RC C3879: 'Review of Wentworth et al', Anonymous Referee #1, 28 Jul 2014

"Page 7549 line 26 to 7550 line 2: Can you quantify what more stable and variable metrological conditions mean? It would also be nice to give an idea about how this variability may impact the flux estimates."

Author Response: In August the air temperature ranged between 9°C and 30°C whereas in September it ranged from 2°C and 29°C. Likewise, the soil temperature varied from 16°C to 26°C and 9°C to 26°C in August and September, respectively. Furthermore, there were fewer days of precipitation during August relative to September. Since χ is dependent on soil temperature, more variability in soil temperature would lead to more variability in flux estimates in terms of both magnitude and direction (given the same NH_3 mixing ratio).

These lines have been changed to clarify these points: "*The soil was sampled more frequently towards the end of the campaign since meteorology (i.e. precipitation, air temperature) was more variable and was expected to perturb the Γ_{soil} to a greater extent than in August when meteorological conditions were more consistent. Specifically, the ranges in air and soil temperature were larger in September than in August.*"

"Page 7550 lines 23-27: "The inherent assumptions is …" How does this assumption impact the results presented here? A sensitivity calculation to bound the uncertainty in this assumption should be done. For example, how would a 50% reduction in the available NH4 for exchange with the atmosphere alter the conclusions of this study?"

Author Response: A sensitivity experiment was performed for one set of soil extractions. The three samples were extracted in both the 0.25% KCl solution as well as deionized water (DIW). The soil [NH_4^+] measured with the DIW extraction was between 30-45% of that measured with the 0.25% KCl extract solution. It is likely that the ionic strength of soil pore water is less than or equal to that of the KCl solution but much stronger than DIW. In other words, the uncertainty in this assumption could, *at most,* lower the measured Γ_{soil} by a factor of 2 or 3 if the soil pore water is best represented by DIW. We have confidence that the KCl solution sufficiently mimics the ability of the soil pore water to liberate NH_4^+ from the soil matrix, and that the majority of uncertainty in Γ_{soil} stems from the spatial heterogeneity of the itself (see figure 3a).

Several sentences have been added to this section to further explain this assumption: "*An additional extraction into deionized water (DIW) was performed on one set of soil samples. The [NH_4^+] measured in the DIW extract was between 30-45% of that measured with the KCl extraction. Extraction into DIW is an absolute lower bound on soil [NH_4^+] since higher ionic strength solutions will desorb more NH_4^+, and soil pore water has a much higher ionic strength than DIW.*"

"Page 7553 first paragraph in section 3.1: Are there environmental variables that correlate with the observed variability in Γ_{soil}?"

Author Response: We are hesitant to attempt linking any environmental variables to observed variability in Γ_{soil} since the spatial variability in soil pH and $[NH_4^+]$ is large. Furthermore, it would be hard to conclusively attribute any specific environmental variables to variability in Γ_{soil} given we only sampled soil on six different occasions.

"Page 7554 line 24: At what depth was the soil temperature measured?"

Author Response: Soil temperature was measured at 10 cm in 5 different locations within the fetch of the sonic anemometer (radius of 30 feet). This was mentioned on page 7551 line 9.

"Page 7554 line 28 – page 7555 line 4: The diurnal trends could be related to the soil moisture content. Soil moisture could also impact the soil compensation point because it determines the volume of soil NH4 that is available for air-surface exchange and impacts the diffusion of air through the soil media."

Author Response: Since we have chosen to represent hourly Γ_{soil} as a linear interpolation between the six Γ_{soil} measurements, our data would not capture any diurnal trends related to soil moisture content and instead is a result of diurnal trends in soil temperature and NH_3 mixing ratios. It is possible that the soil moisture content could alter Γ (and therefore χ). However, one must consider that $\Gamma = [NH_4^+]/[H^+]$, so simply increasing the volume of water would also alter $[H^+]$ in a similar fashion and it is the $[NH_4^+]/[H^+]$ ratio that dictates the available NH_4^+ for air-surface exchange. The water content will impact the diffusion of NH_3 through the soil which we have parameterized with $R_{soil} = 60$ s m^{-1} (see page 7549, line 12). However, because we hold R_{soil} constant throughout the study, the dependence of diffusion on water content is not captured.

