

Authors' response to the interactive comment of W. Bussink on "A process-based model for ammonia emission from urine patches, GAG (Generation of Ammonia from Grazing): description, validation and sensitivity analysis"

We thank Dr Bussink for his detailed and insightful comments, especially for bringing our attention to several relevant studies that we have now been able to mention in the revised manuscript. Our answers followed by our modifications of the manuscript are provided point-by-point below.

Comment: *"Sometimes it [urea] is no more than 50% of the total N excretion (on pure grass diets it can be much higher). This means that other components like allantoin, creatine and creatinine become more important (see i.e. Whitehead et al., 1989) and can make up to more than 15% of the N in urine (Bristow et al., 1992). These components can also decompose to urea, resulting in ammonia emission (Whitehead, 1989)."*

Our answer: We completely agree with the reviewer that decomposition of urine components other than urea can contribute to the TAN (Total Ammoniacal Nitrogen) budget as clearly shown by Whitehead et al. (1989). However, according to Whitehead et al. only allantoin can have a comparable influence on ammonia emission (from the solutions of these compounds with the same N concentration, over 8 days 15% of the applied N was emitted from urea and 11% from the allantoin); that of the other two components, creatine and creatinine, is rather small (over 8 days 4% and less than 1% of the applied N was emitted as NH₃, respectively). In addition, according to Dijkstra et al. (2013) the proportion of allantoin in urinary nitrogen is considerably lower than that of urea, 2.2-14.2% compared to 57.8-93.5% and the proportions for creatine and creatinine are even lower.

Change to the manuscript:

At the sentence on page 10078 in line 10: "To further focus our model onto the key reactions, we simulate urine chemistry considering only the water and urea available in the beginning, and the products of urea breakdown afterwards." We add the following paragraph after line 10:

"Whitehead et al. (1989) showed that not only urea but other urinary nitrogen components, such as allantoin, creatine and creatinine, can contribute to NH₃ emission through their decomposition. However, Whitehead et al. found that only allantoin can have a comparable influence on NH₃ volatilization (from the solutions of these compounds with the same N concentration, over 8 days 15% of the applied N was emitted from urea and 11% from the allantoin); that of the other two components, creatine and creatinine, is rather small (over 8 days 4% and less than 1% of the applied N was emitted as NH₃, respectively). In addition, according to Dijkstra et al. (2013) the proportion of allantoin in urinary nitrogen is considerably lower than that of urea, 2.2-14.2% compared to 57.8-93.5% and the proportions for creatine and creatinine are even lower. Therefore, to further focus our model onto the key reactions, we simulate urine chemistry considering only the water and urea available in the beginning, and the products of urea breakdown afterwards."

Comment: *“Furthermore the composition of urine influences the urea hydrolysis rate (Whitehead et al., 1989; Dijkstra et al., 2013) and own unpublished results. However, due to the setup of the validation - cow urine of 5 g/l (Laubach 2012) was enriched with artificial urea to obtained a urine-urea solution with 10 gN/l. So in fact a “pure” urea solution was used. – a urea based model was tested against an urea solution, resulting in a negligible effect of other N constituents in urine. But, using this model for other situations may lead to an underestimation of TAN and thereby to an underestimation of the driving force for ammonia emission.”*

Our answer: As Dr Bussink pointed out, a clear consequence of the findings of Whitehead et al. (1989) is that if all the urinary nitrogen is assumed to be in the form of urea, the model will possibly underestimate ammonia emission. Whitehead et al. suggests that this is caused by the presence of hippuric acid in real urine, the effect of which is not taken into account in our model. According to this study the difference in the cumulative volatilization of ammonia (expressed as the proportion of the total nitrogen content of urine) between cattle urine and a urea solution (without hippuric acid) is about 10%. However, a comparable difference was reported when these authors compared urea+hippuric acid solutions with different N contents as well as different hippuric acid contents.

