We would like to thank both anonymous referees for their valuable comments on the manuscript. Referee comments are given in bold, the answers in standard font. The first points by Referee 2 were numbered from #1 to #6. The page and line numbers in the answers refer in this document to the revised manuscript version below.

### Answer to Referee 1 (Part A)

Abstract, line 31. The statement regarding the potential for QCL to be applied for NH3 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 NH3 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.

We added 'at sites with strong nearby ammonia sources leading to relatively high mean background concentrations and fluxes.' (P1L32) Indeed we are currently conducting a field campaign at a forest site without local sources and we are able to reliably measure very low concentrations in a range from 0 to 10 ppb.

# 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.

According to the Reynolds number (approx. 2400 - 2700) the flow was not fully turbulent (with Re<sub>crit</sub> > 3000), but also not laminar. High damping occurs usually because of imperfect turbulent flow regime and not completely excludable adsorption effects in the sampling line. Over time, especially the inlet gets clogged with aerosols, dust etc., which may cause unintended reactions of ammonia. However, due to the relatively short measurement period, we do not expect that increased clogging at the inlet alters the offset of NH<sub>3</sub> loss through reactions with particles and wall adsorption effects on the one hand and NH<sub>3</sub> production through the volatilization of NH<sub>4</sub>NO<sub>3</sub> aerosols on the other hand as is already discussed on page 4, lines 11-28.

In the EC-community gases like H<sub>2</sub>O measured with a closed-path device usually undergo spectral damping and are corrected for in a similar way.

Ferrara et al. (2012; 2016), also using an Aerodyne QCL, reported similar total damping factors.

On Page 5, line 27, we added '..., which usually occurs due to imperfect turbulent flow regime and possible wall sorption effects in the sampling line.'

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 NH3 concentration fluctuations and calculate NH3 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 75ngNH3/m2/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.

We added information on instrument precision on page 4, line 3*ff*. 'The main frequencies of the flux contributing eddies were in a range of 0.01 to 1 Hz. Precision, i.e. measurement sensitivity, of the instrument is 0.042, 0.021, 0.016, and 0.010 ppb in 1, 10, 20, and 60 s, respectively.'

We added information on flux detection limit and random error on page 6, line 3*ff*: 'The random flux error was computed according to the method after Finkelstein & Sims (2001) and the corresponding limit of detection was determined after Langford et al. (2015) as 1.96 times the flux error (95% confidence limit) resulting in a median value of 7.75 ng N m<sup>-2</sup> s<sup>-1</sup>. Alternatively, an upper flux detection limit for half-hourly values can be calculated by using only night-time data under stationary conditions (3 – 7 m s<sup>-1</sup> wind speed) and wind from the west-southwest sector, where local ammonia sources were negligible and concentrations were low (< 15 ppb). The standard deviation was 16.5 ng N m<sup>-2</sup> s<sup>-1</sup>, so the 2 $\sigma$ -uncertainty range is 33.0 ng N m<sup>-2</sup> s<sup>-1</sup>.'

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

We used the N-input dependent parameterization from Eq. (8) of Massad et al. (2010):

$$\Gamma_{\rm s} = 246 + 0.0041 \cdot N_{\rm in}^{3.56}$$

where the annual dry and wet N input to the ecosystem  $N_{in}$  (kg N ha<sup>-1</sup> a<sup>-1</sup>) was estimated to be approximately 25 kg N ha<sup>-1</sup> a<sup>-1</sup> by Hurkuck et al. (2014) at the same site, leading to a stomatal emission potential  $\Gamma_s$  of 634 mol mol<sup>-1</sup>.

We added on page 6, line 25: '...as well as the stomatal compensation point (N-input dependent)'.

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

Yes, thanks, this was a mistake. Changed to '...vertical exchange with higher layers...'. (now page 8, line 2)

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 NH3 to shift to the particle phase. Do the DELTA measurements of HCl, SO2, and HNO3 support this statement? Were there particle measurements collected that might help shed some light on this question?

The DELTA measurements do not strongly support this statement as they always cover measurement periods of four weeks. Short occurrences of high concentrations of particles are not identifiable. Hurkuck et al., 2014, who were measuring at weekly time resolution in 2012 and 2013, recorded in the first year especially high HNO<sub>3</sub>-concentrations in late April and early May, compared to February and March. So there might have been sufficient acid gas species to enhance the conversion from ammonia to ammonium.

# The statement regarding volatilization of aerosol in the heated inlet line is a little confusing, as this would tend to bias the measured NH3 high. Some clarification is needed here.

It was already mentioned on page 4 lines 22 – 28, that we possibly overestimate the concentration because of this volatilization effect, but in the case of formation of acidic salts we would regain some of the 'lost' ammonia. This might be a little bit too confusing in this sentence, so we will leave this part out and write on page 8, line 14-17: 'With higher temperature a larger amount of acidic gas or particle species are present in the atmosphere, which usually leads to reactions of ammonia to ammonium salts such as ammonium nitrate. (Kim et al., 2011)'

# 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?

The diurnal concentration pattern is generally highly influenced by the two periods with high concentration between 06 and 15 March and 30 March and 08 April. This can also be observed in Fig. 4, period II and III also exhibit this peak in contrast to the other periods. In these two periods the high concentrations are related to the northeast wind sector, where the next agricultural sources are closest (approx. 1.5 km distance). We separated the diurnal concentration into northeast ( $0 - 90^{\circ}$ ) and  $90 - 360^{\circ}$  wind sectors to illustrate that the late afternoon peak is mainly driven by local ammonia sources located northeast of the tower (see Fig. A1). Fig. A1 is included in the supplementary material as Fig. S1 and we added on page 8., lines 6-9: 'The conspicuous afternoon peak cannot be explained by turbulent mixing, but it is strongly linked to the northeast wind sector, where agricultural sources are closest (approx. 1.5 km distance, see also Fig. S1 in supplement). Therefore this is assumed to be an artifact caused by these agricultural point sources.'



Fig. A1: Mean diurnal variation of ammonia concentrations separated by wind direction.

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?

To our knowledge this was the first time it was observed with high-resolution flux measurements. There are emissions as well as depositions during rain events in a range of -75 to 25 ng N m<sup>-2</sup> s<sup>-1</sup>, with a median of -8.6 ng N m<sup>-2</sup> s<sup>-1</sup>. The range is smaller compared to the residual data set, but the median was in a similar magnitude of -14.2 ng N m<sup>-2</sup> s<sup>-1</sup>, so we suppose the data during precipitation to be valid. During precipitation-emission periods temperatures were moderate between 3 and 15 °C, concentrations relatively low between 3 and 11 ppb. The wind direction was mostly west to north, where very few point sources are located. So probably relatively unpolluted air reached the site and led to a gradient between the highly polluted area and the "clean" air, so that some emission occurred.

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.

The statistical analysis was not supposed to explain the patterns of the fluxes as we focus on the methodology and these considerations were only used to show the plausibility of the flux data. We just wanted to know if there are significant influences by the meteorology. The results only tell us, that we cannot exclude the influence of the mentioned meteorological variables. As shown in Fig. 7 (manuscript) especially the diurnal variation of the fluxes and the concentrations appear to be controlled by temperature, net radiation and friction velocity but it is not possible to state to which extend the one or the other value contributes to the flux, because there are highly non-linear processes involved. Only mean-values show this effect because in addition the data is strongly scattered, therewith also some requirements for different statistical tests like for example normal distribution for ANOVA (so we chose the alternative Kruskal-Wallis test) are not met. An in depth analysis would be interesting but we are afraid that this would distract the reader from the main methodological focus of this work.

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?

See above. We added the necessary explanation concerning this peak.

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?

We agree with the reviewer that from a mass balance point of view it might not be applicable, but it was also stated: 'However, more likely is a coincidence of flux drivers and high concentration levels which were high due to advection from the local sources.' Hence, we do not fully apply this statement from Milford et al. (2004) to our site conditions. We included the following changes for clarification on page 12, lines 19-23: 'However, Milford's (2004)

statement that the concentration may still determine the flux during deposition periods, whereas during emission periods it may be the ammonia flux itself, which is controlling the concentration, is also likely be applicable for our site during deposition periods. In emission periods, a coincidence of flux drivers and high concentration levels, which were high due to advection from the local sources, is the more realistic reason for the relationship in Fig.10 (right panel).'

# 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?

Advection affects in the first place concentration and thereby indirectly also the flux. We always had the local sources in mind, that's why we mention it several times in the manuscript. We added at page 12, lines 23-27: 'The nearest agricultural ammonia point source was 1.5 km away from the tower. With a measurement height of 2.5 m none of the sources were located within the flux footprint, thus we can largely exclude effects from flux heterogeneity such as a direct contribution of the sources to the measured vertical fluxes. However, there might be still large scale transport processes as outlined in a study by Mohr et al. (2015) that influence ammonia concentrations at the site.'

# 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.

We agree with the reviewer that the site has to have a very large compensation point for these emissions to occur. There are generally two simple ways to derive the canopy compensation point from flux and concentration measurements: (i) Look for situations when the sign of the flux changes from deposition to emission or vice versa and assume the measured air  $NH_3$  concentration at these times to be equal to the canopy compensation point, or (ii) invert the single-layer resistance-in-series analogue (details below).

(i) Without separating into emission and deposition and without bin-averaging, the points are too scattered to estimate any compensation point. We tried again to plot the fluxes against the concentration for a smaller flux range (-10 to 10 ng N m<sup>-2</sup>s<sup>-1</sup>) without bin-averaging (see figure A2 below), but again we cannot derive a compensation point from it, emission and deposition seems to be divided. Only for single days compensation points appear, but with poor R<sup>2</sup>. Fig. A2 is included as Fig. S2 in the supplementary material.



Fig. A2: Half-hourly scatter plot showing the dependency of  $NH_3$  fluxes (only in a range of -10 to 10 ng N m-2s-1) on  $NH_3$  concentration, red line: linear regression above for emission, below for deposition, for coefficients and  $r^2$  see legend

(ii) We were able to derive a continuous time-series of the canopy compensation point, as proposed by Anonymous Referee 2, using the relation  $\chi_c = F_t \cdot (R_a \{z - d\} + R_b) + \chi_a \{z - d\},$ where  $\chi_c$  (µg m<sup>-3</sup>) is the canopy compensation point at the notional height of trace gas exchange  $z_0'$  (m),  $\chi_a \{z - d\}$  (µg m<sup>-3</sup>) the air NH<sub>3</sub> concentration measured at the aerodynamic reference height z - d (m),  $F_t$  (µg m<sup>-2</sup> s<sup>-1</sup>) is the total NH<sub>3</sub> flux measured by the eddy covariance system,  $R_a\{z - d\}$  (s m<sup>-1</sup>) is the aerodynamic resistance at the reference height, and R<sub>b</sub> (s m<sup>-1</sup>) is the quasi-laminar resistance to NH<sub>3</sub> exchange. From this, we were also able to calculate the canopy emission potential as described by Anonymous Referee 2. The results indicate that indeed there appears to be a very large canopy compensation point that closely follows the air NH<sub>3</sub> concentration, which triggers emission events and effectively reduces deposition in the way that it prevents NH<sub>3</sub> from depositing at the maximum allowed deposition velocity allowed by turbulence ( $v_{d,max} = (R_a + R_b)^{-1}$ ; Fig. A3, panel 1). In other words: In a unidirectional framework, this high canopy compensation point increases the effective canopy resistance R<sub>c</sub> (Fig. A3, panel 2), and it appears to have a much larger influence on the observed fluxes than the atmospheric resistances. The constant (stomatal) emission potential from the Massad et al. (2010) model is much lower than the observed canopy emission potentials, and the stomatal compensation point is only a function of temperature, not of the ambient NH<sub>3</sub> concentration, which may be an indicator that, at this site, there is another, ambient concentration-dependent bidirectional pathway that is not being modelled (e.g. wet surfaces; as described, for example, by Burkhardt et al. (2009) for the case of leaf wetness).



Fig. A3: Upper panel: Deposition velocity, negative values indicate emission, and maximum deposition velocity, middle panel: canopy resistance, negative values are not shown, as they are not defined in the resistance framework and mostly correspond to phases of emission, lower panel: canopy compensation point derived from measured data. Note that the upper and middle panels are based on a one-layer deposition-only and the lower panel to a one-layer canopy compensation point framework (cf. Sutton et al. 1993).

A comparison of method (i) and (ii) is not really possible. Loubet et al. (2012) showed that it is generally possible, but they restricted it to data under relatively dry conditions - a criterion, which was never fulfilled at this peatland site during our campaign - and R<sup>2</sup> of the daily regressions not smaller than 0.5, for which this dataset was too scattered.

We added figure A3 to our manuscript as Fig. 8 and included the discussion on canopy resistance and the canopy compensation point.

We added on page 10, lines 18-20: 'Compared to  $v_{d,max} (v_{d,max} = (R_a + R_b)^{-1})$  the deposition velocity is, with a few exceptions, always smaller, confirming the plausibility of the data (see Fig. 8 panel 1).'

On page 10, lines 23-31: 'A continuous time-series of the canopy compensation point was derived (Fig. 8, panel 3), using the relation after Nemitz et al. (2000) for a single-layer canopy compensation point resistance model  $\chi_c = F_t \cdot (R_a\{z-d\} + R_b) + \chi_a\{z-d\}$ , where  $\chi_c$  (µg m<sup>-3</sup>) is the canopy compensation point at the notional height of trace gas exchange  $z_0'$  (m),  $\chi_a\{z-d\}$  (µg m<sup>-3</sup>) the air NH<sub>3</sub> concentration measured at the aerodynamic reference height z - d (m),  $F_t$  (µg m<sup>-2</sup> s<sup>-1</sup>) is the total NH<sub>3</sub> flux measured by the eddy covariance system,  $R_a\{z-d\}$  (s m<sup>-1</sup>) is the aerodynamic resistance at the reference height, and  $R_b$  (s m<sup>-1</sup>) is the aerodynamic resistance to NH3 exchange. From this, also the canopy emission potential could be calculated. The results indicate that there appears to be a very large canopy compensation point (compared for example with Loubet et al. (2012)) that closely follows the air NH3 concentration, which triggers emission events and effectively reduces deposition in the way

that it prevents NH3 from depositing at the maximum allowed deposition velocity allowed by turbulence (see Fig. 8 panel 1).'

On page 11, lines 1-2: 'As can be seen in Fig. 8 the canopy resistance increases from the beginning and is already on a high level in period II. Note that here  $R_c$  is derived from a deposition- only model approach (cf. Sutton et al., 1993).'

### 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?

Regarding the stomatal emission potential parameterization, see above.

Regarding modelled emissions: There are in fact very few short periods where the stomatal compensation point is larger than the air ammonia concentration, however, due to the relatively high stomatal resistance during the measurement period, the emissions occurring under these conditions are insignificant in magnitude compared to the total flux, and especially compared to the measured emission flux densities.

We can derive a non-constant canopy emission potential as proposed by Referee 2 that appears to be linked to air ammonia concentrations. This is indeed not compatible with the Massad et al. (2010) model, but we cannot unambiguously attribute this to the stomatal pathway based on our data.

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.

Thanks for pointing to these apparent contradictions. Looking at this again, we found in fact some wrong data used for the creation of the model regression line. Now we corrected this and there are no discrepancies anymore between figure 10 and 11 anymore (see Fig. A4). Thanks for discovering that!



Fig. A4: New figure 10 in the manuscript.

Page 11, line 29. The authors note that some analysis of nighttime resistances was conducted which indicated that the Rw 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 Rw approach is not appropriate for this site. How low should Rw be to optimize the agreement with the measurements? Can Rw 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?

