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Modeling the dynamic chemical interactions of atmospheric ammonia and other trace gases with measured leaf surface wetness in a managed grassland canopy

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Abstract

Ammonia exchange fluxes between grassland and the atmosphere were modeled 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. The leaf surface water storage was calculated from measured leaf wetness data using an exponential parameterisation.

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 and after the cut, but unrealistically high stomatal compensation points were needed after the cut in order to match measured fluxes. Significant improvements 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.

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. 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 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^+

5   concentration, temperature and pH, which determine the stomatal compensation point (Sutton et al., 1993, Sutton et al., 1995). The importance of cuticular processes at humidities well below water vapour saturation has been demonstrated by an increasing number of studies in the last years, indicating the presence of liquid water on plant surfaces under seemingly "dry" conditions (Erisman and Wyers, 1993, van Hove et al.,

10 1989, Burkhardt and Eiden, 1994). 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).

Leaf surfaces at different heights within the canopy are differently affected by hu-
15 midity generated by soil evaporation, plant transpiration, and ambient atmospheric humidity, and thus a vertical gradient in leaf surface wetness is to be expected. Water vapour transfer, evaporation and recondensation within the canopy influences the internal cycling of ammonia (cf. Denmead et al., 1976) due to its high solubility in water. For example, it is known that the soil is an important water vapour source for the
20 formation of dew, a process having been called "distillation" (Long, 1958, Monteith, 1957). Similarly, 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 or transpired from the leaves (Burkhardt et al., 1999). On leaf surfaces, water film development is in part determined by salts and solutes originating from atmospheric
25 deposition and cuticular leaching, and the dissolved ions and other solutes in turn influence the solubility of ammonia through control by pH. Any dynamic changes of canopy liquid water storage can lead to enhanced deposition or degassing of ammonia (Sutton et al., 1998).

Leaf surface wetness is expected to have been a major driver of ammonia fluxes

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during the GRAMINAE field experiment over managed grassland near Braunschweig, Germany, in 2000 (Sutton et al., 2008a[1], 2008b[2]). Prior to the grass cut, NH_3 deposition prevailed (Milford et al., 2008[3]), 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[4]; Mattsson et al.,

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[1]Sutton, M. A., Nemitz, E., Theobald, M. R., Milford, C., Dorsey, J. R., Gallagher, M. W., Hensen, A., Jongejan, P. A. C., Erisman, J. W., Mattsson, M. E., Schjoerring, J. K., Cellier, P., Loubet, B., Roche, R., Neftel, A., Herrmann, B., Jones, S. K., Lehman, B. E., Horvath, L., Weidinger, T., Rajkai, K., Burkhardt, J., Löpmeier, F. J., Dämmgen, U.: Dynamics of ammonia exchange with cut grassland: Strategy and implementation of the GRAMINAE Integrated Experiment, Biogeosciences Discuss., submitted, 2008a.

[2]Sutton, M. A., Nemitz, E., Milford, C., Erisman, J. W., Hensen, A., Cellier, P., David, M., Loubet, B., Personne, E., Schjoerring, J. K., Mattsson, M. E., Dorsey, J., Gallagher, M., Horvath, L., Weidinger, T., Dämmgen, U., Neftel, A., Herrmann B., Lehman, B., Burkhardt, J.: Dynamics of ammonia exchange with cut grassland: Synthesis of results and conclusions, Biogeosciences Discuss., submitted, 2008b.

[3]Milford, C., Theobald, M. R., Nemitz, E., Hargreaves, K. J., Horvath, L., Raso, J., Dämmgen, U., Neftel, A., Jones, S. K., Hensen, A., Loubet, B., and Sutton, M. A.: Ammonia fluxes in relation to cutting and fertilization of an intensively managed grassland derived from an inter-comparison of gradient measurements, Biogeosciences Discuss., submitted, 2008.

[4]David, M., Loubet, B., Cellier, P., Mattsson, M., Nemitz, E., Roche, R., Riedo, M., Schjoerring, J. K., and Sutton, M. A.: Analysis of ammonia fluxes with intensively managed grassland using dynamic chambers, I. Sources and sinks of ammonia at canopy level, Biogeosciences Discuss., submitted, 2008.

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2008[5]), and these processes need to be accounted for to make realistic estimates in ammonia exchange models.

In this paper, a single layer ("big leaf") chemistry and exchange model (Flechard et al., 1999) is applied in a first approach, simulating 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 modeling of leaf surface water storage is replaced by an empirical static parameterisation based on continuously measured leaf wetness. In order to better reflect ammonia emission from litter, the original "big leaf" model is upgraded to a stratified approach with two layers, i.e. foliage and litter, 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.

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 29 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, $3.06\,\mathrm{m^2\,m^{-2}}$) down to 7 cm (LAI, $0.14\,\mathrm{m^2\,m^{-2}}$). 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. The bulk of this equipment was

[5]Mattsson, M., Herrmann, B., Jones, S. K., Borrella, S., Bruhn, D., Dorsey, J., Neftel, A., Sutton, M. A., and Schjoerring, J. K.: Contribution of different grass species to plant-atmosphere ammonia exchange in intensively managed grassland, Biogeosciences Discuss., submitted, 2008.

