Authors' response to the review by Referee #3 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 and extensive comments. We have carried out some new, explanatory model runs as suggested by the reviewer. We believe that these new model results have considerably improved the clarity of our manuscript. Our answers followed by our modifications of the manuscript are provided point-by-point below. 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.)

Specific comments

Comment 1: *The structure of the model with regard to transport from the soil and processes within the soil needs to be more clearly described. On p 65 l 15+, the text describes a system where urea or TAN can leave the "source layer", and then seems to be no longer available for emission. Is this correct? This loss is not apparent in Fig. 2. In section 2.4 on the TAN budget (p 72+), there is no mention of loss of TAN or urea in this way. Please clarify.*

> **Our answer:** We change Fig. 1 and the related explanation in Section 2 (as also mentioned in our response to Referee #2). Yes, the reviewer is correct, TAN that infiltrates under the source layer, is no longer available for ammonia emission.

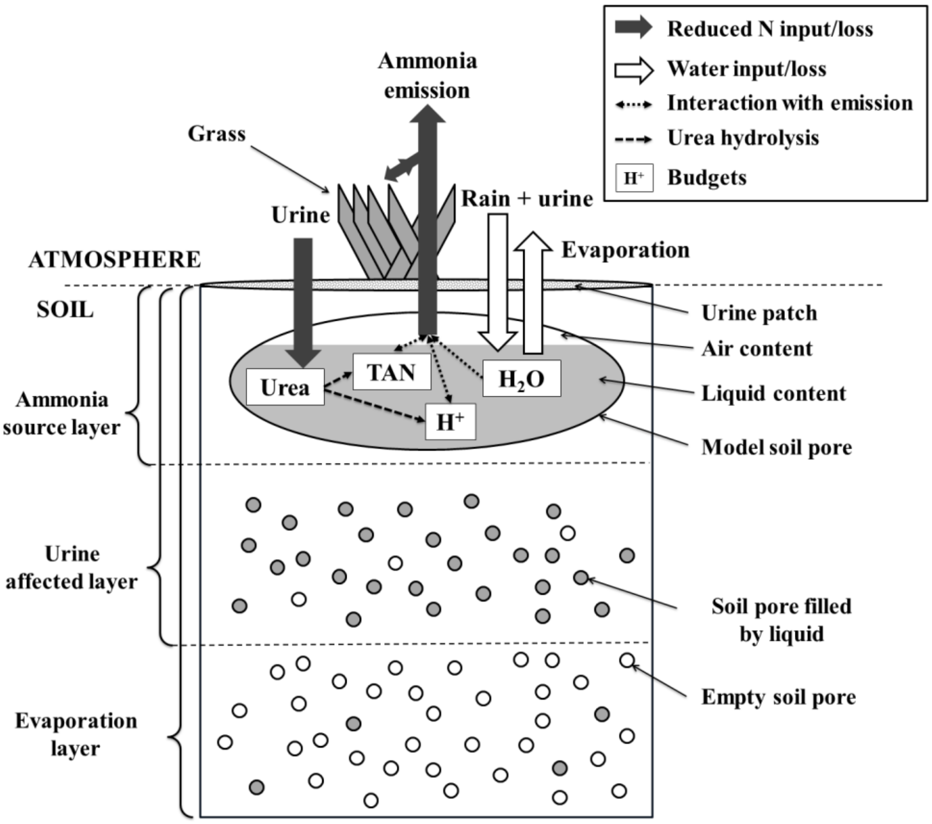


Figure C1. Schematic of major relationships in the GAG model. Empty soil pores in the middle layer represents that the maximum water content in the model is field capacity instead of being saturated. Whilst in the bottom layer the soil pores filled by liquid represents that the lowest water content is at the permanent wilting point instead of being completely dry. For more details on schematic see the text of Section 2.

Change to the manuscript:

To clarify the loss of TAN under the source layer we modify Fig. 1 as shown above (together with the modified caption) and accordingly, we add the following sentence to page 65, line 14 as a closing sentence to the paragraph:

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

We also add on page 65 to line 18 after "assumed to be nitrified": "and no longer available to NH_3 emission"

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.

Comment 2: *[…] it is not clear that your simple approach of using a single layer with a single (soil) resistance is sufficient. In fact, comparison of measured emission and model predictions suggest it may not be (Fig. 4).*

Our answer: Fig. 4 shows that the model well captured the measured values before the rain event, and it underestimates the observations afterwards. As we explained in the manuscript (page 83, line 9-14) we believe that this underestimation was caused by a possible restart of urea hydrolysis that was neglected in the original model run. We demonstrated this point by running the model with a scenario where we assumed that urea hydrolysis restarted after the rain event (page 88, line 7-13). With this modification the agreement was better not only with the measured ammonia exchange flux (Fig. 10d), but also soil pH and TAN budget (Fig. S2 in the supplementary material).

Change to the manuscript:

To clarify the difference between the measurements and modelled values we change on page 88 from line 10 the following part:

"The simulation resulting from this assumption is consistent with the idea of the possible restart of breakdown of the fresh urea penetrating to the soil dissolved in rain water (for emission flux see Fig. 10d in Sect. 6, for TAN budget and pH see Fig. S2)."

to:

"With this assumption the modelled values were in better agreement with observations not only in the case of NH_3 exchange flux (Fig. 10d) but also the TAN budget and soil pH (see both at Fig. S2). These results clearly support the idea of the possible restart of breakdown of the fresh urea penetrating to the soil dissolved in rain water."

Comment 3: *Can you clarify why you believe this approach is sufficient, instead of a more complex and realistic representation of the distribution and transport of soil solutes? Perhaps* *you should you change the perspective of your discussion to evaluate whether or not this approach is sufficient.*

Our answer: We completely agree with the reviewer that the model would be more realistic by incorporating a soil model that simulates water movement and solution mixing in the soil. However, - as we also pointed out 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 equation describing these processes, which could be a basis for further development of 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, our aim with this work was to develop a model with an appropriate level of complexity that can be applied also for regional scale. This application will be likely to require a certain level of model simplification. From this point of view, linking the model with a soil submodel would be not just labour-intensive but also make it more difficult to find the way to simplify the model to regional scale.

Change to the manuscript:

To clarify the importance of model simplicity we add the following paragraph 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.”

In response to why we do not use a more complex soil model, 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: *You cited the work Rachpal and Nye did in the 1980s developing a model for a similar system. I understand that your approach to transport outside of the soil is more detailed. But you use a much simpler approach for transport within the soil. But what is the advantage of your approach for urea and TAN transport within the soil? Simplicity only? I think this topic needs discussion, including more details on the differences between the approaches.*

Our answer: Yes, the advantage of our modelling approach is simplicity. Regarding the soil processes, the reasons why we kept our model at this, lower level of complexity are explained in our response to the previous comment, which is clarified with the changes in the manuscript outlined above.

Change to the manuscript:

In addition to our previous modifications, to clarify the difference between the mentioned model and GAG we also change the Conclusion section as explained in our response to Comment 11.

Comment 5: *Furthermore, it is not completely clear to me if Δz describes both the thickness of the emitting layer of soil and also the resistance, or just the latter. It is not physically realistic to say that Δz is both the thickness of the emitting layer and also the distance NH_3 has to diffuse to exit the soil. If TAN were really present only in a thickness of < Δz, none of it would have to be transported as far as Δz to be emitted. Clarify please.*

Our answer: We thank the reviewer for pointing out this missing piece of information. We assume that the liquid in the "model soil pore" is at the bottom of the source layer.

Change to the manuscript:

To replace the missing piece of information, we add to page 65, line 21 after "in the source layer (Fig. 1)": "We assume that all the liquid content is at the bottom of the model soil pore / source layer."

Comment 6: *It seems a bit odd to me to include the masses of individual aqueous species as state variables (e.g., Eqs. 39-44) (since presumably you assume equilibrium at all times and locations) but I think I follow the approach. I think a more straightforward approach is to use total solute concentrations as state variables and then calculate species concentrations using a separate set of equilibrium equations.*

Our answer: We use the amount of substance in mol, and not mass (page 78, line 23). As during evaporation and rain events, the volume of both of the liquid and the gaseous phase changes we found it clearer to use the total amount of substance (in mol) of all the simulated compounds instead of their concentration. For further clarification on units used in the model see our response to Comment 33.

