Review on manuscript acp-2016-197 by Richter et al.

« Surface-atmosphere exchange of ammonia over peatland using QCLbased eddy covariance measurements and inferential modelling »

General comments

This manuscript presents the results of a 2.5 month long ammonia flux measurement campaign over a peatland with an eddy covariance method implementing a new inlet system intended to reduce aerosol and henceforth water interactions with ammonia on tube walls, a limiting issue for flux ammonia measurements by eddy covariance with quantum cascade laser until now. The authors show quite convincingly that the new inlet system is adapted for NH_3 flux measurements by Eddy Covariance but recognise a potential bias due to evaporation of NH_4^+ from small aerosols in the heated line which they estimated to be lower than 21% on the concentration but did not give an estimation on the flux uncertainty. The dynamics of the measured ammonia concentration and fluxes are analysed in terms of correlation with meteorological conditions and discussed with regards to the influence of nearby farms and ecosystem functioning. They investigate the relationship between NH_3 concentrations and fluxes but without using the useful framework of resistance modelling, which they use only for estimating the cumulated ammonia deposition.

This manuscript reports thoroughly designed and conducted experiments and is to my knowledge a unique reporting of continuous NH_3 flux measurements by eddy covariance over such a long period. The analysis and discussion of the flux and concentration dynamics is interesting but lacks overall quantification of the emission potential and surface resistances. Moreover, the analysis would be greatly improved by better discussing the flux uncertainties and analysing the hourly dynamics of the deposition velocity rather than the flux which is concentration dependent. In my opinion, this manuscript could be greatly improved by answering the following issues, prior to publication:

- The quality of the flux measurements which is critical due to the novelty of the inlet system is however difficult to figure out completely for the reader. The way the time lag is calculated is not completely clear in the current manuscript, and the lag is an essential parameter in the flux which could change its magnitude by a large fraction, especially with noisy signals. It would be good to show some covariance peaks and may be the dynamics of the lag (in a supplementary material section?). Similarly, a median value of the high frequency damping factor is given without much details, nor discussion and comparison to previous literature (Ferrara et al., 2012;Whitehead et al., 2008). I would suggest showing the dynamics of the high frequency damping (it could be a box plot of hourly values for instance). The random uncertainty is also given as a 15% estimate, but there are some methods to evaluate the uncertainty in the flux, which are especially designed for fluxes with large instrumental noise. I would suggest to get example on Langford (2015), and to report flux detection limit. Some of these methods can be turned on in EddyPro, so this should not represent too much work.
- The analysis of the correlation of the fluxes with the meteorological conditions is quite instructive but lacks a deeper insight into the surface exchange parameters. Indeed, a first essential test is a comparison of the deposition velocity $V_d(z)$ with the maximum deposition velocity for ammonia $V_{dmax}(z)$, which represents the maximum transfer rate and can simply be evaluated as $(R_a(z) + R_b\{NH_3\})^{-1}$, where $R_a(z)$ and $R_b\{NH_3\}$ are the aerodynamic and boundary layer resistances for ammonia, respectively (e.g. (Loubet et al., 2012)). Similarly, analysing the statistics of the deposition velocity would probably give more insight into the exchange processes than the ammonia flux because of the large variability of the atmospheric concentration which is influenced by the local sources. An analysis of the daily variations of the deposition velocity would be very instructive. This would especially be helpful for understanding the links between Figure 9 and 10, which is not clear in the current manuscript.
- The resistance analogy would also be very helpful to better evaluate the surface emission potential $\Gamma(z_0)$ and its dynamics. Indeed the canopy compensation point could be estimated as $C_c = F_{NH3} \times (R_a(z) + R_b\{NH_3\}) + C_{NH3}(z)$, and the emission potential retrieved from that using the thermodynamical gas-to-liquid and acid-base equilibrium constants. See Sutton *et al.* (2009), Loubet *et al.* (2012) or Personne *et al.* (2015). The compensation point could be also estimated by analysing daily flux versus concentration relationships (similar to Figure 10 but for each day). This would ease a lot the understanding of the seasonal evolution of the ammonia flux, and its relationship with ecosystem functioning. It will as well help controlling the quality of the flux measurements.
- In a complementary analysis, surface conductance (g_c, the inverse of the resistance R_c) could be estimated (assuming a zero emission potential in the canopy under deposition conditions) based on

$V_d(z)$ and $V_{dmax}(z)$. Indeed, then $g_c^{-1} = V_d(z)^{-1} - V_{dmax}(z)^{-1}$ (Massad et al., 2010). This would withdraw part of the influence of u_* on the exchange dynamics, which is embedded in $V_d(z)$, and hence better show changes in ecosystem exchange parameters, and especially cuticular exchange.

