Authors' response to the review of Referee 1, Christophe Flechard on "Process-based modelling of NH₃ exchange with grazed grasslands"

We thank the referee for the thorough and insightful comments. We believe that following his suggestions our manuscript will be significantly improved. 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 and tables are listed at the end of this document.

Comment 1: *p2*, *cN* (*gN dm-3*): *is this total N including all N-containing forms, or just urea-N content of urine?*

Our answer: Since in the model we assume that urine consists of urea and water at the moment of the deposition of the urine patch, this refers to the urea-N content of urine. The following changes clarify that this is the only form of urea N considered in the model.

Change to the manuscript:

On P2, we modify the descriptions of the symbols as follows (text inserted in bold):

c_N (g N dm ⁻³)	N content of the urine (assumed to be in the form				
	of urea)				
CN^{Ave}	Average urinary N concentration (assumed to be in				
	the form of urea) in urine patches deposited in the				
	same time step				
c_N^{Dil} (g N dm ⁻³)	Urine N content (assumed to be in the form of				
	urea) after dilution in the soil				
c_N^k (g N dm ⁻³)	Urinary N concentration (assumed to be in the				
	form of urea) in the k^{th} urine patch				

For further clarification, on P5 in L7, after the end of the sentence we add the following sentence:

"Following the considerations of Móring et al. (2016), the model handles urine as a water solution of urea, i.e. the urinary N content is assumed to be in the form of urea."

Comment 2: *p2*, for clarity's sake, please indicate here that Ft is the total net flux over the canopy at patch scale in GAG_patch (while Fnet is the equivalent for field scale in GAG_field)

Our answer: Agreed. Please see our modification below.

Change to the manuscript:

On P2, we modify the description of F_t as follows (text inserted in bold):

 $F_t(\mu g N m^{-2} s^{-1})$ Total NH₃ exchange flux over the canopy **above a**

single urine patch

Comment 3: *p5, 110 '...is considered as the only sink term.' Here it would be useful to mention that drainage/leaching of TAN and urea out of the source layer in the case of (heavy) rainfall filling porosity and entrainment of N into deepers soil layers are not considered, and whether, or why, it is reasonable to do so.*

Our answer: We agree to add information on the assumption for the GAG model for a single urine patch. However, this part of the manuscript is an overview of the model, which summarizes the approach of Móring et al. (2016). Therefore, we add here a short comment which refers to further details in that paper.

Change to the manuscript:

On P5 from L5 we change:

"The GAG model (Móring et al., 2016) is a process-based NH₃ 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..."

On P5 in L12, after "can hold" we add:

"Since during the development of the GAG model simplicity was a key aspect, the effect of the vertical movement of the liquid within the soil (leaching and capillary rise) as well as the mixing of urea and the products of its hydrolysis within the solution was neglected."

Comment 4: *p6, l2 '...it would be preferable to neglect the overlap...' : it is not preferable, just easier!*

Our answer: To solve a problem, we consider that an easier way is preferable if it gives a reasonable approach for the solution. We believe that our corrected approach, as described in our answers to Comment 5 and 6, is a reasonable solution for the handling of the issue of the overlap of the urine patches.

Change to the manuscript:

We add the following amendment to On P6 in L3 (inserted text in bold):

"Thus, it would be preferable to neglect the overlap of the patches if the error from this simplification can be shown to be small".

Comment 5: *p6, 125, and p7, 112: 10 LSU/ha as 'worst case scenario' is not a valid or representative value for the maximum grazing density in Europe. Intensive and rotational grazing practices can give rise to much higher animal numbers per ha, though for shorter periods of time. See example given in Bell et al., Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-350, 2016, with grazing densities above 20-40 LSU/ha.*

Our answer: If we assume that an intensive grazing period lasts for 3 days (as mentioned by the reviewer in Comment 6), it is possible to apply Eq. 1 and 3 with the maximum A_{patch} values from Table 1 to estimate the number of LSU/ha that is associated with the same level of error due to patch overlap. Neglecting patch overlap for such a period would imply that 57 and 113 LSU/ha can be on the field to keep the error under 5% and 10%, respectively. In case of sheep, the same numbers will be 26.1 and 51.7 LSU/ha, respectively. For cows the resulting grazing densities are above the values mentioned by the reviewer, therefore, even in the worst case for short periods of rotational grazing, the error will be under 5%. For sheep, calculating with 44 LSU/ha, the highest grazing density in Bell et al., the error will be 8%, which is still reasonable for the worst case scenario.

While patch overlap can therefore be generally neglected for continuous grazing and short periods of rotational grazing, we acknowledge that there may be extreme cases of intense extended grazing where patch overlap could become relevant.

Change to the manuscript:

On P7 in L14, after "no over-lap case", before the last sentence of the paragraph we add:

"In addition, it should be stressed that in the above calculation the case of rotational or intensive grazing was not taken into account when the grazing density can be above 20-40 LSU/ha (e.g. Bell et al., 2016), whilst the animals are typically on the field only for only a few days. If it is assumed that an intensive grazing period typically lasts for a maximum of 3 days, using Eq. 1 and 3, with the maximum A_{patch} values from Table 1, in case of cows, 57 and 113 LSU/ha can be on the field to keep the error – originating from the neglect of the overlap between the urine patches - under 5% and 10%, respectively. In case of sheep the same numbers will be 26.1 and 51.7 LSU/ha, respectively. For cows, the resulting grazing densities are above the 40 LSU/ha, therefore, even in the worst case, the error will be under 5%. For sheep, calculating with 44 LSU/ha, the highest grazing density in Bell et al. (2016), the error will be 8%, which can be still considered reasonable for the worst case scenario. While patch overlap can therefore be generally neglected for continuous grazing and short periods of rotational grazing, we acknowledge that there may be some extreme cases of intense extended grazing where patch overlap could become relevant."

Comment 6: *p7, 18-9, related to the above : 'As a consequence, the total area of the patches grows in the first eight days, then it remains constant while the animals are on the field'. This is true of extensive grazing, but in intensive management, grazing duration may be just 2-3 days.*

Our answer: Please see our answer and the suggested modifications for Comment 5.

Comment 7: *p8*, *l25-29*: the terminology *Ft* vs *Fnet* vs *Fnon* is slightly confusing, see e.g. the sentence "...Fnon was derived in the same way as the net NH3 flux (*Ft*)...", is it possible to use less ambiguous symbols?

Our answer: We think that the symbols used for the description of GAG_field, F_{net} , F_{non} and F_{patch} are clearly distinguishable from each other. However, we agree with the reviewer that referring to the symbol F_t used by Móring et al. (2016) in the description of GAG_patch might cause confusion. To avoid this, we modify the text as showed below.

Change to the manuscript:

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 NH₃ flux over a urine patch in GAG_patch, described by Eq. (1)-(7) in Móring et al. (2016), together with the following simplifications:"

Comment 8: p9, l24: related to the above, '...GAG_patch calculates the patch emission (Ft(ti)...': is Ft actually the patch (gross) emission, or the total net flux including exchange with vegetaion? I believe it is the latter, so for clarity's sake please write '...GAG_patch calculates the patch net flux (Ft(ti)...'?

Our answer: As it was indicated earlier in the text of the manuscript (P8 L28) it is the net NH_3 flux over the urine patch, which yes, includes the exchange with the vegetation. We clarify this in the text.

Change to the manuscript:

On P9, in L23-24, we change the sentence to:

"Finally, $F_{patch}^{j}(t_i)$ was determined by Eq. (10), which expresses that before the deposition of the urine patch, the area is handled as non-urine area (first condition), and afterwards GAG_patch calculates the net NH₃ flux over the urine patch ($F_t(t_i)$, second condition)."

Comment 9: *p9, l1: '...over the non-urine area the dynamic simulation of soil chemistry is not needed...': it would be needed, to better resolve background exchange fluxes (instead of default /constant Gamma_g values); it's just that we don't have adequate understanding, models and data to do it. Please rephrase.*

Our answer: We agree with the reviewer and clarify our meaning accordingly. We had meant that this is not required according to our model structure. We had not meant to comment on whether dynamic modelling of background soil chemistry would be useful. Please see the rephrased sentence below.

Change to the manuscript:

On P9 in L1-2, we change the sentence as follows:

"Since over the non-urine area undisturbed soil chemistry is assumed, the dynamic simulation of soil chemistry in GAG_field is not needed. Therefore, the original version of the two-layer canopy compensation point model by Nemitz et al. (2001) is used. While dynamic simulation of undisturbed soil chemistry would be a useful avenue for further research, it is not addressed in the present study."

Comment 10: *p9, l17: add '(assuming no overlap)' after '...the area of the field that is not covered by any urine patches.'*

Our answer: Please our modification below.

Change to the manuscript:

On P9 in L17, we change the sentence as follows (inserted text with bold):

"The size of A_{non} in the given t_i time step is the area of the field that is not covered by any urine patches (assuming no overlap):"

Comment 11: *p10, l1: 'When calculating Ft(ti) a slight modification is also required...' : a small modification compared with what? with GAG patch?*

Our answer: Yes, with the GAG_patch model. Please see our modification below.

Change to the manuscript:

On P10 in L1 we change the sentence as follows (inserted text with bold):

When calculating $F_t(t_i)$ a slight modification is also required **compared with the GAG_patch model**, regarding the urea added with a single urination (U_{add}).

Comment 12: p10, l5-6: sentence not clear: why does B=Bmax 'prevent infiltration'? Do you mean rather that the model formulation cannot account for/simulate infiltration when the B=Bmax situation occurs?

Our answer: 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 NH₃ 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 NH₃ emission from the soil."

