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Atmospheric Measurement Techniques Discussions

Interactive comment on "Measurements and quality control of ammonia eddy covariance fluxes: A new strategy for high frequency attenuation correction" *by* Alexander Moravek et al.

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We thank A. Neftel and A. Hensen for their critical comment. We highly value the discussion on NH_3 flux measurements and on the comparability between methods. Precise and accurate measurements of ammonia and its fluxes are challenging, which underlines the importance that these issues are discussed.

Before answering the comments in more detail below, we summarize first the findings from further analysis which were not presented the original version of the manuscript and underline the plausibility of the presented fluxes:

1. **Agreement with resistance modelling:**

   Soil fluxes: NH_3 fluxes were inferred from measured soil emission potentials (soil NH_4^+ / soil pH) under bare soil conditions and are in the same range as measured fluxes. Using measurement of soil temperature, the ambient NH_3 mixing ratio and the commonly used parameterization of the aerodynamic and quasi-laminar boundary layer resistances, the median absolute NH_3 predicted flux (on days when the emission potential was measured in the first month of measurements) was 13.2 ng m^{-2} s^{-1} (mean 13.6 ng m^{-2} s^{-1}). This compares well to a median absolute flux of 4.1 ng m^{-2} s^{-1} (mean 13.0 ng m^{-2} s^{-1}) from eddy covariance measurements during the same period. More discussion about the NH_3 soil fluxes is provided in a manuscript that is currently prepared by the authors.

   Full canopy fluxes: A more complex resistance model was used to model the bidirectional ammonia exchange in presence of the corn canopy. Preliminary results show that both measured and predicted fluxes are in the same range with maximum daytime fluxes being typically less than a factor of three different. More details on the compensation point model will be presented in a manuscript that is currently being prepared by the authors.

2. **Agreement with WindTrax simulations:**

   Following the suggestion of Neftel & Hensen, we performed a WindTrax simulation for a selected period of the flux measurements. Since no background measurements were made, we performed the simulation for different background scenarios, which enables us to discuss the plausibility of the presented fluxes. We compiled the method and results in the Supplementary Material. The results in Fig. S1 show the estimated daytime NH_3 fluxes for 28 and 30 May using

different assumptions of the NH_3 background mixing ratio. The NH_3 mixing ratios measured using the QCL ranged between about 2 and 10 ppbv for both days. Considering only the high emission periods, the WindTrax flux estimates are about 1.5 times higher than the measured flux for the peaks on both 28 and 30 May under the scenario where a background NH_3 mixing ratio of 0 ppbv is assumed. Since a background of 0 ppbv represents the highest possible WindTrax flux estimates, the real NH_3 fluxes are expected to be lower. According to the eddy covariance flux measurements, the best agreement between WindTrax estimates and flux measurements was for a background NH_3 mixing ratio between between 2 and 4 ppbv.

3. **Comparison with offline relaxed eddy accumulation fluxes:**

   A previous study conducted by Zhu et al. (2000) measured NH_3 fluxes from the same location after urea fertilization. They used an offline relaxed eddy accumulation (REA) technique, where the up- and downdraft NH_3 was captured directly by dry coated denuders, a technique which is not subject to high frequency attenuation. While their fluxes are on average slightly higher than the ones observed in this study, still the range is comparable and a percentage loss of 0.8 % of the fertilizer nitrogen input was calculated. This value is also lower than reported in some other studies and suggests that site characteristics are responsible for the generally lower NH_3 emission fluxes at this site.

The above mentioned analyses and observations show that the measured NH_3 fluxes are in a plausible range, and that a general underestimation by a factor of 10 is not likely as suggested by Neftel & Hensen.

