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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 Reviewer #1 for their detailed comments and suggestions for improving the manuscript. We addressed their comments as follows:

Comment: *page 6, line 34: The details of the zero air inlet design are quite crucial for the success of the proposed HFA method. However, unlike stated in this sentence, no corresponding details are visible in Fig. 1. The authors should give a close-up view of*

the gas inlet and the attached inlet for the zero gas. In addition it needs to be specified, how the zero gas unit (heating catalyst) was operated during periods of normal EC measurements (outside the zeroing periods).

Response: We included a close-up view of the inlet piece in Fig. 1. Since we used a slightly different glass inlet as compared to Ellis et al. (2010), the zero air was introduced through a PFA T-fitting at the front of the inlet. Therefore, we updated this sentence in the manuscript. The heating catalyst was running continuously, where the NH_3 scrubbed air was vented into ambient air during periods of normal EC measurements. We added a note at the end of the paragraph.

Comment: *page 11, Eq. 8: The presented correction of the cospectra using sqrt[T(f)] only accounts for the damping of the fluctuation amplitudes. However a first order filter as characterised in Eqs. 5 and 6 also leads to a phase shift in the damped frequencies (e.g. Horst, 1997; Massman and Ibrom, 2008). Because the constant phase angle shift corresponds to different lag times for different frequencies, this effect is only partly compensated by the empirical lag time correction. Thus especially for HFA over a large frequency range, as observed here, the unaccounted phase shift can be important. This effect should be addressed in the manuscript.*

Response: We thank the reviewer for this comment. Indeed, the used transfer functions do not include the phase shift of a first order filter. Using a transfer function for the phase shift is complex, especially since the lag time correction accounts for some of the flux loss caused by the phase shift. Instead of applying the described transfer functions to the co-spectrum, we therefore updated the simulation method by applying a low pass filter to the 30 min time series in the time domain and subsequently performing a cross-correlation analysis to account for the lag time shift as it is done with the real flux data. Using this approach, both the effect of the phase shift and the lag time correction are accounted for. Using this new approach in the flux loss simulation, we updated Fig. 9 and the empirical relationship between the flux

attenuation factor and the D value (Fig. 10 and Eq. 12 in the revised manuscript). As a result of the updated flux correction, fluxes increased by a further 25 % (median value) over the corrected values presented in the original manuscript. Final flux values were updated accordingly in the entire manuscript. The method section 2.4.2 was updated using the time domain approach. Since the calculation of the transfer function is not necessarily needed with the time domain approach, the method was renamed to "time response method" in the entire manuscript. The description of results in Sect. 3.2.3 was also updated accordingly.

Comment: *Page 19, line 5-6: Concerning the results of the ogive method, it is stated here that the results from least-squares regression (corresponding to an arithmetic averaging) strongly deviated from the median. This is not surprising because the ogive results represent ratios of (very noisy) half-hourly cospectra. Such data usually have a non-Gaussian (non-symmetric) distribution. Therefore the application of a simple least-squares regression in Fig. 6 is not adequate. Instead, the calculation of binned medians (as e.g. used in Fig. 8) or a median regression would be much more suitable (eventually with separation of stable and unstable cases). In that way, a dependence on windspeed possibly could be detected. Also for the analysis of the temporal behavior (before/after inlet cleaning) a running median filter should be applied to the ogive data. Generally: if two approaches for HFA are inter-compared and rated, they should both be evaluated in an adequate and careful way. Thus the evaluation of the ogive method needs to be improved as suggested.*

Response: We agree that using binned median or a median regression could be more adequate for interpreting the ogive results. We therefore updated Fig. 6 showing the box plot statistics of the flux attenuation factor against binned wind speed data. We then used a quartile (median) regression to retrieve the linear relationship against wind speed. Using this approach the dependency of the attenuation factor on the wind speed is slightly stronger (factor of -0.033 instead of -0.028). We updated the

coefficients in Eq. 11 (of revised manuscript) and its description. Still, the similarity of the new linear regression coefficients with previously used coefficients supports our finding that the flux attenuation determined with the ogive method is less than with the proposed time response method.