Comment 13: *p10, l6: "...prevents infiltration, resulting in no N input to the system and consequently no NH3 emission': surely you don't mean that B=Bmax means no NH3 emission?*

Our answer: We meant NH₃ emission <u>from the soil</u>. In GAG_patch the NH₃ emission from the soil is clearly driven by the breakdown of urea and the subsequent NH₃ emission. Therefore, in the GAG_patch model if there is no urea-N input to the source layer, then there is no soil emission.

To distinguish the net NH₃ emission and soil NH₃ emission in GAG_patch, we modify the text.

Change to the manuscript:

On P10 from L5, to the end of ii) we add "from the soil" as shown in our response to Comment 12.

Comment 14: *p10, 19-10: '...the GAG_patch model modified for the non-urine area...': not very clear what this means?*

Our answer: To simulate the NH₃ exchange with the non-urine area, we modified the GAG_patch model, as we indicate on P8 in L26-27. To clarify this, we modify the text.

Change to the manuscript:

On P10 in L9-10 we change the following piece of text:

"Therefore, the water budget calculated by the GAG_patch model modified for the nonurine area right before the j^{th} patch deposition"

as follows:

"Therefore, the water budget for the non-urine area (simulated by the modified version of the GAG_patch as described above), right before the j^{th} patch deposition"

Comment 15: *p10*, *l11*: why was dilution only treated in the first time step in GAG_patch ? And can you please state explicitly on *l12* (just before Eq. 11) that dilution is now treated in GAG_field at all time steps and not just at the time of urination ? (if I understand correctly)

Our answer: In this section, we gave a detailed description of how to handle the diluting effect of rain events *when it happens in the same time with urine application* (P10, point i)). In the description of GAG_patch by Móring et al. (2016), U_{add} was not defined as a function of time, since it was defined only for the first time step of a single urine patch. As over the field urine patches are deposited in every time step, U_{add} will be different for every urine patch depending on when the urine patch was deposited (t_j as defined in the our manuscript on P8 in L18 and used in Eq. 11 for U_{add}). We modify the text for better clarity.

In addition to the above, we would like to clarify that after urine deposition the diluting effect is simulated by the model, accounting for the water budget and the TAN budget in every time step (see Móring et al., 2016). In this way, dilution is treated in GAG_field in each time-step where liquid is added: either rain or urine or both.

Change to the manuscript:

On P10 in L12 after "applied to the surface" we modify the text as follows:

"This means that in Móring et al. (2016) U_{add} was not defined as a function of time. Therefore, in the field-scale model, where urine patches are deposited in every time step, U_{add} was calculated for all of urine patches deposited in every t_j as:" **Comment 16:** *p10, l18: which 'second point', what does this refer to?*

Our answer: to ii) on P10. No other numbered lists were used in the text previously. To make this clearer, we modify the text.

Change to the manuscript:

On P10 in L7, we change "to address the first point" to "to address point i)".

Similarly, on P10 in L18, we change "resulting from the second point" to "resulting from point ii)".

Comment 17: *p12, l9: the interval 03/09 13-17:00 is not shown anywhere on the figures, thus need not be mentioned here. Please delete.*

Our answer: Indeed. We delete the cited piece of text and amend the following sentence accordingly.

Change to the manuscript:

On P12 in L9 we delete "and over 03/09 13:00 - 17:00".

On P12 in L21-22 until "hourly time step" we change the text to:

"The individual gap was interpolated from the values from the previous and next time step, whilst over the long period of missing data in χ_a (25 consecutive hourly time steps)"

Comment 18/1: *p12, 111: "...values were assumed to be zero." This is not a reasonable assumption to make, as doing so will necessarily lead, in the model, to the maximum possible net emission (through the maximum possible soil-vegetation-atmsophere gradient). I believe this effect is clearly visible on Figures 8a, 9a, 12a, 13a, where in each case there is a sharp, step-wise, instantaneous increase in modelled flux from large deposition to large emission (step change > +100 ng m-2 s-1) around midday on 27/08, followed by a steep, instantaneous decline one day later around midday on 28/08. The timing of these step changes coincides exactly with the period of missing concentration data, where the authors assume Xa=0, with the strong and immediate effect of boosting net emission b. This is clearly not right. The authors should either: i) start the modelling period at 13:00 on 28/08, or ii) fill this 1-day gap in Xa by assuming Xa equals the mean background concentration in the area at this time of year (2-3 g m-3 according to C. Milford, PhD thesis, The University of Edinburgh, 2004). In either case, all flux figures should be redrawn, and all subsequent sensitivity analyses should be recalculated because the results of this day will affect the total.*

Our answer: Agreed. Since one of the condition for the model application is that grazing should start on the field at the beginning of the model period (P10, L10), we decided to replace the assumed zero values to the average of the existing measurements over the modelling period P2001. We believe that this assumption is more realistic than assuming the background concentration from the literature. Based on this modification, we recalculate all the model results related to P2002.

Change to the manuscript:

On P12 in L11, we change "the values were assumed to be zero" to "the values were replaced by the average of the measured values of χ_{air} over P2002 (1.71 µg m⁻³)".

In addition, we recalculate all the model results related to P2002 as shown at the end of this document: Figures 8-13 and Table 3.

Comment 18/2: This raises another important issue. The measured Xa values were used as inputs to drive the emission and bi-directional exchange models; however, in most cases, the concentrations were measured downwind from the S. field, since the prevailing wind was southwesterly, i.e. the measured Xa values were enhanced with respect to background through the emissions occurring on the S. field, and thus were themselves partly a result of the emission. The concentration gradient across a grazed field may be several g/m3, as shown by Bell et al., Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-350, 2016. There is thus clearly a problem of recursive logic in using the downwind concentration as input, in such a situation where there is a strong horizontal gradient. There is no easy way out of this issue since the model does not address advection, but at least i) the issue must ne mentioned in the text, and ii) a sensitivity analysis must be run and added to Section 4, in which the model will be run with a range of other Xa values e.g. Xa' = 0.5*Xa, 0.6*Xa, 0.7*Xa etc, or Xa - 0.1g/m3, Xa - 0.2g/m3, xa - 0.3g/m3, etc... This will likely have the effect of increasing emissions throughout (as already shown by the Xa=0 bias on 27-28/08), and may thus incidently improve the comparison to flux data late August/early September 2002.

Our answer: As we highlight in the manuscript, we agree with the reviewer concerning the error originating from the neglect of the heterogeneity of the simulated field due to the urine patches (P8 L5-7). To address the reviewer's comment, we therefore extend this part of the text to clarify the effect of this heterogeneity on the atmospheric NH₃ concentration above the field. In addition, we carry out a sensitivity analysis to explore the effect of χ_{air} on the NH₃ exchange over the field.

Change to the manuscript:

On P8 from L5 we change "Since a grazed field, due to the urine patches, is not a uniform source of NH₃, an error of the estimation of the total NH₃ flux can originate from the exclusion of the horizontal advection" as follows:

"One of the challenges of simulating bi-directional exchange at the field scale is that fluxes are both driven by atmospheric concentrations (especially for deposition) and affect atmospheric concentrations (especially for emission) (e.g. Loubet et al., 2009). In addition, due to the urine patches, a grazed field is not a uniform source of NH₃. One of the consequences is that the atmospheric concentration of NH₃ is not homogenous over the field (see e.g. Bell et al., 2016). Both effects result in a horizontal advection of NH₃, neglecting which leads to an error of the estimation of the total NH₃ flux. At the field scale, this affect can be explored by explicit consideration of horizontal gradients (Loubet et al., 2009) or by sensitivity analysis to the values of χ_{air} . In application to regional scale models, the overall effect of bi-directional exchange can be incorporated as emission/deposition feeds back to the simulated value of χ_{air} ."

On the same page in L8 after the end of the sentence we add:

"To investigate of the effect of χ_{air} on the simulated NH₃ flux a sensitivity analysis for χ_{air} was carried out (Section 4.2.1)."

On P13 in L10, after the last sentence we add:

"Finally, a perturbation experiment was carried out for χ_{air} (Section 4.2.1)."

We added the results to Table 3 (see at the end of this document).

On P13 in L14 we change 428 g N to 127 g N. (Because of the modified χ_{air} dataset, this is how the total net NH₃ exchange changed over the field in P2002.)

On P13 in L15, we add after the last sentence:

"In the case of the perturbation experiments for χ_{air} , χ_{air} was modified by the $\pm 10\%$ and $\pm 20\%$ of its average over both periods. These average concentrations in P2002 and P2003 were 1.73 µg NH₃ m⁻³ and 1.51 µg NH₃ m⁻³, respectively."

On P17 after L26 we add the following paragraph:

"As for χ_{air} , in Table 3 the percentage differences for P2002 over the whole field suggest a significant effect on ΣF_{net} . However, comparing the absolute hourly change to that for P2003, it can be concluded that the absolute influence was similar in the two modelling periods. It can be also clearly seen that the absolute hourly changes over the urine patches are negligibly small in both P2002 and P2003 compared to the absolute changes observed for the whole field. This suggests that the value of χ_{air} affects ΣF_{net} mainly through the non-urine area, rather than the urine patches."

On P23 after L10 (to the Discussion) we add the following paragraph:

"In GAG_field, the horizontal dispersion of NH₃ on the field was neglected, and as such, the homogeneity of χ_{air} was assumed. However, the perturbation experiments showed that χ_{air} can considerably affect the total NH₃ exchange over the non-urine area. This suggests that including the effect of horizontal advection to the model could possibly improve the simulation of NH₃ exchange over a grazed field. This effect is treated directly when such a bi-directional model as GAG_field is incorporated into a regional atmospheric chemistry transport model, through the influence of surface emission/deposition on the simulated value of near-surface χ_{air} ."

