The original reviewer comments are given in black text. Responses to these comments are given throughout this document in blue text. Sections added or significantly altered in the manuscript are given in underlined blue text in quotations.

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 #2

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This manuscript examines the potential for ammonia accumulation in dew with subsequent release to the atmosphere during surface drying. The authors examine this process using a combination of laboratory and field dew chemistry measurements, measurement of dew amount, and atmospheric measurements of ammonia. The experiment is well designed and the results and conclusions are, for the most part, well supported by the data, which are of high quality. The manuscript is well written and appropriate for Atmospheric Chemistry and Physics. I recommend publication subject to treatment of the following comments.

Page 3, Line 30: "Most larger scale (regional or global) chemical transport models (CTMs) still employ. . ." The authors should acknowledge that the models are evolving. For example, CTMs commonly used for North America contain a bidirectional framework for NH3 fluxes (see Pleim et al, 2013, doi:10.1002/jgrd.50262; Zhang et al., 2010, doi: 10.1029/2009JD013589).

We agree with the referee and have added the following (page 4, line 2):

"However, some recent studies have successfully incorporated a bi-directional NH_3 exchange framework into regional and global CTMs (Bash et al., 2013; Wichink Kruit et al., 2012; Zhu et al., 2015)."

Rain measurements should be briefly described in Materials and Methods.

We agree with the referee and have added the following (page 9, line 7):

"If rain had occurred during the night, then rain samples were also collected off of the dew collector in a similar fashion the following morning. Rain samples were unambiguously identified using data from the dewmeter described below."

Page 13, Line 11: ". . .NH3 deposited into dew overnight should not necessarily be counted towards the total N-deposition budget. . .". This is an important statement (and there is a similar statement on Page 14, Lines 25-27) that begs the question, how might the dew measurements differ from real processes in both the grass field and surrounding forest? Is it reasonable to expect that some dew is transferred from the canopy to the ground where the NH4+ would be more likely to remain in the ecosystem? How might the amount and timing of dew in the grass field differ from the surrounding forest?

The referee raises several good questions that we intend to investigate in subsequent studies. There are several scenarios that could cause discrepancies between dew measurements and ambient dew:

1. If real dew dissolves a substantial amount of salts already present on vegetative surfaces (i.e. particulate matter deposited during the daytime). Since the collector is rinsed prior to deployment, the dew collector will not capture this effect. This would likely cause a change in Frac(NH_3) and an underestimation of $[NH_4^+]_{dew}$. However, the Frac(NH_3) will not change if the salt components are non-volatile.
2. If dew is transferred to the ground (as the referee points out). This would cause an overestimation of V_{dew}. However, even if dew is transported to the soil surface, it will likely remain at or near the surface and could still be subject to evaporation at sunrise.
3. If there is a large difference in the accumulation/evaporation of dew on different vegetative surfaces (i.e. grass and forest, as the referee points out). The amount and timing of dew depends on a variety of meteorological factors (temperature, RH, wind speed, cloud conditions). Although meteorological factors are likely similar between the grass and surrounding forest, a dense forest canopy could hinder dew formation at the surface and on lower branches due to trapping of IR radiation.

More research is needed to quantitatively explore the impact of these scenarios. We have added a sentence to emphasize the need for additional research (page 13, line 15):

"Additional research is needed to examine the effects of: 1) salts already present on vegetative surfaces on dew composition, 2) dew transfer from leaf to soil prior to evaporation, and 3) different canopies (e.g. forest, tall grass) on the amount and timing of dew accumulation and evaporation."

Regarding the interpretation of the atmospheric measurements of NH3, it is likely that during some periods the emission footprint driving the variability in atmospheric NH3 extends well outside of the grass field in which the dew measurements were made. This may be further complicated by topographically induced advection of NH3 from upslope/downslope as well. For these reasons, and because the field is surrounded by forest, some discussion of the representativeness of the measurements relative to the larger surrounding ecosystem is warranted.

