Response to Referee Report

We thank the Referees for their helpful suggestions and detailed comments. We have enumerated the points made by the referees below, and provided our responses to each point in blue text. We have also provided a revised manuscript with changes highlighted (starting on pg. 13 of this file).

Referee #1

This article by Battaglia, Weber, Nenes and Hennigan explores effects of water-soluble organic compounds on aerosol acidity by means of thermodynamic modeling. Two data sets from field measurements distinct by acidity (Baltimore & Beijing) are used to provide information about inorganic constituents, aerosol mass concentration and the water-soluble organic fraction. The authors provide new insights into the effects of organic compounds on aerosol water content and the activity coefficient of H+. This topic is of interest for the atmospheric chemistry community, since aerosol acidity has been linked to a range of chemical and physical properties of particulate matter, but relatively few studies have attempted to quantify the effects of organic/inorganic mixing on aerosol pH. While certain effects of inorganic/organic aerosol mixing have been excluded in this work, e.g. liquid-liquid phase separation and lower relative humidity conditions, the study by Battaglia et al. provides interesting findings for single-phase aqueous aerosol by using a combination of state-of-the-art thermodynamic models. It is shown for the cases studied that the pH is largely controlled by the inorganic aerosol species, which is in agreement with other related studies (Pye et al., 2018). The manuscript is generally well structured and provides a good introduction about the need for understanding the effects of organic acids and non-acids on pH. However, the descriptions lack some details with regard to the methods employed and would benefit from additional discussion about the choice of a rather limited number of specific organic non-acids and dicarboxylic acids and how these may affect the simulation results.
I am in support of the publication of this work after my minor points on methods and assumptions have been addressed by the authors. General and specific comments are provided below.

General Comments

1.) Factorial design method (pages 8, 9).
A factorial modeling experiment design was used to represent different combinations and concentration levels of organic compounds. Since this is not a widespread approach used by atmospheric chemists, it would be adequate to provide a better description of what was done exactly and why. For example, on page 9 is stated: “...and combined in factorial fashion: each organic acid concentration level combination of the three organic acids, and vice versa for the non-acid organic species. Combinations of organic acids and non-acid organic species were not explicitly considered here.”

This could be phrased much better for clarity and perhaps an example could be provided to make clear what is meant (e.g. that the approach involves independent combinations, rather than permutations) and what is "factorial" about this method. Also, references to adequate literature describing this approach are missing.

We have added clarifying statements as to the nature and structure of the factorial design method, giving attention to the statistical design terms of 'factors' and 'values.' Additionally, we have provided a highly-cited textbook on statistical design that discussed factorial design of experiments. The updated text (lines 187-193) now reads, "A matrix was constructed to examine multiple combinations of the selected organic component composition levels (factorial design), and their effects evaluated on the basis of organic-to-inorganic ratio (OIR) or organic mass fraction, both computed on a dry particle basis. This full factorial design consists of three factors for each acid or non-acid condition (the identity of each species), each with discrete possible values (air concentrations in µg m^{-3}), where the experiment incorporates all possible combinations of these values across all factors (Keppel, 1991)."

And (lines 220-226): "For each geographic region, 11 different concentrations were chosen for each WSOC compound (0-4 µg m^{-3} for Baltimore; 0-40 µg m^{-3} for Beijing), and combined in factorial fashion: each organic acid concentration level combination of the three organic acids were examined in combination with every other level of the remaining two, and vice-versa for the non-acid organic species. Combinations of organic acids and non-acid organic species were not explicitly considered here; only combinations of organic acids with organic acids, or combinations of non-acids with non-acids were examined experimentally."

2.) Liquid-liquid phase separation (LLPS)

Phase separation was not considered in the calculations from this study, but the topic is discussed in the introduction, which is valuable. It is well-known that non-ideal mixing in organic/inorganic solutions can cause LLPS, as the authors also point out. However, what remains unclear is how the authors concluded that their cases are not affected by phase separation. Page 8, line 8 – 12: "The RH in all simulations was fixed at either 70%, 80%, or 90%, with inorganic system inputs calculated and invariant at each RH level based on the initial input data from either Baltimore or Beijing to ensure deliquescence of inorganic aerosol particles, to understand the sensitivity of the model-predicted aerosol pH to changes in RH (ALW), and to avoid liquid-liquid phase separation as a potential cause of organic-influenced aerosol pH changes (Pye et al., 2018)."

It should be clarified how avoiding LLPS is related to deliquescence of inorganic particles. How sure are the authors that LLPS would not occur, say at 70% RH, in their systems when high amounts of organics are present? Was this checked quantitatively? For example, the authors could confirm that organic activity coefficients remain less than ~5 – 10, since studies like

Donahue et al. (2011, https://doi.org/10.5194/acp-11-3303-2011) suggest that “Somewhere between 5< γ <10 phase separation becomes very likely”. The LLPS constraints from You et al. 2013 (mentioned much later on page 19) could also be useful for the discussion in this context.