Comment 19: *p12, l21: related to the above comment: delete the reference to substitution by zero.*

Our answer: We change this as explained in our response to Comment 18/1.

Change to the manuscript: As stated above.

Comment 20: p12, l30-33: Gamma_g for the non-affected grassland is a key parameter for the NH3 recapture within the field, and the authors use a value of 3000 based on a comparison of model and measurements early June 2003. It would be useful to see these data as Supplementary Material, together with alternative runs using e.g. Gamma_g = 500, 1000, 5000.

Our answer: We create a plot for the calibration experiment, together with the alternative model runs requested by the reviewer, and add it to the supplementary material. Please see Fig. S1 at the end of this document.

In addition, due to the opposite wind speed (from the direction of the North Field instead of the South Field), at the end of the calibration period as mentioned in the manuscript (P12, L32) there were no measured fluxes to compare with the model results. Therefore, we shortened the period so that it ends with the last measured flux that is representative for the South field. We modify the text accordingly.

Change to the manuscript:

We add Fig. S1 to the supplementary material (see at the end of this document).

On P12, from L32 we change the following:

"The time period of 01/06/2003 00:00 – 09/06/2003 00:00 fulfilled this criteria. These preliminary model experiments indicated a close agreement between the measured and simulated NH₃ fluxes with a Γ_g of 3000. Therefore, this value of Γ_g was applied in the baseline simulations with GAG_field."

as follows:

"The period of 01/06/2003 00:00 – 08/06/2003 16:00 fulfilled these criteria. These preliminary model experiments indicated a reasonable agreement between the measured and simulated NH₃ fluxes with a Γ_g of 3000 (see Fig. S1 in the supplementary material). Therefore, this value of Γ_g was applied in the baseline simulations with GAG_field. To investigate the model sensitivity to this choice of Γ_g , a sensitivity analysis was carried out in Section 4.2.2."

Comment 21: *p14, l2 & l12: why must there be a 'conversion', what does it mean to 'convert'* SENSnet to SENSpatch? I don't quite see why SENSnet needs to be made 'compatible' with SENSpatch. The sensitivity of Fnet (GAG_field) to model parameters is the sensitivity of Fnet (GAG_field) to model parameters; there is no need for further transformation? Perhaps the authors need to start this argument on p13, l31 by writing that they wish to compare the model sensitivities of "...Fpatch in the case of the multiple patches simulated within GAG_field and the single urine patch simulated by GAG_patch...", and that in order to do this a mathematical transformation is needed to extract the sensitivity of Fpatch from the overall sensitivity of Fnet. Thus the argument will become clearer.

Our answer: We believe that from the comparison of the results for GAG_patch from Móring et. al (2016) and the results from our current study, valuable conclusions can be drawn for the model behaviour of GAG_field in response to the perturbation of the patch-related model parameters. In this part of the manuscript we attempted to highlight that the direct comparison of the two is not possible, since over the field the total net exchange is also affected by the NH₃ exchange over the non-urine area.

At this point of the manuscript our purpose was to show the relationship between *Sens_{net}* and *Sens_{patch}*, avoiding to create an overly-complex table with data separately for the whole field and the urine patches. However, we also agree that our approach may cause

confusion for the readers. Therefore, we added the $Sens_{patch}$ values to Table 3, as shown at the end of this document. In addition, we think that it is an important conclusion, that for the patch-related parameters the ratio of $Sens_{net}$ and $Sens_{patch}$ is a close-to-constant value, therefore, we modify Section 4.2. accordingly.

Change to the manuscript:

We change Table 3 as showed at the end of this document.

We extend 4.2 with a subsection titled "General remarks" as shown in our answer to Comment 30.

Comment 22: p15, l8, presumably these scale parameters are the geometric standard deviation (sigma=0.786) and geometric mean (=1.154)? The text should say so. Then the start of the next sentence says "The mean of cN ...", I presume but can't be certain that this signifies the arithmetic mean? Again should be clarified.

Our answer: The "scale parameters" (as referred to in statistics) σ and μ are the arithmetic standard deviation and the arithmetic mean of the normal distribution of $log(c_N)$. We think that this information might confuse the readers with a less advanced mathematical knowledge, and is not necessary to understand the purpose of this calculation. Therefore, we clarify this in the list of symbols at the beginning of the manuscript.

We agree that the definition of mean(c_N) should be clarified in the text, which is indeed the arithmetic mean.

Change to the manuscript:

On P3 after the description of σ and μ we add:

"(the arithmetic standard deviation and the arithmetic mean of the normal distribution of $log(c_N)$, respectively)"

On P15 in L8 we add "arithmetic" before "mean of c_N ".

Comment 23: Equation 21: geometric or arithmetic mean?

Our answer: Please see our response to Comment 22.

Comment 24: *p15, l15-16, the mean cN of 11 g dm-3 is the arithmetic mean, and the 'scale parameter' of 2.089 is the geometric mean?*

Our answer: As noted in our response to Comment 22, $c_{N=11g} \text{ dm}^{-3}$ refers to the arithmetic mean, while $\mu=2.089$ refers to the arithmetic mean of $\log(c_N)$.

Comment 25: *p15, l19: why 30 cN time series (why not 50 or 2000)?*

Our answer: 30 is an arbitrary choice as a sample size but widely used to calculate statistics.

Comment 26/1: p16, l2: '...broad accordance with the observations.' Please provide the regression R^2 , slope for model vs measurements, as well as RMSE and other such statistics classically used for model evaluation.

Our answer: As suggested, we calculate the model statistics and create a scatter plot to summarise the measurements against the model results. Also, we extend the text of the manuscript accordingly.

Change to the manuscript:

We add a scatter plot together with the model statistics. Please see Fig. N3. at the end of this document. Please see our further modifications in our response to Comment 26/2.

Comment 26/2: Was there any filtering of the flux data for periods of low wind speed, strong nocturnal stability or any such quality criteria for flux-gradient measurements? (it looks as though the flux time series is completely uninterrupted apart from aforementioned periods of AMANDA down time)

Our answer: No, there was not any filtering, which we implement now according the following criteria:

- according to the footprint analysis, the field contributed at least 67% to the measured flux,
- u*>0.15 m s⁻¹ for at least 45 minutes,
- $L^{-1} < 0.2 \text{ m}^{-1}$, and
- $u > 1 \text{ m s}^{-1}$.

Change to the manuscript:

On Fig 8. we denote the flux measurements that - based on the quality check detailed above - turned out to be robust (meeting all the above criteria) and less robust (failing one or more of the above criteria). Please see the modified version of Fig. 8 at the end of this document.

We calculate the model statistics for all of the measured data and separately for only the robust data. Please see Fig. N3 at the end of this document.

We also modify the text accordingly. On P12 after L18 we add the following paragraph:

"In addition, a quality check was carried out on the measured flux dataset, distinguishing the time periods with low wind and strong stability. A flux measurement was considered robust if it met all of the following criteria:

- according to the footprint analysis, the field contributed at least 67% to the measured flux,
- $u^* > 0.15 \text{ m s}^{-1}$ for at least 45 minutes,
- $L^{-1} < 0.2 \text{ m}^{-1}$, and
- $u > 1 \text{ m s}^{-1}$.

The fluxes failing to meet one or more of the above criteria were considered as less robust. The robust and less robust data determined in this way, can be seen in Section 4.1.1 on Fig. 8."

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..."

On the same page after the last sentence of the first paragraph we add:

"When the last 6 values before this event as well as the less robust data were removed from the dataset, the calculated statistics reflected a much promising model performance."

On the same page, we change the first sentence of the second paragraph as follows:

"Similarly to P2002, the model statistics implies a relatively low model performance (Fig. N3b) for P2003 as well, however, according to Fig. 8b, the simulation generally agreed with the observations within 50 ng m⁻² s⁻¹. The removal of the less robust data from the dataset, resulted in improved model statistics (Fig. N3b), suggesting a better agreement between the model and the measurements."

Comment 27: *p16, l27-28: '...could explain part of the difference between the simulation and measurements on this day (Fig. 8), if the model overestimated the deposition component of the net flux.' The difference could just as well be due to an underestimation of the gross emission from urine patches, there is no telling which; possibly a combination of both.*

Our answer: Agreed.

Change to the manuscript: On P16, we remove L26-28.

Comment 28: p16, l29-32 and also section 4.2.4, on the diurnal variations of net emission: is it possible/likely that there is a diurnal variation in urination frequency, with animals being e.g. more actively grazing during day than night, or other temporal urination patterns? Could this be tested by using e.g. UF(day) = 2*UF(night)? The impact of higher urination frequency during daytime would be compounded by the effect of higher temperatures.

Our answer: We agree, that it would be interesting to test how the modelled NH_3 fluxes would respond to an assumed diurnal pattern of urination frequency. However, we believe that this is out of the scope of the present study. However, in Section 4.2.4. we investigated the sensitivity of the total net NH_3 exchange to the changes in the applied average hourly urination frequencies.

Change to the manuscript:

Please see the suggested changes in our response to Comment 37.

Comment 29: *p18, l2: change to "...are between 1-2 orders of magnitude larger than..."*

Our response: We do the correction as suggested by the reviewer.

Change to the manuscript:

On P18 in L2 we change "significantly larger than" to "1-2 orders of magnitude larger than".

