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Interactive comment on "The underappreciated role of nonvolatile cations on aerosol ammonium-sulfate molar ratios" *by* Hongyu Guo et al.

Anonymous Referee #1

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Large discrepancy existed between observed and model-predicted molar ratios of NH4+/SO42- (R) for the southeastern US datasets. The observed R differed among instruments, with averages ranging from 0.93 for AMS ground data to 1.7 for PILS data. In comparison, ISORROPIA predicted R are always near 2. To explain this discrepancy, mainly two hypothesis are proposed, namely the organic-film hypothesis (Pye et al., 2017) and the non-volatile cations (NVC) hypothesis (as shown in this manuscript). By including in the measured NVC, the authors could now decrease predicted R from 1.97 to 1.85, which is still higher than the corresponding observation of 1.7. The remaining difference could possibly be due to the presence of organic-film, or the size heterogeneity.

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Considering the large disagreement in observation data, neither of the above hypothesis could be fully validated. However, they are still of scientific interests and worth publishing, as they both provided robust explanations to be further examined; while several concerns need to be addressed before that.

(1) What's the average activity coefficient of NH3ÂůH2O(aq) and NH4+? Does that change with NVC levels? If so, how would the theoretical S-curve be influenced, or what's the potential range of S-curve in this study? In comparison, the S-curve range based on the activity coefficient of H+ as given in Pye et al. (2017) should also be indicated.

(2) At high or low pH ranges, the partitioning fraction of NH3(g) can be extremely low or large, but can never reach 0% or 100%. What's the accuracy of the ISORROPIA model? Or, at what value would the model treat the ratio actually as 0% or 100%? Since the observation data can never be zero, what's the discrepancy of predicted NH3 and observation NH3 at those extreme conditions, for gas- and aerosol-phase respectively? Similarly, how about the HNO3-NO3- pair?

(3) Adding Fig. 3 in the authors' comment to Pye et al. (2017) would help improve the current manuscript. To my eye, the theoretical S-curve in that figure is to the right edges of the corresponding observation data. What if the aerosol water associated with organics are taken into account? That dilution effect would increase pH, shift the corresponding observation data points to the right and may result in better agreement. In addition, the authors claim that corresponding S-curve of Pye et al. (2017) can be derived by shift the S-curve of 0.8 pH units. This argument looks confusing and should be better described.

(4) The authors attributed the data with R over 2 to "measurement uncertainty and error propagation at low SO42- concentrations". However, based on data shown in Figure 1, these periods are not the periods with the lowest SO42- concentration (and thus largest uncertainty). Also, these periods correspond to periods with negative inferred

Na+. The arbitrary exclusion of these data is problematic. Basically that is to say that ambient aerosols can never be neutral or basic. As mentioned in other papers (Allen et al., 2015), sometimes the sea-salt episodes can be observed. How could the authors prove that cation-abundant situations are wrong? Does those data have any common distinct features from others? The data can be discarded for better reasons, not just due to that they look abnormal.

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