We kindly refer the reader to another paper by Schrader et al. (2016, under review) which deals with this exact question and has just been published in ACPD under doi:10.5194/acp-2016-403. Quantitatively speaking, mean, median and geometric mean (calculated here to deal with zero-values as  $\left(\exp\left(\frac{1}{n}\sum_{i=1}^{n}\log(R_w+1)\right)\right) - 1\right)$  of observed nighttime  $R_c \ (\approx R_w,$ assuming that the stomata are mostly closed at night) were 606, 419 and 402 s m<sup>-1</sup>, respectively, and mean, median and geometric mean modelled nighttime  $R_w$  were > 10<sup>4</sup>, 497 and 1172 s m<sup>-1</sup>. Note that we did not impose an upper value on modelled R<sub>w</sub>, so median values are likely the most comparable quantity here. We think the agreement of modelled and measured fluxes is overall quite satisfactory after mid-March 2014, which is also reflected in the comparison of R<sub>w</sub> values (Fig. A5), considering the uncertainties in the measurements, the gap-filling procedure, and in some input parameters for the model. Simply decreasing minimum R<sub>w</sub> leads to a better fit to the measurements in Periods I and II, but an increasing mismatch later in the time-series. Increasing the stomatal emission potential, even to unreasonably high levels, and decreasing the stomatal resistance to increase this pathway's contribution to the total flux does not lead to a significant improvement of the modelled flux estimates. Following Referee 2's suggestions on further calculations, we were able to derive a significant non-zero canopy emission potential from our measurements, which appears to follow air ammonia concentration levels. This observation is not compatible with the Massad et al. (2010) model, where the only emission potential is the stomatal emission potential, which is constant throughout the year and is set through its parameterization on annual N inputs.

We added on page 13 line 16: 'A detailed investigation on  $R_w$  parameterizations can be found in Schrader et al. (2016, under review).'



Fig. A5: Comparison of observed and modelled  $R_w$  during nighttime, when  $R_a + R_b < 200$  s m<sup>-1</sup>,  $u_* > 0.1$  m s<sup>-1</sup> and  $S_t < 10$  W m<sup>-2</sup>. Left panel: Time series of observed and modeled  $R_w$ , with a mismatch in the first two weeks due to the minimum  $R_w$  in the model. Right panel: Histograms of observed and modeled  $R_w$  with 30 s m<sup>-1</sup> bins.

### Answer to Referee 2 (Part B)

### # 1

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?).

A strong drift between sonic anemometer acquisition system and QCL clocks was observed during the measurement period which led to drifts in the position of the maximum of the covariance function for the ammonia flux (see Fig. B1, approx. 3 s per day). In order to correct for this clock drift Figure B1 was divided into 9 subsections and a linear trend was fitted to the apparent time lag in each section. Then each half-hourly NH3 time series was shifted with the fitted time lag resulting in near-zero time lags in the corrected datasets (Fig. B2). For the final flux calculation in EddyPro, we still had to set a range around zero for the time lag, in which the program again filtered the one with maximum covariance or took the default of 0. We modified the text in the manuscript to clarify this procedure on page 5, line 14ff. as follows: 'The effective time lag, i.e. the residence time of the air sample in the tubing before it reaches the analyzer cell, was determined via comparing the maximum covariance of between the data series of the vertical wind speed (w) and temperature (T) with that of w and the NH3 concentration was determined by searching the maximum (absolute) covariance as a function of the time shift. A strong and irregular drift in the form of a sawtooth wave was observed found for the lag time of maximum covariance (Fig. 2b), which is attributed to diverging drifts of the system clocks of between the system clock of the sonic anemometer's data acquisition computer and the QCL clock. Thus, the drifting time lag was divided into subsections (one for each tooth) and a linear trend was fitted to the apparent time lag in each section. Then each half-hourly NH3 time series was shifted with this estimated time lag using a specifically designed R-script (R Core Team, 2012) resulting in near-zero time lags in the corrected datasets time series were shifted against each other on a half hourly basis to force a commonly expected relatively stable lag time using a specifically designed R-script (R Core Team, 2012). After a further covariance maximization procedure, a smaller less varying time lag remained. In EddyPro a range of -2 to 4 s was chosen.'

Also attached is Fig. B3 showing an example of covariance functions of vertical wind speed and temperature as well as vertical wind speed and  $NH_3$  concentration. Another example was included in the revised manuscript as Fig. 2b.



Fig. B2: Samples indicate the shift needed to maximize the covariance between vertical wind speed and NH<sub>3</sub> concentration for every 10 minute period. This shift includes the difference between the two system clocks of the sonic and the ammonia data acquisition systems. As the measurement frequency was 10 Hz, 200 samples equal 20 s delay time. Straight lines (red) were fitted to sections where the points accumulated.



Feb 18 Feb 23 Feb 28 Mar 05 Mar 10 Mar 15 Mar 20 Mar 25 Mar 30 Apr 04 Apr 09 Apr 14 Apr 19 Apr 24 Apr 29 May 04

dates





EP\_2014-02-20\_0830.txt

Fig. B4: Example for covariance functions, red line indicates  $\overline{w'T'}$  and black line  $\overline{w'c_{NH_3}}'$ 

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).

Ogives were calculated for every half hour. Since individual ogives (cumulative cospectra) of a 30 min-interval are very noisy and uncertain (even when smoothed over the frequency scale), it is generally necessary to perform a strict quality selection and averaging the resulting damping factors over certain periods or classes. Only cases with significant fluxes

(for  $NH_3$  and T) and with fairly stationary conditions were selected. In the end we decided to apply the median damping factor on the complete dataset because we couldn't find a clear dependency on horizontal wind speed nor atmospheric stability (as already mentioned in the manuscript). We assume there might have been a dependency to relative humidity but unfortunately our measurement period covers only humidity data in a very small range (high RH values). We added some illustration of the damping factor behavior in the revised manuscript as Fig. 2c.

We also added in the text the comparison to Ferrara et al. (2012; 2016) on page 5, line 30-31: 'A median damping factor of 0.67 was found which is similar to the damping factors Ferrara et al. (2012; 2016) reported for their NH3 QCL system.'

For details on the ogive-method the reader is referred to Ammann et al. (2006).

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.

Yes agreed, see answer to Referee 1 to Page 5, Section 2.3.

### #2

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 Vd(z) with the maximum deposition velocity for ammonia Vdmax(z), which represents the maximum transfer rate and can simply be evaluated as  $(Ra(z)+Rb{NH3})-1$ , where Ra(z) and  $Rb{NH3}$  are the aerodynamic and boundary layer resistances for ammonia, respectively(e.g. (Loubet et al., 2012)).

See Fig. A3 in Answer to Referee 1. This figure and the discussion around it is now included in the manuscript. The upper part shows the deposition velocity and the maximum deposition velocity. As we would expect, the latter is bigger than the deposition velocity, only in ten instances (0.2%) the maximum deposition velocity was smaller. These data was excluded.

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.

We already had a deeper look at this very interesting point, however, diurnal deposition velocities didn't give more insight, and they showed nearly the same (inverse) pattern as the flux (see Fig. B4). The linear regression was also very similar, only the Kruskal-Wallis-test differed a little with respect to precipitation and the length of the time period after the last rain. Following also to other suggestions, Fig.8 and 10 were rearranged anyway, thereby leading to some further insight into the plausibility of the flux with regard to the (maximum) deposition velocity, the canopy resistance and the canopy compensation point.



Fig. B4: Mean diurnal variation of ammonia deposition velocities, negative values indicate emission, with standard deviation (upper left panel), separated by periods (upper right panel), by precipitation (lower left panel), and by days after last rain (lower right panel).

### #3

The resistance analogy would also be very helpful to better evaluate the surface emission potential  $\Gamma(z0)$  and its dynamics. Indeed the canopy compensation point could be estimated as Cc=FNH3×(Ra(z)+Rb{NH3}) + CNH3(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.

See Fig. A3 and discussion to Figure 10 in Answer to Referee 1.

### #4

In a complementary analysis, surface conductance (gc, the inverse of the resistance Rc) could be estimated (assuming a zero emission potential in the canopy under deposition conditions) based on Vd(z) and Vdmax(z). Indeed, then gc-1=Vd(z)-1-Vdmax(z)-1(Massad et al., 2010). This would withdraw part of the influence of u\*on the exchange dynamics, which is embedded in Vd(z), and hence better show changes in ecosystem exchange parameters, and especially cuticular exchange.

We have looked at surface conductances  $g_c$  (see Fig. B5, below), but found that  $R_c$  was a better basis for the discussion (See #2 and Fig. A3 in Answer to Referee 1).



Fig. B5: Canopy conductance

### # 5

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 Vd(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.

(1) Unfortunately there were some wrong data used for the creation of the model regression line. Now there are no discrepancies anymore between figure 10 and 11 anymore. See Fig. A4 in Answer to Referee 1.

(2) There is no intercept due to the separation into emission and deposition fluxes. More on this topic in Answer to Referee 1, discussion on Figure 10.

Emissions can also be seen in Fig. 3 in the manuscript. Daily dynamics are displayed as mean diurnal courses in Fig. 4 and 6. Additionally we provide a section of one example week for this answer to the review and in the supplementary material: Fig. B8 and Fig. S4.

### #6

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.

Yes, we discussed this in the revised manuscript, see Fig. A3 and discussion to Figure 10 in Answer to Referee 1.

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).

Yes, we discussed this in the revised manuscript, see Answer to Referee 1, discussion on Page 11, line 12.

### **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.

They were unfortunately not explicitly measured in this study and therefore not included in the manuscript, but we would expect a pH of 3.5 to 4.5.

• 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.

We added a statement in the method section that it is actually a mixing ratio (relative to dry air) but we will keep the term concentration, which is recorded as mol  $NH_3$  per mol dry air. The QCL system automatically corrects for water vapor dilution in the air sample and outputs mol  $NH_3$  per mol dry air. We wrote on page 3, line 30-31: 'They were recorded as mol  $NH_3$  per mol dry air, also termed as mixing ratio, due to an online internal correction for water vapor dilution provided by the QCL.'

## • P4L30. What is the inlet box size? Could you discuss briefly the potential impact on the flux measurements?

Inlet Box size: 39 cm x 34 cm x 21 cm (added to Fig.1) We are aware that this box right next to the sonic anemometer is a source of disturbance. We tried to find a compromise between sensor separation and unhindered inflow. That's why the box is mounted below the sonic anemometer at the north side, a less common wind direction at this site (5.6% of the campaign), so only few data was influenced. We addedinformation on page 4, line 33: 'The inertial inlet box was mounted next to it on the north side, a less common wind direction at the site (5.6% of the campaign), placing the sample air inlet westward 40 cm below the center of the sonic anemometer array.'

• P5L7-12: The way the two timeseries 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.

Please see answer to # 1, part 1 (starting at page XI).

• 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.

Please see answer to # 1, part 2 (starting at page XIII).

## • 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.

Please see answer to # 1, part 2 (starting at page XIII).

## • P5L29: Clarify if gap-filling was also performed for NH3 and if so how. Gap-filling was performed. The chosen method was mean-diurnal-variation (MDV, window size was +/- 5 days) (Falge et al., 2001; Moffat et al., 2007). This information can be found at P6L16 in the manuscript.

## • P6L6: Be careful that Ra is a function of the measurement height z. Consider using the notation Ra(z).

Thanks, we changed it to  $R_a(z-d)$ .

## • P6L7 - 12: The parameters of the Wesely model should be given here: the minimum resistance and the response to radiation.

We used the original formulation of the Wesely (1989) model with a minimum  $R_s$  for H<sub>2</sub>O of 200 s m<sup>-1</sup>, scaled by the ratio of the molecular diffusivities of H<sub>2</sub>O and NH<sub>3</sub>:

$$R_{s} = 200 \cdot \frac{D_{H_{2}0}}{D_{NH_{3}}} \cdot \left(1 + \left(\frac{200}{S_{t} + 0.1}\right)^{2}\right) \frac{400}{T \cdot (T - 40)}$$

where  $S_t$  is global radiation in W m<sup>-2</sup>,  $D_x$  is the molecular diffusivity of H<sub>2</sub>O and NH<sub>3</sub> in air, respectively, in m<sup>2</sup> s<sup>-1</sup>, and T is the surface temperature in °C. Note that we were not able to optimize these parameters due to a lack of data in the dry range, where cuticular deposition is restricted, so this pathway does indeed have some uncertainty. A +/- 100 % change in the minimum stomatal resistance leads to a change in total cumulative flux between -7 % and +19 % (for 300 s m<sup>-1</sup> and 100 s m<sup>-1</sup>, respectively). We added '..., with a minimum stomatal resistance of 200 s m<sup>-1</sup>,...' on Page 6, Line 27. Further information and equation is shown in supplementary material.

## • 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.

We assume you mean the sentence before, as also Referee 1 got confused. We left the last part out and only write: 'With higher temperature a larger amount of acidic gas or particle species are present in the atmosphere and usually leads to reactions of ammonia to ammonium salts such as ammonium nitrate. (Kim et al., 2011)'

## • P7L33-34: The work of Flechard et al. (1999), Wu et al. (2009), and Burkhardt et al. (2009) should be mentioned here.

Very good point, these references were included.

# • P9L1-5. Could you be more quantitative here? Are the levels comparable with Duyzer (1994)? What is the amount of NH3 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.

Duyzer et al. (1994) reported 16 kg  $NH_3$  ha<sup>-1</sup>yr<sup>-1</sup>, so they found even more than 2.5 times more than we did in our study. We are not sure what is meant by ecosystem compensation point, but we assume you mean the stomatal emission potential

$$\Gamma_{\rm s} = 246 + 0.0041 \cdot N_{\rm in}^{3.56}$$

We can make a rough estimate about the N<sub>in</sub>: Duyzer et al. (1994) report dry deposition fluxes of 16 kg NH<sub>3</sub> ha<sup>-1</sup> yr<sup>-1</sup> and 3.8 kg NH<sub>4</sub><sup>+</sup> ha<sup>-1</sup> yr<sup>-1</sup>, corresponding to an N input by dry deposition of reduced nitrogen of around 20 kg N ha<sup>-1</sup> yr<sup>-1</sup>. They also state that the input by dry deposition is roughly 50 % of wet deposition, so total reduced nitrogen input would be roughly 50 kg NH<sub>3</sub> ha<sup>-1</sup>yr<sup>-1</sup>. Assuming that reduced nitrogen deposition is the major pathway of N<sub>r</sub> deposition at their site, this translates into a stomatal emission potential of at least 4828 mol mol<sup>-1</sup> using the Massad model (likely higher due to deposition of other N<sub>r</sub> species) or a stomatal compensation point of around 10 µg m<sup>-3</sup> at 15 °C, whereas at our site total N-input was estimated to be 25 kg N ha<sup>-1</sup> yr<sup>-1</sup> by Hurkuck et al. (2014), leading to a stomatal emission potential of 634 mol mol<sup>-1</sup> or a stomatal compensation point of 1.4 µg m<sup>-3</sup> at 15 °C. Note that Duyzer et al. (1994) estimated the average (canopy) compensation point at their site to be 0.4 µg m<sup>-3</sup>.

We added the reported deposition rates by Duyzer et al. (1994) in the manuscript on page 9 line 28. Since we are not completely sure what was meant by ecosystem compensation point, we cannot compare values from the suggested authors with it (we also couldn't find these term in their references). We will include these references in the section about surface wetness on page 7 line 33. The same dataset that was used in Wu et al. (2009) was also discussed in Walker et al. (2006) and is already discussed in the manuscript.

