Response to Anonymous Referee #2

Song et al.

Comments are in black and responses are in blue.

This paper provides insight into the acidity of aerosols in Beijing. Table 1 provides a nice summary of previously published values which range from very acidic (-1) to basic (7.6). The paper uses ISORROPIA and E-AIM to estimate pH and provides discussion on how organic compounds may modify pH. The paper is well written, fairly thorough, and detailed. The Monte Carlo approach provides additional confidence in the results. A number of (mostly clarifying) comments are listed below.

Thanks for these positive comments for our manuscript. Our responses to specific comments are provided below.

One role for organic compounds in modifying pH was missing from the discussion. Specifically, on page 11, the authors list three ways in which organics can modify pH: (1) adding aerosol water, (2) participating in charge balance (e.g. dissociation of organic acids), and (3) by changing the aerosol phase state. The third area could use clarification (see detailed comments), but a fourth way (that seemed to be missing) is through modification of the chemical environment and therefore by modifying the activity coefficients of the inorganic species. This could be scoped out using the AIOMFAC model.

It is a very good comment. E-AIM assumes that the inorganic ions and organic solutes do not influence each other. Their molality-based activity coefficients are thus equal to those calculated for the systems water + inorganic ions only, and water + organic solutes only (Clegg et al., 2001). In the revised manuscript, we add the fourth way in Sect. 3.4 when discussing the effect of organics on particle pH calculation. Specifically, we modified this sentence to "*Organics may affect particle pH in several ways: (1) by increasing the absorption of aerosol water; (2) by participating in the charge balance and modifying the activity coefficients of inorganic ions in the aqueous phase; and (3) by changing the aerosol phase state (liquid-liquid phase separation)*", and added "*Note that E-AIM assumes that the organics in the aqueous solution do not affect the activity coefficients of inorganic ions (Clegg et al., 2001). Using the AIOMFAC model (web.meteo.mcgill.ca/aiomfac), Pye et al. (2018) recently showed that the interaction of inorganic ions with water-soluble organic compounds resulted in a 0.1 unit increase in pH for aerosols in the southeast United States*".

S. L. Clegg, J. H. Seinfeld, and P. Brimblecombe (2001) Thermodynamic modelling of aqueous aerosols containing electrolytes and dissolved organic compounds. J. Aerosol Sci. 32, 713-738.

Pye, H. O. T., Zuend, A., Fry, J. L., Isaacman-VanWertz, G., Capps, S. L., Appel, K. W., Foroutan, H., Xu, L., Ng, N. L., and Goldstein, A. H.: Coupling of organic and inorganic aerosol systems and the effect on gas–particle partitioning in the southeastern US, Atmos. Chem. Phys., 18, 357-370, doi:10.5194/acp-18-357-2018, 2018.

The authors should also be more forceful in their statements regarding what is a reasonable pH calculation and what is likely erroneous (see specific comment 1).

The abstract and conclusion have been revised to highlight the appropriate applications of thermodynamic modeling and the reasonable range of aerosol water pH inferred from such method. Revisions made in the manuscript:

> ***"Abstract.*** *pH is an important property of aerosol particles but is difficult to measure directly. Several studies have estimated the pH values for fine particles in North China winter haze using thermodynamic models (i.e., E-AIM and ISORROPIA) and ambient measurements. The reported pH values differ widely, ranging from close to 0 (highly acidic) to as high as 7 (neutral). In order to understand the reason for this discrepancy, we calculated pH values using these models with different assumptions with regard to model inputs and particle phase states. We find that the large discrepancy is due primarily to differences in the model assumptions adopted in previous studies. Calculations using only aerosol phase composition as inputs (i.e., reverse mode) are sensitive to the measurement errors of ionic species and inferred pH values exhibit a bimodal distribution with peaks between −2 and 2 and between 7 and 10, depending on whether anions or cations are in excess.*

Calculations using total (gas plus aerosol phase) measurements as inputs (i.e., forward mode) are affected much less by these measurement errors. In future studies, the reverse mode should be avoided whereas the forward mode should be used. Forward mode calculations in this and previous studies collectively indicate a moderately acidic condition (pH from about 4 to about 5) for fine particles in North China winter haze, indicating further that ammonia plays an important role in determining this property. The particle phase state assumed, either stable (solid plus liquid) or metastable (only liquid), does not significantly impact pH predictions. The unrealistic pH values of about 7 in a few previous studies (using the standard ISORROPIA model and stable state assumption) resulted from coding errors in the model, which have been identified and fixed in this study."