The referee brings up an excellent point. We have addressed the LLPS condition for the non-acid simulations quantitatively in revision in the following ways: using the parameterization of Bertram et al. ACP 2011, who define separation RH (SRH) as a function of O:C, we compute the mass-weighted O:C for all of our simulations, and compare the SRH to the simulation RH. We have noted that LLPS is highly unlikely to occur for the organic acid cases based on the experiments performed by You et al. ACP 2013.

For the initial Baltimore simulations, out of 1330 simulations utilizing 1-pentanol in the non-acid organics mixture, 372 are non-LLPS (28%) while 958 (72%) are projected to experience LLPS. Based on these results, we have altered our experimental approach by replacing 1-pentanol in the analysis with a more atmospherically-relevant compound with a higher O:C ratio: 2-methyltetrol (1-methylbutane-1,2,3,4-tetrol). This significantly increases the number of model cases that are not projected to experience LLPS. In performing this new analysis, we remove points that fall into the “likely LLPS” bin according to the Bertram et al. (2011) parameterization.

In changing the analysis, we have added a section under Methods where we explicitly discuss LLPS, and the approach we take in applying the Bertram et al. (2011) parameterization. We have extended the discussion to utilize more of the explanations from Pye et al. ACP, 2018 and Zuend and Seinfeld ACP 2012 who discuss the presence of H^+ and water in both electrolyte- and organic-rich phases in systems that have undergone LLPS. We have added the following text (lines 346-363) to the Methods section:

“**Evaluation of LLPS and Accommodations for LLPS Scenarios**

The O:C ratio is a key factor that determines whether LLPS occurs in organic-containing particles (Song et al., 2018a; Freedman, 2017). We followed the parameterization found experimentally by Bertram et al. (2011) to evaluate the presence of LLPS in our simulations. This method uses the overall mixture O:C ratio to determine the separation RH of the mixture. If the modeled (in this case, specified/enforced) system RH is lower than the parameterized RH, LLPS is likely to occur. This was performed for each of the non-acid mixtures for both Baltimore and Beijing data to verify the claim that LLPS was not anticipated to occur. For each point in the non-acid model evaluations, the LLPS condition of Bertram et al. (2011) was employed, and the RH_{LLPS} predicted by the method compared against the system RH/H_2O activity reported by AIOMFAC. For cases where the parameterized RH_{LLPS} was higher than the predicted system RH, LLPS was anticipated to occur, and the point was flagged and excluded from further analysis. Out of 1331 simulations, Baltimore had 55% (*n* = 732), 70% (*n* = 932), and 75% (*n* = 998) simulations that met the non-LLPS criteria at 70%, 80%, and 90% RH respectively. Beijing had 85% (*n* = 1131), 89% (*n* = 1185), and 93% (*n* = 1238) of simulations meet the non-LLPS conditions at 70%, 80%, and 90% RH respectively. Experimental work by You et al. (2013) indicates that glutaric acid, malonic acid, oxalic acid, or their mixtures do not undergo LLPS at any of the RHs investigated."

3.) Acids vs. non-acid organics
In the abstract and similarly on page 18, line 19, it is stated that "surprisingly, non-acidic WSOC compounds were found to have a larger effect on pH than organic acids owing to their stronger impacts on $\gamma H+$". It is not made clear what is surprising, please clarify. Also, how robust is this result given the choice of rather small, polar and hygroscopic organic diacids in this study. Would the same explanation hold true if a diacid of lower O:C ratio (less hygroscopic) were used? Moreover, the finding may depend on how ISORROPIA, E-AIM, UNIFAC and AIOMFAC treat organic acids (accounting for dissociation or not); see specific comments.

We have extended and enhanced this portion of the analysis by replacing 1-pentanol in the organic non-acid case with 2-methyltetrol to create a more atmospherically relevant particle composition - this has changed the results to lead to the initially hypothesize result of increasing aerosol pH with increasing organic non-acid concentration. Similarly, we have used the E-AIM model predictions of pH in the organics acids case (modeling the Beijing data in E-AIM rather than ISORROPIA) to incorporate the explicit dissociation of organic acids (as AIOMFAC was found to not include those reactions). This result is only relevant for diacids of relatively low-volatility and high solubility; for larger acids with higher O:C it is likely that the results would be equally contradictory as in the cases using 1-pentanol vs. 2-MT. The statements in the conclusion have been changed to reflect the additional analyses performed with 2-MT and the use of E-AIM pH for the organic acids cases.

Specific Comments

1.) Page 2, line 23: define the meaning of "aerosol strong acidity or total acidity"

The statement has been changed to include the definitions as follows: "pH, the parameter serving to define and describe the acidity of aqueous solutions, often has no direct correlation with proxy measurement methods such as aerosol strong acidity (H^+ contributed by strong acids that dissociated completely at any pH level) or aerosol total acidity (dissociated H^+ and undissociated H^+ bound to weak acids) (Hennigan et al., 2015;Song et al., 2018)."