- Figure 10 puzzles me for several reasons, but I might not have understood correctly how it was built:
  (1) I cannot figure out why the modelled flux is smaller than the measured one with a constant offset (in Fig 10-right), while it shows larger values in Figure 11 at the beginning. I also interpret a constant offset as an additional pathway with a constant flux, but cannot reconcile this with the model of Massad *et al.* (2010) as used here.
  (2) I cannot understand why no intercept (flux crossing the zero line) can be seen in Figure 10(left) while in Fig 8 we see negative $V_d(z)$. It is probably due to the separation between emission (Fig10. Right) and deposition (Fig10. Left) fluxes. The authors should clarify how Fig. 10 is constructed. Especially important would be to show some dynamics of the daily flux and concentration with emissions. Currently only averages are shown (except for Vd(z)) and no emissions can be seen except in Fig. 6c and in the error bars of Fig 6a. An example of daily dynamics would be most helpful.
- The authors should also discuss further, based on more quantified surface parameters, whether the flux is linked to a surface compensation point or some other features. Especially, the magnitude of the advection fluxes should be evaluated. Indeed, if the NH3 concentration peaks of up to 85 ppb are due to concentration advected from nearby farms and agricultural activities, advection fluxes can be expected to be large. To evaluate these a footprint model could be used, the advection fluxes would then be the footprint of the farm (or fields spread with organic manure) multiplied by the source strength of these, which could be evaluated by a simple emission factor analysis. This would allow evaluating whether advection is an issue or not. I would suggest the authors to look at (Hensen et al., 2009;Loubet et al., 2009).

Detailed comments

- Section 2.1: The ground pH and NH4+ are important parameters for interpreting NH3 fluxes. Were any of these measured? If so, they should be reported.
- P3L29: The authors should rather use “mixing ratio” rather than concentration. Also are these expressed per mol of dry air or per mol of ambient air? Please discuss this point as this makes a difference in the flux calculation which should be done with mixing ratio per mol of dry air (Gu et al., 2012;Kowalski and Serrano-Ortiz, 2007). Especially important is the dilution effect due to water.
- P4L30. What is the inlet box size? Could you discuss briefly the potential impact on the flux measurements?
- P5L7-12: The way the two time-series were shift is not sufficiently detailed here. Especially, could the authors explain how the expected time lag was chosen? Also, it would be important to show that this procedure did not strongly affect the flux. Could the authors please discuss this point further? The authors may consider adding a graph showing several covariance peaks for emission and deposition conditions.
- P5L15-20. Please give more details on the damping factor and how it evolved during the campaign. Some additional graphs could be proposed in a supplementary material section.
- P5L20-23. The uncertainty on the flux is critical for NH3 which is not a routine measurement. I suggest taking example on (Langford et al., 2015) and related references for computing the error on the flux and evaluating the flux detection limit.
- P5L29: Clarify if gap-filling was also performed for NH3 and if so how.
- P6L6: Be careful that R_a is a function of the measurement height z. Consider using the notation $R_a(z)$.
- P6L7-12: The parameters of the Wesely model should be given here: the minimum resistance and the response to radiation.
- Section 3.1: Since the local farms and agricultural fields play an important in the interpretation of the mixing ratios.
- P7L27-28: This sentence is unclear. Please rephrase.
- P7L33-34: The work of Flechard *et al.* (1999), Wu *et al.* (2009), and Burkhardt et al. (2009) should be mentioned here.
- P9L1-5. Could you be more quantitative here? Are the levels comparable with Duyzer (1994)? What is the amount of NH_3 received in this study? What would be the ecosystem compensation point predicted by Massad *et al.* (2010) with this deposition? Please also discuss this issue with reference to Wu et al. and Burkhardt et al.