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placed at "Site 1" (Sutton et al., 2008a[1]); in practice, the sensors 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 of Site 1, 200 m to the south and 50 to 100 m to the north. A further, smaller array of instruments was located at "Site 2", approximately 250 m east of Site 1 and close to the eastern edge of the field, which was bounded to the east by a deciduous shelterbelt approximately 8 m tall. The groups and the abbreviations used for each are described elsewhere (Sutton et al., 2008a[1]) 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 rigorous 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[3]). Bioassay measurements to determine the apoplastic concentrations especially of NH_4^+ and pH were conducted by infusion and subsequent removal with a centrifuge (Mattsson et al., 2008[5]), while the vertical structure of the plant canopy and bioassays was also determined (Herrmann et al., 2008[6]). In addition to ammonia, air concentrations and fluxes of acid gases were measured (Sutton et al., 2008a[1], 2008b[2]).

2.1 Surface wetness measurements

Leaf surface water was collected for chemical analysis mainly after clear, calm nights. Samples included dew, surface water after rain, and, in some instances, guttation from the leaves. Actual radiative dew formation was observed on 5 days (21, 23, 24, 25,

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[6]Herrmann, B., Mattsson, M. E., Jones, S. K., Cellier, P., Milford, C., Sutton, M. A., Schjoerring, J. K., and Neftel, A.: Vertical structure and diurnal variability of ammonia emission potential within an intensively managed grass canopy, Biogeosciences Discuss., submitted, 2008.

26 May). The sampling was done manually by stripping the droplets with a pipette from grass leaves and bringing them to a plastic vial (Burkhardt and Eiden, 1990), with sample sizes of about 500 μl being large enough for the subsequent chemical analysis to be carried out. The chemical composition of the dew, rain and guttation samples was determined in two stages: pH was measured immediately using a small aliquot of about 10 μl, which was subsequently discarded to avoid pollution from the used microelectrode. Samples were then frozen and chemical analysis for NH_4^+, K^+, Ca^{2+}, Cl^-, NO_3^-, SO_4^{2-} was done later in the laboratory.

Leaf wetness measurements were carried out using clip sensors with a distance of about 5 mm between the electrodes, which were 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 heights ($\sim$10 cm, $\sim$25 cm, $\sim$40 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 the stomatal influences 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 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).

For the introduction of the normalized leaf wetness values (LW) into the NH_3 model an exponential function was adapted, which converted LW into the "effective" water volume (storage) interacting with ammonia (cf. van Hove and Adema, 1996). For this reason, a surface water storage capacity of 0.1 mm per unit leaf area was assumed (Barfield et al., 1973; Wohlfahrt et al., 2006). The increase of water storage was assumed to be an exponential function of the leaf wetness signal. This is a consequence of the characteristics linking the signal with relative humidity, and the increase of water volume of deliquescent salts with increasing humidity (Burkhardt and Eiden, 1994, Sutton et al., 1995, Winkler, 1988).

2.2 Model

Fluxes were modeled using the dynamic chemical canopy compensation point model, of Flechard et al. (1999). 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., 2008[5].

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 which equals the sum of the component fluxes (Sutton et al., 1995). The difference with conventional canopy resistance or canopy compensation point models (Sutton et al., 1993, Sutton et al., 1995), is that the leaf cuticular

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concentration χ_d is different from 0, allowing desorption as well as deposition from the non-stomatal part of the leaf.

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; Burkhardt and Drechsel, 1997). 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. These processes, however, are poorly understood and only coarsely parameterized, and 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. One justification for the pH limitation lies in the fact that base cation leaching has been mainly observed as a passive defence mechanism against acid rain on leaf surfaces, limiting foliar injury; the other is that a continuous and unlimited supply of cations at higher pH values would raise pH unrealistically.

The program determines the duration of each new time step, such that each new equilibrium concentration does not differ by more than 10% from the concentration at the previous step. In wet conditions, time steps of up to a few minutes are possible, but in dry conditions time steps become infinitesimally small. The dynamic chemistry module is therefore set to stop being the driving force for trace gas exchange when conditions become too dry, i.e. as soon as the ionic strength given by the amount and composition of the dissolved salts exceeds 0.3 M, or if more than 50 model iterations would be needed to calculate the equilibrium. In that case, however, the cuticle is not considered as entirely inactive for NH_3 (and other gas) fluxes; here, instead of the dynamic bi-directional ($\chi_d > 0$) scheme based on Henry's law, the model switches to a conventional empirical R_w scheme (Nemitz et al., 2001), which is deposition-only ($\chi_d = 0$) with respect to the cuticle.

In practice, during the drying-out phase that occurs between the "fully-wet" chemistry of dew or rain, and the "dried-out" cuticular bed of particles and ammonium salts, ammonia may desorb for a while until the surface is fully dry. It is during this phase that gaseous exchange ceases to be controlled, in the model, by ideal solution chemistry,

because processes in high-activity solutions on leaf surfaces are still poorly under-stood. Then during later conditions of increasing humidity (e.g. sunset or after rain),
the surface re-wets, allowing a renewed driving of ammonia exchange through dynamic modeling (cf. Sutton et al., 1998, Flechard et al., 1999). However, during the runs pre-sented here, the leaf surface was almost always more or less wet, so that wet chemistry was calculated, except for the 2-layer run shown in Fig. 6.