## • P9L12: It is difficult to see a change on Fig. 8. Please consider re-graphing this figure.

Fig. 8 from the manuscript was re-graphed (Fig. A3) but not to emphasize the change or the tipping point. We added on page 19, line 14: '(Fig. 8, tipping point in this depiction not visible, see also supplement Fig. S3)'

# • 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:

We tried both methods, please see Fig. A3 and discussion in Answer to Referee 1.

# • 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.

Unfortunately we have only monthly wet deposition, so we cannot directly link the higher wet deposition to 15 March, so we rephrased the sentence on page 10 line 10*ff*.:

'Similar to findings in Kim et al. (2011), precipitation after 15 March significantly reduced ammonia concentrations in ambient air while probably the ratio of wet to dry deposition increased.'

• P9L21-33 and P10L1-5: Showing the maximal exchange velocity Vdmax(z)=(Ra(z)+Rb{NH3})-1 would be important to show the plausibility of the flux. Moreover, you can then calculate the canopy resistance Rc or the canopy conductance gc as gc-1=Vd(z)-1-Vdmax(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  $\Gamma(z0)$  which could be estimated from the canopy compensation point  $Cc(z0)=FNH3\times(Ra(z)+Rb{NH3}) + CNH3(z)$ , with the relationship  $Cc(z0)=\Gamma(z0)\times10-3.4362+0.0508T{z0 in °C}$ . This will probably help understanding the surface exchange dynamics and also test the plausibility of the flux and concentration measurement as Cc should remain positive.

Please see Fig. A3 and discussion to Figure 10 in Answer to Referee 1.

• 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.

Please see answer to #2 (starting at page XVI).

### P10L7: explicit the term $\alpha$ .

 $\alpha$  is the significance level, that is typically 0.05, which was also chosen in this study.

### • P10L28: Vd would be indeed good to show together with the flux!

Time series of  $v_d$  together with the flux is shown in the supplementary section, see Fig. B6, as Fig. S3.



Fig. B6: Half-hourly ammonia fluxes (upper panel) and half-hourly ammonia deposition velocities (lower panel) during the whole campaign.

• 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(z0)) 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(z0) 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\*.

This is a very good point and we integrated this in our discussion on page 12 lines 4-7: 'On the other hand it could be a consequence of a stomatal or ground compensation point which follows the daily surface temperature course. The temperature itself increases with increasing  $u_*$ , also during nights with clear sky, therewith the compensation point increases, which leads to less uptake and less deposition respectively.'

## • P11L2-4: Indeed. Vmax(z) is a measure of this exchange velocity and comparing Vd(z) with Vmax(z) would easy this discussion.

Together with the new figure for  $v_d$  this was included. See also Fig. A3 and discussion to Figure 10 in Answer to Referee 1.

• 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).

Please see discussion to Figure 10 in Answer to Referee 1.

• 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 NH3 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.

Yes, we discussed this in the revised manuscript, see Answer to Referee 1, discussion on Page 11, line 12.

• 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.

Please see answer to # 5 (page XVI).

• 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 Rw, 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 Rw from night time measurements together with Ra and Rb or alternatively Vmax(z) and gc.

Mean diurnal fluxes, measured and modelled, are shown in Fig. B7. The first 9 hours match very well but then the maximum of the modelled flux is lower and delayed compared to the measured flux. The model is not able to reproduce the emission peak during midday and predicts stronger deposition, limited by the  $R_{w,min}$  set in the Massad-Model. For one week of half-hourly fluxes, measured and modelled see below (Fig. B8). For measured canopy compensation points see Fig. A3, for  $R_w$  Fig. A5. For more investigation on the model the reader is referred to Schrader at al. (in review, 2016). Fig. B8 is shown in the supplementary section as Fig. S4.



Fig. B7: Mean diurnal variation of measured and modelled flux over the whole campaign.



Fig. B8: Measured ammonia concentrations (upper panel), comparison of measured and modeled half-hourly ammonia fluxes (middle panel) and cumulative ammonia flux (lower panel) based on half-hourly data during one week of the measurement campaign.

## • P12L1-2: Please show data from the Delta denuders (in a supplementary section?) or at least give range of concentrations.

On P8L31 values of the only comparable periods are given and also the  $NH_4^+$  to  $NH_3$  ratio is given on P4L24.

### • P12L8-9: Please explicit how you extrapolated to the entire year?

Assuming a stable exchange rate during the whole year, we extrapolated the nine weeks ammonia exchange to an entire year, so it was a simple time integration. 'Extrapolating our measurement-based campaign total time proportionally to an entire year, under the assumption of stable exchange rates, results in a net deposition estimate of approx. 5.3 kg NH<sub>3</sub>-N ha<sup>-1</sup>.' Of course we will never observe a stable exchange rate during the whole year, due to climatic variation during the year and especially due to the many sources around. This number is only for getting an idea of the dimension of the annual exchange rate.

## • 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.

We only measured for 3 month including a huge gap, so we didn't really measure long-term and therefore we didn't write anything like that in the manuscript. There were a lot of difficulties that need to be solved in the future like temperature stability in the QCL-Box, humidity, cleaning of the inlet and the laser cell and pump maintenance, so we cannot give any long-term prognosis. We currently use the instrument in a 2-yr campaign at a forest site with very low N input and continuously work on solutions for the above-mentioned issues. The sentence – as it is written – can be understood as an outlook, not necessarily as a result.

### Tables

# • Table 1. Table and Figure legend should be self-standing: Please explain what are cNH3,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.

We addes the explanation in brackets in the title:

"Characterization for four subperiods of the measurement campaign (I to IV) with different NH<sub>3</sub> concentration ( $c_{NH_3}$ , mean, standard deviation, maximum and minimum) and weather regimes (mean air temperature  $\overline{T}_a$ , sum of precipitation P and net radiation R<sub>n</sub>)." We also added a column with the number of points.

# • Table 2. Explain on what variable was the Kruskal-Wallis test made (the NH3 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 Cc(z0), the emission potential $\Gamma(z0)$ or the canopy conductance gc. Please also explicit what are "p-value" and "Post-Hoc" in the legend Figures

The test was made on the ammonia flux. We will added this and an explanation for p-value (probability value) and Post-Hoc (Post-Hoc-Test result) in the title: 'Data classification and results of Kruskal-Wallis test on the NH<sub>3</sub> flux; the null hypothesis of identical population is rejected, when the p-value is below the significance level of  $\alpha = 0.05$ , the Post-hoc-test confirms if the distributions in all groups are significantly different, if not, the equal groups are listed (see Section 3.2 for further details and Tab. S1 for tests on other variables).' We tried different analyses also for the deposition velocity (see above). We added a similar table for the other variables to the supplementary material as Tab. S1.

### • Throughout the text and legends change concentration for mixing ratio.

See above.

## • Consider adding a Figure with the map of the field and the surrounding including farms and agricultural fields

We refer the reader to Hurkuck et al. (2014) for an aerial photograph.

# • 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.

We agree to add some more information in the description below. There is one additional tube from the pump to the inlet box, in the box the bypass air and the particles out section are combined and together sucked to the pump. We added a modified overview in the revised manuscript (Fig. 1) and some information to the description: 'Schematic overview of the measurement setup. An ultrasonic anemometer (height 2.5 m) is mounted closely to the heated 'inertial inlet' box (39 cm  $\times$  34 cm  $\times$  21 cm) containing a critical glass orifice to reduce the pressure regime inside the sample line (total length 3.5 m) to 5.3 to 8 kPa. After passing the critical orifice, a sharp turn of the sample lineflow path leads to a reduction of particles

(>300 nm) of approx. 50 %, thereby reducing unintentional chemical interactions. The heated tubing (black tube) leads the sample air (flow rate = approx. 17 I min-1) to the Quantum Cascade Laser (QCL), which is housed in an air-conditioned (AC) box. The bypass air and the particles out flow are combined in the inertial inlet box and together sucked to the pump (left part of the grey tube).'

• 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.

Please see #1 section 2 (page XIII). For an explicit description of the applied ogive method we refer to Ammann at al. (2006).

## • Figure 3. This is a very nice graph. It would be helpful to add legend on the right hand side.

After giving it quite some thought, we have no idea what the content of a legend in this figure could be as we think the figure is self-explanatory. We added axes labels on the right hand side instead.

## • Figure 5. Why splitting the wind direction in periods and not the NH3 mixing ratio windrose?

## Here the map of the surrounding would be much needed to help understanding the NH3 wind rose.

Period 4 is then not visible for example (because the concentrations are very low compared to the other periods) and the whole right diagram gets very unclear.

## • Figure 7. How do you explain the afternoon peak in NH3 mixing ratio. May be I missed it in the text.

See Answer to Referee 1 to Page 7, discussion of diurnal variability.

• 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 Vmax(z).

See above answer to P9L12 and new Fig. 8 shown in Answer to Referee 1 Fig. A3. When writing the manuscript we considered adding a plot of meteorological variables, but the campaign is too long to show all the data in one graph that clearly visualizes any effects of the driving flux variables. Therefore we decided to show only mean values.

# • 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 Vd(z).

We already had the suggestion from a co-author to do the same figure with  $v_d$ , but it didn't change the insights, so we decided to keep the plot with fluxes. The percentages are explained in the figure descriptions: 'Values in upper row specify percentages of data in the respective u-category given below.' We added the suggested legend.

• 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.

See discussion to Figure 10 in Answer to Referee 1. We changed the axis labels to letters with overbars to clarify that these values are mean values.

•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.

See above. Fig. B8.

### 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., 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.

Duyzer, J.: Dry deposition of ammonia and ammonium aerosols over heathland, JOURNAL OF GEOPHYSICAL RESEARCH -ALL SERIES-, 99, 18-757, 1994.

Falge, E., Baldocchi, D., Olson, R., Anthoni, P., Aubinet, M., Bernhofer, C., Burba, G., Ceulemans, R., Clement, R., Dolman, H., Granier, A., Gross, P., Grünwald, T., Hollinger, D., Jensen, N.-O., Katul, G., Keronen, P., Kowalski, A., Lai, C. T., Law, B. E., Meyers, T., Moncrieff, J., Moors, E., Munger, J. W., Pilegaard, K., Rannik, Ü., Rebmann, C., Suyker, A., Tenhunen, J., Tu, K., Verma, S., Vesala, T., Wilson, K., and Wofsy, S.: Gap filling strategies for defensible annual sums of net ecosystem exchange, Agricultural and Forest Meteorology, 107, 43-69, 2001.

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, Agricultural and Forest Meteorology, 158–159, 30-42, 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, Agriculture, Ecosystems & Environment, 219, 1-13, 2016.

Finkelstein, P.L., Sims, P.F.: Sampling error in eddy correlation flux measurements, Journal of Geophysical Research, 106, 3503-3509, 2001.

Hurkuck, M., Brümmer, C., Mohr, K., Grünhage, L., Flessa, H., and Kutsch, W. L.: Determination of atmospheric nitrogen deposition to a semi-natural peat bog site in an intensively managed agricultural landscape, Atmospheric Environment, 97, 296-309, 2014.

Kim, J.-S., Bais, A. L., Kang, S.-h., Lee, J., and Park, K.: A semi-continuous measurement of gaseous ammonia and particulate ammonium concentrations in PM2.5 in the ambient atmosphere, Journal of Atmospheric Chemistry, 251-263, 2011.

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, 2015.

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, 2012.

Massad, R.-S., Nemitz, E., and Sutton, M. A.: Review and parameterisation of bi-directional ammonia exchange between vegetation and the atmosphere, Atmos. Chem. Phys. 10, 10359–10386, doi:10.5194/acp-10-10359-2010, 2010.

Milford, C.: Dynamics of atmospheric ammonia exchange with intensively-managed grassland, Doctor of Philosophy, The University of Edinburgh, 218 pp., 2004.

Moffat, A. M., Papale, D., Reichstein, M., Hollinger, D. Y., Richardson, A. D., Barr, A. G., Beckstein, C., Braswell, B. H., Churkina, G., Desai, A. R., Falge, E., Gove, J. H., Heimann, M., Hui, D., Jarvis, A. J., Kattge, J., Noormets, A., and Stauch, V. J.: Comprehensive comparison of gap-filling techniques for eddy covariance net carbon fluxes, Agricultural and Forest Meteorology, 147, 209-232, 2007.

Mohr, K., Suda, J., Kros, H., Brümmer, C., Kutsch, W. L., Hurkuck, M., Woesner, E., Wesseling, W., 2015. Atmospheric nitrogen inputs and ways of their reduction in raised bogs of northwestern Germany – a case study from an intensively managed agricultural region (in German). Braunschweig: Johann Heinrich von Thünen-Institut, 108 p, Thünen Report 23.

Schrader, F., Brümmer, C., Flechard, C. R., Wichink Kruit, R. J., van Zanten, M. C., Richter, U., Hensen, A., and Erisman, J. W.: Non-stomatal exchange in ammonia dry deposition models: Comparison of two state-of-the-art approaches, Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-403, in review, 2016.

Walker, J. T., Robarge, W. P., Wu, Y., and Meyers, T. P.: Measurement of bidirectional ammonia fluxes over soybean using the modified Bowen-ratio technique, Agricultural and Forest Meteorology, 138, 54 -68, 2006.

Wesely, M.: Parameterization of surface resistances to gaseous dry deposition in regional-scale numerical models, Atmos. Env. (1967), 23(6), 1293–1304, doi:10.1016/0004-6981(89)90153-4, 1989.

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, 2009.

### Surface-atmosphere exchange of ammonia over peatland using QCL-

### based eddy covariance measurements and inferential modeling

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Abstract. Recent advances in laser spectrometry offer new opportunities to investigate ecosystem-atmosphere exchange of environmentally relevant trace gases. In this study, we demonstrate the applicability of a quantum cascade laser (QCL)

- 15 absorption spectrometer to continuously measure ammonia concentrations at a-high time resolution and thus to quantify the net exchange between a semi-natural peatland ecosystem and the atmosphere based on the eddy-covariance approach. Changing diurnal patterns of both ammonia concentration and fluxes were found during different periods of the campaign. We observed a clear tipping point in early spring with decreasing ammonia deposition velocities and increasingly bidirectional fluxes that occurred after the switch from dormant vegetation to  $CO_2$  uptake, but was triggered by a significant
- 20 weather change. While several biophysical parameters such as temperature, radiation, and surface wetness were identified to partially regulate ammonia exchange at the site, the seasonal concentration pattern was clearly dominated by agricultural practices in the surrounding area. Comparing the results of a compensation point model with our measurement-based flux estimates showed considerable differences in some periods of the campaign due to overestimation of non-stomatal resistances caused by low acid ratios. The total cumulative campaign exchange of ammonia after nine weeks, however,
- differed only in a 6 % deviation with 911 and 857 g NH<sub>3</sub>-N ha<sup>-1</sup> deposition being found by measurements and modeling, 25 respectively. Extrapolating our findings to an entire year, ammonia deposition was lower than reported by Hurkuck et al. (2014) for the same site in previous years using denuder systems. This was likely due to a better representation of the emission component in the net signal of eddy-covariance fluxes as well as better adapted site-specific parameters in the model. Our study not only stresses the importance of high-quality measurements for studying and assessing land surface-
- 30 atmosphere interactions, but also demonstrates the potential of QCL spectrometers for continuous observation of reactive nitrogen species as important additional instruments within long-term monitoring research infrastructures such as ICOS or NEON at sites with strong nearby ammonia sources leading to relatively high mean background concentrations and fluxes.

