Authors' response to the review of Referee 2 on "Process-based modelling of NH_3 exchange with grazed grasslands"

We thank the referee for the valuable comments. Our responses and the changes we make to address the referee's comments are provided below point-by-point. The cited literature as well as the modified and the newly-created figures are listed at the end of this document.

Comment 1: "*The manuscript is sometimes hard to read and may be shortened; especially the description and results on the sensitivity analysis may be more synthetic.*" (Cited from the section "General comments").

Our answer: Apart from Comment 11, the reviewer did not specify the exact parts of the manuscript that should be shortened. However, we are open for the reviewer's additional suggestions.

Comment 2: *P5L9: I would suggest telling in a few words what limitations may imply the fact that no water infiltration is taken into account.*

Our answer: The GAG model applied and extended to the field scale is described in Móring et al., (2016) as well as in the PhD thesis by Móring (2016). In these studies the possible consequences of this – and the other model assumptions – are investigated in detail. In this part of the manuscript only a general description of the model is provided to set the context for the work described in the following part of the manuscript.

Change to the manuscript:

On P5 from L5 we change:

„The GAG model (Móring et al., 2016) is a process-based NH_3 emission model for a single urine patch that is capable of…"

as follows:

"The GAG model, applied and extended to the field scale in this study, is a process-based NH_3 emission model for a single urine patch. An in-depth description of the model, together with a comprehensive sensitivity analysis can be found in Móring et. al (2016) and Móring (2016). The GAG model is capable of…"

Comment 3: *P6L5-L6. I suggest writing which parameter is modelled with a negative binomial (area covered by patch?)*

Our answer: Please see our modification below.

Change to the manuscript:

On P6 we insert text to L5-6 (inserted text in bold):

"A way to estimate the temporal evolution of the urine-covered proportion of the field is to use a negative binomial distribution function **for the time-space distribution of the urine patches** as suggested by…"

Comment 4: *P8 EQ5: From the equation I understand that n (over the sum symbol) and n(tj) are not the same. Please clarify.*

Our answer: Indeed, this could be confusing for the readers. Please see our modifications below.

Change to the manuscript:

In Eq. 5 we change *n* (over Σ) to *m*:

$$F_{net}(t_i) = \frac{F_{non}(t_i)A_{non}(t_i) + \sum_{j=1}^{m} F_{patch}^{j}(t_i)n(t_j)A_{patch}}{A_{field}}$$

In accordance, the size of the matrix considered for the calculation will be m × m, so on P8 in L16 we change "*n* × *n*" to "*m* × *m*", as well as we modify Fig. 5 as shown at the end of this document.

Comment 5: *P9 EQ6 and L6-8: Since χ_{z0} is an equilibrium point between the ground and the atmosphere, I do not understand how it could be parameterised. To me it should depend on the flux and the concentration above. Please clarify and explain clearly the assumptions behind the calculation of the fluxes from non-urine patches area and how these are linked to the urine patches area. May be a resistance scheme in a supplementary material would help the understanding: from what I can understand from the current manuscript, the resistance scheme would be as in the GAG patch model of Moring et al. (2016) with an additional "leg" with a resistance R_{ac} + R_{bg} and a potential χ_g, starting from χ_{z0}. Is that correct? This would imply in particular that the horizontal distance between urine patches and non-urine patches is supposed null. Once the hypotheses clearly explicated I would also suggest discussing in the discussion section what implication this would have.*

Our answer: As pointed out in the manuscript on P8 from L2: "it was assumed that the total flux over the field is the sum of the emission from the urine affected area (calculated by GAG) and the exchange with the non-urine area (derived by GAG, assuming constant emission potentials, as explained later, in Section 3.1)", which is in accordance with Eq. 5. This means that the NH_3 exchange flux is calculated separately for the non-urine area and for every single urine patch, so a different χ_{z0} is derived separately for the non-urine area and for every single urine patch deposited on the field. For the urine patches GAG_patch is used (as described by Móring et al. 2016) and for the clean area its modified version is applied.

