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Modelling the dynamic chemical interactions of atmospheric ammonia with leaf surface wetness in a managed grassland canopy

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Abstract. Ammonia exchange fluxes between grassland and the atmosphere were modelled on the basis of stomatal compensation points and leaf surface chemistry, and compared with measured fluxes during the GRAMINAE intensive measurement campaign in spring 2000 near Braunschweig, Germany. Leaf wetness and dew chemistry in grassland were measured together with ammonia fluxes and apoplastic NH_4^+ and H^+ concentration, and the data were used to apply, validate and further develop an existing model of leaf surface chemistry and ammonia exchange. Foliar leaf wetness which is known to affect ammonia fluxes may be persistent after the end of rainfall, or sustained by recondensation of water vapour originating from the ground or leaf transpiration, so measured leaf wetness values were included in the model. pH and ammonium concentrations of dew samples collected from grass were compared to modelled values.

The measurement period was divided into three phases: a relatively wet phase followed by a dry phase in the first week before the grass was cut, and a second drier week after the cut. While the first two phases were mainly characterised by ammonia deposition and occasional short emission events, regular events of strong ammonia emissions were observed during the post-cut period. A single-layer resistance model including dynamic cuticular and stomatal exchange could describe the fluxes well before the cut, but after the cut the stomatal compensation points needed to numerically match

measured fluxes were much higher than the ones measured by bioassays, suggesting another source of ammonia fluxes. Considerably better agreement both in the direction and the size range of fluxes were obtained when a second layer was introduced into the model, to account for the large additional ammonia source inherent in the leaf litter at the bottom of the grass canopy. Therefore, this was found to be a useful extension of the mechanistic dynamic chemistry model by keeping the advantage of requiring relatively little site-specific information.

1 Introduction

The deposition and emission of ammonia to/from vegetated surfaces are controlled not only by stomatal characteristics, but also by non-stomatal surfaces such as the leaf cuticle or the underlying soil (Sutton et al., 1993, 1998). While trace gas exchange through stomates is linked to the diurnal course of photosynthesis and transpiration, non-stomatal exchange is not actively controlled by the plant. Both pathways are continuously influenced by physiological signals (e.g. drought induced abscisic acid formation in the roots, affecting stomatal aperture) and environmental changes, while turbulent and laminar transport impose physical constraints on the potential rates of bi-directional exchange with the atmosphere. Plants exchange NH_3 via stomata, depending on the apoplastic NH_4^+ concentration, temperature and pH, which determine the stomatal compensation point (Sutton et al., 1993, 1995). The importance of cuticular processes



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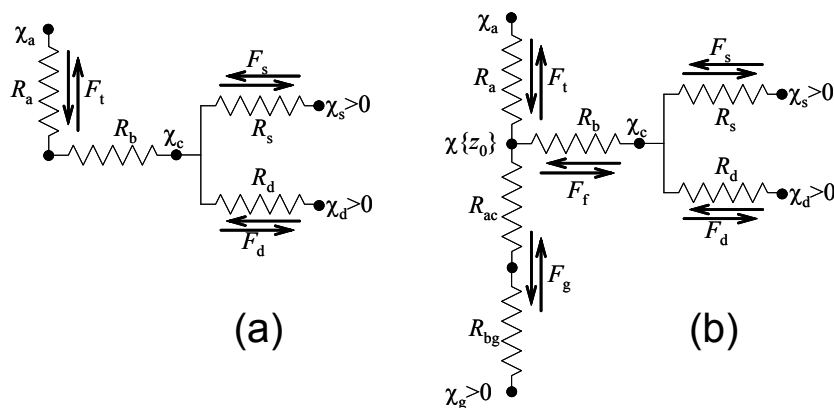


Fig. 1. Diagrams of canopy compensation point models for biosphere/atmosphere NH₃ exchange. (a): “big leaf” type model of Flechard et al. (1999) with dynamic chemical model and bi-directional transfer resistance R_d for cuticular deposition (b): two-layer canopy compensation point models for biosphere/atmosphere NH₃ exchange, adapted from Nemitz et al. (2001).

at humidities well below water vapour saturation has been demonstrated by a number of studies (e.g. van Hove et al., 1989; Burkhardt and Eiden, 1994), often showing an exponential increase of the deposition velocity of NH₃ and other water soluble trace gases with increasing relative humidity (RH), both in the laboratory (van Hove and Adema, 1996) and in the field (Erisman and Wyers, 1993; Wyers and Erisman, 1998; Altimir et al., 2006). This is due to microscale liquid water layers formed on external plant surfaces by the condensation of water vapour originating from the atmosphere or plant transpiration, and facilitated by hygroscopic particles on the leaves (Burkhardt et al., 1999). The presence of thin water layers at low humidities can be demonstrated with special sensors measuring the electrical conductance on leaf surfaces (Burkhardt and Gerchau, 1994; Altimir et al., 2006), and the water lasts longer on grassland compared to forest leaf surfaces (Klemm et al., 2002; Wichink Kruit et al., 2008). Nevertheless, there is substantial uncertainty about the thickness of these water layers. The process of physical adsorption (or physisorption) is physically well described by a BET (Brunauer/Emmett/Teller) isotherm with RH-dependent exponential increase (Brunauer et al., 1938). However, physisorption can only explain a few nanometers of liquid water, whereas the “effective water layer” for ammonia absorption on leaves is in the range of several micrometers (van Hove and Adema, 1996). This leaves a so far unresolved gap between the physically explained process and experimental observations.

Leaf surface wetness was expected to be a major driver of ammonia fluxes during the GRAMINAE field experiment over managed grassland near Braunschweig, Germany, in 2000 (Sutton et al., 2008a, b), since any dynamic changes of canopy liquid water storage can lead to enhanced deposition or degassing of ammonia (Sutton et al., 1998). Water vapour transfer, evaporation and recondensation within the canopy influences the internal cycling of ammonia (cf. Den-

mead et al., 1976) due to its high solubility in water. A vertical gradient in leaf surface wetness is to be expected, as leaf surfaces at different heights within the canopy are differently affected by humidity generated by ambient atmospheric humidity, soil evaporation, and plant transpiration. Thin water films, which are precursors of visible dew, may result from the re-condensation of water originating from within the canopy, either from the soil (Long, 1958; Monteith, 1957) or transpired from the leaves (Burkhardt et al., 1999). On leaf surfaces, water film development is partly determined by salts and solutes originating from atmospheric deposition and cuticular leaching, and the dissolved ions and other solutes in turn control the solubility of ammonia by their influence on pH (Burkhardt and Eiden, 1994; Sutton et al., 1993). In this paper, a single layer (“big leaf”) chemistry and exchange model (Flechard et al., 1999) is applied in a first approach, to simulate the dynamic surface chemistry and the gradients driving ammonia exchange, based on the energy balance equation and building on notional concentrations (“compensation points”) in crucial positions along the exchange path. The original version of the model determined the water layer depth on basis of the energy balance and precipitation, and water absorbed by deliquescent aerosols in the drier conditions. In the present paper the dynamical modelling of leaf surface water storage is replaced by an empirical static parameterisation based on continuously measured leaf wetness (Fig. 1a): In order to better reflect ammonia emission from litter, the original “big leaf” model (Fig. 1a) is upgraded to a stratified approach with two layers, based on the approach by Nemitz et al. (2001) and incorporating the dynamic chemistry module for foliage water films, but not for the leaf litter. This resulted in a two-layer (foliage + litter) dynamic chemical canopy compensation point model (Fig. 1b), with the modelling of chemistry restricted to the living canopy foliage.

2 Methods

The field site at the FAL Federal Agricultural Research Institute near Braunschweig, Germany was a *Lolium perenne*-dominated agricultural grassland, which was cut on the 29th May 2000 (i.e. 10 days after the beginning of the experiment), from a canopy height of 70 cm (single-sided leaf area index, LAI=3.06 m² m⁻²) down to 7 cm (LAI=0.14 m² m⁻²). The vegetation started to grow again towards the end of the campaign. A large array of micrometeorological equipment was deployed over the canopy by several groups from different European research institutes (Sutton et al., 2008a). The instruments were distributed along a roughly north-south axis and covered a distance of about 100 m along a transect through the field. The available fetch was approximately 300 m to the west and east, 200 m to the south and 50 to 100 m to the north. The groups and the overall measurement program are described elsewhere (Sutton et al., 2008a) together with further description of the sward and prevailing conditions at the site.