Page 7555 lines 9-10: Why would the peak be larger than in September, if this peak originates from NH4 in the dew? Was there more dew or higher morning time humidity values in August?

Author Response: It is possible that the rate at which dew/fog evaporates has an impact on the morning peak. For example, the dew/fog could evaporate more quickly during warmer periods (August) and result in a "sharper" morning spike relative to cooler periods. Based on the available data, there was no discernible difference between either the quantity of dew or RH in August versus September. It is important to note there are almost certainly other processes contributing to this morning spike (see page 7559, lines 3-4).

"Page 7555 lines 28-29: The autumn deposition flux estimated by Wichink-Kruit et al. (2007) appear to be much larger, nearly a factor of 5, than the deposition fluxes estimated in this study. Perhaps this can be explained by differences in the ambient concentrations in the fall between the two studies."

Author Response: The reviewer raises a good point and we agree with the hypothesis. The average autumn NH_3 concentrations from Wichink Kruit et al. (2007) are 6.3 ± 3.8 μg m-3 (~9 ppb). The values from this study are significantly lower (2.3 ± 1.8 ppb for September). This discrepancy in NH_3 levels between the studies is consistent with the higher deposition fluxes measured by Wichink Kruit et al. (2007).

"Page 7557 lines 2-4: Another explication that is often made, typically outside the atmospheric measurement community, is that NH3 deposits near its source. However, I think that the relatively high background concentrations measured here argues in favor of a local and relatively heterogeneous sources, likely bidirectional exchange."

Author Response: We agree with the reviewer. There is a large diversity in lifetime estimates of NH_3, in part because deposition velocities vary widely between different surface types. However, it is typically thought that the lifetime is on the order of 1 day (Lefer et al., 1992) which means it is unlikely that the majority of NH_3 deposits near (within 1 km) of its source.

"Page 7557 first full paragraph: This paragraph could be made more concise. The authors are making an order of magnitude estimate here and there really is no need to discuss the 3m equilibria calculations. The system never reaches equilibria any ways as evident from the differences between the ambient concentration and compensation points. I think that a general statement that the soil NH4 pool is large and modulates the ambient NH3 concentration would be more reasonable."

Author Response: The back-of-the-envelope calculations for the 3 m height are provided to show the reader that a near-surface gradient in $[NH_3]$ is possible based on soil-atmosphere fluxes. We agree that the system never reaches equilibria based on soil-atmosphere exchange framework we have adopted in this study.

"Page 7558 line 27: Figures 3b and 3c indicates that the observed increase in the mixing ratio in the morning was greater than 0.5ppb"

Author Response: The calculation estimating a 0.5 ppb increase from dew evaporation is assuming the NH_3 is evenly distributed in a 1000 m deep boundary layer. In reality, the NH_3 would not be evenly distributed and a gradient would exist near the surface (i.e. higher NH_3 close to the surface). Since the AIM-IC inlet is close to the surface (3 m), one would expect an increase larger than 0.5 ppb from dew evaporation.

"Page 5, lines 17-25: Another study that explicitly measured soil flux under a crop canopy is: Walker, J.T., Jones, M.R., Bash, J.O., Myles, L., Luke, W., Meyers, T.P., Schwede, D., Herrick, J., Nemitz, E., Robarge, W., 2013, Processes of ammonia air-surface exchange in a fertilized Zea Mays canopy, Biogeosciences, 10, 981-998. The authors also estimate the portion of the emission that is taken up by the canopy and the portion that is emitted out the top of the canopy. I'm not sure I agree with your statement in lines 23-25."

Author Response: We agree that there have been several studies that explicitly measure/model soil-air NH_3 exchange (i.e. Walker et al., 2013). However, there are studies that neglect soil NH_3 emissions because of dense canopy (see Nemitz et al., 2000 and references therein). We have changed the manuscript to clarify this point:

"*Indeed, there have been a limited number of studies strictly examining soil-atmosphere bi-directional exchange. One reason is that if a significant canopy (i.e. forest or crops) is present, a significant fraction of soil NH_3 emissions are expected to be recaptured by the canopy before leaving it (Nemitz et al., 2000). For instance, Walker et al. (2013) estimated that ~76 % of soil NH_3 emissions are recaptured by the canopy in a fertilized corn field during peak leaf area index (LAI).*"

"Section 2.1: Please add a description of the precipitation regime and the typical percent canopy cover."