Comment 7: *[...] equations (47) through (49) seem to be related to equilibrium constraints, but their derivation is unclear and they do not seem accurate. You state that these equations are derived from the mass action expressions in Table S2 (p 78 l 28+), but there is a B_{H2O} present in your equations that seems out of place. Please check.*

Our answer: As we explained in the manuscript (page 79, line 1) the concentration of an X dissolved component is calculated as: [X] = B_x / B_{H2O}. Based on this, the form of the first equilibrium equation in Table S2 will be:

$$K\left(NH_4^+\right)=\frac{\frac{B_{NH_{3(aq)}}}{B_{H_2O}}\frac{B_{H^+}}{B_{H_2O}}}{\frac{B_{NH_4^+}}{B_{H_2O}}}$$

After dividing by $1/B_{H2O}$ and reorganizing the equation we get Eq. 47. Following the same steps, Eq. 48 and Eq. 49 can be derived from the second and third equilibrium equation in Table S2, respectively.

Comment 8: *Also, can you provide details on which reactions are quantified by rR5 etc.? I think they refer to the reactions in Table S2, but the sign of at least rR3 seems wrong in at least Eqs. (39) and (40).*

Our answer: We agree with the reviewer on the first question; this needs clarification in the text. In the questioned equations r_{R3} means that during the reaction R3, while one molecule of H_2CO_3 is produced ($+r_{R3}$ in Eq. 39) one molecule of HCO_3^- is consumed ($-r_{R3}$ in Eq. 40).

Change to the manuscript:

We change at page 78, from line 24:

"r_{Rx} (mol) is the production or consumption of a given compound in reaction X"

to:

"r_{Rx} (mol) is the production or consumption of the compound predicted by the given equation in the reaction X (following the numbering of reactions in Table S2)."

Comment 9: *Lastly, can you explain in more detail how was buffering capacity incorporated? I see in Eq. (50), but how you got from soil buffer capacity to this expression is not clear.*

Our answer: Buffering capacity moderates the change of H^+ ion concentration. When H^+ ions are produced in the system during urea hydrolysis and the related equilibrium processes, to balance this change H^+ ions are consumed by buffers, and similarly, when H^+ ions are consumed in the system, buffers releases H^+ ions. In the model this buffering effect is expressed by the term of $\beta_{patch}(pH(ti)-pH(ti-1))$ in Eq. 46 (for B_{H+}) (where t_i is the ith time step). This term is positive when the H^+ ion concentration decreases (pH increases), and it is negative in the opposite case.

Change to the manuscript:

To clarify the incorporation of buffering capacity to the model equations, on page 78 in 17 we add before "We defined β" we add the following:

"Buffering capacity moderates the change of H^+ ion concentration. When H^+ ions are produced in the system during urea hydrolysis and the related equilibrium processes, to balance this change H^+ ions are consumed by buffers, and similarly, when H^+ ions are consumed in the system, buffers releases H^+ ions. In the model this buffering effect is expressed by the term of $\beta_{patch}(pH(ti)-pH(ti-1))$ in Eq. 46. This term is positive when the H^+ ion concentration decreases (pH increases), and it is negative in the opposite case."

Comment 10: *Is it correct that patch size (area) does not change resistance? Is this realistic for areas that are so small?*

Our answer: The atmospheric resistances (R_a, R_b, R_{ac} and R_{bg}) – as we also explained in our response to Referee #2 - 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.

Change to the manuscript:

We 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 11: *Can you summarize the differences between your model and previous work, including improvements and simplifications? Some of this is done in your conclusions section, but this material should be moved (probably to the discussion) and expanded.*

Our answer: We thank the reviewer for this suggestion. We will expand the comparison. We believe that with the additional information provided (see below) we sufficiently highlight the main improvements and simplifications in the GAG model compared to the models published earlier in the literature. We also provide the readers with the references of the previous models, therefore, they have the chance to explore the differences between the models in a greater depth if they wish. In addition, we restructure the Conclusions section as we outlined in our response for Comment 50.

Change to the manuscript:

On page 93, we change the two paragraphs between line 11 and 25 to the following ones:

"In contrast to the NH_3 volatilization models published earlier for urea affected soils (Sherlock and Goh, 1985; Rachhpal and Nye, 1986), our model, incorporating a canopy compensation point model, accounts for the effect of the meteorological parameters on net canopy exchange of NH_3. Compared with the model constructed by Laubach et al. (2012), GAG is capable of simulating the influence of vegetation on NH_3 exchange. In addition, our model also simulates soil pH, the TAN and the water content of the soil, allowing it to predict net NH_3 emission, instead of operating only in "inverse" mode, calculating soil parameters based on flux measurements.

Rachhpal and Nye (1986) suggested a solution for dynamic modelling of soil pH with a set of continuity equations. However, in their approach the dissociation coefficients, as well as the urea hydrolysis rate, were independent of temperature. Even though the GAG model accounts for the same chemical reactions, it incorporates a different mathematical description and accounts for the missing temperature dependencies.

Dynamic simulation of soil pH is novel among the NH_3 exchange models on the ecosystem scale. In the PaSim ecosystem model (Riedo et al., 2002) pH is treated as a constant, and the same is true for the VOLT'AIR model (Génermont and Cellier, 1997) developed for simulating NH_3 emission related to fertilizer and manure application. Furthermore, the framework of GAG is simpler and requires less input data than the VOLT'AIR model. Therefore, for grazing situations, it is much easier to adapt GAG on both field and regional scale.

As our final goal is to apply the model to regional scale, simplicity was a key aspect of the model development, avoiding extra steps of model simplification in the later stages of our project. Therefore, the model operates with a single layer approach in the soil. Although this is a simpler approach compared to the some of the above mentioned models (Rachhpal and Nye, 1986, Génermont and Cellier, 1997 and Riedo et al., 2002), the model code is easily amendable, which enables to add new modules to GAG in the future."

Comment 12: *Please consider adding a list of abbreviations. There are many variables and parameters used in your model and it is difficult to keep track. Additionally, you may want to repeat variable definitions in the notes to some tables.*

Our answer: We agree with the reviewer. We will provide a list of abbreviations.

Change to the manuscript:
We add the list of abbreviations to the main text as a table seen in at the end of this document, right after our responses.

Comment 13: *p 61 l 13 Or ammonia and carbon dioxide (see section on urea hydrolysis products below).*

Our answer: As the reviewer pointed out, in an equilibrium model, like GAG it does not matter what we handle as the product of urea hydrolysis: bicarbonate and ammonium or carbamate and ammonia. However, we agree with the reviewer, strictly taken, the products of the enzymatic process of urea breakdown are the latter.

Change to the manuscript:

At page 61, from line 12 we change:

"the dissociation and dissolution equilibria related to the two products of urea hydrolysis: ammonium and bicarbonate."

to:

"the dissociation and dissolution equilibria related to ammonium and bicarbonate produced during urea hydrolysis."

Comment 14: *p 61 l 19. Instead of "parameter" I believe you mean "variable" or even "state variable".*

Our answer: Please see our modification below.

Change to the manuscript: On page 61, in line 19 we replace “parameter” with “variable”.

Comment 15: *p 61 l 23+. Please explain this TAN limitation more clearly. I believe you mean that in your results most of the available TAN was lost, so sensitivity to weather was low. This is an important result and probably an important limitation of your model approach. Why do you use “presumably”? You have a model, you can determine the exact response, perhaps with some more runs.*

Our answer: We thank the reviewer for making this point. We have done some new model runs to show what causes the difference between the previously reported Q_{10} values and the one we found in this study. We have run the model with three times and five times higher urinary N concentration (allowing more TAN in the later stages of the modelling period) and then we repeated the runs assuming a 10°C higher air and soil temperature. As it can be seen from Table C1 shown below, the difference in the Q_{10} values is negligibly small. This means that the reason, why the reported and the simulated temperature sensitivity differ, is not because of a model limitation, affecting the simulation of the TAN budget.

Table C1: Comparison of the total emission (g N) from a single urine patch from the model runs assuming different N content of the urine deposited with the original temperature and +10°C scenario (both in air and the soil temperature). We also calculated Q_{10} as the ratio of the total emission for the original and the amended temperature scenario.