- P9L12: It is difficult to see a change on Fig. 8. Please consider re-graphing this figure.
- P9L17: A shift of the stomatal compensation point could be evaluated by retrieving the daily compensation point as explained in the general comments. Two methods are possible:
- P9L19-20: The data on wet to dry deposition are not shown here. Please consider adding these to the supplementary material or at least giving numbers to support the sentence.
- P9L21-33 and P10L1-5: Showing the maximal exchange velocity $V_{dmax}(z) = (R_a(z) + R_b\{NH_3\})^{-1}$ would be important to show the plausibility of the flux. Moreover, you can then calculate the canopy resistance R_c or the canopy conductance g_c as $g_c^{-1} = V_d(z)^{-1} - V_{dmax}(z)^{-1}$, during deposition periods (especially at the start of the campaign). This would probably better show the dynamics of the ecosystem exchange parameters, together the surface emission potential $\Gamma(z_0)$ which could be estimated from the canopy compensation point $C_c(z_0) = F_{NH3} \times (R_a(z) + R_b\{NH_3\}) + C_{NH3}(z)$, with the relationship $C_c(z_0) = \Gamma(z_0)\times10^{-3.4362 + 0.0508\, T\{z0 \text{ in } °C\}}$. This will probably help understanding the surface exchange dynamics and also test the plausibility of the flux and concentration measurement as C_c should remain positive.
- P10: This study on the parameters influencing the ammonia exchange would benefit from being made on the deposition velocity which would less depend on the variable atmospheric concentration.
- P10L7: explicit the term α.
- P10L28: Vd would be indeed good to show together with the flux!
- P10L29-33: The daily evolution of the flux with decreasing deposition or even small emission around noon and deposition at night could be a consequence of a stomatal or ground compensation point which evolves following the daily surface temperature ($T(z_0)$) pattern and is much larger at noon than during the night. This explanation also reconciles the observed dependency of the flux to u_*, observed both during day and night (Fig. 9): indeed, the surface temperature $T(z_0)$ will increase with increasing u_* at night with clear sky due to better mixing and hence less radiative cooling. During the day, the increase of surface temperature is mostly linked with incoming solar radiation and peaks at the same time as u_*.
- P11L2-4: Indeed. V_{max}(z) is a measure of this exchange velocity and comparing $V_d(z)$ with $V_{max}(z)$ would easy this discussion.
- P11L5-15; I cannot figure out how to interpret this Figure. I would suggest the authors to try showing the same relationship without separating emissions and depositions to show whether there is or not a compensation point and try to evaluate it. It would be interesting to try to build a figure for some representative days based on 30-min data and see whether the change from deposition to emission appears at a given concentration (the definition of the compensation point).
- I can imagine that the advection indeed could indeed lead to such dependency. But it would then be interesting to evaluate the potential for advection based on a simple footprint model such as Kormann and Meixner (2001), which is available as an excel spreadsheet (Neftel et al., 2008). If you just multiply the value of footprint of the surrounding agricultural field or farms by an estimated magnitude of the NH_3 fluxes there, you could evaluate the potential effect of the advection on your flux. See also in Loubet *et al.* (2009) and in Sutton *et al.* (2009) for a discussion on advection.
- Section 3.3: Indeed, it is likely that the cuticular resistance may be overestimated in Massad et al. (2010), as was also found by Loubet et al. (2012) and Personne et al. (2015). However I cannot figure out how to reconcile Fig 10 which shows globally larger deposition fluxes by the model and Fig 11 which shows larger measured deposition fluxes overall. This probably comes from the averaging procedure which splits emissions and deposition in Fig. 10.
- Moreover it would be very instructive here to have comparison of daily dynamics of the modelled and measured flux. This would also allow testing hypothesis with the model, as for instance diminishing R_w, or adding a compensation point and compare to the observations. Fig. 6 could for instance be duplicated and compared with the model flux or alternatively some example days could be chosen.
- P11L29-30: As mentioned above you should show the inferred R_w from night time measurements together with R_a and R_b or alternatively $V_{max}(z)$ and g_c.
- P12L1-2: Please show data from the Delta denuders (in a supplementary section?) or at least give range of concentrations.
- P12L8-9: Please explicit how you extrapolated to the entire year?
- P13L2: You mention in the conclusion the long term stability of the QCL but none was said about it in the manuscript. Either consider withdrawing from the conclusions or add a discussion in the manuscript.