2.) P3, l6: "to obtain the pH of an aerosol distribution". Since distribution is mentioned, would the same pH be expected for all aerosol particles over a considerable size range (e.g. ultrafine vs. larger accumulation mode particles)? Do the input data from measurements account for size modes?

This phrase has been changed to read “to obtain aerosol pH values.” We agree with the Referee that aerosol pH does vary with particle size, but it was not our intention to include the added dimension of ambient aerosol size distributions into our analysis (not one of the aims of this investigation). For the purposes of this article, the aerosols are treated as belonging to a single aggregate aerosol phase.

3.) P3, l10 - 15: the aerosol thermodynamic models are introduced. At this point it is appropriate to define the acronyms and to cite the key references describing the models, which are missing; see associated websites. Also, citing Ganbavale et al. (2015) in the context of AIOMFAC and its web model seems inadequate as that study does not concern organic-inorganic mixtures.

The initial introduction to the models has been modified to say: “The Extended Aerosol Inorganics Model (E-AIM, http://www.aim.env.uea.ac.uk/aim/aim.php) (Wexler and Clegg, 2002;Friese and Ebel, 2010) and the ISORROPIA-II model (Greek for ‘equilibrium,’ http://isorropia.eas.gatech.edu) (Fountoukis and Nenes, 2007) are widely used to calculate aerosol pH for atmospheric and experimental particle distributions (Guo et al., 2017;Guo et al., 2016;Guo et al., 2015;Wang et al., 2016). The Aerosol Inorganics-Organics Mixtures Functional groups Activity Coefficient (AIOMFAC) model (http://www.aiomfac.caltech.edu/model.html) offers the most extensive treatment of organic-inorganic interactions (Zuend et al., 2008;Zuend et al., 2011) of models to date, but is primarily an activity coefficient model that does not solve full thermodynamic equilibrium calculations or phase diagrams as E-AIM and ISORROPIA do.”

4.) Pages 3 and 4 (first paragraph): AIOMFAC is discussed as only being an activity coefficient model, which seems correct, but the authors forgot to mention that there are equilibrium models based on AIOMFAC, including the one used by Pye et al. (2018), Hodas et al. (2015), Zuend et al. (2010, 2012) and others. The study by Pye et al. used both ISORROPIA and AIOMFAC-based equilibrium models to estimate aerosol pH. It seems that the authors only refer to the online model of AIOMFAC, which could be made clear. Also, do ISORROPIA, E-AIM, AIOMFAC solve the ion association/dissociation equilibria, like bicarbonate and bisulfate in aqueous systems? What about organic acid dissociation? There is an E-AIM model version for specific acids, but it seems that organic acid dissociation is not considered explicitly by the models, right? Discussion of this could be important for pH calculations in the context of diacids (of different pKa values) and when contrasting the effects of acidic vs. non-acidic organics.

The version of AIOMFAC used here was the online model, used exclusively as an activity coefficient model. ISORROPIA, E-AIM, and AIOMFAC all solve the ion association/dissociation problem, especially for the bisulfate/sulfate system which is of importance. E-AIM treats explicitly the partial dissociation of species used here in both the single and double deprotonated anion forms are included in the outputs. AIOMFAC treats all organic acids as undissociated species, which informed further additions to this work detailed elsewhere.

The following clarifying statements have been added to the section to further detail the use of the models:

"While AIOMFAC has been used in combination with thermodynamic equilibrium models such as ISORROPIA-II (Pye et al., 2018), these are custom modifications to the models, and not reflected in the online versions used in this study."

"An additional consideration between the models is their treatment of organic acids. E-AIM offers support for limited (n = 8) organic acid species, and treats the dissociation equilibrium of organic acids. In contrast, AIOMFAC treats organic acids as non-dissociating, a model difference that is discussed in detail below. Note that the ion dissociation equilibria of inorganic species (such as HSO_4^-/SO_4^{2-}) are explicitly considered in the equilibrium calculates of all three models employed in this study."

5.) P4, l 15: Define LLPS

We have added the definition of liquid-liquid phase separation preceding the first use of the initialism LLPS.

6.) P5, l 5: Rephrase "increasing particle phase partitioning"; what kind of partitioning is meant? gas-particle, liquid-liquid?

We refer here to gas-particle phase partitioning of organic species. This comment has been clarified to say "increasing gas-particle phase partitioning."

7.) P6, l12: Rephrase "S-curves" - these are known as sigmoid curves.

We have replaced the phrase 'S-curves' with the more accurate phrase 'sigmoid curves.'

8.) P6, l16: how was the threshold uncertainty of 0.5 pH units determined? Cite a reference.

This sentence has been removed.