Comment: *page 8, line 3-6: With respect to its potential influence on the HFA, it would be of interest to show (or quantitatively describe) the temporal variations of observed lag times.*

Response: After (1) synchronizing the two data acquisition systems and (2) applying the described quality control, the standard deviation of the lag time between the NH_3 mixing ratio and the vertical wind speed measurements was 1.1 s. Since a larger HFA leads to a flatter cross-correlation peak, a larger variation of the time lag during times with high D values would be expected. However, this could not be observed. Therefore, we think that the variations in the lag time are dominated by other factors. For example, part of the variation (about 0.5 s) can be explained by changes in the wind speed influencing the lag time between the sonic anemometer and inlet position. We added a description on the variation of the lag time in the manuscript.

Comment: *page 9, line 21: How stable was the 'background' signal (y_0) of the QCL during the study? Its variability would be an indication for the systematic uncertainty and the total accuracy of the QCL measurements.*

Response: We agree that a stable operation of the QCL is crucial for reliable and accurate QCL measurements. However, as described in the methods section, during the operation of QCL the automated background schedule was activated, which already accounts for the drift and is a common procedure for QCL measurements. This procedure is enabled to maximize the accuracy, given that used zero air is free of NH_3. To correct for a potential drift of the QCL between two automated background periods,

the background mixing ratios were linearly interpolated between two consecutive background measurements and subtracted from the NH_3 mixing ratios. Due to the precise temperature control the QCL was generally running in a very stable way. As a result, even during the periods when automated backgrounds were collected only every three hours, the drift was typically less than 0.3 ppbv over the three hour period.

Comment: *page 10, Eq. 7: The representation of the two different response times (exp. functions) by the combined transfer function in Eq. 7 yields an adequate result in practice for the present study. However, the additive combination of individual transfer functions is conceptually problematic. It e.g. implies that the fast τ_1 filter only acts on a fraction (1-D) of the concentration fluctuations. However, if this filter (as suggested by the authors) can be attributed to the air mixing in the analyser detection cell, it physically acts on all fluctuations. Therefore, a multiplicative combination of the transfer functions would be conceptually more adequate in my view, and it would be compatible to the classical transfer function method (Moore, 1986; Moncrieff et al., 1997). At least the relation and differences between additive vs. multiplicative combination of transfer functions should be discussed.*

Response: We agree with the reviewer that a multiplicative combination would be conceptually more adequate, however only if both τ_1 and τ_2 are determined independently. In our analysis, both τ_1 and τ_2 were determined using the double exponential decay function from the time response. Since they are linked by the D value they are not independent from each other. While τ_1 can be estimated by the sample cell (+sample tube) volume, pressure and flow rate, we cannot determine τ_2 from the time response measurements independently from τ_1. Therefore, using the double exponential time response model as a concept, we find that the presented additive approach is more appropriate in defining a combined transfer function.

Note: In the updated manuscript we applied the low-pass filter in the time domain instead of using transfer function (in reaction to comment above on phase shift). The

filters for τ_1 and τ_1 were still combined additively and scaled by the D value.

Comment: *Although the focus of this study is the HFA method, it would be suitable to give information about the possible sources of NH_3 in May and August (Fig. 3) as a difference to other months showing deposition. Therefore, the timing, type and amount of fertilizer applications to the corn field (before or during measurement period) should be reported.*

Response: The plausibility of measured fluxes is important for the presented technical paper, which is why we addressed this in more detail in the answer to the comment of Neftel Hensen and added a paragraph on the plausibility of NH_3 fluxes in Section 4.3.2. Due to the complexity of the bi-directional exchange of NH_3, it is out of the scope of this paper to discuss the underlying processes of NH_3 in more detail, but will be discussed in a subsequent paper under preparation by the authors. Information on the fertilization time (25 May), type (granular urea) and amount (155 kg N ha^{-1}) are given in Sect. 2.1.2.