	Original	+10C	Q10
Base run	95.81331	120.9791	1.262654
3x Ncontnet	290.4477	370.8033	1.276661
5x Nconent	489.6987	613.7874	1.253398

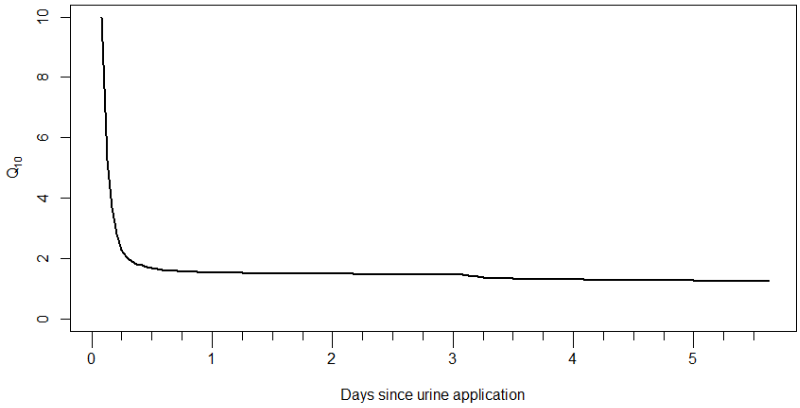


Figure C2: Calculated Q_{10} values for the cumulative NH_3 emissions over the period.

We have also calculated the Q_{10} values for the cumulative ammonia emissions for every time step (Fig. C2), and we found that ammonia emission is more sensitive to temperature in the first six hours than in the later stages. Considering, that over a grazed field urine patches are deposited in every time step, creating a peak in the individual patch emissions, the total emission for the whole field will be more sensitive to temperature than that for a single urine patch. This can explain the difference between the Q_{10} in the literature and the current model simulation.

Change to the manuscript:

At page 90 we remove the lines 14-20 starting from "The combined temperature…". Instead, we add the following together with the above shown table and figure:

We derived Q_{10} by running the model with 10°C higher air and soil temperature. The resulted value of 1.26 compared to that reported by Sutton et al. for grazing (4.7 for sheep sites) suggest a rather modest temperature sensitivity. The model showed similarly modest sensitivity when we tested it with three and five times higher N concentration in urine (Table C1). Based on this results it can be concluded that the lower Q_{10} values are not a consequence of the limited TAN available in the later stages of the modelling period.

A possible explanation for the difference between the reported and the simulated temperature sensitivity can be the temporal development of Q_{10} over time (Fig. C2). We calculated the Q_{10} values for every time step as the ratio of the cumulative emissions from the higher temperature model version and the original one, and we found that NH_3 emission is more sensitive to temperature in the first six hours than in the later stages. Considering, that over a grazed field urine patches are deposited in every time step, creating a peak in the individual patch emissions, the total emission for the whole field will be more sensitive to temperature than that for a single urine patch.

Comment 16: *p 61 l 25. Could clarify, e.g., "... provides a smaller temperature dependence than what has been reported in the literature."*

Our answer: As the cited part of the manuscript is in the abstract, we make a small, clarifying change there and in the main text – as outlined below - give a clear comparison of the temperature-dependency simulated by GAG and reported in the literature.

Change to the manuscript:

At page 61, from line 25 we change:

"a modest overall temperature dependence in total NH_3 emission compared with the values in the literature."

to:

"a modest overall temperature dependence in total NH_3 emission compared to what was reported in the literature earlier."

At page 90 line 17 we change:

"This value is rather smaller than the temperature dependencies for many volatilisation situations reviewed by Sutton et al. (2013)"

to:

"This value is rather smaller than that was reported by Sutton et al. (2013) for grazing ($Q_{10} = 4.7$ for sheep sites)."

Comment 17: *p 62 l 13-15. Not clear "In spite of its small proportion of emission, since two thirds of the grasslands are estimated to be grazed (Hellsten et al., 2008), grazing affects a significant percentage of the country."*

Our answer: We re-phrase this sentence for clarity.

Change to the manuscript:

At page 62, from line 13 we change:

"In spite of its small proportion of emission, since two thirds of the grasslands are estimated to be grazed (Hellsten et al., 2008), grazing affects a significant percentage of the country."

to:

"Although this proportion in the total national emission is rather small, since two thirds of the grasslands are estimated to be grazed (Hellsten et al., 2008), NH_3 emission from grazing affects a significant percentage of the country."

Comment 18: *p 62. Not clear what you mean: "as it was confirmed by both laboratory and field experiments (Farquhar et al., 1980; Sutton et al., 1995),"*

Our answer: The whole sentence is: "Ammonia exchange between atmosphere and surface, as it was confirmed by both laboratory and field experiments (Farquhar et al., 1980; Sutton et al., 1995), is a bidirectional process and dependent largely on meteorological factors, especially temperature." It is not obvious for any gas that its transfer between the atmosphere and surface is bidirectional and controlled by meteorology. In the case of ammonia it was confirmed by both laboratory and field experiments. We rephrase the sentence.

Change to the manuscript:

On page 62, from line 16 we change:

"Ammonia exchange between atmosphere and surface, as it was confirmed by both laboratory and field experiments (Farquhar et al., 1980; Sutton et al., 1995), is a bidirectional process and dependent largely on meteorological factors, especially temperature."

to:

"As demonstrated by both laboratory and field experiments (Farquhar et al., 1980; Sutton et al., 1995), ammonia exchange between atmosphere and surface is a bidirectional process and dependent largely on meteorological factors, especially temperature."

Comment 19: *p 62 l 1-3. Is this the only constraint for application at this scale? Do you think the model has been validated/evaluated sufficiently?*

Our answer: Yes, we believe that if all the input parameters can be obtained at larger scales, the model can be applied to larger scales. Of course, as we explained above (see Comment 3), for regional scale application the model needed to be simplified to a certain level. Beside the model validation (Section 4), we carried out a comprehensive sensitivity analysis to the uncertain parameters and assumptions within the model (Section 5).

Therefore, we think that we highlighted the weak points of the model that should be considered at larger scale application.

Comment 20: *p 62-63. The sentence starting with "To maintain the chemical equilibria. . ." and the following one are not clear. What do you mean "to maintain the chemical equilibria"? And what is "This" that leads to a high compensation point? Isn't it simply the relatively high concentration of NH3 (aq) in the urine patch?*

Our answer: In the mentioned two sentences we wanted to highlight for the readers the relationship between the equilibrium system of urine solution and the related ammonia emission. When ammonium is produced in the system, the equilibrium previously established within the system is disturbed; therefore, a new equilibrium state has to be formed. If more ammonium is produced, the whole equilibrium system shifts to form gaseous NH_3 above the solution ("to maintain the chemical equilibria"), or in other words, raising the compensation point. We rephrase the sentences for clarity.

Change to the manuscript:

At page 62, from line 27 we change:

"In a urine patch ammonium (NH_4^+) is produced by urea hydrolysis. To maintain the chemical equilibria between NH_4^+ and dissolved as well as gaseous NH_3, production of NH_3 by ureolysis is accompanied by NH_3 release from the urine solution to the gas phase. This leads to a high compensation point (usually higher than the ambient air concentration) above the urine patch, generally leading to NH_3 emission over a urine patch."

to:

"In a urine patch ammonium (NH_4^+) is produced by urea hydrolysis. Because of the equilibrium between NH_4^+ and NH_3, increasing NH_4^+ concentration results in an NH_3 compensation point that is usually higher than the ambient air concentration above the urine patch. This generally leads to NH_3 emission from a urine patch."

Comment 21: *p 63 l 22. For "dissolution" do you mean "volatilization"? Or, to avoid implying a direction, you could use "partitioning".*

Our answer: Please see our modification below.

Change to the manuscript:

At page 63, in line 22 we change "dissolution" to "partitioning".

Comment 22: *p 64 l 7-8. Running in in reverse implies absorption to me.*

Our answer: Following the suggestions of Reviewer #2, we avoid to use "inverse model", the proposed changes to the manuscript are listed below.

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".

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" (which follows the exact wording of Laubach et al., 2012).