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, with normalized values between 0 and 1 (see methods), provide the model input for leaf water storage, instead of the original energy balance approach by Flechard et al. (1999). 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). The following parameterisation of the effective water film thickness (V_{H2O}, mm) was used, using the normalized leaf wetness (LW) signal:

$$V_{H2O}(LW) = a \times \exp(b \times LW) \tag{1}$$
$$LW = 0.02 \rightarrow V_{H2O} = 0.02\,\text{mm}$$
$$LW = 0.15 \rightarrow V_{H2O} = 0.08\,\text{mm}$$
$$LW = 1 \rightarrow V_{H2O} = 0.1\,\text{mm (water holding capacity per unit leaf area)}$$

The first value is taken to be representative of a "dry" surface, after the following rationale: the observed relationship between relative humidity (RH, 1 m) and LW (30–45 cm) showed that a normalized LW signal of 0.02 corresponds to a relative humidity of 28%, which is close to the driest conditions before the cut. This LW signal of 0.02 is then assumed to translate into a V_{H2O} of 0.02 mm, based on the data by van Hove and Adema (1996) who observed NH_3 absorption and calculated an "effective leaf wetness" layer of 20 μm for an equally low relative humidity.

Using this approach, the parameterisation used for conditions before the grass was cut is based on the BET isotherm for adsorption derived by Altimir et al. (2006) for the same type of wetness sensors, as V_{H2O} is scaled up to the whole canopy by multiplying by the Leaf Area Index (LAI):

$$V_{H2O}(mm) = LAI * 0.0031 \times Exp(3.5061 \times LW) \tag{2}$$

This means that with a wetness signal of 0, the "effective thickness" of the water film would be reduced to 3.1 μm, which would thus represent an incompressible "minimum leaf water storage" with an effective thickness of the order of reported values in the literature (van Hove and Adema, 1996). At high humidities, the maximum value of 100 μm reflects the water holding capacity of the leaves.

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). This resulted in a two-layer (foliage + litter) dynamic chemical canopy compensation point model (Fig. 1b), with the modeling of chemistry restricted to the living canopy foliage. 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:

$$\chi_c = \frac{\chi_a (R_a R_b)^{-1} + \chi_g (R_b R_g)^{-1} + \chi_s \left[(R_a R_s)^{-1} + (R_b R_s)^{-1} + (R_g R_s)^{-1}\right] + \chi_d \left[(R_a R_d)^{-1} + (R_b R_d)^{-1} + (R_d R_g)^{-1}\right]}{(R_a R_b)^{-1} + (R_b R_g)^{-1} + (R_a R_s)^{-1} + (R_b R_s)^{-1} + (R_g R_s)^{-1} + (R_a R_d)^{-1} + (R_b R_d)^{-1} + (R_d R_g)^{-1}} \tag{3}$$

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}:

$$R_g = R_{ac} + R_{bg} \tag{4}$$

with

$$R_{ac}\{d + z_0\} = \frac{\alpha\{d + z_0\}}{u*} = \frac{40Hc}{0.45u_*} \tag{5}$$

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 parametrisation for R_{ac} is adapted from measurements in grassland during this experiment (Nemitz et al., 2008a[7]), and α=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:

$$R_{bg} = \frac{Sc - \ln\left(\delta_0/z_1\right)}{ku_{*g}} \tag{6}$$

where k the von Karman constant (0.41), Sc is the Schmitt number ($Sc = v_a/D_\chi$, with v_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. $\delta_0 = D_\chi/(ku_{*g})$, while z_1 is the upper height of the logarithmic wind profile (Nemitz et al., 2001). The parametrisations for u_{*g} and z_1 given by Milford (2004) were used here such that:

$$u_{*g} = u/20 \tag{7}$$

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[7]Nemitz, E., Dorsey, J. R., Flynn, M. J., Gallagher, M. W., Hensen, A., Owen, S., Dämmgen, U., and Sutton, M. A.: Aerosol fluxes and gas-to-particle conversion above grassland following the application of NH_4NO_3 fertilizer, Biogeosciences Discuss., submitted, 2008a.

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

$$z_1 = Hc/5 \qquad (8)$$

The bioassay measurements within the measurement campaign provided values of Γs at 305 (SE 1.5) for the apoplast of green leaves, and 5193 (SE 392) for senescent leaves (Mattsson et al., 2008[5]). The first value was used to describe Γ_s for the whole precut 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[8])) to estimate χ_s. The estimates of Γ for different plant, litter and soil compartments through the campaign were compared (Sutton et al., 2008b[2]) 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 modeling framework.

3 Results

3.1 Results of leaf wetness measurements

During the first part of the pre-cut phase (20–25 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 26–29 May, leaf wetness was generally below 0.5. (Fig. 2a). After the cut, there was a strong diurnal pattern of leaf wetness, with no further rain before 5 June and consequently low values throughout the day, and high values at night. The values measured on filter papers usually confirmed this, although during days without rain the mean LW values recorded on the leaves

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[8]Nemitz, E., Hargreaves, K. J., Neftel, A., Loubet, B., Cellier, P., Dorsey, J. R., Flynn, M., Hensen, A., Weidinger, T., Meszaros, R., Horvath, L., Fruehauf, C., Sutton, M. A., and Gallagher, M. W.: Inter-comparison of measurements and assessment of the turbulent exchange and energy balance of an intensively managed grassland, Biogeosciences Discuss., submitted, 2008b.

