Authors' response to the review by Referee #2 on "A process-based model for ammonia emission from urine patches, GAG (Generation of Ammonia from Grazing): description, validation and sensitivity analysis"

We thank the reviewer for their insightful comments including the timeliness and usefulness of this model. We feel the manuscript is much improved with the additions suggested by the reviewer. Our responses are provided point-by-point below, followed by our modifications of the manuscript. All the references mentioned in our response are listed at the end of the document. (We use the truncated page numbers as the reviewer suggested.)

Major comments

Comment: 1) a): *The authors state (P64, L20f) that the present model "can be applied on both field and regional scales. However, it is not clear, how the urine patch model is supposed to be applied on larger scales (e.g. with full temporal and spatial resolution or in a statistically integrated/parameterized form). Thus a (short) outline should be added on how the application to larger scales and/or the incorporation into larger scale models can or should be done.*

Our answer: We thank the reviewer for making this valuable point. We give an outline of these question to the manuscript.

Change to the manuscript:

We add the following sentence to the page 64 in line 21 after "… and regional scales.":

"On field scale our approach is to apply the model for every urine patch deposited over the modelling period (involving statistical consideration), whilst for regional scale we are currently working to incorporate the field scale model into the EMEP4UK atmospheric chemistry transport model (Vieno et al., 2010, 2014)."

Comment: 1 b): *The name "Ammonia generation from grazing (GAG)" is a bit misleading for the present specific model describing ammonia emission (or exchange) of urine patches only. It needs to be considered whether fresh urine patches (less than 10 days old) are really the only ammonia source on grazed fields. What about the dung patches and the grassland areas which are not very recently affected by excreta?*

Our answer: We agree with the reviewer that the name of the model (Generation of Ammonia from Grazing, GAG) does not account for all the aspects of ammonia exchange on a grazed field. Nevertheless, when we were choosing a name for our model our aim was to find a short and memorable name for it. In addition, the model is known in a wider researcher community (especially within the ÉCLAIRE project) by this name, and a change to it would lead to confusion.

As we mentioned in our paper (page 62, line 24) the dominant source of ammonia on a grazed field are urine patches rather than dung, as concluded by Petersen et al. (1998) and Laubach et al. (2013), and referred to in the manuscript. The not recently affected areas play a role in ammonia exchange on a grazed field, but this is beyond the scope of this current manuscript.

In addition, it should be noted that by including treatment of each of i) urine volatilisation, ii) bi-directional fluxes via a stomatal compensation point and iii) cuticular deposition, our model does indeed allow development of a more generalized description of ammonia exchange with grazed systems.

Comment 2:

- In my opinion, no representative stomatal or cuticular compensation point can be derived for an area recently covered by urine.

- For the (short range) re-deposition of urine derived ammonia, the area directly downwind of the urine patch is more important than the patch area itself due to very effective horizontal displacement of the air column by the mean wind (even for heights of a few centimeters above ground) and the much lower compensation point.

- The way in which the aerodynamic resistances (Ra and also Rac) are used here appears erroneous. These resistances are defined for a vertical turbulent transport over a spatially homogeneous (and virtually infinite) surface. This is not appropriate for isolated small patches. There the exchange is clearly dominated by horizontal advection (from/to the surrounding areas not affected by urine) and not by turbulent transport.

Due to these reasons I suggest to either omit the ammonia exchange with vegetation on the patch area or to improve it by considering the short-range deposition downwind of the patch.

Our answer: To the first bullet point: The stomatal compensation point according to Massad et al. (2010) (as referred in the manuscript) is a function of fertilization, which is taken into account in the model (Eq. 16.). We are not aware of any experimental results which would suggest that this assumption is not valid for a urine patch. We did not assume a separate compensation point for the cuticle. Although some of the authors have developed ammonia exchange models that include bi-directional cuticular exchange (e.g. Sutton et al., 1998; Flechard et al., 1999; Burkhardt et al., 2009), our focus in developing GAG has been to examine a simpler approach that could most easily be applied for regional upscaling.

To the second bullet point and the last sentence: We agree with the reviewer that the model would be more realistic by incorporating the effects of dispersion. However, such a development would require extensive modelling work which is beyond the scale of the current effort. Our aim with this work was to develop a simple model that – as we pointed out also above – can be applied also for regional scale. This application will likely require a certain level of model simplification. From this point of view, developing a within-canopy dispersion model would be not just labour-intensive but also make it more difficult to find the way to simplify the model to regional scale.