9.) P8, l18: What is "the standard table of AIOMFAC organic species"? this is unclear

This comment has been clarified to reflect that the organic species selected were chosen by their availability in the predefined list of organic species included in the AIOMFAC web interface.

10.) P10, l9: Clarify meaning of “Metastable mode” in this context. This seems to be a technical term used with ISORROPIA, but jargon should be avoided.

“Metastable” is not just jargon – it is used to describe a system that is not at a global equilibrium point. In this case, metastable means the system may be supersaturated with respect to the solubility of dissolved ions, but salts do not form. A simplified definition of ‘metastable mode’ (the formation of solids in the model being disabled) was added for clarifying purposes: “The formation of solids in the model was disabled (leading to potential supersaturated aerosols, metastable mode operation), based on the justifications in previous studies (Guo et al., 2015; 2018b)”.

11.) P11, l16: “The selected species and order of allocation of the ionic species appears to be dependent solely on the researcher, and a priori knowledge of which molecular species are likely to exist in the aerosol particle as the dissociated ionic species.” It is unclear what a priori knowledge is needed. Do the authors mean that the choice of species allocation affects model predictions or not?

The following clarifying statement has been added: “The selection of species is unlikely to affect model outcomes, as this is simply a way to account for the ionic species present in the AIOMFAC model inputs, which require matched cation-anion pairs, and are expected to be fully-dissociated in the aqueous phase during model evaluation.”

12.) P17, l1 - 4: The statements in this sentence appear to contradict each other. Is the increase of oxalic acid from 1 to 2 μg/m3 not a discrete increase in concentration? Revise.

We have revised this statement to reflect the change from the AIOMFAC model to the E-AIM model for prediction of aerosol pH in the organic acids case. The use of E-AIM eliminates the presence of this unusual collection of points, and results in the removal of the poorly-worded section of the original manuscript.

13.) P17, l9 - 11: “Taken together, this may indicate that the system pH changes to such a point that one of the acids which may not previously have been fully dissociated begins to do so, spontaneously lowering system the pH by nearly 0.4 pH units”. Are you referring to inorganic acids here or to the dicarboxylic acids? If the latter, is AIOMFAC even computing the dissociation of acids (explicitly or implicitly)?

We have addressed this comment by specifically stating that this could be the effect of organic acid dissociation. However, further insights into the working of the AIOMFAC model reveal that the model does not explicitly treat these processes. Subsequently, it may be the result of a transitional point in the HSO_4^-/SO_4^{2-} equilibrium. We have accounted for this by utilizing the E-

AIM model, which does explicitly treat the acid dissociation of the selected organic acids for the prediction of aerosol pH in the organic acid cases.

14.) P18, l10: rephrase

This section has been rephrased in the following way: “The magnitudes of these observed pH changes, with the exception of the Beijing organic acids case at high (> 25 µg m^{-3} acids concentration) is not expected to significantly alter particle conditions or lead to changes in particle chemistry, except when the pH is close to the point where a given species is almost equally partitioned between the gas and particle phases (*i.e.* on the center/vertical portion of the titration-style sigmoid curves). This effect is demonstrated in the work of Guo et al. (2018b) and Vasilakos et al. (2018): when the pH lays on or near the inflection point of the sigmoid curve, a change of 0.5 pH units will have significant effect on species partitioning; however, when the pH is in the near-horizontal portions of the curve above or below the rapid transitional region, a change of 0.5 pH units will have negligible effect on partitioning, and thus particle chemistry.”

15.) P19, l5: “the situation becomes more complicated as there exists no accepted definition of pH for a predominantly-organic phase in which the solvent is the organic aerosol constituents rather than ALW.”
This referee considers this statement to be incorrect. Isn’t the definition by IUPAC the accepted definition of pH, which was also used in this study? The definition of pH by IUPAC seems to be applicable in either situation; it solely depends on the H+ activity. Further, any (organic) phase containing dissolved H+ likely also contains some amount of water.

The Referee is correct and our manuscript has been corrected to state that pH could be defined in either phase. The statement in question has been corrected to say: “As LLPS scenarios still require equilibrium between both predominantly-aqueous and predominately-organic phases, there is both water and inorganic ions (including H^+) in the organic phase, and organics in the inorganic-rich aqueous phase (Zuend and Seinfeld, 2012;Pye et al., 2018). Thus the IUPAC definition of pH could be applied to either phase so long as H^+ activity could be defined, necessitating an understanding of if and when LLPS occurs, and the phase for which pH is being reported.”

16.) P19, l10: Didn’t Pye et al. (2018) consider also cases with a single aqueous phase? Their Figure 3 suggest they had both LLPS and single phase cases for the SOAS field study.

Pye et al. (2018) did consider both cases within their SOAS investigation. Our investigation differs in that we seek only to pursue cases in which LLPS did not occur. We have modified our analysis using the LLPS condition specified by Bertram et al. (2011) to investigate only points where LLPS did not occur.

