Response to A. Nenes, H. Guo, A. Russell and R. Weber

Song et al.

Comments are in black and responses are in blue.

We would like to commend Song et al. for their extensive analysis that goes deep into the model code and data. The importance of understanding aerosol pH is key to understanding of aerosol growth and impacts, as has been demonstrated in a growing body of literature. This literature, however, also exposes knowledge gaps. Following are some comments and thoughts about the analysis that in our opinion require attention, especially on the impact and importance of the H^+ activity coefficient. Addressing these points, may require considerable rewriting and refocusing of the paper, but we feel it will eventually substantially enhance the contribution.

We thank Nenes et al. for their comments, which are very useful for improving the quality of this manuscript. The comments on the H^+ activity coefficients are especially helpful. Our responses to the specific points raised by Nenes et al. are given below.

Algorithm changes to ISORROPIA-II routines.

We would like to thank the authors for their very detailed explanation of the pH calculation issue, and the resolution provided. This clearly shows the value of having open source codes so that they are continuously used and tested by the community. The alternative approach in the standard code was used in the routines identified, because loss in precision in calculating the SQRT function (at low concentrations of aerosol precursors and when solid precipitates formed, e.g., NH_4Cl), made partitioning calculations at times inaccurate and noisy. Although the alternative approach captured partitioning, pH was clearly not, so adopting the standard calculation approach used in the subcases with higher RH values is appropriate; however, provision still needs to be shown to avoid loss of precision (e.g., Taylor expansion approximations or renormalization instead of SQRT). We will address this in the upcoming version of ISORROPIA-II.

We thank Nenes for sharing us the source codes of ISORROPIA, which allowed us to examine and identify the coding errors in the model.

Application of thermodynamic models when interpreting data.

We were very pleased to see that the analysis of Beijing data carried out here fully supports our prior work on how to use observational data to constrain pH, namely: *i*) avoiding usage of molar ratios and ion balances as pH proxies (Guo et al., 2015; Hennigan et al., 2015; Guo et al., 2016; Weber et al., 2016; Guo et al., 2017b), and, *ii*) the large pH errors that can result when aerosol-only concentrations from observations are used in open-system thermodynamic calculations (i.e., “reverse mode” calculations that are not subject to a global constraint of mass balance (Pilinis et al., 2000; Hennigan et al., 2015)).

We agree with Nenes et al. on this.

It should also be noted that the secondary effect of water-soluble organics on aerosol pH is also consistent with the recent work of Pye et al. (2017). Note that the reference to Pye et al. (2017) should refer to the following publication: Coupling of organic and inorganic aerosol systems and the effect on gas–particle partitioning in the southeastern US, Atmos. Chem. Phys., 18, 357-370, https://doi.org/10.5194/acp-18-357-2018, 2018.

The effect of water-soluble organic compounds is discussed in more detail in the revised manuscript. Please see the responses to anonymous reviewer #2.

One conclusion that the authors come to is that the pH calculations are not sensitive to the assumption of metastable and stable state. As presented, this can be misinterpreted by the reader that partitioning evaluations are not valuable for constraining aerosol pH. Partitioning calculations can sufficiently constrain pH, but only when predictions of aerosol water and semivolatile partitioning (of NH_3-NH_4^+, HNO_3-NO_3^-, and HCl-Cl^- if possible) are reproduced by observations (as shown in e.g., Guo et al. (2015) and other studies) – and a sufficient fraction of the partitioned aerosol species is associated with the aqueous phase. When aerosol water measurements are lacking or too uncertain, then showing that when **aqueous phase semivolatile partitioning by itself** (i.e., provided by the metastable solution) reproduces aerosol observations, aerosol pH is sufficiently constrained. **The pH values calculated for the metastable solution, for cases where partitioning is consistent with observations, provide the most plausible estimates of acidity.** pH values for the stable solution, especially when the liquid water content becomes very small (hence aqueous-phase partitioning a secondary contribution to the total partitioning), are subject to considerably more uncertainty – even if the pH corresponding to the metastable and stable solutions agree.