This assumption also means that all the χ_{z0} values are driven by the compensation points at the given point of the field ($\chi_p, \chi_g, \chi_{sto}$) and the air concentration of NH_3, χ_a. The effect of the neighbouring patches or non-urine area via horizontal dispersion on χ_{z0} in a given point is neglected. As we argue in the manuscript, to account for this effect is not straightforward, and would involve the application of a dispersion model (P8 L7). However, following the suggestion of Reviewer 1, we carried out a sensitivity analysis for χ_a that could give an approximate picture on how the NH_3 exchange would change with a higher χ_{air} (the effect of the urine patches over the non-urine area via horizontal dispersion) or a lower χ_{air} (the same effect of the non-urine area over the urine patches).

Change to the manuscript:

On P8 in L3-5 we change the following sentence:

"Therefore, it was assumed that the total flux over the field is the sum of the emission from the urine affected area (calculated by GAG) and the exchange with the non-urine area (derived by GAG, assuming constant emission potentials, as explained later, in Section 3.1)."

as follows:

"Therefore, it was assumed that the total flux over the field is the sum of the emission from the urine affected area and the exchange with the non-urine area. Over the urine affected area the GAG model was applied to every single urine patch and for the non-urine area a modified version of the GAG model was used, assuming constant emission potentials, as explained later, in Section 3.1."

On P8, from L27 we change the last sentence of the paragraph to:

"Based on this, F_{non} was derived in the same way as F_t, the net NH_3 flux over a urine patch in GAG_patch, described by Eq. (1)-(7) in Móring et al. (2016), together with the following simplifications:"

We add the applied resistance models to the supplementary material (see Fig. S1 at the end of this document), and on P9 in L9, we add to the end of the sentence:

"(see the applied resistance model in the Supplementary Material on Fig. S1)"

For the modifications related to the sensitivity analysis for χ_a, please see our response to Comment 18/2 by Reviewer 1.

Comment 6: *P10L1-20: The second point "ii)" is unclear. Does that mean that the total amount of liquid will be larger than the soil capacity and since no runaway and infiltration is considered this water will "disappear". Could you rephrase in a clearer way?*

Our answer: Point ii) means that in GAG_patch the source layer cannot hold more water than $B_{H2O}(max)$ since for the incoming liquid there is no more soil pore to fill. This means that if urine deposition occurs when $B_{H2O}= B_{H2O}(max)$, there is no infiltration, resulting in no N input to the system. We clarify this in the text.

Change to the manuscript:

On P10 from L5, we change ii) as follows:

"may lead to the maximal water content ($B_{H2O}(max)$) in the NH_3 source layer. In the formulation of GAG_patch this means that for the incoming liquid there is no more soil pore to fill, i.e. there is no infiltration. Therefore, when a urine patch is deposited while the water content is at B_{H2O}(max), will result in no N input to the system and consequently, no NH_3 emission from the soil."

Comment 7: *P10L18-20. This sentence is unclear. Please rephrase. In particular I do not understand what "the minimum amount of urine that is always allowed to penetrate" is, and how it is linked with the water budget. I would also suggest justifying why the minimum amount is chosen as 5% and what implication this has.*

Our answer: We modify the cited part of the text for better clarity. As for the 5%, it was an arbitrary choice. As explained above, in the original form of the GAG model if the NH_3 source layer's water content is at $B_{H2O}(max)$, no urine can infiltrate, and consequently, the model will derive zero urea-driven soil emission. It would be unrealistic to assume that in reality infiltration is prevented to the soil after every rain event (might happen after heavy rain or an elongated rain event), i.e. in most of the cases urine can infiltrate to the soil. However, if urine penetrates to a wet soil, the NH_3 emission flux might be weaker for two reasons: 1) due to the soil wetness, the urine might dilute after its deposition, and 2) the high water content is associated with large soil resistance, leading to a weaker NH_3 emission flux. Therefore, we think that the choice of 5% of $B_{H2O}(max)$ is large enough to avoid zero soil emission, but small enough to represent the described effects.

On P10 we change extend L18-19 as follows:

"To avoid the possible error resulting from the second point, it was assumed that instead of no infiltration, a small amount of water is always allowed to penetrate to the soil. This amount was chosen to be the 5% of $B_{H2O}(max)$, as shown in Eq. 13. This assumption is necessary since in reality in most of the cases there is infiltration to the soil (except after heavy rain or an elongated rain event), therefore, there is NH_3 emission from the soil even if the urine patch deposited to a very wet soil. However, in this case, the NH_3 emission flux from the soil might be weaker for two reasons: 1) due to the soil wetness, the urine might dilute after its deposition, leading to a lower χ_p and 2) the high water content is associated with large soil resistance, leading to a weaker NH_3 emission flux. Therefore, the choice of 5% of $B_{H2O}(max)$ could be reasonably large to avoid zero soil emission, but reasonably small to represent the described effects."