Comment 23: *p 64 14-18. I think you should describe how the chemistry and soil transport components differ, if not here, elsewhere.*

Our answer: Please see our modifications mentioned in our response to Comment 11.

Comment 24: *p 64 l 24-26. "As soil ... content." not clear. I think I understand what you mean, but this need to be clarified.*

Our answer: Agreed.

Change to the manuscript:

At page 64, from line 24 we add the following clarifying clause after "available":

"– especially for a high resolution grid that would be required for regional scale application –"

Comment 25: *p 64-65 last/first sentence. I understand that your main interest was effects of weather, but if the soil processes are not accurately represented, the response to weather may be inaccurate. For an example, think about the TAN mass limitation to emission in your results that reduces the sensitivity of predicted emission to changes in weather.*

Our answer: We agree with the referee on this point. We address this under the model results presented in our response to Comment 15.

Comment 26: *p 65 l 16. Is this really similar to Riedo et al.? From my reading of their paper, they seemed to include multiple soil layers (and transport among them).*

Our answer: It is similar from the point of view that Riedo et al. (2002) also assumed a specific source layer in their model. We agree that this might not be clear enough, so will rephrase the sentence in the manuscript.

Change to the manuscript:

On page 65, in line 16 we change the text in the brackets to the following:

"similarly to Riedo et al. (2002), who also assumed a source layer on the top of their multilayer system"

Comment 27: *p 66 l 10. Is exchange with foliage one way only as implied by the figure? Clarify.*

Our answer: The exchange with the foliage is depicted on two figures in the manuscript, Fig. 1 and Fig. 3. On Fig. 1 there is bidirectional exchange with the foliage, the arrow between the thickest arrow ("Ammonia emission") and the "Grass" is double ended. We thicken the end of the arrow (see the Figure C1 shown above). On Fig. 2 in the manuscript there is bidirectional exchange with the canopy as a whole (F_f, double ended arrow between χ_{z0} and χ_c), there is deposition to the cuticule (F_w, arrow pointing downward from χ_c) and bidirectional exchange with the stomata (F_{sto}, double ended arrow between χ_{sto} and χ_c).

Change to the manuscript:

We change Fig. 1 to the one shown in our response to Comment 1.

Comment 28: *p 67 l 7. Is the assumption of steady-state reasonable? Why?*

Our answer: This assumption enables us to calculate the NH_3 flux in every time step by solving a linear system of equations instead of a system of partial differential equations. In the application of the two-layer canopy compensation point model this is a widely used approach (as also suggested by Massad et al., 2010). The assumption is reasonable because within a time step (1 hour) the changes are close to linear. We clarify this in the manuscript.

Change to the manuscript:

On page 67 in line 7 we change "steady state in every time step (1 h)" to "that the changes are close to linear within a time step (1h)".

Comment 29: *Equation (8). What value was used for a?*

Our answer: As we mentioned in the manuscript (page 67, line 13), all the model constants used within the 2LCCPM are listed in the supplementary material in Table S1. The value we used for *a* is 0.074, as listed in the "for R_w and R_{sto}" section of the table, in the 2nd row.

Change to the manuscript: To make this point more clear, we draw the borders of the row "for R_w and R_{sto}" to highlight it as a section header within Table S1.

Comment 30: *Equation (11). What are the units and possible values for the different gs? In this equation, are they really all multiplied? Can you give a name or clearer description for the gs parameters? The text suggests "phenological state", "temperature", and others that are incorrect.*

Our answer: We thank again the reviewer for noting this missing piece of information. We agree that there is need to add further conditions for calculating g_s in the supplement. We add these and also we clarify in the main text the role of g_{temp}, g_{light}… etc.

Change to the manuscript:

At page 69, we change the text from line 6 to 10, to:

"Stomatal conductance Eq. (11) is defined based on the relative conductances that express how the openness of the stomata changes in the function of the phenological state of the plant (g_{pot}) (assuming that grass could grow equally over the year, $g_{pot} = 1$), light (g_{light}), temperature (g_{temp}), vapour pressure deficit (g_{VPD}) and soil water potential (g_{SWP}). The combined effect of these, through the openness of stomata, controls g_s between its maximal value (g_{max}) and its minimal value (g_{max} × gmin):"

Change to the supplementary material:

We change Eq. S17 to:

$$g_{temp} = \min\left\{ g_{\min}, \left(1 - \left(\frac{T - T_{opt}}{T_{opt} - T_{\min}} \right)^2 \right) \right\}$$

And Eq. S18 to:

$$g_{VPD} = \begin{cases} g_{\min} & if \quad VPD > VPD_{\min} \\ 1 & if \quad VPD < VPD_{\max} \\ \left(\frac{(1 - g_{\min})(VPD_{\min} - VPD)}{VPD_{\min} - VPD_{\max}} + g_{\min} \right) & otherwise \end{cases}$$

Comment 31: *p 70 l 4+. I guess that emission potential Γs is meant to be proportional to the equilibrium concentration of free ammonia (NH3 (aq)). Is that correct? But this approach ignores temperature effects. And then below, on the same page, this variable is defined differently. Please clarify.*

Our answer: Eq. 14 (as we mentioned in the manuscript it is used in the form as it was published by Nemitz et al., 2001) is derived from the equations for the equilibrium coefficients (Table S2, second column) and their temperature dependent from (Table S2, third column) (as we also explain it in the manuscript on page 70, in line 1-4). In this way, the formulation of the compensation point (which in the mentioned equations is $[NH_{3(g)}]$) consists of the temperature dependent terms and Γ, which is the ratio of the NH_4^+ and H^+ concentrations. Therefore, yes, Γ is independent of temperature, but the compensation point is temperature dependent, accounting for both the temperature response of the Henry and dissociation equilibria. (And yes, Γ is proportional to the concentration of $NH_{3(aq)}$.)

As we explained in the manuscript (page 70, line 8-12), compared to the original application of 2LCCPM, where Γ was a measured parameter, in this case we have no information on the N status or the pH of the apoplastic fluid from the site, neither we will have any at regional scale application. Therefore, we had to find an approach to estimate it. As we explain it in the manuscript, we chose for this purpose the parametrization by Massad et al. (2010).

Change to the manuscript:

At page 70, in line 11, after “As” we add the following clarifying clause:

“As there were no Γ measurements in the experiment we used for validation (nor would such measurements be available for regional scale application) and …“

Comment 32: *Section 2.3 Here, Γp is defined two different ways. Please clarify.*

Our answer: Following the mentioned expressions for [TAN] and K(NH_4^+) in the manuscript (page 71, line 8-9):

$$\frac{[TAN]}{K(NH_4^+)+[H^+]}=\frac{[NH_4^+]+[NH3_{(aq)}]}{\frac{[NH3_{(aq)}][H^+]}{[NH_4^+]}+[H^+]}=\frac{[NH_4^+]+[NH3_{(aq)}]}{\frac{[H^+]}{[NH_4^+]}\left([NH3_{(aq)}]+[NH_4^+]\right)}=\frac{1}{\frac{[H^+]}{[NH_4^+]}}=\frac{[NH_4^+]}{[H^+]}$$

Where the first expression is Γ_p as in Eq. 19 in the manuscript and the last expression is Γ_p according to its definition (page 71, line 7).

Comment 33: *p 71 l 13 and elsewhere. You use the term “budget” for your state variables B, e.g. BTAN. But are these more accurately described as simply mass within the soil? To me “budget” here would be a description of the mass of TAN in each pool at some time, e.g., 1 g in soil, 0.5 g leached, 0.5 g in plants, 2 g emitted.*

Our answer: We defined all the budgets in the manuscript, so that the reader will know what the variables denoted by B mean. To clarify the units of the different budgets, we add also the units to the list of the abbreviations.

Change to the manuscript:

We include all the units of the different budgets into the list of abbreviations (together with the units of all the other variables and parameters). See the list at the end of the document, right after our responses.

Comment 34: *p 71 bottom. Is it correct that BH2O is in kg and other masses in g? Please give units (or point me to where they are given if I overlooked it).*

Our answer: It is in dm^3 which is practically, kg. It is mentioned at page 71, in line 14. We include this to the list of the abbreviations too.

Change to the manuscript:

We include this unit together with the units of all the other variables and parameters within the model to the list of abbreviations. See the list of abbreviations after our responses.