We partially disagree with Nenes et al. on this.

We think partitioning evaluations are important for evaluating the rationality of pH calculations in thermodynamic modeling. A good model–observation comparison of semivolatile species partitioning is a necessary condition for a good estimate of pH, but not a sufficient condition. When using the standard source codes, although model calculations can well reproduce the partitioning of semivolatile species for both particle phase states, the predicted pH values can be significantly different, for example, on average 4.6±0.4 (metastable) and 7.0±1.3 (stable) during 2012 winter in Xi'an, China (Wang et al., 2018). On the other hand, when using the revised source codes of ISORROPIA, model calculations under both states can well reproduce the partitioning of semivolatile species and also predict very similar pH values.

It is important to note that the predicted partitioning of semivolatile species is almost identical for both particle phase states. Guo et al. (2017c) mentioned that the partitioning of aerosol inorganic concentrations (e.g., NH_4^+, NO_3^-) using the metastable mode agreed better with the observations, when compared to those using the stable mode. We believe that the model–observation comparisons in Figure S1 of Guo et al. (2017c) were conducted inappropriately for the stable mode because only aqueous phase concentrations were used. However, the total particle phase (aqueous + solid) concentrations should be used in order to be consistent with ambient observations. The same results were also given in a recent study by Wang et al. (2018). In fact, since the forward thermodynamic calculations take the measured total (gas + particle) concentrations as model inputs, good model–observation comparisons for gas phase concentration (e.g., NH_3(g)) definitely mean that the model can well reproduce the observed particle phase concentrations (e.g., NH_4^+(p)).

We think thermodynamic model calculations with either stable or metastable state assumption can provide reasonable estimates of aerosol water pH, and the predicted pH values for the stable solution are NOT subject to "considerably more uncertainty" when the aerosol water content is small, at least for the winter haze conditions considered in our study. In order to better describe our point of view, here we conduct some more model calculations using ISORROPIA. The inputs are the average temperature and the average concentrations of total H_2SO_4, HNO_3, and NH_3 from our field measurements during haze episodes, and varied RH values from low to high. Figure R1 shows the comparisons of the predicted pH, AWC, ionic strength, and partitioning of NH_3 for both stable and metastable solutions.

As shown in Figure R1a–b, the predicted pH values for the stable and metastable solutions are exactly the same when the RH is larger than about 80% (when the RH is larger than the deliquescence RH for all the salts and both of the solution includes an aqueous phase only). When the RH is between about 60% and about 80% (when both aqueous and solid phases are present for the stable solution), the predicted pH values for the stable solution are on average 0.02 ± 0.00 greater than those for the metastable solution. This difference in pH is small relative to the uncertainty resulting from other factors (e.g., measurements of gas and aerosol species and meteorological parameters). Note that in Figure R1c for some cases the AWC in the stable solution is more than one order of magnitude lower than that in the metastable solution, and that for the same cases in the stable solution the "aqueous-phase partitioning a secondary contribution to the total partitioning", as can be seen in Figure R1e–f.

We also would like to emphasize that there has been no observational evidence so far to suggest whether the Beijing winter haze fine particles are in a metastable or stable state. It is also unlikely to figure out particle phase states from theoretical calculations because of the very large variability of ambient RH (see Section 2.2 of our paper) and the difficulty in estimating the efflorescence RH for multicomponent salts (Seinfeld and Pandis, 2016 Chapter 10). Therefore, at the current stage, a practical approach is to predict the aerosol water content and pH for both stable and metastable states, which can provide a way to estimate the uncertainty of these variables due to the assumption of different phase states.