We agree with the referee and have added the following to clarify emission footprint and explicitly discuss the influence of upslope/downslope flow (page 15, line 8):

"It is likely that during some periods the emission/deposition footprint of the atmospheric and dew measurements extends beyond the grassland clearing and into the surrounding forest. While we did not find that the overnight loss rate of ammonia depended on dew amount, the deposition rate of ammonia likely depends on surface type, so estimates of moles of NH_3 deposited per m^2 from the dew collector may not be representative of the surrounding forest. Upslope and downslope flow conditions could also explain some of the variability in nocturnal NH_3 since the latter is prevalent during the nighttime and delivers cleaner air from the west of RMNP.

Subsequent work should be performed to examine the representativeness of grassland dew measurements to the larger surrounding ecosystem."

Discussion of NH3 loss rates beginning Page 16, Line 9. The finding of similar loss rates on dew and dry nights is interesting and to me a bit surprising. The implication that dew results in a net lower deposition flux to the ecosystem is important from both a budget standpoint and process modeling. The calculated loss rates, assumed to reflect deposition, are based on a mass balance framework that may be considerably more complicated in complex terrain. For example, the rate could be affected by advection of NH3 depleted air from upslope rather than deposition. In my opinion, this aspect of the paper would benefit from further analysis.

We agree that the nocturnal NH_3 loss rate is affected by more than just deposition, and could be affected by upslope/downslope advection as the referee suggests. Therefore, we have added an additional point to our list of assumptions (page 15, line 25):

"…and 4) no influence from horizontal advection (i.e. upslope/downslope flow) on NH_3"

The authors should consider including some discussion of meteorological conditions associated with dew versus dry nights. Are wind speed and direction similar?

The average nocturnal wind speed on dew nights was less than dry nights (1.3 m s^{-1} versus 2.2 m s^{-1}). On the other hand, average wind direction was from the NW for both dew nights (307º) and dry nights (313º) indicating downslope flow in both instances. The average maximum nocturnal RH on dew nights was 75%, significantly higher than on dry nights (53%).

Regarding NH3 deposition processes, I agree with the suggestion that Ra and Rb dominate over the surface resistance at night. This is another instance where an examination of meteorology may be helpful. Comparison of Ra and Rb on dew versus dry nights would provide some insight into potential differences in exchange processes. Were the CASTNET meteorological measurements active during the study period or were there other measurements from which Ra and Rb may be calculated? If not, even a basic analysis of wind speed and direction during dew versus dry nights would be informative. The results suggest that, assuming the atmospheric resistances are similar on dew versus dry nights, similar rates of non-stomatal deposition occur when the surface is wet versus dry.

Unfortunately R_a and R_b cannot be reliably calculated during the study since there was no instrumentation with which to measure friction velocity. As stated above, winds were calmer on dew nights while the average wind directions were similar. We agree with the referee that this is important to discuss and have added the following to the manuscript (page 16, line 13):

"The average nocturnal wind speed on dew nights was lower than on dry nights (1.3 m s^{-1} versus 2.2 m s^{-1}). Lower wind speeds typically result in a higher R_a and R_b. It is possible that increased aerodynamic and quasi-laminar resistances on dew nights are partially compensated for by a lower surface resistance due to dew, such that the overall canopy resistance is similar on dew nights and dry nights. Average nocturnal wind direction was from the NW (i.e. downslope flow) on both dew nights (307º) and dry nights (313º). The average nocturnal maximum for RH was

75% on dew nights and only 53% on dry nights. The lower wind speeds and higher RH on dew nights are consistent with the meteorological conditions favourable for dew formation."

Can the authors speculate regarding the "dry" process? Of the nights with no surface wetness presented in figure 4b, what were typical maximum values of relative humidity?

See our above response for the typical maximum RH values. Deposition on dry nights could be either through adsorption to the leaf cuticle or soil constituents or through dissolution into soil pore water. It is also possible that enhanced downslope flow on dry nights is partially responsible for nocturnal NH_3 loss at RMNP. The following has been added to the manuscript (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."

References

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