

Responses to Referee #1

We thank the referee for the thoughtful and constructive comments. Before a point-by-point response to the issues raised, we would like to articulate the main points of our work:

- Including NVCs in the thermodynamic model largely resolves the molar ratio discrepancy, based on our data set, which is representative of the southeast. Only small amounts of NVC are often required, therefore the practice of omitting NVCs from fine mode calculations (which may seem unavoidable for many datasets) induces important biases in molar ratios, which have to be considered in any relevant interpretations (especially on the role of organics).
- The bias in R (ISORROPIA predicted R with Na^+ minus ISORROPIA predicted R without Na^+ , where $R = \text{NH}_4^+/\text{SO}_4^{2-}$, mole/mole) is highly correlated with measured Na^+ ($r^2 = 0.93$), but not correlated with OA mass or OA mass fraction. Furthermore, the difference in observed R from a ratio of 2 (R observed minus 2) is correlated with NVCs and not correlated with OA mass or OA mass fraction. Both results provide strong evidence for NVCs, and not OA, as the underlying driver of the molar ratio discrepancy.

We have addressed the comments (numbered, below), with referee comments in quotes and italics, and our responses in plain text.

1. *“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. Considering the large disagreement in observation data, neither of the above hypothesis could be fully validated.”*

The above statistics are for the whole Fig. 1 period including many data points where we had to estimate Na^+ since the measured Na^+ was below our LOD. Focusing only on the periods with measured Na^+ above LOD (reliable NVC concentrations), there is no statistical difference between predicted and measured R (t- test $\alpha = 0.05$).

See also our response to the comments from Daniel Jacob and Rachel Silvern (Figure I in that response), where we also discuss differences in R between model-predicted and observations and also point out that a significant fraction of the differences in R between some data sets (e.g., AMS PM_1 vs various $\text{PM}_{2.5}$ data) can be attributed to the differences in measured particle size ranges.

In summary, our NVC analysis can fully explain the discrepancy in molar ratio predictions for either PM_{2.5} or PM₁ data sets.

2. *“What’s the average activity coefficient of NH₃ in H₂O(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”*

The activity coefficient of dissolved NH₃, $\gamma(\text{NH}_3)$, has a negligible effect on the S curve and so not considered (Guo et al., 2017). For example, at 298 K, the acid dissociation constant of NH₄⁺, $K_a = 5.69 \times 10^{-10}$ mole L⁻¹ (Clegg et al., 1998), results in $\frac{K_a}{\gamma_{\text{NH}_3}} \ll \frac{\gamma_{\text{H}^+}[\text{H}^+]}{\gamma_{\text{NH}_4^+}}$ as long as the solution is not too basic. SOAS fine particles were very acidic with pH on average 0.94 ± 0.59 (SD). The measured Na⁺ (above zero) for the SOAS study doesn’t change $\frac{\gamma_{\text{H}^+}}{\gamma_{\text{NH}_4^+}}$ significantly; including or excluding Na⁺ gives the same $\frac{\gamma_{\text{H}^+}}{\gamma_{\text{NH}_4^+}}$ of 1.38 ± 0.12 (no statistical difference as confirmed by t-test at $\alpha = 0.05$).

3. *“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?”*

Theoretically, the partitioning fraction of NH₃ may never be 0 or 100%, but practically this is not an issue. We only use the semivolatile pairs with fractions close to 50% to constrain our pH predictions since this is the region of greatest sensitivity (e.g. (Guo et al., 2015)). Propagated uncertainty in the partitioning fraction can be determined from both gas and particle measurement uncertainties. The average propagated uncertainty in $\epsilon(\text{NH}_4^+)$ is ~4% (absolute value, not percentage of $\epsilon(\text{NH}_4^+)$) for SOAS, the pH prediction is accurate within 0.08 for $\epsilon(\text{NH}_4^+)$ at 50% and 0.22 for $\epsilon(\text{NH}_4^+)$ at 10%. A similar result is derived for HNO₃-NO₃⁻ partitioning (0.07 for $\epsilon(\text{NO}_3^-)$ at 50% and 0.22 for $\epsilon(\text{NO}_3^-)$ at 10%).

4. *“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.”*

To actually do this properly we need the Pye et al. (2017) data set, which is not yet available. Furthermore, this paper does not directly address the claims of Pye et al. (2017).

