influencing forest NH$_3$ emissions in different phenological phases and in different landscape settings. In particular, MMSF is located in a remote region while DK-Sor is located in an agricultural region characterized by large atmospheric NH$_3$ depositions in the growing season (Hansen et al. 2013). Thus, only MMSF (not DK-Sor) show NH$_3$ emissions in the green (mid-season) period, and only DK-Sor (not MMSF) show NH$_3$ emissions in the leaf-fall period (see Hansen et al. 2013; 2015). In order to analyze the sources of the observed NH$_3$ flux emissions of the two different (remote and anthropogenic) deciduous forests, we used the biophysical bi-directional surface model SURFATM-NH$_3$ in combination with a physiologically based leaf photosynthesis-stomatal conductance model (Collatz et al. 1991) for simulating the NH$_3$ and CO$_2$ fluxes in different phenological stages. The good agreement for the energy and NEE fluxes between measurements and simulations gives confidence in the model representation of the physical and physiological processes that are important for simulating and analyzing the observed forest - atmosphere NH$_3$ exchange.
4.1 Forest – atmosphere NH3 fluxes

4.1.1 MMSF – a natural green forest canopy

Overall, the daytime magnitude of the NH3 fluxes from the green canopy at MMSF (up to 50 ng NH3-N m⁻² s⁻¹) and the diurnal pattern of the NH3 fluxes from the forest were simulated moderately well with SURFATM-NH3 ($R^2 = 0.45$). In particular, daytime stomatal NH3 emissions are well simulated (in the range 36 and 46 ng NH3 m⁻² s⁻¹), however slightly overestimated during midday, whereas measured nighttime NH3 emissions (up to 30 ng NH3-N m⁻² s⁻¹) were not represented by the model (Figure 5a). Nighttime emissions of NH3 are rarely reported in the scientific literature because deposition fluxes exceed emission rates in most studies. Exceptions are crop fields and managed grasslands where fertilization causes NH3 volatilization from soil and fertilizers during both day and night (e.g., David et al. 2009; Sutton et al. 2009). In contrast, the MMSF station represents a remote natural site with very low atmospheric NH3 concentrations ($\approx 0.5$ μg NH3-N m⁻³) and inferior NH3 deposition (Figure 6a). If the atmospheric NH3 concentration is lower than the NH3 compensation point, natural ecosystems may act as a source of NH3 (Langford and Fehsenfeld 1992). Sites with low N supply are generally expected to have low NH3 compensation points (e.g., Massad et al. 2010a; Zhang et al. 2010). The sources of NH3 emissions are further discussed on the basis of observed and modelled NH3 emissions in section 4.2.

4.1.2 DK-Sor - a senescent forest influenced by anthropogenic NH3 depositions

For DK-Sor, NH3 depositions up to 250 ng NH3-N m⁻² s⁻¹ were measured during the first five days when PAI was $\sim 3$ m² m⁻² (Figure 5b). The model was not able to represent these deposition rates. Indeed, the measurements exceed the maximum possible flux permitted by turbulent transfer ($F_{\text{max}} = -c_{\text{NH3}}/r_a$) in this period, as discussed in Hansen et al. (2013), however this simple analysis assumes horizontal and vertical homogeneity and no chemical reactions within the gradient. Following these days, emissions of up to 670 ng NH3-N m⁻³ were observed during the leaf fall period. The emission events during DOY 306–308 and 316–318 are well simulated by SURFATM-NH3 using PAI to scale the influence of litter on the ground layer emission potential. Modelled emissions were strongly controlled by turbulence assessed by the friction velocity. However, the emission fluxes measured during DOY 314–316 are not captured by the model. During these days, the air temperature
4.2 Sources of forest - atmosphere NH₃ fluxes

Simulated forest component NH₃ fluxes (Figure 6a) show that, for MMSF, NH₃ emissions up to 50 ng NH₃-N m⁻² s⁻¹ dominate the daytime net flux due to stomatal release of NH₃ from the leaves, whereas the contribution of simulated soil emissions is insignificant. SURFATM-NH₃ simulates very little cuticular absorption during night and morning, but relatively high observed NH₃ emissions at night suggest that cuticular desorption is more important (section 4.1) and responsible for nighttime emissions up to 30 ng NH₃-N m⁻² s⁻¹ for this dense natural forest ecosystem.

For DK-Sor, being a small forest surrounded by intensively cultivated crop fields, emissions up to 150 ng NH₃-N m⁻² s⁻¹ were observed in the leaf fall period corresponding to approximately 130 % of the net flux at midday. During/after leaf fall, the ground layer contributes almost solely to the modelled NH₃ emissions (Figure 6b). Stomatal NH₃ fluxes are insignificant in the leaf fall period but the average cuticular absorption amount to 30 ng NH₃-N m⁻² s⁻¹. Due to the cold and humid weather (Table 1), modelled cuticular deposition is nearly constant with no diel variation.

Less knowledge exists about soil and litter emissions of NH₃ in (semi-)natural ecosystems. Both emission pathways depend strongly on the seasonal variation in canopy physiological functioning and the building of a leaf litter layer on the forest floor that potentially contributes as a source for NH₃ emissions.

