**Biogeosciences
Discussions**

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*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.**

Received and published: 3 November 2008

We thank reviewer # 2 for the thorough evaluation and the detailed comments. We made a thorough revision of the paper removing several mistakes, including the indicated typos. We changed the calculation scheme used to incorporate leaf water measurements into the model, and recalculated all figures. The switch of the model from a bi-directional Rd scheme to a deposition-only Rw scheme at ionic strengths was given up, so the model calculates wet chemistry throughout. We introduced table 2 in order to quantify and compare model performance. The paper becomes also clearer as several of the accompanying papers have been published meanwhile in BGD.

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

General comments:. The purpose of the paper is to investigate surface chemistry dynamic information, which we improve when adding the second layer to the model of Flechard (1999). In the new version of the paper, we changed Fig. 1a which was misleading. We include much more quantitative information by adding a new table (table 2) which compares modeled and measured fluxes by correlation, sign (deposition/emission) and mean difference. Different model approaches (energy balance, LW/BET, RH/BET, vpd) are compared. Within the larger scope of the overall project, the paper of Personne et al. (Personne E., Loubet B., Herrmann B., Mattsson M., Schjoerring J.K., Nemitz E., Sutton M.A. Cellier P.: SURFATM-NH3: a model combining the surface energy balance and the bi-directional exchanges of ammonia at the field scale; submitted to Biogeosciences Discussions) is looking into non-dynamic modelling in more detail.

General comment about the figures: Equal scales and the same variables in figures that can/should be compared with each other are used. Measured fluxes appear in black.

Specific comments: We agree and changed the title to Modeling the dynamic chemical interactions of atmospheric ammonia with leaf surface wetness in a managed grassland canopy.

Abstract: We changed the description. Now reads: 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. Considerable 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

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of the mechanistic dynamic chemistry model by keeping the advantage of requiring relatively little site-specific information. By changing Fig. 1a which was misleading, we think it is now clearly shown that the starting point is the existing one-layer dynamic model, including surface chemistry, but modified by the leaf wetness measurements. This is improved by adding a second layer.

Methods: The methods section has been shortened considerably.

p 2507, l 8-10: Rephrased. Now: 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.

p 2507, l 17: Now reads: The compensation points needed to numerically match measured fluxes were much higher than the ones measured by bioassays, suggesting another source of ammonia fluxes.

p 2507, l 18: Now: Considerable 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. Quantification in terms of percentage would be in the range of several thousands, compared to the single layer with measured gamma of 305. This is the reason why we did not quantify by numbers here.

p 2508, l 2: Explanation for: physiological signals: (e.g. abscissic acid affecting stomatal aperture) was added to the text.

p 2508, l 13: Citation has been added - we had not been aware of this recent publication when submitting the manuscript.

p 2511, l 12: A detailed record of the flux uncertainties is reported by Milford et al. (2008) and summarized by Sutton et al. (2008b). The analysis showed that the scatter between four replicate gradient systems varied throughout the experiment, though

typically fluxes were estimated with +/- 20% to +/-60% relative standard deviation between instruments. Further comparison with relaxed eddy accumulation measurements and with a near surface inverse dispersion model showed consistent to the gradient method. Word rigorous was removed.

p 2511, l 19: now: of other trace gases (HNO3, SO2, HONO, HCl)

p 2511, l 22-23: We agree. The apparent contradiction between clear, calm nights and surface water after rain is better explained now: Samples included dew, sometimes guttation from the leaves, and, in some instances surface water after rain, which had not completely evaporated before the night.

p 2512, l 27-30: This is right, there are still different factors within the normalised signal, but it is likely that by the definition of the maximum value the pressure factor is removed. It is still not clear what are the main causes leading to liquid water vapour formation on leaves far below saturation, nor are the patterns of the water on the surface. A main factor is likely to be due to deposited particles. Factors like transpiration which are known to contribute are not so much a problem, because the liquid water formed will be effective for ammonia deposition. Below saturation (RH=1), ion concentrations in the film are near to saturation, even just above the deliquescence point. For a significant increase of the electrical conductance signal ammonia concentrations as high as 50 ppm were needed (Burkhardt and Eiden, Atmos. Environ., 1994), so with the actual concentrations NH3 fluxes should not cause much noise in the signals. Averaging over a range of sensors on the basis of normalised signals will help to remove these unwanted effects.

