

Interactive comment on “Determination of field scale ammonia emissions for common slurry spreading practice with two independent methods” by J. Sintermann et al.

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We thank the referees for their careful evaluation of the manuscript and their constructive comments. In the following, we address all comments of all three referees individually and indicate the corresponding revisions in the manuscript.

Anonymous Referee 1

Specific Comments

(1.1) Sections 2.1.2 and 2.1.3: What is the accuracy of the FTIR, and is it path-length

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dependent? What is the accuracy of the background instrument (Picarro)? Together, these determine the accuracy of upwind-downwind concentration differences fed into WindTrax.

»Response: Concerning the Picarro instrument, we added the following information in Section 2.1.3: "The accuracy was estimated to 10%. In a side-by-side intercomparison with the HT-CIMS on the field under background conditions, absolute deviations were generally below 2 ug/m³." Concerning the FTIR instrument: The accuracy of the FTIR is path-length dependent. For the used configuration it was estimated to ≤10% (this value was added in Section 2.1.2). Unfortunately an empirical check in the field by direct inter-comparison with the Picarro or other point sampling reference instruments in the field was not possible. During background phases (no slurry emissions) the ambient concentrations were mostly below the detection limit of 15 ug/m³; and during emission phases, the path integrated FTIR concentrations were not directly comparable to point measurements. Due to the generally larger downwind concentration and the higher detection limit of the FTIR, the uncertainty of the downwind-background concentration difference is supposed to be dominated by the FTIR measurement.

(1.2) p.2642 L5: Table 2 is mentioned before Table 1, they should be swapped.

»Response: done

(1.3) p.2642 L19: "FAO, ISRIC and ISSS" is not in reference list.

»Response: is now included

(1.4) Section 2.2: Were background readings compared between the various NH₃ instruments? This is important because the background is measured with a different instrument type.

»Response: There was a period of side-by-side measurements by the HT-CIMS and the cavity ring-down analyser a few days prior to and some days after the fertilisation where the measurements agreed with maximum concentration differences of around 2

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ug/m³. The limit of detection of the FTIRs was too high to determine the background NH₃ levels which ranged between about 3 and 15 ug/m³. We modified the text as detailed above in Comment (1.1).

(1.5) Section 2.3.1, 2nd paragraph: The comments on flux divergence and footprint are all correct. This makes for a very complex data analysis. I wonder what accuracy should be expected from that?

»Response: In our opinion, the accuracy of such complex experimental methods (for the field scale) can only be assessed by intercomparing results with independent methods, as presented in the Results section (Figs. 7-9).

(1.6) Eq. (1): May I suggest to replace "FP" by a single-letter symbol (not "F"), for a clear distinction between footprint terms and flux terms.

»Response: We agree; "FP" is replaced by the greek "Phi"-Symbol.

(1.7) Eq. (2): Please explain the rationale for the bi-exponential approach (why two decay processes?). It is done later (p. 2659), but one sentence here would help. Was a simple exponential fit found to produce poor results?

»Response: The description of the temporal dynamics of the slurry emission was primarily an empirical approach here. The choice of the function type was based on expert judgement (visual inspection) of the measured data and on the goodness of fit. As outlined, the choice of the bi-exponential function was furthermore supported by previous flux measurements at the Oensingen grassland site (Spirig et al., 2010) roughly suggesting a temporal emission behaviour in exponential to bi-exponential form. In principle, a simple exponential or a Michaelis-Menten (see Sogaard et al., 2002) function could as well serve to describe emissions. However, especially at the event on 6 August, the bi-exponential function was clearly better suited as a parameterisation of the track emissions. The use of a function containing two decay process as well goes along with the explanation provided in the Discussion section. For clarification we

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modified/amended the text in Section 2.3.1 as follows: "In the present study, supported by visual inspection of the measured fluxes, we used a bi-exponential decay function (for a discussion of possible related processes see Sect. 4.3) with a total of four fittable parameters as course of $F_{volat}(t)$..."; "The choice of the specific function for the course of F_{volat} will be justified by good correspondence of fit and measurements."

(1.8) p.2649 L20: What is c at 20 m a.g.l. needed for, since upwind concentration was measured separately?