4.2.1 Ground layer NH₃ emissions

Walker et al. (2008) measured the soil NH₃ emission potential of a forest exposed to large NH₃ deposition and found it to be 20 (n = 34) at a depth of 5 cm, however other studies indicate much higher emission potential of decomposing litter layers (e.g., Zhang et al. 2010). For instance, Wang et al. (2011) observed higher emission potential of (newly) fallen leaves (Γₔ = 300) compared to senescing leaves (Γₛ = 200) at the DK-Sor site. Since it may take 1.3-2 years before forest leaf litter is totally decomposed (Müller 2003), the seasonal development
of forest floor $\Gamma_g$ is however not known. Any ground layer NH$_3$ emissions may be absorbed by the overlying leaf layers of closed canopies (Nemitz et al. 2001; Personne et al. 2009). In case of much higher estimates for $\Gamma_g$ (6000-30000) than measured for the DK-Sor forest ($\Gamma_g = 300$) by Wang et al. (2011), the modelled nighttime forest NH$_3$ emissions of MMSF would be sensitive to the emission potential of the ground layer (Figure 7c). Using such high estimates for $\Gamma_g$, the simulated NH$_3$ emissions of MMSF (Figure 7c) would however exceed the daytime NH$_3$ flux observations considerably (Figure 5a). Thus, the observed nighttime NH$_3$ fluxes of the green forest canopy at MMSF are rather caused by foliar emissions or related to transitions in the gaseous-aerosol phases of atmospheric NH$_3$ not included in the model.

### 4.2.2 Foliar NH$_3$ emissions

Foliar emissions during daytime are very sensitive to stomatal emission potential and stomatal conductance (Figure 7a). In this study, $\Gamma_s$ was set to 400 to represent a mid-season green forest canopy, following leaf measurements at DK-Sor (Wang et al. 2011). The use of similar parameter value for $\Gamma_s$ at MMSF and DK-Sor is supported by nearly similar leaf nitrogen concentration of the two sites (Table 1). During nights, this emission source diminishes due to stomatal closure, however a number of recent gas exchange studies suggested that simulated stomatal conductance may be underestimated at night (e.g., Charusombat et al. 2010; Wu et al. 2011), and a significant loss of water through stomata can take place that may not be measured by eddy covariance systems due to low turbulence at night (Caird et al. 2007; Dawson et al. 2007; Fisher et al. 2007). Measurements of LE at MMSF do not indicate considerable nighttime transpiration, e.g., average nighttime LE varies from -2.5 to 10 W m$^{-2}$ in the study period. Nevertheless, similar rates of eddy-covariance nighttime LE measured in Californian AmeriFlux sites were found to significantly underestimate nighttime transpiration as a percent of daily total when compared to sapflow-based analyses for oak-savannah (underestimation by 12 %) and Pinus Ponderosa (underestimation by 20 %) (Fisher et al. 2007). Even though the simulated nighttime stomatal conductance, transpiration and stomatal NH$_3$ flux may be underestimated in this study, the large proportion of observed nighttime relative to daytime NH$_3$ emission flux at MMSF (Figure 5a) suggest that other processes are also involved at night. Assuming no (or low) nighttime stomatal NH$_3$ emissions in this case (and no significant soil emissions – see 4.2.1), cuticular desorption could be responsible for the observed nighttime NH$_3$ emissions. This process is not represented in SURFATM-NH$_3$ that was earlier applied for modelling NH$_3$ fluxes of agricultural sites where cuticular
adsorption is the dominant process. Emission of NH$_3$ from cuticles requires low cuticular resistance and that NH$_3$ concentrations at the leaf surface exceed those in the surrounding air. Sources of higher leaf surface NH$_3$ concentrations may occur from stomatal NH$_3$ emissions or from deposited aerosols that are converted to gaseous NH$_3$ at the leaf surface.

### 4.2.1 Leaf surface wetness and dew formation

The high solubility of NH$_3$ in water causes leaf surface wetness to be very important for the estimation of NH$_3$ fluxes. During night, radiative cooling reduces temperature, increases relative air humidity and causes dew formation. Leaf wetness caused by morning dew was found to increase the NH$_3$ deposition (e.g., Burkhardt et al. 2009), and there is recent evidence that dew can work as a nighttime NH$_3$ reservoir which is released back to the atmosphere during early morning dew evaporation (Wentworth et al. 2016). Dew formation starts when 100% relative air humidity (RH) is reached at the actual leaf surface which normally corresponds to about 90% RH of the surrounding air (Burkhardt and Hunsche 2013). At MMSF, nighttime RH approaches 100% following the rain event at night (at 1 h) on DOY 251, and RH increases to above 90% throughout the following 3 nights. The largest nighttime NH$_3$ emissions are however seen on DOY 248–251 (Figure 5a) where RH is lower, e.g., it reaches maxima of 75%, 70% and 85% on DOY 248–251.