Author Response: The site at CARE has no overlying canopy (no trees or shrubs). August was very dry relative to September. We have added a daily cumulative rainfall time series to figure 3(a). In addition, the rainfall regime has been clarified in the last paragraph in section 2.1:

"*The site itself is surrounded by 60 hectares of semi-natural, non-fertilized grassland with no overlying canopy. The month of August was relatively dry with cumulative precipitation totalling 8 mm, whereas September had 75 mm of precipitation.*"

"Page 8, line 30: Why did you choose .25% KCL solution? The issue of the appropriate NH4+ extraction is discussed in the supplemental information section of Cooter et al (2010) and in Flechard et al. (2013) both of which are already in your references."

Author Response: We chose the 0.25% KCl solution because it is sufficient to desorb all the available NH_4^+ from the soil matrix since it gave the same NH_4^+ loadings as extracting with a 2% KCl solution (which is common practice in the literature). Our detection limits for NH_4^+ were worse with a 2% KCl extraction because the large K^+ peak interferes with the NH_4^+ peak in ion chromatography. Hence it is preferable to use a lower concentration of KCl when quantifying soil nitrogen with ion chromatography. We already made reference to the work by Flechard et al. (2013) in this section with regards to the appropriate extraction method, but now have also added reference to Cooter et al. (2010) – we thank the reviewer for pointing this out.

"Section 2.4: You do not mention wet and dry atmospheric N deposition. I would not expect there to be very much deposition at this location, but a little extra N as opposed to no N addition at all can make a difference. If you do not have any measurements, are there estimates or model simulated values? If not, can you discuss the role of atmospheric deposition in N flux from natural (non-fertilized) systems?"

Author Response: The Canadian Air and Precipitation Monitoring Network (CAPMoN) collects precipitation samples daily at the CARE facility (http://www.on.ec.gc.ca/capmon/login/login.aspx). The following passage has been added to the end of section 3.2:

The average NH_4^+ wet deposition rates from 2001-2011 for August and September are 12.4 ± 4.6 ng m^{-2} s^{-1} and 11.3 ± 5.4 ng m^{-2} s^{-1}, respectively. In the context of our results (fluxes of 2.6 ± 4.5 ng m^{-2} s^{-1} in August and -5.8 ± 3.0 ng m^{-2} s^{-1} in September), the site at CARE has net NH_3 deposition in both months when one considers both wet deposition and bi-directional exchange. In other words, the magnitude of wet deposition fluxes is roughly 2-5 times larger than the magnitude of bi-directional exchange. However, it is important to note that wet deposition occurs in discrete events, whereas dry exchange is continuous.

Wichink Kruit et al. (2012) modelled $\chi_{stomata}$ as a function of long-term NH_3 concentration (i.e. pollution climate) in their updated version of LOTOS-EUROS. In other words, it is likely χ for a non-fertilized system is influenced by total atmospheric deposition of reactive N over long time scales. However, as discussed in section 3.3 (2nd paragraph) the soil NH_3 pool is much larger than the NH_3 pool in the boundary layer so deposition on the timescale of this study is unlikely to have a large impact on χ_{soil}.

"Section 3.1: Precipitation is important to note as well as temperature. The role of precipitation events and emission pulses is discussed in Cooter et al. (2010) and Walker et al (2013)(see above). Rain (.4mm) occurred on the day of your peak observation on August 13. The August 28th observation occurred 1 day after 54mm of rain was reported. You generally expect an emission pulse following a rainfall event. If there is any atmospheric N available for wet removal (NH3 or NH4+), that would also act as a small N addition."

Author Response: We are grateful to the reviewer for pointing out this trend. We have added several sentences to the 1st paragraph in section 3.2 detailing the emission pulses on August 13th and 28th following rain. A similar pulse occurs on the afternoon of September 22nd following 10.9 mm of rain. The new addition reads:

"Precipitation can also be important factor for NH_3 fluxes – both Cooter et al. (2010) and Walker et al. (2013) observed emission "pulses" of NH_3 over agricultural soils within 24 hours after rainfall. Elevated [NH_3] levels are seen on August 13, August 28, and September 22 following 0.4 mm, 5.0 mm and 10.9 mm of rain. Reasons for this could include increased soil NH_4^+ available for exchange, increased diffusion of NH_3 through soil, and/or increased N inputs to the surface as a result of wet deposition."