We have modified the statement to clarify this point. The new statement reads as: "This work stands apart from, but connects to related works. Pye et al. (2018) specifically examined the effects of LLPS, but the present study examines a different particle regime altogether (single aqueous phase with water, inorganics, and organics); instances where LLPS were predicted to occur were excluded from the analysis for this reason."

17.) P21, l15: It is unclear how a "forced metastable condition" would help to avoid LLPS. These are two independent processes/states. Clarify.

This statement has been clarified to tie metastable operation to the formation of solid precipitates only. The metastable condition does not have bearing on avoiding LLPS, but rather to avoid precipitate formation, which could alter aqueous phase activity values. The statement has been clarified to read: "Because we have forced the metastable mode on our use of the models, the system mixing state becomes another potentially significant source of error. Here we have considered only internally mixed aerosol particles without LLPS, a case that may not exist given the concentration of organic species utilized in the model study; formation of solid precipitates may occur, which has the potential to drastically alter the aqueous phase activity values."

18.) P22, l20: "for especially glassy aerosols" – unclear how viscosity and glassy aerosols are related to pH in this context. Glassy aerosols would indicate significant equilibration time scale effects, but what does that have to do with pH?

This statement has been modified to remove the phrase 'glassy aerosols.' We agree with the Referee that glassy phase states would indicate significant equilibration time scales, and that in this context, the relation to pH does not make sense.

19.) P23, l4: While the authors show that the aerosol pH value is mostly determined by inorganic species, the present study and previous work cover a relatively limited set of organic compounds and conditions. Hence, general conclusions should be stated carefully. One aspect that warrants further study and discussion concerns the partitioning of organic acids that may dissociate significantly at relatively high pH (say > 4) as well as the effects of amines acting as bases similar to ammonia. Therefore, it may be premature to conclude that exclusion of organics for future aerosol pH predictions is always justified. A disclaimer in that context may be appropriate.

We have taken strides to address this point in our reanalysis of the organic acid conditions utilizing E-AIM for model prediction of pH. We have added the clarification that AIOMFAC does not explicitly treat the dissociation of organic acids, and thus in our previous analysis we were not seeing the effects of this acid dissociation. By utilizing E-AIM, our re-analysis shows that there is a more pronounced effect on aerosol pH for the Beijing case, where the pH is in the

> 4 regime. This use of E-AIM for re-analysis shows more clearly the effect different pH regimes have on the organic acid cases. However, the results for Beijing remain relatively unpronounced until unrealistic quantities of organic acids are present. We have also clarified these statements made in the Conclusions section to better represent the results of the re-analysis employed.

Referee #2

In “Effects of Water-soluble Organic Carbon on Aerosol pH”, the authors examine changes in pH due to water solute organic acid with inorganic-organic single-phase aerosol systems, at conditions from two locations: Baltimore (more acidic) and Beijing (less acidic). In the manuscript, the authors detail use of three widely used thermodynamic models: E-AIM, ISORROPIA, and AIOMFAC for calculations of water content, activity coefficients, and pH. The results should that the impact of the organic content explored here on pH was minimal, and continues to support the role of the inorganic compounds in determining pH. However, there are some unanswered questions regarding the calculation methods, and in particular the role of dissociation equilibria of the organic acids, that should be clarified or handled in more depth. The paper would be of interest to the Atmospheric Chemistry and Physics readership, and should be considered for publications after the following are addressed.

1.) Organic acids and dissociation:
It was stated that “non-acidic WSOC were found to have a larger effect...than organic acids” due to their larger impact on H+ activity. However, it is not clear how the models used handle the concentration and the concentration, ionic strength, and pH dependent dissociation of the weak organic acids. Clarify how AIOMFAC treats the organic acids. Selection of organic acids can be put into E-AIM, both with an UNIFAC treatment, and a fitted treatment, which, I believe, treats the organic acid as non-dissociating and partially-dissociating. It would be helpful to see the impact of the two treatments in the pH results. It may be that different treatment of the dissociation equilibrium may result in more significant changes in pH by the organic acid.

The Referee makes an excellent point, and our analysis has been modified. AIOMFAC does not explicitly treat the dissociation of the organic acid species. We have switched to using E-AIM for the aerosol pH model predictions in the organic acid cases. Subsequently, we find that the organic acid dissociation has an approximately equal effect for Baltimore (where pH is low from the start), and a more obvious effect for Beijing (where pH is higher initially). By accounting for this dissociation explicitly via the E-AIM model, we observe that the hypothesized trends in pH (*e.g.* that organic acid addition should decrease pH which it is initially high, and that non-acid organics addition should generally increase pH) hold.