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were mostly higher than the filter paper values (Fig. 2a and b). No clear indications of stomatal activities could be derived from comparing wetness sensors clipped to leaves and filters, respectively.

Figure 3 shows the humidity dependence of LW during the pre-cut phase for different heights, as well as the overall relationship derived and used in the model. 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 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, high leaf surface wetness prevails even at low air humidities, and also the increase of LW with increasing rh starts earlier than at the higher levels. It is obvious that leaf wetness depends more strongly on air humidity for the upper leaves than within the canopy. The overall approximation for all values 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 (including in 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

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
5 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.

10 ## 3.3 Modeling

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

Figure 4a shows the calculated leaf surface water storage derived from leaf wetness
measurements ("empirical V_{H2O}") using Eq. (2) before the grass cut. The water stor-
age as calculated by the dynamic energy balance model, using micrometeorological
15 measurements to determine condensation, dewfall and evaporation, is also shown for
comparison. Two different regimes can be seen in the precut period, one with a wet-
ter phase in the first two days (23–25 May), and a drier one in the second half (26–29
May). Apart from strong dewfall on 23 May, and wetness caused by rainfall, leaf surface
water storage is calculated to be below 0.1 mm during most of the time (Fig. 4a).
20   When comparing the measured ammonia fluxes and the simulations from the single-
layer model in the pre-cut phase (Fig. 4b) using a Γ_s value of 305, a general agreement
with respect to deposition and emission episodes can be observed. During the wetter
first period, deposition was the dominating flux. By contrast, from 26 May, deposition
decreased and occasional emission events were measured, which were not very well
25 reproduced by the modeling approach. The aerodynamically maximum possible flux,
$F_{max} = -V_{max} * \chi_a$ where $V_{max} = 1/(R_a + R_b)$), shows higher values in the second period,
caused by higher wind speeds. At the same time, a relative decrease of the measured
fluxes occurred relative to this maximum deposition, which can be attributable to the
drier conditions (Fig. 4b).
  Figure 4c shows separately the modeled stomatal and cuticular fluxes of ammo-

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nia which sum up to the total modeled flux indicated in the previous graphs. During daytime, the model indicates cuticular emission periods. However, these rarely result in simulated net emission periods due to re-capturing of the released ammonia by the stomata ($\chi_c > \chi_s$). The notional concentrations χ_s and χ_d, and the measured air concentration at 1 m height (χ_a) are shown for the whole precut period in Fig. 4d. Net emissions are simulated when both χ_s and χ_d are higher than χ_a (e.g. 26 May, 11:30 a.m.).

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. Ionic strength was below 0.1 during the whole pre-cut period (Fig. 4e), thus always remaining below the model threshold of 0.3, and allowing an uninterrupted modeling of surface wet chemistry. This was different in the dynamic energy balance approach, in which water storage was probably underestimated and ionic strength exceeded 0.3 M most of the time, preventing the surface chemistry from being calculated, even on days with visible dew. The measured dew pH values are also shown on Fig. 4e alongside modeled pH. The modeled and measured values show good agreement on 23 and 24 May, when V_{H2O} was relatively high, above 0.1 mm; there was however substantial discrepancy for the next two dew events on 25 and 26 May, when V_{H2O} was much lower, below 0.05 mm.

3.3.2 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 Γ_s=5000. Given the scale of difference between this value and the measurements (Mattsson et al., 2008[5]), 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. 1), which was provided by the leaf litter after the cut, when grass residues were left to decay on the

ground.

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

The two-layer model was applied to the post-cut period, using the measured stomatal Γ_s of 305, while for the litter Γ_g was assumed to be 5193 and equivalent to the value measured for senescent leaves (Mattsson et al., 2008[5]). 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 soil temperatures lead to 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 and 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. 6e). In this phase, however, the surface was often dry and the ionic strength of leaf surface solution often high, so that the modeling of wet chemistry was precluded a significant fraction of the time (25%), especially during the daytime from 1 June onwards, and in such cases modeled pH is much less reliable.

3.3.4 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). Under this situation, it was assumed 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 modeled ammonia fluxes, although there are several periods differing both in sign and size of

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the fluxes (Fig. 7a). Especially around noon and during the early afternoon, higher emission rates were calculated than those measured or even during deposition periods.

¹⁰ These modelled emissions were dominated by Fg, 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 May, although litter NH_3 emissions (Fg) are substantial, almost all is recaptured

¹⁵ by the leaf surfaces (Fd) and by stomatal uptake (Fs). 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

²⁰ 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).

3.3.5 Influence of leaf wetness on modeled fluxes

Evaporation of rain or of dew droplets in the morning always leads to an extremely

²⁵ strong concentration process within a short time period, leading to 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 ammonia. 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 modeled ammonium concentrations in the

⁵ water film with the measured concentrations in dew during the precut period, there was a good general agreement when leaf wetness values of the lower canopy were used for modeling, while the mean leaf wetness values would lead to higher concentrations (Fig. 8). The difference between one- or two-layer models was not significant in this

case.

4 Discussion

Field measurements of surface water pH and ion concentrations have provided a first direct validation for the dynamic chemical module of the compensation point model. Dew pH was found to be higher (6.6) than that of rain collected on leaf surfaces (5.2). The ionic composition of dew is influenced by aerosol and gas deposition before and during the dew event, as well as leaching and uptake of ions across the plant surface (Wisniewski, 1982; Takeuchi et al., 2003; Hughes and Brimblecombe, 1994; Burkhardt and Drechsel, 1997; Burkhardt and Eiden, 1990). 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 condensors 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.