In addition to morning dew formation, leaf wetness can be caused by microscopic (invisible) water films that are formed by deliquescence of hygroscopic leaf surface particles at high RH or as a result of transpiration (Burkhardt and Hunsche 2013). For instance, measurements of leaf surface wetness on potato over five days clearly showed two diel peaks with one leaf wetness peak being related to midday transpiration and the other leaf wetness peak being related to increasing RH at night (Burkhardt and Hunsche 2013). It is striking that this observed microscopic leaf wetness pattern resembles a bimodal diel curve also observed in the measured NH$_3$ emissions at MMSF (Figure 5a). Several studies have indicated that such microscopic water films on leaf surfaces may also enhance the emission of NH$_3$ depending on the concentration of dissolved ions (Sutton et al. 1998; Sutton et al. 2009; Burkhardt and Hunsche 2013; Wentworth et al. 2016). Unfortunately, we do not know how the ammonium concentrations vary overnight, however high ammonium concentration of microscopic leaf water could explain the observed nocturnal NH$_3$ emissions at MMSF. Theoretically, the deliquescence of aerosols happens when RH reaches the deliquescent relative humidity (DRH) which is e.g. 62% for NH$_4$NO$_3$ particles and 80% for (NH$_4$)$_2$SO$_4$ particles (at 298 K) (Hu et
al. 2011). At DRH, the solid particles are transformed to larger aqueous solutions (microscopic droplets or water films) with high ion concentration. Hu et al. (2011) measured the hygroscopic growth curve for different ammonium salt particles in laboratory, and they observed gradually decreasing particle size of highly volatile particles such as NH$_4$NO$_3$ aerosols in response to increasing RH (below DRH). This led to the suggestion that small (< 50 nm) volatile ammonia particles such as NH$_4$NO$_3$ aerosols evaporate during the RH increasing process whereas this was not observed for the less volatile (NH$_4$)$_2$SO$_4$ particles (Hu et al. 2011). With increasing RH above DRH, the saturated solution droplets grow due to additional water condensation onto the salt solution (Hu et al. 2011), however the growth rate was less than expected for very small (< 50 nm) volatile NH$_4$NO$_3$ particles. When RH reaches 100 %, dew is formed. Burkhardt and Hunsche (2013) hypothesized that microscopic leaf wetness occurs on almost any plant worldwide, often permanently, and that it significantly influences the leaf surface-air exchange processes. Further studies are needed to investigate the role of RH on the deliquescence of deposited volatile ammonia particles and the likely occurrence of highly concentrated solutions on leaf surfaces.

### 4.2.2 Gaseous - aerosol phase interactions

The condensation nuclei for microscopic water typically result from deposited aerosols and may form highly concentrated solutions (Burkhardt and Hunsche 2013). Aerosol concentrations of NH$_4^+$ previously measured at MMSF indicated that the gaseous and aerosol phase concentrations of NH$_3$/NH$_4^+$ were of similar magnitude, but that the aerosol phase typically dominated (Hansen et al. 2015). Measured HNO$_3$ fluxes at MMSF showed deposition during daytime and emission during night (Hansen et al. 2015). This leads to the suggestion that the apparent nighttime HNO$_3$ and NH$_3$ emissions are caused by dissociation of aerosol NH$_4$NO$_3$ at (or near) the cool and humid leaf surfaces, and that this source of NH$_3$ could be responsible for the observed nighttime NH$_3$ emissions at MMSF. This proposed mechanism may also be related to the suggestion that increasing RH alters the chemical equilibrium and accelerates the evaporation of very small volatile particles such as NH$_4$NO$_3$ aerosols (Hu et al. 2011). It was also earlier suggested by Pryor et al. (2011) that NH$_3$ emission fluxes at MMSF could be caused by NH$_4$NO$_3$ aerosol evaporation.
4.2.3 Vapor pressure deficit and relative humidity

In the current study, we used measurement-based values for simulating ground layer and stomatal NH$_3$ emissions (measured at DK-Sor), and we find that these cannot explain the observed nighttime NH$_3$ emissions. However, the vapor pressure deficit, VPD (Pa) is found to be strong positively correlated with both the average nighttime LE ($R^2 = 0.82$) and the average nighttime NH$_3$ flux ($R^2 = 0.90$). The average nighttime LE and $F_{NH3}$ are also strongly correlated ($R^2 = 0.88$) whereas $H$ and $F_{NH3}$ are not correlated ($R^2 = 0.09$). These relations suggest a strong association between VPD, LE and $F_{NH3}$ at night that may be related to VPD-driven transpiration and foliar NH$_3$ emissions being supported by high ammonium concentrations at the leaf surface due to the formation of microscopic leaf wetness (by transpiration) and deliquescence of ammonia particles. In the case that NH$_3$ loss to the air occurs by e.g. NH$_4$NO$_3$ aerosol deliquescence and evaporation at night, the observed nighttime NH$_3$ emission would be strongly affected by in-canopy and leaf surface chemical reactions that are excluded in our model. In SURFATM-NH$_3$, the leaf surface NH$_3$ concentration is assumed to be zero. For further analysis, the development and application of more advanced physical and chemical models is required to represent microscopic leaf wetness (Burkhardt et al. 2013) and leaf surface NH$_3$ concentrations that are in equilibrium with the dissolved NH$_3$ concentrations at the leaf surface (Wichink Kruit et al. 2010) in order to simulate and analyze the importance of bi-directional cuticular NH$_3$ gaseous exchange. Model representation of inorganic chemistry interactions on the leaf surface requires many input parameters and excessive computation time, and the development of simpler empirical approaches are also needed for application in atmospheric transport models (Massad et al. 2010a; Wichink Kruit et al. 2010).