»Response: The remark is justified. The F_{mi} calculation was repeated using the background concentration measured by the cavity ring-down instrument assuming a constant vertical background NH₃ profile. The method section is changed accordingly and the results given in Table 3 are updated, but do not change significantly as the concentration gradient and hence the flux is largely determined by $c(z_0')$, which is not significantly influenced by the background NH₃ concentration. The related discussion is kept as it was.

(1.9) Section 3.1: The crop area treated on 4 Aug is upwind of the grass area treated on 6 Aug. Fig. 1 suggests that the background instrument was upwind of both areas, on both days. How can you be certain that the crop area did not contribute to the NH3 fluxes measured on 6 Aug? Sure, you observed a decline in the evening of 4 Aug, but NH3 emissions will increase again the next day(s) as temperature rises.

»Response: The position of the background measurement (cavity ring-down instrument) was actually moved on 6 Aug from the first position upwind of the cropland to a second position between both fields (directly upwind of the grassland). In this way the background measurement accounted for remaining emissions from the cropland field. We added this second position in Fig. 1 and adjusted the text in Section 2.2 accordingly. However, it has to be noted that already on the 5 Aug, concentrations on the cropland field had strongly declined (to c. 20 ug/m³) and were even lower on the following day. Thus there was only a very minor influence on the background concentration

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for the grassland field emission.

(1.10) Section 3.1, last sentence: *Can you explain how the F_{ini} values relate to Fig. 4. They are about twice the peak values shown there. Are they just hypothetical fitting parameters? What happens before the peak is reached?*

»Response: Indeed the F_{ini} values are fitting parameters of the bi-exponential functions and represent the (footprint-corrected) emission of the slurry at $t=0$ (immediately after application). In contrast, the values in Fig. 4 are directly measured EC fluxes, which are not yet footprint corrected and averaged over 10 minutes. Both the time averaging (time lag) and the lacking footprint correction lead to the lower value of the measured fluxes.

(1.11) p.2651 L20-21: '6%, 6% and 22%', etc: *percentages of what?*

»Response: These percentages are deviations between fitted and measured FTIR concentrations, which is now stated explicitly in the text. The according statement in Sect. 3.1 was also clarified.

(1.12) Section 3.4.1, *"The bLS model was used... matched within 10way to use WindTrax, and the result is encouraging. Just note that, hypothetically, if an EC bias and a WindTrax bias were present and cancelled each other, that would go undetected!"*

»Response: We agree with the referee that hypothetically cancelling errors could occur and would not be detected. However this is an intrinsic problem of all micrometeorological flux measurement methods, since usually no absolute reference or calibration for field-scale fluxes is available. Therefore constraining the uncertainty of such method by intercomparison with other independent methods (and models) is common scientific practice. However, there is additional confidence in the accuracy of the used models provided by other (independent) studies reported in the literature (see references in the manuscript).

(1.13) Section 3.4.1, end of first para and Table 5: *It is a bit misleading to take a*

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regression slope directly as a measure of relative error when there is a significant intercept present (unless the intercept represents a known source of bias, in which case it should be corrected for first). Linear regression also gives the largest weight to the largest values. A better test would be to take the ratio of the two methods for each run and then give the mean and SD of this ratio (and its trend over time, if one exists).

»Response: We agree with the referee that the quantification of uncertainty was not adequate. However, the solution suggested by the referee would in turn put too much weight on the lowest values (because they could show large deviation of the slope (ratio) even for very small absolute deviations), which are not very relevant for the quantification of total ammonia emission here. As an improved solution we now describe the uncertainty estimated from the deviation between the two measurements by two values: 1) the deviation of the regression slopes from the 1:1 line representing a systematic relative effect and 2) the root mean squared error (RMSE) of individual points from the regression line indicating a non-systematic absolute error similar to a detection limit. The full uncertainty then can be quantified as combination of the two effects. Accordingly, the calculation of the regression lines in Fig. 9 and the corresponding results in Table 5 have been changed. As a consequence, the corresponding values in the manuscript are adjusted to the new evaluation (with no major quantitative changes) and the text in the Abstract and Sections 3.4.1, 4.2, and 5 is modified accordingly.

