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Interactive comment on “The role of dew as a nighttime reservoir and morning source of atmospheric ammonia” by G. R. Wentworth et al.

Anonymous Referee #1

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In this manuscript, the authors presented several lines of evidence in supporting their argument that dew is a nighttime reservoir and a morning source for atmospheric ammonia (NH₃). They have demonstrated by the laboratory experiments using artificial dew solutions that the release of ammonia from drying dew can be predicted from dew ion composition. Their field measurement results have shown that ambient NH₃ levels decreased in both dry and dew event nights, and then increased in only the mornings following the dew event nights, and the time of release coincided with dew evaporation. Furthermore, the morning increases in NH₃ levels can be quantitatively explained by the releases of ammonia in the dews. The laboratory experiments and field measurements were well designed, the results and data were of high quality, and the manuscript is well prepared. I would recommend the publication of this manuscript in *Atmospheric Chemistry and Physics*. I have several comments need to be addressed, although they are relatively minor and would not change the general conclusions of this study.

Specific comments:

1. NH₃ release from drying dew: dry zero air used in the experiment was likely to lower the relative humidity (RH) in the artificial turf to an unreasonable level, and might result in an unrealistically high release fraction. In the real world, the grass canopy surface should be relatively moist because of plant transpiration. One monolayer or more of water could stay on the leaf surface at RH \geq 40%. The existence of water layers may affect the release of NH₃. If dew drying was conducted using zero air at 50% RH, the resulting release fraction might be more realistic. The authors should examine and discuss the potential effect.

Monolayer coverage of water, in a canopy with a leaf area index of 1.5 m² m⁻², would represent only 7.6x10⁻⁴ g m⁻² of water, more than a factor of a million less water than typical dew volumes, so a relatively minimal amount of ammonia would be associated with this based on bulk solubility. Ammonia could remain at the surface through adsorption of a monolayer coverage of water, in which case the fraction that actually volatilized would be lower than that predicted by the lab experiments. At RMNP the daytime RH was quite low (< 40 %), so the importance of adsorption of NH₃ to surface water was likely less significant than it could be at other sites. Subsequent laboratory experiments should investigate this effect by carrying out the drying with air at 50 % RH.

2. HCO_3^- contribution in equation 2: When in equilibrium with atmospheric CO_2 , the HCO_3^- concentration is an exponential function of pH. In artificial dew solutions (Table S1), the pH values are mostly higher than 6.35, the pK_{a1} of H_2CO_3 , and thus HCO_3^- could be important. However, the average pH of the collected dew samples is 5.19 (page 12, line 24), well below the pK_{a1} of H_2CO_3 , and thus the contribution from HCO_3^- to the anion concentration should be negligible.

We agree with the referee. The HCO_3^- equivalent loading was a non-negligible fraction for the lab dew because the pH of the synthetic dews were mostly above 6.4. On the other hand, ambient dew collected at RMNP was sufficiently acidic to mitigate the importance of HCO_3^- in the ion balance. For reference, the median $[\text{HCO}_3^-]$ for ambient dew was $5.4 \mu\text{M}$ compared to $100 \mu\text{M}$ for the synthetic laboratory dews.

3. NH_3 deposition: It is interesting to note that there was no difference in the average nighttime NH_3 loss rate between dew event nights and dry nights. Then the questions become: Was the loss of NH_3 due to its deposition to the grass canopy or due to the movement air masses (nighttime down slope flow)? If it was due to its depositional loss, similar amount was released back to the atmosphere in the morning following a dew event night, but not following a dry night; then where was the lost NH_3 during a dry night?

Given the approximate mass balance closure (on dew nights) between NH_3 lost from the atmosphere and NH_4^+ gained in dew, it is likely that deposition is a significant contributor to the observed nighttime loss of NH_3 . The fact the observed loss rate constant ($\sim 0.5 \text{ h}^{-1}$) is comparable to literature deposition velocities for NH_3 (Schrader and Brümmer, 2014) is further evidence that deposition is a significant contributor to the nocturnal loss of NH_3 . However, as the reviewer points out, it is not possible to unambiguously associate the nocturnal loss of NH_3 with deposition.