### **1** Introduction

Increased agricultural production and energy consumption over the last century led to a dramatic increase in anthropogenic reactive nitrogen (N) production (Erisman et al., 2008). Atmospheric N deposition can be a major driver of change in most natural and semi-natural ecosystems and may considerably alter species composition, biodiversity, and ecosystem

- 5 functioning with regard to causing nutrient imbalances. As ammonia (NH<sub>3</sub>) mainly originates from agricultural activities, it has received more and more attention in the past 20 years (e.g., Sutton et al., 2011). It is estimated that in 2008 65 Mt NH<sub>3</sub>-N were emitted globally to the atmosphere (Sutton et al., 2013), a large proportion (60 %) of it from anthropogenic sources. Around 1910 the creation and therefore release of NH<sub>3</sub> experienced a steep rise due to the Haber-Bosch-process (Galloway et al., 2003). While ammonia emissions doubled since 1950 (Asman et al., 1998), Sutton et al. (2013) predict the emission of
- 10 132 Mt  $NH_3$ -N  $yr^{-1}$  by 2100. Ammonia is an essential part of the nitrogen cascade with reactive nitrogen ( $N_r$ ) tending to accumulate in both, ecosystems and atmosphere, mainly because denitrification in soils cannot balance out industrial N creation (Galloway et al., 2003) causing a severe environmental problem for future generations. Additionally, reactive N is widely spread through hydrologic and atmospheric transport processes (Galloway et al., 2003). Ammonia can cause foliar injury, increase sensitivity to drought, reduce frost hardiness, lead to structure change in plant communities and loss in
- 15 biodiversity, especially regarding sensitive nutrient-poor ecosystems like peatbogs (Krupa, 2003). Furthermore, deposited ammonia causes ecosystem acidification, fertilization, and eutrophication (Galloway et al., 2003), while air and water quality deterioration also impact human health (Erisman et al., 2013).

Until now only little is known about the temporal and spatial variability of  $NH_3$  concentrations and exchange fluxes between different ecosystems and the atmosphere. Estimates to what extent  $NH_3$  is being emitted from plant canopies under common

- 20 environmental conditions remain highly uncertain (e.g., Flechard et al., 2013). This is due to the fact that continuous halfhourly, micrometeorological measurements of NH<sub>3</sub> exchange, e.g. based on the aerodynamic gradient or eddy-covariance (EC) technique, have largely remained experimental and were limited to selected research sites and to measurement campaigns of typically a few weeks to a few months due to technical complexity and to the large equipment and operational costs involved (e.g., Sutton et al., 2007; Flechard et al., 2011; Marx et al., 2012; Brümmer et al., 2013). Other well-
- 25 established techniques like denuder, impinger or filter sampling in combination with ion chromatography analysis usually provide concentration values and flux rates at poor time resolution and require labor- and cost-intensive chemical analyses (e.g., Dämmgen and Zimmerling, 2002; Tang et al., 2009; Hurkuck et al., 2014). Over the last few years, substantial progress has been made in the use of tunable diode laser absorption spectrometers (TDLAS) and quantum cascade lasers (QCL). The precision and fast response of these approaches have allowed first EC measurements of field scale N<sub>2</sub>O and CH<sub>4</sub> fluxes
- 30 (Denmead et al., 2010; Kroon et al., 2010; Neftel et al., 2010; Merbold et al., 2014) and are expected to become a standard method within integrated observation networks such as ICOS in Europe or NEON in North America. Eddy-covariance measurements of NH<sub>3</sub> fluxes, however, have been extremely limited and are still subject to considerable uncertainty (Famulari et al., 2004; Ellis et al., 2010; Sintermann et al., 2011; Ferrara et al., 2012) mainly due to issues regarding the tube

inlet design, sampling high frequency flux losses and tube wall and air chemistry (e.g., Marx et al., 2012 and references therein).

In this study, we demonstrate the applicability of a quantum cascade laser (QCL) absorption spectrometer to continuously and fast measure turbulent fluctuations at background-level  $NH_3$  concentrations and thus the net exchange between a semi-

- 5 natural peatland ecosystem and the atmosphere, with the eddy-covariance technique. Specifically, we (1) test the QCL performance to measure NH<sub>3</sub> concentration fluctuations and calculate NH<sub>3</sub> fluxes and net deposition during the observation period, (2) investigate the biophysical controls on NH<sub>3</sub> concentrations and fluxes, and (3) compare the measured fluxes with results from a local application of a two-layer NH<sub>3</sub> canopy compensation point model using the parameterization after Massad et al. (2010). The general objective is to better understand the mechanisms of peatland-atmosphere NH<sub>3</sub> exchange
- 10 under the influence of highly intensive agricultural land management in the surrounding area.

### 2 Materials and methods

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### 2.1 Site description and local climate

Tower-based fast response measurements of ammonia concentrations were conducted from 18 February to 8 May 2014 at an ombrotrophic, moderately drained peatland located in Northwest Germany near the city of Meppen (52°39'19.98"N, 7°10'56.65"E, 14 m.a.s.l.). The site is surrounded by intensive agricultural land and livestock holdings. Local vegetation is dominated by bog heather (Erica tetralix), purple moor-grass (M. caerulea), cotton grass (Eriophorum vaginatum,

- Eriophorum angustifolium) and is further characterized by some smaller, mostly solitary trees like birches (B. pubescens), and Scots pines (Pinus sylvestris). The peat layer depth is approx. 4 m. The area around the tower has a fetch of 650 m including some small paths, tree lines and hedgerows. Facing towards the main wind direction (SSW) 230 m can be regarded
  as totally homogenous. Details on fetch and footprint analysis are given in Hurkuck et al. (2014).
- From 1981 to 2010 the annual average air temperature ( $T_a$ ) and the mean annual precipitation in the area were 10.0 °C and 800 mm, respectively (German Weather Service, station Lingen, 2015). For the respective months of observation (February to May), the long-term average air temperatures were 2.7 °C, 5.7 °C, 9.3 °C, and 13.6 °C, respectively. Except for May, monthly mean air temperatures in 2014 were higher (4.1 °C, 6.3 °C, 10.9 °C, and 12.3 °C) than the 30-yr averages. Monthly
- 25 precipitation (36 mm, 31 mm, 39 mm, and 124 mm) was lower in February, March and April than the long-term observations (53 mm, 67 mm, 45 mm and 58 mm). As most of the precipitation was recorded after the campaign on 8 May, the measurement period was considerably drier than the long-term mean.

#### 2.2 Measurements of ammonia and microclimate

Ammonia concentrations were measured at high temporal resolution with a QCL absorption spectrometer (model mini QC-30 TILDAS-76) from Aerodyne Research, Inc. (ARI, Billerica, MA, USA). <u>They were recorded as mol NH<sub>3</sub> per mol dry air</u>, <u>also termed as mixing ratio, due to an online internal correction for water vapor dilution provided by the QCL</u>. Laser detectors were thermoelectrically cooled at 25 °C. A 76-m path length and 0.5 L multiple pass absorption cell for sampling at an operation pressure of approx. 40 Torr was used. The QCL is able to offer up to 10 Hz resolution with the detection limit in the sub-ppb range and a precision of 0.04 ppb when averaged over 1 s (McManus et al., 2008). The main frequencies of the flux contributing eddies were in a range of 0.01 to 1 Hz. Precision, i.e. measurement sensitivity, of the instrument is

- 5 0.042, 0.021, 0.016, and 0.010 ppb in 1, 10, 20, and 60 s, respectively. Along with its compact design, the QCL forms an appropriate basis for eddy-covariance measurements in the field (Ellis et al., 2010, Ferrara et al., 2012). A dry vacuum scroll pump (TriScroll 600, Agilent Technologies, Santa Clara, United States) was used to transport the sample air with a flow rate of approx. 17 1 min<sup>-1</sup> through 3-m long tubing (1 cm inner diameter) to the laser cell and back outside through an exhaust device. For further conceptual details see McManus et al. (2008) and Zahniser et al. (2005) as well as Ellis et al. (2010) for a
- 10 performance test.
  - To prevent damage to the laser cell from particles, it is necessary to filter the ambient air. Because of the stickiness of NH<sub>3</sub> and its high reactivity, it is not possible to use any conventional membrane filter. Aerodyne Research, Inc. developed a specific inertial inlet (Fig. 1) that removes particles with an aerodynamic diameter larger than 300 nm and that reduces pressure inside tubing and laser cell. After a short PTFE inlet, a critical orifice made of glass ensures that the pressure in the
- 15 system is decreased to a range of approx. 5.3 to 8 kPa, which significantly reduces wall adsorption effects (Warland et al., 2001) and is required for the operation of the laser cell. After passing the critical orifice, the sample air is forced to make a sharp turn, thereby losing 10 % of its volume, going straight to the pump, and approx. 50 % of the particles (> 300 nm) (Ellis et al., 2010; Ferrara et al., 2012; von Bobrutzki et al., 2010). Heating the inertial inlet box (at approx. 40 °C) and the anti-adhesive PFA tubing that leads the sample air to the QCL's analyzer cell minimize water condensation or absorption
- 20 (Massman and Ibrom, 2008, Ibrom et al. 2007), thus avoiding interactions of ammonia with surfaces (Walker et al., 2006; Norman et al., 2009; Ellis et al., 2010). Ellis et al. (2010) compared different tubing variants and reported significant improvement when using heated tubing at 40 °C, which reduced unintended interactions to around 10 % at 30 ppb. A side effect is, that at low atmospheric pressures NH<sub>4</sub>NO<sub>3</sub> aerosols can be volatilized, if not removed by the inertial inlet, and thereby produce NH<sub>3</sub>. DELTA denuder measurements (details below) showed a NH<sub>4</sub><sup>+</sup> to NH<sub>3</sub> ratio of 0.17 up to 0.24 during
- the campaign. Assuming that 100 % of the  $NH_4^+$  aerosols passed the inlet and were volatilized, there was on average an overestimation of 21% of  $NH_3$  concentration, which is the same rate Walker et al. (2006) found in their investigation and is an acceptable compromise between  $NH_3$  loss due to wall sorption effects and ammonia alterations through  $NH_4NO_3$ volatilization. This affects not only the concentration but also the flux, because  $NH_4NO_3$  particles are also deposited. In this study, we performed calibration with zero air every 8 hours, i.e. at 00:00, 08:00 and 16:00 local time for 60 s per interval
- 30 (data not shown) as well as internal system calibration through the laser itself by aligning the NH<sub>3</sub> absorption peak of the sampled air to the standard of the HITRAN database (Rothman et al., 2009).
   An ultrasonic anemometer (model R3, Gill Instruments, Lymington, UK) was installed at 2.5 m above ground. The inertial

inlet box was mounted next to it on the north side, a less common wind direction at the site (5.6 % of the campaign), placing

the sample air inlet <u>westward</u> 40 cm below the center of the sonic anemometer array. To protect the inlet from rain, a teeinlet was attached, which allowed to feed in calibration gas (see above).

Additional measurements of  $NH_3$  concentrations with monthly time resolution were conducted by means of passive samplers (e.g., Dämmgen et al., 2010) and DELTA denuder (**DE**nuder for Long-Term Atmospheric sampling, e.g., Tang et al., 2009).

5 A detailed description of the measurement setup of meteorological parameters such as air and soil temperature, radiation components, precipitation, water table depth as well as the operation of carbon dioxide and water vapor eddy-covariance measurements is presented in Hurkuck et al. (2014, 2016).

#### 2.3 Data acquisition, analysis and flux calculation

Sonic anemometer data were recorded by the EddyMeas software, which is an embedded application of the software package EddySoft (Kolle and Rebmann, 2009). The QCL was controlled by Aerodyne's TDL Wintel software with ammonia concentration data being recorded at a frequency of 10 Hz on the QCL computer. Anemometer and concentration time series needed alignment to a reference timestamp, before the software EddyPro (LI-COR Inc.) could be used to compute halfhourly exchange fluxes. Block averaging and 2-D coordinate rotation were applied.

The <u>effective</u> time lag, i.e. the residence time of the air sample in the tubing before it reaches the analyzer cell, was determined via comparing the maximum covariance of between the data series of the vertical wind speed (w) and temperature (T) with that of w and the NH<sub>3</sub> concentration was determined by searching the maximum (absolute) covariance as a function of the time shift. A strong and irregular drift in the form of a sawtooth wave was observed found for the lag time of maximum covariance (Fig. 2b), which is attributed to diverging drifts of the system clocks of between the system elock of the sonic anemometer's data acquisition computer and the QCL clock. Thus, the drifting time lag was divided into

- 20 <u>subsections (one for each tooth) and a linear trend was fitted to the apparent time lag in each section. Then each half-hourly</u> <u>NH<sub>3</sub> time series was shifted with this estimated time lag using a specifically designed R-script (R Core Team, 2012)</u> <u>resulting in near-zero time lags in the corrected datasets time series were shifted against each other on a half hourly basis to</u> <u>force a commonly expected relatively stable lag time using a specifically designed R script (R Core Team, 2012)</u>. After a further covariance maximization procedure, a smaller less varying time lag remained. In EddyPro a range of -2 to 4 s was
- 25 chosen.

The ogive method from Ammann et al. (2006) was applied to empirically investigate the high-frequency damping of NH<sub>3</sub> concentration measurements which usually occurs due to imperfect turbulent flow regime and possible wall sorption effects in the sampling line. Cumulative cospectra of  $\overline{w'NH_3'}$  were scaled to the corresponding  $\overline{w'T'}$  cospectra in the medium-low frequency range (see example ogives in Fig. 2a) for quality filtered cases. The resulting relative deviations at the highfrequency end are quantitative measures of the flux damping factor. A median damping factor of 0.67 was found which is similar to the damping factors Ferrara et al. (2012; 2016) reported for their NH<sub>3</sub> QCL system. As no clear dependency of the damping factor on horizontal wind speed (Fig. 2c) nor atmospheric stability could be observed, a constant correction factor

of 1/0.67 was applied to all NH<sub>3</sub> flux values as a simplified approach. The random uncertainty of the correction factor was

estimated to 15%, but a potential systematic deviation (part of the damping not appropriately detected by the ogive method) cannot be fully excluded.

The random flux error was computed according to the method after Finkelstein & Sims (2001) and the corresponding limit of detection was determined after Langford et al. (2015) as 1.96 times the flux error (95% confidence limit) resulting in a

- 5 median value of 7.75 ng N m<sup>-2</sup> s<sup>-1</sup>. Alternatively, an upper flux detection limit for half-hourly values can be calculated by using only night-time data under stationary conditions  $(3 7 \text{ m s}^{-1} \text{ wind speed})$  and wind from the west-southwest sector, where local ammonia sources were negligible and concentrations were low (< 15 ppb). The standard deviation was 16.5 ng N m<sup>-2</sup> s<sup>-1</sup>, so the 2 $\sigma$ -uncertainty range is 33.0 ng N m<sup>-2</sup> s<sup>-1</sup>.
- To guarantee a high level of data quality, fluxes were flagged according to criteria presented in Mauder and Foken (2006).
  Data from April 11 to 28 were excluded from analysis due to several technical difficulties such as power outages, pump failure or insufficient temperature control inside the analyzer housing. 33.9 %, 44.3 %, and 10.9 % of data were flagged with grade 0, 1, and 2, respectively. Data with quality flags 0 and 1 were used for further analysis, while flag 2 data were discarded. Because the stationarity tests included in the flagging protocol by Mauder and Foken (2006) might not be applicable for NH<sub>3</sub> due to possibly higher variability of the flux over short time scales, flag 1 was generally not discarded.
- 15 The remaining 10.9 % of data were not used due to insufficient turbulence ( $u_* < 0.1 \text{ m s}^{-1}$ ). The data gaps (except for the lost data in April) were filled with the mean diurnal variation (MDV, window= +/- 5 days) method (Falge et al., 2001; Moffat et al., 2007). Campaign data were grouped into four periods (Tab. 1) of 9 to 25 days depending on different concentration patterns and meteorology.