Comment 8: *P12L29-30: I would have thought that the "unfertilised grassland class" of Massad et al. (2010) would not be adapted here as this grassland does receive nitrogen. Please justify and also discuss the possible implications of choosing a "managed grassland class" in the discussion section.*

Our answer: This value of Γ_{sto} is used exclusively for the non-urine area (P9 L15-16). The choice of using Γ_{sto} values for unfertilised grassland, is in accordance with the assumption we made for the formulation of GAG_field, that is, over the non-urine area there is no considerable nitrogen input (P8 L26). In addition, the sensitivity analysis showed that the total net NH_3 exchange is not particularly sensitive to the changes of Γ_{sto} applied in the perturbation experiments.

Change to the manuscript:

On P12 from L29 we extend the sentence (see the inserted text in bold):

"For the constant Γ_{sto} for the non-urine area of the field, **where no considerable N input is assumed**, the values from the emission potential inventory by Massad et al. (2010) for unfertilized grasslands were averaged."

Please note that Table 3 was modified following the suggestion by Reviewer 1. The new table can be found at the end of our response to Reviewer 1. Based on this, on P17 after the last sentence of Section 4.2.1 we add the following piece of text:

"As it can be seen, for Γ_{sto} the resulted changes in ΣF_{net}, depending on the modelling period, are about 5-15% of the perturbations applied to Γ_{sto}. This means that using a 5 times larger Γ_{sto} (+400% perturbation, assuming a soil richer in N) was used in the model runs, the resulted ΣF_{net} were about 20-60% larger, with an overall hourly difference of 0.4 g N."

Comment 9: *P16L2: "of the modelled and measured": I suggest adding 'NH₃ exchange' here.*

Our answer: Following the suggestion of Reviewer 1 (Comment 26/1), we calculated model statistics and extended the text accordingly. Based on this, please see our modification below.

Change to the manuscript:

On P16 in from L2 we change:

"In the case of P2002 (Fig. 8a) the model was in a broad accordance with the observations. It captures…"

as follows:

"In the case of P2002, although the model statistics imply a weak model performance (Fig. N3a), the visual comparison of the modelled and measured NH_3 exchange (Fig 8a) suggests a broad accordance between the two datasets. The model captures…"

Comment 10: *P18L10: I suggest changing lower and higher to low and high.*

Our answer: Please see our modification below.

Change to the manuscript:

On P18 in L10 in the first sentence we change "lower" to "low" and "higher" to "high":

"Considering point 1), if pH(*t0*) is **low**, i.e. [H+] is **high**, during urea hydrolysis more H^+ ion can be consumed."

Comment 11: *P18L16-20 and L21-25: I found these two paragraphs unclear. Could you clarify?*

Our answer: Since the reviewer did not point out which parts of the cited two paragraphs need clarification exactly, we modify the text so that it gives more insight on how the buffering effect is taken into account in the GAG model, and we attempt to give our explanations in more details.

Change to the manuscript:

On P18 in L5 we change the following sentence:

"Following Móring et al. (2016), the effect of buffering on the H^+ ion budget in the NH_3 source layer can be expressed with the term (pH(t_i)-pH(t_{i-1})) × β_{patch}, where $\beta_{patch} = \beta \times A_{patch} \times \Delta z$."

As follows:

"In Móring et al. (2016), the H^+ ion budget depends on the H^+ ion consuming and producing processes related to the products of urea breakdown. On top of these, the effect of the buffers in the soil is expressed with an additional term: (pH(t_i)-pH(t_{i-1})) × β_{patch}, where $\beta_{patch} = \beta \times A_{patch} \times \Delta z$."