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. However, the Braunschweig experiment has demonstrated that the existence and stratification of different NH_3 sources need to be considered in order to improve modeling 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 parameterizations uncertain. As can be seen from Fig. 4 the measured emission

events often occur during periods of increasing Vmax. i.e. increased turbulence flushes
NH$_3$ out from deep within the canopy from litter emissions. The application of the 2-layer model led to significant 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., 2008[5]) which is much smaller than inferred from litter measurements (Sutton et al., 2008b[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 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). 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).

The model sensitivity to different parameters, including SO$_2$ concentration and leaching rates, was tested. Sulphur dioxide oxidation by O$_3$, as prescribed in the model (Adema and Heeres, 1995), was fast, of the order of 15% min^{-1} on average, and

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O_3 levels during the experiment (mean ambient concentration of 26 ppb during the field campaign) were not limiting, given the low ambient SO_2 concentrations (mean 0.45 ppb over the whole campaign). To further assess the importance of SO_2 on ammonia fluxes, the 2-layer pre-cut model was also run with five-fold the measured half-hourly SO_2 concentrations. The higher SO_2 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 SO_2 oxidation rates would result in increased pH and thus reduced NH_3 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, 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.

References

Adema, E. H. and Heeres, P.: Dry deposition of sulphur dioxide and ammonia on wet surfaces and the surface oxidation kinetics of bisulphite, Atmos. Environ., 29, 1091–1103, 1995.

Altimir, N., Kolari, P., Tuovinen, J.-P., Vesala, T., Bäck, J., Suni, T., Kulmala, M., and Hari P.: Foliage surface ozone deposition: a role for surface moisture?, Biogeosciences, 3, 209–228, 2006,
http://www.biogeosciences.net/3/209/2006/.

Barfield, B. J., Payne, F. A., and Walker, J. N.: Surface water storage capacity of selected crop leaves under irrigation sprays, Agr. Meteorol., 12, 105–111, 1973.

Beysens, D., Ohayonc, C., Muselli, M., and Clus, O.: Chemical and biological characteristics of dew and rain water in an urban coastal area (Bordeaux, France), Atmos. Environ., 40, 3710–3723, 2006.

Burkhardt, J. and Drechsel, P.: The synergism between SO_2 oxidation and manganese leaching on spruce needles – A chamber experiment, Environ. Pollut., 95, 1–11, 1997.

Burkhardt, J. and Eiden, R.: The ion concentration of dew condensed on Norway spruce (Picea abies (L.) Karst.) and Scots pine (Pinus sylvestris L.), Trees, 4, 22–26, 1990.

Burkhardt, J. and Eiden, R.: Thin water films on coniferous needles, Atmos. Environ., 28, 2001–2011, 1994.

Burkhardt, J. and Gerchau, J.: A new device for the study of water-vapor condensation and gaseous deposition to plant-surfaces and particle samples, Atmos. Environ., 28, 2012–2017, 1994.

Burkhardt, J., Kaiser, H., Goldbach, H., and Kappen, L.: Measurements of electrical leaf surface conductance reveal recondensation of transpired water vapour on leaf surfaces, Plant Cell Environ., 22, 189–196, 1999.

Denmead, O. T., Freney, J. R., and Simpson, J. R.: Closed ammonia cycle within a plant canopy, Soil Biol. Biochem., 8, 161–164, 1976.

Erisman, J. W. and Wyers, G. P.: Continuous measurements of surface exchange of SO_2 and NH_3 – implications for their possible interaction in the deposition process, Atmos. Environ. A-Gen., 27, 1937–1949, 1993.

Flechard, C. R.: Turbulent exchange of ammonia above vegetation, Ph.D. thesis, University of Nottingham, UK, 231 pp., 1998.

Flechard, C. R., Fowler, D., Sutton, M. A., and Cape, J. N.:. A dynamic chemical model of bi-directional ammonia exchange between semi-natural vegetation and the atmosphere, Q. J. Roy. Meteor. Soc., 125, 2611–2641, 1999.

Hughes, R. N. and Brimblecombe, P.: Dew and guttation – formation and environmental significance, Agr. Forest Meteorol., 67, 173–190, 1994.

Long, I. F.: Some observations on dew, Meteorol. Mag., 87, 161–168, 1958.

Klemm, O., Milford, C., Sutton, M. A., Spindler, G., and van Putten, E.: A climatology of leaf surface wetness, Theor. Appl. Climatol., 71, 107–117, 2002.

Magarey, R. D., Russo, J. M., and Seem, R. C.: Simulation of surface wetness with a water budget and energy balance approach, Agr. Forest Meteorol., 139, 373–381, 2006.

Milford, C.: Dynamics of atmospheric ammonia exchange with intensively-managed grassland,

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10   Ph.D. thesis, University of Edinburgh, UK, 218 pp., 2004.

Monteith, J. L.: Dew, Q. J. Roy. Meteorol. Soc., 83, 322–341, 1957.

Monteith, J. L. and Unsworth, M. H.: Principles of environmental physics, Edward Arnold, London, UK, 291 pp., 1990.

