Biogeosciences
Discussions

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

Anonymous Referee #1

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This paper presents results from a 12 day experiment to determine NH3 emissions from a circular pasture of about 800 m2 grazed for 3 days by 12 cattle. It is related to the publication of Laubach et al., Agricultural and Forest Meteorology 156, 1-17, 2012, and the main methodology is similar here. The vertical horizontal NH3 flux profile was measured by so-called Leuning samplers in the centre of a circular plot in order to apply the integrated horizontal flux (IHF) approach for emission determination. Feed (cut pasture) uptake was controlled and feed nitrogen content and other parameters were measured to describe the N intake and to relate measured NH3 emissions to the estimated excreted N amount. A bimodal emission course was observed, and with the help of control urine and dung patches and associated pH the authors attempt to distinguish between NH3 emissions from urine and dung. Finally, a simple flux resistance model is inferred and the resistance of the dung crust towards NH3

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emission is estimated.

General comments:

The presented paper is of scientific relevance because there is relatively scarce information on NH3 emissions from grazing cattle directly evaluated under agricultural field conditions. As cattle husbandry is responsible for a significant fraction of the unwanted and generally large agricultural NH3 release it is essential to experimentally discriminate between volatilisation pathways. Deriving information to further confine and explain such emissions is a valuable contribution to the community and fits into the scope of BG. The paper is well structured and written in concise and proper language. Applied methodology is used in an appropriate setup to address the research questions. A unique feature is the indirect distinguishing between emissions from pasture fractions exposed to dung and urine, respectively. The findings are well discussed and literature is sufficiently considered. Overall I recommend to publish the manuscript in BG with minor revisions addressing issues outlined in the following.

Specific comments:
Methodological remarks and questions:

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

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

- 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.

- 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.

- 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?

- 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? 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?

- 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.

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? 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. 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 NH_3.

Further points:

- p.13289, l.1: also soil properties are important
- p.13291, l.15: was it then generally observed that the cattle spread evenly to feed on the grass?
- p.13294, l. 19: the vertical profile of NH_3 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".
- 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 NH_3 emissions.
- 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 NH_3 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

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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.
- 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 NH_3 volatilisation. The reference is appropriate here, but the sentences should be rephrased to avoid confusion.
- 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.
- 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 NH_3 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 NH_4 in the stored sample. The measured non NHx-N could then come from NO_3.
- 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:NH_3 from stored slurry and dung is much smaller than found inside and in proximity to cattle stables, thus does not explain corresponding high ratios.
- p.13308: I understand the authors' decision to concentrate on NH_3 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

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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?

Technical corrections:

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