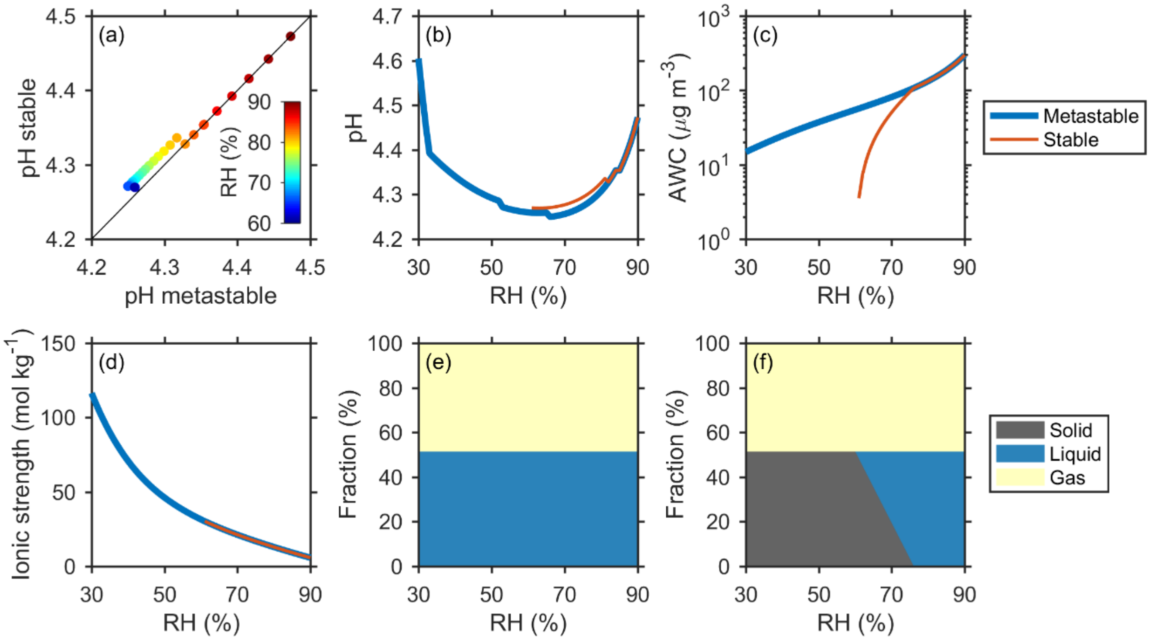

Figure R1. Comparisons of the ISORROPIA-predicted pH (a–b), AWC (c), ionic strength (d), and partitioning of NH_3 (e–f) under assumptions of the metastable and stable phase states. The model inputs include total H_2SO_4 = 30 μg m^{-3}, total HNO_3 = 51 μg m^{-3}, total NH_3 = 47 μg m^{-3}, temperature = 278 K, and varied RH. The inputs are calculated from our field measurements during haze episodes (RH > 60%) as the average temperature and the average concentrations of total H_2SO_4, HNO_3, and NH_3. Na^+ and K^+ are accounted for as equivalent NH_4^+, and Cl^- as equivalent NO_3^-.

Activity coefficient discussion

The authors extensively comment on the usage of $\gamma_{H+} = 1$ in some of the calculations behind ISORROPIA-II. In fact, the assumption that $\gamma_{H+} = 1$ is thought to be a major source of pH discrepancy between ISORROPIA and E-AIM (it's even stated in the abstract). The data presented does not really support this for the following reasons:

1. γ_{H+} varies by ±0.2 units over the ionic strengths considered (0-20), Figure 2b, while pH differences between the models are typically larger than 0.2 units.

2. The correlation of pH discrepancy between ISORROPIA-II (as calculated with the formula of Guo et al. (2015)) and E-AIM with γ_{H+} *does not* indicate a causal relationship.

3. If $\gamma_{H+} = 1$ was indeed the reason for the discrepancy, then at an ionic strength of ~20, when γ_{H+} ~1, the pH discrepancy between ISORROPIA and E-AIM should be zero (Figure 2b). This is not the case at all.