4.3 Seasonal development of the bulk NH$_3$ emission potentials $\Gamma_s$ and $\Gamma_g$

A number of bi-directional NH$_3$ exchange models have been developed (e.g., Flechard et al. 2013; Nemitz et al. 2000b; Massad et al. 2010a; Sutton et al. 1995; Sutton and Fowler 1993; Wichink Kruit et al. 2010). The parameterization of seasonal dynamics during the growing season to estimate canopy NH$_3$ compensation point are often vastly simplified (Simpson et al. 2012), however new parameterizations are being developed for application to atmospheric transport models (Wichink Kruit et al. 2010). In practice, ecosystem (soil-vegetation) N and NH$_4^+$ pools are ever changing and $\Gamma$ may undergo diel, seasonal and annual cycles. Modelling
approaches dealing with temperature response of emission potentials should therefore theoretically also deal with temporal $\Gamma$ dynamics in the various parts of an ecosystem (Flechard et al. 2013; Massad et al. 2010b; Wichink Kruit et al. 2010). Satellite observations have identified deforestation as an important source to atmospheric NH$_3$ (e.g., van Damme et al. 2015) and that the NH$_3$ emissions from large scale forest fires are important to include in atmospheric models (van Damme et al. 2014a). All these findings suggest that forest regions should be dynamically included in atmospheric models by taking into account governing processes in relation to both deposition and emission of NH$_3$.

Ammonia emission potentials of the ground layer ($\Gamma_g$) and stomata ($\Gamma_s$) are crucial input parameters in bi-directional NH$_3$ exchange models, in order to simulate the NH$_3$ compensation points of the ground layer and the stomata, respectively. However, realistic measurements of those are difficult and demanding to obtain and only few data exists. Wang et al. (2013) measured the pH and NH$_4^+$ concentration in the leaf apoplastic solution for the DK-Sor and two coniferous forest sites in order to study the seasonal variation in stomatal NH$_3$ compensation point. For DK-Sor, they found for the years 2008 and 2009, i.e., very close to the investigated period in this study, that $\chi_s$ peaked in the early-season during leaf expansion (6.8 $\mu$g NH$_3$ m$^{-3}$) and again in the late-season during leaf senescence (5.2 $\mu$g NH$_3$ m$^{-3}$) while in the mid-season, $\chi_s$ was lower (around 2.1 $\mu$g NH$_3$ m$^{-3}$). During leaf senescence N is translocated from the leaves into other parts of the trees leading to lower N concentrations decreasing tissue NH$_4^+$ concentrations especially in leaves from the canopy top (Wang et al. 2013). This pattern followed the variation in $\chi_s$ determined in parallel on the basis of the gas exchange measurements. Because of the difficulty to measure apoplastic concentrations, the significant correlation between $\Gamma_s$ and the more easily measurable total foliar [NH$_4^+$] (Loubet et al. 2002; Mattsson et al. 2009; Wang et al. 2011) can be used to estimate $\Gamma_s$. In this study we used the seasonal measurements of Wang et al. (2011) to set $\Gamma_s = 400$ for representing a green forest canopy (MMSF) and $\Gamma_s = 200$ to represent a senescing forest canopy (DK-Sor). Apart from observed seasonal variations in $\Gamma_s$, differences in leaf N status of the two forests (2.2% for MMSF and 2.5% for DK-Sor) support the use of different $\Gamma_s$ values. To improve model simulations, this parameter should be measured for each site and maybe even parameterized with seasonal variation.

The other source for NH$_3$ is the ground layer ($\Gamma_g$) and particularly the decomposing litter that we described with the parameter $\Delta LPAI$. Mattsson et al. (2009) showed that the emission
potential of litter could be up to 45-60 times higher than for green leaves and stems of an
intensively managed grass land. Here we chose a $I_{g,\text{min}}$ value of 300, corresponding to
measurements of newly fallen leaf litter at DK-Sor, and $I_{g,\text{max}}$ was estimated by trial and
error method ($I_{g,\text{max}} = 18000$). An emission potential of 18000 is high, however, in the range
of values found for senescing plant material (e.g., Sutton et al. 2009; Zhang et al. 2010).

5 Conclusions
Simulations with the SURFATM-NH$_3$ model in combination with a canopy stomatal model
show that the atmospheric NH$_3$ flux above a natural green forest canopy (MMSF) was
dominated by the stomatal exchange (up to 50 ng NH$_3$-N m$^{-2}$ s$^{-1}$). For a senescent canopy
influenced by anthropogenic NH$_3$ depositions in the growing season (DK-Sor), the ground
layer, or more specifically the fresh decomposing litter layer, was the largest contributor (up
to 150 ng NH$_3$-N m$^{-2}$ s$^{-1}$) to the total simulated NH$_3$ emissions from the forest to the
atmosphere. The measured day-time pattern of the NH$_3$ flux for MMSF indicates a strong
stomatal control by environmental factors with a strong diel signal (radiation, temperature,
humidity, CO$_2$). However, the model underestimated the observed nighttime emissions of
NH$_3$ for the green forest canopy (MMSF). We hypothesize that cuticular desorption is
responsible for these observed NH$_3$ emissions at night. Recent studies found that nights with
high RH caused morning evaporation of dew to be an important NH$_3$ source (Wentworth et al.
2016). In our study, nighttime NH$_3$ emissions were observed at nights without dew formation
(e.g., higher VPD) and may be related to foliar NH$_3$ emissions induced by a combination of
nighttime transpiration and deliquescence of aerosols leading to high ion concentrations of
microscopic leaf surface water (Burkhardt and Hunsche 2013). Emissions of NH$_3$ due to
microscopic leaf wetness have to our knowledge not been observed before, however, it seems
likely that in-canopy gaseous-aerosol interactions may cause the formation and evaporation of
aqueous aerosols and in particular microscopic leaf water at the cool and humid leaf surfaces.
Atmospheric NH$_3$ concentrations at MMSF are consistently low which suggests that cuticular
desorption may also take place during daytime where transpired water condenses on leaf
surfaces (Burkhardt et al. 1999). However, further investigations including detailed process
based measurements and the modelling of bidirectional cuticular NH$_3$ fluxes are needed in
order to obtain more knowledge on this topic.
The NH$_3$ fluxes measured in DK-Sor showed a less pronounced diurnal pattern, however, a pattern where the flux turns from depositions to emissions parallel to the decreasing PAI and an increasing depth of the leaf litter layer on the forest floor comprising an important NH$_3$ source during leaf fall for deciduous forests. The model was not able to represent the deposition rates before leaf fall but simulated well the emission events following on leaf fall using PAI to scale the influence of litter on the ground layer emission potential. We conclude from this study that deciduous forests potentially comprise a natural source of NH$_3$ to the atmosphere, and that it is crucial to take into account the bi-directional exchange processes related to both the stomatal, cuticular and ground layer pathways in order to realistically simulate natural forest–atmosphere fluxes of NH$_3$. We conclude that the combination of flux measurements and modelling is a robust approach in order to understand the important, however difficult to measure all relevant processes and parameters of the NH$_3$ exchange with the atmosphere. More specialized studies of measurement campaigns measuring particularly the bulk ground layer emissions potential ($I_g$) as well as the potentials for the two individual ground layer contributors; the soil and the litter layer, are needed in order to obtain improved model parameterizations.