Nemitz, E., Milford, C., and Sutton, M. A.: A two-layer canopy compensation point model for describing bi-directional biosphere-atmosphere exchange of ammonia, Q. J. Roy. Meteorol. Soc., 127, 815–833, 2001.

Nemitz, E., Sutton, M. A., Schjoerring, J. K., Husted, S., and Wyers, G. P.: Resistance modeling of ammonia exchange over oilseed rape, Agr. Forest Meteorol. 105, 405–425, 2000.

Schjoerring, J. K., Husted, S., and Mattsson, M.: Physiological parameters controlling plant-atmosophere ammonia exchange, Atmos. Environ., 32, 491–498, 1998.

Sutton, M. A., Pitcairn, C. E. R., and Fowler, D.: The exchange of ammonia between the atmosphere and plant communities, Adv. Ecol. Res., 24, 301–393, 1993.

Sutton, M. A., Schjørring, J. K., and Wyers, G. P.: Plant – atmosphere exchange of ammonia, Philos. T. R. Soc. A., 351, 261–275, 1995.

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

Takeuchi, M., Okochi, H., and Igawa, M.: Deposition of coarse soil particles and ambient gaseous components dominating dew water chemistry, J. Geophys. Res., 108(D10), 4319, doi:10.1029/2002JD003058, 2003.

van Hove, L. W. A., Adema, E. H., Vredenberg, W. J., and Pieters, G. A.: A study of the adsorption of NH_3 and SO_2 on leaf surfaces, Atmos. Environ., 23, 1479–1486, 1989.

van Hove, L. W. A. and Adema, E. H.: The effective thickness of water films on leaves, Atmos. Environ., 30, 2933–2936, 1996.

Winkler, P.: The growth of atmospheric aerosol particles with relative humidity, Phys. Scripta, 37, 223–230, 1988.

Wisniewski, J.: The potential acidity associated with dews, frosts, and fogs, Water Air Soil Poll., 17, 361–377, 1982.

Wohlfahrt, G., Bianchi, K., and Cernusca, A.: Leaf and stem maximum water storage capacity of herbaceous plants in a mountain meadow, J. Hydrol., 319, 383–390, 2006.

Wyers, G. P. and Erisman, J. W.: Ammonia exchange over coniferous forest, Atmos. Environ., 32, 441–451, 1998.

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Table 1. Mean aqueous concentrations (and standard deviations) in dew, guttation, and rain from leaves, measured on 21, 22, 23, 24, 25, and 26 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
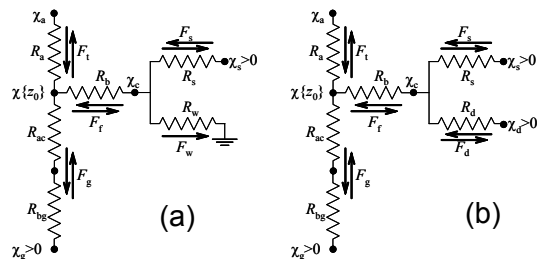
Fig. 1. Diagrams of two-layer canopy compensation point models for biosphere/atmsophere NH_3 exchange. **(a)** model of Nemitz et al. (2001) treating leaf cuticle as a sink with deposition resistance Rw; **(b)** dynamic chemical model reported in the present study with explicit treatment of leaf surface equilibrium concentration χd and bi-directional transfer resistance Rd, adapted from Flechard et al. (1999).
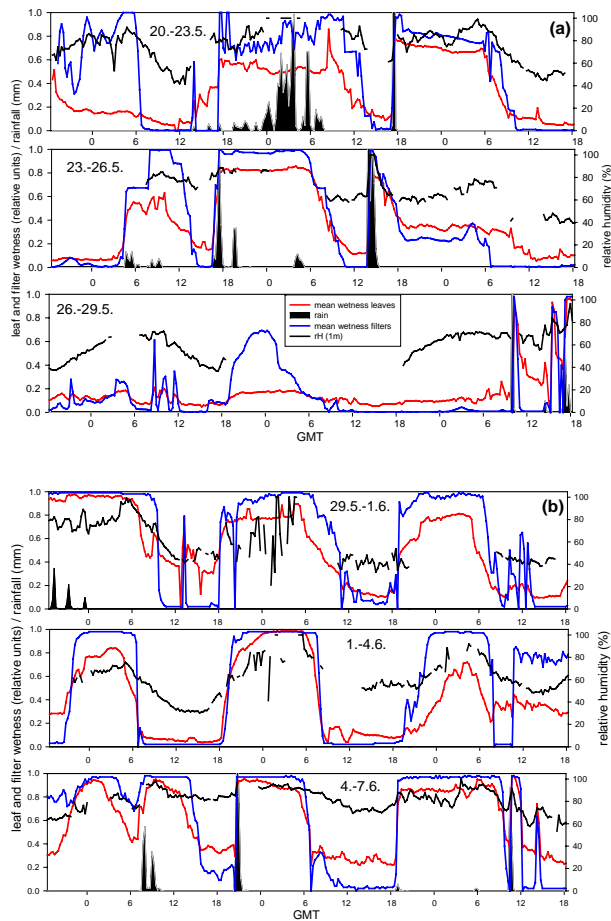
Fig. 2. Leaf wetness (LW, mean values of all heights) measurements on leaves and on paper filters, relative humidity at 1 m, and rain distribution (black signature at the bottom) during **(a)** the pre-cut phase and **(b)** the post-cut phase of the GRAMINAE experiment.