On dry nights, the NH_3 can deposit to leaf cuticles or to the soil. In the absence of dew, the NH_3 may remain adsorbed to the cuticle, sorbed to soil constituents, or dissolved in soil pore water. This has been clarified in the text (page 16, line 13):

“Deposition of NH_3 on dry nights could be to either leaf cuticles and/or soil pore water. However, it is not possible to unambiguously attribute the nocturnal NH_3 loss solely to deposition. Enhanced downslope flow of cleaner air on dry nights cannot be ruled out as a contributor to nocturnal NH_3 loss.”

It is possible that dew accumulation prevents or at least lessens deposition to cuticles or soil on dew nights. However, addressing this hypothesis requires further investigation.

4. Ion balance in dew samples: It seems that cations and anions are not in balance in many of the collected dew samples (Figure 2). HCO_3^- is only $\sim 2 \mu\text{M}$ at pH ~ 5.2 , and thus it is unlikely to make up the difference. What could be the missing ions?

The missing ions could be longer-chain organic acids (other than acetate and formate) such as succinate, maleate, malonate, and pyruvate. To our knowledge, there are no reported literature values for these species in dew. However, a recent study by Boris et al. (2016) measured the chemical composition of fog water near the ocean and reported average fog water TOC of 17.0 mg C L⁻¹ with an average total organic acid concentration of 121 μM, excluding acetate and formate. By comparison, dew at RMNP had an average of 6.23 mg C L⁻¹. Organic acids at RMNP could be a result of the oxidation of VOC emissions from the forest surrounding the site.

A second possibility are unmeasured anionic species from wind-blown dust, such as silicates, which could be counter ions for soil mineral cations included in the ion balance (Ca²⁺ and Mg²⁺). Unfortunately, to our knowledge, there are also no constraints on these species in dew.

A brief discussion has been included in the text (page 13, line 3):

“Figure 2 reveals a persistent ion imbalance for ambient dew samples. On average, about 25% more anion is needed to achieve ion balance with the measured cations. This implies that some anions are unaccounted for in the system. Possible explanations include: 1) longer chain organic acids (e.g. succinate, maleate, malonate, and pyruvate) and/or 2) silicates from wind-blown dust.”

A future study has been planned to perform lab drying experiments on ambient dew. These subsequent measurements will allow us to: 1) perform a more complete chemical analysis (i.e. for organic acids and silicates) and 2) determine whether ions that are unaccounted for will affect NH₃ release from dew evaporation (i.e. evaluate Eq. 2 for ambient samples). Drying experiments could not be done for the RMNP dew since NH₄⁺ was too dilute to detect NH₃/NH₄⁺_(residue) after drying and extraction.

5. pH values of the dew and rain samples: It is expected that rainwater to be highly acidic (mostly below pH 5, Table S3), due to high concentrations of NO₃⁻ and SO₄²⁻, the anions of strong acids, balanced by high concentrations of NH₄⁺, the cation from a weak base (Table S2). It is surprising to see the low pH in the dew samples (Table 1), as the combined equivalents of NO₃⁻ and SO₄²⁻ are lower than those of Ca⁺⁺, Mg⁺⁺, K⁺ and Na⁺ in many dew samples (Figure 2).

A possible explanation for the acidic pH in ambient dew despite ($2 \cdot \text{Ca}^{2+} + 2 \cdot \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+$) > ($2 \cdot \text{SO}_4^{2-} + \text{NO}_3^-$) is the presence of longer-chain organic acids. In addition, undetected silicates could be significant contributors for the anion balance. The sources and impacts of these species have been discussed in response to the previous comment (#4).

References

Boris, A. J., Lee, T., Park, T., Choi, J., Seo, S. J. and Collett, J. L. Jr.: Fog composition at Baengnyeong Island in the eastern Yellow Sea: detecting markers of aqueous atmospheric oxidations, Atmos. Chem. Phys., 16, 437-453, 2016.

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