"Conclusions. *This study suggests that the significant discrepancy of fine particle pH, ranging from about 0 (highly acidic) to about 7 (neutral), calculated in previous studies of North China winter haze is due primarily to differences in the ways in which the E-AIM and ISORROPIA thermodynamic equilibrium models have been applied. The reverse mode calculations (only using aerosol phase composition as inputs) lead to erroneous results of pH since they are strongly affected by ionic measurement errors (especially under ammonia-rich conditions), and therefore should be avoided in future winter haze studies. The forward mode calculations (using the total (gas plus aerosol phase) compositions as inputs) account for additional constraints imposed by the partitioning of semi-volatile species and are affected much less by the measurement errors, and therefore, should be used in future studies. The forward mode calculations in this and previous studies collectively indicate, during North China winter haze events, that aerosol particles are moderately acidic with pH values ranging from about 4 to about 5. The assumed particle phase state (stable or metastable) does not significantly affect the pH calculations of ISORROPIA after coding errors in its standard model being fixed. A few previous studies, in which the standard ISORROPIA model was used and the stable state was assumed, predicted unrealistic pH values of around 7, and should be re-evaluated. In agreement with previous studies, we confirm that ammonia plays an important role in determining particle pH under winter haze conditions in northern China."*

Specific comments:

1. Page 1, line 29: The authors indicate reverse mode calculations "exhibit a bimodal distribution with peaks between -2 and 2 and between 7 and 10." This reads as if these peaks are plausible values. Consider adding "depending on whether cations or anions were in excess" to highlight that the bimodal values are artifacts.

Revised accordingly.

2. Page 1, line 34-35 "The phase state assumed, which can be either stable (solid plus liquid) or metastable (only liquid), does not significantly impact pH predictions of ISORROPIA." Presumably this is true only at high RH? Figure 4a does not provide "stable" pH estimates below 60% RH and Figure 4b indicates the metastable and stable aerosol water differs (and is nonzero) between 40 and 70%.

This statement is true for a large RH range. In Figure 4b, the predicted metastable and stable aerosol water contents are zero for 30% and 40% RH bins (the *x* and *y* axis is not intersected at zero). For the RH bin at 50% (i.e., 45%-55%), the aerosol water content is 2.8 $\mu g\ m^{-3}$ (a small value but nonzero). We did not show in Figure 4a the pH estimates for this RH range because there were many cases with no liquid phase in the stable state (the mutual deliquescence RH is around 50%). The average pH value for this RH range is 4.3 for the stable state (calculated using the available cases), which is ~0.2 unit smaller compared to that for the metastable state. Thus we think phase state does not *significantly* (compared to the reported 3 to 4 units' difference in some previous studies) impact pH predictions of ISORROPIA. We added a supplementary figure in the revised manuscript in order to clarify and emphasize this point and please see the details in the responses to Nenes et al.

3. Page 3, line 27-30. The collection efficiency of the AMS is known to be a function of the ammonium to sulfate ratio (e.g. Middlebrook et al., 2012 https://www.tandfonline.com/doi/pdf/10.1080/02786826.2011.620041). Was this factored in?

The several factors described in Middlebrook et al. (2012) which may affect the collection efficiency (CE) of the AMS have been considered when the CE of 0.5 was chosen in our AMS analysis. One sentence has been added here: "*A* *constant collection efficiency of 0.5 was chosen because (1) particles were dried before being analyzed, (2) the mass fraction of NH_4NO_3 was smaller than 0.4, and (3) the particle acidity was not high enough to affect CE substantially*".

4. Page 4, line 12: What effects of organic compounds does E-AIM consider? Dissociation of acids? Does it treat the effects of organics on inorganic activity coefficients?