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Appendix A

Description of the two-layer bi-directional NH\textsubscript{3} model

The two-layer bi-directional NH\textsubscript{3} exchange model simulates the total net atmospheric NH\textsubscript{3} flux ($F_T$; ng m\textsuperscript{-2} s\textsuperscript{-1}) as a sum of each of the forest component fluxes; the stomatal NH\textsubscript{3} flux ($F_s$; ng m\textsuperscript{-2} s\textsuperscript{-1}), the cuticular NH\textsubscript{3} flux ($F_w$; ng m\textsuperscript{-2} s\textsuperscript{-1}) and the ground NH\textsubscript{3} flux ($F_g$; ng m\textsuperscript{-2} s\textsuperscript{-1}) which are all related to the NH\textsubscript{3} canopy compensation point ($\chi_c$; ng m\textsuperscript{-3}) (Nemitz et al. 2000b):

\[
\chi_c = \frac{\chi_g (r_b r_g)^{-1} + \chi_s (r_b r_s)^{-1} + (r_s r_w)^{-1} + (r_b r_s r_w)^{-1}}{(r_a r_b)^{-1} + (r_a r_s)^{-1} + (r_b r_s)^{-1} + (r_b r_g r_w)^{-1}} \tag{A1}
\]

\[
F_s = \frac{\chi_c}{r_s} \tag{A2}
\]

\[
F_w = \frac{\chi_c}{r_w} \tag{A3}
\]

\[
F_g = \frac{\chi_c}{r_g} \tag{A4}
\]

where $r_a$ (s m\textsuperscript{-1}) is the aerodynamic resistance of the canopy, $r_b$ (s m\textsuperscript{-1}) is the quasi-laminar boundary layer resistance of the canopy, $r_s$ (s m\textsuperscript{-1}) is the stomatal resistance, $r_w$ (s m\textsuperscript{-1}) is the cuticular resistance, $r_g$ (s m\textsuperscript{-1}) is the ground layer resistance which represents a series of the in-canopy aerodynamic resistance and the quasi laminar boundary-layer resistance of the ground layer (Nemitz et al. 2001). $\chi_g$ and $\chi_s$ (ng m\textsuperscript{-3}) are the ground layer compensation point and the stomatal NH\textsubscript{3} compensation points, respectively.

Appendix B

Description of the coupled photosynthesis-stomatal conductance model

The coupled leaf photosynthesis and stomatal resistance model (Collatz et al. 1991) was parameterized for the specific forest sites using measured plant area index, PAI (m\textsuperscript{2} m\textsuperscript{-2}) as a proxy of the leaf area index (LAI). The model uses input data of the air temperature, $T_a$ (°C), soil temperature, $T_s$ (°C), leaf temperature, $T_L$ (°C), relative humidity, $R\text{HI}$ (%), photosynthetic active radiation, $PAR$ (W m\textsuperscript{-2}), sensible heat flux, $H$ (W m\textsuperscript{-2}), wind speed, $u$ (m s\textsuperscript{-1}), friction...
velocity, $u^*$ (m s$^{-1}$), and $PAI$ (m$^2$ m$^{-2}$), to simulate the stomatal conductance, $g_s$ (m s$^{-1}$) and the
leaf photosynthesis (or net carbon assimilation), $A_n$ ($\mu$mol m$^{-2}$ s$^{-1}$), in an iterative setup (Figure
9). $A_n$ is estimated as the minimum of three potential capacities and the leaf dark respiration,
$R_D$ ($\mu$mol m$^{-2}$ s$^{-1}$), (Collatz et al. 1991, Farquhar et al. 1980b):

