**Biogeosciences
Discussions**

Interactive comment on "Ammonia emissions from cattle urine and dung excreted on pasture" by J. Laubach et al.

J. Laubach et al.

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Reply to Anonymous Referee #1

We are delighted by the reviewer's positive General Comments, and appreciate the thoughtful and in-depth queries in the Specific Comments, which we address individually, below.

Methodological remarks and questions: - p.13291, l.19: briefly explain how digestibility is defined and what exactly is being measured

Reply: Dry-matter (DM) digestibility is defined as the proportion of feed DM consumed that can be absorbed by the animal. Near-infrared spectroscopy (NIRS) is a standard technique in the agricultural sciences and industry to determine several important pa-

rameters in feed composition. NIRS measures the reflectance of a sample across an IR waveband. The combinations of reflectances at certain wavelengths are highly correlated to certain composition properties of the sample, and by means of empirical calibration can be used to predict these properties (see e.g. Norris et al. 1976). These days, standard databases providing such calibration data are available for a wide range of sample types. Our judgment was that the readership of this journal would probably not require explanation of the expressions "digestibility" and "NIRS", but if the Editor disagrees with that judgment then we will be happy to add the essence of this reply to the manuscript.

- p.13292, l.11: it should be stated whether the "imported" urine was also from non-lactating cows with similar diet? Had it been tested to have the same initial pH as urine excreted from the cattle in the field? That is an important point regarding pH development and urea content of the control patches that are used to interpret the course of NH3 emissions from the field experiment. Has the urine been analysed for N content and if so, how compared that with the estimated urinary N excretion? If no such urine parameters have been measured, briefly outline the expected comparability of in-situ excreted urine and the urine collected at Lincoln University dairy farm.

Reply: The imported urine was from lactating cows. We know neither the pH of the imported urine nor of that excreted in situ. However, we believe that the initial urine pH is not particularly relevant to the course of subsequent NH3 volatilisation. The pH reached within the urine patch itself is the main driver of NH3 volatilisation and that is related to the urea content of the urine and the pH buffering capacity of the soil. The animals in the circular plot were fed the same quality and type of herbage that the lactating cows were eating, therefore we assume that the N content (and pH) of their urine was similar.

- p.19293, l.4: was the pH electrode checked for drift throughout the experiment?

Reply: Yes. The calibration of the electrode was checked prior to each daily batch of

samples that were analysed.

- p.13294: I have one concern about how the IHF has been applied in the experiments: as described in Laubach et al. (Agricultural and Forest Meteorology 156, 1-17, 2012) the horizontal flux was measured at 5 heights. In order to derive the total horizontal flux the profile has to be integrated vertically up to a height where background is reached. In this paper this is done by summation of the results from each measurement height multiplied by the corresponding layer depth (delta-z). This approach assumes that the five layers, given by delta-z, show a height-constant horizontal flux measured at the respective height. With this simplification and the limited amount of measurement heights it is unclear, however, whether the vertical horizontal flux profile is accurately enough resolved. In contrast to the present experiment, the IHF references (Beauchamp et al., 1979; Denmead, 1995) provided in the both papers interpolate the entire vertical profiles before integration. This can e.g. be done by fitting a function through the measurement points. How is the here applied simplification justified? Have the authors compared both approaches? Are there references for the applied method? What is the introduced systematic and random uncertainty? This should be accounted for in the final flux uncertainty.

Reply: The details of how the mass-budget, or IHF, method was implemented are the same as described and discussed in Laubach and Kelliher (2004). Please find a detailed reply (including equations and a figure) in the Supplement.

- p.13295, l.1: how was ensured that the background concentration was not influenced by the pasture emissions during the long, e.g. >5h intervals. Generally, how confident are the authors about having a "clean" background measurement? It would make sense to include wind speed, –direction, and background mast position into Fig. 1. to give an impression about the according dynamics.