Ammonia fluxes were determined using four gradient denuder systems in parallel. These were combined with turbulence measurements using ultrasonic devices. At least three ammonia flux systems were always operating in parallel. After quality control, a joint dataset containing the consensual “best flux estimate” was agreed upon, using the arithmetic mean of the available filtered flux measurements by the different groups (Milford et al., 2008). Bioassay measurements were conducted to determine the apoplastic concentrations especially of NH₄⁺ and pH by infusion and subsequent removal with a centrifuge (Mattsson et al., 2008a), while the vertical structure of the plant canopy and bioassays was also determined (Herrmann et al., 2008). In addition to ammonia, air concentrations of other trace gases (HNO₃, SO₂, HONO, HCl) were measured (Sutton et al., 2008a, b).

2.1 Surface wetness measurements

Leaf wetness measurements were carried out using electrodes with a distance of about 5 mm directly clipped to the leaf surfaces (Burkhardt and Gerchau, 1994). An AC voltage of about 4 V, 2 kHz was applied and the electrical conductance recorded by means of a data logger. The sensors respond to changes in the electrical conductances of the mesophyll, the cuticle and any wetness within the leaf boundary layer. Leaf wetness usually is the dominating influence, but the signal may be affected by stomatal aperture, environmental humidity, and the ion concentration in surface moisture (Burkhardt et al., 1999).

Before the cut, the single sensors were applied at three different height ranges (0–15 cm, 15–30 cm, 30–45 cm above ground). In addition, some leaf wetness sensors were clipped onto filter paper and placed in the upper grass layer. The filter paper mimics a leaf during dew formation as it undergoes radiational energy loss in the same humidity surroundings.

However, it is hygroscopic and there are no contributions from either tissue nor from transpiration, compared with a real leaf. The comparison aimed at distinguishing stomatal transpiration which might interfere with atmospheric moisture (Burkhardt et al., 1999). After the cut, the sensors were deployed at only one height, on live grass blades.

The recorded leaf wetness values were normalized, leading to a data range between 1 (visible wetness at water holding capacity), and 0 (completely dry surfaces, zero conductance), in order to reduce unwanted instrumental factors, such as the pressure applied to the leaf (Klemm et al., 2002).

The normalized leaf wetness values (LW, dimensionless) were then converted into the “effective” water volume vH₂O (lm⁻² or mm) interacting with ammonia (cf. van Hove and Adema, 1996). We assumed multilayer physical adsorption (physisorption) described as exponential increase with RH (Brunauer et al., 1938). One complete layer of physisorbed water molecules was assumed at 70% RH and two complete layers at 85% RH (Altimir et al., 2006). At 100% RH, we assumed X complete layers of water molecules, with X being a full number fixed by an optimisation process (5 < X < 25). The exponentially RH-dependent water film thickness determined by this procedure describes well the observed behaviour, but would only mount up to a few nanometers. Therefore it was “scaled up” to meet the ‘effective water film thickness’ of 100 μm at 100% RH, a round value similar to the 123.9 μm derived by van Hove and Adema (1996, Fig. 1b). 100 μm is also the approximate leaf water storage capacity of leaves (Barfield et al., 1973; Wohlfahrt et al., 2006), although this is species dependent due to differences in wettability (Flechard et al., 1999).

Technically, LW values were first transformed into RH based on the exponential relation described in Sect. 3.1:

$$\text{RH} = 0.127 * \ln(\text{LW}/(3.68 \times 10^{-4})) \quad (1)$$

The exponential relation resulting from the BET isotherm was combined. This gave an overall dependence of

$$v\text{H}_2\text{O}(\text{LAI} = 1) = a \times \exp(b \times \ln(\text{LW}/(3.86 \times 10^{-4}))), \quad (2)$$

which needs to be adjusted to the leaf area index of the canopy. The parameters a and b were determined by the assumption of X, the amount of physisorbed water layers at 100% RH. Unless otherwise stated, the formula for X=16 was used (see Sect. 3.3.1), resulting in

$$v\text{H}_2\text{O} = \text{LAI} \times 3.13 \times 10^{-4} \times \exp(0.73 \times \ln(\text{LW}/3.86 \times 10^{-4})) \quad (3)$$

with LAI being the leaf area index, vH₂O being the effective water film thickness (mm) and LW being the normalized leaf wetness signal.

For comparison, we also calculated vH₂O directly from RH values using the BET approach but not LW. In addition and alternatively to the BET approach, the curve described by van Hove and Adema (1996; Fig. 1b) was also used (“vpd

Table 1. Mean aqueous concentrations (and standard deviations) in dew, guttation, and rain from leaves, measured on 21th, 22th, 23th, 24th, 25th, and 26th May (pre-cut period). Due to logarithmic scale of pH, calculated standard deviation is derived from $[H^+]$.

	pH	NH_4^+ (mg kg ⁻¹)	K^+ (mg kg ⁻¹)	Ca^{2+} (mg kg ⁻¹)	Cl^- (mg kg ⁻¹)	NO_3^- (mg kg ⁻¹)	SO_4^{2-} (mg kg ⁻¹)
Dew	6.6 (6.4–7.0)	3.55 (1.74)	0.66 (0.36)	1.31 (0.87)	1.08 (0.95)	0.32 (0.31)	1.53 (0.91)
Guttation	5.5 (5.3–5.9)	1.40 (0.48)	0.79 (0.72)	3.12 (2.45)	3.32 (2.58)	0.19 (0.15)	3.34 (2.87)
Rain from leaves	5.2 (4.9–7.7)	1.69 (0.28)	0.18 (0.07)	0.14 (0.06)	0.06 (0.09)	0.20 (0.10)	0.70 (0.26)
Wet only		1.01	0.36	1.12	0.31	0.82	0.94
Bulk rain		1.03	0.38	1.37	0.43	1.05	1.07

approach”). In order to compare modelled leaf water chemistry with the real water composition on leaf surfaces, we collected dew samples from leaves after clear, calm nights. Samples included dew, sometimes guttation from the leaves, and in some instances surface water after rain, which had not completely evaporated before the night. Actual radiative dew formation was observed on 5 days (21th, 23th, 24th, 25th, 26th May). The sampling was done manually by stripping the droplets with a pipette from grass leaves (Burkhardt and Eiden, 1990), for subsequent chemical analysis. pH was measured immediately within a small aliquot, the rest of the samples was frozen and chemical analysis for NH_4^+ , K^+ , Ca^{2+} , Cl^- , NO_3^- , SO_4^{2-} was done later in the laboratory.

2.2 Model

Fluxes were modelled using the dynamic chemical canopy compensation point model of Flechard et al. (1999) (Fig. 1a). The stomatal compensation point (χ_s) is the gaseous concentration in equilibrium with dissolved ammonia in the apoplast, and is pH- and T-dependent (e.g. Nemitz et al., 2001; Sutton et al., 1995; Schjoerring et al., 1998). Given the temperature sensitivity of χ_s , in practice it is convenient to use the apoplastic ratio $[NH_4^+]/[H^+]$ referred to as Γ_s , as the model input coupled with the standard temperature function. Here we use the Γ_s values determined by another group during the GRAMINAE experiment (Mattsson et al., 2008b).

The chemistry module for the surface water films calculates trace gas chemical equilibria at each time step; at the water surface, the notional gaseous concentration of ammonia in equilibrium with dissolved ammonia (χ_d) is calculated from Henry’s law (Flechard et al., 1999). The resulting canopy compensation point χ_c is then calculated from all notional concentrations and transfer resistances in the network (Fig. 1a). The difference between χ_c and the atmospheric NH_3 concentration (χ_a), divided by the sum of the atmospheric transfer resistances R_a and R_b , determines the direction and magnitude of the total ammonia flux (F_t) which equals the sum of the component fluxes F_s and F_d (Sutton et al., 1995). The difference with conventional canopy resistance or canopy compensation point models (Sutton et al., 1993, 1995), is that the leaf cuticular concentration χ_d is different from 0, allowing desorption as well as deposition from the non-stomatal part of the leaf.

The model is initialised at a period with high leaf wetness and assuming chemistry according to mean measured (wet-only) rainfall concentrations (Table 1). Aqueous chemistry in surface wetness includes dissolved SO_2 , O_3 , HNO_3 and their exchange with the atmosphere and aqueous reactions, such as the heterogeneous oxidation of SO_2 to SO_4^{2-} (Flechard et al., 1999) by ozone, whereas H_2O_2 and the metal ion catalysed oxidation by oxygen (Martin, 1984; Burkhardt and Drechsel, 1997) was not included due to limited data availability. Cuticular leaching of base cations and exchange of H^+ and NH_4^+ with the leaf interior and through the cuticle are included in the model, and parameterised according to Flechard et al. (1999). For practical and numerical reasons, the exchange by default only takes place below a pH of 4.5, and only above a canopy-equivalent water storage of 0.1 mm. The program limits the concentration difference between time steps to 10%, i.e. in dry conditions time steps often become very small. Contrary to the original model by Flechard et al. (1999), there is no switch to a deposition-only ($\chi_d=0$) empirical R_w scheme (Nemitz et al., 2001), when the ionic strength exceeds 0.3 M; but the model calculates wet chemistry throughout.