The N content of urine ranges widely, not just amongst different animals, but also for different urination events by the same animal (Betteridge et al., 1986 and Hoogendoorn et al., 2010) (the incorporation of this effect to our field scale model is currently being studied in further work). This means that assuming an average N concentration of 8 g, according to Whitehead et al. (1989) can result in a 10% overestimation in the cumulative volatilization of ammonia if the real nitrogen concentration was as low as 2 g/l.

Similarly, in the case of the different ratios of hippuric acid and urea: if we assume that the hippuric acid N is an average of 0.8% of the urea N (based on the data published by Dijkstra et al. (2013) this proportion varies between 1.4 - 0.36%), according to Whitehead et al. (1989), the overestimation of the cumulative ammonia emission can be 10% if the proportion of hippuric acid was minimal in reality.

As the effect of hippuric acid on urea hydrolysis is not widely investigated in the literature, at the moment the current approach is the best we can achieve to simulate the decomposition chemistry in urine. Although the field scale model would most likely underestimate ammonia emission due to the exclusion of hippuric acid, this underestimation may be partly balanced by the sources of overestimation in the model. Nevertheless, the detailed analysis of the effect of the composition and N content of urine is beyond the scope of our current study.

Change to the manuscript:

We add the following paragraphs after line 14 on page 10086:

“Finally, it has to be pointed out that we neglect an effect where the presence of hippuric acid in urine may increase urea hydrolysis and consequently, NH₃ emission (Whitehead et al., 1989). Whitehead et al. found that ignoring this triggering effect can lead to up to -10% difference in the cumulative NH₃ volatilization (expressed as the proportion of the total nitrogen content of urine) compared to real urine containing the same amount of urinary N.

In the measurement campaign (Laubach et al. 2012) an artificial urine solution was spread on the experimental plot that was enriched with additional urea, so we validated

a urea based model against a concentrated urea solution. Therefore, the difference in modelled and measured NH_3 fluxes, originating from this simplification, is possibly negligible, though it could be relevant if the model is applied in real grazing situation. However, Whitehead et al (1989) reported comparable differences in NH_3 emissions when they compared urea+hippuric acid solutions with different total N contents as well as different hippuric acid ratios.

The N content of urine ranges widely, not just amongst different animals, but also for different urination events by the same animal (Betteridge et al., 1986 and Hoogendoorn et al., 2010). This means that assuming an average N concentration of 8 g, according to Whitehead et al. (1989) can result in a 10% overestimation in the cumulative volatilization of ammonia if the real nitrogen concentration was as low as 2 g/l. Similarly, in the case of the different ratios of hippuric acid and urea: if we assume that the hippuric acid N is an average of 0.8% of the urea N (based on the data published by Dijkstra et al. (2013) this proportion varies between 1.4 - 0.36%), according to Whitehead et al. (1989), the overestimation of the cumulative ammonia emission can be 10% if the proportion of hippuric acid was minimal in reality.

As the effect of hippuric acid on urea hydrolysis is not widely investigated in the literature, at the moment the current approach is the best we can achieve to simulate the decomposition chemistry in urine. Although the field scale model would most likely underestimate ammonia emission due to the exclusion of the effect influence of hippuric acid, this underestimation may be partly balanced by the sources of overestimation in the model. Nonetheless, this uncertainty should be addressed when the model is applied on field scale.”

Comment: “Page 10070, line 20: N_{app} is equal to the nitrogen content of urine. This presumes that all N is directly available, which is certainly not the case. It is not clear to me why not TAN is used instead of total nitrogen content of urine.”

Our answer: We thank the reviewer for noting this point. The definition of N_{app} originates from Massad et al. (2010), who proposed it as a part of a parametrization, describing an empirical relationship between the total N applied to the ecosystem (N_{app}) and the observed maximal stomatal ammonia emission potential ($\Gamma_{sto}(\max)$, see Eq. 16 in our manuscript). In our study we applied the parametrization to a urine patch in which the “total N applied to the ecosystem” equals to the total N content of the urine.