### 2.4 Modeling ammonia exchange

- A state-of-the-art dry deposition inferential model driven by measured NH<sub>3</sub> concentrations and local micrometeorological conditions was applied to assess plausibility of the flux measurements. We used the parameterization of a two-layer canopy compensation point model from Massad et al. (2010), which simplifies to a one-layer big leaf model for unmanaged ecosystems (i.e., no soil layer is considered explicitly below the canopy; *cf.* Nemitz et al., 2000). Aerodynamic-, quasi-laminar-, and cuticular resistance ( $R_a(z-d)$ ,  $R_b$ , and  $R_w$ , respectively) were parameterized as described in Massad et al. (2010)
- for semi-natural/moorland vegetation as well as the stomatal compensation point (N-input dependent). Stomatal resistance  $(R_s)$  was modeled using the simple global radiation and temperature dependent formulation of Wesely (1989, see supplement for further details), with a minimum stomatal resistance for H<sub>2</sub>O of 200 s m<sup>-1</sup>, since detailed measurements of vegetation characteristics which are necessary for more complex approaches (e.g., Emberson et al., 2000) were not available for the study period.  $R_s$  and  $R_w$  were calculated with temperature and relative humidity at the mean notional height of trace gas
- 30 exchange, estimated from measurements at the reference height and measured turbulent sensible (*H*) and latent (*LE*) heat fluxes as described in Nemitz et al. (2009).

### **3** Results and discussion

### 3.1 Diurnal and seasonal pattern of ammonia concentrations

On a half-hourly basis, ammonia concentrations ranged from 2 to 85 ppb with short term (10 Hz) maxima reaching up to 110 ppb. The highest values were found in the beginning of March (Period II) and in the beginning of April (end of Period III),

- 5 which coincided well with the peak of fertilization activities on nearby agricultural fields including the spreading of organic manures from livestock farming (Fig. 3; for details on farming practices see Hurkuck et al., 2014). The base concentration level outside the fertilization periods ranged mostly between 7 and 15 ppb and is well represented by mean values of Periods I and IV.
- The highest mean diurnal variability of ammonia concentrations was found in Period II with peak concentrations being observed in the late afternoon (>30 ppb from 5 to 15 March; Fig. 4). Concentrations were lowest at night during the whole observation period. While in Period III the average mean diurnal course exhibited less variability than in Period II, almost stable concentrations on a low level (7 to 12 ppb) were found in Periods I and IV.

The frequency distributions of wind directions and ammonia concentrations for the whole observation period are shown in Fig. 5. The typical main wind direction from the 200 to 280° sector is clearly visible. However, only the lowest

- 15 concentrations (<15 ppb, average for  $10^{\circ}$  wind sectors) were observed under southwesterly winds, whereas peak concentrations were found under winds from the east and northeast. This finding is consistent with observations from previous years using denuder systems (*cf.* Hurkuck et al., 2014). The reason for the concentration dependency on wind direction is the land use in close vicinity to the measurement site. While southwest of the tower and outside the protected zone, the area is characterized by active peat cutting, thus no elevated ammonia concentrations can be expected, east and
- 20 northeast of the tower a number of farm houses with livestock buildings, manure storage areas and adjacent fertilized land are located in a distance of approx. 2 km. The pattern of Fig. 5 is also revealed in the progression of wind direction and concentrations over time (data not shown). At the beginning of the campaign, i.e. Period I and early Period II, the predominant wind direction was south and southwest while concentrations were relatively low (Fig. 3). Later on, i.e. from late Period II onwards, wind direction was much more variable with sporadic episodes from the northeast sector, when peak
- concentrations between 60 and 110 ppb occurred. Despite the fact that frequent winds from the northeast were recorded in Period IV, it was also the time of the lowest concentration levels ( $\bar{c}_{NH_3}$ = 8.0 ppb). This is an indication that the main fertilization activities on the adjacent fields had been terminated during that time.

Similarly diurnal variability of ammonia concentrations with peak values during afternoon over a variety of ecosystems has been observed by other authors (e.g., Sutton et al., 2000; Wolff et al., 2010). There are most likely several reasons for the

30 observed pattern in this study. First and foremost, concentration levels are highly influenced by agricultural activities in the surrounding area. Farmers usually fertilize their land during the day, thereby causing ammonia volatilization, which is then transported and detected at the study site. With a stable nighttime planetary boundary layer, ammonia in the lower atmosphere is likely being deposited causing decreasing concentrations. With no further penetration from higher layers containing higher loads, concentrations remain low from midnight to sunrise (Fig. 4). When temperatures rise, turbulent mixing of the planetary boundary layer starts and <u>horizontal-vertical</u> exchange with higher layers increases, which, consequently, leads to rising ammonia concentrations over the day. On the other hand, continuous sources like mechanically ventilated stables could cause an opposite pattern with the planetary boundary layer acting as a lid and leading to a

- 5 concentration build up at night. As no information was available of ventilation types of stables, we assume that land applied manure during the day dominates the concentration signal in Fig. 4. <u>The conspicuous afternoon peak cannot be explained by</u> <u>turbulent mixing, but it is strongly linked to the northeast wind sector, where agricultural sources are closest (approx. 1.5 km distance, see also Fig. S1 in supplement). Therefore this is assumed to be an artifact caused by these agricultural point <u>sources.</u></u>
- 10 Beside the strong influence of agricultural management on seasonal concentration variability, temperature is usually a substantial driver. Higher temperature indirectly leads to higher NH<sub>3</sub> concentrations (Fig. 7), because it is often related to low relative humidity and thus favors ammonia release from the condensed phase towards the gas phase. But increasing air temperature can also be linked to lower NH<sub>3</sub> concentrations, especially observed in this study in late April and early May (Period IV). With higher temperature a larger amount of acidic gas or particle species are present in the atmosphere-<u>, which</u>
- <sup>15</sup> <u>usually leads to reactions of ammonia to ammonium salts such as ammonium nitrate</u> and usually leads to reactions of ammonia to ammonia to ammonium nitrate, part of which might even be recorded because of re volatilization inside the higher temperature and lower pressure in the sampling line (Kim et al., 2011; Norman et al., 2009). We observed higher NH<sub>3</sub> concentrations when it was dry and/or cold, whereas rainy conditions led to lower ammonia concentration levels, which confirms findings reported by Mosquera et al. (2001). In our study, high concentrations were at the same time
- 20 triggered by local sources northeast of the tower as described above. This phenomenon was particularly observed in the second half of Period III under decreasing air temperatures. Another driver for the observed concentration pattern might be leaf surface wetness. Peatlands in general, particularly during

colder parts of the year, are moist environments where ammonia can easily be taken up by wet surfaces. On the other hand, it is released back to the atmosphere when surface water, e.g. dew, evaporates during morning and midday hours (Walker et

- 25 al., 2006; Wentworth et al., 2014; Flechard et al. 1999; Wu et al. 2009; Burkhardt et al. 2009), which then causes again rising ammonia concentrations as observed in this study (Fig. 4). Other authors observed the concentration peak earlier in the morning, e.g., Walker et al. (2006) and Wolff et al. (2010) at arable land and grassland, respectively. The observed peak in our study might have been shifted because of the much higher humidity at our peatland site, indicated by small water pools, causing a longer duration of the evaporation process.
- 30 The monthly integrated ammonia concentration of 16.8 ppb in March from QCL measurements was in good agreement with those values measured by DELTA denuder and passive samplers. The latter approaches resulted in 14.5 and 15.2 ppb for DELTA and passive samplers, respectively, indicating their robustness and validity as low-cost methodologies for longterm air quality monitoring. As the time of exposure of DELTA denuders and passive samplers was not consistent with our QCL measurements due to instrument failures and campaign duration in February, April, and May, as well as due to highly

variable concentrations during that time, we could not directly compare QCL numbers with those from the monthly integrating methods.

### 3.2 Ammonia exchange and its biophysical controls

Half-hourly measured ammonia fluxes ranged mainly within -80 and 20 ng N m<sup>-2</sup> s<sup>-1</sup> with only very few values as low as -300 and as high as 300 ng N m<sup>-2</sup> s<sup>-1</sup> (upward fluxes positive, Fig. 3, lower panel). On average the peatland was a sink with a mean flux of -17.4 ng N m<sup>-2</sup> s<sup>-1</sup>. At the beginning of the campaign (Period I and II), ammonia deposition was consistently recorded (<-20 ng N m<sup>-2</sup> s<sup>-1</sup>; Fig. 3), while in Periods III and IV the average deposition decreased to values >-10 ng N m<sup>-2</sup> s<sup>-1</sup> and the exchange became clearly bi-directional.

We observed considerable diurnal variability in ammonia fluxes throughout the campaign. The average diurnal flux showed 10 moderate uptake around -25 ng N m<sup>-2</sup> s<sup>-1</sup> from midnight to 10 a.m., near-neutral exchange around noon, and highest uptake of -40 ng N m<sup>-2</sup> s<sup>-1</sup> in the late afternoon and early evening hours (Fig. 6 and 7). Separated by episodes, Period II showed the largest amplitude, whereas Period IV revealed only little variability over the daily course. Separated by surface wetness, considerably higher uptake was observed in the late afternoon and early evening when there was no precipitation recorded at the site than during times when it was raining. Furthermore, ammonia exchange shifted from around zero to net emissions at

15 noon during rain events. Typically rain events were mostly associated with winds from the south-west, where the influence of the agriculture is lowest. We also used the elapsed time after the last recorded rain as a proxy for leaf surface wetness (Fig. 6). We found that higher ammonia uptake coincided with a larger number of days passed since last rain. Springtime ammonia uptake at sites that were highly influenced by fertilization and other local sources of ammonia in the

surrounding area has been reported earlier, e.g. by Mosquera et al. (2001), who found considerable average deposition fluxes

- 20 at their semi-natural grassland site. Beside management, they showed that higher surface wetness in spring amplified local ammonia deposition, while net emission was typically found only in summer (see also Wichink Kruit et al., 2007). An undisturbed peatland site is likely to be a higher ammonia sink than managed grasslands due to a lower nitrogen status and therefore lower ammonia compensation point. However, with the chronically high atmospheric nitrogen loads caused by agriculture over several decades our peatland is presumably not such an efficient sink anymore. With this assumption and
- 25 the decreasing uptake over the progression of the measurement campaign (box plots in Fig. 3), saturation effects might have played a role in biosphere-atmosphere exchange characteristics. Flechard and Fowler (1998) already showed that peatland vegetation under its common wet conditions may not necessarily be an 'almost perfect sink' as was reported by Duyzer (1994) due to nitrogen saturation effects in heathland plants caused by persistently high ammonia deposition (approx. 13 kg N ha<sup>-1</sup> yr<sup>-1</sup>, 2.5 times more than in this study) induced by local sources.
- 30 Regarding the diurnal flux patterns observed in this study, significantly different exchange characteristics have been reported elsewhere. For example Horvath et al. (2005) and Wichink Kruit et al. (2007) found highest deposition rates in early morning hours due to dew formation at their grassland sites with decreasing deposition and even emission afterwards

through drying leaves and stomatal release. Their finding, i.e. the ecosystem emits only under dry conditions is contrary to our observations (Fig. 6 and 7).

Regarding the entire campaign, a significant tipping point in ammonia exchange was found on 15 March, where higher deposition rates changed to much lower deposition and bi-directional exchange (*cf.* Fig. 8 and 11; Section 3.3). This tipping

- 5 point followed 10 days after the onset of spring, occurring on 5 March, as indicated by CO<sub>2</sub> uptake shown as significant gross primary productivity (GPP) in Hurkuck et al. (2016) and was mainly triggered by a significant weather change. A huge pressure drop and daily minimum air temperatures exceeding 5 °C for the first time in that particular year were recorded. While conditions were dry until 15 March, 25 mm precipitation was recorded during the following nine days. Thus, a likely reason for decreasing uptake after 15 March might have been a shift of the stomatal compensation point of the local active
- peatland vegetation due to higher temperatures as was shown by Milford (2004). Similar to findings in Kim et al. (2011),
   precipitation after 15 March significantly reduced ammonia concentrations in ambient air while <u>probably</u> the ratio of wet to dry deposition considerably increased.
  - The tipping point from higher to much lower ecosystem ammonia uptake was also observed in the course of deposition velocities ( $v_d$ ) (Fig. 8 upper panel, tipping point in this depiction not visible, see also supplement Fig. S3). Mean  $v_d$  is defined
- as the ammonia flux divided by concentration over a given period and is still a valuable indicator to verify dry deposition inferential models such as AUSTAL2000 (Janicke, 2002), even in the case of bi-directional exchange (in the case of emission flux,  $v_d$  is negative). In our study mean  $v_d$  decreased from approx. 0.5 cm s<sup>-1</sup> at the beginning of the campaign to approx. 0.2 cm s<sup>-1</sup> on 15 March and remained relatively constant until the end of the campaign. <u>Compared to  $v_{d,max}$  ( $v_{d,max} =$ </u>
- $(R_a + R_b)^{-1}$ ) the deposition velocity is, with a few exceptions, always smaller, confirming the plausibility of the data (see 20 Fig. 8 upper panel). These deposition velocity values are significantly lower than those reported by Schrader and Brümmer
- (2014), who found a median and weighted average of 0.7 and 0.9 cm s<sup>-1</sup>, respectively, for the category 'semi-natural' (n=19) in their literature review. In that study, single site values of  $v_d$  were ranging between 0.1 and 1.8 cm s<sup>-1</sup>. <u>A continuous time-series of the canopy compensation point was derived (Fig. 8, lower panel), using the relation after Nemitz</u>
- et al. (2000) for a single-layer canopy compensation point resistance model  $\chi_c = F_t \cdot (R_a\{z d\} + R_b) + \chi_a\{z d\}$ , where  $\chi_c (\mu g m^{-3})$  is the canopy compensation point at the notional height of trace gas exchange  $z_0'(m), \chi_a\{z - d\}, (\mu g m^{-3})$  the air NH<sub>3</sub> concentration measured at the aerodynamic reference height *z*-*d* (m),  $F_t (\mu g m^{-2} s^{-1})$  is the total NH<sub>3</sub> flux measured by the eddy covariance system,  $R_a [z-d]$  (s m<sup>-1</sup>) is the aerodynamic resistance at the reference height, and  $R_b$  (s m<sup>-1</sup>) is the quasilaminar resistance to NH<sub>3</sub> exchange. From this, also the canopy emission potential could be calculated. The results indicate that there appears to be a very large canopy compensation point (compared for example with Loubet et al. (2012)) that
- $\frac{1}{30} \frac{\text{closely follows the air NH_3 concentration, which triggers emission events and effectively reduces deposition in the way that it prevents NH_3 from depositing at the maximum allowed deposition velocity allowed by turbulence (see Fig. 8 upper panel). The observed tipping point on March 15 is also likely another indicator of increased canopy resistance (<math>R_c$ ) over time, which
  - effectively reflects the increase of the canopy compensation point, which may be related to both stomatal and non-stomatal



influences. As can be seen in Fig. 8 (middle panel) the canopy resistance increases from the beginning and is already on a high level in period II. Note that here  $R_c$  is derived from a deposition- only model approach (*cf.* Sutton et al., 1993). Over a coniferous forest, Wyers and Erisman (1998) described an increase in nocturnal  $R_c$ , which was interpreted as a consequence of pre-deposited ammonia leading to an alkaline saturation of leaf surfaces. For drying canopy, the same authors also found