Changes in leaf wetness force the model to simulate increased deposition or release of ammonia, the magnitude of which depends on pH, temperature and atmospheric turbulence. In the present application, the normalized leaf wetness data obtained from clip measurements provide the model input for leaf water storage, instead of the original energy balance approach by Flechard et al. (1999) as discussed in Sect. 3.2. This value is then converted to the amount of water or the “effective water film thickness” relevant for ammonia dissolution or release (van Hove and Adema, 1996) as described in the methods section. To account for the NH_3 emission potential caused by decomposing plant material at the bottom of the grass canopy, a litter layer was added to the one-layer model of Flechard et al. (1999), following the scheme by Nemitz et al. (2001) (Fig. 1b). Nemitz et al. (2001) had solved the two-layer resistance model in χ_c assuming a zero NH_3 concentration and consistent sink behaviour at the cuticle. Following the terminology of Sutton et al. (1998) and Flechard et al. (1999), we added a non-zero cuticular water film equilibrium concentration χ_d , coupled with an exchange resistance R_d , so that the χ_c equation from Nemitz et al. (2001) becomes:

$$\chi_c = \frac{\chi_a (R_a R_b)^{-1} + \chi_g (R_b R_g)^{-1} + \chi_s \left[(R_a R_s)^{-1} + (R_b R_s)^{-1} + (R_g R_s)^{-1} \right] + \chi_d \left[(R_a R_d)^{-1} + (R_b R_d)^{-1} + (R_d R_g)^{-1} \right]}{(R_a R_b)^{-1} + (R_b R_g)^{-1} + (R_a R_s)^{-1} + (R_b R_s)^{-1} + (R_g R_s)^{-1} + (R_a R_d)^{-1} + (R_b R_d)^{-1} + (R_d R_g)^{-1}} \quad (4)$$

where R_a is the aerodynamic resistance above the canopy, R_b is the laminar boundary layer resistance for foliage, R_s is the resistance to stomatal gaseous transfer, and R_g is the sum of the in-canopy aerodynamic transfer resistance R_{ac} and of the resistance of the ground laminar boundary layer R_{bg} :

$$R_g = R_{ac} + R_{bg} \quad (5)$$

with

$$R_{ac} \{d + z_0\} = \frac{\alpha \{d + z_0\}}{u_*} = \frac{40 Hc}{0.45 u_*} \quad (6)$$

where α is a factor of proportionality between R_{ac} and the inverse of friction velocity $1/u_*$ (Nemitz et al., 2001), and Hc is canopy height (m). The parameterisation for R_{ac} is adapted from measurements in grassland during this experiment (Nemitz et al., 2008a), and $\alpha = 40$ was estimated for a canopy height of 0.45 m. Equation (3) thus provides an R_{ac} that is scaled according to height (Milford, 2004). The laminar boundary layer resistance at ground level is given by Nemitz et al. (2001) as:

$$R_{bg} = \frac{Sc - \ln(\delta_0/z_1)}{k u_{*g}} \quad (7)$$

where k the von Karman constant (0.41), Sc is the Schmitt number ($Sc = \nu_a/D_\chi$, with ν_a the kinematic viscosity of air and D_χ the molecular diffusivity of NH_3). The term u_{*g} is defined as an in-canopy friction velocity, assuming that a logarithmic wind profile exists within the canopy with a slope of u_{*g}/k . The lower boundary of this profile is found at the height δ_0 above ground where eddy diffusivity equals D_χ , i.e. $\delta_0 = D_\chi/(k u_{*g})$, while z_1 is the upper height of the logarithmic wind profile (Nemitz et al., 2001). The parameterisations for u_{*g} and z_1 given by Milford (2004) were used here such that:

$$u_{*g} = u/20 \quad (8)$$

where u is horizontal wind speed at a reference height above the canopy, and

$$z_1 = Hc/5 \quad (9)$$

The bioassay measurements provided values of Γ_s of 305 (SE 1.5) for the apoplast of green leaves, and 5193 (SE 392) for senescent leaves (Mattsson et al., 2008b). The first value was used to describe Γ_s for the whole pre-cut period, and the

second one for the description of the litter in the post-cut period. The Γ_s values were combined with canopy temperature ($T(z'_o)$, Nemitz et al., 2008b) to estimate χ_s . The estimates of Γ for different plant, litter and soil compartments through the campaign were compared (Sutton et al., 2008b) and showed extremely large values for litter (Γ_g , c. 2×10^5 after cutting), and these are also tested here within the two-layer modelling framework.

The model performance was evaluated comparing measured and simulated values of ammonia fluxes. Agreement of flux direction, root mean square difference, and correlation were quantified.

3 Results

3.1 Results of leaf wetness measurements

During the first part of the pre-cut phase (20–25th May), there was first a relatively humid period with occasional showers, several dew events and leaf wetness values between 0.5 and 1 about half of the time. Between 26–29th May, leaf wetness was generally below 0.5 (Fig. 2a).

Directly after the cut, there was a short rainfall which ceased during the night, followed by a strong diurnal pattern of leaf wetness, with low values throughout the day, high values at night, and no further rain before 5th June. The values measured on filter papers usually showed the same patterns, although during days without rain the mean LW values recorded on the leaves were mostly higher than the filter paper values (Fig. 2a, b). No clear indications of stomatal activities could be derived from comparing wetness sensors clipped to leaves and filters, respectively, as would have been the case in an obvious dependence on photosynthetically active radiation (Burkhardt et al., 1999).

Figure 3 shows the humidity dependence of LW during the pre-cut phase for different heights. Data measured during rainfall and up to 2 h after the end of each rain event were excluded from the analysis. This was due to the fact that intercepted rain stays on the leaves for some time, even if the humidity has decreased in the meantime, resulting in values along a horizontal line at $\text{LW}=1$, as still can be noted for the lowest level (0–15 cm). An exponential increase with air humidity can be noted at all three heights. At the lowest level, the increase of LW with increasing RH starts earlier than at the higher levels, and high leaf surface wetness prevails even