Reply: Whether the background is "clean" does not really matter. What we need is the local upwind concentration at the time. Of course, we imply that Cb is constant with

height. That is a reasonable assumption as long as sources/sinks in the surroundings are much smaller than those we aim to measure. Wind speed and direction varied widely throughout the experiment, with synoptic conditions and local diurnal wind patterns. The position of the background sampler was adjusted as needed (choice of 4 masts), which is said in the manuscript. We do not believe that a figure showing the time series of wind speed and direction would aid the reader with the understanding of the volatilisation results.

- p.13295, l.17: how and for how long were the samples stored? Was the potential for nitrification or amine degradation in the samples inhibited?

Reply: The samples were analysed with the ion-specific electrode within hours of retrieving the samplers. After that they were stored in a freezer. No specific nitrification or amine degradation inhibitors were included prior to storage. The samples contained excess oxalic acid, probably more than 75 % of the original amouts that the sampler had been charged with. This makes it likely that the pH of the stored solution was less than 1.25 (= first pKa of oxalic acid). We cannot confirm this because we did not measure pH of the samples, but if the samples were so strongly acidic then microbial activity would have been suppressed and both nitrate and amine levels preserved. A few selected samples were re-analysed with the clinical chemistry analyser (CCA) within 3 weeks, to see whether CCA results would make more sense than the electrode results. The whole set of samples was finally analysed by the CCA two months later (and results for those samples that had been selected earlier were reproduced consistently).

- p.13298, l.13 and Fig. 2: Uncertainties for the calculated NH3 emissions are given here. In Sect. 2.5 the authors refer to the companion paper for further methodological details. It is nevertheless worthwhile for the reader to know how the emission errors are composed, especially since the chemical analytics in this study differ from those in the first paper. It would probably be sufficient to mention which parameters go into the error propagation. Also, the used precision of the wet chemistry NH4 analyser (given

by the manufacturer as mentioned in Sect. 2.6, or from replicate laboratory analysis, and/or instrument calibration?) should be stated more clearly. Do the authors include an uncertainty for the IHF method, i.e. uncertainty in the vertical profile shape into their error propagation?

Reply: The error estimation was computed exactly as described by Laubach et al. (2012), and we will add half a sentence on p.13298 to indicate this. The precision of the Randox analyser (CCA) was assumed as specified by the manufacturer (1 to 4 %), and since this is less than the 4.5 % relative error assigned to the Leuning sampler collection process, the exact value within this range does not cause much variability in the error propagation. The end result is indeed quite similar to that estimated for the electrode (which has an assumed reading error of 2.3 %, as stated in Section 2.6). An uncertainty for the profile shape (slab approximation) is not included, for reasons stated above, but an uncertainty for the extrapolated horizontal flux above the top measurement height (the sixth term of the summation in Eq. 1) is included where applicable (i.e. in runs where C5 exceeded Cb significantly).

Also, the NH3-N loss values relative to the estimated excreted N are given with uncertainties (Table1 and in the Section). Has the uncertainty from the amount of excreted N been included here?

Reply: Yes it has, and the relative error of the excreted N (as given in Table 1) makes the dominant contribution to the relative error of the N loss fraction.

- p.13304: for the gas-phase equilibrium NH3 concentration calculation: have the authors considered that the solution was probably far from being an ideal solution, and therefore had a reduced ionic strength? If not so, the corresponding gas phase concentration would be even more an overestimation.

Reply: We agree that the aqueous medium within the dung interior is definitely not an "ideal solution" as understood by physical chemists, but we are not aware of a practical and justifiable method to correct for ionic strength departures from ideality for

systems such as dung pat interiors. Rather than having a "reduced ionic strength" as the reviewer suggests, it is more likely that the aqueous medium within the dung pats would have had a greater ionic strength than required by the "ideal solution" definition, due to other ion species present, but the net effect on the activities of NH4+ and OH− is unclear.

Issues regarding the usual agricultural practice and representativeness of the experiment:

- p.13297, l.23: 111 kg/ha excreted N seems to me quite a high number as this would mean to have about 150 animals fed with cut pasture on one ha for 3 days. Would such a practice be common for feedlots?