Comment 30: Sections 4.2.1, 4.2.2, 4.2.3: these sections describe the sensitivity of GAG_field to soil physical and chemical parameters, which is very well and fine. However the authors also try to compare this sensitivity to the results obtained for GAG_patch in Moring et al (2016), and claim that the observed differences in sensitivity can be assigned to upscaling. I have a major reservation with this approach, because GAG_patch was run on a dataset from New Zealand in Moring et al 2016. The authors are aware of this limitation because they adjust soil parameters one by one in order to make the two datasets comparable (e.g., very different initial pH values of 6.65 and 4.95, or Theta_urine of 0.18 and 0.3, etc), but as far as I understand they did not go as far as to -re-run GAG_patch and its sensitivity analysis specifically for and using only Scottish data (not just soil inputs, but also weather, stocking density, etc). The comparison of sensitivity for the different scales (patch and field) can only make sense (in terms of the impact of upscaling) if data from the same site are used.

My recommendation therefore is

- either focus on the sensitivity of GAG_field, and leave aside the comparison with GAG_patch results from Moring et al, or at least make it clear that differences cannot be assigned to upscaling

-or re-run the GAG_patch sensitivity analysis using only input data from the Scottish site (forget about GAGpatch results from Moring et al 2016), such that upscaling can be invoked to explain differences for the same soil/weather/grazing conditions In either case the authors would have to re-think/re-draw/re-calculate Tables 3, 4, 5, 6, and rewrite sections 4.2.1 through 4.2.3.

Our answer: We agree that we did not describe the idea well-enough behind our model comparison in the manuscript, therefore, we rewrite the Sections 4.2.1-4.2.3 and add further, explanatory figures to the manuscript. In our modifications, the logic we follow is:

- The comparison of the result from the sensitivity analysis for the patch-related parameters is important, since we believe that in this way important lessons can be learned on the behaviour of the model.
- There are three main differences in the GAG_field simulations and the GAG_patch model experiments:
 - 1) in GAG_field the total net NH₃ exchange consists of not only the total NH₃ emission over the urine patches, but also the total net NH₃ exchange over the non-urine area,
 - 2) in GAG_field multiple urine patches are deposited in every time step, whilst in GAG_patch a single urine patch is simulated,

- and the two models were applied for two different sites with different circumstances: GAG_field was applied for a grazed grassland at Easter Bush, Scotland and GAG_patch was evaluated for a grassland at Lincoln, New-Zealand.
- To address these differences point-by-point:
 - 1) We derive the Sens_{patch} values for the GAG_field simulations as explained in our response to Comment 21.
 - 2) For the parameters β , θ_{fc} , and θ_{pwp} we calculate the corresponding sensitivities (Sens_{patch}^{single}). See the new figures Fig. N1 and Fig. N2 at the end of this document. Apart from showing the difference between the sensitivity of the area covered by urine patches (multiple patches) and the single urine patches, this will give an insight on how the model sensitivity responds to upscaling.
 - 3) The Sens_{patch}^{single} values calculated in the previous point are now comparable with the Sens_{patch}^{single} values for GAG_patch (as published by Móring et al., 2016), and the differences will reflect on the different circumstances at the two experimental site, Easter Bush, UK (GAG_field) and Lincoln, NZ (GAG_patch).
- To explore what could cause the differences in the *Sens*_{patch}^{single} for the urine patches in the GAG_field and GAG_patch simulations, the general model behaviour should be investigated. As such, it is equivalent to rerun the original GAG_patch with parameters from Easter Bush, or pick a urine patch deposited in the GAG_field simulation and rerun the patch scale model for it with parameters from Lincoln. Therefore, we keep Table 4 and 6 in the manuscript in their original form.

Change to the manuscript:

We rewrite Section 3.3.1 from the second paragraph as follows (the parts kept from the original manuscript is indicated with grey):

"The perturbation experiments were carried out as follows: the investigated parameter was modified with $\pm 10\%$ and $\pm 20\%$, whilst the other parameters were kept the same. At the end of every simulation, the total NH₃ exchange (ΣF_{net}) was calculated by summing the modelled hourly NH₃ fluxes in the given modelling period. The difference compared with the baseline simulations was expressed in two ways. Firstly, it was calculated as the percentage of ΣF_{net} in the baseline model integrations (127 g N and 403 g N net emission for the whole field in the baseline simulations for P2002 and P2003, respectively), denoted as *Sens_{net}*. Secondly, the differences were derived as the absolute average hourly change, i.e. ΣF_{net} in the actual perturbation experiment minus ΣF_{net} in the baseline simulation, divided by the length of the modelling periods (199 hours and 126 hours in P2002 and P2003, respectively).

In addition to the percentage differences for the whole field, similarly, the proportional change (*Sens*_{patch}) in the total NH₃ emission was calculated separately for the area covered by the urine patches (ΣF_{patch}) as well. In the baseline simulations, the total NH₃ emission

from the urine patches were 717g N and 846 g N in P2002 and P2003, respectively. Finally, for β , θ_{fc} , and θ_{pwp} , the percentage differences in the total NH₃ emission ($\Sigma F_{patch}^{single}$) were calculated for every single urine patch deposited over both modelling periods, denoted as *Sens*_{patch}^{single}.

When the results from the sensitivity analysis for GAG_field and GAG_patch is compared (latter carried out by Móring et al., 2016), differences can occur for three reasons:

- 1) in GAG_field the total net NH₃ exchange consists of not only the total NH₃ emission over the urine patches, but also the total net NH₃ exchange over the non-urine area,
- 2) in GAG_field multiple urine patches are deposited in every time step, whilst in GAG_patch a single urine patch is simulated,
- and the two models were applied for two different sites with different circumstances: GAG_field was applied for a grazed grassland at Easter Bush, Scotland and GAG_patch was evaluated for a grassland at Lincoln, New-Zealand.

For point 1), an insight can be gained if $Sens_{net}$ and $Sens_{patch}$ is compared. The differences originating from point 2) can be investigated based on the comparison of $Sens_{patch}$ and $Sens_{patch}^{single}$ derived for the single urine patches deposited in each time step of P2002 and P2003. Finally, the differences between the results of the perturbation experiments with GAG_patch in Móring et. al (2016) and those calculated for every urine patch in P2002 and P2003 ($Sens_{patch}^{single}$) will reflect the effect of the different circumstances at the two sites GAG_field and GAG_patch were applied for (point 3)."

Before Section 4.2.1. we add the following subsection:

"General remarks

Based on Table 3, some preliminary, general conclusions can be drawn. Firstly, a near constant ratio of *Sens_{net}* and *Sens_{patch}* can be observed for the urine-patch related parameters. These are the parameters that are used in the formulation of GAG_field only for the urine patches: Δz , β , *REW*, θ_{fc} , θ_{pwp} , and pH(t_0) (initial soil pH). These have an effect on the NH₃ exchange for the whole field only through the NH₃ emission from the urine patches.

The value of Δz , *REW*, θ_{fc} , and θ_{pwp} influences the water budget, which is considered in the calculation of the stomatal resistance for both the non-urine area and the patches (Móring et al., 2016). However, preliminary results indicated that without the urine patches (assuming only non-urine area), the change in the total NH₃ exchange over the field in response to the perturbations applied to these parameters were negligibly small (under 1% in absolute value). Therefore, the effect of Δz , *REW*, θ_{fc} , and θ_{pwp} on the total NH₃ exchange over a grazed field through the non-urine area can be ignored.

In essence, when Δz , β , *REW*, θ_{fc} , θ_{pwp} , and pH(t_0) perturbed, the changes of the total exchange flux are attributed exclusively to the changes in the emission flux over the urine patches. Therefore, as shown in the following, for these parameters the ratio of *Sens_{net}* and *Sens_{patch}* is close to constant. Since the net NH₃ exchange over the whole field equals

to the sum of the NH₃ emission from the urine patches and the NH₃ exchange over the non-urine area (Fig. 4), the total NH₃ exchange over the whole field (ΣF_{net} , Eq. 16) over a time interval is equal to the sum of the total NH₃ exchange over the non-urine area (ΣF_{non}) and the total NH₃ emission from the urine patches (ΣF_{patch}). Therefore, based on Eq. (16), when a urine-patch-related parameter is perturbed, the resulting differences (ΔF) in ΣF_{patch} and ΣF_{net} will be the same.

$$\sum F_{\text{net}} = \sum F_{\text{non}} + \sum F_{\text{patch}}$$
(1)

Using ΔF , Sens_{patch} and Sens_{net} can be expressed as:

$$Sens_{patch} = \frac{\Delta F}{\sum F_{patch}}$$
(2)

$$Sens_{net} = \frac{\Delta F}{\sum F_{net}}$$
(3)

Based on these, it can be clearly seen that the ratio of $Sens_{net}$ and $Sens_{patch}$ equals to the ratio of ΣF_{patch} and ΣF_{net} . These ratios are 5.6 and 2.1 for P2002 and P2003, respectively, which is in accordance with the $Sens_{net}$ and $Sens_{patch}$ values in Table 3.

Secondly, in Table 3 it can be also seen that the absolute hourly changes (values in brackets) for the patch-related parameters are about 2-3 times larger in P2003 than P2002. The main reason for this is that on an hourly basis in P2003 the deposition rate of the urine patches was larger than in P2002. On average, in P2003 and P2002, 21 and 8 urine patches were deposited in an hour, respectively. The ratio of the two, 2.625, is in agreement with the observed ratio in the hourly changes for P2002 and P2003.

