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

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Comments on ‘The underappreciated role of nonvolatile cations on aerosol ammonium-sulfate molar ratios’, by Guo et al. (2017)

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Guo et al. (2017) criticize the results from the recent paper by Silvern et al. (2017) that built on the previous work by Kim et al. (2015). Silvern et al. (2017) found that the ammonium-sulfate molar ratio (R) in aerosol over the Southeast US in summer averages only 1.04 ± 0.21 mol mol-1, despite a large excess of ammonia, whereas thermodynamic models such as ISORROPIA predict that R should approach 2 under these conditions. Silvern et al. (2017) further showed that R steadily decreased during the 2003-2013 period even as SO2 emissions decreased, inconsistent with thermodynamic models.

Guo et al. (2017) argue that the apparent inconsistency of observed R with thermodynamic models can be reconciled by taking into account non-volatile cations (NVCs) in the aerosol charge balance. They show that taking into account NVCs reconciles model and observed R at their SOAS site in the Southeast and for the WINTER aircraft campaign in the Northeast.

In our opinion, however, the paper does not resolve the discrepancies with thermodynamics found by Kim et al. (2015) and Silvern et al. (2017). Specifically:

1. Both Kim et al. (2015) and Silvern et al. (2017) included observed NVCs in their charge balance ratios and found them to have little effect because NVCs are present in very low concentrations relative to NH4+. Guo et al. (2017) do not acknowledge that both Kim et al. (2015) previously examined the effect of NVCs. The effect of NVCs was shown specifically in Figure 7 of Kim et al. (2015) and in p. 5110 of Silvern et al. (2017). So the inclusion of NVCs in the charge balance calculation is not new. It is also discussed by Pye et al. (ACPD 2017, https://doi.org/10.5194/acp-2017-623). Guo et al. (2017) may consider them ‘underappreciated’ (viz. the title) but they must invoke ‘inferred’ NVC concentrations over 4.5 times measured values in order to reconcile R at their SOAS site with thermodynamic calculations (bottom of page 4).

2. The ‘inferred Na+’ from Guo et al. (2017) seems like a self-fulfilling prophecy. Here Na+ (taken as a proxy for NVCs) is specified not from observations but from a charge balance 2[SO42-]+[NO3-]-[NH4+] excluding [H+]. Of course in that case the predicted R will match the observed values but that is nothing more than fitting NVC to match the observed R. The problem is that these fitted values of NVCs are much higher than observed. Guo et al. [2017] make the case that [H+] in the charge balance must be

small but this is based on inferred Na+ so the argument seems circular.

3. Guo et al. (2017) start from a value R = 1.70 mol mol-1 for a select time range at their SOAS site, and it does not take much correction to bring this value to approaching 2 through inclusion of NVCs. However, the CSN observations across the Southeast and the AMS observations from SOAS reported by Silvern et al. (2017) indicate much lower mean values of 1.04 ± 0.21 mol mol-1 and 0.93 ± 0.29 mol mol-1 respectively. This is not acknowledged by Guo et al. (2017). Silvern et al. (2017) noted the discrepancy with the higher values of R observed at the SEARCH sites and analyzed the differences in the measurement protocols, concluding that the R values could be biased low in the CSN data and biased high in the SEARCH data. Weber et al. (2016) reported a value of R = 1.54 for one representative SEARCH site in summer 2013 and Guo et al. (2015) reported R = 1.4 for SOAS. Pye et al. (2017) also pointed out this large difference in R between data sets. Guo et al. (2017) should acknowledge this difference in observed values of R between datasets because it has major implications for their assertion that NVCs can solve the problem.

4. The most puzzling and interesting behavior of R noted by Silvern et al. (2017) is its decrease over the 2003-2013 period as SO2 emissions decrease while ammonia emissions stay flat. Guo et al. (2017) need to acknowledge this discussion of the trend by Silvern et al (2017). The top panel of Figure 5 in Guo et al. (2017) shows that ISORROPIA cannot properly predict the trend, supporting the argument made by Silvern et al. (2017) that observed trends show a departure from equilibrium behavior. In order to capture observed trends, Guo et al. (2017) require n an increasing concentration of NVCs with time (an increasing ‘inferred Na+’) that is inconsistent with observed concentrations at SEARCH sites.

Beyond these specifics, Guo et al. (2017) misrepresent the results of Silvern et al. (2017) in three general ways:

5. They suggest that Silvern et al. (2017) did not think of NVCs. This is apparent

in the title “The underappreciated role...” and the fact that nowhere in the paper is it acknowledged that Silvern et al. (2017) and previously Kim et al. (2015) quantified the effect of NVCs on R – see comment 1 above.

6. They suggest (specifically in the abstract) that Silvern et al. (2017) is solely about the organic film hypothesis with claims that retardation of equilibrium would somehow not apply to water vapor or nitric acid. In fact, Silvern et al. (2017) only presented the organic film as a tentative hypothesis to explain the decrease in R over the 2003-2013 period (see their Abstract). Also, they did not claim that it would not retard equilibrium for H2O and HNO3, and instead simply discussed the implications for H2O and HNO3 as an open question (see their last paragraph).

7. They imply that Silvern et al. (2017) do not understand the basics of H2SO4-NH3 thermodynamics and the implications for pH, but this seems based on inadequate reading of the paper. Contrary to what Guo et al. (2017) state (see for example page 5, lines 20-22), Silvern et al. (2017) did not claim that thermodynamics imply complete neutralization of sufate by ammonia resulting in elevated pH. In fact Silvern et al. (2017) took pains to show that the thermodynamic argument is not about pH but about R. See their Figure 1 which shows a pH value below 2 even when total ammonia is in large excess. Guo et al. (2017) claim that Silvern et al. (2017) are using R as “acidity proxy” to get at pH (page 2, lines 9-12) but Silvern et al. (2017) in fact emphasize that their paper is not about pH. The Guo et al. (2017) paper suggests that the controversy is about pH (page 8, lines 5-7) but it is not; it’s about R.

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