

Interactive comment on “A process-based model for ammonia emission from urine patches, GAG (Generation of Ammonia from Grazing): description, validation and sensitivity analysis” by A. Móríng et al.

Anonymous Referee #3

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1 General comments

The paper describes in some detail what may be a useful model. In my opinion the model has some significant problems that need to be addressed through more careful evaluation and probably changes to the model itself. The most important is the the single-layer lumped-parameter approach to soil resistance. Additionally, I think model evaluation could be improved, both in terms of the scenarios evaluated and discussion of the implications.

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2 Specific comments

In these comments I've omitted the "100" from the start of all page numbers.

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 | 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.

Regardless of whether TAN can be lost from the upper layer by infiltration, 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). 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 change the perspective of your discussion to evaluate whether or not this approach is sufficient.

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.

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 $< \Delta z$, none of it would have to be transported as far as Δz to be emitted. Clarify please. If these

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Your approach to calculating soil solution pH is not described in sufficient detail. 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. Apart from this point, 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 | 28+), but there is a B_{H_2O} present in your equations that seems out of place. Please check. Also, can you provide details on which reactions are quantified by r_{R5} etc.? I think they refer to the reactions in Table S2, but the sign of at least r_{R3} seems wrong in at least Eqs. (39) and (40). 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.

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

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.

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.

p 61 | 13 Or ammonia and carbon dioxide (see section on urea hydrolysis products below).

p 61 | 19. Instead of “parameter” I believe you mean “variable” or even “state variable”.

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p 61 | 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.

p 61 | 25. Could clarify, e.g., "... provides a smaller temperature dependence than what has been reported in the literature."

p 62 | 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."

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),"

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

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?

p 63 | 22. For “dissolution” do you mean “volatilization”? Or, to avoid implying a direction, you could use “partitioning”.

p 64 | 7-8. Running in reverse implies absorption to me.

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

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

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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.

p 65 | 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).

p 66 | 10. Is exchange with foliage one way only as implied by the figure? Clarify.

p 67 | 7. Is the assumption of steady-state reasonable? Why?

Equation (8). What value was used for a ?

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

p 70 | 4+. I guess that emission potential Γ_s is meant to be proportional to the equilibrium concentration of free ammonia (NH_3 (aq)). Is that correct? But this approach ignores temperature effects. And then below, on the same page, this variable is defined differently. Please clarify.

Section 2.3 Here, Γ_p is defined two different ways. Please clarify.

p 71 | 13 and elsewhere. You use the term “budget” for your state variables B , e.g. B_{TAN} . 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.

p 71 bottom. Is it correct that B_{H_2O} is in kg and other masses in g? Please give units (or point me to where they are given if I overlooked it).

p 72 | 10. Why was a value of 4 mm selected? Is it based on model fit for days 1

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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.

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?

p 77 | 15+. Consider a different, simpler explanation: urea hydrolysis produces CO_2 and NH_3 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).

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

p 81 | 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?

p 82 | 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

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layer” need to be the same as the “diffusion distance”?

p 82 | 19-20. Here r is Person’s correlation coefficient, right? A value of 0.54 ($r^2 = 0.29$) is not high. You need to clarify the observations here—presumably they were individual measurement intervals.

p 82 | 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.

p 83 | 5. Do you mean “variables” and not “parameters”?

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?

Section 5.2 See my comments at the top of this section on possible problems with the model structure.

p 87 | 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?

p 87 | 3. What is “This” in “This is also suggested...”? Not clear.

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.

p 93 paragraph around | 20. This seems out of place. And “online” does not seem to be the proper term. Do you mean “dynamic”?

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Conclusions. 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?

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). Please consider whether you overstate the advantages of your model.

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).

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 modeled response variable is. What is the observational unit here? Are individual observations from measurement periods?

2.1 Comments on the supplement

p 2. Not clear what virtual temperature is.

Table S1. Give units for D_g . What is heat capacity for–soil?

Equation (S9). Missing molar mass?

Table S2. There are a few problems here. Some may just require clarification.

1. What do square brackets [mean here? I assume molar concentration (mol/L) but you also use them for gaseous species.

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2. Did you apply any correction for non-ideal behavior, 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.
3. Related to 1. Assuming the numerator for the definition of H in R4 and R5 is activity, how was it defined? Presumably it was just partial pressure.
4. 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 ($0.082057 \text{ L atm K}^{-1} \text{ mol}^{-1}$)? Also, is the exponent correct? I would expect you to divide H in $\text{atm} (\text{mol dm}^{-3})^{-1}$ by RT to convert atm to (mol dm^{-3}) but here it is multiplied.

Table S3. The footnote symbols could be confusing.

3 Technical corrections

p 61 | 7 “Total Ammoniacal Nitrogen” switch to lowercase.

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

p 66 | 9 and elsewhere. Give version of R used (functions can change).

p 68 | 8. Give reference for diffusivities.

p 73 | 1 Replace "negligible" with "negligibly"

p 85 | 22. Do you mean "In contrast"?

p 86 | 23. By "online" do you mean "dynamic"?

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