

## ***Interactive comment on “Surface-atmosphere exchange of ammonia over peatland using QCL-based eddy covariance measurements and inferential modeling” by Undine Richter et al.***

**Anonymous Referee #1**

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In this study, a closed-path QC-TILDAS system is used to measure bi-directional NH<sub>3</sub> fluxes by eddy covariance over peatland. The subject is appropriate for Atmospheric Chemistry and Physics. Given the importance of NH<sub>3</sub> deposition with respect to ecosystem processes and a general lack of information on dry deposition, the data are potentially of use to the scientific community with regard to understanding NH<sub>3</sub> air-surface exchange in natural ecosystems near local sources (i.e. at high atmospheric NH<sub>3</sub> concentrations). The authors note several interesting results which differ from previous studies in natural ecosystems, including the observation of NH<sub>3</sub> emissions during wet conditions. While the results are compelling and could be of interest to a broad community of ecologists and atmospheric scientists, there are several issues

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noted below that need to be addressed before the paper is acceptable for publication.

Abstract, line 31. The statement regarding the potential for QCL to be applied for NH<sub>3</sub> flux measurements within long-term research networks such as NEON may be a bit strong. The concentrations at which the instrument has been applied in this study are not generally representative of NEON sites, in fact they are much higher. The current paper does indeed demonstrate the potential for use at sites influenced by local NH<sub>3</sub> sources, where concentrations are relatively high, but further characterization of the instrument performance at low concentrations would be necessary to suggest applicability at sites typical of NEON.

Page 4, line 5. At the flow rate and tubing dimensions noted, was the sample flow fully turbulent? The authors note a high frequency damping factor of 0.67 derived from ogive analysis on page 5 but do not explain the cause. A little more information here would be helpful.

Page 5, Section 2.3. As stated in the introduction, one of the three objectives of the paper is to “test the QCL performance to measure NH<sub>3</sub> concentration fluctuations and calculate NH<sub>3</sub> fluxes. . .”. In this regard, some additional information on instrument performance and relation to flux calculations is warranted. Specifically, the only mention of precision comes at the top of page 4, line 2, referenced to McManus et al. (2008). A more detailed description of instrument precision would be informative. For example, what is the precision at sampling rates corresponding to frequencies of the flux contributing eddies (see Ferrara et al., 2012)? Related to precision is the flux detection limit. For their setup and site conditions, Ferrara et al (2012) estimated the flux detection limit to be 0.25u\*, or about 75ngNH<sub>3</sub>/m<sup>2</sup>/s, which is large relative to the fluxes reported in the present study. The authors should include an estimate of flux detection limit in their results.

Page 6, section 2.4. How is the stomatal compensation point parameterized? What value is used for emission potential ( $\gamma$ )?

Page 7, line 15. “horizontal exchange with higher layers...” Do the authors mean vertical exchange?

Page 7, line 22 – 27. The authors note that they observed low air concentrations at high temperatures in late April/early May. They go on to suggest that this might be related to higher concentrations of acid gases and a tendency of NH<sub>3</sub> to shift to the particle phase. Do the DELTA measurements of HCl, SO<sub>2</sub>, and HNO<sub>3</sub> support this statement? Were there particle measurements collected that might help shed some light on this question? The statement regarding volatilization of aerosol in the heated inlet line is a little confusing, as this would tend to bias the measured NH<sub>3</sub> high. Some clarification is needed here.

Page 7, discussion of diurnal variability. The authors discuss possible reasons for lower concentrations at night and for the morning increase in concentration. What might be driving the relatively rapid increase during the evening (1600 – 1800) as illustrated in figures 4 and 7?

Page 8, line 20 – 23. The authors mention that emission was observed during rain events. Are the flux measurements valid during active precipitation? Assuming that the measurements are valid, what process would be driving the emission?

Page 9, line 9. “.. the ecosystem emits only under dry conditions in contrary to our observations..” The observation of emission during periods of rain or surface wetness is significant. Are there other published examples where this was observed in natural ecosystems?

Page 10, statistical analysis (Table 2). To me, the statistical analysis does not help explain the patterns of the fluxes. The statistical tests indicate that the groups are different but do they differ in a way that is physically meaningful? What are the results telling the reader about the fluxes? How much of the variability in the fluxes can be explained by their relationships to these variables? If the authors wish to employ statistics to explain the flux patterns, a more well developed and rigorous analysis, which

accounts for collinearity in the independent variables, is needed.

Page 10, line 16. “.. whereas peaks in concentration, although rather forming a bimodal pattern, follow the shape of the air temperature with a 2-3 hour lag”. The concentration pattern is very much bimodal, with the evening peak representing a process that is obviously important (as these are mean values) and uncorrelated with temperature. As in my previous comment, some discussion of the cause of this evening mode, which contains the highest concentrations observed diurnally, is warranted. It is too highly amplified and brief to represent boundary layer dynamics. Is it a persistent influence from local sources?

Page 11, line 10. “whereas during emission periods it may be the ammonia flux itself, which is controlling the concentration. . .”. Does this make sense from a mass balance standpoint? Assuming some depth of the boundary layer and no advection, could the measured flux reproduce the observed air concentration?

Page 11, line 12. “...high concentration levels due to advection from local source”. Have the authors considered advection as a potential source of error in the flux measurements themselves?

Figure 10. Can the relationship between concentration and flux be used to derive an estimate of the surface compensation point? Regarding the increase in emissions with concentration, it seems a very large compensation point would be needed for the surface to continue emitting at an air concentration of 35 ppb. Some explanation of this feature of the plot would be helpful.

Page 11, line 22. “.. the model does not exhibit any emission”. Some additional detail on the model parameterization is needed. What is the stomatal emission potential ( $\gamma$ ) and how was it derived? Does the lack of emission in the model suggest that this parameter should be adjusted?

Page 11, discussion of measured versus modeled fluxes. The results shown in Figure

10 and 11 are difficult to reconcile at first read. The left hand panel of figure 10 shows larger deposition fluxes (more negative) estimated by the model, relative to the measurements, across the entire range of concentrations. The error bars mostly do not overlap. However, figure 11 shows a combination of model overestimation and underestimation of daily mean fluxes across periods. Some explanation of the differences in these plots would be helpful.

Page 11, line 29. The authors note that some analysis of nighttime resistances was conducted which indicated that the  $R_w$  produced by the Massad et al scheme is too large for this site. What were the calculated resistances? This seems like a good opportunity to examine why the Massad et al  $R_w$  approach is not appropriate for this site. How low should  $R_w$  be to optimize the agreement with the measurements? Can  $R_w$  and the stomatal emission potential be changed together in a way that better reproduces deposition and emission? If so, does this inform not only the model improvement but also the processes that may be driving the fluxes?

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