In the following we divided our reply to the individual comments into several sections:

Comment: *The paper focusses on the frequency behavior of the NH_3 covariance function. The paper follows up the work by Shaw et al, 1998 and Ferrara et al. (2012) that had a similar focus. We have question marks regarding the order of magnitude of the presented fluxes in this paper and, indirectly for all these papers. Shaw et al. presented a very well designed and careful analysis of the EC data. All necessary information is given and the inferred correction of 45 % due to high frequency damping is convincing. But the NH_3 emission fluxes in Shaw et al. are extremely high for a non-fertilized natural grassland situation (145 g $m^{-2}s^{-1}$). We rather expect deposition fluxes. We do speculate that Shaw et al. overlooked that their NH_3 signal was due to a water interference and thus measured water fluxes that are indeed emission fluxes with the reported signature.*

Response: We disagree that all NH_3 eddy covariance (EC) flux measurements reported in the literature are not plausible. E.g. Zöll et al. (2016) presented NH_3 EC fluxes over peatland, which agree well with inferred fluxes from resistance modelling. They used a continuous wave QCL,which was also used in this study. The continuous wave QCL has a much higher precision than the pulsed-laser instrument used by Ferrara et al. (2012), which could partly explain the difference in performance. In general, from our experience, the measurement of NH_3 fluxes with EC requires a measurement system in optimal conditions. Furthermore, differences in the setup, the inlet system and material, and the spectroscopic technique may be the cause why some presented flux data are questionable.

Regarding the mentioned interferences with water vapour fluxes, there are different ways in which water vapour fluxes may impact the QCL fluxes, which we could exclude for our system: (1) There is no spectroscopic interference with water peaks in the window we use to fit our absorption spectrum. (2) The effect of water vapour fluxes on air density fluctuations: this effect is small for NH_3 fluxes as it was shown by Pattey

et al. (1992). (3) Interferences of water vapor may vary the pressure broadening coefficient used in spectral fit. (4) Chance for impact of water vapour fluxes on the NH_3 fluxes, if water molecules influence the absorption/desorption process of NH_3 on the inlet surface. We performed tests to evaluate the potential influence of water vapour fluxes on NH_3 fluxes. This was done by adding a steady flow of 10 ppbv NH_3 calibration air to the inlet and observing the effect on NH_3 fluxes. We chose conditions where low NH_3 mixing ratios (< 2 ppbv) prevailed, no NH_3 flux was detected (characterized by random noise of NH_3 time series) but a significant water vapor flux (during daytime, when leaf stomata are opened and turbulent mixing was high) was expected. The increased NH_3 during these standard addition test would allow for stronger NH_3 interaction with the inlet and sample cell walls, and the potential effect of water vapor fluxes should be visible during these conditions. However, our tests showed that the measured NH_3 flux was within the flux detection limit as before the NH_3 addition. From this we conclude that there was no significant effect of the water vapor flux on the NH_3 fluxes.

Comment: *Ferrara et al. 2012 presented EC NH_3 flux data using a pulsed Aerodyne QCL system. They focus on different algorithms for the damping correction. Two years later the same authors presented a new flux analysis, this time based on concentration measurements in combination with a dispersion model (bls). Apparently both papers used the same raw data set. But the fluxes in the 2014 paper (bls) are roughly one order of magnitude higher. They are in the expected range of NH_3 emission fluxes after fertilization with urea. This is a strong indication that the calculated EC fluxes from the first paper do underestimate the true fluxes by roughly one order of magnitude.*

Response: As we mentioned in this paper, there are significant differences from our system setup to the setup by Ferrara et al. (2012). E.g. Ferrara et al. (2012) used laminar flow conditions, which may have led to an underestimation of fluxes if the high frequency attenuation (HFA) correction is not adequately accounted for by the ogive

method as we conclude it in this paper. The performance of the ogive method is further affected by the noise of the instrumentation, which is significantly larger with the pulsed laser QCL used by Ferrara et al. (2012) as opposed to the continuous wave laser QCL used in this study. For those reasons we propose the use of the time response method for the HFA correction of NH_3 fluxes.

In addition to instrumental differences, the measured ambient NH_3 mixing ratios during the peak emissions of Ferrara et al. (2012) were larger by approximately one order of magnitude or more, reaching up to roughly 150 ppbv, while mixing ratios at our site were typically below 10 ppbv. Differences in prevailing NH_3 levels could be one reason for the potentially different performance of EC flux measurements. Ferrara et al. (2016) found using a different NH_3 flux data set that measured EC fluxes agreed reasonably well for higher NH_3 fluxes with WindTrax simulations. In our opinion, this underlines that the quality of NH_3 EC flux measurements depends on the individual operational parameters and environmental conditions, which opposes the statement by Neftel & Hensen that NH_3 EC fluxes are generally underestimated by one order of magnitude.