Comment 35: *p 72 l 10. Why was a value of 4 mm selected? Is it based on model fit for days 1 and 2? Clarify. And if so, how can you use the same data set for both calibration and validation? Does it really provide a sufficient validation? This is definitely a problem for at least, and from looking at data sources in the supplement, possibly for other parameters as well.*

> **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 36: *p 73 top. This description isn't entirely clear. So it is possible to lose more TAN than is present in a single time step, and if this happens, emission is "shut off" in the next one? If so, this is not a very elegant approach–doesn't it add artificial oscillations to your results? Since you are using R, you could use the ODE solvers in the deSolve package instead. Or, if you want a fixed time step for simplicity, can't you just limit emission in a time step to the total available TAN? Or have I misunderstood your equations?*

> **Our answer:** We thank again the reviewer for pointing this out. We include a model equation that does not allow the system to emit more ammonia than TAN is available in the TAN budget. Also, we note that in Eq. 24, the first condition is unnecessary (as the model is not able to produce higher emission than the TAN budget the first condition will be never fulfilled). We clarify this in the manuscript.
>
> **Change to the manuscript:** We change Eq. 24 to:
>
> $$B_{TAN}(t_i) = N_{prod}(t_i) + B_{TAN}(t_{i-1}) - F_g(t_{i-1}) \times A_{patch}$$
>
> and we add the following equation:
>
> $$F_g = \begin{cases} \dfrac{B_{TAN}(t_{i-1})}{A_{patch}} & if\left(B_{TAN}(t_{i-1}) - F_g(t_{i-1}) \times A_{patch}\right) < 0 \\ \dfrac{\chi_p - \chi_{z_0}}{R_{ac} + R_{bg} + R_{soil}} & otherwise \end{cases} \qquad \text{(Eq. C1)}$$
>
> On page 77, from line 2 we remove the sentence "In the first time step (right after depositing urine), as well as if all the TAN was emitted as NH_3 in the previous time step, B_{TAN} equals to N_{prod}." and we add the following instead:
>
> "The model does not allow to emit more NH_3 than TAN is available in the source layer, as it is described by Eq. C1."

Comment 37: *p 77 l 15+. Consider a different, simpler explaination: urea hydrolysis produces CO2 and NH3 in a ratio of 1:2. Ammonia is a base, and so pH rises during hydrolysis as NH_3 accumulates. The emission rate of NH_3 increases due to both an increase in total TAN and increase in pH. Emission of NH_3 (loss of a base) reduces pH, and also emission rates. You can debate whether urease produces these products or NH_4^+ and HCO_3^- . My understanding is that* *the actual products are* NH_3 *and* NH_2COO^-*. And carbamate (*NH_2COO^-*) is in equilibrium with* NH_3 *and* HCO_3^- *. For an equilibrium model it doesn't matter anyway (and this is almost true in reality too–the exception is the slow dehydration of* H_2CO_3*).*

Our answer: The explanation here approaches the phenomena from the point of view of the governing equilibrium chemical reactions, since the simulation of pH is developed based on these reactions. We agree, that we could give a simpler explanation, but at this section of the manuscript we find it helpful to outline for the reader the issues relevant for pH modelling based on the equilibrium reactions. As for the question of the products of urea hydrolysis, we proposed a change above in the abstract (Comment 13), and here we make a small amendment too.

Change to the manuscript:

On page 77, to line 15 after "urea molecule is decomposed" we add "(based on R0 in Table S2)". Also, to line 19 before "NH_4^+" we add "the produced".

Comment 38: *p 80 l 20. The word "lookup" is not a good description of what the uniroot() function does. How about using "finds" as in its help file?*

Our answer: Agreed.

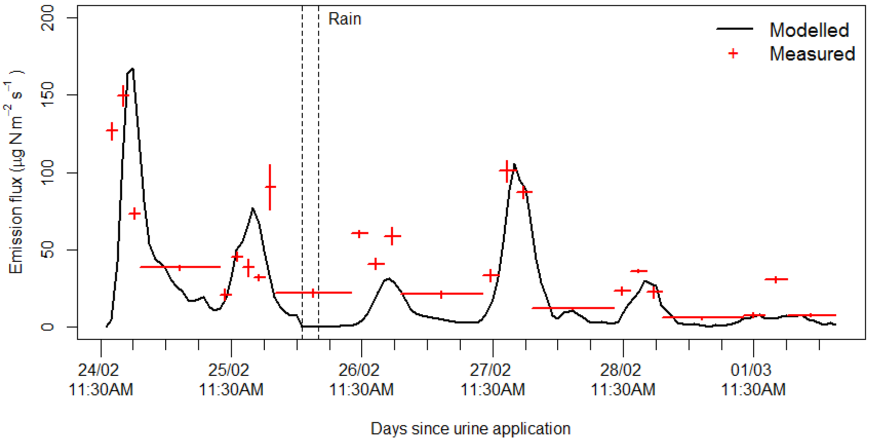
Change to the manuscript:

On page 80, in line 20 we change the word "look up"to "find".

Comment 39: *p 81 l 27+. Why not evaluate using measured and predicted average fluxes over each interval? I believe that these are the values reported in Laubach (e.g., their Fig. 2). Why introduce error (by using predictions from the middle of an interval) when it can be avoided?*

Our answer: Averaging the model results would lead to another type of error and the readers can say that the comparison does not show how the model really works, as the results were biased by the averaging. To give a wider basis to the readers to judge how the model works, we add intervals to the measured fluxes, illustrating the period for which the measurements are representative for.

Change to the manuscript:



On Fig. 4. we change Fig. a) as show above.

And we modify its caption as follows:

"Figure 4. Comparison of modelled and measured values for NH_3 emission flux with the corresponding sampling periods of the measurements (a), soil pH (b), TAN budget and NH_x-N (c), and volumetric water content of the top 5 mm layer of the soil (d). The vertical error bars stand for the standard deviation in the measurements."

Comment 40: *p 82 l 12+. So validation of water and TAN emission was done using two different values for Δz? That doesn't seem appropriate. Does the thickness of your "source layer" need to be the same as the "diffusion distance"?*

Our answer: To compare the water content measurement for the top 5 mm soil layer with model results for the top 4 mm would not be right, since in the model we assume that the evaporated water is released always from the top of the layer. This means that the same water loss via evaporation will not result in the same volumetric water content at the 4 mm and the 5 mm layer. Therefore, we had two options to validate the model: to estimate the water content of the top 4 mm layer based on the measurements or run the model with a layer of 5 mm thickness. As we are not aware of a technique to do the first solution, we decided to run the model, assuming a 5 mm of thickness. The choice is well established considering that none of the other model parts have effect on the water budget. We clarify this in the manuscript. As for the second question, the two are the same as we explained above (see Comment 5).

Change to the manuscript:

At page 82, from line 12 we remove the sentence "To validate […] to the soil" and we add the following paragraph:

"To validate θ we had to consider that the θ measurements were taken by using a sharp-edged metal ring that was pushed to about 5mm to the soil. As the model simulates the water content of a 4 mm thick layer, the same water loss via evaporation would not result in the same volumetric water content as was measured in the 5 mm depth sample. Since none of the other soil modules have effect on the water budget, we ran the model also with a Δz of 5 mm to get results that are comparable with the measurements."

Comment 41: *p 82 l 19-20. Here r is Person's correlation coefficient, right? A value of 0.54 (r2 = 0.29) is not high. You need to clarify the observations here–presumably they were individual measurement intervals.*

Our answer: Yes, it is the Person's correlation coefficient. We clarify this in the text. Considering that the model uses a simple approach for explaining a complex phenomenon, this can be regarded as a "relatively high" correlation as we put also in the manuscript (page 82, line 19). For the individual measurement intervals, see the modified figure proposed above (Comment 39).

Change to the manuscript:

On page 82 from line 18 we change the sentence "We got […] measurements." to the following one:

“The results of the model validation are summarized in Fig. 4 and Table 3. GAG captures the emission relatively well. Considering, that compared to the complexity of the phenomena, we use a simple model, the Person’s correlation coefficient (hereafter referred to as “correlation”) for NH_3 flux, can be considered as relatively high ($r=0.54$, $p=0.01$).”