E-AIM considers the dissociation of organic acids and treats the produced organic anions by the Pitzer, Simonson and Clegg (PSC) equations. E-AIM assumes that the inorganic ions and organic solutes do not influence each other. Their molality-based activity coefficients are thus equal to those calculated for the systems water + inorganic ions only, and water + organic solutes only (Clegg et al., 2001).

S. L. Clegg, J. H. Seinfeld, and P. Brimblecombe (2001) Thermodynamic modelling of aqueous aerosols containing electrolytes and dissolved organic compounds. J. Aerosol Sci. 32, 713-738.

The above information has been added in the revised manuscript.

5. Page 5, equations: Add "charge equivalent" before "measured ion concentrations" to indicate that sulfate, Ca, Mg have been multiplied by 2.

Revised accordingly.

6. Section 3.2.1 and Figure 2: Do E-AIM and ISORROPIA predict different H+ concentrations? To what degree? How much of the difference between ISORROPIA and E-AIM is due to including gamma_H+ different than 1 in reporting pH vs the activity coefficient of H+ actually modifying the thermodynamics? In other words, if you plotted E-AIM and ISORROPIA and set the activity coefficient to 1 in both for plotting purposes only, what would the difference be?

We have provided a detailed response to this question in the response to Nenes et al. Please refer to that.

7. Figure 3: Could ISORROPIA or E-AIM predictions be overlaid on the plot? What measurement technique is the measured NH_4^+ fraction from? Is it different than the AMS value?

In the revised manuscript, we have added the average pH values from different model calculations to this figure. It is now noted in the caption of this figure that "*the measured average aqueous fraction … is calculated with the gas phase NH_3 and $PM_{2.5}$ NH_4^+ concentrations*." The AMS pH value is similar, although it is not shown.

8. Page 10, before section 3.4: Emphasize and clearly state what your best estimate of aerosol pH is.

One more sentence has been added: "*The appropriate applications of thermodynamic modeling indicate a moderately acidic condition (pH from about 4 to about 5) for fine particles in North China winter haze.*"

9. Page 11, line 6-8: See above comment about a missing organic modification to pH.

See our responses to the general comment about the impacts of organics on pH above.

10. Page 11, line 17: What fraction of the total aerosol water is due to organic compounds?

The data has been added in the revised manuscript: "*we find that the aerosol water associated with these species is only about 14 ± 3% (median ± median absolute deviation) of that associated with inorganic salts*".

11. Page 12, near line 7. What is your hypothesis regarding liquid-liquid phase separation and the effect on pH? Isn't your default configuration essentially liquid-liquid phase separation into and organic-rich and inorganic-rich phase? This ties in with the fourth possible way organics affect pH (via activity coefficients if organic compounds coexist in the inorganic phase).

The aerosol solution under liquid-liquid phase separation can be separated into two phases: organic-rich and inorganic-rich, which may have different pH values (although such effect remains unclear). The study we cited here (Dallemagne et al., 2016) showed that the organic-rich phase had a pH value higher by 0.4 unit compared to the single phase situation. This effect is not the same as the fourth possible way, which is the influence of water-soluble organics on the activity coefficients of inorganic ions in the aqueous phase (inorganic-rich).

12. In the supporting information, can you provide the exact ISORROPIA file names and line numbers and what the content was modified?

The standard ISORROPIA source code is password protected at *http://isorropia.eas.gatech.edu/index.php?title=Code_Repository*, but there is a version of ISORROPIA-II implemented by Pye et al. (2009) in the GEOS-Chem chemical transport model and fully publicly accessible at: *http://acmg.seas.harvard.edu/geos/doc/man/.* The ISORROPIA-II code is under the directory *ISOROPIA/*. Thus we have published bug fixes for ISORROPIA-II stable mode and the exact line numbers and contents can be found at: *http://wiki.seas.harvard.edu/geos-chem/index.php/ISORROPIA_II*

Pye, H. O. T., H. Liao, S. Wu, L. J. Mickley, D. J.Jacob, D. K. Henze, and J. H. Seinfeld, Effect of changes in climate and emissions on future sulfate-nitrate-ammonium aerosol levels in the United States, J. Geophys. Res., 114, D01205, 2009.

The above information has been added in the revised manuscript and the supplement.