Comment: *In order to decide whether the estimated flux detection limit (closely related to the flux uncertainty) is plausible, some exemplary time series with measured half-hourly fluxes should be presented. These would be more informative in the present context than the statistical diurnal cycles in Fig. 3.*

Response: We showed the statistical diurnal cycles instead of an exemplary time series to give an overview of the variable magnitude and direction NH_3 fluxes over the growing season in relation to the flux detection limit. In our opinion, this gives a better overview of the performance of the eddy covariance system and quality of the flux measurements than a selected time series. However, we agree that the shown flux boxplot statistics are not ideal for the comparison with the median flux detection limit since they combine values from both positive and negative fluxes. We therefore

updated Fig. 3 and its description in Sect. 3.1 using the absolute NH_3 flux values for the boxplot statistics, while the percentages of flux periods with emission or deposition are given for each month. Furthermore, to make clear that the shown fluxes are before the application of the HFA correction, we additionally indicated this in the title of Sect. 3.1.

Comment: *page 11, line 24: This precision only represents the precision at zero concentration while the precision at higher ambient concentrations could be larger. This should be specified.*

Response: The precision over the course of the experiment was determined from the zero air measurements. We found that the precision of the NH_3 QCL does not change at higher NH_3 mixing ratios. This was tested by applying a known constant NH_3 mixing ratio (8 ppbv) through the calibration port of the glass inlet. We added a note that the precision was independent of the measured NH_3 mixing ratio.

Comment: *A separate quantification of the HFA factor with the τ_1 transfer function alone would be of interest in order to partition the total damping into 'classical' damping effects applicable to all trace gases and wall sorption effects only applicable to NH_3.*

Response: This case, where only τ_1 is responsible for the HFA, is considered in the case of D = 0. Hence, in Eq. 12 (of revised manuscript) the damping that is not due to the wall effects and applicable also to other trace gases is described by "$\alpha_{tr} = -0.47 \cdot u + 0.93$". We added a note explaining this in Sect. 3.2.3.

Comment: *page 13, lines 6-7: Were the distinct temporal variations in D found only after fixing τ_1 and τ_2 to overall constant values, or were they equally found with variable τ_1 and τ_2?*

Response: Thank you for asking this question. τ_1 and τ_2 were only fixed for the HFA simulation (Sect. 3.2.3). The shown temporal variation of D was retrieved without fixing τ_1 and τ_2 in Eq. 2 (Sect 2.3). However, we tested this and found that fixing τ_1 and τ_2 to the median values resulted in a comparable temporal variation of the D value.

Comment: *page 13, lines 17-18: In my view the dependence of the D value from the NH_3 concentration in Figure 8 is not so clear as stated in this sentence. To get a better impression from Fig. 8, it would be useful to indicate the number of data (n) in each bin.*

Response: In Fig. 8 we included the number of data points used in each bin. As one might suspect, there are less data points at high NH_3 mixing ratios where the variation is less. The larger uncertainty of the double exponential fit with small mixing ratio changes may be the cause of the observed larger variation of D values at lower mixing ratios, as we had noted in the text of the manuscript.

Comment: *page 13, line 26: "time constants were fairly constant over time" is a strange statement. I suggest to replace "time constants" by "response times".*

Response: We improved the wording of this sentence. We prefer to use the term "time constant" since it has a more accurate definition, namely the time required for the NH_3 measurement to respond to 63.2% of its final value.

Comment: *Figure 7: What was the reason for the decrease and subsequent increase of D at the end of August?*

Response: From 23 to 28 August, the D value was decreasing, which is against the increasing trend of D over the month of August. We were not able to determine a specific reason for the temporary decline and subsequent increase. Possible is a

change in ambient air characteristics that would influence the wall interaction. However, the fact that we cannot attribute a single factor (such as NH_3 ambient mixing ratios, humidity, temperature or operational changes) to the change in time response, shows the complexity of NH_3 time response. This is also one important reason, why we conclude in the paper that using an experimental approach like the time response method is necessary to adequately correct the high frequency attenuation of NH_3 eddy covariance fluxes.

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