Comment 42: *p 82 l 20-21. This description doesn’t seem accurate. From the figure, it looks like the model underestimates emission for all days after day 2. How does total emission compare? This would seem to be an important variable to compare. The equation given in Table 3 suggests the comparison is not good, but please give values of both measured and calculated total emission.*

Our answer: The rain event is in the middle of the second day. We state in the text: “The model slightly overestimates the fluxes before the rain event and it rather underestimates the measured values after it.” We are pointing to the period after the second day using the rain event and not simply saying that “after the second day” because we believe that the rain event had a significant effect on the ammonia emission, as we explain it in the same section, on page 83 from line 9, and proved our point with a model experiment (explained on page 88 from line 7).

The equation in Table 3 suggest an overall underestimation. Nevertheless, we agree that it is useful to include the total emission estimates.

Change to the manuscript:

At page 82, in line 21 after “event” we add: “on the second day”.

In addition, in the same line before the sentence “However…” we add:

“The total emissions over the whole period from a single patch (modelled: 1.78 g N, measured: 3.88 g N) was underestimated.”

Comment 43: *p 83 l 5. Do you mean “variables” and not “parameters”?*

Our answer: Please see our modification below.

Change to the manuscript:

At page 83, in line 5 we change “parameters” to “variables”.

Comment 44: *p 84 last paragraph. So do you even need the complexity of the equations for calculating atmospheric resistance? Would the use of simpler approaches change the results at all?*

Our answer: As we explained in the introduction, during the model development we predominantly focused on the accurate modelling of the effect of meteorological variables. Therefore, our answer is yes, we consider this complexity of equations to be relevant. However, it can be also argued to what extent these equations are complex: R_{ac} was assumed to be inversely proportional to u_* (as mentioned on page 68, in line 1) and R_{bg} can be also expressed by a single equation if we substitute the formulas of Eq. S14 and Eq. S15 to Eq. S13, which we wrote as three separate equations for better transparency.

We agree that the derivation of R_a is more complex than those of R_{ac} and R_{bg} but R_a plays a role also in the NH_3 exchange with the vegetation. Due to the decrease of soil emission, the effect of the exchange with vegetation on total emission is becoming comparable with that of the soil emission toward the end of the period (Figure S1.). Since the model will be applied elsewhere for longer periods than it was here, it is important to keep the simulation of R_a as realistic as possible.

In addition, we pointed out in the manuscript (page 84, in line 20-22), that the atmospheric resistances can approach values of the soil resistance when weak wind (large atmospheric resistances) is coupled to dry soil conditions (small soil resistance). This is especially true for R_{ac} that even exceeds the value of R_{soil} on the 4th and the 5th day (Fig. 5).

Comment 45: *p 87 l 6-10. This response implies pressure accumulation in soil pores and seems implausible. Why not modify the model to at least allow soil air to be forced out as gas pore volume decreases?*

Our answer: We agree that this could be an interesting topic for future investigation. However, considering the likely scale of the effect and the need to balance resources presently available to us, we have focused on other suggestions of the referees as being of higher priority.

Comment 46: p 87 l 3. *What is "This" in "This is also suggested..."? Not clear.*

Our answer: Please see our modification below.

Change to the manuscript:

At page 8, from line 3 we change the sentence "This is also […] blue line." to:

"A sudden drop can be seen in the simulated pH at the beginning of the rain event (Fig. 4b), which tends to disappear if there is no rainfall over the modelling period (Fig. 9a, blue line)."

Comment 47: *p 87-88, last/first paragraph. Another possible explanation is that the solution infiltrates deeper than Δz, and diffusion or even advection (both in water and gas phase) transport it close to the surface. This seems like a simpler explanation. It would mean that the single layer lumped-parameter approach of your model is insufficient.*

Our answer: As the model works with a "single layer lumped-parameter approach" the mentioned explanation cannot be tested within the present formulation of the model. However, we supported our point for the restart of urea hydrolysis by a model simulation (as explained on page 88, in line 7-13).

In addition, if we use the urea decomposition function for the total urea applied within a urine patch (15 g), at the beginning of the rain event there will be only around 0.002 g urea in the soil. We do not believe that this amount of urea (even if all of it is transported to the surface) could explain the simultaneous and significant increase of the soil's mineral NH_x-N content and soil pH that was observed at the site. Or if more urea was transported to the surface: we are not aware of any process in the soil that would prevent urea hydrolysis in the deeper soil layers.

We do, however, agree that further work would be beneficial on the recycling processes of urea and TAN and NH_x between deeper and surface soil, but consider that this must be addressed as part of the future research challenges.

Comment 48: *p 93 paragraph around l 20. This seems out of place. And "online" does not seem to be the proper term. Do you mean "dynamic"?*

Our answer: We are not aware of any ecosystem scale NH_3 exchange model that is capable of simulating soil pH.

Change to the manuscript:

On page 93, line 29 we change the word "online" to "dynamic".

Comment 49: *How can your model underestimate NH3 emission but accurately predict TAN in the soil? To me this means that one of those measurements is wrong, or that the model is right for the wrong reasons. In this case I suspect that there is significant TAN below 4 mm that was not measured or measured and not reported. In that case is comparison with TAN in the top 5 mm really useful at all?*

Our answer: Ammonia emission depends not only on the TAN content of the soil but also the soil pH. In the mentioned period, the pH was underestimated in the model (Fig. 4 b), which leads to underestimation in the NH_3 emission flux as well (Fig. 4 a)). On the other hand, we agree there might be more TAN below 4 mm in the soil, but, as it was neither measured nor modelled, we have no information about it. As noted above (Comment 47), we agree that it would be beneficial for future studies to give more attention the transport processes of TAN between deeper and surface soil layers.

Comment 50: *The conclusions section is too long and contains material more appropriate for the discussion section, I think. The comparison of your model to others is useful (although I don't think it belongs in this section). Pease consider whether you overstate the advantages of your model.*

Our answer: We agree with the reviewer. See our modification below.

Change to the manuscript:

We rename the Conclusion section to Discussion and add the following paragraphs as a new, shorter Conclusion section:

"We report the description of a process-based, weather-driven ammonia exchange model for a urine patch that is capable of simulating the TAN and the water content of the soil under a urine patch and also soil pH.

The model tests suggest that ammonia volatilization from a urine patch can be affected by the possible restart of urea hydrolysis after a rain event as well as CO_2 emission from the soil.

The vital role of temperature in NH_3 exchange is supported by our model results; however, the GAG model provides only a modest overall temperature dependence in total NH_3 emission compared with the literature. This, according to our findings, can be explained by the higher sensitivity to temperature close to urine application than in the later stages. In addition, we found that wind speed and relative humidity are also significant influencing factors. These relationships need to be further tested in relation to field measurements.

For simplicity to allow subsequent regional upscaling, the model operates with a single soil layer approach, neglecting water movement and solution mixing in the soil. Although this is a limitation of the current model version, the model code is easily amendable, which facilitates to add new modules to GAG in the future.

Considering that all the input parameters can be obtained for larger scales, GAG is potentially suitable for field and regional scale application, serving as a tool for further investigation of the effects of climate change on ammonia emissions and deposition."

Comment 51: *Table 1. Are all these values from Laubach et al.? Looking through that paper, I do not see some of them (urea hydrolysis constant, source layer thickness at least).*

Our answer: We thank the reviewer for noting this point. We agree that the caption of the table needs further details and we therefore modify it.

Change to the manuscript:

We change the caption of Table 1. to:

"Urine patch details from the experiment of Laubach et al. (2012) (or from other sources as listed in the footnote) and site specific model constants."

We also add to the footnote linked to Δz:

"Assumed in this study."

Comment 52: *Table 3. Is r Pearson's correlation coefficient? Please clarify. What are units on water content? What is "Equation" column? Presumably it is least-squares regression equation. Which variable is y, which is x? For TAN budget, it is not clear what the modelled response variable is. What is the observational unit here? Are individual observations from measurement periods?*

Our answer: We add these pieces of information to the caption of the table. Individual measurement periods were only in the case of the measurement of NH_3 exchange flux (as mentioned in Table 2). As we showed above (Comment 39), we add these sampling periods to the figure. The response variables in every case were the same as were plotted on Fig. 4.

