Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "Importance of Ammonia Gas-Particle Conversion Ratio in Haze Formation in the Rural Agricultural Environment" *by* Jian Xu et al.

Anonymous Referee #1

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This paper investigates the effect of NH3 concentration on NH3 partitioning to the particle phase and the influence of other factors, such as the concentration of a group of PM2.5 inorganic aerosol (sulfate, nitrate, ammonium; SNA) and ambient conditions in a region with very high NH3 plus NH4+ concentrations (ie, ammonia emissions). The title implies that the paper will investigate the overall influence of ammonia on PM2.5 haze, but this is never really done; eg, what fraction of the PM2.5 mass is ammonium, how does high ammonium affect the particle concentrations of Cl-, NO3-, what faction of the PM2.5 mass are these species? The analysis includes a thermodynamic model, with the focus of the paper solely on predictions of NH3/NH4+. Since the thermodynamic predictions depend on sulfate and nitrate, along with ammonium, (and possibly

chloride) these species should be included in the data presentation and discussion, but are largely ignored. For example, one should also present the partitioning (S curves) of nitrate, and possibly even chloride since it's concentrations are also fairly high (Fig 2) since these species are critical to the thermodynamic predictions and are highly hygroscopic and affect the aerosol liquid water. Overall the data is interesting, but the data analysis should be much more comprehensive and in depth.

Specific Comments

Was there even any mention of the sulfate concentration in this study?

The ACR is widely used in this paper and defined in the Abstract as the ammonia gas-particle conversion ratio, but that is ambiguous, explicitly define it in the Abstract. I strongly suggest the authors use a more common term, epsilon(NH4+), why make up new terminology?

How was the TEOM sample air dried? What was the temperature if dried? How would it affect mass concentrations of semivolatile species, such as NH4NO3?

Although PM2.5 mass and various gas phase species measurement methods are discussed, the data are really never considered in any important way, so why discuss the measurement method?

Figure 2. No explanation is given on why both gas/particle data are compared for ammonia but not for chloride or nitric acid. Also it would be insightful to plot ACR predicted vs measured, and plot and discuss the gas phase components of Cl- and NO3-, as was done for NH4+/HNO3. These comparisons, are also important to assess the model.

Since concentrations of the important other inorganic ions other than just NH4+ are not presented, the analysis in this paper is largely superficial. For example, roughly what is the form of the ammonium in the particle, is it ammonium nitrate, ammonium sulfate, ammonium chloride? Why not give a pie chart of the inorganic species concentrations,

as noted above regarding sulfate, no data on these other important species are given.

In Fig 4 the number of data points are not considered in the statistical results. Instead of plotting the error bar as the standard deviation plot it as the standard error, or better yet make bar-whisker plots instead. Does average = mean (mean is the more explicit term)? There is clearly a temp trend in this Fig, which should be explicitly discussed, ie, this plot simply shows that lower T more partitioning to the aerosol higher leading to high SNA and lower NH3 (if SNA is dominated by NA and not S).

Line 152. ISORROPIA is used for the predictions (ie, LWC, pH) and activity coefficients for the S curve are taken from E-AM. Is it reasonable to mix these two models? How do these activity coefficients compare to that predicted by ISORROPIA.

Line 135. The statement that NH3 concentration can be interpreted as the strength of the NH3 emissions is true only if only a small fraction of the total NH3 can be in the particle phase, which ACR shows is not true.

The table in the supplemental data is cut off and not all is legible.

Fig 6. The comparison between the S curve and the data is claimed to be good (relatively well constrained), but is it? Compare this result to other published identical plots and discuss why there appears to be more (or maybe less) discrepancy in this study. S curves of nitrate and possibly chloride should be included since the data exits and they can also be used to assess the thermodynamic model.

Lines 162-165. This explanation does not make sense. The model predicts the equilibrium state, which should exist at all time since the time scales to reach it are about 30 minutes. How will long range transport effect that. The authors need to investigate the thermodynamic model predictions better and come up with a better discussion.

Line 169. If the authors are going to accept the Silvern et al theory of a film impeding uptake of NH3, then they cannot accept the results of their thermodynamic analysis. Or they must assume that it affects only a fraction of the aerosol. This needs more

explanation.

Overall, the explanations for the discrepancy is largely just throwing out ideas and not assessing quantitatively the effect. For example, if the AWC is 35% higher how does that affect the S curve and data in Fig. 6. How will a different Henry's law affect the S curve in Fig 6 (ie which way is it shifted, to better or worse agreement with the data)?

Line 183 to 185. How does the affect of ALW on secondary aerosol formation (ie, I assume here from the references the authors are referring to SOA formation) affect the ACR?

Fig 9, ACR vertical axis is not colored the same way as the line on the plot (black and not yellow), whereas for the other plotted components there is consistency.

Section 3.3 Please explain the logic why similar diurnal trends in SNA, ACR and AWC at night supports the self amplifying feedback loop in SNA formation. Also how specifically does daytime photochemistry lead to a discrepancy if it is always assumed that the aerosol is in equilibrium?

SNA includes sulfate. How does sulfate play a role in this feedback mechanism?

The idea of feedback (or sometimes called co-condensation) leading to more uptake of NH3 by the added liquid water is not a new concept. It happens for any semi-volatile species that when partitioned to the particle phase significantly increases the water uptake. Thus, since sulfate is not semi-volatile and highly hygroscopic the species involved must generally have significantly higher concentrations then sulfate. Essentially here the effect is due to ammonium nitrate uptake, the same process discussed in Guo et al. (2017), yet here the focus is just on NH3/NH4+, the role of nitrate and possibly chloride in this process should also be included in the analysis. Note, that the molecular weight of NO3- is > NH4+ (thus most have focused on NO3- since one is generally concerned with effects on PM mass. Since the authors seem to think this is an important result from this work, they should discuss this process in much more detail and

cite other papers that have also investigated the process. See, for example Topping et al (2013).

Guo, H., J. Liu, K. D. Froyd, J. Roberts, P. R. Veres, P. L. Hayes, J. L. Jimenez, A. Nenes, and R. J. Weber (2017), Fine particle pH and gas-particle phase partitioning of inorganics in Pasadena, California, during the 2010 CalNex campaign, Atm. Chem. Phys., 17, 5703-5719.

Topping, D., P. Connolly, and G. McFiggans (2013), Cloud droplet number enhanced by co-condensation of organic vapours, Nature Geoscience, 6, 443-446.