2.) Effects due to selected method/models:
There remains an underlying question of if the results (e.g., the minimal impact of WSOC on aerosol pH) is due to the method and models used, versus being representative of the true pH in the Baltimore and Beijing conditions. It would be helpful to compare results with various treatments of organic acid dissociation equilibrium (see above comment) as well as organic-inorganic mixtures. For the later, one can add organic compounds to E-AIM, by way of using UNIFAC functional groups – how do the results from this method compare to the that with a combined E-AIM for the inorganic, AIOMFAC for the organic method used here? E-AIM was used for the Baltimore date, and ISORROPIA for the Beijing data – how do the results vary if this was switched? For example, a model-based impact likely explains the isolated group of points in Fig 4 (page 16 line 21 – page 17 line 11) – is that same group of points found with oxalic acid is treated using a different model?

We agree with the Referee's comment, however, the suggested analysis is not possible. The online version of AIOMFAC treats organic acids as non-dissociating species. ISORROPIA does not provide inclusion of organic acids. E-AIM treats organic acids as dissociating species, able to contribute H^+ through full or partial dissociation. Therefore, direct comparison of predictions with the different models would be expected to be quite different. See our response to Referee #2, comment 1 above, as well.

3.) Effects of the inorganic salts and the model organics chosen:
How much impact did the choice of method to go from individual ions to salts (page 11) have on the results? How does this compare to results if the ions were evenly distributed into all the possible salt combinations? For the organics, more information on why the three particular non-acids were chosen. (line 22, page 8) Also, why were organic acids and non-organic acids not considered together? (line 5, page 9). Is it expected that having the mixture would impact the results?

We feel that the choice of salts exists primarily as an 'accounting' method to transform the outputs of the E-AIM or ISORROPIA model into inputs that AIOMFAC can interpret. As we have used measured (average) compositions, we selected salt species known to exist in inorganic aerosols; consideration of all the various salt combinations would have be prohibitive in the time frame for publication. Similarly, the exploration of organic acids and non-acid organics was not considered for similar reasons, in addition to leaving further analysis for future works once the method employed in this current study was peer-reviewed and published. However, we anticipate that having the mixtures would impact the results (*e.g.* as non-acid organics display an increase in pH placed against the downward or flat trend observed by organic acid addition).

We have addressed the Referee comments by adding the following to the discussion:

“The selection of species is unlikely to affect model outcomes, as this is simply a way to account for the ionic species present in the AIOMFAC model inputs, which require matched cation-anion pairs, and are expected to be fully-dissociated in the aqueous phase during model evaluation.”

“Levoglucosan ($C_6H_{10}O_5$), tetrahydrofuran ($(CH_2)_4O$), and 2-methyltetrol (1-methylbutane-1,2,3,4-tetrol, $C_5H_{12}O_4$), three organic species observed in ambient aerosols, were selected as the non-acid organic species.”

Minor Comments

1.) Define what is meant by “...the thermodynamic equilibrium problem…” (line 2, page 4).

This statement was revised to explicitly state AIOMFAC is an activity coefficient model and does not solve the equilibrium calculations of E-AIM or ISORROPIA. The new line reads: “AIOMFAC offers wide support for organic components, but is an activity coefficient model that does not solve the equilibrium partitioning calculations for which the other models were designed.”

2.) What are the typical organic to inorganic mass ratios of the two region (line 1, page 9)

The following statement was added to answer the Referee’s question: “For Beijing, typical organic mass fractions can be on the order of 50-70% of total aerosol mass (Zhou et al., 2018), and 20-60% of total aerosol mass for continental mid-latitude locations like Baltimore (Carlton et al., 2009).”

3.) How much H+ was typically added for electroneutrality (line 19-20, page 9), compared to the other cations? Was it significant? Please comment.

The following clarifying statement was added: “The amount of H^+ added was a not-insignificant amount, comprising approximately 65% of the amount of NH_4^+ included in the model for Baltimore, but makes sense given the expected acidic nature of Eastern US, sulfate-rich aerosols.”

4.) “AIOFAC” typo, line 9, page 13

This typo has been corrected to say AIOMFAC.