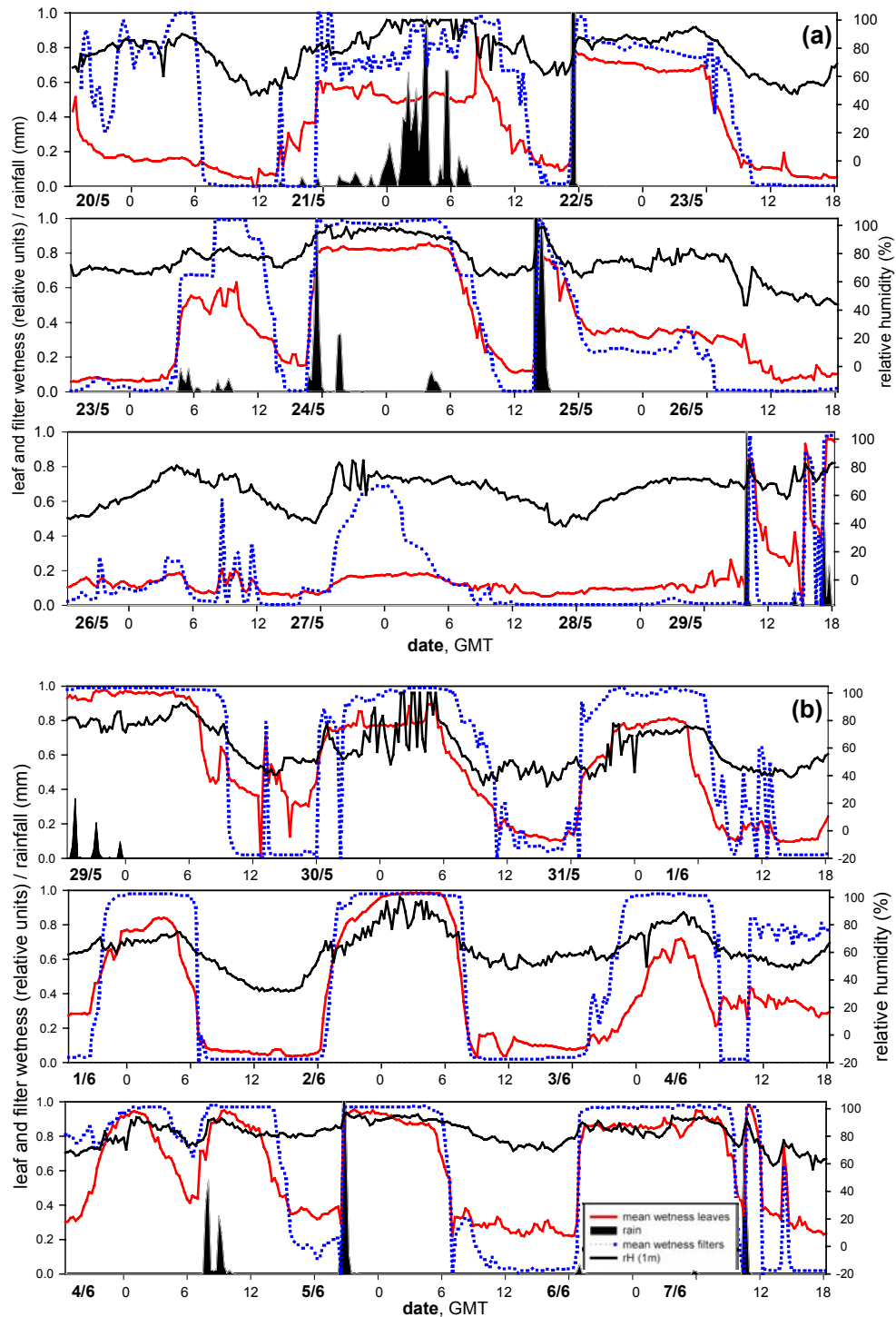


Fig. 2. Leaf wetness (LW, mean values of all heights) measurements on leaves and on paper filters, relative humidity at 1 m, and rain distribution (black signature at the bottom) during (a) the pre-cut phase and (b) the post-cut phase of the GRAMINAE experiment. Legend is placed in lowest sketch.

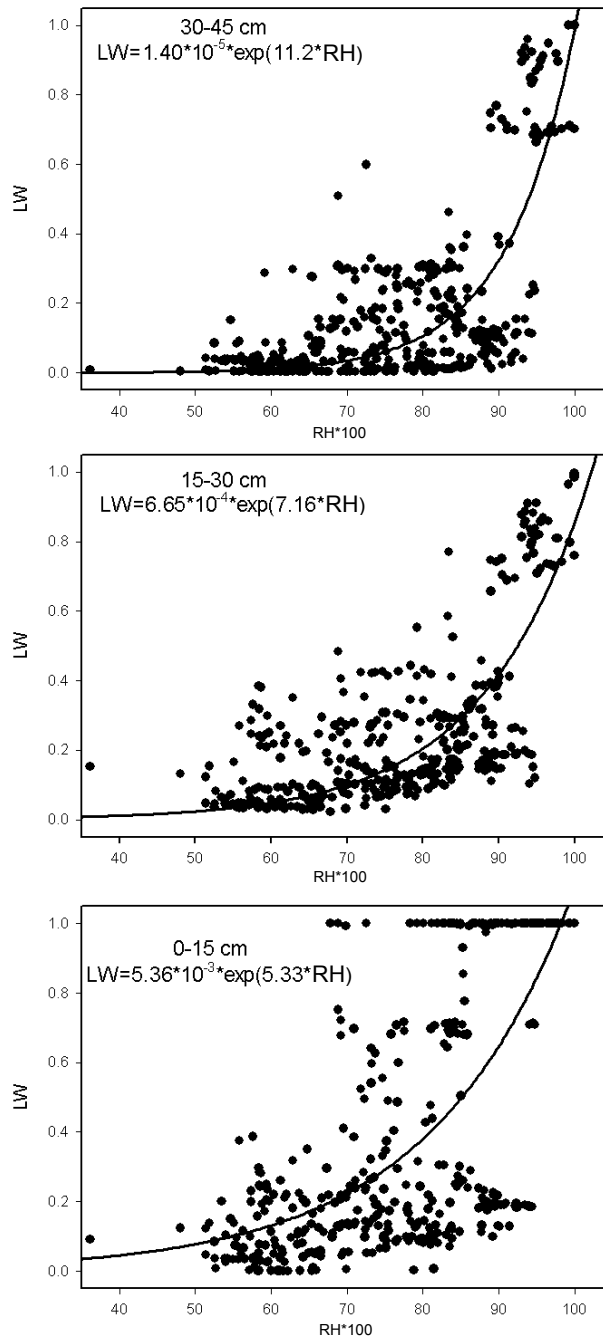


Fig. 3. Relation between normalized leaf wetness (LW) and relative humidity at the notional height of gas exchange ($RH(z'_0)$) for leaf wetness sensors installed at different heights within the grass canopy (0–45 cm) during the pre-cut phase. LW values during precipitation events and within 2 h after the last rain event were not included.

at low air humidities. The overall approximation combining values from all three heights

$$LW = 3.68 \times 10^{-4} \times \exp(7.9 \times RH) \quad (10)$$

was very close to the relation for the middle leaf layer. It should be noted here that the RH values used on the abscissae of Fig. 3 are referenced to z'_0 , the notional mean height

of gas exchange in a single-layer, “big leaf” model (Monteith and Unsworth, 1990). There are, however, strong vertical gradients of RH within the canopy, with the higher values expected near the ground in grassland, which could explain at least partly why the exponential relationships of LW differ when expressed relative to the relative humidity of a common height.

In the following analysis (and including Fig. 2), all leaf surface wetness values have been combined to form one single leaf wetness parameter for the whole depth of the canopy. This means that the influence of in-canopy turbulence on the vertical distribution of leaf wetness is neglected, and that all heights are included into the measurements with the same weight.

3.2 Dew measurements

The chemical analysis of dew was intended to validate the wet chemistry part of the model. Dew measurements, compared to the chemistry of bulk rain from a wet-only collector, indicate higher concentrations of ammonium, potassium and chloride, and lower concentrations of nitrate (Table 1). The independently sampled guttation from grass also showed higher ammonium and sulphate concentrations than in wet-only samples. Leaf surface pH was significantly higher in dew than in guttation, while pH from rain collected on leaves showed considerable variation. Concentrations of ammonium and other cations were only 8% lower on average in wet-only samples than in bulk rain, while this difference was 27% for nitrate and other anions, reflecting the influence of dry deposition in the bulk samples. The mean concentrations found in the wet-only collector were used to initialise the chemistry of the model.

3.3 Modelling

3.3.1 Parameterisation of water adsorption

The frequently observed exponential dependence of ammonia deposition on relative humidity (e.g. Wyers and Erisman, 1998; Milford et al., 2001) is likely to be caused by an exponential increase of liquid water on the leaf surfaces. This increase has the characteristics of the exponential physisorption with RH described by a BET isotherm (Brunauer et al., 1938; Altimir et al., 2008). However, the BET isotherm only explains a few layers of physisorption, equivalent to a few nanometers of physically adsorbed water, which is not enough to explain the cuticular deposition fluxes observed. The “effective” water volume for ammonia absorption has been calculated in the range of several micrometers (van Hove and Adema, 1996). So, while there are consistent reports on the influence of humidity and microscale water on trace gas fluxes, there is a gap between the physically explained adsorption of water, and the resulting effects.

To describe the humidity influence on water adsorption, we chose the values derived by Altimir et al., (2006), assuming “one layer” sorption at RH=0.7, “two layer” sorption at RH=0.85, and “X layer” sorption at RH=1. In addition, the “effective water layer” of RH=1 was set to 0.1 mm adsorbed water layer as described in Sect. 2.1. The value of X was

varied between the original suggestion of 5 (Altimir et al., 2006) and 25, and applied to the pre-cut period (20th to 29th of May).

The results are shown in Table 2. The overall agreement of measured and modeled fluxes for direction of fluxes, differences, and correlation was highest for X=16. This value, which is also incorporated in Eq. (3), Sect. 2.2, is used for the calculations in the paper unless otherwise stated. The agreement was also better compared to model runs which used directly the RH values (not LW) together with the BET approach (which gave best results for X=5), and the alternative approach (not using BET) of a vapour pressure deficit dependent curve for the effective water layer given by van Hove and Adema (1996) (Table 2).

3.3.2 Application of the single-layer model to the pre-cut period

Fig. 4a shows the calculated leaf surface water storage derived from leaf wetness measurements (“empirical V_{H_2O} ”) using Eq. (2) before the grass cut.

The water storage as calculated by the dynamic energy balance model, using micrometeorological measurements to determine condensation, dewfall and evaporation, is also shown for comparison. Two different regimes can be seen in the pre-cut period, one with a wetter phase in the first three days (23–25 May), and a drier one in the second half (26–29 May). Apart from wetness caused by rainfall, v_{H_2O} is calculated to be below 0.1 mm during most of the time (Fig. 4a).