Change to the manuscript:

We change the caption of Table 3 to:

"Model validation statistics: root mean square error (RMSE), Pearson's correlation coefficient (r), the equation of the fitted least-squares equation (x - observation, y - model) and the level of significance of the correlation."

In the table we change "soil water content" to "volumetric water content (m^3 m^{-3})"

We add the following foot note to Table 3:

"All the modelled and measured variables are the same as shown in Fig. 4. In the case of the emission flux, we compared the measured flux in the given measurement period with the value simulated at the time of the midpoint of the corresponding measurement period as explained in Table 2. "

Comments on the supplement

Comment 53: *p 2. Not clear what virtual temperature is.*

Our answer: The virtual temperature of the moist air is the temperature that the dry air would have if its pressure and density was the same as that of the moist air. We add this to the supplementary material.

Change to the supplementary material:

Before Eq. S9 we add after T_{V}:

", which is the temperature that the dry air would have if its pressure and density was the same as that of the moist air."

Comment 54: *Table S1. Give units for Dg. What is heat capacity for–soil?*

Our answer: Please see our modification below.

Change to the supplementary material:

We add in Table S1 the unit to D_g: m^2 s^{-1} and extend the text in the brackets for c_p: "heat capacity of air".

Comment 55: *Equation (S9). Missing molar mass?*

Our answer: No, it is the specific gas constant of dry air R is expressed as J kg^{-1} K^{-1}.

Change to the supplementary material:

Before Eq. S10 we modify "gas constant" to "specific gas constant of dry air".

Comment 56: *Table S2. [...] 1. What do square brackets [mean here? I assume molar concentration (mol/L) but you also use them for gaseous species.*

Our answer: [ ] means that all the concentrations, including that of the gaseous species are in mol dm^{-3}.

Change to the supplement:

To clarify what square brackets mean, we add the caption of Table S2: "(squared brackets denotes that the concentration of every compound is in mol dm^{-3})".

Comment 57: *Table S2. [...] Did you apply any correction for non-ideal behaviour, i.e., did you use activity coefficients? This requires an estimate of ionic strength, but even an approximate estimate would be more accurate than none.*

Our answer: We thank the reviewer for this comment. For the manuscript we did not apply any correction for non-ideal behaviour, but following the reviewer's suggestion, we did a test simulation with the highest activity coefficients derived for the highest ion concentrations (0.2 mol dm^{-3}) published by Kielland (1937) (the highest ionic concentration in the modelled solution was 0.14 mol dm^{-3}). With this modification, the difference, in the total NH_3 emission was - 4.7% and the average change in pH was - 0.019. Considering that the ion concentration decreases toward the end of the modelling period, and consequently, the activity coefficients converge to 1, we neglect the effect of non-ideal behaviour in the solution in the present study.

Change to the manuscript:

At page 78 after line 21 we add the following paragraph:

"As urine is a relatively concentrated solution, non-ideal ionic behaviour may have an effect on the chemical equilibria. To test this in the model, we did a test run with the maximum activity coefficients derived for the highest ion concentrations (0.2 mol dm^{-3}) published by Kielland (1937) (the highest ionic concentration in the modelled solution was 0.14 mol dm^{-3}). With this modification, the difference, in the total NH_3 emission was - 4.7% and the average change in pH was - 0.019. Considering, that the ion concentration decreases toward the end of the modelling period, and consequently, the activity coefficients converge to 1, we neglect the effect of non-ideal behaviour in the solution."

Comment 58: *Table S2. [...] Assuming the numerator for the definition of H in R4 and R5 is activity, how was it defined? Presumably it was just partial pressure.*

Our answer: As we explained in our response to Comment 56 [ ] means that all the concentrations, including those of the gaseous species in the definition of H in R4 and R5 are in mol dm^{-3}. For further clarification on this question see our answer to the next comment.

Comment 59: *Can you clarify your conversion factor c_{con}? Giving units in the conversion would be good. I think 8.314 is the gas constant and the other terms (other than temperature) just change units of the gas constant. Why not use the necessary units from the start (0.082057 L atm K^{-1} mol^{-1})? Also, is the exponent correct? I would expect you to divide H in atm (mol dm^{-3})$^{-1}$ by RT to convert atm to (mol dm^{-3}) but here it is multiplied.*

Our answer: We thank to the reviewer for noting this point. In the manuscript in the equations (not in the model code) we accidentally swap the gaseous and aqueous concentrations in the definition of the Henry constants for R4 and R5, which means that in the temperature dependent equations mol dm^{-3} atm^{-1} has to be converted to mol dm^{-3} (mol dm^{-3})$^{-1}$.

We converted atm to mol dm^{-3} as follows. First we converted atm to Pa:

1 atm = 1.01×10^5 Pa

Then this was converted to mol m^{-3}. Based on the ideal gas law, pressure has to be divided by RT, where R is the gas constant (8.314 J K^{-1} mol^{-1}) and T is the temperature (K).

Based on $\frac{n}{V} = \frac{p}{RT}$ we get $\frac{1.01 \times 10^5 Pa}{8.314 \frac{J}{Kmol} \times T(K)} = \frac{1.01 \times 10^5 \frac{N}{m^2}}{8.314 \frac{Nm}{Kmol} \times T(K)} = \frac{1.01 \times 10^5}{8.314 \times T} \frac{mol}{m^3}$

And finally we converted m^3 to dm^3:

$$\frac{1.01 \times 10^5}{8.314 \times T} \frac{mol}{m^3} = \frac{1.01 \times 10^5}{8.314 \times T} \frac{mol}{10^3 dm^3} = \frac{0.001}{8.314} \times \frac{1.01 \times 10^5}{T} \frac{mol}{dm^3}$$

This conversion factor has a (-1) power, as atm is in the denominator in the Henry constant.

Change to the supplementary material:

In Table S2 we change the equations for R4 and R5 to:

$$H\left(NH_{3(g)}\right) = \frac{\left[NH_{3(aq)}\right]}{\left[NH_{3(g)}\right]}$$

$$H\left(CO_{2(g)}\right) = \frac{\left[H_2CO_3\right]}{\left[CO_{2(g)}\right]}$$

And we change the conversion factor to:

$$c_{con} = \left(\frac{0.001 \frac{m^3}{dm^3}}{8.314 \frac{J}{Kmol}} \times \frac{1.013 \times 10^5 \frac{Pa}{atm}}{T_{soil}} \right)^{-1}$$

Technical corrections

Comment 60: *p 61 l 7 "Total Ammoniacal Nitrogen" switch to lowercase.*

Our answer: Please see our modification below.

Change to the manuscript:

At page 61 in line 7 we change "Total Ammoniacal Nitrogen" to "total ammoniacal nitrogen".

Comment 61: *Fig. 2. Resolution is poor and perhaps font size is too small. Can you use a vector image (eps, pdf)?*

Our answer: We submitted the figure following the requirements of the journal. The figure is readable on a usual A4 page. We can confirm this with the technical editor during the production stage.

Comment 62: *p 66 l 9 and elsewhere. Give version of R used (functions can change).*

Our answer: Please see our modification below.

Change to the manuscript:

At page 67 in line 9 and page 80 in line 19 after "programming language R" we add: "(version 3.1.2 (2014-10-31))".

Comment 63: *p 68 l 8. Give reference for diffusivities.*

Our answer: We add the reference to the diffusivity of ammonia. For the ratio of the diffusivity of ozone and ammonia we gave the reference in Table S1 in the supplementary material.

Change to the supplementary material:

We add to the footnote under Table S1 linked to D_{NH3}: "Spiller (1989)", and to the Reference section of the supplementary material:

Spiller, L.L.: Determination of Ammonia/Air Diffusion Coefficient Using Nafion Lined Tube, Analytical Letters, 22, 2561-2573, 1989.

Comment 64: *p 73 l 1 Replace "negligible" with "negligibly"*

Our answer: Please see our modification below.

Change to the manuscript:

At page 73, in line 1 we change "negligible" to "negligibly".

Comment 65: *p 85 l 22. Do you mean "In contrast"?*

Our answer: Please see our modification below.

Change to the manuscript:

At page 85, in line 22 we change "by" to "in" following the request of the referee.

Comment 66: *p 86 l 23. By "online" do you mean "dynamic"?*

Our answer: We change this as mentioned above (Comment 48).