5. *“The authors attributed the data with R over 2 to “measurement uncertainty and error propagation at low SO_4^{2-} concentrations”. However, based on data shown in Figure 1, these periods are not the periods with the lowest SO_4^{2-} 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? Do 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.”*

The observed PILS-IC data points with R over 2 are within the measurement uncertainty range and are periods of lower sulfate concentrations than average. For example, lowest sulfate was record near June 19 midnight and R slightly above 2. We don't find the R above 2 points distinctly different from other periods, e.g., enhanced Na^+ or NO_3^- was not simultaneously observed, indicating no significant change in aerosol composition (see Figure I below).

Similar results are found for other measurements of $PM_{2.5}$ ions during SOAS, e.g., MARGA data (Allen et al., 2015). The figure below shows good consistency between PILS and MARGA measured R and Na^+ . MARGA and PILS sulfate and ammonium also agree well; ODR fits, $MARGA\ SO_4^{2-} = (1.00 \pm 0.01)\ PILS-IC\ SO_4^{2-} + (0.51 \pm 0.02\ \mu g\ m^{-3})$, $r^2 = 0.96$; $MARGA\ NH_4^+ = (1.04 \pm 0.01)\ PILS-IC\ NH_4^+ + (0.21 \pm 0.01\ \mu g\ m^{-3})$, $r^2 = 0.91$, see our comment to Pye et al. (2017) for a plot.)

The sea-salt episodes mentioned by Allen et al. (2015) are included in our studies. Consistently low pH was predicted despite the occasionally enhanced Na^+ level. In response to reviewer 2 question of mixing state, we have added more details on the topic to the manuscript. Finally, including or removing the data when R is over 2 does not change the findings of the paper.

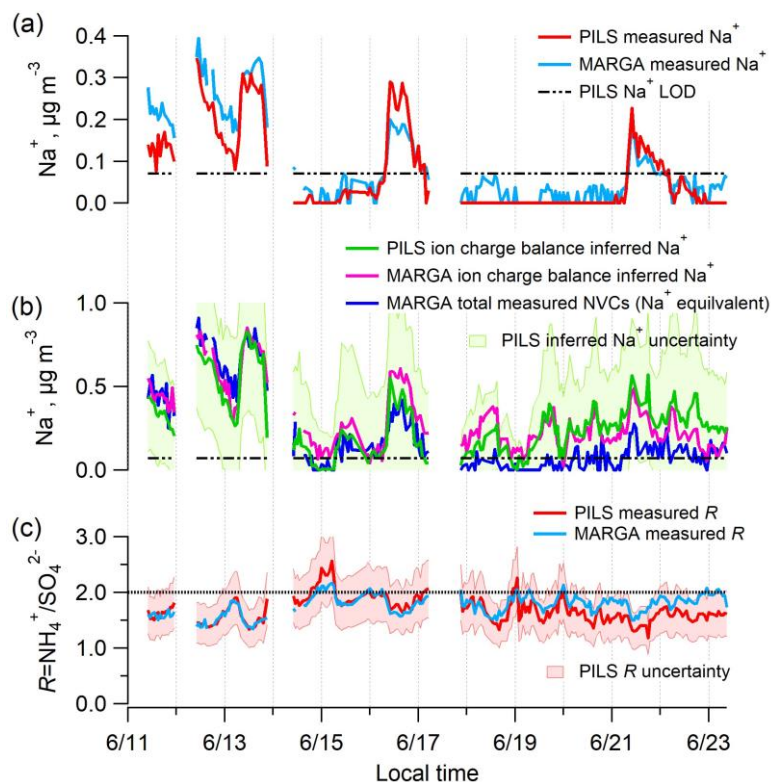


Figure I. (a) Comparison of PM_{2.5} PILS and MARGA Na⁺. (b) Comparison of inferred Na⁺ (from ion charge balance; Na⁺ = 2SO₄²⁻ + NO₃⁻ + Cl⁻ - NH₄⁺, nmol m⁻³) by PILS and MARGA to total measured NVCs by MARGA (represented by Na⁺), and (c) comparison of PILS and MARGA ammonium-sulfate molar ratios (*R*). Data are from the SOAS study.

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