The modelled ammonia fluxes using leaf wetness measurements and the energy balance showed similar agreement with the measurements (Fig. 4b), with slightly better values for the leaf wetness based model (Table 2). Using a Γ_s value of 305, a general agreement with respect to the magnitude of the fluxes can be observed. During the wetter first period, deposition was the dominating flux. By contrast, from 25 May, deposition decreased and occasional emission events were measured, which is better reproduced by the energy balance approach. In the second period, a relative decrease in the measured flux indicates that there is a decrease in the surface uptake efficiency which might be explained by the occurrence of relative drier conditions and this part is better reproduced by using the LW measurements. Table 2 also shows reasonably good agreement of hypothetical Γ_s values in the range of 1000 within the single layer model in the pre-cut period.

Based on the LW measurements, Fig. 4c shows separately the modeled stomatal and cuticular fluxes of ammonia which sum up to the total modelled flux indicated in the previous graphs. During daytime, the model indicates stomatal emission periods. However, these rarely result in simulated net emission periods due to re-capturing of the released ammonia by the cuticle ($\chi_c < \chi_s$). The notional concentrations χ_s and χ_d , and the measured air concentration at 1 m height (χ_a) are shown for the whole pre-cut period in Fig. 4d.

Table 2. Evaluation of model performance based on agreement of flux direction, root mean square difference, and correlation between measured and simulated values of ammonia fluxes during the pre-cut period. Bold numbers indicate the optimum values calculated for the approach using leaf wetness (LW) values and the BET isotherm from Eq. (2) with Gamma 305 (1-layer), and X physisorbed layers at 100% RH.

Section	approach	X (“physi-sorbed layers”)	Correctness of flux direction (%)	Mean square difference ($\text{ng m}^{-2} \text{s}^{-1}$)	Correlation coefficient (r^2)	Graph shown in Fig.
3.3.1	LW/BET	5	76.3	26.1	0.252	
3.3.1	LW/BET	6	76.3	25.4	0.251	
3.3.1	LW/BET	8	76.3	20.2	0.325	
3.3.1	LW/BET	10	75.0	18.8	0.333	
3.3.1	LW/BET	16	76.0	16.8	0.317	4b
3.3.1	LW/BET	20	76.9	17.0	0.296	
3.3.1	LW/BET	25	75.6	17.5	0.259	
3.3.1	RH/BET	5	73.1	11.2	0.243	
3.3.1	RH/BET	6	76.3	50.2	0.275	
3.3.1	RH/BET	8	76.3	51.1	0.276	
3.3.1	vpd (van Hove and Adema, 1996)	–	76.3	60.5	0.271	
3.3.2	Energy balance (Flecharde et al., 1999)	–	63.1	16.9	0.298	4b
3.3.2	$\Gamma_s = 800$	16	79.2	12.7	0.336	
3.3.2	$\Gamma_s = 1000$	16	76.9	12.1	0.349	
3.3.2	$\Gamma_s = 1200$	16	73.7	12.1	0.357	
3.3.2	$\Gamma_s = 1500$	16	68.0	12.8	0.356	
3.3.5	2-layer, LW/BET, $\Gamma_g = 5193$	16	61.9	15.6	0.403	7a
4	2-layer, LW/BET, $\Gamma_g = 200\,000$	16	23.7	846.1	0.344	

The available wetness in relation to the ions present on the leaf surface determines the liquid phase concentrations, and hence the ionic strength in the solution (Fig. 4e). The measured dew pH values are also shown on Fig. 4e alongside modelled pH. The modelled and measured values showed good agreement on 23rd and 24th May, whereas substantial discrepancy was apparent for the next two dew events on 25th and 26th May. By changing the usually applied initial chemistry of the model to a pure NaCl solution of the same ionic strength, the modelled pH agreed with the measured pH on 25th May and approached it on 26th May, indicating the sensitivity of the model results to this factor (Fig. 4e).

3.3.3 Application of the single-layer model to the post-cut period

When applying the 1-layer model to the post-cut period with the measured Γ_s value of 305, the agreement with measured fluxes was poor (Fig. 5).

In order to obtain a better agreement with the observed strong emission events, it is necessary to increase Γ_s to unrealistically high values, as illustrated in Fig. 5 using $\Gamma_s=5000$. Given the scale of difference between this value and the measurements (Mattsson et al., 2008b), the discrepancy cannot

be ascribed to uncertainties in the measured Γ_s , but rather points to the need to include a further separate NH_3 source in the model (Fig. 1b), which was provided by the leaf litter after the cut, when grass residues were left to decay on the ground.

3.3.4 Application of the 2-layer model to the post-cut period

Motivated by parallel studies which identified the importance of leaf litter emissions for the post-cutting period (David et al., 2008; Herrmann et al., 2008; Sutton et al., 2008b), a two-layer model with litter as a second source was applied to the post-cut period. The measured stomatal Γ_s of 305 was used, while for the litter Γ_g was assumed to be 5193 and equivalent to the value measured for senescent leaves (Mattsson et al., 2008b). The performance of the model is shown in Fig. 6. Generally, measured and simulated fluxes are in good agreement.

The strongest discrepancies appeared during daytime, when the recorded ground surface temperatures were lower than $T(z_0')$, which was extrapolated from air temperature using the measured sensible heat flux and transfer resistances R_a and R_b . Higher ground surface temperatures lead to