On P18 from L16 we change the paragraph:

"These larger changes in soil pH generate a larger buffering effect ((pH(t_i)-pH(t_{i-1})) × β_{patch}), i.e. a larger term in the H^+ budget, which makes the system more sensitive to a modification of β trough β_{patch}. This was confirmed in the model experiment A (Table 4). In this simulation GAG_patch was run with the initial pH of 4.95 used in the baseline simulation with GAG_field. Although the response of NH_3 exchange was relatively weak to the modifications of β, it was stronger than in the original perturbation experiment for GAG_patch (Table 3)."

as follows:

"These larger changes in soil pH generate a larger buffering effect ((pH(t_i)-pH(t_{i-1})) × β_{patch}), i.e. a larger term in the H^+ budget. This means that in the GAG_field simulations, this term has a stronger effect in the H^+ budget, consequently, when β is modified (through β_{patch}), the system gives a stronger response, which means that the model is more sensitive to the perturbation of β. This was confirmed in the model experiment A (Table 4). In this simulation GAG_patch was run with the initial pH of 4.95 used in the baseline simulation with GAG_field. Although the response of NH_3 exchange was relatively weak to the modifications of β, it was stronger than in the original perturbation experiment for GAG_patch (Table 3)."

On P18 from L21 we change the paragraph:

"Regarding point 2), the definition of β_{patch} expresses the buffering effect of the solid material of the soil on the liquid content. Since in the model β_{patch} is independent of the liquid content of the soil, within the source layer the same buffering effect takes place even if less urine stored in it. In a smaller amount of urine, the H+ ion budget (expressed in mol H^+) and the variations in it are proportionally smaller too. Therefore, the governing role of the same buffering capacity in the case of a smaller amount of urine becomes stronger, resulting in a stronger model sensitivity to β."

as follows:

"Regarding point 2): the definition of β_{patch} expresses the buffering effect of the solid material of the soil on the liquid content. As it can be seen from the formula $\beta_{patch} = \beta \times A_{patch} \times \Delta z$, β_{patch} depends clearly on Δz, but it does not depend on the liquid content of the soil. This means that in the model, in a source layer with the same Δz, the same buffering effect takes place even if less urine stored in it. In a smaller amount of urine, the H^+ ion budget (expressed in mol H^+) and the variations in it are proportionally smaller too. Therefore, the governing role of the same buffering capacity in the case of a smaller amount of urine becomes stronger, resulting in a stronger model sensitivity to β."

Comment 12: *Table 5: Explain what is β in the table legend.*

Our answer: The reviewer must have meant here Table 4. Please see our modification below.

Change to the manuscript:

In the legend of Table 4 in the second row after β we add: "(buffering capacity)".

Comment 13: *Figure 4: I would suggest adding a resistance scheme to better explain the model.*

Our answer: Following the suggestion of the reviewer in Comment 5, we add the resistance schemes to the supplementary material. Please see these in Fig. S1, at the end of this document.

Change to the manuscript: As stated above.

Comment 14: *Figure 8: I suggest adding the input variables of the model here or in a supplementary material (u_*, T_a, RH, rain, ...) as well as the potentials $\chi(z)$, χ_{z0}, χ_g, χ_p. This will ease the understanding of the flux dynamics.*

Our answer: The model input data are the meteorological variables identified for GAG_patch in Móring et. al (2016). The value of u_* is simulated by the model. We create a plot for the meteorological input variables together with the fluxes, and we add these figures to the supplemetary material.

As for the potentials: as pointed out in our answer to Comment 5, in a given time step, χ_{z0} is different above every urine patch depositied in the different time steps, as well as above the non-urine area (see Comment 5). Similarly, χ_p varies among the urine patches in a given time step. Therefore, χ_{z0} and χ_p cannot be plotted on a single figure, and to create plot only for the non-urine area (for χ_{z0}, and χ_g) would not make much sense on its own. However, we agree that a figure, showing the measured ambient atmospheric NH_3 concentration (χ_a), which was an input variable as well, could provide useful information for the readers.

Change to the manuscript:

Please see Figure S2 and S3 at the end of this document. We add these figures to the supplementary material. (Please note that in the caption of these figures Fig. 8a and Fig. 8b refer to the improved version of these figures as showed in our response to Reviewer 1.)

On P11 in L13, we add after the last sentence:

"The measured input data is illustrated in the supplementary material, in Fig. S1 and S2."

References

Móring, A. 2016. Process-based modelling of ammonia emission from grazing. PhD, University of Edinburgh.

Móring, A., Vieno, M., Doherty, R. M., Laubach, J., Taghizadeh-Toosi, A. & Sutton, M. A. 2016. A process-based model for ammonia emission from urine patches, GAG (Generation of Ammonia from Grazing): description and sensitivity analysis. Biogeosciences, 13, 1837-1861.