p 2513, l 3 and 6-7: This part has been changed, and the new procedure is explained in detail in the text. There is an exponential relationship between RH and ammonia deposition (van Hove and Adema, 1996; Wyers and Erisman, 1998), and an exponential relationship between RH and vH2O by physisorbed water layers described by the BET isotherm (Altimir et al., 2006). The relationship between RH and LW is also exponen-

tial. However, the relation between LW and vH2O is not necessarily exponential, and the approach used was mistaken. The approach used now is that LW values (measured liquid water) are used to calculate the corresponding RH (water vapour) value which is then translated to vH2O (liquid water again; what the NH3 molecule senses ). For the last two steps we refer to published values. We compare different ways of describing this, including the vpd approach by van Hove and Adema, 1996, and the physisorption (BET isotherm) approach described in Altimir et al., 2006. The latter works better for the description of the NH3 fluxes measured in the field. The procedure as well as the evaluation of model performance are explained in the methods section. On the basis of the new approach, all calculations were redone and figures changed accordingly.

p 2513, l 24: This is in fact misleading. We changed Fig. 1a in agreement with focus of the paper on dynamic models, so Fig. 1a now is from Flechard et al. (1999).

p 2514, l 5-27: One of the reasons why the model description of Neirynck and Ceulemans (2008) may seem more clear is that they summarize a different (and simpler) model to the one we have used, being an implementation of the paper by Sutton et al. (1998, Atmos Environ, 32(3)). A full description of the basic model we use here can be found in Flechard et al. (1999) as already cited. We think, this part is clearer now after having it partly shortened, and more detailed in other aspects. The citation is included.

p 2515, l 7; This sentence was completely removed.

p 2515, l 11-12: we agree and removed this part.

p 2515, l 9-28: We agree with this statement of the reviewer. The nature of water films has not really been recognized until now. There are very few mechanistic studies how they evolve, while their effect has been described much more often. In our opinion, and based on earlier experiments, the most important origin of water films are deposited hygroscopic aerosols which attract water vapour more efficiently than the pristine leaf and also release it rapidly once the surrounding air humidity decreases. A similar

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measuring principle has been used by radiosonde humidity sensors on LiCl cristals. In the early stage of adsorption to hygroscopic salts, the water layer is a saturated solution, and small amounts of dissolved gas are not likely to change the electrical conductance strongly. See also comment in response to page 2512, l 27-30.

p 2515, l 20: This section has been completely changed now and is no longer relevant. The reference value LW = 0.15 and vH2O = 0.08 mm had been based on the 70% RH value which seems to be a switching point in terms of water films (possibly connected to the deliquescence point of important atmospheric aerosols like NaCl, NaNO3).

p 2515, l 23-25: There was indeed a mistake, which also changes equation (2). LW = 0.00031 would be needed for RH of 28%. As described above, the relation between RH and LW has been changed.

p 2516, l 4: BET (after Brunauer Emmett Teller; 1938) isotherm describes chemisorption and (important here) physisorption of gaseous molecules to solids. Described in detail in the text.

p 2516, l 12: We mention now that the water holding capacity is species dependent.

p 2516, l 24-26 and p 2517: This reference is cited but we kept the explanation of the variables in due to their first appearance.

p 2518, l 18: There was rainfall directly after the cut and this has been corrected. The labels have been changed. RH was not unusually low, between 30 and 100%. It was measured by krypton hygrometers (as part of EC systems).

p 2519, l 1-3: Different patterns between sensors on leaves and filter papers had been observed before and were indicative for stomatal influence on the measurements. This was tested here, but there were no very clear results. Although not used further in this paper, it might be of interest in the future.

p 2519, l 13-15: Leaf wetness persisted on the lower leaf stages even when relative humidity had already decreased. We added this to the text.