$$A_n = \min \{J_E, J_C, J_S\} - R_D \quad \text{(B1)}$$

$J_E$ is the light-limited assimilation rate ($\mu$mol m$^{-2}$ s$^{-1}$), $J_C$ is the rubisco-limited assimilation
rate ($\mu$mol m$^{-2}$ s$^{-1}$), and $J_S$ is the assimilation rate due to the limitation of the export of
assimilates inside the leaf ($\mu$mol m$^{-2}$ s$^{-1}$) simulated as (Collatz et al. 1991):

$$J_E = a \alpha Q \frac{C_{i-}^{\Gamma^*}}{C_{i} + 2 \Gamma^*} \quad \text{(B2)}$$

$$J_C = \frac{V_{c,\max} (C_{i-}^{\Gamma^*})}{C_{i} + K_c \left(1 + \frac{O_2}{K_0}\right)} \quad \text{(B3)}$$

$$J_S = 0.5 V_{c,\max} \quad \text{(B4)}$$

where $\alpha$ is the leaf absorptivity of PAR, $\alpha$ ($\mu$mol m$^{-2}$ s$^{-1}$) is the maximum quantum yield,
$Q$ is PAR, $C_i$ (Pa) is the internal CO$_2$ pressure, $\Gamma^*$ (Pa) is the CO$_2$ compensation point, $V_{c,\max}$
($\mu$mol m$^{-2}$ s$^{-1}$) is the maximum carboxylation rate of Rubisco, $O_2$ is the oxygen intercellular
partial pressure (Pa), and $K_C$ (40.4 Pa) and $K_O$ (24,800 Pa) are the Michaelis constant for CO$_2$
fixation and oxygen inhibition, respectively. $R_D$ can experimentally be determined by gas
exchange measurements of leaves, but here it is determined by a fraction of $V_{c,\max}$ following
Collatz et al. (1991):

$$R_D = 0.015 V_{c,\max} \quad \text{(B5)}$$

The stomatal conductance is simulated following Ball et al. (1987):

$$g_s = m \frac{A_n h_s}{C_s} + b \quad \text{(B6)}$$

where $h_s$ (%) is the relative humidity at the leaf surface, $C_s$ (Pa) is the CO$_2$ partial pressure on
the leaf surface, and $m = 7$ and $b = 0.01$ mol m$^{-2}$ s$^{-1}$ are constants.

The leaf temperature, $T_L$ (°C), is simulated as:

$$T_L = \frac{H r_{abh}}{\rho c_p} + T_a \quad \text{(B7)}$$

where $r_{abh}$ (s m$^{-1}$) is the total resistance to heat, $\rho$ (kg m$^{-3}$) is the air density, and $c_p$ is the
specific heat for air at constant pressure (J kg$^{-1}$ K$^{-1}$).
$V_{c,max}$ is strongly dependent on the availability of leaf nitrogen and leaf temperature. Hence it is expected that $V_{c,max}$ at 25 °C is higher for the DK-Sor site than for the MMSF site, since the DK-Sor site is located in an agricultural region exposed to large NH3 deposition (Skiba et al. 2009). The applied parameter values for $V_{c,max}$ at 25 °C for DK-Sor (100·10^{-6} \text{ mol m}^{-2} \text{ s}^{-1}) and MMSF (70·10^{-6} \text{ mol m}^{-2} \text{ s}^{-1}) are within the range of values found and used for this plant functional type (PFT) in other terrestrial biosphere models (Kattge et al. 2009; Rogers 2014).

Three different parameterizations of the soil and ecosystem respiration were furthermore tested in order to obtain the best representation; two of them based on the temperature-controlled soil ($R_s$) or ecosystem ($R_{eco}$) respiration model from Lloyd and Taylor (1994) and one total ecosystem respiration ($TER$) parameterized for DK-Sor by Wu et al. (2012):

\[ R_s = R_{10} \times \exp \left( 308.56 - \left( \frac{1}{T_{ref} - T_0} - \frac{1}{T_s - T_0} \right) \right) \]  
\[ R_{eco} = R_{eco,ref} \times \exp \left( 308.56 - \left( \frac{1}{T_{ref} - T_0} - \frac{1}{T_{air} - T_0} \right) \right) \]  
\[ TER = R_{eco,ref} Q_{10}^{\frac{T_s - T_0}{10}} \]  

where $R_{10}$ (µmol m^{-2} s^{-1}) is the soil respiration at 10°C, $T_s$ (°C) is soil temperature, $T_{ref}$ (°C) is the reference temperature set to 10°C as in the original model, $T_0$ (°C) is a regression constant of -46.02°C (Lloyd and Taylor 1994), $T_{air}$ (°C) is the ambient air temperature, $R_{eco,ref}$ (µmol m^{-2} s^{-1}) is the respiration at $T_{ref}$ estimated from nighttime data, and $Q_{10}$ is the temperature sensitivity parameter and set to a constant value of 2. The parameterization of $TER$ by Wu et al. (2012) was used for DK-Sor, and the general parameterization ($R_{eco}$) was used for MMSF.

Subtracting the simulated soil respiration ($R_s$) from $A_c$ (canopy net photosynthesis per ground area) being $A_n$ (leaf net photosynthesis per leaf area) upscaled to the canopy scale using $LAI$ as proposed by Sellers et al. (1992), the net CO2 exchange was calculated at canopy scale ($NEE = -A_c + R_s$) and can be directly tested with eddy covariance CO2 flux measurements (Pilegaard et al. 2011).

References


Table 1: Site location and characteristics during the measurement periods. Mean including standard deviation is given for *PAI*, temperature and rain.