Effects of Water-soluble Organic Carbon on Aerosol pH

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Abstract

Water soluble organic carbon (WSOC) is a ubiquitous and significant fraction of fine particulate matter. Despite advances in aerosol thermodynamic equilibrium models, there is limited understanding on the comprehensive impacts of WSOC on aerosol acidity (pH). We address this limitation by studying submicron aerosol that represent the two extremes in acidity levels found in the atmosphere: strongly acidic aerosol from Baltimore, MD, and weakly acidic conditions characteristic of Beijing, China. These cases are then used to construct mixed inorganic/organic single-phase aqueous particles, and thermodynamically analyzed by the E-AIM and ISORROPIA models in combination with activity coefficient model AIOMFAC to evaluate the effects of WSOC on the H^+ ion activity coefficients (γ_{H+}) and activity (pH). We find that addition of organic acids and non-acid organic species concurrently increases γ_{H+} and aerosol liquid water. Under the highly acidic conditions typical of the eastern U.S. (inorganic-only pH ~1), these effects mostly offset each other, giving pH changes of < 0.5 pH units even at organic aerosol dry mass fractions in excess of 60%. Under conditions with weaker acidity typical of Beijing (inorganic-only pH ~4.5), the non-acidic WSOC compounds had similarly minor effects on aerosol pH, but organic acids imparted the largest changes in pH compared to the inorganic-only simulations. Organic acids affect pH in the order of their pKa values (oxalic acid > malonic acid > glutaric acid). Although the inorganic-only pH was above the pK_a value of all three organic acids investigated, pH changes in excess of 1 pH unit were only observed at unrealistic organic acid levels (aerosol organic acid concentrations > 35 μg m^{-3}) in Beijing. The model simulations were run at 70%, 80%, and 90% relative humidity (RH) levels and the effect of WSOC was inversely related to RH. At 90% RH, WSOC altered aerosol pH by up to ~0.2 pH units, though the effect was up to ~0.6 pH units at 70% RH. The somewhat offsetting nature of these effects suggests that aerosol pH is sufficiently constrained by the inorganic constituents alone under conditions where liquid-liquid phase separation is not anticipated to occur.

1. Introduction

The acidity of atmospheric particles plays a critical role in many physicochemical processes. Some of these processes include sulfur oxidation and halogen chemistry, with important implications for the formation of sulfates (Chameides, 1984) ; the oxidation of volatile organic compounds (VOCs), and ozone formation in marine environments (Keene et al., 1998); the gas-particle partitioning of many semi-volatile species (Ahrens et al., 2012; Keene et al., 2004); and, enhancements to secondary organic aerosol (SOA) formation (Hallquist et al., 2009). The inorganic salt constituents in atmospheric particles, such as ammonium sulfate ($(NH_4)_2SO_4$) and ammonium bisulfate (NH_4HSO_4), contribute to particle acidity and water content, with effects on aerosol radiative forcing (Seinfeld and Pandis, 2016). In addition to the physicochemical effects within particles, their bulk acidity can affect health, both of environmental ecosystems and the human populations therein either directly (Gwynn et al., 2000; Peters et al., 1996; Schindler, 1988; Spengler et al., 1996; Fang et al., 2017; Johnson et al., 2008), or by their effects on nutrient deposition (Myriokefalitakis et al., 2016; Myriokefalitakis et al., 2018; Kanakidou et al., 2016; Nenes et al., 2011).

pH, the parameter serving to define and describe the acidity of aqueous solutions, often has no direct correlation with proxy measurement methods such as aerosol strong acidity (H^+ contributed by strong acids that dissociated completely at any pH level) or aerosol total acidity (dissociated H^+ and undissociated H^+ bound to weak acids) (Hennigan et al., 2015; Song et al., 2018b). The most accurate predictions of aerosol pH come from aerosol thermodynamic equilibrium models constrained by both aerosol and gas-phase measurements (i.e., “forward mode” calculations), or from the measured gas-particle partitioning of semi-volatile species, including ammonia, nitric acid, or oxalic acid, which provide direct insight to the pH (Hennigan et al., 2015). Both approaches utilize aerosol and gas-phase composition measurements, along with the temperature and relative humidity, to obtain aerosol pH values. Consistent pH values are obtained when the assumptions about aerosol mixing and equilibrium are met (Guo et al., 2018a; Guo et al., 2018b).

Different aerosol thermodynamic equilibrium models have been developed through the years, each with a unique sets of assumptions, simplifications and approach to obtain the composition at thermodynamic equilibrium. The Extended Aerosol Inorganics Model (E-AIM, http://www.aim.env.uea.ac.uk/aim/aim.php) (Wexler and Clegg, 2002; Friese and Ebel, 2010) and the ISORROPIA-II model (Greek for ‘equilibrium,’ http://isorropia.eas.gatech.edu) (Fountoukis and Nenes, 2007) are widely used to calculate aerosol pH for atmospheric and experimental particle distributions (Guo et al., 2017; Guo et al., 2016; Guo et al., 2015; Wang et al., 2016). The Aerosol Inorganics-Organics Mixtures Functional groups Activity Coefficient (AIOMFAC) model (http://www.aiomfac.caltech.edu/model.html) offers the most extensive treatment of organic-inorganic interactions (Zuend et al., 2008; Zuend et al., 2011) of models to date, but is primarily an activity coefficient model that does not solve full thermodynamic equilibrium calculations or phase partitioning as E-AIM and ISORROPIA do. At present, E-AIM, ISORROPIA, and AIOMFAC are widely used for atmospheric applications due to their demonstrated predictive capabilities and their accessibility: they are freely available online, and include resources and user guides to facilitate their application and use.