		NH_3 emission from the urine patches					**NH_3 exchange with the non-urine area**
		Time of the deposition of the urine patches					
		$t_{j=1}$	**$t_{j=2}$**	**$t_{j=3}$**	**…**	**$t_{j=n}$**	
Time since the beginning of the modelling period	**$t_{i=1}$**	**$F_{patch}^{j=1}(t_{i=1})$**	$F_{non}(t_{i=1})$	$F_{non}(t_{i=1})$	…	$F_{non}(t_{i=1})$	$F_{non}(t_{i=1})$
	$t_{i=2}$	**$F_{patch}^{j=1}(t_{i=2})$**	**$F_{patch}^{j=2}(t_{i=2})$**	$F_{non}(t_{i=2})$	…	$F_{non}(t_{i=2})$	$F_{non}(t_{i=2})$
	$t_{i=3}$	**$F_{patch}^{j=1}(t_{i=3})$**	**$F_{patch}^{j=2}(t_{i=3})$**	**$F_{patch}^{j=3}(t_{i=3})$**	…	$F_{non}(t_{i=3})$	$F_{non}(t_{i=3})$
	…	…	…	…	…	…	…
	$t_{i=m}$	**$F_{patch}^{j=1}(t_{i=m})$**	**$F_{patch}^{j=2}(t_{i=m})$**	**$F_{patch}^{j=3}(t_{i=m})$**	…	**$F_{patch}^{j=n}(t_{i=m})$**	$F_{non}(t_{i=m})$
Number of patches deposited in t_j		$n(t_{j=1})$	$n(t_{j=2})$	$n(t_{j=3})$	…	$n(t_{j=m})$	0

Figure 5. Schematic for the temporal development of NH_3 fluxes (in every i^{th} time step, t_i) as derived by GAG_field. $F_{patch}^j(t_i)$ stands for the NH_3 flux from the urine patches deposited in the j^{th} time step (t_j), and $F_{non}(t_i)$ stands for the NH_3 flux from the non-urine area. The bottom row shows how many urine patches were deposited in the given j^{th} time step ($n(t_j)$). Fluxes with striped background are calculated by GAG_patch, and the fluxes with clear background are calculated by a modified version of GAG_patch for non-urine area (explained in the text).