Reply: Not in New Zealand, where feedlots are rare anyway. The feed in feedlots would normally be different. The experiment was designed to closely represent grazing practice while being able to estimate feed intake well. An important reason to use a high stocking rate (perhaps unrealistically high, see below) was to create a well-resolvable NH3 signal from the excreta.

On p.13290 it is mentioned that the provision of feed rather resembles feedlot conditions, but the whole experimental design would be more similar to rotational grazing management. I would appreciate to be given some numbers e.g. for average stocking density / grazing period at typical systems in New Zealand or elsewhere in order to classify the experimental arrangement. On p.13300, l.25 the authors compare their results with those from similar former studies and implicitly deem the excretion rate in the present experiment unrealistically high. In that respect it would be good to know for the reader if the smaller excretion rate in the quoted experiments was due to a smaller stocking density or shorter grazing period? This could be an important difference between the experiments, since a higher stocking density and longer grazing periods increase the possibility for urine and dung interaction (being excreted on same spots), therefore increasing the rate of urea hydrolysis because of the interaction of

urinary urea and faecal urease. A few more words about the representativeness and most important implications of the applied stocking rate / grazing duration could put the present experiment into a broader context.

Reply: We agree with the reviewer that the main issue with an unrealistically high stocking density is the increased probability for "double-hits" of excreta, and in particular for urine-dung interaction. We are happy to follow the suggestion to discuss this in the manuscript. We will make two insertions to that effect. In the first paragraph of Section 2.1 it will read: "... For the first three days, 12 non-lactating cattle with average live-weight of 470 kg were kept in the experimental plot. The stocking density represented by this setup (150 animals ha-1) was typical for rotational grazing practice in New Zealand, but the cattle-presence period was 3 to 6 times longer than the feed supply in a real-world grazing situation would normally last. This longer period was chosen so that a sufficient amount of urine and dung was deposited to produce a well-resolvable NH3 emission signal. Implications of the higher excreta density are discussed in Section 4.1." In Section 4.1, we will insert a passage in the 2nd paragraph, after the unchanged sentence "The N excretion rate (urine and dung combined) reported by Bussink (1992; 1994) was typically 40 to 80 kg ha-1, roughly half of that in the present experiment." The new passage is: "The excreta density in the latter was higher because of the unrealistically long period of animal presence. A consequence of this was an increased probability for urine and dung being co-deposited in the same location, which could have increased the rate of urea hydrolysis because of the interaction of urinary urea and faecal urease. This probability can be estimated from the respective numbers of urinations and defecations and the average dung pat size. An approximate count of dung pats, after the cattle had departed, gave N = 445 ($\pm$23). Dung pat size was not measured and is guessed as a = 0.1 m2. Given the fenced surface area A = 785 m2, the dung cover fraction was thus p = N a/A = 0.057. This is the probability for a single urination to occur in a defecation's location (regardless of the timing of both events). For cattle, urination counts are typically about 80 % of defecation counts (Haynes and Williams, 1993; White et al., 2001), which gives an

estimated total of 356 urinations. Using the binomial probability distribution, it results that the most likely number of urine patches being co-located with a dung pat was 20. The occurrence of 20 co-locations would imply that 5.6 % of all urine-N and 4.5 % of all dung-N was potentially subject to interaction with each other. However, even if such interaction altered the volatilisation rate considerably (e.g. doubled it), the effect of that on the total N volatilised would still be small (of order 5 %)." The new passage contains sentences about the dung cover fraction from Section 4.4 in the original manuscript. There, they will be replaced with a reference to the new (earlier) mention.

A second point that might deviate from a normal agricultural situation is the fact that the 5 cm canopy height is likely to favour higher emissions than a similar situation with higher vegetation, as a higher vegetation could, for example, lower the peak surface temperature and intercept some emitted NH3.

Reply: We agree that vegetation height can have these effects. However, in rotational grazing, when the cattle leave after a day or so, the vegetation height is of order 5 cm, so except for Day 1 the experiment provided realistic conditions in this respect.

Further points:

- p.13289, l.1: also soil properties are important

Reply: We agree, this will be added.