"Page 12, lines 10-12. If the "nearby site" is not one referenced in Van Hove et al., 2002, then please provide a reference for this study."

Author Response: The measurements from a "nearby site" refers to soil samples taken in another non-fertilized grassland in Southwestern Ontario 30 km southwest of the CARE facility. The samples were taken as part of this study but could not be taken at CARE since we were not allowed access to the site outside of business hours and the frequency of sampling (every 6 hours) would require site access 24/7.

"Pg 12: I believe the ammonium concentration to be used in computing gamma is the concentration of NH4+ in the soil water. How do you get that concentration from your extraction method with no consideration of soil water? Do you assume that the soil is always saturated? If so, then your gamma values may be too low."

Author Response: The reviewer is correct – the $[NH_4^+]$ used to compute Γ is the ammonium concentration in soil pore water. However, for the Γ calculation $[NH_4^+]$ is normalized to $[H^+]$ (the concentration of H^+ in the pore water) so the Γ calculation can also be computed by dividing the NH_4^+ concentration in mol/kg wet soil by the H^+ concentration in mol/kg wet soil. The second approach is simpler because our methodology yields concentrations in mol/kg wet soil.

"Pg 12 lines 29-31 and page 13 lines 1-14: Your table 1 suggests a somewhat higher soil pH in August than in September (.5 units). Is this a significant difference? If it is significant, then what is the source of the temporal change?"

Author Response: Due to the spatial variability of soil pH this is not a significant difference. In some instances (e.g. September 20), the soil pH can vary almost an entire unit amongst samples taken on the same day.

"You mention the importance of temperature. It is roughly the air temperature (unless you adjusted to the leaf surface) for the leaf exchange and soil temperature for the soil exchange. At what depth was the soil temperature shown in figure 3a sampled?"

Author Response: The soil temperature was measured in 5 locations within the fetch (10 metres) of the anemometer. Each sensor was placed 10 cm deep and the soil temperature reported is the average from the 5 sensors. This is already mentioned on page 7551 line 9.

References:

Nemitz, E., Sutton, M. A., Schjoerring, J. K., Husted, S. and Paul Wyers, G.: Resistance modelling of ammonia exchange over oilseed rape, Agric. For. Meteorol., 105, 405–425, 2000.

"We read with great interest the manuscript "Soil-atmosphere exchange of ammonia in a non-fertilized grassland: measured emission potentials and inferred fluxes" by G. R. Wentworth et al. It provides an observational large scale characterization of NH3 (and other chemicals) during a 50-day campaign over a non-fertilized grassland in Ontario, CA. The results show that the emission potential for non-fertilized grasslands is way below (up to 2 orders of magnitude) the values proposed in previous studies for fertilized lands. The NH3 fluxes obtained during the campaign were also validated against previous literature showing a relative good agreement. An analysis using a Lagrangian model assesses the air parcel history and therefore identifies the possible impact of various emission sources on the chemical composition. The authors have found that NH3 – contrarily to all the other chemicals investigated - does not show a bias due to the different air mass directions, suggesting that the NH3 near surface is mainly controlled by emission/deposition rather than horizontal advection or entrainment. This is somewhat surprising since non-fertilized grasslands have a lower emission potential if compared to fertilized lands – as also mentioned in this manuscript. Maybe some extra clarification can be given.

Despite the characterization, the authors have discussed only qualitatively the morning increase of NH3. Several explanations are suggested – dew evaporation, volatilization of NH4NO3, surface emission and NH3 rich-air entrainment at the top of the boundary layer – however, the contribution of the various processes to the diurnal variability of NH3 have not been well quantified. We believe these features can be explored more carefully – and in a quantitative fashion - by the use of mixed-layer theory (Barbaro et al 2013 and references therein). This type of analysis has also been performed for other chemical species (see van Stratum et al 2012 – Figure 6). By doing so, the specific contributions to the diurnal variability of NH3 driven by turbulent mixing, advection and chemistry are quantified on time.