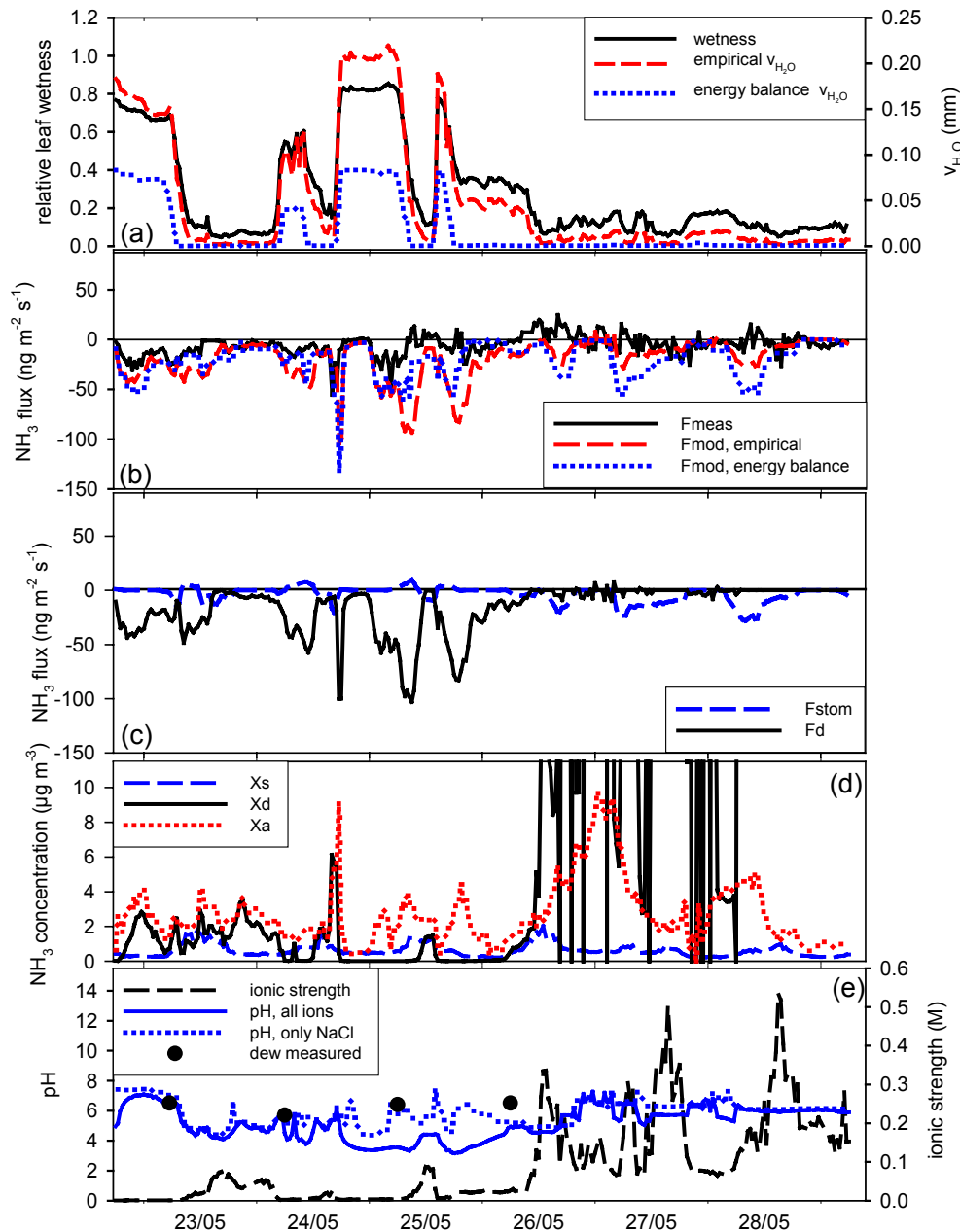


Fig. 4. Comparison of measured and modeled (single-layer) parameters during the pre-cut phase. **(a)** Relative leaf wetness (LW) measurements; calculated canopy water storage based on LW (“empirical”) and based on micrometeorological data (“energy balance”). **(b)** Measured and modeled flux, based on LW and micrometeorological data. **(c)** Modeled stomatal and cuticular fluxes during the pre-cut period. **(d)** Stomatal and cuticular compensation points during the pre-cut period, together with air concentration χ_a (1 m). **(e)** Ionic strength, measurements of dew pH and two calculations of pH based on different chemistry (see text). (c), (d), and (e) are based on LW measurements.

higher emissions from the litter and overestimation of ammonia emissions (Fig. 6a). While stomatal fluxes were simulated to be small throughout, significant emission from the ground leaf litter took place which was partially recaptured within the canopy, even with little surface water (Fig. 6b, e). pH in the water film was between 5 and 8 under these conditions, reaching highest values during times of low water film

thickness (Fig. 6 e) whereas on 2nd June it decreased to 3.4, with the ionic strength reaching 4.0 M. At such high concentrations, the modelling of wet chemistry is probably not very reliable.

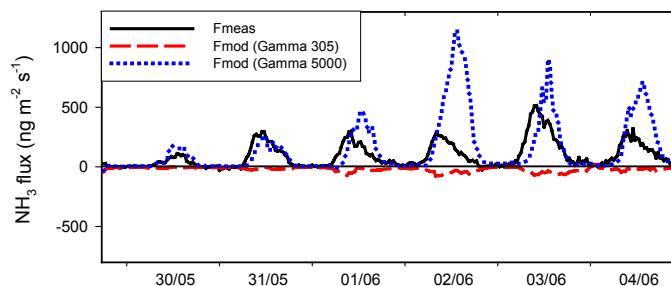


Fig. 5. Measured and modeled NH_3 fluxes in the post-cut period, using the single-layer model and the measured Γ_s , 305 as well as a hypothetical Γ_s , 5000.

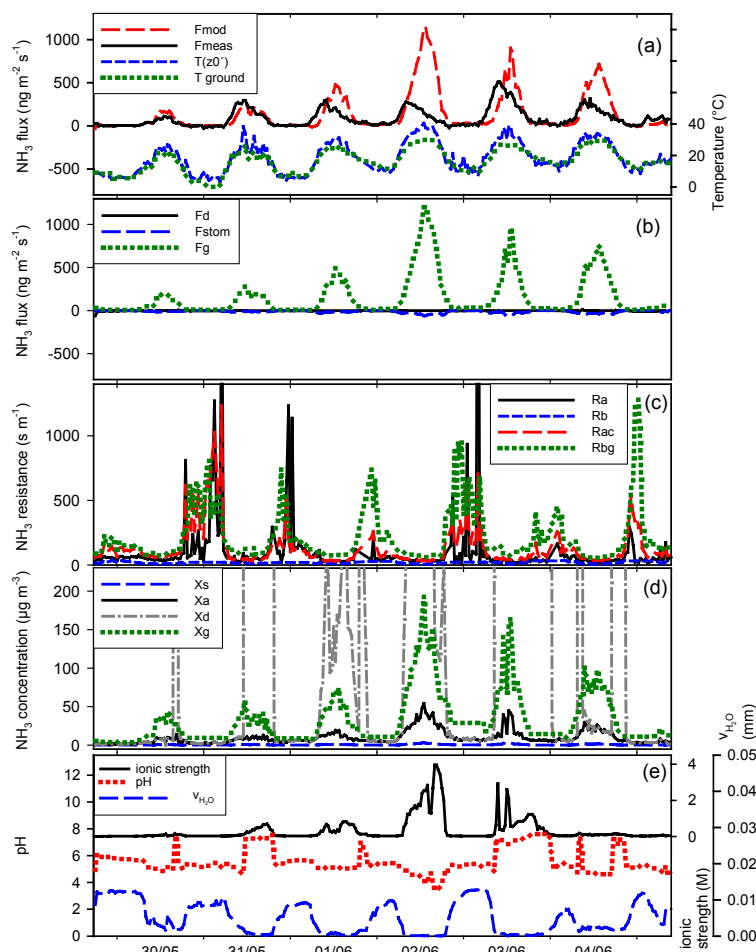


Fig. 6. (a): Measured NH_3 fluxes and modeled fluxes using the 2-layer model, as well as comparison of $T(z_0')$ and T_{ground} . Calculations were made using the measured stomatal Γ_s of 305, and litter Γ_g of 5193, respectively. (b) Partitioning of NH_3 fluxes between stomata, cuticle, and ground (litter) and (c) contributing resistances. (d) Notional ammonia concentrations along the different points of the exchange path. (e) Water volume, ionic strength, and pH of the water layer.

3.3.5 Application of the 2-layer model to the pre-cut period

The 2-layer model was also applied to the pre-cut period (Fig. 7), assuming that the Γ_g for litter was the same as after the cut.

In this case, it would be expected that larger R_{ac} and R_{bg} values would limit litter emissions, while much of the NH_3 emitted by litter would be recaptured within the grass canopy (Nemitz et al., 2000). Applying the same parameterisation of the 2-layer model as above to the pre-cut period, there is

generally a good agreement between measured and modelled ammonia fluxes, although there are several periods differing both in sign and size of the fluxes (Fig. 7a). While emission and deposition periods are predicted less accurately, the correlation between measured and modelled flux is better for the 2-layer model (Table 2).

Especially around noon and during the early afternoon, emission was calculated at higher rates than measured, or even during deposition periods. These modelled emissions were dominated by F_g , respectively (Fig. 7b). In the pre-cut period, R_{ac} and R_{bg} are confirmed as having much stronger influence on the net fluxes (Fig. 7c). Although there are periods of substantial disagreement between the model and the measured fluxes, the overall agreement in the dynamics is encouraging. Thus on 23 and 24 May, although litter NH_3 emissions (F_g), are substantial, much of it is recaptured by the leaf surfaces (F_d) and by stomatal uptake (F_s). By contrast, when the canopy is dry, and turbulence at a maximum (small R_{ac} , R_{bg}), some periods occur where the litter NH_3 emission escapes from the canopy. Such emission periods occur 25–27 May, and are broadly simulated by the model, as is the switch from deposition to emission on 26 May. Overall, the major discrepancy is probably related to the need to include the litter emission as a dynamic process, in which Γ_g is not a constant. By comparison with the post-cut period, this would imply smaller simulated emissions (in better accord with the measurements).

3.3.6 Influence of leaf wetness on modelled fluxes

Evaporation of rain or of dew droplets in the morning always leads to an extremely strong concentration process within a short time period, with increasing water activity, increasing interaction of ionic components and volatilisation of dissolved gases. Dew samples can only be taken when visible water is available, which would be reflected in very high leaf wetness values, so they represent minimum concentrations of ammonium. For pH, the overall composition of the ions present in the solution is decisive for the direction the H^+ concentration change will take, rise or fall, and thus also for the effect on ammonia fluxes. When comparing modelled ammonium concentrations in the water film with the measured concentrations in dew during the pre-cut period, there was a good general agreement when leaf wetness values of the lower canopy were used for modelling, while the mean leaf wetness values would lead to higher concentrations (Fig. 8).