- 5 an increase in  $R_c$  in a heathland study (Erisman and Wyers (1993), which is consistent with Walker et al. (2006). Our observations showed that the tipping point occurred in a relatively dry period and also that ammonia uptake remained low during rain events ten days later. This might indicate that at a certain point ammonia exchange was partly no longer controlled by surface wetness but by the pH on non-stomatal surfaces. However, stomatal plant physiological effects in the form of the seasonal onset of CO<sub>2</sub> uptake as mentioned above was likely be caused by the change in weather and therefore be 10 probably the main reason for the tipping point.
- The statistical significance of the ammonia flux dependency on meteorological variables when classified into different ranges of values was checked by means of a Kruskal-Wallis-Test (Tab. 2, see also Tab. S1 for deposition velocity, canopy resistance, canopy compensation point and emission potential). The null hypothesis of identical population was rejected in all cases when the p-value was below the commonly used significance level of  $\alpha = 0.05$ . A Post-hoc-test confirmed that the
- 15 distributions in all groups, except for '1–2 days' and '2–5 days' in the category 'days after last rain', were significantly different. Thus, all criteria, i.e. the biophysical factors air temperature, precipitation, surface wetness, and radiation, had a statistically significant influence on ammonia exchange. However, fluxes were not well correlated with air temperature, radiation or concentration ( $R^2 < 0.1$ ) when using simple regression analysis. Milford et al. (2001) reported that these variables usually regulate the ammonia exchange but could not find a good correlation between flux and temperature or
- 20 radiation either because of many non-linear interrelations (*cf.* Milford, 2004; Yamulki et al., 1996). This can be confirmed by visually inspecting the diurnal cycles shown in Fig. 7. The course of ammonia fluxes is more closely coupled to net radiation and  $u_*$ , whereas peaks in concentration, although rather forming a bimodal pattern, follow the shape of air temperature with a 2–3 hour lag. Furthermore, solubility of ammonia is related to temperature, which in turn drives the opening of stomata (Fowler et al., 1998), although the response of radiation is much stronger and the temperature effect on stomatal conductance
- is often confounded by the stronger vapor pressure deficit effects. With increasing temperature ammonia is less dissociated in the available water reservoirs and the plants are able to easier release it to the atmosphere. Radiation and temperature are also driving local turbulence, i.e.  $u_*$ , which appears also to be a controlling factor for both ammonia concentration and fluxes (Fig. 9). While concentrations were lowest under low turbulence, even when analyzed for single periods, maxima were observed in the 0.1 to 0.2 m s<sup>-1</sup> class with slightly decreasing values under increasing
- 30 turbulence, which is a natural phenomenon due to better mixing and transport in the boundary layer, whereas low concentrations under low turbulence at night are likely an artefact of the local fertilizer management that is usually applied during the day. Highest uptake fluxes, however, were found under low  $u_*$ , whereas lowest uptake was found under high  $u_*$ . This is confirmed by separating day and nighttime data with highest uptake of ammonia clearly occurring during the night

(left and middle panel of Fig. 9). The same patterns were found when plotting  $u_*$  vs. normalized fluxes, e.g.  $v_d$  (not shown). Decreasing uptake with increasing  $u_*$  is rather an unusual finding and could be indicating that the control of turbulence is significantly masked by the strong influence of plant physiological regulation (VPD response of stomata) and agricultural practices at our study site with co-occurring gradual ammonia saturation of the leaf surface. On the other hand it could be a

- 5 consequence of a stomatal or ground compensation point which follows the daily surface temperature course. The temperature itself increases with increasing  $u_*$ , also during nights with clear sky, therewith the compensation point increases, which leads to less uptake and less deposition respectively. Further, at low turbulence local transport from nearby fields and farms into the peatland occurs, at high turbulence a high proportion is going directly from the sources into long-distance transport. At daytime this is mirrored by the flux, thus it seems like the influence of  $u_*$  on the ammonia flux is small
- 10 compared to concentration. At nighttime there is no tendency except a generally higher flux compared to daytime, which may be an effect of wet surfaces rather than any turbulence effect. It has been reported even for agricultural sites that medium to high turbulence favors the magnitude of exchange fluxes, regardless of direction, i.e. emission or deposition (*cf.* Brümmer et al., 2013).

The interdependency of the ammonia flux and concentrations is shown in Fig. 10. We separated emission from deposition 15 periods and bin-averaged the concentration data (for an extract without bin-averaging see supplement Fig. S2). Our

- observations are consistent with Milford (2004) who also found both increasing emission and deposition under elevated concentration, also when separating by wind direction (data not shown). It remains a matter of speculation whether the flux controls the concentration or vice versa as the relationship is highly controlled by plant nitrogen status and at least to some extent by biometeorological variables as mentioned above. However, Milford's (2004) statement that the concentration may
- 20 still determine the flux during deposition periods, whereas during emission periods it may be the ammonia flux itself, which is controlling the concentration, is also likely be applicable for our site during deposition periods. In emission periods, may also be applicable for our site. However, more likely is a coincidence of flux drivers and high concentration levels which were high due to advection from the local sources, is the more realistic reason for the relationship in Fig.10 (right panel). The nearest agricultural ammonia point source was 1.5 km away from the tower. With a measurement height of 2.5 m none of the
- 25 sources were located within the flux footprint, thus we can largely exclude effects from flux heterogeneity such as a direct contribution of the sources to the measured vertical fluxes. However, there might be still large scale transport processes as outlined in a study by Mohr et al. (2015) that influence ammonia concentrations at the site. What is needed at this point is not just an observation on one field and one ecosystem, but a landscape-scale or regional-scale model of emission, dispersion, chemistry, exchange and deposition, which makes it possible to work on this question interactively.

### 30 3.3 Measured vs. modeled fluxes and cumulative exchange

The comparison of measured and modeled daily mean and cumulative half-hourly ammonia fluxes is given in Fig. 10 and 11 (for one week with half-hourly values see supplement Fig. S4). We found a considerable mismatch between modeled and measured fluxes with the latter showing higher uptake in Period I and lower uptake in Period III than model outputs. In

contrast, during Periods II and IV measured and simulated fluxes run fairly parallel, with the exception of a short period of overestimated deposition during last week of March, indicating that, on average, during these times the model is able to reproduce the measured fluxes well. The interdependency of modeled ammonia fluxes and measured concentrations is very similar to the measured ones except that the model does not exhibit any emission and the fluxes are generally lower with

- 5 increasing concentrations (Fig. 10). We do not see the larger measured deposition fluxes during Periods I and II as being indicative of faulty measurements. Instead, we suspect that under the local pollution climate during the measurement period, the model predicts a too large non-stomatal resistance ( $R_w$ ). The Massad et al. (2010) parameterization uses a so-called acid to ammonia ratio (AAR), i.e. the molar ratio of the sum of HNO<sub>3</sub>, SO<sub>2</sub>, and HCl concentrations to the NH<sub>3</sub> concentration, to scale the minimum allowed  $R_w$  in the model. The very low AAR (0.07 to 0.11) measured at the peatland site increases the
- baseline (acid ratio = 1) minimum  $R_w$  of 31.5 s m<sup>-1</sup> roughly 9- to 14-fold. A comparison with non-stomatal resistances inferred from night-time measured fluxes and modeled  $R_a(z-d)$  and  $R_b$  (*cf.* Wichink Kruit et al., 2010) reveals that this is too large for periods I and II (not shown here); however, in Periods III and IV, when temperatures rise and thermodynamic equilibria are shifted towards ammonia in the gas phase – increasing apparent  $R_w$  and decreasing deposition on the external leaf surfaces – the model is able to reproduce the measured  $R_w$  well. Furthermore, HNO<sub>3</sub>, SO<sub>2</sub> and HCl concentrations were
- 15 only measured on a monthly basis using DELTA denuders, thus introducing some uncertainty to the estimated acid ratio and therefore modeled  $R_w$ . A detailed investigation on  $R_w$  parameterizations can be found in Schrader et al. (2016, under review). Regarding the canopy compensation point (Fig. 8, lower panel) it must be considered that in a unidirectional framework, this high canopy compensation point increases the effective canopy resistance  $R_c$  (Fig. 8, middle panel), and it appears to have a much larger influence on the observed fluxes than the atmospheric resistances. The constant (stomatal) emission potential
- 20 <u>from the Massad et al. (2010) model is much lower than the observed canopy emission potentials, and the stomatal</u> compensation point is only a function of temperature, not of the ambient  $NH_3$  concentration, which may be an indicator that, at this site, there is another, ambient concentration-dependent bidirectional pathway that is not being modelled (e.g. wet surfaces; as described, for example, by Burkhardt et al. (2009) for the case of leaf wetness).
- The cumulative exchange after approx. 9 weeks of observation resulted in total deposition of 911 and 857 g NH<sub>3</sub>-N ha<sup>-1</sup> for 25 measurements and model output, respectively, thus matching relatively well over a longer period despite considerable deviation in Periods I and II. Hurkuck et al. (2014) estimated annual ammonia deposition of 8.5 kg N ha<sup>-1</sup> at the same study site using denuder filter systems in combination with inferential modeling. They found considerable seasonal variability and also accounted agricultural practices in the surrounding area as the main driver for ammonia exchange variability. Extrapolating our measurement-based campaign total time proportionally to an entire year results in a net deposition estimate
- 30 of approx. 5.3 kg NH<sub>3</sub>-N ha<sup>-1</sup>. Reasons for the mismatch might be the fact that our measurements are based on a much higher time resolution leading to a more accurate representation of emission components in the net signal of the eddycovariance fluxes. Additionally,  $R_w$  is based on a much more complex parameterization in Massad et al. (2010), including AAR and a correction for temperature and leaf area index, than those methods used in Hurkuck et al. (2014). However, even

with an approx. 3.2 kg N ha<sup>-1</sup> yr<sup>-1</sup> lower ammonia deposition, our study site remains a substantial total nitrogen sink. Adding the numbers presented in Hurkuck et al. (2014), i.e. another 2.4 kg N ha<sup>-1</sup> yr<sup>-1</sup> dry deposition of HONO, HNO<sub>3</sub>, and NH<sub>4</sub>NO<sub>3</sub> aerosols as well as 14 kg N ha<sup>-1</sup> yr<sup>-1</sup> as wet deposition, total nitrogen deposition results in approx. 21.7 kg N ha<sup>-1</sup> yr<sup>-1</sup>, thereby more than four times exceeding the ecosystem-specific critical load of 5 kg N ha<sup>-1</sup> yr<sup>-1</sup> (*cf.* Bobbink et al., 2010; UNECE, 2004).

### **4** Conclusions

5

Eddy-covariance flux measurements of ammonia using a QCL in combination with an 'inertial inlet box' were conducted at a peatland site in an agricultural landscape. This methodology has high potential for (1) an establishment in long-term observation networks with the aim to improve nitrogen budgets and transfer calculations at local and regional scale as well

- 10 as (2) providing deeper insight into the mechanisms of ammonia transfer and the ecosystems' responses to ammonia loads in the atmosphere by offering continuous flux observations at unprecedentedly high temporal resolution. In the present study, we interpret changing diurnal patterns of ammonia concentration and fluxes as well as a tipping point followed by decreasing deposition velocities and increasing canopy resistance, as a sign of non-stomatal leaf surface NH<sub>3</sub> saturation in response to elevated NH<sub>3</sub> from agricultural activities (i.e. manure spreading), but also by delayed plant physiological effects after the
- 15 onset of the growing season. Temperature, radiation, and surface wetness were identified to partially regulate ammonia exchange at the site; however, the seasonal concentration pattern was clearly dominated by emissions from agricultural practices in the surrounding area. Overestimations of non-stomatal resistances due to low acid to ammonia ratios were assumed to be responsible for deviations between modeled and measured flux estimates. On a total cumulative campaign basis the estimated ne NH<sub>3</sub> exchange differed only by 6 % between the model and independent flux measurements. Lower
- 20 QCL-based deposition values than those of using denuder systems were likely due to a better representation of the emission component in the net signal of eddy-covariance fluxes as well as better adapted site-specific model parameters, particularly  $R_w$ . Further research is needed on long-term stability of the QCL system and on avoidance of unintended reactions of ammonia within the inlet and sample tube.

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### 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.
- 5 Asman, W. A. H., Sutton, M. A., and Schjørring, J. K.: Ammonia: emission, atmospheric transport and deposition, New Phytologist, 139, 27-48, 1998.
  - Bobbink, R., Hicks, K., Galloway, J., Spranger, T., Alkemade, R., Ashmore, M., Bustamante, M., Cinderby, S., Davidson,
    E., Dentener, F., Emmett, B.A., Erisman, J.W., Fenn, M., Gilliam, F.S., Nordin, A., Pardo, L., de Vries, W.: Global assessment of nitrogen deposition effects on terrestrial plant diversity: a synthesis, Ecol. Appl. 20, 30–59, 2010.
- Brümmer, C., Marx, O., Kutsch, W., Ammann, C., Wolff, V., Flechard, C. R., and Freibauer, A.: Fluxes of total reactive atmospheric nitrogen (ΣNr) using eddy covariance above arable land, Tellus B, 65, 19770, 2013.

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.

- 15 Dämmgen, U. and Zimmerling, R.: Vertical Fluxes of Air-Borne Acidifying and Eutrophying Species in the Schorfheide Nature Reserve in Brandenburg, Germany, JOURNAL OF APPLIED BOTANY, 76, 190-202, 2002.
  - Dämmgen, U., Thöni, L., Seitler, E., Lumpp, R., Bullinger, M., and Gilke, K.: Performance characteristics for the determination of ammonia concentrations in ambient air Part 2: Passive sampler measurements, Gefahrstoffe Reinhaltung der Luft, 70, 367-372, 2010.
- 20 Denmead, O. T., Macdonald, B. C. T., Bryant, G., Naylor, T., Wilson, S., Griffith, D. W. T., Wang, W. J., Salter, B., White, I., and Moody, P. W.: Emissions of methane and nitrous oxide from Australian sugarcane soils, Agricultural and Forest Meteorology, 748-756, 2010.
  - Duyzer, J.: Dry deposition of ammonia and ammonium aerosols over heathland, JOURNAL OF GEOPHYSICAL RESEARCH -ALL SERIES-, 99, 18-757, 1994.
- 25 Ellis, R. A., Murphy, J. G., Pattey, E., van Haarlem, R., O'Brien, J. M., and Herndon, S. C.: Characterizing a Quantum Cascade Tunable Infrared Laser Differential Absorption Spectrometer (QC-TILDAS) for measurements of atmospheric ammonia, Atmos. Meas. Tech., 3, 397-406, 2010.

- Emberson, L. D., Wieser, G., and Ashmore, M. R.: Modelling of stomatal conductance and ozone flux of Norway spruce: comparison with field data, Environmental Pollution, 109, 393-402, 2000.
- Erisman, J. W. and Wyers, G. P.: Continuous measurements of surface exchange of SO2 and NH3; Implications for their possible interaction in the deposition process, Atmospheric Environment. Part A. General Topics, 27, 1937-1949, 1993.