Finally, based on the results of Table 3, it is clear that $Sens_{net}$ is substantially affected by ΣF_{net} . For example, when χ_{air} was perturbed by -20%, the absolute changes in ΣF_{net} were similar in P2002 and P2003 (+1.06 and +1.16 g N hr⁻¹, respectively), however, there was an enormous difference in the resulted $Sens_{net}$ values (+166% and +36%). This suggests that when the model behaviour is compared for P2002 and P2003, the $Sens_{net}$ values can be interpreted only together with the hourly absolute changes of ΣF_{net} . To visually compare these absolute changes with the values on Fig. 8, the hourly average error of the measurements can be taken as a base: ± 2.86 g N and ± 2.46 g N in P2002 and P2003, respectively, after conversion from flux (ng NH₃ m⁻² s⁻¹) to total emission for the whole field."

We rewrite Sections 4.2.1-4.2.3 as follows (modifications indicated with blue):

"4.2.1 Sensitivity to Δz , REW, pH(t₀), Γ_{sto} and Γ_{soil} , χ_{air} , LAI and h

According to Table 3, compared with the other patch-related parameters, for GAG_field, ΣF_{net} turned out to be the least sensitive to the changes in Δz and *REW*. The *Sens*_{patch} values were similar in the case of the perturbation experiments with GAG_patch, with an overall, slightly stronger sensitivity than was found in the case of GAG_field.

In the case of pH(t_0), ΣF_{net} was found to be very sensitive to the $\pm 10\%$ and $\pm 20\%$ modifications (Table 3). However, it has to be pointed out that these changes in the value

of pH(t_0) (±0.5 unit for a ±10% modification and ±1 unit for ±20%), can be considered as a large increase in the soil pH, taking into account that during intensive urea hydrolysis 2-3 units change can be expected (Fig. 11).

The constant Γ_{sto} and Γ_{soil} affect NH₃ exchange over the whole field exclusively through its effect on the NH₃ exchange over the non-urine area. As the results show (Table 3), the model is only slightly sensitive to Γ_{sto} , whilst Γ_g can have a considerable effect on NH₃ exchange.

As for χ_{air} , in Table 3 the percentage differences for P2002 over the whole field suggest a significant effect on ΣF_{net} . However, comparing the absolute hourly change to that for P2003, it can be concluded that the absolute influence was similar for the two periods. It can be also clearly seen that the absolute hourly changes over the urine patches are negligibly small in both P2002 and P2003 compared to the absolute changes observed for the whole field, suggesting that χ_{air} affects ΣF_{net} mainly through the non-urine area, rather than the urine patches.

The effect of LAI on ΣF_{net} turned out to be weak. The resulting percentage differences are negligibly small compared to the extent of the perturbations applied. Similarly, a relatively weak sensitivity was found for *h*. However, in this case, it has to be noted that the resulting percentage differences are about half of the perturbations. This means that in the case of e.g., a canopy height of 5 cm, which is -83% shorter than the *h* used in the baseline simulations, could lead to considerable changes in the NH₃ exchange flux, especially toward the end of the period when the grass is shorter on the field due to the continuous grazing.

4.2.3 Sensitivity to β

In the case of β , strong sensitivity was detected in ΣF_{net} (Table 3), and the values of *Sens*_{patch} were significantly larger than the *Sens*_{patch}^{single} values reported for GAG_patch. According to Fig. N1b and Fig. N2b, the sensitivity of the total NH₃ emission for the single urine patches in most of the cases were similar (close to the values of *Sens*_{patch}), except in the time steps where the values became scattered, in some cases with extremely high values. The scattered pattern largely disappeared when the precipitation was assumed to be zero, leaving behind the high peaks associated with the events of dew fall (Figs. N1a and N2a). These results suggest that *Sens*_{patch}^{single} is affected by the volumetric water content at the time of the deposition of the urine patch. Furthermore, comparing the patch sensitivities illustrated in Figs N1b and N2b, with those reported by Móring et al. (2016), a large difference occurs over the urine patches observed at the two different sites, Lincoln (NZ) and Easter Bush (UK). Therefore, in the following two questions are investigated:

- What causes the difference between the patches at the two different sites?
- What causes the high peaks in the sensitivity to β ?

For both questions, the general model behaviour was examined through a series of model experiments with GAG_patch (Table 4).

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: $(pH(t_i)-pH(t_{i-1})) \times \beta_{patch}$, where $\beta_{patch} = \beta \times A_{patch} \times \Delta z$. Based on these, the main factors that can regulate the governing role of buffering in the evolution of soil pH in the NH₃ source layer and subsequently, NH₃ exchange, are

- 1) $pH(t_i)$ - $pH(t_{i-1})$, and
- 2) β_{patch} .

Considering point 1), if $pH(t_0)$ is lower, i.e. $[H^+]$ is higher, during urea hydrolysis more H^+ ion can be consumed. This results in a larger increase in soil pH shortly after the urine patch deposition. In the baseline simulations with GAG_patch and GAG_field pH(t_0) was 6.65 and 4.95, respectively. On Fig. 11 it can be observed that in most of the urine patches deposited in the baseline simulations with GAG_field, the difference between the initial and maximum soil pH was about 3 units, whilst in the case of the baseline experiment with GAG_patch (with the higher pH(t_0)) it was only 2 (Móring et al., 2016).

These larger changes in soil pH generate a larger buffering effect $((pH(t_i)-pH(t_{i-1})) \times \beta_{patch})$, 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 NH3 exchange was relatively weak to the modifications of β , it was stronger than in the original perturbation experiment for GAG_patch (Table 3).

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 .

The maximum volume of urine that can be stored in the NH₃ source layer (θ_{urine}) can be calculated as the difference of θ_{fc} and θ_{pwp} . The values of θ_{urine} in the baseline experiments with GAG_field and GAG_patch were 0.18 and 0.3, respectively. This, based on the above consideration, suggests a stronger response in $\Sigma F_{patch}^{single}$ to the perturbation of β for the GAG_field experiments than the GAG_patch experiment. This effect was explored in the model experiment B (Table 4), in which the baseline simulation with GAG_field (Table 2). The results show a small difference in $\Sigma F_{patch}^{single}$ in response to the change of β , but it is still larger than in the sensitivity analysis carried out for the baseline simulation with GAG_patch (Table 3), supporting the effect described above. When the influence of pH(t_0) and the soil water content characteristics were examined

together (model experiment C, Table 4), their effect added up, reaching a $\pm 10\%$ difference in ΣF_{patch} when β was modified by $\pm 20\%$.

The model was tested also with a higher θ_{pwp} (model experiment D, Table 4), assuming that half of the available space for urine in the model soil pore is filled with water, allowing only half of θ_{urine} to infiltrate. This can represent a situation on the field when a urine patch is deposited after a rain event, when only half of the soil pore is empty. As expected, due to the smaller amount of urine, with this modification the sensitivity to β became even stronger.

Overall, these findings show that the difference in $Sens_{patch}^{single}$ in response to the perturbations of β between the GAG_field and GAG_patch simulations are mainly caused by the difference in θ_{fc} and θ_{pwp} as well as pH(t_0) at the two different sites. Furthermore, the above results highlight that the sensitivity of $\Sigma F_{patch}^{single}$ to β can vary between wide ranges over the individual urine patches on the same field, depending on the water content of the soil at the time of the given urination event.

4.2.4 Sensitivity to θ_{fc} and θ_{pwp}

In the case of θ_{fc} and θ_{pwp} , the perturbation experiments suggested an extremely strong sensitivity of ΣF_{net} (Table 3), especially in P2003, where the absolute changes exceeded the 2 g N hourly rate in several cases. Some of the changes in these parameters resulted in a ΣF_{net} that was double or almost triple (+191% in P2003 when θ_{fc} was changed by +20%) of the ΣF_{net} for the baseline simulation. Furthermore, Sens_{net} was below -100% in many cases, suggesting that in response to the modifications of θ_{pwp} and θ_{fc} the originally positive total net exchange turned to deposition. The values of Senspatch for both P2002 and P2003 were less extreme than Sensnet, however these still suggest a substantially stronger sensitivity of $\Sigma F_{patch}^{single}$ to the modifications of θ_{fc} and θ_{pwp} in the GAG_field model experiments than the GAG patch experiments. Figs. N1c-d and Figs. N2c-d show a similar pattern in the Sens_{patch}^{single} values for θ_{fc} and θ_{pwp} to those for β : most of the values are close to the corresponding Senspatch value, however, extreme values appear during the events of precipitation and dew fall, which affect the soil water content at time of the deposition of the urine patches. Similarly to β , the sensitivities observed in the GAG patch experiment at the Lincoln site are significantly lower than those depicted on Figs. N1c-d and Figs. N2c-d for Easter Bush. In the following these findings are further explored in additional model experiments with GAG patch.

The value of θ_{fc} and θ_{pwp} influence NH₃ exchange over a urine patch predominantly through θ_{urine} , affecting the amount of urea available for hydrolysis in the NH₃ source layer. Therefore, the difference in the response of $\Sigma F_{patch}^{single}$ to the changes in θ_{fc} and θ_{pwp} at the two sites, might be caused by the difference in the values of θ_{fc} and θ_{pwp} . As it was pointed out above, in the baseline simulation with GAG_patch $\theta_{urine} = 0.4$, and over the field scale $\theta_{urine} = 0.18$. In the perturbation experiments, when θ_{fc} and θ_{pwp} are modified this fillable space in the source layer is also affected. As it can be seen in Table 5, the ±10% and ±20% modifications of θ_{fc} and θ_{pwp} resulted in proportionally smaller differences in θ_{urine} in the case of the GAG_patch experiment at Easter Bush than the GAG_field simulation at Lincoln, suggesting a weaker response in $\Sigma F_{patch}^{single}$ for the Lincoln site. This effect was explored within a series of model experiments with GAG_patch (Table 6), in which the θ_{fc} and θ_{pwp} used in the baseline simulation with GAG_patch (0.4 and 0.1, respectively) were changed to those applied in the baseline simulation with GAG_field (0.37 and 0.19, respectively). All the other parameters and input variables were kept the same as in the baseline simulation with GAG_patch. The experiments were carried out in two cases for both θ_{fc} and θ_{pwp} : 1) when the initial water content of the soil $(\theta(t_0))$ was assumed to be the θ_{pwp} ($\theta(t_0) = 0.19$) and 2) when half of the available space was filled by liquid ($\theta(t_0) = 0.28$), e.g. by rain water from a preceding rainfall.