(1.14) Section 3.4.1, last 3 sentences and Fig. 10: *This is an interesting test, but deviations from the 1:1 line could be caused by any of the following: bias of the EC flux correction, bias of WindTrax, or bias of the footprint model used to relate EC flux to surface emission rate. So, to really arrive at the desired conclusion about EC flux bias, one would need to show independently that WindTrax and the footprint model were consistent with each other.*

»Response: We agree with the reviewer that this would be desirable, but testing the consistency between a flux footprint model and a concentration footprint model (like WindTrax) at least requires additional model adjustments and is beyond the scope

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of the present study. For the evaluation and comparison of different types of diffusion-transport model we refer to the corresponding literature (e.g. Kljun et al., 2003). On the other hand it is an intrinsic problem that field-scale (micrometeorological) flux measurements include model components and cannot be validated directly because usually no reference flux is available. Therefore it is common practice to approximate the uncertainty of such complex methods by inter-comparison with other independent methods on the same spatial scale (see also Comment 1.12).

(1.15) p.2656 L10: *"to more than 50%": why not give the actual maximum error? "More than" can be anything.*

»Response: 50% is replaced by 76% as the largest uncertainty given in Milford et al. (2009).

(1.16) p.2658 L7, *"fetch... quite small that day": Fig. 1 gives the impression that on both days the FTIR paths were along the downwind edge of the slurry strips, and that the strips all had similar lengths, so why would the fetch on 6 Aug have been shorter?*

»Response: The wind direction on both days was not exactly along the strip orientation but was shifted towards east (see Fig.1). Therefore the FTIR line concentration measurements were also partly influenced by the easterly neighbouring field. This had a larger relative influence at the grassland field, because the FTIR path was shorter. For clarification we changed the text as follows: "...because the relative influence of source areas outside the fertilised field (due to easterly wind components) were larger for the short FTIR path on that day, producing a smaller effective fetch for the line concentration measurement (see Fig. 1)."

(1.17) Section 5, 2nd para: *Does the result of the methods comparison lead to a recommendation? Is EC to be favored because it is more accurate? Or is either method OK, provided the accuracy of the instrumentation is good enough? Is it possible to give guidance what accuracy would be required, for either method?*

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»Response: We modified the conclusion text to clarify that we attribute the observed difference between the two methods in our experiments predominantly to the bLS/FTIR method based on the consistency test with the impinger concentrations. However, we think that a general recommendation for one method cannot be derived from experiments at one single site and with one specific application. In practice (like in our case) the choice of method is often constrained by the availability of instruments, know-how, and the type of field site and scientific question. A broader discussion of different methods for slurry emission measurements is presented in another paper submitted to the Special Issue "Nitrogen and global change" in Biogeosciences.

(1.18) Section 5, end of 2nd para, *"very small contributions on the subsequent day": Better replace "very small" with "less than x%". Do the authors have any proof how small the emissions were then, or is this just an assumption? If the latter, then this should be removed from the Conclusions.*

»Response: The sentence is modified: "... with contributions $\leq 1\%$ loss of TAN on the subsequent day". As stated in Sect. 3.3 the EC/HT-CIMS system had measured the NH₃ emissions over the next day following the fertilisations.

(1.19) Section 5, para beginning with "Generally,": *Not only must the instrumentation be fast and accurate enough, but it seems that one also requires a rather complex analysis of footprint geometry and decay evolution, which makes it next to impossible to develop a "routine" procedure. In other words, one needs 1) expensive instruments, 2) a lot of expertise, and 3) many scientist-hours, to obtain the emission rates for a single slurry spreading. Do the authors see a way forward to reduce any of the requirements 1) to 3)?*

»Response: We agree with the referee and consider that as the major experimental challenge for the next few years. We added a corresponding statement in the Conclusion section. "For both methods applied here, the analytical instruments are relatively expensive and need a high level of maintenance in the field. Thus an important fu-

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ture challenge will be to establish either of the two methods with easier-to-use (and cheaper) analytical instruments. For the bLS method, also point concentration measurements instead of open-path line measurements could be used. However, a high temporal resolution (about 15 min or better) is necessary for properly evaluating the temporal dynamics."

For favorable situations with constant meteorological conditions (wind speed, stability, wind direction) and constant source area geometry, we are positive that reliable flux estimates with a precision in the order of 30% can be done using an automated impinger sampling system in combination with an ultrasonic anemometer using WindTrax to calculate the fluxes. Our analysis shows a good correspondence between the impinger and EC approach.

(1.20) Table 3: Are the huge numbers in Rows 2-4 of the τ_2 column correct? If so, what do they mean?

