

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.

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Here we respond to the reviewer comments on at a time.

Reviewer Comment: “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 9C and 30C whereas in September it ranged from 2C and 29C. Likewise, the soil temperature varied from 16C to 26C and 9C to 26C in August and September, respectively. Furthermore, there were fewer days of precipitation during August relative to September. Since χ is de-

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pendent 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 NH3 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.”

Reviewer Comment: “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 $[\text{NH}_4^+]$ 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 $[\text{NH}_4^+]$ 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

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$[\text{NH}_4^+]$ since higher ionic strength solutions will desorb more NH_4^+ , and soil pore water has a much higher ionic strength than DIW."

Reviewer Comment: "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 $[\text{NH}_4^+]$ 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.

Reviewer Comment: "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.

Reviewer Comment: "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 NH_4^+ 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 $\Gamma = [\text{NH}_4^+]/[\text{H}^+]$, so simply increasing the volume of water would also alter $[\text{H}^+]$ in a similar fashion and it is the $[\text{NH}_4^+]/[\text{H}^+]$ 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 $R_{\text{soil}} = 60 \text{ s m}^{-1}$ (see page 7549, line 12). However, because we hold

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R_{soil} constant throughout the study, the dependence of diffusion on water content is not captured.

Reviewer Comment: "Page 7555 lines 9-10: Why would the peak be larger than in September, if this peak originates from NH_4^+ 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).

Reviewer Comment: "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 $6.3 \pm 3.8 \mu\text{g m}^{-3}$ ($\sim 9 \text{ ppb}$). The values from this study are significantly lower ($2.3 \pm 1.8 \text{ ppb}$ 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).

Reviewer Comment: "Page 7557 lines 2-4: Another explication that is often made, typically outside the atmospheric measurement community, is that NH_3 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."

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Author Response: We agree with the reviewer. There is a large diversity in lifetime estimates of NH₃, 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 NH₃ deposits near (within 1 km) of its source.

Reviewer Comment: "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 [NH₃] 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.

Reviewer Comment: "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 NH₃ is evenly distributed in a 1000 m deep boundary layer. In reality, the NH₃ would not be evenly distributed and a gradient would exist near the surface (i.e. higher NH₃ 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.

Reviewer Comment: "Page 7560 Line 10: Again, I do not think that the deposition fluxes are that similar but this may be due to higher ambient NH₃ concentrations measured by Wickink Kruit et al (2007)."

Author Response: We agree, and have changed the language in this sentence to reflect

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the differences in NH₃ deposition during the fall, which are likely a result of higher NH₃ during the Wickink Kruit et al. (2007) study.

References:

Lefer, B. L., Talbot, R. W., Munger, J. W.: Nitric acid and ammonia at a rural northeastern US site, *J. Geophys. Res.*, 104, 1645-1661, 1999.

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