4 Discussion

Ammonia fluxes, ammonium concentrations and pH in leaf surface water could be reasonably well described by the different model versions, but an accurate scheme to describe leaf surface water storage is essential, especially when the

canopy is drying out. Prior to the grass cut, NH_3 deposition prevailed (Milford et al., 2008), so that cuticular exchange processes at the top of the canopy may have dominated the net exchange. After the cut, conditions would have changed substantially, as cells with a high solute content were massively broken down and would also take part in the exchange with the atmosphere directly, bypassing the stomatal pathway. There was additionally the effect of a direct exposure of decomposing plant material in the existing leaf litter on the soil surface, through the removal of the upper part of the canopy and consequent reduction of within-canopy transfer resistance (Nemitz et al., 2001). Thus, the litter is likely to have contributed large amounts of ammonia to the total fluxes following cutting (David et al., 2008; Mattsson et al. 2008a). The Braunschweig experiment has demonstrated that the existence and stratification of different NH_3 sources need to be considered in order to improve modelling results. Breakage of cells and decomposing organic material on the ground lead to ammonia emissions often exceeding the stomatal contributions of the plants. Parts of the emissions are recaptured by the leaf surface and internal structures in the canopy. Especially in higher canopies, internal turbulence is difficult to determine and parameterisations are uncertain. Measured emission events often occur during periods of increased turbulence which flushes NH_3 out from deep within the canopy from litter emissions. The application of the 2-layer model led to an improvement of the model performance, indicating the important role of a second ammonia source near the ground. Figure 6 demonstrates that litter emissions can easily explain the measured fluxes after cutting. Conversely, the value for senescent leaves of Γ_g (Mattsson et al., 2008b) which is much smaller than inferred from litter measurements (Sutton et al., 2008b; see also evaluation for $\Gamma_g=2 \times 10^5$ in Table 2) is confirmed by the model run. This may be explained by the fact that the value of Γ_g is itself a dynamically varying parameter rather than a constant under plant regulation, as is more logically the case for Γ_s . Thus litter emissions and drying of the surface in the morning may exhaust the litter NH_4^+ pool, which is replenished during the following night in cool and wet conditions. This reason, together with the completion of desorption from the leaf cuticular pool, would explain why the measured emissions decrease in the late afternoon, and why the model overestimates the measured fluxes for the afternoons where the surface is warmest.

The model simulated only few and small net emission events in the pre-cut phase, which was caused by the fact that disappearing water which would lead to cuticular desorption most frequently happen in the mornings simultaneously to the opening of the stomata which may take up the released ammonia. Furthermore, a slightly or moderate acidic pH was often calculated, also preventing ammonia from desorption.

Leaf wetness measurements are used as a prediction method mainly in phytopathology, as many plant diseases are promoted by the presence of liquid water (e.g. Huber

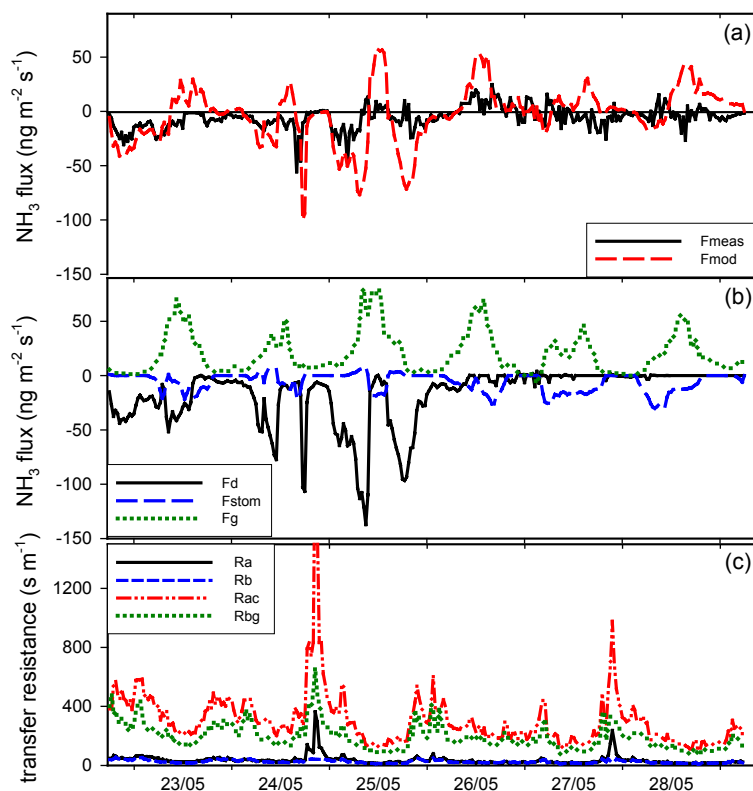


Fig. 7. (a) Measured and modeled fluxes applying the 2 layer model to the pre-cut period. (b) Partitioning of internal modeled fluxes. (c) Contributing resistances to NH_3 transfer.

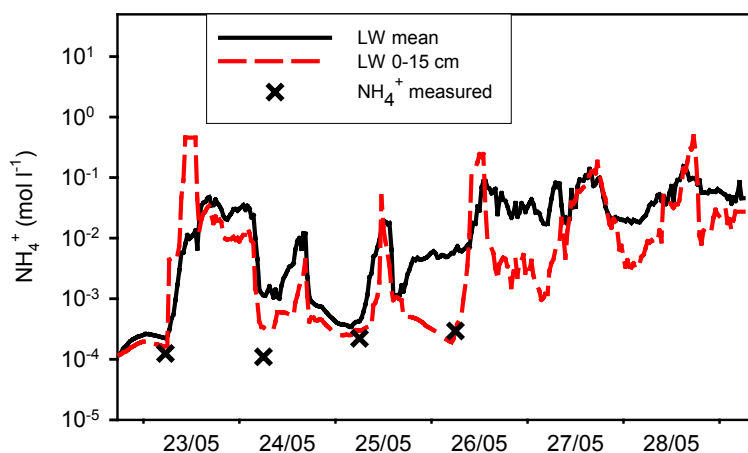


Fig. 8. Measured ammonium concentrations in dew and modeled NH_4^+ concentrations in the leaf water layers, using mean wetness (LW) values and those from the lower layer (0–15 cm). Note logarithmic scale.

and Gillespie, 1992; Andrews and Harris, 2000; Lindow and Brandl, 2003; Chelle, 2005), but they are also increasingly used in micrometeorological investigations due to their importance for fluxes of water soluble trace gases (e.g. Altimir et al., 2006; Wichink Kruit et al., 2008). The information gained by the leaf wetness sensors was included into

the model. This is a more direct approach compared to the determination by the energy balance, and yields higher and probably more realistic values of leaf surface water storage in macroscopically “dry” conditions, because recondensation phenomena within the canopy are not detected by routine micrometeorological techniques. Recondensation may happen

from soil evaporation (Monteith, 1957; Long, 1958) as well as from stomatal transpiration (Burkhardt et al., 1999). A better overall agreement of LW measurements compared to the energy balance was noted, although not in all situations. The main problems involved with directly applying leaf wetness sensors on the leaves are reproducibility, frequent maintenance intervals, and heterogeneity. The actual existence of liquid water on leaf surfaces is determined by the specific microstructure of the surface, the salts on it, and the wetness caused by condensing transpiration which can not be completely simulated from RH alone nor from artificial wetness sensors. Therefore, leaf wetness measurements should ideally be included into measurement networks. Where this is not possible, relative humidity can be used as a highly correlated factor to ammonia exchange with leaf surfaces. One might also think about a factor to include wetness after rain (causing a deviation from the pure RH-vH₂O scheme).

However, especially the reasons for the large difference between the physically explained water adsorption to leaf surfaces and the observed differences on trace gas absorption related to relative humidity and thus most likely caused by the liquid water layer, remain unexplained. The most likely explanation is the absorption of water by hygroscopic salts, which might have the capacity to absorb enough water by deliquescence, and together with pH effects might allow for large ammonia absorption. However, a thorough theoretical and experimental analysis of this possibility is still lacking. Although the wetness clips do provide a direct assessment of leaf wetness changes, a comprehensive, mechanistic and dynamic understanding of all wetting events (rain, dew, guttation, recondensation) as well as drying influences, is needed for model applications outside field campaign studies (e.g. Magarey et al., 2006).

Field measurements of surface water pH and ion concentrations provided a direct validation for the dynamic chemical module of the compensation point model. Macroscopic wetting of leaves consists of different contributions including different possible sources of water – rain, dew, fog, transpiration, and guttation – and of dissolved substances, particulate matter and gases from the atmosphere or the soil, exudates, and passively leached ions from the plant (Wisniewski, 1982; Takeuchi et al., 2003; Hughes and Brimblecombe, 1994; Burkhardt and Drechsel, 1997; Burkhardt and Eiden, 1990). The model simulates many of them, but especially initial concentrations (consisting of dissolvable residues on the leaf) are difficult to quantify. Dew pH was found to be higher (6.6) than that of rain collected on leaf surfaces (5.2). Hughes and Brimblecombe (1994) measured pH between 4.6 and 5.9 for bulk samples of dew and guttation taken from grassland dominated by *Poa* spp. In a study using artificial dew water condensers in SW France, Beysens et al. (2006) found higher mean dew pH values (6.3) than in rain (5.4), although the comparison is not straightforward because there was no interaction with living plant tissue. In addition, Beysens et al. (2006) reported almost systematically lower ion

concentrations in dew than in rain, whereas the present study showed the opposite (Table 1), confirming the importance of deposited particles, together with ion exchange between leaf tissue and surface water through the cuticle. The difference between measured pH of dew and the model may be caused by incomplete knowledge about ionic residues on the leaves. The sensitivity of the model to this factor is shown in Fig. 4e, indicating that for example NaCl-dominated dry deposition from the sea prior to the dew event could have caused a considerably different pH of the water film as compared to calculations based on measured rainfall chemistry.