As it can be seen in Table 6, with the $\theta(t_0) = \theta_{pwp}$ model setting the sensitivity to both θ_{fc} and θ_{pwp} became higher than in the case of the original perturbation experiment with GAG_patch (Table 3). This sensitivity became even stronger when urine was deposited to a half-filled source layer ($\theta(t_0) = 0.28$). These results suggest that one of the reasons for the large differences in Sens_{patch}^{single} between the GAG_field simulations and the GAG_patch simulation could be the different θ_{fc} and θ_{pwp} values over the two sites. In addition, the findings in Table 6 also imply that depending on the rain events and how they modify the initial water budget in the soil before a urination event, the sensitivity of NH₃ exchange to the perturbations of θ_{fc} and θ_{pwp} over the individual urine patches, deposited on the same field over the modelling period, can vary widely."

Finally, we divide the discussion to two subsections and extend it. After the first paragraph of Section 5.2 we add:

"5.2.1. General conclusions

The results of the perturbation experiments were compared with those from Móring et al. (2016) for GAG_patch. In general, it can be concluded that the differences in the sensitivity of the two models can originate from three sources: 1) the effect of the nonurine area on the total net NH₃ exchange over the whole field, 2) the different response in the total NH₃ exchange of the urine patches as a group, and as individual urine patches, and 3) the different soil characteristics at the two experimental sites, Easter Bush, UK (GAG_field) and Lincoln, NZ (GAG_patch).

For point 1) it was shown in general that if a patch-related parameter (Δz , *REW*, β , pH(t_0), θ_{fc} , θ_{pwp}) is perturbed, even if the resulting change in the total NH₃ emission over the urine patches is the same, the percentage difference over the whole field will be larger if the deposition to the non-urine area is stronger. This is because a larger deposition term results in a smaller total net NH₃ exchange over the whole field, suggesting a proportionally larger change in the total over the whole field in response to the perturbation of the given parameter.

Regarding point 2) a 3) additional perturbation experiments were carried out for θ_{fc} , θ_{pwp} , and β . Overall, these suggest that the sensitivity of the total NH₃ exchange of an individual urine patch is similar to the sensitivity of the urine patches as a group if the investigated urine patch is deposited when the water content of the source layer is minimal (θ_{pwp}). However, over a urine patch, the total NH₃ exchange can be extremely sensitive to the perturbations of θ_{fc} , θ_{pwp} , β , if it is deposited shortly after an event of rain fall (or dew fall), which increases the water content of the source layer at the time of urine deposition. Since in the baseline simulations with GAG_field the source layer was

dry most of the time (water content at θ_{pwp}), the sensitivity for the group of urine patches was similar to the sensitivity of most of the individual urine patches deposited over the modelling periods.

The results also showed that difference between the sensitivities to θ_{fc} , θ_{pwp} , and β over the urine patches in the GAG_field simulations and the GAG_patch simulation is associated with the different values of θ_{fc} , θ_{pwp} at the two experimental sites. Furthermore, the different pH of the undisturbed soil at Lincoln and Easter Bush could lead to high differences in the resulted sensitivities to β over the individual urine patches at the two sites.

In conclusion, two main reasons can be identified for the large differences in the observed sensitivity of the total net NH₃ exchange to θ_{fc} , θ_{pwp} , and β between the baseline simulations with GAG_field and GAG_patch. The differences are caused by firstly, the fact that over the field scale in the net exchange the deposition to the non-urine area is also included, and secondly, the different soil characteristics at the two sites."

After this we insert the title of the second subsection:

"5.2.2. Parameter-specific findings"

Finally, on P24 from L2 we change the following two sentences:

"Over the field scale the response of the NH₃ fluxes was extremely strong to the perturbation of these parameters. This high sensitivity was attributed to the maximum amount of urine that the NH₃ source layer can hold, which depends on θ_{fc} and θ_{pwp} , or if the soil volumetric water content is higher than θ_{pwp} before a urination event, the initial water content of the soil ($\theta(t_0)$)."

as follows:

"The results suggested that the sensitivity of the total NH₃ exchange over a urine patch is regulated by the maximum amount of urine that the NH₃ source layer can hold, which depends on θ_{fc} and θ_{pwp} , or if the soil volumetric water content is higher than θ_{pwp} before a urination event, the initial water content of the soil ($\theta(t_0)$)."

Comment 31: p18, l6-7: '...the main factors that can regulate the governing role of buffering in the evolution of soil pH in the NH3 source layer ... are ... pH(ti) - pH(ti-1) ...': this turn of phrase is strange, because it is buffering that controls/reglates/modulates the change in pH over a time interval, not the other way around, semantically.

Our response: Following the logic of the text on P18 from L5 this is logical: the effect of buffering in the model is described by the expression mentioned also in the manuscript (P18 L6):

 $(pH(t_i)-pH(t_{i-1})) \times \beta_{patch.}$

The part $(pH(t_i) - pH(t_{i-1}))$ describes the change of pH. This expression is based on the definition of buffering capacity, which is the released/consumed H⁺ (mol) by the buffers in the solution as a response to 1 unit change of pH in a dm³ of solution, which implies

that the stronger are the H⁺ consuming and producing terms in the system, the stronger will be the "buffering effect". This was used in Móring et al. (2016), where the "buffering effect" is considered as an additional term in the H⁺ budget on top of the other H⁺ consuming and producing terms, as shown in the referred study in Eq. 47:

 $B_{H^{+}}(t_{i}) = B_{H^{+}}(t_{i-1}) - i_{C}(t_{i}) + (-r_{R3} + r_{R2} + r_{R1}) + \beta_{patch}(pH(t_{i}) - pH(t_{i-1}))$

Comment 32: *p18, l16, similarly to the above comment, '...These larger changes in soil pH generate a larger buffering effect...' sounds strange; it is the extent of buffering that controls pH change*

Our answer: As pointed in our answer to the pervious comment, the stronger are the H^+ consuming and producing terms in the system, the stronger will be the "buffering effect". In this case, the cited part of the manuscript describes that due to the more active urea hydrolysis in the GAG_field simulations than in the GAG_patch experiment, more H^+ ion is consumed in a time step, which means that the buffers in the system will produce more H^+ , i.e. the buffering effect will be larger. Nevertheless, to avoid confusion by readers we modify the text.

Change to the manuscript: Please see the modifications we propose following the suggestion of Reviewer 2, in our response to Comment 11 by Reviewer 2.

Comment 33: p20, l20: Fig. 12 does not show a comparison of GAG_field vs measurements

Our answer: Agreed, we meant to refer to Fig. 8 here. We correct this in the text.

Change to the manuscript: On P20 in L20 we change "Fig 12." to "Fig 8."

Comment 34: *p24, l2-3: 'Over the field scale the response of the NH3 fluxes was extremely strong to the perturbation of these parameters'. This is true, but as pointed out above, it is not adequately demonstrated that this response is stronger at field than at patch scale, because the NZ and UK sites are different.*

Our answer: We change this sentence as also showed in our response to Comment 30.

Change to the manuscript: "Over the field scale the response of the NH₃ fluxes was extremely strong to the perturbation of these parameters. This high sensitivity was attributed to the maximum amount of urine that the NH₃ source layer can hold, which depends on θ_{fc} and θ_{pwp} , or if the soil volumetric water content is higher than θ_{pwp} before a urination event, the initial water content of the soil ($\theta(t_0)$)."

as follows:

"The results suggested that the sensitivity of the total NH₃ exchange over a urine patch is regulated by the maximum amount of urine that the NH₃ source layer can hold, which depends on θ_{fc} and θ_{pwp} , or if the soil volumetric water content is higher than θ_{pwp} before a urination event, the initial water content of the soil ($\theta(t_0)$)." **Comment 35:** *p24, l27-28: 'The observed sensitivities [of GAG_field] turned out to be much higher than was found in the case of GAG_patch': again, this is misleading because it gives the impression that the only reason for the difference is scale (patch vs field), which is not the case.*

Our answer: In the cited sentence, we simply use the name of the two models, GAG_patch and GAG_field. The difference mentioned in this sentence is explained in the next sentence.

Comment 36: Same paragraph: 'The different sensitivities over the two scales can be explained by the different initial soil pH and the different soil physical characteristics': ergo, the difference has nothing to do with scale, but with soil characteristics.

Our answer: Please see our suggestion below.

Change to the manuscript:

On P24 in L28 after the sentence ending with "in the case of GAG_patch" we add:

"The reason for these different sensitivities is dual. Firstly, the difference originates from the different scales. When a model parameter, affecting the NH₃ emission from the urine patches is perturbed, the resulting change in the total net NH₃ exchange over the whole field will be larger compared to that in the total NH₃ emission from the urine patches. The reason for this is the negative deposition term in GAG_field over the non-urine area."

And in the same paragraph we change the sentence cited by the reviewer as follows:

"Secondly, and more importantly, the different sensitivities observed for the two models can be explained by the environmental circumstances at the two sites the model were applied for, i.e the different initial soil pH and the different soil physical characteristics at the two sites which determine the maximum volume of urine that can be stored in the NH₃ source layer."