- p.13291, l.15: was it then generally observed that the cattle spread evenly to feed on the grass?

Reply: Yes, and after the cattle left, we did a partial survey of dung pat locations, in 4 pie-shaped sectors of the circle (each of 5 % area). The observed dung pat distribution did not differ from a distribution predicted on the assumption of uniform deposition probability everywhere within the circle. We will add a sentence to this effect.

- p.13294, l. 19: the vertical profile of NH3 background concentration is in most cases not height-constant, but rather not very pronounced, therefore it is treated as constant.

It would be more correct to say e.g. "assumed height constant".

Reply: Agreed, the text will be changed accordingly. See also our reply above concerning "clean" background.

- p.13300, l.5: it would be good to have an indication of the durations of the cited experiments in order to get an impression whether mineralised organic N contributed by roughly similar fractions to the NH3 emissions.

Reply: By "organic N" we presume the reviewer is referring to the organic N in dung. For the experiments we cite here, the NH3 emission measurements were of varying duration, but always of sufficient duration to fully characterise and quantify the volatilisation event associated with each type of N-containing substrate (either urine of dung). NH3 volatilisation events following urine deposition are typically of shorter duration than NH3 volatilisation events following dung application. But the numbers we provide here are correct. For the studies we report here, the proportions of urine-N emitted as NH3 significantly exceeded the proportions of dung-N emitted as NH3.

- p.13301-13302: the authors argue that the smaller, second emission peak on day 9 originates mainly from dung emissions and use the pH developments as supporting argument. I agree with that interpretation. One could even go further (as is done in the section 4.4 to derive the crust resistance) and couple the assumed transition between emissions from urine and dung with the respective pH developments. Urine patch pH falls and stays below 7.75 from day 6 on, and dung interior pH exceeds pH 8 around 3 to 4 days after excretion. The dissociation equilibrium predicts rather little dissociated NH3 below pH 7.75, and given that a large fraction of urinary N had probably been volatised in the first 3 days, would it be feasible to estimate the emission source transition not by a sharp step, but pH-dependent transition curve estimates between days 4 and 8? The two approaches probably yield a lower/upper dung emission range.

Reply: This is a good suggestion in principle, but our feeling is that this would go too far into modelling with too many not that well-constrained parameters. (The unknowns

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would include possible mismatches between the pH of the "imported" urine and the in-situ urine, as noted by the reviewer above.)

- p.13303, l.3: Spirig et al. measured high initial volatilisation rates from field-applied slurry and a fast emission decrease, but no parameters associated with urea hydrolysis or pH development were measured. When slurry is applied to fields as fertiliser, urea hydrolysis is usually already completed and the resulting high TAN content, pH, and high temperatures in the field can result in rapid NH3 volatilisation. The reference is appropriate here, but the sentences should be rephrased to avoid confusion.

Reply: Thank you, the sentence will be changed to: "The same is true for surface-applied slurry (Spirig et al., 2010), where the urea hydrolysis is often already completed at the time of application".

- p.13304, l.24: a roughness length of 2 cm seems rather large for a grass canopy of 5 cm height. Mostly, it is more in the order of 1/10 of the canopy height. Was the canopy height outside the circle different? Was the wind profile used for z0 determination disturbed by obstacles (fence, cows,. . .)? Please discuss this briefly, as it may have consequences for the resistance determination.

Reply: The grass had been mown to 5 cm in the fenced circle and in a similar-sized area surrounding the wind profile mast, which included the locations of the experimental dung pats and urine patches. The canopy height "seen" by the wind profile was thus similar to that "seen" by the NH3 sampler profile. We agree that a roughness length of 2 cm appears implausible for 5 cm canopy height. The main explanation for this is that the terrain was not perfectly flat. There were undulations at the decimetre scale, and these contributed to increased roughness. Additional minor contributions may have come from the taller grass outside the mown areas, and from the presence of the cattle (Laubach and Kelliher 2004 estimated, for a cattle herd of similar stocking density as in the present experiment, that the flow-obstacle effect of the cattle would explain a roughness length of about 2 cm.) We are convinced that the roughness length, derived