- Erisman, J.W., Sutton, M.A., Galloway, J., Klimont, Z. and Winiwarter, W.: How a century of ammonia synthesis changed the world. Nature Geoscience, 1(10): 636-639, 2008.
- Erisman, J. W., Galloway, J. N., Seitzinger, S., Bleeker, A., Dise, N. B., Petrescu, A. M. R., Leach, A. M., and de Vries, W.:
   Consequences of human modification of the global nitrogen cycle, Philosophical Transactions of the Royal Society
   B: Biological Sciences, 368, 20130116, 2013.
- Falge, E., Baldocchi, D., Olson, R., Anthoni, P., Aubinet, M., Bernhofer, C., Burba, G., Ceulemans, R., Clement, R., Dolman, H., Granier, A., Gross, P., Grünwald, T., Hollinger, D., Jensen, N.-O., Katul, G., Keronen, P., Kowalski, A., Lai, C. T., Law, B. E., Meyers, T., Moncrieff, J., Moors, E., Munger, J. W., Pilegaard, K., Rannik, Ü., Rebmann, C., Suyker, A., Tenhunen, J., Tu, K., Verma, S., Vesala, T., Wilson, K., and Wofsy, S.: Gap filling strategies for defensible annual sums of net ecosystem exchange, Agricultural and Forest Meteorology, 107, 43-69, 2001.
  - Famulari, D., Fowler, D., Hargreaves, K., Milford, C., Nemitz, E., Sutton, M. A., and Weston, K.: Measuring eddy covariance fluxes of ammonia using tunable diode laser absorption spectroscopy, Water, Air & Soil Pollution: Focus, 4, 151-158, 2004.
- 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, Agricultural and Forest Meteorology, 158–159, 30-42, 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, Agriculture, Ecosystems & Environment, 219, 1-13, 2016.
- 25 Finkelstein, P.L., Sims, P.F.: Sampling error in eddy correlation flux measurements, Journal of Geophysical Research, 106, 3503-3509, 2001.
  - Flechard, C. R. and Fowler, D.: Atmospheric ammonia at a moorland site. II: Long-term surface-atmosphere micrometeorological flux measurements. Royal Meteorological Society, 759-791, 1998.

- 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, Quarterly Journal of the Royal Meteorological Society, 125, 2611-2641, 1999.
- Flechard, C. R., Nemitz, E., Smith, R. I., Fowler, D., Vermeulen, A. T., Bleeker, A., Erisman, J. W., Simpson, D., Zhang, L.,
  Tang, Y. S., and Sutton, M. A.: Dry deposition of reactive nitrogen to European ecosystems: a comparison of inferential models across the NitroEurope network, Atmos. Chem. Phys., 11, 2703-2728, 2011.
  - Flechard, C. R., Massad, R.-S., Loubet, B., Personne, E., Simpson, D., Bash, J. O., Cooter, E. J., Nemitz, E., and Sutton, M. A.: Advances in understanding, models and parameterizations of biosphere-atmosphere ammonia exchange, Biogeosciences, 10, 5183-5225, 2013.
- 10 Fowler, D., Flechard, C. R., Sutton, M. A., and Storeton-west, R. L.: Long term measurements of the land-atmosphere exchange of ammonia over moorland, Atmospheric Environment, 32, 453-459, 1998.
  - Galloway, J. N., Aber, J. D., Erisman, J. W., Seitzinger, S. P., Howarth, R. W., Cowling, E. B., and Cosby, B. J.: The nitrogen cascade, BioScience, 2003. 341–356, 2003.
- GermanWeatherService,15http://www.dwd.de/DE/leistungen/klimadatendeutschland/langj\_mittelwerte.html;jsessionid=3A217F56F6F162BCBB87547E9FECAB9F.live21062?nn=495662&lsbId=343278, last access: 16 Dec 2015, 2015.
  - Horváth, L., Asztalos, M., Führer, E., Mészáros, R., and Weidinger, T.: Measurement of ammonia exchange over grassland in the Hungarian Great Plain, Agricultural and Forest Meteorology, 130, 282-298, 2005.
- Hurkuck, M., Brümmer, C., Mohr, K., Grünhage, L., Flessa, H., and Kutsch, W. L.: Determination of atmospheric nitrogen
   deposition to a semi-natural peat bog site in an intensively managed agricultural landscape, Atmospheric Environment, 97, 296-309, 2014.
  - Hurkuck, M., Brümmer, C., and Kutsch, W. L.: Near-neutral carbon dioxide balance at a semi-natural, temperate bog ecosystem, Journal of Geophysical Research Biogeosciences, 121,doi: 10.1002/2015JG003195, 2016.
  - Ibrom, A., Dellwik, E., Jensen, N.O., Flyvbjerg, H. and Pilegaard, K.: Strong low-pass filtering effects on water vapour flux
- 25 measurements with closed-path eddy correlation systems. Agricultural and Forest Meteorology, 147: 140 -156, 2007.
  - Janicke, L.: Lagrangian dispersion modelling. Landbauforsch Völkenrode, 235, 37-41, 2002.
- Kim, J.-S., Bais, A. L., Kang, S.-h., Lee, J., and Park, K.: A semi-continuous measurement of gaseous ammonia and particulate ammonium concentrations in PM2.5 in the ambient atmosphere, Journal of Atmospheric Chemistry, 251-30 263, 2011.

- Kolle, O. and Rebmann, C.: EddySoft Documentation of a Software Package to Acquire and Process Eddy Covariance Data, MPI-BGC, 2009.
- Kroon, P. S., Schuitmaker, A., Jonker, H. J. J., Tummers, M. J., Hensen, A., and Bosveld, F. C.: An evaluation by laser Doppler anemometry of the correction algorithm based on Kaimal cospectra for high frequency losses of EC flux measurements of CH4 and N2O, Agr. Forest Meteorol., 150, 794–805, 2010.

25

- Krupa, S. V.: Effects of atmospheric ammonia (NH3) on terrestrial vegetation: a review, Environmental Pollution, 124, 179-221, 2003.
- 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, 2015.
- 10 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, 2012.
  - Marx, O., Brümmer, C., Ammann, C., Wolff, V., and Freibauer, A.: TRANC a novel fast-response converter to measure total reactive atmospheric nitrogen, Atmos. Meas. Tech., 5, 1045-1057, 2012.
- 15 Massad, R. S., Nemitz, E., and Sutton, M. A.: Review and parameterisation of bi-directional ammonia exchange between vegetation and the atmosphere, Atmos. Chem. Phys., 10, 10359-10386, 2010.
  - Massman, W.J. and Ibrom, A.: Attenuation of concentration fluctuations of water vapor and other trace gases in turbulent tube flow. Atmos. Chem. Phys., 8, 6245–6259, 2008.
- Mauder, M. and Foken, T.: Impact of post-field data processing on eddy covariance flux estimates and energy balance closure, Meteorologische Zeitschrift, 15, 597-609, 2006.
  - McManus, J. B., Shorter, J. H., Nelson, D. D., Zahniser, M. S., Glenn, D. E., and McGovern, R. M.: Pulsed quantum cascade laser instrument with compact design for rapid, high sensitivity measurements of trace gases in air, Appl Phys B, 92, 387-392, 2008.
  - Merbold, L., Eugster, W., Stieger, J., Zahniser, M., Nelson, D. D., and Buchmann, N.: Greenhouse gas budget (CO2, CH4 and N2O) of intensively managed grassland following restoration, Global Change Biology, 20, 1913-1928, 2014.
    - Milford, C., Hargreaves, K. J., Sutton, M. A., Loubet, B., and Cellier, P.: Fluxes of NH3 and CO2 over upland moorland in the vicinity of agricultural land, Journal of Geophysical Research. Atmospheres, 106, 24169 –24181, 2001.
    - Milford, C.: Dynamics of atmospheric ammonia exchange with intensively-managed grassland, Doctor of Philosophy, The University of Edinburgh, 218 pp., 2004.

- Moffat, A. M., Papale, D., Reichstein, M., Hollinger, D. Y., Richardson, A. D., Barr, A. G., Beckstein, C., Braswell, B. H., Churkina, G., Desai, A. R., Falge, E., Gove, J. H., Heimann, M., Hui, D., Jarvis, A. J., Kattge, J., Noormets, A., and Stauch, V. J.: Comprehensive comparison of gap-filling techniques for eddy covariance net carbon fluxes, Agricultural and Forest Meteorology, 147, 209-232, 2007.
- 5 Mohr, K., Suda, J., Kros, H., Brümmer, C., Kutsch, W. L., Hurkuck, M., Woesner, E., Wesseling, W., 2015. Atmospheric nitrogen inputs and ways of their reduction in raised bogs of northwestern Germany – a case study from an intensively managed agricultural region (in German). Braunschweig: Johann Heinrich von Thünen-Institut, 108 p, Thünen Report 23.
- Mosquera, J., Hensen, A., van den Bulk, W. C. M., Vermeulen, A. T., and Erisman, J. W.: Long Term NH3 Flux Measurements above Grasslands in The Netherlands, Water, Air, & Soil Pollution: Focus, 1, 203-212, 2001.
  - Neftel, A., Ammann, C., Fischer, C., Spirig, C., Conen, F., Emmenegger, L., Tuzson, B., and Wahlen, S.: N2O exchange over managed grassland: Application of a quantum cascade laser spectrometer for micrometeorological flux measurements, Agricultural and Forest Meteorology, 150, 775-785, 2010.
  - Nemitz, E., Sutton, M. A., Schjoerring, J. K., Husted, S., and Paul Wyers, G.: Resistance modelling of ammonia exchange over oilseed rape, Agricultural and Forest Meteorology, 105, 405-425, 2000.

- Nemitz, E., Hargreaves, K. J., Neftel, A., Loubet, B., Cellier, P., Dorsey, J. R., Flynn, M., Hensen, A., Weidinger, T., Meszaros, R., Horvath, L., Dämmgen, U., Frühauf, C., Löpmeier, F. J., Gallagher, M. W., and Sutton, M. A.: Intercomparison and assessment of turbulent and physiological exchange parameters of grassland, Biogeosciences, 6, 1445-1466, 2009.
- 20 Norman, M., Spirig, C., Wolff, V., Trebs, I., Flechard, C., Wisthaler, A., Schnitzhofer, R., Hansel, A., and Neftel, A.: Intercomparison of ammonia measurement techniques at an intensively managed grassland site (Oensingen, Switzerland), Atmos. Chem. Phys., 9, 2635-2645, 2009.
  - R Core Team: R: A language and environment for statistical computing, R Foundation for Statistical Computing, Vienna, Austria. ISBN 3-900051-07-0, http://www.R-project.org/, 2012
- Rothman, L.S., Gordon, I.E., Barbe, A., Benner, D.C., Bernath, P.F., Birk, M., Boudon, V., Brown, L.R., Campargue, A., Champion, J.-P., Chance, K., Coudert, L.H., Dana, V., Devi, V.M., Fally, S., Flaud, J.-M., Gamache, R.R., Goldman, A., Jacquemart, D., Kleiner, I., Lacome, N., Lafferty, W., Mandin, J.-Y., Massie, S.T., Mikhailenko, S.N., Miller, C.E., Moazzen-Ahmadi, N., Naumenko, O.V., Nikitin, A.V., Orphal, J., Perevalov, V.I., Perrin, A., Predoi-Cross, A., Rinsland, C.P., Rotger, M., Simeckova, M., Smith, M.A.H., Sung, K., Tashkun, S.A., Tennyson, J., Toth, R.A., Vandaele, A.C., Vander Auwera J.: The HITRAN 2008 molecular spectroscopic database. J. Quant. Spectrosc. Ra. 110, 533–572, 2009.
  - 19

- Schrader, F. and Brümmer, C.: Land Use Specific Ammonia Deposition Velocities: a Review of Recent Studies (2004–2013), Water Air Soil Pollut, 225, 1-12, 2014.
- Schrader, F., Brümmer, C., Flechard, C. R., Wichink Kruit, R. J., van Zanten, M. C., Richter, U., Hensen, A., and Erisman, J.
   W.: Non-stomatal exchange in ammonia dry deposition models: Comparison of two state-of-the-art approaches, Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-403, in review, 2016.

Sintermann, J., Spirig, C., Jordan, A., Kuhn, U., Ammann, C., and Neftel, A.: Eddy covariance flux measurements of ammonia by high temperature chemical ionisation mass spectrometry, Atmos. Meas. Tech., 4, 599–616, 2011.

Sutton, M. A., Flower, D., and Moncrieff, J. B.: The exchange of atmospheric ammonia with vegetated surfaces. I: Unfertilized vegetation, Quarterly Journal of the Royal Meteorological Society, 119, 1023-1045, 1993.

- Sutton, M. A., Nemitz, E., Milford, C., Fowler, D., Moreno, J., San José, R., Wyers, G. P., Otjes, R. P., Harrison, R., Husted, S., and Schjoerring, J. K.: Micrometeorological measurements of net ammonia fluxes over oilseed rape during two vegetation periods, Agricultural and Forest Meteorology, 105, 351-369, 2000.
- Sutton, M. A., Nemitz, E., Erisman, J. W., Beier, C., Bahl, K. B., Cellier, P., de Vries, W., Cotrufo, F., Skiba, U., Di Marco, C., Jones, S., Laville, P., Soussana, J. F., Loubet, B., Twigg, M., Famulari, D., Whitehead, J., Gallagher, M. W.,
  Neftel, A., Flechard, C. R., Herrmann, B., Calanca, P. L., Schjoerring, J. K., Daemmgen, U., Horvath, L., Tang, Y. S., Emmett, B. A., Tietema, A., Peñuelas, J., Kesik, M., Brueggemann, N., Pilegaard, K., Vesala, T., Campbell, C. L., Olesen, J. E., Dragosits, U., Theobald, M. R., Levy, P., Mobbs, D. C., Milne, R., Viovy, N., Vuichard, N., Smith, J. U., Smith, P., Bergamaschi, P., Fowler, D., and Reis, S.: Challenges in quantifying biosphere–atmosphere exchange of nitrogen species, Environmental Pollution, 150, 125-139, 2007.
- 20 Sutton, M. A., Howard, C. M., Erisman, J. W., Billen, G., Bleeker, A., Grennfelt, P., van Grinsven, H., and Grizzetti, B.: The European Nitrogen Assessment : Sources, Effects, and Policy Perspectives, Cambridge University Press, Cambridge, UK, 2011.
- Sutton, M. A., Reis, S., Riddick, S. N., Dragosits, U., Nemitz, E., Theobald, M. R., Tang, Y. S., Braban, C. F., Vieno, M., Dore, A. J., Mitchell, R. F., Wanless, S., Daunt, F., Fowler, D., Blackall, T. D., Milford, C., Flechard, C. R., Loubet,
  B., Massad, R., Cellier, P., Personne, E., Coheur, P. F., Clarisse, L., Van Damme, M., Ngadi, Y., Clerbaux, C., Skjøth, C. A., Geels, C., Hertel, O., Wichink Kruit, R. J., Pinder, R. W., Bash, J. O., Walker, J. T., Simpson, D., Horváth, L., Misselbrook, T. H., Bleeker, A., Dentener, F., and de Vries, W.: Towards a climate-dependent paradigm of ammonia emission and deposition, Philosophical Transactions of the Royal Society B: Biological Sciences, 368, 20130166, 2013.
- 30 Tang, Y. S., Simmons, I., van Dijk, N., Di Marco, C., Nemitz, E., Dämmgen, U., Gilke, K., Djuricic, V., Vidic, S., Gliha, Z., Borovecki, D., Mitosinkova, M., Hanssen, J. E., Uggerud, T. H., Sanz, M. J., Sanz, P., Chorda, J. V., Flechard, C.