Comment 37: Table 2: it seems the model used constant canopy height and LAI over the whole modelling period, this is surprising since cattle will consume grass, so the values should decrease from start to end, which would impact model results. Also, a leaf area index of 1m2 m-2 is very small, there would be hardly anything to eat for 50 cows for a week! I would venture that these values were measured at the end of the grazing period? It might be reasonable to rerun the model with starting LAI and canopy height values of 3 m2 m-2 and 0.2m, respectively, and assume a linear decrease until the end of the period?

Our answer: We thank the reviewer for this comment, especially because it pointed out a mistake in the Table 2, in which an earlier version of the input data was included. Indeed, we also realised that the measured leaf area index (*LAI*) and canopy height values (*h*) indicate too little grass on the field, therefore, instead of these, in our simulations in both modelling periods we used data as suggested by Massad et al. (2010) for summer grasslands (*LAI* = $3.5 \text{ m}^2 \text{ m}^{-2}$, *h*=0.3 m, as also in the simulation with GAG_patch in Móring et al., 2016). This choice is also supported by the fact that when the model will be applied to regional scale within an atmospheric chemistry transport model, it is highly unlikely that measured *LAI* and *h* values will be available over a large region. As such

over regional scale similar constants from the literature will be used. We modify Table 2 accordingly.

We agree with the reviewer that the effect of grazing, and its effect through the decreasing canopy height and leaf area index could have a considerable effect on the NH₃ flux over the field. Similarly to our answer to Comment 28, it would be interesting to investigate the effects of real grazing situations (together with daily pattern in urination frequencies) but this is out of the scope of our current study. We agree though that such investigations could be good material for a further study. Nevertheless, to illustrate the general effect of *h* and *LAI* on the net NH₃ exchange over the field, we carry out additional perturbation experiments for these two parameters.

Change to the manuscript:

From Table 2 we remove the values for *LAI* and *h*. (The caption says that the parameters that are not defined in the table are the same as defined for GAG_patch in Móring et al., 2016).

On P13, in L8 we extend the sentence as follows (the added text with bold):

"LAI (leaf area index) and h (canopy height) were also examined"

We add to the end of Section 4.2.1 the following paragraph:

"The effect of LAI on ΣF_{net} turned out to be weak, the resulting percentage differences are negligibly small compared to the extent of the perturbations applied. Similarly, a relatively weak sensitivity was found for *h*. However, in this case, it has to be noted that the resulting percentage differences are about half of the perturbations. This means that in the case of e.g., a canopy height of 5 cm, which is -83% shorter than the *h* used in the baseline simulations, could lead to considerable changes in the NH₃ exchange flux, especially toward the end of the period when due to the continuous grazing the grass is shorter on the field."

In Section 5.2, we add the following paragraph before the last one:

"For the presented simulations with GAG_field a hypothetical grazing situation was assumed, in which there is no temporal variation in UF, c_N and A_{patch} . However, UF, c_N and the volume of urine deposited by an animal can have a diurnal cycle (Misselbrook et al., 2016), latter with a potential effect on A_{patch} (Li et al., 2012). In addition to these parameters, LAI and h was handled as constant for the whole modelling period, whilst these parameters are decreasing since due to grazing, there is less and less grass on the field toward the end of the modelling period. To assess the possible influence of these assumptions on ΣF_{net} , additional sensitivity experiments were performed with GAG_field."

Then we rewrite the last paragraph as follows:

"According to the results, whilst the uncertainty originating from the choice of a constant A_{patch} and UF is considerable, the uncertainty coupled with the value of c_N is extremely large. Nevertheless, model simulations with randomized N concentrations implied that this uncertainty might be considerably smaller in reality than it was suggested by the sensitivity analysis. For *LAI* and *h*, it was found, that LAI has a negligible effect on ΣF_{net} ,

whereas h can substantially affect the NH₃ exchange over the field. Therefore, future work should investigate how the modelled NH₃ exchange responds when a real grazing situation assumed, including a diurnal cycle of UF, c_N and A_{patch} as well as temporal changes of LAI and h."

Comment 38: Tables 3,4,5 to be recalculated to show GAG_patch results using fully Scottish input data (soil parameters + weather data + grazing/field data + NH3 concentration data, etc), instead of using GAG patch sensitivity values from NZ site of Moring et al 2016

Our answer: Please see the modified version of Table 3 at the end of this document. We keep Tables 4-6 in the manuscript in their original form as explained in our answer to Comment 30.

Change to the manuscript: As stated above.

Comment 39: Figure 5, bottom line, second cell from right: presumably this is n(tj=n)?

Our answer: Agreed. Reviewer 2 pointed out that we used n for the number of the urine patches as well as for the maximum number of the time steps within the modelling period. Therefore, we change the latter to m. Following this, please see our modification below.

Change to the manuscript:

In Fig. 5, in the bottom row, we change " $n(t_{j=4})$ " to " $n(t_{j=m})$ " and every *n* in brackets to *m*. See the new figure at the end of this document.

Comment 40: *Figure 6, add scale*

Our answer: We change Fig. 6 as shown at the end of this document.

Change to the manuscript: As stated above.

Comment 41: *Figure 7, the geometric mean value (mu) of 2.089 seems to be abnormally small for this distribution, I would expect the geomean nearer 5-6, close to the median?*

Our response: As pointed out in our response to Comment 22, μ does not denote the geometric mean, but the arithmetic mean of $log(c_N)$.

Comment 42: Figures 8 through 13 to be redrawn using a non-zero concentration for the missing Xa data on 27-28/08/2002

Our answer: Please see the modified versions of Figs. 8-13 at the end of this document.

Change to the manuscript: As stated above.

Comment 43: Figure 8: 'Where the error bars are missing one of the three NH3 concentration denuders were malfunctioning or not registering data at all.' This is slightly misleading, visually, because it is at times when fluxes are most uncertain (calculated from only 2)

concentration heights) that there is no indication of uncertainty on the figure... I would suggest to calculate the mean uncertainty from all fluxes from 3-point gradients (mean of red error bars already present on figure), multiply this value by e.g. a factor of 2, and apply to the rest of the points (in a different color)?

Our answer: We calculate the error bars as suggested and add them to Fig. 8. See the modified figure together with the belonging caption at the end of this document.

Change to the manuscript: As stated above.

References

- Bell, M., Flechard, C., Fauvel, Y., Häni, C., Sintermann, J., Jocher, M., Menzi, H., Hensen, A. & Neftel, A. 2016. Ammonia emissions from a grazed field estimated by miniDOAS measurements and inverse dispersion modelling. Atmos. Meas. Tech. Discuss., 2016, 1-29.
- Li, F. Y., Betteridge, K., Cichota, R., Hoogendoorn, C. J. & Jolly, B. H. 2012. Effects of nitrogen load variation in animal urination events on nitrogen leaching from grazed pasture. Agriculture, Ecosystems & Environment, 159, 81-89.
- Loubet, B., Milford, C., Hensen, A., Daemmgen, U., Erisman, J. -W., Cellier, P., Sutton, M. A. 2009. Advection of NH₃ over a pasture field and its effect on gradient flux measurements. Biogeosciences, 6, 1295-1309.
- Massad, R. S., Nemitz, E. & Sutton, M. A. 2010. Review and parameterisation of bi-directional ammonia exchange between vegetation and the atmosphere. Atmospheric Chemistry and Physics, 10, 10359-10386.
- Misselbrook, T., Fleming, H., Camp, V., Umstatter, C., Duthie, C. A., Nicoll, L. & Waterhouse, T. 2016. Automated monitoring of urination events from grazing cattle. Agriculture, Ecosystems & Environment, 230, 191-198.
- 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.

Table 3. Results of the perturbation experiments with GAG_field. The changes in the total NH₃ flux over the field as a response to a change ($\pm 10\%$ and $\pm 20\%$) in the listed model parameters where expressed as the percentage of the total NH₃ exchange in the baseline simulations with GAG_field and in the brackets as the hourly change in the total net exchange over the whole field (g N hr⁻¹). Results are listed for both modelling periods, P2002 and P2003, separately for the whole field (Sens_{net}) and the urine patches (Sens_{patch}). As a comparison, the results of the sensitivity analysis carried out by Móring et al. (2016) for GAG_patch are also indicated (Sens_{patch}^{single}). In the column 'Effect' the letters denote how the given parameters affect total NH₃ exchange in GAG_field: through the urine patches (P) or the non-urine area (N) or both.

