

***Interactive comment on “Modeling the dynamic chemical interactions of atmospheric ammonia and other trace gases with measured leaf surface wetness in a managed grassland canopy” by J. Burkhardt et al.***

**J. Burkhardt et al.**

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We thank reviewer #3 for the valuable comments. We have cited more papers, more specifically supporting the assumptions made in the paper. We introduced table 2 in order to quantify and compare model performance. We also added a definition of future research priorities to the discussion, based on the findings of presented analysis.

In the following we address the different general and specific points .

General comments: We critically checked for unclear phrases and added new citations to support statements. We added more information from the companion papers as

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requested (e.g. on flux uncertainties). Meanwhile, several of the companion papers have been published in BGD.

Specific comments: Pp 2514, line 5-10; Now reads: Aqueous chemistry in surface wetness includes dissolved SO<sub>2</sub>, O<sub>3</sub>, HNO<sub>3</sub> and their exchange with the atmosphere and aqueous reactions, such as the heterogeneous oxidation of SO<sub>2</sub> to SO<sub>4</sub><sup>2-</sup> (Flechard et al., 1999) by ozone, whereas H<sub>2</sub>O<sub>2</sub> and the metal ion catalysed oxidation by oxygen (Martin, 1984, Burkhardt and Drechsel, 1997) was not included due to limited data availability.

Pp 2514, lines 16-27; We agree and included the following phrase into the discussion: 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. The situation of NH<sub>3</sub> fluxes under conditions with little leaf water available is addressed in more detail in the results and discussion section.

Pp 2515; This phrase referring to Figure 6 has been omitted, due to the changes in chemistry calculation. We gave up the original switch from a bidirectional R<sub>d</sub> to a deposition only R<sub>w</sub> scheme, calculating wet chemistry throughout.

PP 2515; The comparison of vH<sub>2</sub>O between both approaches in figure 4a is now extended to NH<sub>3</sub> fluxes shown in figure 4b and table 2. The difference between the energy balance and the leaf wetness approach is not very large. Therefore, while a detailed study on the leaf wetness influence here gives some insights into processes affecting NH<sub>3</sub> fluxes, the energy balance approach remains a good option for large scale models.

Pp 2516; BET: The process of physical adsorption (or physisorption) is physically well

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described by a BET isotherm with RH-dependent exponential increase (Brunauer, Emmett, and Teller, 1938; the name results from the authors' initials). Explained in the introduction.

Pp 2516; line 15-17; We agree and included this phrase.

Pp 2517; The uncertainties in  $R_a$  and  $R_b$  are rather small compared with resistances like  $R_d$  and  $R_{\text{ground surface}}$  (we set that to zero) for the model.

Pp 2519; line 1; Here we refer to a contribution by stomatal opening and the release of  $H_2O$ . Under laboratory conditions, such an influence of stomatal aperture on leaf wetness measurements has been found (Burkhardt et al., 1999), caused by recondensation of transpired water vapour on the leaf surface. It was one of the aims of the leaf wetness measurements to look for this effect during the field measurements, and the comparison of parallel wetness measurements on filter paper and leaves intended to see if there was a difference caused by the stomata. A diurnal course related to photosynthetically active radiation (PAR) only on leaves, but not on filter paper, would have supported this. Supporting data, however, were too scarce to back such a statement for this field experiment. We made this clearer at several locations in the text now.

Pp 2519; lines 24-25; We used a mean expression based on all leaf wetness measurements (eq. 10 of the new manuscript) to run the model. While we kept stratification in mind and occasionally referred to it as in Fig. 8, this was a possibility to summarise leaf wetness effects of the canopy as a whole.

Pp 2520; end of Section 3.2; The dew and rain chemistry results are now more extensively discussed in the discussion section. Actually the agreement is not so bad given the many processes involved which are difficult to predict. Main uncertainties are the influence of deposited aerosols (not modeled), gaseous deposition (modeled), leaching (modeled) and amount of water (modeled).

Pp 2520; line 15; We included this sentence. The water layers calculated by the energy

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balance model are thinner than the ones deviated from leaf wetness measurements (Fig 4a), caused by the exponential increase of the mathematical expression. However, the calculated flux is not much lower, compared to the calculations based on LW (Fig. 4b of new manuscript).

Pp 2520; We changed this to: In the second period, a relative decrease in the measured flux indicates that there is an decrease in the surface uptake efficiency which might be explained by the occurrence of relative drier conditions.

Pp 2521; We show one possible explanation based on the sensitivity of pH on the assumed chemistry on leaf surfaces in Fig. 4e of the new manuscript. Assuming NaCl as the only constituent of leaf water, the agreement with measured values is much better. Such NaCl dominated water chemistry could result from dry particle deposition from the sea.

Pp 2522; The change was motivated by the identification of the importance of leaf litter emissions for the post-cutting period based on parallel studies (David et al., 2008, Herrmann et al., 2008; Sutton et al., 2008b).

Pp 2523; line 13; The results of the model runs are quantified now in terms of mean difference, correlation, and agreement of signs (deposition/emission) and compared in table 2.

Pp 2524; We illustrated the influence of different particles on pH in model runs shown in fig. 4e of the new paper version, using measured rain water chemistry in one case, and purely NaCl in the comparison. Some background and experimental evidence has been published in earlier papers ( Burkhardt and Eiden, 1990, 1994).

Pp 2526; We agree that we need a section on future priorities. We included the following paragraph: For the improvement of the mechanistic understanding and its inclusion into the model, the following research priorities seem important: 1. closing the knowledge gap between the physically explained water adsorption and the un-

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explained much stronger effects that it has on ammonia deposition, 2. handling the chemistry of concentrated solution, through to complete dryness and evaporation of volatile components (e.g. ammonium nitrate), 3. improving the parameterisation of the cuticular charging resistance  $R_d$ , 4. developing a dynamic treatment of mineralization and desorption of ammonia from decomposing leaf litter, 5. 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.

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