Comment: *Measurements reported in the present paper covered a five-month period of NH_3 fluxes from a large cornfield. The field was fertilized with 155 kg N ha^{-1} urea on May 25^{th}, the measurements started then on May 28^{th}. The present paper by Moravek et al. unfortunately presents no time series of concentrations and fluxes nor calculates cumulative fluxes. A very generous and rough estimation of the cumulative loss from May 28^{th} to May 31^{st} yield a very low percentage of NH_3 loss of the applied urea. Assuming a persistent flux of 50 ng $m^{-2}s^{-1}$ over four days yields a cumulative emission of approx. 150g ha^{-1} or 0.1 % of the applied fertilizer, which is an extremely low amount.*

Response: We agree that the observed percentage loss of NH_3 from the fertilizer application is relatively low compared to estimates for other sites. However, as stated at the beginning of this document, we explained how the NH_3 EC flux

measurements are plausible and within the predictions from WindTrax simulations and the compensation point resistance model. Also, as we noted, Zhu et al. (2000) made measurement at the same location and obtained a flux loss of 0.8 % which is also significantly lower compared to other studies. For this reason, we believe that site specific properties led to the generally low NH_3 fluxes after fertilization. Since it is not within the scope of the paper to discuss the flux magnitudes in respect to expected environmental processes, we did not present a time series in this paper. Instead, the time series and cumulative emissions are being prepared for another publication, where more details are given and the NH_3 fluxes are compared to estimates from other studies. Also, it has to be noted here that the fluxes in the revised paper are increased compared to the first version due to the updated correction method following the comment from Reviewer #1 (median increase of 25 %).

Comment: *We hypothesize that a similar situation as in the Ferrara 2012 paper could have occurred: a reasonably looking NH_3 flux covariance function where the usual high frequency damping correction algorithms seem to work, is severely underestimating the true flux.*

Response: We refer here to our explanation given above on the instrumental and methodological differences of the study by Ferrara et al. (2012) and our study. Next to the instrumental drawbacks of the Ferrara study, the use of the time response method retrieves a reasonable attenuation factor for conditions where fluxes are small. We acknowledge that there could be problems with the time response method if nearly all of the flux would have been lost due to low-pass filtering. However, over the 5 month measurement period many significant NH_3 flux periods were observed that not only showed clear diurnal cycles but also featured co-spectra following the expected shape. This offers strong evidence to us that fluxes could not have been attenuated completely during these periods. Also the fact that the flux correction factors from the time response method were fairly low (ranged from 1.35 to 2.69) excludes the

possibility that the majority of the NH_3 flux was attenuated.

Comment: *The authors do have the possibility for a plausibility control as they have concentrations and turbulence data and could estimate therefore the fluxes with a dispersion model such as Windtrax. As there are no detailed information on the management, nor the meteorological conditions are given, it is impossible for us reader to judge whether the order of magnitude of the presented emission fluxes are in a reasonable range. We are perfectly aware that a plausibility check of the reported deposition fluxes is much more demanding. But time series of deposition velocities at the measurement height would yield interesting information, e.g. on compensation points (see Flechard et al., 2010).*

Response: As we outlined at the beginning of this response, the plausibility of the measured fluxes was investigated. We understand that for the reader it would be nice to have more information on the environmental conditions. Since the flux plausibility is linked to the flux quality control, we added in the last section of the manuscript a paragraph on the flux plausibility. We find it is out of the scope of this paper to go into detail of the environmental factors controlling the measured fluxes. Also, we thank Neftel & Hensen for their suggestion to use a dispersion model such as WindTrax as another way for a plausibility check. In the supplement of the revised manuscript we included the results of the WindTrax simulation, which underline that an underestimation by one order of magnitude, as suggest by this comment, is not likely.