	Effect	Δx	Change in the total net flux in response to the perturbation					
Constants (x)			P2002		P2003		GAG_patch	
			Sensnet	Senspatch	Sensnet	Senspatch	Senspatch	
	Р	-20%	-40% (-0.26)	-7%	-8% (-0.27)	-4%	-12%	
		-10%	-18% (-0.11)	-3%	-4% (-0.12)	-2%	-6%	
212 (unexitess of the source rayer)		+10%	+14% (+0.09)	+2%	+2% (+0.08)	+1%	+5%	
		+20%	+25% (+0.16)	+4%	-2% (-0.06)	-1%	+11%	
	р	-20%	0% (0.0)	0%	-3% (-0.08)	-1.3%	-3%	
<i>PEW</i> (readily evaporable water)		-10%	0% (0.0)	0%	-1% (-0.04)	-0.6%	-2%	
<i>KEW</i> (readily evaporable water)		+10%	0% (0.0)	0%	+1% (+0.04)	+0.6%	+2%	
		+20%	0% (0.0)	0%	+2% (+0.08)	+1.2%	+4%	
	Р	-20%	-173% (-1.11)	-31%	-79% (-2.53)	-38%	-	
<i>pH(to)</i> (initial soil pH)		-10%	-90% (-0.58)	-16%	-42% (-1.36)	-20%	-	
		+10%	+96% (+0.61)	+17%	+48% (+1.53)	+23%	-	
		+20%	+196% (+1.25)	+35%	+100% (+3.21)	+48%	-	
	N	-20%	-3% (-0.02)	-	-1% (-0.02)	-	-	
		-10%	-1% (-0.01)	-	-0.3% (-0.01)	-	-	
Γ_{sto} (stomatal emission potential)		+10%	+1% (+0.01)	-	+0.3% (+0.01)	-	-	
		+20%	+3% (0.02)	-	+1% (+0.02)	-	-	
	N	-20%	-54% (-0.34)	-	-12% (-0.38)	-	-	
Γ_g (soil emission potential)		-10%	-27% (-0.17)	-	-6% (-0.19)	-	-	
		+10%	+27% (+0.17)	-	+6% (+0.19)	-	-	
		+20%	+54% (+0.34)	-	+12% (+0.38)	-	-	
eta (soil buffering capacity)	Р	-20%	+94% (+0.60)	+17%	+50% (+1.61)	+24%	+1%	
		-10%	+46% (+0.29)	+8%	+24% (+0.77)	+11%	+1%	
		+10%	-43% (-0.28)	-8%	-22% (-0.69)	-10%	-1%	
		+20%	-84% (-0.53)	-15%	-41% (-1.31)	-20%	-1%	

Table 3. Continued.

		Δx	Change in the total net flux in response to the perturbation					
Constants (x)	Effect		P2002		P2003		i GAG natch	
			Sensnet	Senspatch	Sensnet	Senspatch		
$ heta_{fc}$ (field capacity)	Р	-20%	-360% (-2.30)	-64%	-153% (-4.88)	-72%	-18%	
		-10%	-190% (-1.22)	-34%	-85% (-2.71)	-40%	-7%	
		+10%	+211% (+1.35)	+37%	+96% (+3.07)	+46%	+6%	
		+20%	+448% (+2.86)	+79%	+191% (+6.09)	+91%	+9%	
	Р	-20%	+364% (+2.32)	+64%	+157% (+5.03)	+75%	+9%	
		-10%	+173% (1.11)	+31%	+76% (+2.43)	+36%	+5%	
θ_{pwp} (permanent wilting point)		+10%	-156% (-1.00)	-28%	-65% (-2.07)	-31%	-4%	
		+20%	-292% (-1.87)	-52%	-118% (-3.79)	-56%	-9%	
	P, N	-20%	+166% (+1.06)	+0.3% (+0.012)	+36% (+1.16)	+0.3% (+0.02)	-	
χ_{air} (ambient atmospheric NH ₃ concentration)*		-10%	+83% (+0.53)	+0.2% (+0.006)	+18% (+0.58)	+0.2% (+0.01)	-	
		+10%	-84% (-0.53)	-0.2% (-0.006)	-19% (-0.61)	-0.2% (-0.01)	-	
		+20%	-167% (-1.07)	-0.3% (-0.012)	-38% (-1.22)	-0.3% (-0.02)	-	
LAI (leaf area index)	P, N	-20%	-1.1% (-0.007)	+0.11% (+0.004)	+0.10% (+0.003)	+0.15% (+0.010)	-	
		-10%	-0.5% (-0.003)	+0.05% (+0.002)	+0.05% (+0.002)	+0.07% (+0.005)	-	
		+10%	+0.5% (+0.003)	-0.05% (-0.02)	-0.05% (-0.002)	-0.07% (-0.005)	-	
		+20%	+1.1% (+0.007)	-0.11% (-0.004)	-0.10% (-0.003)	-0.14% (-0.010)	-	
h (canopy height)	P, N	-20%	-12% (-0.08)	-8% (-0.28)	-9% (-0.28)	-8% (-0.51)	-	
		-10%	-6% (-0.04)	-4% (-0.14)	-4% (-0.13)	-4% (-0.25)	-	
		+10%	+4% (+0.03)	+4% (+0.13)	+4% (+0.14)	+4% (+0.26)	-	
		+20%	+6% (+0.04)	+7% (+0.26)	+8% (+0.26)	+7% (+0.49)	-	

*In both P2002 and P2003 χ_{air} was changed by $\pm 10\%$ and $\pm 20\%$ of the average χ_{air} over each period as explained in Section 3.3.1.

		N	NH ₃ exchange with the			
		Time				
		t _{j=1}	t _{j=2}	t _{j=3}	 t _{j=n}	non-urine area
ing iod	t _{i=1}	$\mathbf{F}_{\text{patch}}^{j=1}(\mathbf{t}_{i=1})$	$F_{non}(t_{i=1})$	$F_{non}(t_{i=1})$	 $F_{non}(t_{i=1})$	$\boldsymbol{F}_{non}(\boldsymbol{t}_{i=1})$
beginı ıg per	t _{i=2}	F _{patch} ^{j=1} (t _{i=2})	F _{patch} ^{j=2} (t _{i=2})	$F_{non}(t_{i=2})$	 $F_{non}(t_{i=2})$	$F_{non}(t_{i=2})$
e the l dellin	t _{i=3}	F _{patch} ^{j=1} (t _{i=3})	F _{patch} ^{j=2} (t _{i=3})	$\mathbf{F}_{\text{patch}}^{j=3}(t_{i=3})$	 $F_{non}(t_{i=3})$	$F_{non}(t_{i=3})$
e sinc he mo			,		 	
Time of tl	t _{i=m}	F _{patch} ^{j=1} (t _{i=m})	$\mathbf{F}_{\text{patch}}^{j=2}(t_{i=m})$	$F_{patch}^{j=3}(t_{i=m})$	 $F_{patch}^{j=n}(t_{i=m})$	$F_{non}(t_{i=m})$
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 NH₃ fluxes (in every ith time step, t_i) as derived by GAG_field. $F_{patch}{}^{j}(t_{i})$ stands for the NH₃ flux from the urine patches deposited in the jth time step (t_j), and $F_{non}(t_{i})$ stands for the NH₃ flux from the non-urine area. The bottom row shows how many urine patches were deposited in the given jth 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 6. Satellite photo of the Easter Bush site. The map was generated by Google Maps, indicating the two halves of the field and the place of the instruments on the border of the two denoted by the small yellow rectangle. (The figure is taken from the metadata file by CEH.)



Figure 8. Comparison of the measured and modelled NH₃ fluxes in the modelling periods P2002 (a) and P2003 (b). The uncertainty of the flux measurements is depicted as error bars. Yellow error bars indicate the cases where one of the three NH₃ concentration denuders were malfunctioning or not registering data at all. For these, the error was estimated as the average of the observed errors (red error bars) multiplied by an arbitrary factor of two. A measured flux was considered to be robust if it met the criteria of the quality control for low wind speed and strong stability as described in Section 3.2.2.



Figure 9. Simulated NH₃ exchange fluxes over the urine patches, the non-urine area and the whole field in the modelling periods P2002 (a) and P2003 (b).



Figure 10. Simulated NH₃ fluxes from urine patches deposited in the same time step in the modelling periods P2002 (a) and P2003 (b). Each line indicates NH₃ fluxes from urine patches deposited in a given time step (expressed for the whole field), while the different colours indicate the days of the urination events. The number above the plots show how many cattle were grazing in the given time intervals.



Figure 11. Simulated soil pH in the NH_3 source layer under urine patches deposited in the same time step in the modelling periods, P2002 (a) and P2003 (b) in the baseline experiments with GAG_field. The different colours indicate the days of the urination events. Each line indicates soil pH under urine patches deposited in a given time step, while the different colours indicate the days of the urination events.



Figure 12. Simulated NH₃ exchange fluxes from the baseline simulation with GAG_field with a constant c_N (black line), and 30 model experiments in which c_N was randomized for every time step (orange lines) for the modelling periods P2002 (a) and P2003 (b).



Figure 13. NH₃ exchange fluxes simulated by GAG_field with the original dynamic approach for soil pH (Baseline), and when constant values of soil pH were assumed: pH 7.5 (GAGf_pH7.5), pH 7.0 (GAGf_pH7.0) and pH 8.0 (GAGf_pH8.0). Simulations were carried out for both modelling periods, P2002 (a) and P2003 (b).



Figure N1: Results of the perturbation experiments for every single urine patch deposited over P2002. The results are shown in comparison with the volumetric water content of the soil at the time of urine patch deposition, changing in response to the events of precipitation and dewfall (a). The investigated parameters were: the buffering capacity (β , b), the field capacity (θ_{fc} , c) and the permanent wilting point (θ_{pwp} , d). On figures b)-d), a point represents the percentage difference in the total NH₃ emission from the urine patch deposited in the given time step, and lines denotes the same, assuming zero precipitation over the modelling periods.



Figure N2: Results from the same experiments illustrated in Fig. N1, for P2003.



Figure N3: NH₃ fluxes simulated by GAG_field against the measured NH₃ fluxes in P2002 (a) and P2003 (b). Green and blue dots represent the data for all time steps when measured fluxes where available. The green dots indicate only those time steps in which the measured flux was considered robust as shown in Fig. 8 (on Fig. a, the remaining data points on 27/08/2002 were also excluded as explained in Section 4.1.1). The figures show the fitted lines to the data points (thick black line for all of the data points, green dashed line for the green data points) in comparison with the 1:1 line (red line). The statistics indicated are the equation of the fitted lines (y), the Pearson correlation (R), the relative mean squared error (RMSE) and the level of significance of the relationship between the measured and modelled values (p) in the colour of the corresponding fitted line.



Figure S1: Model results for the calibration period with GAG_field, using different values for the soil emission potential (Γ_g).