Considering points 1, 2, 3 together, one can actually conclude that about 0.2 pH units discrepancy between ISORROPIA-II and E-AIM may arise from the assumption of $\gamma_{H+} = 1$ for the RH (ionic strength) range considered, while the rest of the discrepancy may be related to the predicted concentration of H^+. This may even suggest that $\gamma_{H+} = 1$ is not a leading cause of discrepancy. In support of this, we find it very interesting that when one compares the γ_{H+} values from E-AIM (Figure 2c) and from AIOMFAC (Figure S6), log(γ_{H+}) differs by about 0.6 units at an ionic strength of 20 M (E-AIM gives 0.1 and AIOMFAC gives -0.5; note the -0.6 difference in log(γ_{H+}) means +0.6 pH compared to E-AIM), which seems to be consistent with the 0.6 higher pH comparing ISORROPIA to E-AIM at the same ionic strength. Could it just be then that the calculation of γ_{H+} by E-AIM is more uncertain than implied? The Beijing haze polluted period has an ionic strength close to 40 M, which brings γ_{H+} close to 1 according to Figure S6.

Assuming $\gamma_{H+} = 1$ to diagnose pH from ISORROPIA (single point) translates to an uncertainty of less than 0.5 pH units over a large range of RH or ionic strength (Figure S6).

We agree with Nenes et al. that our data analysis does not support the statement in the original manuscript that the assumption of $\gamma_{H+} = 1$ is the major source of pH discrepancy between E-AIM and ISORROPIA. The Section 3.2.1 has been extensively revised and this statement has been removed from the abstract and conclusion. In the revised manuscript, we conduct additional model calculations using E-AIM version II (for H^+ - NH_4^+ - SO_4^{2-} - NO_3^- - H_2O aerosol), because this version can be used assuming a metastable state and thus predict pH at low RH values. It was not insightful to introduce a third model, AIOMFAC, to help explain the differences in predicted pH between ISORROPIA and E-AIM. Figure R2 below the difference in pH predicted by ISORROPIA and E-AIM as well as several other parameters. What we find from this additional data analysis is that the difference in predicted pH is: (1) systematic and related to RH, (2) related to both H^+ concentrations and activity coefficients, and (3) smaller than one unit for the cases tested. We note in the revised manuscript that "*The exact factors contributing to ΔpH remain unclear, since these two thermodynamic models differ in many ways (e.g., their methods in calculating the activity coefficients for ionic species other than* H^+*)*", and that "*the above analysis is based on the data sets collected in Beijing winter and may not apply to other conditions*".

