

Interactive comment on “Fine particle pH for Beijing winter haze as inferred from different thermodynamic equilibrium models” by Shaojie Song et al.

Anonymous Referee #2

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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. 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

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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. 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).

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.
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%.
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?
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?
5. Page 5, equations: Add “charge equivalent” before “measured ion concentrations” to indicate that sulfate, Ca, Mg have been multiplied by 2.
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 γ_{H^+} different than 1 in reporting pH vs the activity

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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?

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?

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

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

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

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 an 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).

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

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