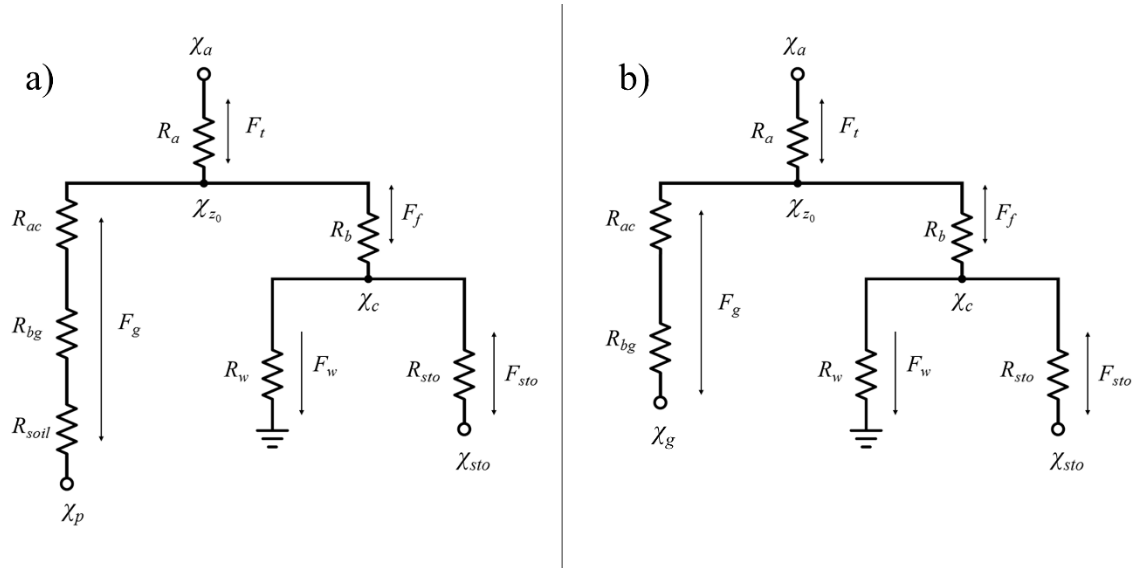

Figure S1. Resistance models applied for the simulation of the NH_3 exchange flux a) over the urine patches (as used in GAG_patch in Móring et al., 2016) and b) over the non-urine area (as suggested by Nemitz et al. 2001). The indicated resistances are: the aerodynamic resistance (R_a), the quasi-laminar resistance (R_b) over the canopy, aerodynamic resistance within the canopy (R_{ac}), quasi-laminar resistance at the ground (R_{bg}), soil resistance (R_{soil}), resistance to water and wax on the leaf surface (R_w) and stomatal resistance (R_{sto}). The gaseous NH_3 concentrations illustrated are: the ambient air concentration (χ_a), the canopy compensation point (χ_{z0}), the compensation point above the vegetation (χ_c), the compensation point in the model soil pore under a urine patch (χ_p), the stomatal compensation point (χ_{sto}) and the compensation point on the ground in the non-urine area (χ_g). The fluxes shown are: the total net exchange above the given canopy (F_t), the emission flux from soil (F_g), the exchange flux above the vegetation (F_f), the deposition flux to the leaf surface (F_w) and the stomatal flux (F_{sto}). For the definition of the resistances, fluxes and concentrations on Fig. a) and b, see Móring et al. (2016) and Section 3.1 in the present study, respectively.

