

## ***Interactive comment on “Soil-atmosphere exchange of ammonia in a non-fertilized grassland: measured emission potentials and inferred fluxes” by G. R. Wentworth et al.***

**G. R. Wentworth et al.**

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Here we respond to the reviewer comments one at a time:

Reviewer Comment: “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.”

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Author Response: We agree that there have been several studies that explicitly measure/model soil-air NH<sub>3</sub> exchange (i.e. Walker et al., 2013). However, there are studies that neglect soil NH<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> emissions are recaptured by the canopy in a fertilized corn field during peak leaf area index (LAI).”

Reviewer Comment: “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.”

Reviewer Comment: “Page 8, line 30: Why did you choose .25% KCl solution? The issue of the appropriate NH<sub>4</sub><sup>+</sup> 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<sub>4</sub><sup>+</sup> from the soil matrix since it gave the same NH<sub>4</sub><sup>+</sup> loadings as extracting with a 2% KCl solution (which is common practice in the literature). Our

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detection limits for NH<sub>4</sub><sup>+</sup> were worse with a 2% KCl extraction because the large K<sup>+</sup> peak interferes with the NH<sub>4</sub><sup>+</sup> 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.

Reviewer Comment: “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<sub>4</sub><sup>+</sup> wet deposition rates from 2001-2011 for August and September are  $12.4 \pm 4.6$  ng m<sup>-2</sup> s<sup>-1</sup> and  $11.3 \pm 5.4$  ng m<sup>-2</sup> s<sup>-1</sup>, respectively. In the context of our results (fluxes of  $2.6 \pm 4.5$  ng m<sup>-2</sup> s<sup>-1</sup> in August and  $-5.8 \pm 3.0$  ng m<sup>-2</sup> s<sup>-1</sup> in September), the site at CARE has net NH<sub>3</sub> 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<sub>3</sub> concentration (i.e. pollution climate) in their updated version of LOTOS-EUROS. In other words, it is likely  $\chi$  for a non-fertilized system is influenced by total atmospheric depo-

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sition of reactive N over long time scales. However, as discussed in section 3.3 (2nd paragraph) the soil NH<sub>3</sub> pool is much larger than the NH<sub>3</sub> pool in the boundary layer so deposition on the timescale of this study is unlikely to have a large impact on  $\chi$  soil.

Reviewer Comment: “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 (NH<sub>3</sub> or NH<sub>4</sub><sup>+</sup>), 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<sub>3</sub> fluxes – both Cooter et al. (2010) and Walker et al. (2013) observed emission “pulses” of NH<sub>3</sub> over agricultural soils within 24 hours after rainfall. Elevated [NH<sub>3</sub>] 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<sub>4</sub><sup>+</sup> available for exchange, increased diffusion of NH<sub>3</sub> through soil, and/or increased N inputs to the surface as a result of wet deposition.”

Reviewer Comment: “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.

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Reviewer Comment: "Pg 12: I believe the ammonium concentration to be used in computing gamma is the concentration of NH<sub>4</sub><sup>+</sup> 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<sub>4</sub><sup>+</sup>] used to compute  $\Gamma$  is the ammonium concentration in soil pore water. However, for the  $\Gamma$  calculation [NH<sub>4</sub><sup>+</sup>] is normalized to [H<sup>+</sup>] (the concentration of H<sup>+</sup> in the pore water) so the  $\Gamma$  calculation can also be computed by dividing the NH<sub>4</sub><sup>+</sup> concentration in mol/kg wet soil by the H<sup>+</sup> concentration in mol/kg wet soil. The second approach is simpler because our methodology yields concentrations in mol/kg wet soil.

Reviewer Comment: "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.

Reviewer Comment: "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,

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G.: Resistance modelling of ammonia exchange over oilseed rape, *Agric. For. Meteorol.*, 105, 405–425, 2000.

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