Comment: *During the Dronten experiment (2016, NL) we have observed situations where reasonably looking EC NH_3 flux data clearly underestimated the fluxes by roughly one order of magnitude. (Hensen, 2018) We used a pulsed Aerodyne QCL system (similar generation as used by Ferrara et al., 2012, 2014). The device was placed in the center of a manured circle (diameter 40m) and the inlet was placed 1m*

above ground. The scope of the measurements was not the vertical fluxes, but to gain information on the horizontal diffusive flux that is an important correction for the Integrated horizontal flux approach. The evaluated fluxes need to be corrected by three factors: i) similar as in Ferrara et al. (2012) the concentration by the Aerodyne evaluation routine is severely underestimated, most likely due to a wrong fitting routine, ii) a footprint correction, as the measured flux is a mixture of contribution from the fertilized circle and the area around them, iii) the high frequency loss that was calculated with an "ogive" approach. These three corrections yielded roughly an upscaling of the raw flux by a factor of 10. Still compared to three other independent approaches (IHF, plume measurements, bls-approach with line integrated concentration measurements) the EC fluxes turned out to be an order of magnitude to small (phd thesis Michael Bell:https://www.theses.fr/2017NSARD083). We speculated that in the inlet line, roughly 10% of the ambient NH_3 variations passed and are damped as described in this paper. But 90% is so strongly attenuated, that the flux memory is lost. We successfully simulated this by manipulating raw temperature time series from Sonic anemometers. In the supplement we added an extract of the presentations of the results at the EGU 2017 Vienna meeting (https://meetingorganizer.copernicus.org/EGU2017/EGU2017-9321.pdf) As we have no running projects on ammonia available anymore (due to retirement and institutional restructuration) we cannot continue to investigate causes of this behavior and cannot offer a mechanistic explanation which is, in our opinion crucial in order to obtain good EC flux estimates for Ammonia.

Response: We thank Neftel & Hensen for sharing the findings from their field measurements and also providing details on their setup. Regarding the flux correction procedure, our measurements differed in the following way: (1) Since we used a continuous wave laser QCL instead of a pulsed laser QCL the span correction is not necessary in the way it is necessary for a pulsed laser QCL (Ferrara et al., 2012). We did check the accuracy of the NH_3 mixing ratio retrieved by the instrument and typically found it to be within 15 % of the value calculated by the algorithm. (2) A correction for flux footprint was not necessary due to the sufficient extent of the corn

field. (3) We used the time response method to correct for the HFA of NH_3 fluxes. The flux loss simulation Neftel & Hensen describe here is what was performed for the retrieval of flux correction factors with the time response method and is illustrated in Fig. 9. In contrast to Neftel & Hensen we used the time constants from the double exponential decay when applying zero air. If we compare our fluxes to the WindTrax simulation as Neftel & Hensen did, we must conclude that the maximal potential flux underestimation is only by a factor of 1.5 (scenario of 0 ppbv background NH_3). However, as we also conclude in our paper, we agree with Neftel & Hensen that more studies are necessary to understand the mechanisms controlling the time response of NH_3, which is important to optimize flux measurements systems so that they can be operated under a large range of environmental conditions.

References

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., 158–159, 30–42, doi:10.1016/j.agrformet.2012.02.001, 2012.

Ferrara, R. M., Carozzi, M., Di Tommasi, P., Nelson, D. D., Fratini, G., Bertolini, T., Magliulo, V., Acutis, M. and Rana, G.: Dynamics of ammonia volatilisation measured by eddy covariance during slurry spreading in north Italy, Agric. Ecosyst. Environ., 219, 1–13, doi:10.1016/j.agee.2015.12.002, 2016.

Pattey, E., Desjardins, R. L., Boudreau, F. and Rochette, P.: Impact of density-fluctuations on flux measurements of trace gases - implications for the relaxed eddy accumulation technique, Boundary-Layer Meteorol., 59(1–2), 195–203, doi:10.1007/bf00120695, 1992.

Zhu, T., Pattey, E. and Desjardins, R. L.: Relaxed eddy-accumulation technique for measuring ammonia volatilization, Environ. Sci. Technol., 34(1), 199–203,

doi:10.1021/es980928f, 2000.

Zöll, U., Brümmer, C., Schrader, F., Ammann, C., Ibrom, A., Flechard, C. R., Nelson, D. D., Zahniser, M. and Kutsch, W. L.: Surface-atmosphere exchange of ammonia over peatland using QCL-based eddy-covariance measurements and inferential modeling, Atmos. Chem. Phys., 16(17), 11283–11299, doi:10.5194/acp-16-11283-2016, 2016.

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