We are not aware of any author having achieved such an approach for urine patches. Nevertheless, we agree that it could form an interesting and challenging project from which useful lessons could be learned, if sufficient future resources could be found to support it. For the moment, however, we needed a more pragmatic and achievable solution.

To the third bullet point: We agree with the reviewer, the atmospheric resistances (R_a, R_b, R_{ac} and R_{bg}) are derived for a larger area. Therefore, we would like to point out that in the calculation of these we do not take into account any urine patch specific parameter or variable, only meteorological and canopy specific variables as well as parameters that were measured or assumed for the whole experimental site. We make the assumption for the model that these parameters and variables are representative for the whole site including the urine patches. From this point of view, the surface where a urine patch is deposited is homogenous, and as a result the air columns over the urine patches have the same turbulent properties as the air column over the whole experimental site.

The approach is, of course, a simplification when it comes to horizontal inhomogeneity of ammonia source strength, but this is also one of the advantages of the 'big leaf' approach: to simply a complex problem to a more tractable form. As noted above, explicit 3-d within-canopy dispersion modelling of ammonia exchange would be interesting, but the trade-off due to substantial added complexity must also be recognized.

To the last sentence: We believe that excluding the effect of vegetation would be likely to lead to a larger error than keeping it in the model, since the model would not then take into account of the way meteorology affects canopy recapture in net ammonia exchange.

Change to the manuscript:

To clarify the importance of model simplicity we add the following sentences to the page 65, line 2:

"As our future aim is to apply the model to regional scale, simplicity to enhance scalability is a key aspect of the model development. For example, from a theoretical perspective, it could be attractive to explicitly model the 3-dimensional dispersion of ammonia between urine patches and adjacent vegetation within the canopy. This would be a much more complex task, which would also require major simplification when developing an upscaled regional application."

We also add a clarifying paragraph about the atmospheric resistances on page 67, after line 15:

"Atmospheric resistances (R_a, R_b, R_{ac}, R_{bg}) are usually derived for homogenous (virtually infinte) surfaces, which is in apparent contradiction with the current application for a single, finite urine patch. In ongoing and future work we will apply the GAG model to field and regional scales, where the meteorological measurements and the canopy specific parameters, required to calculate these resistances, can be obtained for overall canopy types. To apply atmospheric resistances to urine patches, we assume that all the required variables and parameters to calculate them are representative for the whole experimental site including every single urine patch on the field (we also validated GAG against measurements in a field experiment, as detailed in Section 4)."

Comment 3: *In my view the present comparison with the measurements of Laubach et al. (2012) represents rather a model calibration and not a "model validation"! Important model parameters like e.g. the thickness of the source layer Δz or the soil buffering capacity β seem to be adjusted to the measured 6-day dataset. This is problematic because it remains unclear how these parameters behave for different soil types and management conditions.*

Our answer: We thank the reviewer for noting this point. We arbitrary chose 0.004 m for Δz based on literature (as referred on page 72, in lines 5-7). The only other model constant that has not applied from the literature, is the buffering capacity (β), which we defined during test simulations (as we state it on page 78, in line 17). As we had no exact information on either of these parameters we carried out a comprehensive sensitivity analysis to Δz and β in Section 5.2 and 5.3, respectively.

Comment 4: *A weak point of the model seems to be the lacking vertical resolution within the soil. The infiltration and mixing of liquids (urine and rain water) actually depends on the profile of soil water content (not just in the uppermost layer).*

Our answer: We agree with the reviewer that one of the limitations of the model is the simple handling of the water movement and solution mixing in the soil. However, - as we also explained in our responses to the other reviewers - the simulation of water movement, including the effect of capillary force, diffusion of water in the soil as well as the concentration of TAN and urea within the moving liquid is very complex. Shorten and Pleasants (2007) published a system of partial differential equations describing these processes, which could be a basis for further development of soil exchange processes in GAG. Nonetheless, incorporating this model (or any other model of soil water movement) to GAG would require such an extensive modelling work that is beyond the scope of our current study. In addition, as we pointed out above, during the model development simplicity was a key aspect.