»Response: These large numbers are the result of the fitting procedure, signifying that the respective emission courses rather resembled a simple exponential function with an approximately constant offset (on 4 August for $F_{volat, FTIR}$). This issue is addressed in Sect. 3.3 (p.2652).

(1.21) Fig. 5: Do the short-term fluctuations of the fitted curves (red lines) represent changes in footprint contributions due to wind direction fluctuations? Please explain in the text.

»Response: Yes, they do. On p.2651, L.1 we add: "The temporal fluctuations of the fitted fluxes represent changes in track footprint contributions influencing the flux at the EC location (see Fig.4). Associated with a less constant WD, the fluctuations were stronger on 6 August."

Technical Comments

(1.22) p.2639 L16: remove "the" before "both". p.2654 L2: dito.

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»Response: done

Anonymous Referee 2

(2.1) WindTrax also is capable of calculating emissions using single concentration of one point to calculate emission rate, which might be worth to look at the difference of at this point of view to thoroughly understand the performance of these two techniques under a more comparable footprint area.

»Response: We agree that the bLS/FTIR method used here in principle is equally applicable to point concentration measurements. The results of the "forward" WindTrax modelling presented in Fig. 9a and Fig.10 show that point concentrations would probably give good results in "backward" flux calculations, too. However, for taking into account the complex footprint, a function for the temporal development (e.g. bi-exponential) has to be assumed and thus a certain number of concentration points (high temporal resolution) is necessary to perform the fitting procedure. This is a problem e.g. for the impinger measurements usually integrating over 1 hour or longer. Instead, the FTIR yield a temporal resolution of 2 min with reduced fluctuations due to the line integration. We added a corresponding statement in the Conclusion section (see Comment 1.19).

Anonymous Referee 3

Specific comments.

(3.1) p. 2638 L. 13. It would be appropriate to refer to Sogaard et al. (2002) here, as this gives an overview of measured NH₃ emission fluxes from slurry.

»Response: We now cite Sogaard et al. (2002) as this paper refers to the ALFAM database and shows some measured cumulated emissions (slurry applied by trailing hose, injection). Note, that some of the other cited studies at p. 2638 L. 13 are already contained in the ALFAM database.

(3.2) p. 2640 L. 9. It would be nice if some information would be given on possible

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adsorption of NH₃ to the tubings.

»Response: The paragraph is slightly edited and re-structured in order to better indicate that the long 1/2" PFA inlet tube, heated to 150°C belonged to the HT-CIMS EC setup (characterised in Sintermann et al., 2011) in which a strong heating minimised the negative influence of NH₃ adsorption at inner surfaces on the measurement time resolution, thus facilitating EC flux measurements whereas the remaining amount of high-frequency attenuation was quantified and corrected for.

(3.3) First there is referred to Table 2 and after that to Table 1. The order of the Tables should therefore be changed.

»Response: done

(3.4) p. 2642 L. 20. A remark should be made on whether a splash plate is a device that is normally used to spread slurry in Switzerland (in many countries this technique is forbidden).

»Response: We added a corresponding remark: "...with splash plate. This is currently the most common slurry spreading technique in Swiss agriculture."

(3.5) p. 2646 equation (2). Mention why you have chosen the bi-exponential decay here.

»Response: A further explanation has been introduced; see response to referee1 (Comment 1.7)

(3.6) p. 2650 L. 20. It should be motivated why the median NH₃ concentration for the period June to September was taken as a background concentration and not the actual background concentration.

»Response: This calculation and its description has been changed. The background concentration measured with cavity ring-down is now used for the calculation; see response to referee1 (Comment 1.8).

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(3.7) p. 2650 L. 2. It would be nice if the equation for the surface temperature would also be given.

»Response: The equation for temperature is fully analogue to Eq.7, using air temperature at one height and the sensible heat flux to derive surface temperature. We think that, although we use (and show: Table 3) the calculated surface temperature, Eq.7 is sufficient to introduce the general concept. The equation for surface temperature is not central for the paper and therefore we do not think it is necessary to add it to the manuscript.

(3.8) p. 2662 Conclusions. It would be nice if some conclusions could be drawn on the advantages/disadvantages of both methods that also include some notes on how easy they are to work with in the field.

»Response: We added some sentences about that question in the Conclusions sections (see responses to Comments 1.17 and 1.19).

Interactive comment on Atmos. Meas. Tech. Discuss., 4, 2635, 2011.

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