

## ***Interactive comment on “The role of dew as a nighttime reservoir and morning source for 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 (NH<sub>3</sub>). 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 NH<sub>3</sub> 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 NH<sub>3</sub> 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

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be addressed, although they are relatively minor and would not change the general conclusions of this study. Specific comments: 1.  $\text{NH}_3$  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  $\text{RH} \geq 40\%$ . The existence of water layers may affect the release of  $\text{NH}_3$ . 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. 2.  $\text{HCO}_3^-$  contribution in equation 2: When in equilibrium with atmospheric  $\text{CO}_2$ , the  $\text{HCO}_3^-$  concentration is an exponential function of pH. In artificial dew solutions (Table S1), the pH values are mostly higher than 6.35, the  $\text{pK}_{\text{a}1}$  of  $\text{H}_2\text{CO}_3$ , and thus  $\text{HCO}_3^-$  could be important. However, the average pH of the collected dew samples is 5.19 (page 12, line 24), well below the  $\text{pK}_{\text{a}1}$  of  $\text{H}_2\text{CO}_3$ , and thus the contribution from  $\text{HCO}_3^-$  to the anion concentration should be negligible. 3.  $\text{NH}_3$  deposition: It is interesting to note that there was no difference in the average nighttime  $\text{NH}_3$  loss rate between dew event nights and dry nights. Then the questions become: Was the loss of  $\text{NH}_3$  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  $\text{NH}_3$  during a dry night? 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).  $\text{HCO}_3^-$  is only  $\sim 2 \mu\text{M}$  at  $\text{pH} \sim 5.2$ , and thus it is unlikely to make up the difference. What could be the missing ions? 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  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ , the anions of strong acids, balanced by high concentrations of  $\text{NH}_4^+$ , 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  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  are lower than those of  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{K}^+$  and  $\text{Na}^+$

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/acp-2016-169/acp-2016-169-RC1-supplement.pdf>

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