We thank the two anonymous reviewers for their timely comments. We will respond to their comments in a later post as we are conducting additional CMAQ simulations without cations. Here, we respond to the comment of Weber et al.

We thank Weber et al. for bringing more information to this conversation as their recently submitted ACPD paper (Guo et al. 2017) was not publically available when we prepared our paper. We agree that the choice of observational dataset is important. We assert that the role of organic compounds on inorganic aerosol partitioning is secondary to the issue of what observational dataset, particularly aerosol concentrations, is used in the analysis. Note that we used the SEARCH network measurements of gas-phase ammonia, not the MARGA. The differences in gas-phase ammonia from different techniques are summarized in Table S7 of our paper. In decreasing order of abundance: AIM NH_3 > MARGA NH_3 > CIMS NH_3 > SEARCH NH_3. By using the lowest observed NH_3, we give the models the best chance of success. We assert that current thermodynamic models (e.g. ISORROPIA) are adequate to first order. The impact of organics and nonvolatile cations are second order effects and do not reconcile different aerosol observational datasets. We will work to clarify that message in a revision of our paper as well as in this comment.

We do demonstrate that organic compounds have a perturbation on ammonia/ammonium partitioning and pH, mostly via the activity coefficient, which we do not assume is one in the calculation of pH. Thus, we don't think it is appropriate to shift the S-curve in Comment-Figure 3 horizontally by 0.8 as the original S-curve corresponds to an activity coefficient of 1 (Guo et al. indicate a value of 1). A more reasonable shift in the S-curve would be 0.1 to 0.2 pH units for the inclusion of organics (Table 1 including activity coefficients). Thus, there is likely no disagreement between their Comment-Fig. 3 and our model calculations with ISORROPIA or AIOMFAC as long as the pH shown on the x-axis is consistent with the definition used by the models.

We agree that nonvolatile cations play a role in particle pH and partitioning as indicated by Guo et al. (2017), however we do not think they are the driver of discrepancies currently reported in literature (e.g. Silvern et al. 2017, Weber et al. 2016). We conducted box model simulations with and without Ca, K, Mg, Na, and Cl and showed that they do have a minor effect on the resulting ratio of ammonium to 2*sulfate and ammonium vs total ammonia. Figure 2i shows ISORROPIA predictions with all available constituents input (Ca, K, Mg, Na, Cl, SO4, NH4, NO3, HNO3, NH3) while Figure 2j uses only NH4, NH3, and SO4 constituents. The resulting ratio of ammoniums to 2*sulfate and ammonium vs total ammonia is slightly affected by including the additional constituents. Their effect on the ratio of ammonium to 2*sulfate is much smaller than the difference in RN/2S derived from AMS (Figure 2a) measurements compared to MARGA (Figure 2f) measurements.

We do not use the molar ratio of ammonium to sulfate to infer acidity since we explicitly calculate pH, but we do use it as a metric for model evaluation since observations needed to calculate the value are available.

In short, we show that the results of Silvern et al. and other work (such as Weber et al. 2016) can be reconciled by recognizing that the aerosol observations themselves do not provide consistent ammonium and sulfate nor RN/2S (RN/2S=[NH4]/[2*SO4] by mol). In the examination of the role of nonvolatile cations, page 5 of Guo et al. 2017 indicates (with R=NH4/SO4):

> "predicted R was on average … 1.85 ± 0.17 for measured Na+ input, and the highest R at 1.97 ± 0.02 when zero Na+ was used as model input. The average measured R was 1.70 ± 0.23 by PILS-IC and 1.75 ± 0.20 by another PM2.5 water-soluble ion measurement (Allen et al., 2015)."

This ammonium/sulfate ratio of 1.7 from PILS is still significantly higher than the value from AMS: 0.93 (ground) or 1.21 (aircraft) in Silvern et al. or 1.2 (GT-AMS on ground) in our work. The inclusion of measured Na+ lowers R by about 0.1 (Guo et al.) while the differences in measurement-derived R for different techniques are up to 0.8. So while it is important to treat nonvolatile cations and organic compounds to fully understand the inorganic system and improve predictions of pH (and R or RN/2S), our conclusion is that the current debate in literature over ammonium/sulfate ratios and their agreement or disagreement with models is driven by disagreement between different observational datasets.

References

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