R., Fauvel, Y., Ferm, M., Perrino, C., and Sutton, M. A.: European scale application of atmospheric reactive nitrogen measurements in a low-cost approach to infer dry deposition fluxes, Agriculture, Ecosystems & Environment, 133, 183-195, 2009.

- UNECE: Manual on Methodologies and Criteria for Modelling and Mapping Critical Loads and Levels and Air Pollution 5 Effects, Risks and Trends, 52/04, Federal Environmental Agency, Germany, 2004.
- von Bobrutzki, K., Braban, C. F., Famulari, D., Jones, S. K., Blackall, T., Smith, T. E. L., Blom, M., Coe, H., Gallagher, M., Ghalaieny, M., McGillen, M. R., Percival, C. J., Whitehead, J. D., Ellis, R., Murphy, J., Mohacsi, A., Pogany, A., Junninen, H., Rantanen, S., Sutton, M. A., and Nemitz, E.: Field inter-comparison of eleven atmospheric ammonia measurement techniques, Atmos. Meas. Tech., 3, 91-112, 2010.
- 10 Walker, J. T., Robarge, W. P., Wu, Y., and Meyers, T. P.: Measurement of bi-directional ammonia fluxes over soybean using the modified Bowen-ratio technique, Agricultural and Forest Meteorology, 138, 54-68, 2006.
  - Warland, J. S., Dias, G. M., and Thurtell, G. W.: A tunable diode laser system for ammonia flux measurements over multiple plots, Environmental Pollution, 114, 215-221, 2001.
- Wentworth, G. R., Murphy, J. G., Gregoire, P. K., Cheyne, C. A. L., Tevlin, A. G., and Hems, R.: Soil-atmosphere exchange
   of ammonia in a non-fertilized grassland: measured emission potentials and inferred fluxes, Biogeosciences, 11, 5675-5686, 2014.
  - Wesely, M. L.: Parameterization of surface resistances to gaseous dry deposition in regional-scale numerical models, Atmos. Environ., 23, 1293–1304, 1989.
- Wichink Kruit, R. J., van Pul, W. A. J., Otjes, R. P., Hofschreuder, P., Jacobs, A. F. G., and Holtslag, A. A. M.: Ammonia
  fluxes and derived canopy compensation points over non-fertilized agricultural grassland in The Netherlands using the new gradient ammonia—high accuracy—monitor (GRAHAM), Atmospheric Environment, 41, 1275-1287, 2007.
  - Wichink Kruit, R. J., Van Pul, W. A. J., Sauter, F. J., Van den Broek, M., Nemitz, E., Sutton, M. A., Krol, M., and Holtslag,A. A. M.: Modeling the surface-atmosphere exchange of ammonia, Atmos. Environ., 44, 945–957, 2010.
- Wolff, V., Trebs, I., Ammann, C., and Meixner, F. X.: Aerodynamic gradient measurements of the NH3-HNO3-NH4NO3 triad using a wet chemical instrument: an analysis of precision requirements and flux errors, Atmos. Meas. Tech., 3, 187-208, 2010.

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., <u>149, 263-280, 2009.</u>

30

Wyers, P. G. and Erisman, J. W.: Ammonia exchange over coniferous forest, Atmospheric Environment, 32, 441-451, 1998.

- Yamulki, S., Harrison, R. M., and Goulding, K. W. T.: Ammonia surface-exchange above an agricultural field in Southeast England, Atmospheric Environment, 30, 109-118, 1996.
- Zahniser, M. S., Nelson, D. D., McManus, J. B., Shorter, J. H., Herndon, S. C., and Jimenez, R.: Development of a Quantum Cascade Laser-Based Detector for Ammonia and Nitric Acid, Medium: ED, Size: 43 pp., 2005.

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### Tables

### Table 1:

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Characterization for four subperiods of the measurement campaign (I to IV) with different NH<sub>3</sub> concentration ( $c_{NH_3}$ , mean, standard deviation, maximum and minimum) and weather regimes (mean air temperature  $\overline{T}_a$  sum of precipitation P and net radiation  $R_{n_1}$ . Characterisation for four subperiods of the measurement campaign (I to IV) with different NH3 concentration and weather regimes.

Period	Time	<u>n</u>	$\bar{c}_{\mathrm{NH}_3}$	SD of $c_{\rm NH_3}$	Min $c_{\rm NH_3}$	Max $c_{\rm NH_3}$	$\overline{T}_{a}$	Р	R <sub>n</sub>
			(ppb)	(ppb)	(ppb)	(ppb)	(°C)	(mm)	$(MJ m^{-2} d^{-1})$
Ι	Feb 18 – Mar 04	<u>643</u>	11.3	5.6	1.2	34.7	4.5	6.4	1.71
II	Mar 05 – Mar 15	<u>528</u>	22.2	12.1	3.4	87.8	6.3	3.7	4.86
III	Mar 16 – Apr 10	<u>1296</u>	16.5	11.7	2.2	87.4	8.6	35.5	5.19
IV	Apr 29 – May 07	<u>450</u>	8.0	4.2	1.7	21.0	10.3	15.5	8.14

Table 2: Data classification and results of Kruskal-Wallis test <u>on the NH<sub>3</sub> flux</u>; the null hypothesis of identical population is rejected, when the p-value is below the significance level of a = 0.05, the Post-hoc-test confirms if the distributions in all groups are significantly different, if not, the equal groups are listed (see Section 3.2 for <u>further details and Tab. S1 for tests on other variables</u>).

Meteorological variable	Groups			p-value	Post-Hoc
	<u>1</u>	2	<u>3</u>		
Air temperature	<5°C	5 – 10°C	>10°C	< 0.001	All differ
Precipitation	0 mm	>0 mm		< 0.001	All differ
Days after last rain	1 – 2 d	2 – 5 d	>5 d	< 0.001	1=2
Net radiation	$<0 \text{ W} \text{ m}^{-2}$	$0 - 150 \text{ W m}^{-2}$	$>150 \text{ W m}^{-2}$	< 0.001	All differ



Figure 1: Schematic overview of the measurement setup. An ultrasonic anemometer (height 2.5 m) is mounted closely to the heated 'inertial inlet' box (39 cm × 34 cm × 21 cm) containing a critical glass orifice to reduce the pressure regime inside the sample line (total length 3.5 m) to 5.3 to 8 kPa. After passing the critical orifice, a sharp turn of the sample lineflow path leads to a reduction of particles (>300 nm) of approx. 50 %, thereby reducing unintentional chemical interactions. The heated tubing (black tube) leads the sample air (flow rate = approx. 17 l min<sup>-1</sup>) to the Quantum Cascade Laser (QCL), which is housed in an air-conditioned (AC) box. The bypass air and the particles out flow are combined in the inertial inlet box and together sucked to the pump (left part of the grey tube).



Figure 2: <u>a)</u> Normalized flux ogives, i.e. cumulative cospectra, of sensible heat (grey) and NH<sub>3</sub> flux (red). Data were recorded on 18 February 2014, 03:30 – 04:00 pm. The vertical dotted line indicates the frequency at which the two ogives are compared to
 determine the empirical high-frequency damping factor for the NH<sub>3</sub> flux. <u>b</u>) Example of a covariance function of vertical wind speed and ammonia concentration (19 Feb 2014 02:30 pm), after correction, peaking at a time lag of 0 s. c) Variation of the

damping factor separated by wind speed classes. Bold horizontal lines in boxplots show the median, fine horizontal lines indicate lower and upper quartile values, whiskers represent 1.5 times the interquartile range.



Figure 3: Half-hourly measured ammonia concentrations and fluxes. Vertical lines indicate beginning of periods listed in Table 1.
Each period is represented by a boxplot with bold horizontal lines showing the median, fine horizontal lines indicating lower and upper quartile values, whiskers representing 1.5 times the interquartile range and dots with arrows indicating the mean and standard deviation.



Figure 4: Mean diurnal variation of ammonia concentrations separated into different periods.



Figure 5: Frequency distribution of wind direction for each period (left panel, PI (02/18 - 03/04) black, PII (03/05 - 03/15) blue, PIII (03/16 - 04/10) red, PIV (04/29 - 05/07) orange) and ammonia concentration (right panel) for each  $10^{\circ}$  wind sector.



Figure 6: Mean diurnal variation of ammonia fluxes with standard deviation (upper left panel), separated by periods (upper right panel), by precipitation (lower left panel), and by days after last rain (lower right panel).



Figure 7: Mean diurnal cycles of ammonia concentration, ammonia flux, net radiation, air temperature, and friction velocity.

5 Figure 8: Half-hourly NH<sub>3</sub> deposition velocities expressed as NH<sub>3</sub> flux divided by NH<sub>3</sub> concentration during the measurement campaign. Vertical lines indicate the start of Periods II, III, and IV as listed in Table 1.



Fig. 8: Upper panel: Deposition velocity, negative values indicate emission, and maximum deposition velocity, middle panel: canopy resistance, negative values are not shown, as they are not defined in the resistance framework and mostly correspond to phases of emission, lower panel: canopy compensation point derived from measured data. Note that the upper and middle panels are based on a one-layer deposition-only and the lower panel to a one-layer canopy compensation point framework (cf. Sutton et al. 1993).

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Figure 9: Dependency of ammonia concentrations and fluxes on  $u_*$  with panels from left to right showing daytime (Rn > 20 W m<sup>-2</sup>), nighttime (Rn < 20 W m<sup>-2</sup>), and all data, respectively. Bold horizontal lines in boxplots show the median, fine horizontal lines indicate lower and upper quartile values, whiskers represent 1.5 times the interquartile range and dots with arrows indicate the mean and standard deviation. Values in upper row specify percentages of data in the respective  $u_*$  category given below.





Figure 10: Dependency of NH<sub>3</sub> fluxes, measured and modelled, on bin-averaged NH<sub>3</sub> concentrations (bin sizes are 2 ppb for concentrations < 40 ppb and < 20 ppb, in the left and right panel, respectively; for concentrations > 40 ppb bin sizes are 20 ppb) during deposition (100% of the modelled and 84 % of the measured data, left panel) and emission periods (16% of the measured data, right panel), error bars indicate standard error.



Figure 11: Comparison of measured and modeled daily mean NH<sub>3</sub> fluxes (upper panel) and cumulative NH<sub>3</sub> flux (lower panel) based on half-hourly data during the measurement campaign. Vertical lines indicate the start of Periods II, III, and IV as listed in Table 1.

### Parameters of the Weseley model

We used the original formulation of the Wesely (1989) model with a minimum  $R_s$  for H<sub>2</sub>O of 200 s m<sup>-1</sup>, scaled by the ratio of the molecular diffusivities of H<sub>2</sub>O and NH<sub>3</sub>:

$$R_{\rm s} = 200 \cdot \frac{D_{\rm H_2O}}{D_{\rm NH_3}} \cdot \left(1 + \left(\frac{200}{S_{\rm t} + 0.1}\right)^2\right) \frac{400}{T \cdot (T - 40)}$$

where  $S_t$  is global radiation in W m<sup>-2</sup>,  $D_x$  is the molecular diffusivity of H<sub>2</sub>O and NH<sub>3</sub> in air, respectively, in m<sup>2</sup> s<sup>-1</sup>, and T is the surface temperature in °C. Note that we were not able to optimize these parameters due to a lack of data in the dry range, where cuticular deposition is restricted. A +/- 100 % change in the minimum stomatal resistance leads to a change in total cumulative ammonia flux between -7 % and +19 % (for 300 s m<sup>-1</sup> and 100 s m<sup>-1</sup>, respectively).

Table S1: Data classification and results of Kruskal-Wallis test on the deposition velocity, the canopy compensation point, the emission potential and canopy resitance; the null hypothesis of identical population is rejected, when the p-value is below the significance level of α = 0.05, the Post-hoc-test confirms if the distributions in all groups are significantly different, if not, the equal groups are listed (see Section 3.2 for further details).

<b>Deposition velocity</b>	<u>Groups</u>		<u>p-value</u>	Post-Hoc	
	1	2	<u>3</u>		
Air temperature	<u>&lt;5°C</u>	<u>5 – 10°C</u>	<u>&gt;10°C</u>	<u>&lt;0.001</u>	All differ
Precipitation	<u>0 mm</u>	<u>&gt;0 mm</u>		<u>0.811</u>	All equal
Days after last rain	<u><math>1 - 2 d</math></u>	2 - 5 d	<u>&gt;5 d</u>	<u>0.115</u>	All equal
Net radiation	$<0 \text{ W m}^{-2}$	$0 - 150 \text{ W m}^{-2}$	$>150 \text{ W m}^{-2}$	<u>&lt;0.001</u>	All differ
<b>Canopy resitance</b>	<u>Groups</u>		<u>p-value</u>	Post-Hoc	
	1	2	<u>3</u>		
Air temperature	<u>&lt;5°C</u>	<u>5 – 10°C</u>	<u>&gt;10°C</u>	<u>0.149</u>	All equal
Precipitation	<u>0 mm</u>	<u>&gt;0 mm</u>		<u>0.005</u>	All differ
Days after last rain	<u><math>1 - 2 d</math></u>	2 - 5 d	<u>&gt;5 d</u>	<u>&lt;0.001</u>	<u>1=2</u>
Net radiation	$<0 \text{ W m}^{-2}$	$0 - 150 \text{ W m}^{-2}$	$>150 \text{ W m}^{-2}$	<u>&lt;0.001</u>	All differ
Canopy compensation	<u>Groups</u>			<u>p-value</u>	Post-Hoc

<u>point</u>	1	2	<u>3</u>		
Air temperature	<u>&lt;5°C</u>	<u><math>5 - 10^{\circ}C</math></u>	<u>&gt;10°C</u>	<u>&lt;0.001</u>	All differ
Precipitation	<u>0 mm</u>	<u>&gt;0 mm</u>		<u>&lt;0.001</u>	All differ
Days after last rain	<u><math>1 - 2 d</math></u>	2-5 d	<u>&gt;5 d</u>	<u>&lt;0.001</u>	All differ
Net radiation	$\leq 0 \text{ W m}^{-2}$	$0 - 150 \text{ W m}^{-2}$	$>150 \text{ W m}^{-2}$	<u>&lt;0.001</u>	All differ
Emission notantial	Crouns		n-value	Doct Hoo	
<u>Emission potentiai</u>	Groups			<u>p-value</u>	<u>1 05t-110t</u>
	<u>1</u>	2	<u>3</u>	<u>p-value</u>	<u>1 0st-110c</u>
Air temperature	<u>1</u> < <u>5°C</u>	<u>2</u> <u>5 − 10°C</u>	<u>3</u> ≥10°C	<u>&lt;0.001</u>	All differ
Air temperature Precipitation	<u>1</u> ≤5°C 0 mm	2 5 - 10°C ≥0 mm	<u>3</u> ≥10°C	<0.001 <0.001	All differ All differ
Air temperature Precipitation Days after last rain	<u>1</u> ≤5°C 0 mm 1-2 d	$\frac{2}{5-10^{\circ}C}$ $\geq 0 \text{ mm}$ $\frac{2-5 \text{ d}}{2-5 \text{ d}}$	<u>3</u> ≥10°C ≥5 d	<pre></pre> <pre>&lt;</pre> <pre>&lt;</pre> <pre>&lt;</pre> <pre>&lt;</pre> <pre></pre> <p< td=""><td>All differ All differ 1=2</td></p<>	All differ All differ 1=2







Fig. S4: Measured ammonia concentrations (upper panel), comparison of measured and modeled half-hourly ammonia fluxes (middle panel) and cumulative ammonia flux (lower panel) based on half-hourly data during one week of the measurement campaign.