Tables

- Table 1. Table and Figure legend should be self-standing: Please explain what are c_{NH3}, Ta, P, Rn, SD and what the overbars mean. It may also be useful for interpreting graphs (Fig. 6) or statistics to include the number of points per period.
- Table 2. Explain on what variable was the Kruskal-Wallis test made (the NH_3 flux?). It would also be very helpful to do this test on the deposition velocity. But the authors could also consider doing it on the canopy compensation point $C_c(z_0)$, the emission potential $\Gamma(z_0)$ or the canopy conductance g_c. Pleasealso explicit what are "p-value" and "Post-Hoc" in the legend

Figures

- Throughout the text and legends change concentration for mixing ratio.
- Consider adding a Figure with the map of the field and the surrounding including farms and agricultural fields
- Figure 1. It would be helpful to add the heights and the tube length. Also explain or show how are the bypass and "Particles out" channels connected to the pump. Consider also adding the pressure and flow rates on the Scheme. Explicit AC and QCL in the legend.
- Figure 2. I would suggest showing the fitted co-ogive and show explicitly how the frequency damping is evaluated, like in Ammann (2006). Also adding a graph which shows how this frequency damping evolves with time would be very useful. The temperature co-ogive does not see to stabilise completely to 1 at large frequency (we expect from the graph that it may continue growing a bit at larger frequency). Please comment on that in the text.
- Figure 3. This is a very nice graph. It would be helpful to add legend on the right hand side.
- Figure 5. Why splitting the wind direction in periods and not the NH_3 mixing ratio wind rose? Here the map of the surrounding would be much needed to help understanding the NH_3 wind rose.
- Figure 7. How do you explain the afternoon peak in NH_3 mixing ratio. May be I missed it in the text.
- Figure 8. This figure is hard to read. Please consider using lines, a smaller height for the graph and also consider showing additional graphs (as for example in Langford et al. (2009)) of the main drivers (u_*, Ta, RH, Rn,…). This would ease the discussion and help the reader making his mind on the dataset. Also very important in Figure 8 is to add on the same graph window $V_{max}(z)$.
- Figure 9. Consider adding Rn > 20, Rn < 20 and all as legends of the graphs on the graphs themselves. What are the percentage meaning on the top of the graph? Also consider making a similar graph for $V_d(z)$.
- Figure 10. This figure needs clarification, and it might be better not to separate emissions and depositions periods. One would expect a compensation point to appear then. Also consider showing half-hourly data instead of pooling. Moreover one would expect pooling to also give horizontal overbars. Also consider showing specific example for one some days with different behaviour : I would expect Period 1 to be like actual Fig 10 left but period three to show a compensation point.
- Figure 11. Before showing daily averages, it would be good to show daily variations. This could be done over a shorter period or using averages as in Figure 6. Consider showing these in the supplementary material.

References

Ammann, C., Brunner, A., Spirig, C., and Neftel, A.: Technical note: Water vapour concentration and flux measurements with PTR-MS, Atmospheric Chemistry and Physics, 6, 4643-4651, 2006.

Burkhardt, J., Flechard, C. R., Gresens, F., Mattsson, M., Jongejan, P. A. C., Erisman, J. W., Weidinger, T., Meszaros, R., Nemitz, E., and Sutton, M. A.: Modelling the dynamic chemical interactions of atmospheric ammonia with leaf surface wetness in a managed grassland canopy, Biogeosciences, 6, 67-84, 2009.

Ferrara, R. M., Loubet, B., Di Tommasi, P., Bertolini, T., Magliulo, V., Cellier, P., Eugster, W., and Rana, G.: Eddy covariance measurement of ammonia fluxes: Comparison of high frequency correction methodologies, Agric. For. Meteorol., 158, 30-42, 2012.

Flechard, C. R., Fowler, D., Sutton, M. A., and Cape, J. N.: A dynamic chemical model of bi-directional ammonia exchange between semi-natural vegetation and the atmosphere, Q.J.R. Meteorol. Soc., 125, 2611-2641, DOI 10.1002/qj.49712555914, 1999.

Gu, L., Massman, W. J., Leuning, R., Pallardy, S. G., Meyers, T., Hanson, P. J., Riggs, J. S., Hosman, K. P., and Yang, B.: The fundamental equation of eddy covariance and its application in flux measurements, Agric. For. Meteorol., 152, 135-148, 10.1016/j.agrformet.2011.09.014, 2012.