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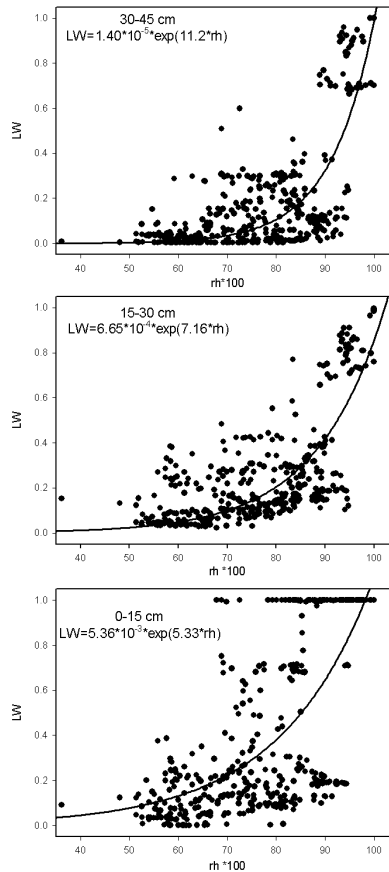
Fig. 3. Relation between normalized leaf wetness (LW) and relative humidity at the notional height of gas exchange (RH(z0') for leaf wetness sensors installed at different heights within the grass canopy (0–45 cm) during the precut phase. LW values during precipitation events and within 2 h after the last rain event have been removed.
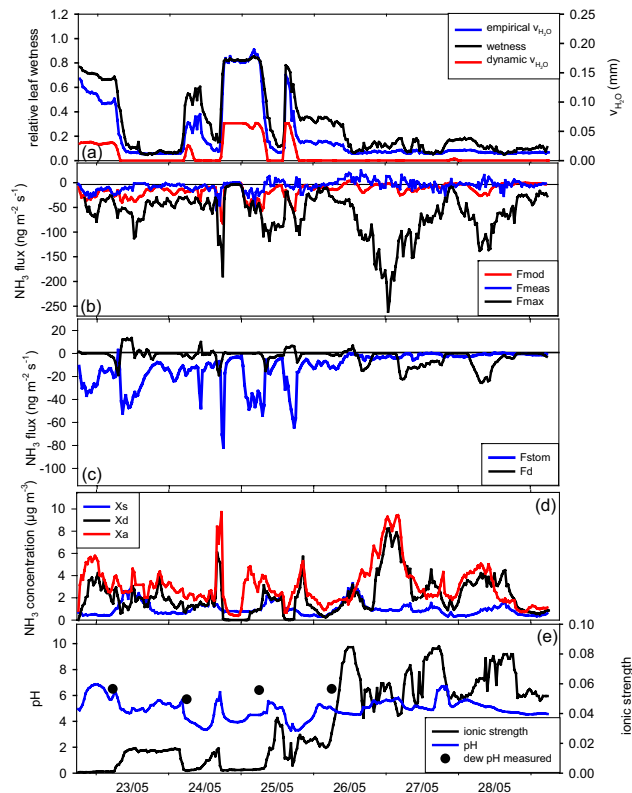
Fig. 4. Comparison of measured and modeled (single-layer) parameters during the pre-cut phase **(a)** relative leaf wetness (LW) measurements; calculated canopy water storage based on LW ("empirical"), and based on micrometeorological data ("dynamic"). **(b)** Measured and modeled flux, compared to the maximal flux allowed by atmospheric turbulence. **(c)** Modeled stomatal and cuticular fluxes during the precut period. **(d)** Stomatal and cuticular compensation points during the precut period, together with air concentration χ_a at 1 m height. **(e)** Ionic strength and calculated pH, and measurements of dew pH.