Change to the manuscript:

In response to this point, we add the following paragraph to page 88 after line 25:

"In addition, a limitation of the calculation of the water budget is that GAG does not account for the water movement in the soil, including the effect of capillary force, diffusion of water in the soil as well as the concentration of TAN and urea within the moving liquid. However, the simulation of these processes is very complex. Shorten and Pleasants (2007) published a system of partial differential equations describing these processes, which could be a basis for further development of GAG."

Comment 4 cntd: *I am somewhat confused about the use of different soil layers: the "urine affected soil layer" (P74 L6), the "source layer" (P74 L19) and the "soil evaporation layer" (P77 L4). It is not clear to me, how these layers of different depth are actually related in terms of soil moisture in the model, because the soil moisture quantities used in the equations are not clearly related to a specific layer. Thus the entire water (and TAN) budget should be presented in a more consistent way with specific depth layer attribution.*

Our answer: We thank the reviewer for noting this point. We have now extended Figure 1. To include the other two layers mentioned in the manuscript (as below). The soil moisture values used in the equations are related to the ammonia source layer.

Change to the manuscript:

To clarify the roles of the different model layers we modified Fig 1. as shown below (together with the modified caption) and accordingly we add the following sentence to page 65, line 14 as a closing sentence to the paragraph:

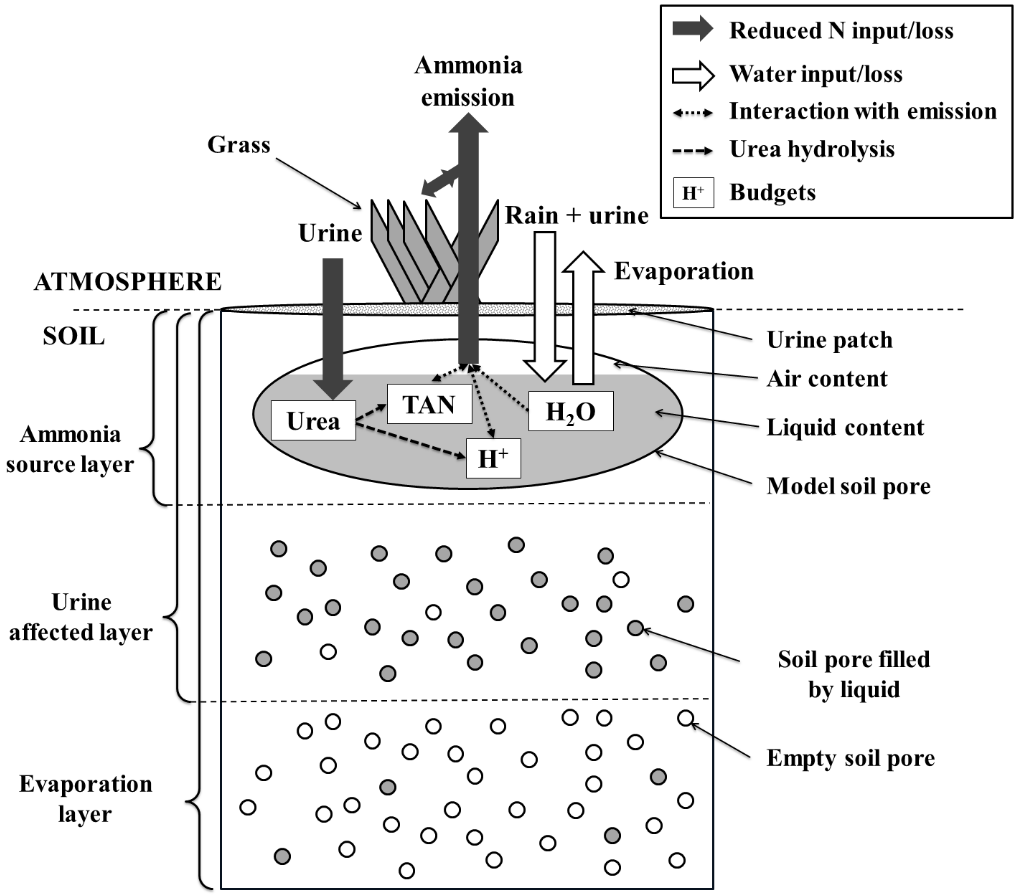

Figure 1. Schematic of major relationships in the GAG model. Empty soil pores in the middle layer represents that the maximum water content in the model is field capacity instead of being saturated. Whilst in the bottom layer the soil pores filled by liquid represents that the lowest water content is at the permanent wilting point instead of being completely dry. For more details on schematic see the text of Section 2.