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from the wind profile, is a correct representation of the flow parameters at the site. Even if that was not the case, the effect of roughness length error on the estimates for the resistances ra and rb would have been minor (in sensitivity tests for a Lagrangian surface-layer model, Laubach and Kelliher 2005 found that $\pm 70\%$ change in roughness length caused only $\pm 15\%$ change in computed emission rates). Besides, for volatilisation from urine patches in dry conditions, the soil resistance dominates over the atmospheric resistances (Laubach et al. 2012), and for volatilisation from dung pats the crust resistance dominates (see present manuscript).

- p.13306, l.23: in the two cases, the Kjeldahl analysis yields a difference between total N and NHx-N of 20 to 100%. This means that in the extreme case, the molar ratio of amines to NH3 was 1:1. The statement on p.13307, l.26 says that a large biased electrode reading could also be provoked by even small amounts of amines. However, the Kjeldahl analysis implies relatively large amine amounts. Another explanation of that difference might be unwanted nitrification of NH4 in the stored sample. The measured non NHx-N could then come from NO3.

Reply: Yes we agree that amines are a tentative explanation for the strange, elevated electrode readings, but we have no direct evidence that amines were actually present in those solutions. We do not know which N species contributed what fractions to the Kjeldahl analyses. We are simply reporting the circumstantial evidence that we have.

- p.13307, l.2: Kuhn et al. differentiated between rumen content, dung, slurry, and hay, but not pure urine. Concluding from that study it is safe to say that rumen juice contains large amounts of TMA posing a high volatilisation (by eructation) potential, and that the emission ratio of TMA:NH3 from stored slurry and dung is much smaller than found inside and in proximity to cattle stables, thus does not explain corresponding high ratios.

Reply: We agree that dung would not explain the presence of high TMA, and said so (p.13307 L.10). We have only indirectly inferred amines as likely candidates for causing

the implausibly high NH3 electrode readings, but no direct evidence of their actual concentrations. Our discussion must therefore remain qualitative and, unfortunately, somewhat inconclusive.

- p.13308: I understand the authors' decision to concentrate on NH3 emissions in the present paper. However, estimates of TMA or amine emissions from agriculture (even if unintended) are extremely rare. I am not aware of any study dedicated to amine emissions from grazing cattle. The authors have in a way calibrated the electrode for TMA using the TMA-HCl standard . Given the difference between electrode and alternative method could be consistently attributed to TMA - so far known to dominate agricultural amine emissions -, wouldn't it be possible to derive a rough (differential) estimation of the potential TMA emissions?

Reply: The problem with this suggestion is that TMA and NH3 equilibria in the electrode solution would affect each other and a simple differential estimate would very likely be incorrect. To follow the reviewer's suggestion empirically, one would need to make some samples containing known amounts of TMA, as well as some with NH3 and TMA combined, and determine the electrode's response to such mixtures. Our first attempts at doing so, three months after the completion of the trial, were frustrated by very significant instrument drift. To do the sort of assessment suggested by the reviewer would require an electrode that was "well-behaved", and much more time than we had available to conclude this study.

Technical corrections:

- p.13297, l.5: a word is missing

Reply: No, that is a misunderstanding, because the reviewer probably interpreted the parentheses to separate a comment from the main sentence. However, the parentheses were intended as mathematical symbols, to indicate "minus" operation executes before "times" operation. To avoid this ambiguity, we will reformulate: "The amount of dung excreted can be estimated as a fraction of DM intake, where the fraction equals

100% minus digestibility."

References:

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Laubach, J., Taghizadeh-Toosi, A., Sherlock, R. R., and Kelliher, F. M.: Measuring and modelling ammonia emissions from a regular pattern of cattle urine patches, Agricultural and Forest Meteorology, 156, 1-17, 2012.

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Please also note the supplement to this comment: http://www.biogeosciences-discuss.net/9/C6267/2012/bgd-9-C6267-2012-supplement.pdf

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