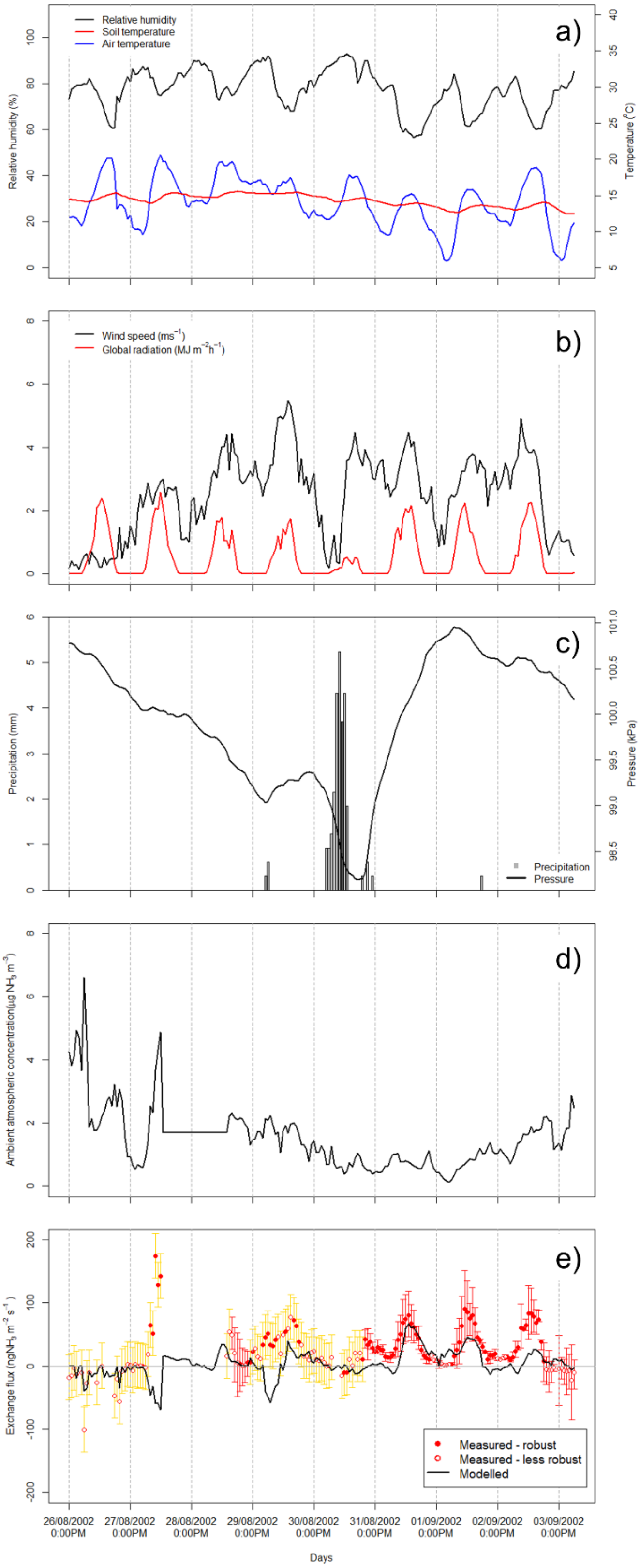

Figure S2. Measured meteorological variables (relative humidity, soil and air temperature (a), wind speed and global radiation (b), precipitation and surface pressure (c)), the measured ambient atmospheric concentration of NH_3 (d) and the measured and simulated hourly NH_3 fluxes (e) in P2002 in Easter Bush as plotted in Fig. 8a.

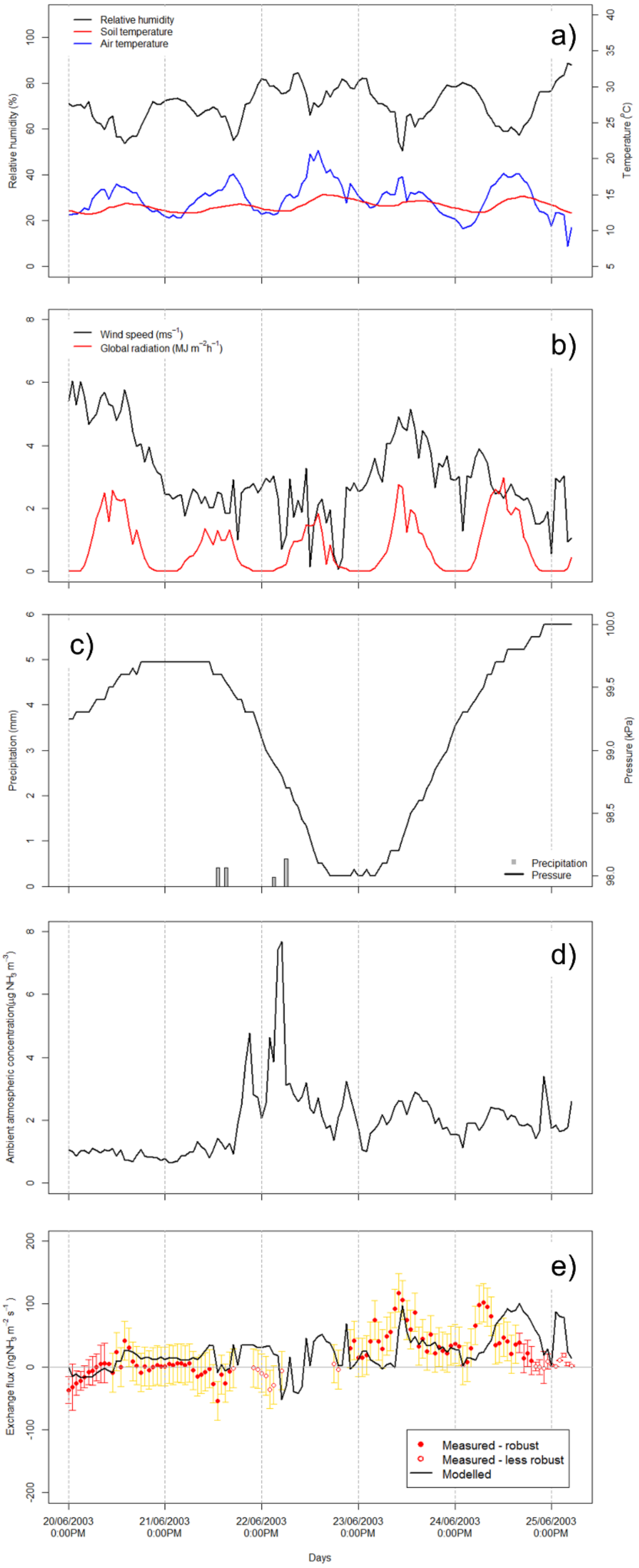

Figure S3. Measured meteorological variables (relative humidity, soil and air temperature (a), wind speed and global radiation (b), precipitation and surface pressure (c)), the measured ambient atmospheric concentration of NH_3 (d) and the measured and simulated hourly NH_3 fluxes (e) in P2003 in Easter Bush as plotted in Fig. 8b.