Specifically, in Sect 3.2 and in Sect. 3.4 the role of the boundary layer dynamics (entrainment and CBL growth) and chemistry on the morning increase of NH3 can be fully quantified. In that context, we would suggest the authors to analyze the NH3 budget.

The conservation equation for NH3 assuming horizontal homogeneity and neglecting advection – as suggested in the manuscript, reads:

$$\frac{\partial \overline{NH3}}{\partial t} = \frac{\overline{w'NH3'}_s - \overline{w'NH3'}_e}{h} + CHEM$$

where the first term on the right hand side is the divergence of the NH3 vertical flux. Note that the flux divergence contains (i) the surface flux ($\overline{w'NH3'}_s$ emission and deposition) controlled by plant and soil processes and (ii) the entrainment flux, controlled by NH3 rich/poor-air entrained from the nocturnal residual layer or free troposphere. The last term stands for the chemical NH3 formation/destruction. By calculating the budget it will be possible to better explore (quantify) the role of the NH3 bidirectional exchange.

To further support our argument, we include here a time evolution of the budget analysis (for NH3) during the convective period over grassland for the Netherlands (manuscript in

preparation). Here, the free tropospheric NH3 concentration (around 1 ppb) is much lower than the CBL values (ranging from 10-20 ppb during the day). The CBL depth ranges from 150 m in the morning up to around 1500 m in the afternoon. We observe that during the morning the bulk-averaged NH3 tendency is explained both by the emission/deposition of NH3 and the entrainment of NH3-poor air from the free-troposphere. Note the role of the CBL growth on the time evolution of the NH3 tendency. The chemistry contribution remains small during the whole convective period but can be relevant depending on specific chemical conditions (e.g. NH4NO3 volatilization and HNO3).

Lastly, the discussion of the results shown in Figures 3-5 can also greatly benefit by the use of mixed-layer theory. For instance, the atmospheric concentrations shown in Fig. 5 can be modeled with a mixed-layer model providing an extra validation component to the manuscript. In case the authors are interested, the mixed-layer code (MXLCH) used in the two references provided here is freely available including a complete documentation.

References:

Van Stratum et al (2012): Case study of the diurnal variability of chemically active species with respect to boundary layer dynamics during DOMINO: Atmos. Chem. Phys., 12, 5329–5341.

Barbaro et al (2013): Impacts of Aerosol Shortwave Radiation Absorption on the Dynamics of an Idealized Convective Atmospheric Boundary Layer Boundary-Layer Meteorol (2013) 148:31–49 DOI 10.1007/s10546-013-9800-7."

Author Response: We are very thankful for this suggestion and agree that the use of mixed-layer theory (MLT) has great applicability in surface-atmosphere exchange studies. However, our data set for this particular study is lacking NH_3 measurements in the free troposphere so it would be hard to accurately parameterize the entrainment flux. Furthermore, there was very little gas-phase HNO_3 (< 0.5 ppb) during our study so we would anticipate the chemistry term in the conservation equation to be small. Therefore, due to a lack of measurements to allow adequate parameterization of key elements of the proposed conservation equation, we suggest that this analysis is outside the scope of this current study. However, we are preparing a manuscript of a field study where concurrent aircraft measurements are available, and are very interested in incorporating this MLT model into our analysis.

"You'll find references to prior studies in undisturbed grasslands worldwide, and a global context for you work in our old review paper:

Schlesinger, W.H. and A.E. Hartley. 1992. A global budget for atmospheric NH3. Biogeochemistry 15: 191-211."

Author Response: We thank you for bringing this review to our attention. The range of NH_3 volatilisation rates from undisturbed grasslands estimated in Schlesinger and Hartley (1992) is 0.3 to 30 ng m^{-2} s^{-1}. This value is in good agreement with our inferred net fluxes during August (2.6 ± 4.5 ng m^{-2} s^{-1}) where volatilisation was observed to dominate over deposition (i.e. net upward flux). Reference to this previous work has been added to end of section 3.2:

"*Furthermore, a review by Schlesinger and Hartley (1992) estimate volatilization rates of NH_3 from undisturbed grasslands are between 0.3 and 30 ng m^{-2} s^{-1}, which encompasses the values from this work and that of Wichink Kruit et al. (2007).*"