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p 2519, l 22-26: The stratification in leaf wetness is shown in order to illustrate possible effects of distillation, uncoupling between humidity and leaf wetness, and further analysis like in Figure 8. For practical reasons, values are combined for the calculations, but stratification should be kept in mind and is discussed later.

p 2519, l 28-29 and p 2520, l 1-9: Introduction to this section: The chemical analysis of dew was intended to validate the wet chemistry part of the model.

In the discussion section, we explain the importance of particulate matter on the leaf: The difference between measured pH of dew and the model may be caused by incomplete knowledge about ionic residues on the leaves. It is shown as an example in Fig. 4e that this could be caused by NaCl-dominated dry deposition, which resulted in considerably different pH of the water film as compared to calculations based on measured rainfall chemistry.

p 2520, l 14: We agree and changed the legend in Fig. 4 accordingly.

p 2520, l 17: We agree and changed two to three .

p 2520, l 18: There is dewfall included but we agree that rainfall was the main contribution. We omitted this statement.

P 2520, l 19: The calculated empirical VH2O can be higher than 0.1mm due to the LAI factor. Before the cut, this leads to a maximum vH2O of 0.3 mm. We made the difference between the LAI-dependent and LAI-independent LW values clearer now when defining the new equations (2) and (3).

p 2520, l 21: We agree with the reviewer. The text has been changed accordingly. Now: The modeled 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 gamma s value of 305, a general agreement with respect to the magnitude of the fluxes can be observed.

p 2520, l 23: 26 May changed to 25 May

p 2520, l 25-29: We agree. We removed Fmax in Fig. 4b and corresponding text. Instead, we now show in Fig. 4b the comparison of fluxes calculated by the energy balance approach and the approach using leaf wetness values.

p 2521, l 5-11: We agree that this is strange and thank the reviewer for noting it. It was due to a mistake, where Fd and Fs fluxes had been erroneously changed in Fig. 4c.

p 2521, l 21: VH20 higher than 0.1 mm, caused by the LAI factor; see comment on P 2520, l 19

p 2521, l 28: We agree with this statement of the reviewer.

p 2522, l 13: We agree and replaced soil temperature by ground surface temperature.

p 2522, l 7-22: For Fig. 6c, a wrong dataset had been used with constant interpolations of missing u* values. This has been changed now. Large ammonia deposition of dry leaves: This was due to an effect related to the switch from the Rd (bi-directional) to the Rw (deposition only) scheme at ionic strengths higher than 0.3 M. This limit had been introduced to the original model due to limited computing power ten years ago, and was justified by the complexity of ionic interactions in highly concentrated solutions. For the new version of the paper we decided to give up this limit, which led to impossible results like the one in question here. We agree with the reviewer that the large deposition amounts calculated here were virtually impossible. In the discussion section, we look at the errors possibly made by calculating wet chemistry in these high concentrations, and identify this as one of the areas where the model could be further improved.

p 2522, l 6(?):While emission and deposition periods are predicted less accurately by the two-layer model (sign correct in 62% of cases, compared to 76% for the one-layer model) , the correlation between measured and modelled flux has improved ($r2=0.403$ for two-layer, $r2=0.317$ for the one-layer model. Other vales see Table 2.

p 2523, l 8: We agree that it is possible that the assumed gamma (ground) is too high,

especially as there is only a small amount of litter in the pre-cut phase.

p 2523, l 8-22: Evaluation of different gamma values within the single layer compensation point model have been included in table 2. There is indeed good prediction at gamma around 1000.

p 2523, l 8: There is two times line 8 on this page but we assume that this comment refers to the lower one. Influence on pH was checked for one layer and two layer models but showed no difference. We agree that the phrase was not placed well here and removed it.

p 2525, l 10-12: For the pre-cut period, correlation between 2-layer model and measured fluxes was better than for the one-layer model. However, sign of fluxes was better predicted by the 1-layer model with measured gamma values. Higher gamma values led to better prediction (table 2). For post-cut fluxes, clear improvement is shown in figs. 5 and 6, compared to the measured gamma value of 305.

p 2525, l 24: Table 2 and Fig. 4b of the revised paper show a comparison between a model run with leaf wetness modeled according to the energy balance method and a model run with the direct scaled leaf wetness measurements.

Interactive comment on Biogeosciences Discuss., 5, 2505, 2008.

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