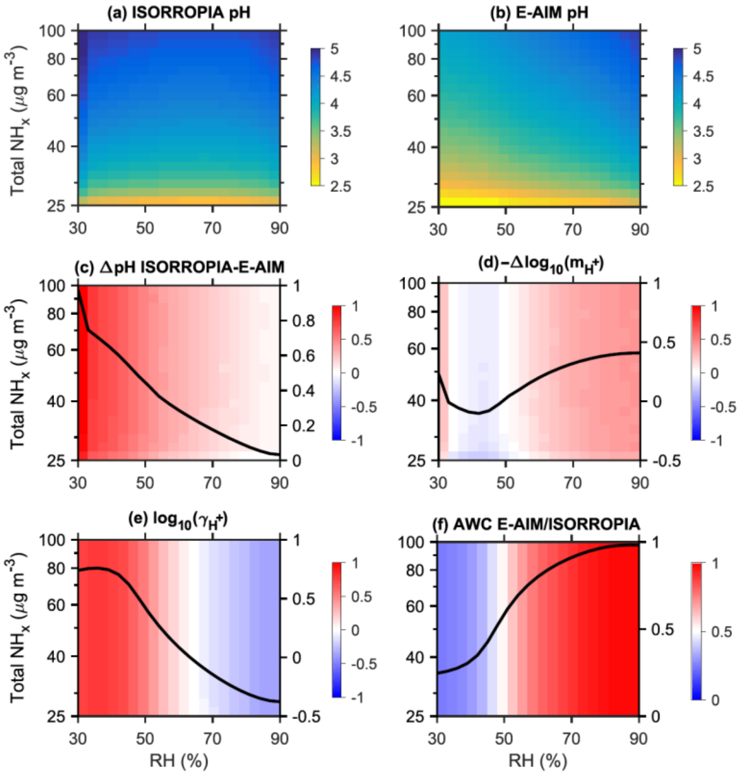

Figure R2. Comparison of predicted pH values and several other parameters from ISORROPIA and E-AIM (version II) under typical Beijing winter haze conditions (NH_x-rich). The curve in each panel (c–f) shows the average value for each bin of RH. The model inputs include total H_2SO_4 = 30 μg m^{-3}, total HNO_3 = 51 μg m^{-3}, temperature = 278 K, and varied RH (from 30% to 90%) and total NH_x concentrations (from 25 to 100 μg m^{-3}). The inputs are calculated from our field measurements during haze episodes (RH > 60%) as the average temperature and average concentrations of total H_2SO_4 and HNO_3. Na^+ and K^+ are accounted for as equivalent NH_4^+, and Cl^- as equivalent NO_3^-.

There is a lack of discussion on the effects of the other ionic species as sources of discrepancy between E-AIM and ISORROPIA-II, which is surprising, given that E-AIM uses the single ion activity approach, while ISORROPIA uses mean activity coefficients of ion pairs. Predictions from the two types of activity coefficient models do show important differences (e.g., Kim et al., 1993).

We agree that the different methods in calculating activity coefficients for ionic species may be a source of difference in predicted pH between E-AIM and ISORROPIA (Kim et al., 1993; Zhang et al., 2000).

The configuration used in ISORROPIA-II (Kusik-Meisner binary activity coefficients with the Bromley mixing rule for multicomponent aerosol) has been shown to provide stable solutions for ionic strengths that far exceed 30, the limit where Pitzer coefficients have been shown to work well (Kim et al., 1993). The latter point of course is quite relevant for the discussion raised by the authors concerning the applicability of the activity coefficient models used by ISORROPIA-II and E-AIM when applied to the high ionic strengths corresponding to RH below 70%.

The Pitzer, Simonson, and Clegg (PSC) method, which is used in E-AIM, overcomes the limitation of molar-based ionic strength and is applicable the over entire concentration range (Zaveri et al., 2005).

Given the above, unless a thorough analysis of how all the activity coefficients water uptake and equilibrium constants contribute to the pH differences between ISORROPIA-II and E-AIM, one cannot really state how much uncertainty in pH arises from the assumption of $\gamma_{H+} = 1$, though it appears to be bounded and much less than the difference in the predicted pH's between the two models. Perhaps it would be better to just plot the predicted particle phase fractions ("$\varepsilon(NH_4^+)$ and "$\varepsilon(NO_3^-)$ as a function of pH) by each model and compare them against the data (following the approach of Guo et al., 2017a). Then one will have a better sense of the pH uncertainty (given by the range between models) for a given value of (observed) ε".

We agree that the pH differences between ISORROPIA and E-AIM cannot be completely explained unless a thorough comparative analysis is made. The main goal of this manuscript is to explain the large pH discrepancy (from about 0 to 7) reported in previous North China winter haze studies. The pH difference in the forward ISORROPIA and E-AIM model calculations is much smaller compared to the other factors (i.e., forward vs. reverse, metastable vs. stable of the standard ISORROPIA) and thus a thorough analysis on this relatively small pH difference between the forward ISORROPIA and E-AIM calculations goes beyond the focus of this manuscript. Both ISORROPIA and E-AIM show a moderately acidic condition for Beijing winter haze particles. It is noted in Figure 1 and Figure S5 that ISORROPIA and E-AIM predict nearly identical $\varepsilon(NH_4^+)$ and $\varepsilon(NO_3^-)$ and both can well capture the observed gas-particle partitioning. Therefore, we think that the difference between ISORROPIA and E-AIM may provide an estimate for the uncertainty of pH.