Change to the manuscript:

To clarify the definition of N_{app} we change this paragraph (page 10070 from line 18):

“ $\Gamma_{sto}(\max)$ (Eq. 16), from Massad et al., 2010a, is determined by the amount of nitrogen applied (N_{app} , in kg N ha^{-1} , see Eq. 17), which in our case is the nitrogen content of the urine calculated as the volume of urine (W_{urine} , dm^3) multiplied by its nitrogen content (c_N , gN dm^{-3}), divided by the area of the urine patch (A_{patch} , m^2) (with 10 as a conversion factor between the different units).”

to this one:

“Massad et al. (2010a) proposed a parametrization, describing an empirical relationship (Eq. 16) between the total N applied to the ecosystem (N_{app} in kg N ha^{-1} , see Eq. 17) and the observed maximal stomatal NH_3 emission potential ($\Gamma_{sto}(\max)$). To apply the formula for a urine patch, we calculated N_{app} as the total N content of the urine - the volume of

urine (W_{urine} , dm^3) multiplied by its nitrogen content (c_N , gN dm^{-3}) - divided by the area of the urine patch (A_{patch} , m^2) (with 10 as a conversion factor between the different units).”

Comment: “The buffering efficiency is determined by i) the cation exchange capacity which depends on clay content and the organic matter content but ii) also on the affinity for ammonium absorption which is clay mineral type dependent.”

Our answer: We also agree with the reviewer that the study of Whitehead and Raistrick (1993) shows clear evidence for a strong relationship between cation exchange capacity (CEC) and ammonia emission. However, we are not aware of a specific quantitative relationship between buffering capacity and CEC, neither the affinity for ammonium absorption, or the clay content or the organic matter content. Therefore, we used a constant buffering capacity in our modelling study. In our manuscript, we have carried out a sensitivity analysis of the effect of the buffering capacity on ammonia emission (in Section 5.3), testing how the model behaves between the two extremes: when there is no buffering in the system and when it is completely buffered.

Change to the manuscript:

We add the following paragraph to the page 10078 after line 17:

“Whitehead and Raistrick (1993) found a strong correlation between the cation exchange capacity (CEC) and NH_3 volatilization as well as a weaker correlation with organic matter, clay and sand content of the soil. However, we are not aware of a specific quantitative relationship between buffering capacity and CEC, or the clay content or the organic matter content. Therefore we address this issue through a sensitivity analysis on the model performance (Section 5.3).”

Comment: “Also the K content of urine can be of importance since it interacts with ammonium to be adsorbed by the soil complex. The result of this adsorption behaviour of soil is that the concentration of TAN in solution will decrease and thereby the driving force for ammonia emission, especially on the more heavy soils.”

Our answer: Whitehead et al. (1989) carried out a comparison experiment between urea solutions with varying content of potassium salts, and they reported a rather small effect on ammonia emission.

Change to the manuscript:

Right after our previous extension, to the same paragraph we add the following two sentences:

“Regarding the effect of the potassium content of urine on buffering capacity and indirectly, NH_3 emission, Whitehead et al. (1989) showed that the potassium salts of urine have a rather small influence on NH_3 volatilization. Based on these, we used a constant buffering capacity in the model.”

Comment: “The results presented suggest that the model can be used in all situations. I don’t agree with that (see also results of Jarvis et al., and Bussink 1994, Whitehead and Raistrick, 1993), soil type and soil buffering should be taken into account. It should be proven that the

modelling results are in principal soil type (and buffering behaviour) independent before extrapolation/usage for other situations takes place.”

Our answer: We do not state that our model is independent of soil type either from the point of view of the water budget (to calculate it soil type dependent characteristics are required as input parameters, such as permanent wilting point, field capacity and porosity) or buffering capacity (if it is measured at the given field site, it can be used as input parameter).

As we mentioned in our manuscript (page 10081 line 2-7), we compared our model results only with the measurements from the experiment of Laubach et al. (2012), because this is the only measuring campaign aiming to investigate ammonia emission from a single urine patch (urine patches deposited relatively close in time) that we are aware of. Producing another independent measuring dataset would require further work that is beyond the scope of this manuscript.

References

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