<table>
<thead>
<tr>
<th>Lat/Lon</th>
<th>MMSF</th>
<th>DK-Sor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>39°53’N, 86°25’W</td>
<td>55°29’N, 11°38’E</td>
</tr>
<tr>
<td>Forest type</td>
<td>Temperate deciduous, mixed</td>
<td>Temperate deciduous, beech</td>
</tr>
<tr>
<td>Canopy height</td>
<td>m</td>
<td>~28</td>
</tr>
<tr>
<td>Tree age</td>
<td>years</td>
<td>80 - 90</td>
</tr>
<tr>
<td>Summer <em>PAI</em></td>
<td>m² m⁻²</td>
<td>4.6</td>
</tr>
<tr>
<td>Soil type</td>
<td></td>
<td>Mesic Typic Dystrochrepts</td>
</tr>
<tr>
<td>Leaf N status</td>
<td>%</td>
<td>2.2</td>
</tr>
<tr>
<td><strong>Measurement period</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dates</td>
<td>5 - 10 September 2013</td>
<td>21 October – 15 November 2010</td>
</tr>
<tr>
<td>DOY</td>
<td>248 – 253</td>
<td>294 – 319</td>
</tr>
<tr>
<td>Mean <em>PAI</em></td>
<td>m² m⁻²</td>
<td>4.5 ± 0.0</td>
</tr>
<tr>
<td>Mean Temp.</td>
<td>ºC</td>
<td>24.5 ± 3.3</td>
</tr>
<tr>
<td>Total Rain</td>
<td>mm</td>
<td>12.8</td>
</tr>
</tbody>
</table>
Table 2: List of input parameters for the SURFATM-NH3 model for the MMSF and DK-Sor model setups. Pedotransfer functions applicable to Danish soil types are used (Madsen and Holst 1988) and some soil parameters for the DK-Sor site were measured in the NitroEurope project (2006-2011) and provided from there.

<table>
<thead>
<tr>
<th>Soil parameters</th>
<th>Unit</th>
<th>Range</th>
<th>MMSF/DK-Sor</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil depth</td>
<td>m</td>
<td>0.86 / 0.80</td>
<td>Thompson et al. (2011) / NitroEurope IP</td>
<td></td>
</tr>
<tr>
<td>Soil density</td>
<td>kg m(^{-3})</td>
<td>1220 / 1038</td>
<td>Measured / NitroEurope IP</td>
<td></td>
</tr>
<tr>
<td>Soil humidity at field capacity</td>
<td>kg (H(_2)O) kg(^{-1}) (soil)</td>
<td>0.15 – 0.4</td>
<td>0.36 / 0.36</td>
<td>Estimated / calculated using pedotransfer function</td>
</tr>
<tr>
<td>Soil humidity at wilting point</td>
<td>kg (H(_2)O) kg(^{-1}) (soil)</td>
<td>0.05 – 0.25</td>
<td>0.22 / 0.24</td>
<td>Estimated / calculated using pedotransfer function</td>
</tr>
<tr>
<td>Thermal soil conductance (wet)</td>
<td>W m(^{-1}) K(^{-1})</td>
<td>1.6 – 2.2</td>
<td>1.60 / 1.00</td>
<td>Monteith and Unsworth (1990)</td>
</tr>
<tr>
<td>Thermal soil conductance (dry)</td>
<td>W m(^{-1}) K(^{-1})</td>
<td>0.2 – 0.3</td>
<td>0.28</td>
<td>Monteith and Unsworth (1990)</td>
</tr>
<tr>
<td>Soil porosity</td>
<td>-</td>
<td>0.25 – 0.5</td>
<td>0.55</td>
<td>Thompson et al. (2011) / Estimated</td>
</tr>
<tr>
<td>Soil tortuosity parameter</td>
<td>-</td>
<td>[2 - 4]</td>
<td>2.00</td>
<td>Estimated</td>
</tr>
<tr>
<td>Soil Roughness</td>
<td>m</td>
<td>[0.001 – 0.5]</td>
<td>0.02</td>
<td>Estimated</td>
</tr>
<tr>
<td><strong>Chemical constants</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(K_H)</td>
<td>-</td>
<td>10(^{-3.14})</td>
<td>Loubet (2000)</td>
<td></td>
</tr>
<tr>
<td>(K_d)</td>
<td>mol l(^{-1})</td>
<td>10(^{-9.25})</td>
<td>Bates and Pinching (1950)</td>
<td></td>
</tr>
<tr>
<td><strong>Vegetation parameters</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Leaf width</td>
<td>m</td>
<td>[0.03 – 0.5]</td>
<td>0.15 / 0.10</td>
<td>Measured</td>
</tr>
<tr>
<td>Canopy height</td>
<td>m</td>
<td>28 / 26</td>
<td>Measured</td>
<td></td>
</tr>
<tr>
<td>Max stomatal conductance</td>
<td>m s(^{-1})</td>
<td>400</td>
<td>Collatz et al. (1991)</td>
<td></td>
</tr>
<tr>
<td>Efficiency coefficient for plant area index</td>
<td>m s(^{-1})</td>
<td>0.25</td>
<td>Estimated</td>
<td></td>
</tr>
<tr>
<td>Radiation attenuation coefficient</td>
<td>-</td>
<td>[0.5 – 0.8]</td>
<td>0.80 / 0.85</td>
<td>Estimated / calculated using radiation data</td>
</tr>
<tr>
<td>Wind attenuation coefficient</td>
<td>-</td>
<td>[1.5 - 5]</td>
<td>2.20</td>
<td>Estimated</td>
</tr>
<tr>
<td><strong>Ammonia emission potentials</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\Gamma_{g,min})</td>
<td>-</td>
<td>300</td>
<td>Estimated</td>
<td></td>
</tr>
<tr>
<td>(\Gamma_{g,max})</td>
<td>-</td>
<td>18000</td>
<td>Estimated</td>
<td></td>
</tr>
<tr>
<td>(\Gamma_s)</td>
<td>-</td>
<td>[0 - 600]</td>
<td>400 / 200</td>
<td>Estimated / Wang et al. (2011)</td>
</tr>
</tbody>
</table>
Table 3: Model error statistics including the number of valid observations, $n$, Pearson correlation coefficient, $R^2$, root mean squared error, $RMSE$, and the Concordance coefficient, $CCC$ (in W m$^{-2}$ for energy fluxes and μg NH$_3$-N m$^{-2}$ s$^{-1}$ for ammonia fluxes). See text (section 3.1.1) and Figure 3 for energy balance closure.