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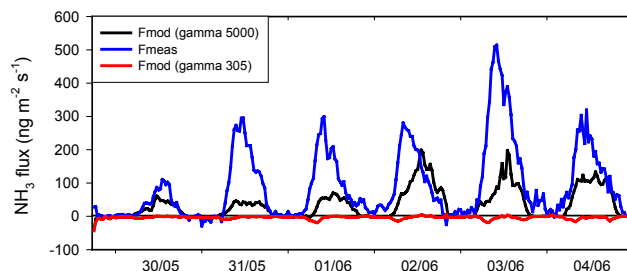
Fig. 5. Measured and modeled NH$_3$ fluxes in the post-cut period, using the single-layer model and the measured Γs 305 as well as a hypothetical Γs 5000.
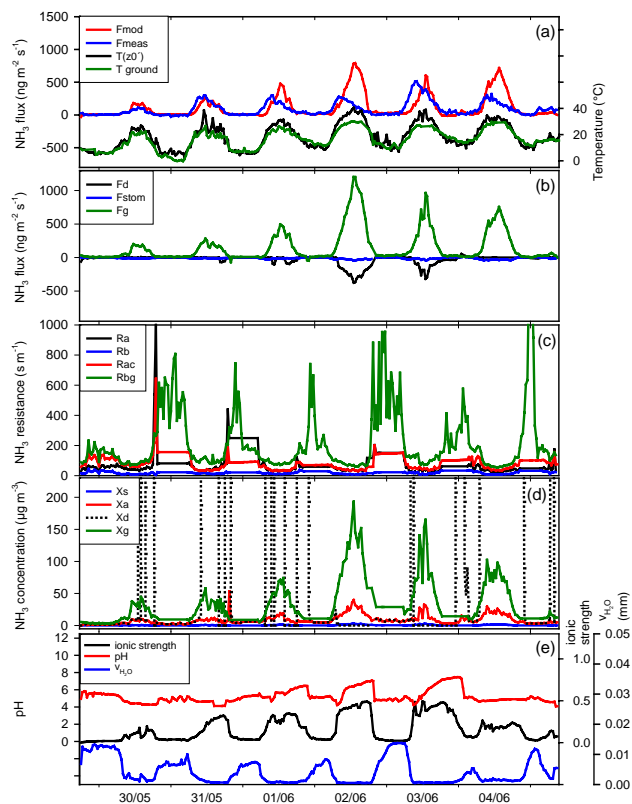
Fig. 6. **(a)** Measured NH$_3$ fluxes and modeled fluxes using the 2-layer model, as well as comparison of T(zo') and Tground. **(b)** Partitioning of NH$_3$ fluxes between stomata, cuticle, and ground (litter) and **(c)** contributing resistances. **(d)** Notional ammonia concentrations along the different points of the exchange path. **(e)** Water volume, ionic strength, and pH of the water layer.
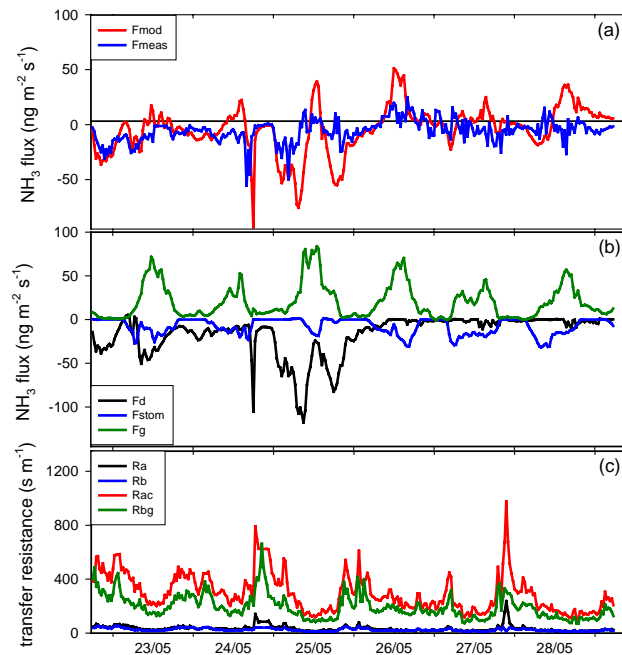
Fig. 7. (a) Measured and modeled fluxes applying the 2 layer model to the pre-cut period. **(b)** Partitioning of internal modeled fluxes. **(c)** Contributing resistances to NH_3 transfer.
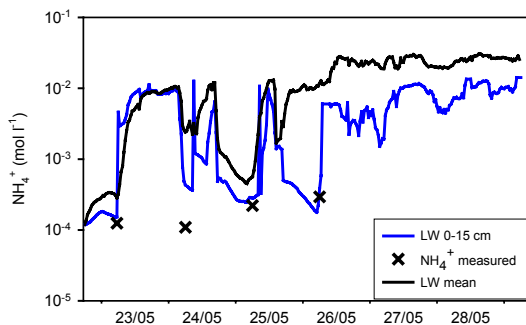
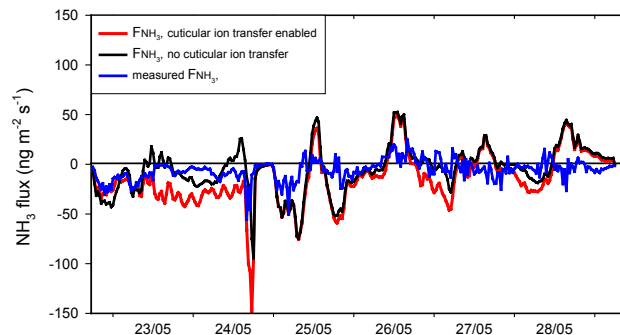**Fig. 8.** Measured and modeled NH_4^+ concentrations in the leaf water layers, using mean wetness values and those from the lower layer. Note logarithmic scale.
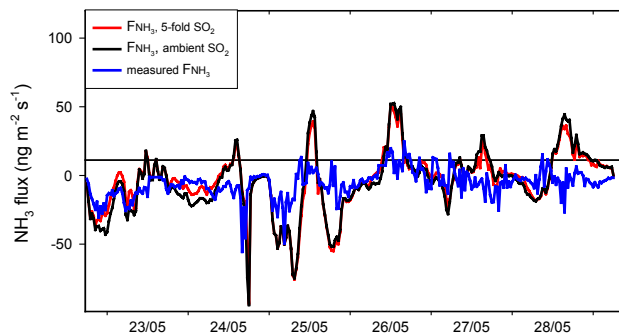
Fig. 9. Modeled NH_3 fluxes using the 2-layer model during the pre-cut period, under actual measured SO_2 concentrations, compared to a run with five-fold SO_2 concentration. Measured fluxes are also indicated.

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.