Specific (but important) comments

- The authors note early in the manuscript that the discrepancy in calculated pH when assuming $\gamma_{H+} = 1$ can be multiple units. This is not supported by the supplementary figure (γ_{H+} from AIOMFAC), where for an ionic strength range of 0-100, log γ_{H+} (hence the contribution of assuming $\gamma_{H+} = 1$ to pH discrepancy) varies within 1 unit. This has always been, by the way, our view – so it is nice to see this confirmed by the analysis presented! Also noted throughout is that pH is overestimated when assuming $\gamma_{H+} = 1$. This is not always true as well; as noted by the supplementary figure (γ_{H+} from AIOMFAC), pH can be underestimated or overestimated by assuming $\gamma_{H+} = 1$, but not more than half a unit.

  Please see the responses to the general comments of activity coefficients above.

- In fact, the average pH estimated by ISORROPIA-II is *actually lower* than that reported for E-AIM (4.2 vs 5.4, for ISORROPIA-II vs E-AIM respectively) inconsistent with pH trends stated above.

  Wrong numbers of pH are quoted from the manuscript. As shown in Section 3.3, the mean pH values of 5.4 (E-AIM) and 4.2 (ISORROPIA) are for the *reverse mode* calculations. The average pH values are 4.0 (E-AIM) and 4.6 (ISORROPIA) for the *forward mode* calculations.

- In ISORROPIA-II, the non-ideal interactions of H+ with all the ions in solution (especially NO3, Cl, HSO4, SO4) is explicitly considered by the Kusik-Meisner and Bromely formulations. $\gamma_{H+} = 1$ is only invoked when the singe ion activity is required. This is not sufficiently noted in the text.

We noted in Section 2.2 that "With ISORROPIA, γ_{H^+} and γ_{OH^-} are assumed equal to unity, whereas the activity coefficients for the other ionic pairs (e.g., H^+–Cl^-) are calculated (Fountoukis and Nenes, 2007)."

- The authors understandably treat NVC (i.e. Ca, Mg, K, Na) as equivalent sodium, because E-AIM cannot explicitly treat Ca, Mg and K. The impact of this assumption can lead to important differences in the predicted thermodynamic state, owing to the strong nonideality of divalent ions and different water uptake characteristics of sodium salts vs. their other counterparts (e.g., Fountoukis et al., 2009).

  We noted in Figure 2 of the original manuscript that K^+ was accounted for as equivalent Na^+ in ISORROPIA, and therefore, for the comparison of pH for E-AIM and ISORROPIA, the model inputs are the same.

- What constitutes a "large/important" and "small/minor" different in pH depends on the context in which the pH is used. Constraining "absolute" pH for ambient aerosol to within less than 0.5 units may prove to be extremely challenging (e.g., the difference in log γ_{H+} between E-AIM and AIOMFAC, the effects of organics on activity and water uptake and so on); so it may most likely be necessary to use a consistent pH calculation method and thermodynamic model when comparing aerosol acidities between models and/or observations.

  Such qualitative expressions have been avoided in the revised manuscript when comparing E-AIM and ISORROPIA.

- The authors caution about the predictions of ISORROPIA-II in metastable mode (for RH below the mutual deliquescence point) owing to the large ionic strengths of the solutions. Although we agree the ionic strengths are high, literature supports that the activity coefficient models used in ISORROPIA-II are stable for ionic strengths above 30, a situation that is also not the case for the Pitzer method (Kim et al., 1993).

  The Pitzer, Simonson, and Clegg (PSC) method, which is used in E-AIM, overcomes the limitation of molar-based ionic strength and is applicable over the entire concentration range (Zaveri et al., 2005).

In closing, we very much appreciate the analysis and it demonstrates an increasing sophistication of which the community is both understanding and discussing the thermodynamics of aerosols and the important topic of aerosol acidity. We also hope that the comments provided here add insight that will considerably strengthen the paper, and provide ideas for future work on the important topic of aerosol acidity.

The authors thank Nenes et al. again for the above comments, which were helpful in improving the quality of this manuscript.

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