"On Fig. 1 this depth in the soil is the bottom of the layer referred to as "urine affected layer"."

and the following sentence to page 66, line 2 after "… by soil evaporation":

"We assume that water evaporates from the "evaporation layer" (as defined by Allen et al., 1998, see in more details in Section 2.5), and the soil dries from the top, that is, during evaporation a dry front moves downwards in the soil."

In addition, we remove the last sentence from the paragraph starting at page 65, in line 15.

Minor comments

Comment: *P61 L17-18: This is a strange formulation. In my understanding it should read "showed that the measured parameters .... are well captured by the model"*

Our answer: We thank the reviewer for noting this point please see our modification below.

Change to the manuscript:

On page 61, in line L17 we change the word "simulated" to "measured".

Comment: *P64 L2 (and entire text): The term 'inverse volatilisation model' is not really appropriate here in my view. A multi-resistance model is an equilibrium model that does not have a clear physical calculation direction (and thus can be equally used in various ways). Not the model itself is inverse but only the specific use of it. Thus one could say instead that "the model was used in an inverse mode to calculate the soil resistance".*

Our answer: We thank the reviewer for pointing out the difference between the two different phrases. We have changed the manuscript accordingly.

Change to the manuscript:

At page 64, in line 3 we change "published an inverse NH_3 volatilization model from urine patches to calculate soil resistance" to: "published an NH_3 volatilization model from urine patches *which was run in an "inverse" mode* to calculate soil resistance".

At page 64, in line 9 we change: "urea hydrolysis in the above mentioned inverse model is based on" to: "urea hydrolysis in the above mentioned model by Laubach et al. (2012) is based on"

At page 72 in line 5 we remove the word "inverse".

Comment: *P64 L7: Isn't that rather the forward than the reversed mode? (see previous comment).*

Our answer: If we consider the model an inverse model, according to our original phrasing the reverse mode would be the real volatilization model, calculating ammonia emission. However, following the new phrasing suggested by the reviewer we change this wording to be consistent across the whole manuscript.

Change to the manuscript:

At page 64, line 7 we change: "Running the model in reverse mode, simulating NH_3 emission" to: "Running the model in *predictive* mode, simulating NH_3 emission" (following the exact wording by Laubach et al., 2012).

Comment: *P66-70: Many parts of this section are just (very detailed) descriptions of previously existing model parts adopted from the literature. If this part is not fully omitted (cf. comment 2) it should be shortened considerably.*

Our answer: As we pointed out in the manuscript (page 67, line 14-15) the parametrization of the two-layer canopy compensation point model is different from the original parametrization (suggested by Nemitz et al., 2001), and our system of parametrizations (even if the parametrizations are taken from the literature) is unique for this application. Therefore, we found it important to keep it in the main text to give a transparent description of the model, from which the model can be reproduced.

Comment: *P80: It would be much more informative for the reader to move Table S2 to the main text, and instead move the Eqs. 39-53 to the suppl. material. The latter equations are not understandable without the corresponding reactions.*

Our answer: As the dynamic simulation of pH within an ammonia exchange model is unique, we found it essential to keep the equations in the main text of the manuscript. We think that by removing it, the simulation of pH would be less understandable for the reader. To make the equations clearer for the reader, we move the Table S2 to the main text as suggested.

Change to the manuscript:

We move Table S2 from the supplementary material to the main text.

Comment: *"P80 L11: Does "no CO2 emission in the basic GHG model" mean that you did not consider the CO2 and carbonate related equations in the pH modelling? As far as I understand, the normal soil respiration (without effect from urine) generally produces a high CO2 concentration in the soil pores that affects the carbonate concentration and pH of the soil water. Did the authors you consider this? And, if yes, how was the soil CO2 concentration determined?"*

Our answer: We do consider the CO_2 and carbonate related equation in the pH modelling, as we describe it in the manuscript (page 80, line 15-21). The whole system of equations has to be solved to determine soil pH. We meant that in the equation for the carbon budget (Eq. 52.) we did not consider a term for CO_2 emission. However, we tested the sensitivity of the model to this exclusion (Section 5.3.). We change the text to make this point clear.