The model sensitivity to other parameters, namely SO₂ concentration and leaching rates, was tested. Sulphur dioxide oxidation by O₃, as prescribed in the model (Adema and Heeres, 1995), was fast, of the order of 15% min⁻¹ on average, and O₃ levels during the experiment (mean ambient concentration of 26 ppb during the field campaign) were not limiting, given the low ambient SO₂ concentrations (mean 0.45 ppb over the whole campaign). To further assess the importance of SO₂ on ammonia fluxes, the 2-layer pre-cut model was also run with five-fold the measured half-hourly SO₂ concentrations. The higher SO₂ concentrations did not have a significant influence on ammonia fluxes (Fig. 9), confirming an observation made previously by Flechard (1998) over a Scottish moorland. However, additional model runs (data not shown) indicate that reduced SO₂ oxidation rates would result in increased pH and thus reduced NH₃ uptake by leaf surface water.

The sensitivity to cuticular ion transfer was more significant. When enabling leaching and cuticular ion uptake at all water volumes and at all pH values below 7 (and not 4.5 as in the model runs presented so far), a strong influence on almost all result parameters can be noted (Fig. 10). In reality ion concentrations will also change due to aerosol dry deposition, which was not accounted for in the model, while the trans-cuticular transfer of cations, although conceptually important, remains very uncertain from the mechanistic and quantitative viewpoints.

Whereas there was a concentration limit in the original model, stopping calculation of wet chemistry at a ionic strength higher than 0.3 M (Flechard et al., 1999), we calculated wet chemistry throughout all conditions. The reliability of these calculations decreases with increasing ionic strength due to the complicated interactions between the ions. A possible improvement would be the inclusion of other models dealing with such concentrated solutions, as often used in aerosol chemistry. Using the Extended AIM Thermodynamics Model (E-AIM; Clegg et al., 1998; Wexler and Clegg, 2002) for the situation with I = 4 M on 2nd June shown in Fig. 6, only crystals would be present with no liquid left, if the actual RH (z_0') = 0.31 is applied. However, RH directly at the leaf surface may be higher due to transpiration. Using the same ionic composition at RH = 0.5, liquid and NaNO₃ salt are calculated to co-exist in equilibrium with pH 2.5, and at RH = 0.9 pure liquid and pH 4.1 are the result of the

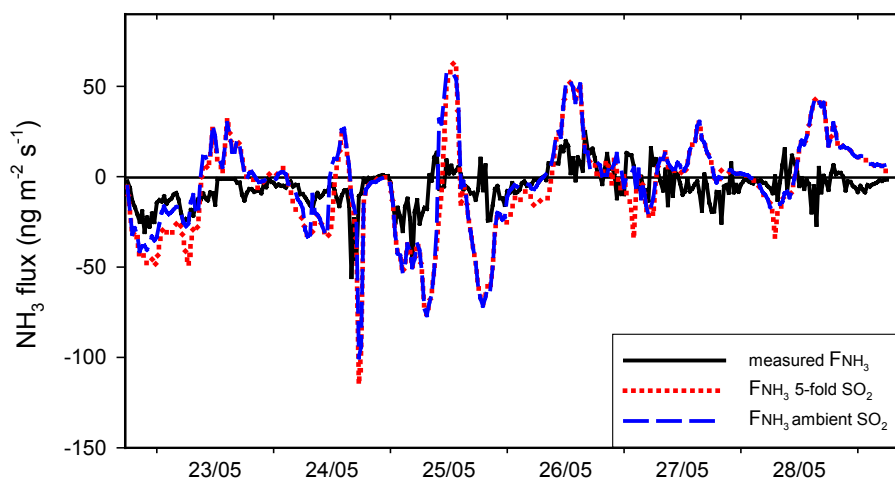


Fig. 9. Modeled NH_3 fluxes using the 2-layer model during the pre-cut period with actual measured SO_2 concentrations, compared to a run with five-fold SO_2 concentration. Measured fluxes are also indicated.

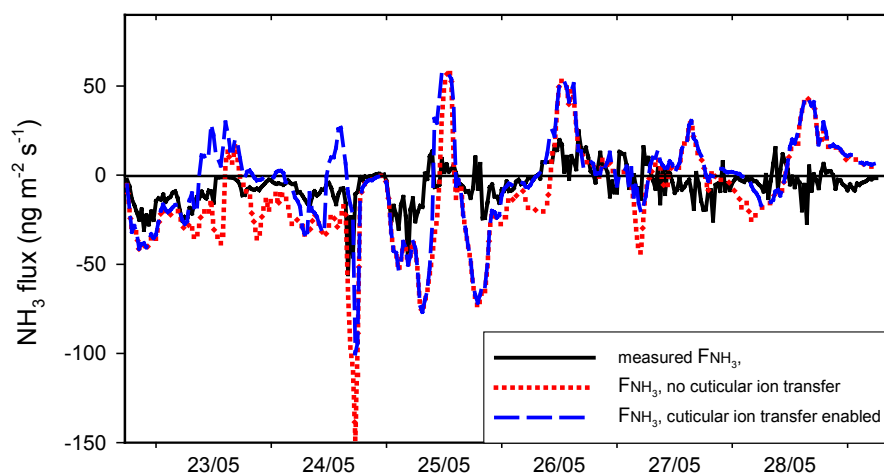


Fig. 10. Modeled NH_3 fluxes using the 2-layer model during the pre-cut period, with and without ion transfer across the cuticle (leaching and uptake). Measured fluxes are also indicated.

E-AIM calculation. Therefore, realistic assumptions about the humidity status within the leaf boundary layer would also be needed.

The present model analysis highlights the complex nature of ammonia biosphere/atmosphere exchange, which is dependent on chemical interactions on leaf surfaces, on exchange with biologically regulated foliar compensation points and exchange with ground surface sources such as leaf litter. The focus of the current model is on the chemical interactions occurring on leaf surfaces. These emphasize the way in which leaf surfaces can be both a source and sink of ammonia rather than only a sink as has been considered in simpler models applying a cuticular resistance (R_w). Although modelled desorption events were rather limited in the present assessment, these may be more significant at regional scales,

for example in particularly dry conditions, favouring desorption from high ionic strength solutions. The consequence of this effect will be to maintain atmospheric ammonia concentrations, increasing the effective atmospheric residence time of ammonia compared with models that only allow for ammonia deposition. For example, replacing a current simple deposition scheme in a regional atmospheric model with a full bi-directional scheme could easily halve rates of dry deposition. It is clear that further work is required to develop the present model approach to deal with desorption from concentrated solutions and dry surfaces, analogous to gaseous loss from aerosol surfaces, but with the added complexity of additional ions (e.g. base cations) on the leaf surface both from dry deposition and from foliar leaching.

The ultimate aim of the model is to understand the processes of bi-directional ammonia exchange, in particular the role of leaf surface adsorption and desorption processes. It is not expected that such a full model would be implemented in a complete regional atmospheric transport and chemistry model, due to the run times involved. However, based on the understanding developed it may in future be possible to develop simpler parameterisations that represent the essential processes investigated here. This must be a priority for future research.

For the improvement of the mechanistic understanding and its inclusion into the model, the following research priorities seem important:

- closing the knowledge gap between the physically explained water adsorption and the unexplained much stronger effects that it has on ammonia deposition,
- handling the chemistry of concentrated solutions, through to complete dryness and evaporation of volatile components (e.g. ammonium nitrate),
- improving the parameterisation of the cuticular charging resistance R_d ,
- developing a dynamic treatment of mineralisation and desorption of ammonia from decomposing leaf litter,
- developing simpler parameterisations that could be applied to more general atmospheric transport and chemistry models,

whereas we think that the within canopy turbulence is not a main uncertainty compared with these which are even more uncertain.

The shown strong influence of leaf surfaces on ammonia exchange, driven by air humidity but more specifically by persisting leaf wetness should be representative for all kinds of grasslands. The reported importance of litter emissions especially after the cut should especially be valid for intensively managed grasslands.

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