List of abbreviations

Abbreviation (unit)	Model variable
$\frac{D_{O_3}}{D_{NH_3}}$	Ratio of diffusivity of O_3 and NH_3
[X] (mol dm^{-3})	Concentration of compound X
A	Parameter for calculating R_w
A_h	Parameter for urea hydrolysis simulation
A_{patch} (m^2)	Area of a urine patch
B_C (mol)	Carbon content of the source layer (originating from urea)
B_{H2O} (dm^3)	Water budget in the source layer
B_{H2O}(max) (dm^3)	Maximal water amount in the source layer
B_{H2O}(min) (dm^3)	Minimal water amount in the source layer
B_{H2O}' (dm^3)	Precalculated water budget in the source layer
B_{H2O}^{Tot} (dm^3)	Total water budget under a urine patch
B_N (mol)	TAN + gaseous ammonia content in the source layer
B_{TAN} (g N)	TAN budget in the source layer
B_{urea} (g N)	Urea budget under a urine patch
B_X (mol) (X= H_2CO_3, HCO_3^-, CO_3^{2-}, $CO_{2(g)}$, NH_4^+, $NH_{3(aq)}$, $NH_{3(g)}$, H^+)	Budget of a chemical compound X under the urine patch
C_d	Effect of day and night on evapotranspiration
c_N (N dm^{-3})	N content of the urine
c_N^{Tot} (g N dm^{-3})	Urine N content after dilution in the soil
c_p (J kg^{-1} K^{-1})	Heat capacity of air
d (m)	Displacement height
D_e (mm)	Cumulative depth of evaporation
D_g (m^2 s^{-1})	Diffusivity of NH_3 in air
E (mm h^{-1})	Soil evaporation rate
e_a (kPa)	Actual water vapour pressure
e_s (kPa)	Saturated water vapour pressure
ET (mm h^{-1})	Actual evapotranspiration rate
ET_0 (mm h^{-1})	Reference evapotranspiration rate
f_c (m^2 m^{-2})	Vegetation coverage
F_f (µg N m^{-2} s^{-1})	NH_3 exchange flux with the foliage
F_g (µg N m^{-2} s^{-1})	NH_3 exchange flux over the ground
F_{sto} (µg N m^{-2} s^{-1})	NH_3 exchange flux with stomata
F_t (µg N m^{-2} s^{-1})	Total NH_3 exchange flux over the canopy
f_w (m^2 m^{-2})	Wetted uncovered soil fraction
F_w (µg N m^{-2} s^{-1})	NH_3 deposition flux deposition to water and waxes on the leaf surface
g (m s^{-2})	Acceleration of gravity
G (MJ m^2 h^{-1})	Soil heat fux
g_{light}	Relative conductance for the effect of light on g_s
g_{max} (mmol O_3 m^{-2})	Maximal stomatal conductance

g_{min}	Minimal relative stomatal conductance
g_{pot}	Relative stomatal conductance for the effect of plant phenological state on g_s
g_s (mmol O_3 m^{-2})	Stomatal conductance for O_3
g_{SWP}	Relative conductance for the effect of soil water on g_s
g_{temp}	Relative conductance for the effect of temperature on g_s
g_{VPD}	Relative conductance for the effect of vapour pressure deficit on g_s
H (J m^{-2} s^{-1})	Sensible heat flux
h (m)	Canopy height
H(X) (mol dm^{-3} (mol $dm^{-3})^{-1}$)	Henry coefficient for the given gas X
i_C (mol)	Carbon input to the urine patch
i_N (mol)	TAN input to the urine patch (TAN production in moles)
K	Karman constant
K(X) (mol dm^{-3})	Dissociation constant for the given compound X
K_c	Crop coefficient
K_{cb}	Transpiration coefficient
K_{cb}(Tab)	Coefficient to calculate ET
K_e	Soil evaporation coefficient
k_h	Urea hydrolysis constant
L (m)	Monin-Obukhov length
LAI (m^2 m^{-2})	Leaf area index
N_{app} (kg N ha^{-1})	Nitrogen applied over a urine patch
N_{prod} (g N)	TAN production
p (kPa)	Surface atmospheric pressure
P (mm)	Precipitation
PAR (µmol m^2 s^{-1})	Photosynthetically active radiation
Q	Specific humidity
R (kg^{-1} K^{-1})	Specific gas constant of dry air
R_a (s m^{-1})	Aerodynamic resistance over the canopy
R_{ac} (s m^{-1})	Aerodynamic resistance in the canopy
R_b (s m^{-1})	Resistance of the quasi-laminar layer over the canopy
R_{bg} (s m^{-1})	Resistance of the quasi-laminar layer in the canopy
Re	Reynolds number
REW (mm)	readily evaporable water
R_{glob} (MJ m^2h^{-1})	Global radiation / solar radiation
RH (%)	Relative humidity
R_n (MJ m^2 h^{-1})	Net radiation
r_{RX} (mol)	Consumption or production of a given compound in reaction X.
R_{soil} (s m^{-1})	Soil resistance
R_{sto} (s m^{-1})	Stomatal resistance
$R_{sto}(O_3)$(s m^{-1})	Stomatal resistance for O_3
R_w (s m^{-1})	Cuticular resistance
$R_{w(min)}$ (s m^{-1})	Minimal cuticular resistance
Sc	Schmidt number

S_{MI}	Soil moisture index
T (ºC)	Air temperature at 2 m
TEW (mm)	total evaporable water
T_{min} (°C)	Temperature for minimal stomatal conductance
T_{opt} (°C)	Temperature for optimal stomatal conducatnce
T_{soil} (ºC)	Soil temperature
T_v (K)	Virtual temperature
u ($m\ s^{-1}$)	Wind speed
u_* ($m\ s^{-1}$)	Friction velocity
u_{*g}	Friction velocity at ground level in the canopy
U_{add} (g N)	Urea added to the source layer
V_{air} (dm^3)	Volume of the air in the source layer
VPD (kPa)	Vapour pressure deficit
VPD_{max} (kPa)	VPD for maximal stomatal conductance
VPD_{min} (kPa)	VPD for minimal stomatal conductance
W_{evap} (dm^3)	Water loss as soil evaporation from the urine patch
W_{rain} (dm^3)	Water input as rain water over the urine patch
W_{urine} (dm^3)	Volume of urine
X	Parameter for calculating the stability functions
z_0 (m)	Surface roughness
z_l (m)	Height of the top of logarithmic wind profile
z_w (m)	Height of wind measurement
A	Parameter for calculating R_{ac}
α_{PAR} ($\mu mol\ m^2\ s^{-1})^{-1}$	Parameter for calculating g_{PAR}
β (mol H^+ (pH unit)$^{-1}$ dm^{-3})	Soil buffering capacity
β_{patch} (mol H^+ (pH unit)$^{-1}$)	Buffering capacity of the source layer
γ (kPa $ºC^{-1}$)	Psychometric constant
Γ_p	NH_3 emission potential in the soil pore
Γ_{sto}	NH_3 emission potential from the stomata
Γ_{sto}(max)	Maximal NH_3 emission potential from the stomata
Δ (kPa $ºC^{-1}$)	Slope of saturation vapour pressure curve
δ_0 (m)	Height where eddy and molecular diffusivity are the same in magnitude
Δz (mm)	Thickness of the source layer
Δz_E (m)	Thickness of evaporation layer
θ ($m^3\ m^{-3}$)	Volumetric water content
θ_{fc} ($m^3\ m^{-3}$)	Field capacity
θ_{por} ($m^3\ m^{-3}$)	Porosity
θ_{pwp} ($m^3\ m^{-3}$)	Permanent wilting point
ν ($m^2\ s^{-1}$)	Kinematic viscosity
Ξ	Soil tortuosity
ρ (kg m^{-3})	Air density
τ (days)	Decay parameter
χ_a (µg N m^{-3})	Air concentration of NH_3
χ_c (µg N m^{-3})	Compensation point above the vegetation
χ_p (µg N m^{-3})	Compensation point in the soil pores
χ_{sto} (µg N m^{-3})	Stomatal compensation point

χ_{z0} (μg N m^{-3})	Canopy compensation point
Ψ_H	Stability function for heat
Ψ_M	Stability function for momentum

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