We did not consider the mentioned effect of soil respiration on CO_2, as we have not come across any study in the literature that showed the importance of soil respiration in the evolution of soil pH in the case of a urine patch. In addition, the urine patch is deposited in the first time step. Therefore, there is no need to consider this effect in the case when there is no urine deposited. Finally, we believe that in the case of a urine patch, in the first 5-8 days, when the great majority of ammonia emission occurs, soil chemistry is predominantly governed by the urea hydrolysis and the related processes rather than soil respiration.

The CO_2 concentration in the soil is derived based on Eq. 42. The solution of the equation ($BCO_{2(g)}$, the CO_2 budget in the soil) can be derived by solving the above mentioned system of equations for soil pH calculations. From this the gaseous CO_2 concentration can be calculated as $[CO_{2(g)}] = BCO_{2(g)} / V_{air,}$ as described on page 79, in line 2.

Change to the manuscript:

To make clear the exclusion of CO_2 emission in the basic GAG model, we change at page 80, line 10: "in the case of carbon budget, we assumed no CO_2 emission in the basic GAG model" to: "in the case of carbon budget *(Eq. 52)* we *did not* assume *a term for* CO_2 emission in the basic GAG model."

Comment: *P80 L21: what does "lg" mean here? Is it the natural logarithm (often denoted by "ln") or the decadal logarithm?*

Our answer: Yes, it is the decadal logarithm, used to calculate pH according to its definition. To make it clear we change it to $\log_{10}$.

Change to the manuscript:

At page 80, in line 21 we modify the equation to: $pH=-\log_{10}(B_{H+} / B_{H2O})$.

Comment: *P81 L2ff. Why did the authors decide to choose only data from such experiments ("where the NH3 emission flux was measured from several urine patches deposited relatively close in time")? Why did they not consider e.g. enclosure measurements of individual/simulated urine patches or field measurements of real grazing fields?*

Our answer: Our aim was to test if the model works for a urine patch, so that when it is applied to field scale during model validation we can exclude the errors originating from the formulation of the patch scale model. To this we needed a dataset with the criteria mentioned above. As we pointed out in the manuscript (page 81, line 5) the study by Laubach et al. (2012) is the only one that we are aware of that describes a measuring campaign aiming to investigate ammonia emission from a single urine patch (urine patches deposited relatively close in time). Producing another independent measuring dataset would require further work that is beyond the scope of this manuscript.

At a real grazed field urine patches are deposited in every time step over a modelling period; therefore, NH_3 flux measurements from this kind of an experiment cannot be used to validate an emission model for a single urine patch. However, as we mentioned in our responses to previous comments, the model is now being tested at the field scale, which will be the subject of a future publication.

Comment: *P82 L12: It would be better to present this relationship as a labelled equation that can be referred to (instead of repeating it on P86).*

Our answer: Agreed.

Change to the manuscript:

On page 82, in line 12, in the brackets instead of the equation we add: "in Eq. C1, F_t^{single} stands for the converted measured flux".

On page 82, before the new section we add the equation:

$$F_t^{single} = F_t \times 804.9 / (156 \times A_{patch}) \quad \text{(C1)}$$

On page 86, in line 2, in the brackets instead of the equation we add: "converted based on the reorganized form of Eq. C1"

Comment: *P83 L6: In which depth was the water content measured in the experiment? Can it be assumed representative for the Δz layer?*

Our answer: We address this question in the manuscript on page 82, line 12-16: "To validate the simulation of θ [volumetric water content] we also ran the model with a Δz of 5 mm (instead of the original setting of 4 mm as shown in Table 1), so that it was comparable with the measurements for which soil samples were taken by using a sharp-edged metal ring that was pushed to about 5 mm into the soil."

Comment: *P90 L9: Correct to "has a considerable effect"*

Change to the manuscript:

At page 90, in line 9, we remove the "s" from the end of "effects".

Comment: *P90 L19f: I do not understand this sentence. Needs rephrasing.*

Our answer: Agreed.

Change to the manuscript:

Following the suggestion of Referee #3 we did new simulations to explore the reason for the weaker temperature sensitivity than was reported in the literature. Please see our results and modifications in our response to the Comment 15 of Referee #3.

Comment: *P107 Fig.4d: Why is there no increase in soil water content at the very beginning of the experiment due to the urine addition?*

Our answer: The urine patch was deposited in the first time step, leading to the maximal water content in the beginning.

References

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