Hensen, A., Loubet, B., Mosquera, J., van den Bulk, W. C. M., Erisman, J. W., Daemmgen, U., Milford, C., Loepmeier, F. J., Cellier, P., Mikuska, P., and Sutton, M. A.: Estimation of NH3 emissions from a naturally ventilated livestock farm using local-scale atmospheric dispersion modelling, Biogeosciences, 6, 2847-2860, 10.5194/bg-6-2847-2009, 2009.

Kormann, R., and Meixner, F. X.: An analytical footprint model for non-neutral stratification, Boundary Layer Meteorol., 99, 207-224, 2001.

Kowalski, A. S., and Serrano-Ortiz, P.: On the relationship between the eddy covariance, the turbulent flux, and surface exchange for a trace gas such as CO2, Boundary Layer Meteorol., 124, 129-141, 10.1007/s10546-007-9171-z, 2007.

Langford, B., Davison, B., Nemitz, E., and Hewitt, C. N.: Mixing ratios and eddy covariance flux measurements of volatile organic compounds from an urban canopy (Manchester, UK), Atmospheric Chemistry and Physics, 9, 1971-1987, 10.5194/acp-9-1971-2009, 2009.

Langford, B., Acton, W., Ammann, C., Valach, A., and Nemitz, E.: Eddy-covariance data with low signal-to-noise ratio: time-lag determination, uncertainties and limit of detection, Atmos. Meas. Tech., 8, 4197-4213, 10.5194/amt-8-4197-2015, 2015.

Loubet, B., Milford, C., Hensen, A., Daemmgen, U., Erisman, J.-W., Cellier, P., and Sutton, M. A.: Advection of NH3 over a pasture field, and its effect on gradient flux measurements, Biogeosciences, 6, 1295-1309, 2009.

Loubet, B., Decuq, C., Personne, E., Massad, R. S., Flechard, C., Fanucci, O., Mascher, N., Gueudet, J. C., Masson, S., Durand, B., Genermont, S., Fauvel, Y., and Cellier, P.: Investigating the stomatal, cuticular and soil ammonia fluxes over a growing tritical crop under high acidic loads, Biogeosciences, 9, 1537-1552, 10.5194/bg-9-1537-2012, 2012.

Massad, R. S., Nemitz, E., and Sutton, M. A.: Review and parameterisation of bi-directional ammonia exchange between vegetation and the atmosphere, Atmospheric Chemistry and Physics, 10, 10359-10386, 10.5194/acp-10-10359-2010, 2010.

Neftel, A., Spirig, C., and Ammann, C.: Application and test of a simple tool for operational footprint evaluations, Environmental Pollution, 152, 644-652, 10.1016/j.envpol.2007.06.062, 2008.

Personne, E., Tardy, F., Genermont, S., Decuq, C., Gueudet, J. C., MASCHER, N., Durand, B., Masson, S., Lauransot, M., Flechard, C., Burkharlt, J., and Loubet, B.: Investigating sources and sinks for ammonia exchanges between the atmosphere and a wheat canopy following slurry application with trailing hose, Agric. For. Meteorol., 207, 11-23, 10.1016/j.agrformet.2015.03.002, 2015.

Sutton, M. A., Nemitz, E., Milford, C., Campbell, C., Erisman, J. W., Hensen, A., Cellier, P., David, M., Loubet, B., Personne, E., Schjoerring, J. K., Mattsson, M., Dorsey, J. R., Gallagher, M. W., Horvath, L., Weidinger, T., Meszaros, R., Daemmgen, U., Neftel, A., Herrmann, B., Lehman, B. E., Flechard, C., and Burkhardt, J.: Dynamics of ammonia exchange with cut grassland: synthesis of results and conclusions of the GRAMINAE Integrated Experiment, Biogeosciences, 6, 2907-2934, 10.5194/bg-6-2907-2009, 2009.

Whitehead, J. D., Twigg, M., Famulari, D., Nemitz, E., Sutton, M. A., Gallagher, M. W., and Fowler, D.: Evaluation of laser absorption spectroscopic techniques for eddy covariance flux measurements of ammonia, Environmental Science & Technology, 42, 2041-2046, 2008.

Wu, Y. H., Walker, J., Schwede, D., Peters-Lidard, C., Dennis, R., and Robarge, W.: A new model of bi-directional ammonia exchange between the atmosphere and biosphere: Ammonia stomatal compensation point, Agric. For. Meteorol., 149, 263-280, 10.1016/j.agrformet.2008.08.012, 2009.