<table>
<thead>
<tr>
<th>MMSF</th>
<th>$n$</th>
<th>$R^2$</th>
<th>RMSE</th>
<th>CCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H$</td>
<td>240</td>
<td>0.78</td>
<td>59.17</td>
<td>0.69</td>
</tr>
<tr>
<td>$LE$</td>
<td>240</td>
<td>0.87</td>
<td>71.83</td>
<td>0.78</td>
</tr>
<tr>
<td>$G$</td>
<td>240</td>
<td>0.40</td>
<td>21.46</td>
<td>0.22</td>
</tr>
<tr>
<td>$F_{NH3}$</td>
<td>209</td>
<td>0.51</td>
<td>14.03</td>
<td>0.43</td>
</tr>
<tr>
<td>DK-Sor</td>
<td>$n$</td>
<td>$R^2$</td>
<td>RMSE</td>
<td>CCC</td>
</tr>
<tr>
<td>$H$</td>
<td>1198</td>
<td>0.17</td>
<td>71.94</td>
<td>0.14</td>
</tr>
<tr>
<td>$LE$</td>
<td>1199</td>
<td>0.07</td>
<td>37.32</td>
<td>0.04</td>
</tr>
<tr>
<td>$G$</td>
<td>1200</td>
<td>0.65</td>
<td>10.97</td>
<td>0.32</td>
</tr>
<tr>
<td>$F_{NH3}$</td>
<td>1020</td>
<td>0.62</td>
<td>94.29</td>
<td>0.60</td>
</tr>
</tbody>
</table>
Figure 1: Parameterization of the ground layer emission potential $\Gamma_g = [\text{NH}_4^+]/[\text{H}^+]$ with the decrease in $\Delta PAI$ exemplified using $PAI$ data from the DK-Sor site.
Figure 2: Comparison of the measured (dots) and the simulated (red lines) energy fluxes (W m$^{-2}$) of sensible heat ($H$) and latent heat ($LE$) for the MMSF and DK-Sor sites. For the DK-Sor site the FAO Penman-Monteith reference evapotranspiration is also shown with (blue line). Measurements of net radiation, $R_n$ (W m$^{-2}$), air temperature, $T$ (degree celcius), wind speed, $Spd$ (m s$^{-1}$), relative humidity, $RH$ (%), and rain (mm) are shown in the lowest graphs.
Figure 3: Scatterplot of the modelled vs. the measured CO₂ flux (μmol m⁻² s⁻¹) for the DK-Sor site for the full year of 2010 (left) and for the MMSF site for the full year of 2013 (right). Black filled symbols show the data points during the measurement periods. $R^2$ is the coefficient of determination, RMSE is the root mean square error, and n is the number of valid sampling points.
Figure 4: Scatter plots comparing the measured available energy ($R_n - G$) to the measured turbulent energy fluxes ($H + LE$) for a) the MMSF site and b) the DK-Sor site during the measurement periods. For (b) the filled circles indicate measurements during periods where the wind speed was 0-5 m s$^{-1}$ and the open circles represent data measured at wind speeds higher than 5 m s$^{-1}$.
Figure 5: Comparison of the measured (dots) and the simulated (lines) NH$_3$ fluxes (ng NH$_3$ m$^{-2}$ s$^{-1}$) for a) the MMSF site and b) the DK-Sor site during the measurement periods.
Figure 6: Simulated mean forest component fluxes (ng NH$_3$-N m$^{-2}$ s$^{-1}$) from the ground layer (light grey), cuticles (dark grey), and stomata (white) for a) MMSF site, which represents a green canopy and b) DK-Sor site, which represents the leaf fall period. The solid line shows the mean NH$_3$ net flux (ng NH$_3$-N m$^{-2}$ s$^{-1}$).
Figure 7: The simulated mean NH$_3$ flux (ng NH$_3$-N m$^{-2}$ s$^{-1}$) for a green forest canopy (MMSF) and for a leaf fall forest canopy (DK-Sor) with different stomata emission potentials ($\Gamma_s$) (a and b) and different ground layer emission potentials ($\Gamma_g$) (c and d). In panel b) all results fall on one single line, indicating that the stomatal NH$_3$ pathway is negligible.