One key difference among the models is their treatment of organics. ISORROPIA does not include organic species. E-AIM functions similarly to ISORROPIA when considering inorganic species, but in addition offers a limited library of organic acids (included by UNIFAC methods or fitted activity equations). AIOMFAC offers wide support for organic components, but is an activity coefficient model that does not solve the equilibrium partitioning calculations for which the other models were designed. While AIOMFAC has been used in combination with thermodynamic equilibrium models such as ISORROPIA-II (Pye et al., 2018), these are custom modifications to the models, and not reflected in the online versions used in this study. These models, and most others, do not treat organics in a way that is comprehensive (that is, simultaneous consideration of activity coefficient calculations and thermodynamic equilibrium calculations). However, these simplified thermodynamic models do seem to capture the partitioning of inorganic species well, even when organic components are present in large quantities, which indicates that pH should be captured well (Guo et al., 2018a). An additional consideration between the models is their treatment of organic acids. E-AIM offers support for limited (n = 8) organic acid species, and treats the dissociation equilibrium of organic acids. In contrast, AIOMFAC treats organic acids as non-dissociating, a model difference that is discussed in detail below. Note that the ion dissociation equilibria of inorganic species (such as HSO_4^-/SO_4^{2-}) are explicitly considered in the equilibrium calculates of all three models employed in this study.

The effects of WSOC on aerosol pH come through two primary means: dilution of the aqueous phase by aerosol liquid water associated with the organic fraction (W_o); and changes to the hydrogen ion activity coefficient and thus hydrogen activity in solution (γ_{H+} and a_{H+}, respectively). The total contribution of organics to aerosol water can be as much as 30-50% of total fine particle aerosol water in the polluted Beijing winter haze events (Tan et al., 2018; Huang et al., 2014), 40-50% in the southeast United States (Nah et al., 2018; Guo et al., 2015), and the eastern Mediterranean (Bougiatioti et al., 2016). The effects of organics (soluble and insoluble) on aerosol pH under conditions of liquid-liquid phase separation (LLPS) are more complex. Free H^+ ion is predicted to have increased association with SO_4^{2-} to form HSO_4^- when organic compounds are in the same phase as inorganic ions, resulting in a 0.1 pH unit increase in aerosol pH (Pye et al., 2018). The isolation of the organic components in a separate phase (LLPS condition) also alters the partitioning behavior of NH_3, a critical component that contributes to aerosol pH. The inclusion, or lack thereof, of organic compounds was predicted to have a greater effect on NH_3 partitioning behavior than the inclusion, or lack thereof, of nonvolatile cations, nitrate, and chloride (Guo et al., 2018a). In addition to these effects, AIOMFAC predicts that any organic presence in the same phase with inorganic constituents drives free H^+ to increased association with sulfate to form bisulfate, a compound predicted to be more miscible with organics than H^+ and small cations. AIOMFAC was used to show that the organic phase of liquid-liquid phase separated particles still contains a significant amount of inorganics, affecting the partitioning medium by inclusion of the inorganic ions and their associated water, lowering the mole fraction and activity of organics, and shifting the gas-particle partitioning of organic compounds with O:C > 0.6 (Pye et al., 2018). In the case where multiple phases do exist, there is anticipated to be a primarily-organic (PO) and primarily-inorganic (PI) phase, each of which contains H^+ in equilibrium with the other phase. In cases where the vast majority of inorganics are partitioned to the PI phase, the pH is not anticipated to change drastically, as H^+ is also required to be in equilibrium with the other phases, which may explain the results of (Pye et al., 2018). In the case of phase separation where the PO phase contains considerable amounts of inorganic species, there exists the possibility of a PI phase with substantially-altered H^+ activity, and therefore, the potential for substantially-altered aerosol pH (*eg.* (Dallemagne et al., 2016). The present study avoids such complexity and instead considers mixed organic-inorganic particles present in a single aqueous phase.

Aerosol pH can also be directly affected by organic acids, whose dissociation produces H^+ ions in the particle aqueous phase. Carboxylic acids represent a highly abundant moiety in atmospheric OA (Yatavelli et al., 2015; Kawamura and Bikkina, 2016; Nah et al., 2018). Although these atmospheric organic acids are typically weaker acids with higher pK_a values than common inorganic acids (H_2SO_4 and HNO_3), they may contribute to particle acidity in some environments (Trebs et al., 2005). However, this effect is not present in all environments and is constrained to situations where the pH is in the range of the pK_a of the acid in question (Nah et al., 2018; Song et al., 2018b). As both organic acids and non-acid organic species are expected to be present, there are competing effects within the particle: dilution by the water fraction associated with organic constituents, direct acidification by the dissolution of organic acids, and the change in γ_{H+} by interactions with the additional species in solution.

Oxalic acid (measured as the oxalate ion) is often the most abundant carboxylic acid in atmospheric aerosols (Bikkina et al., 2015). Several studies utilized E-AIM Model IV to evaluate the effect of oxalic acid on particle acidity (Vasilakos et al., 2018; Song et al., 2018b). With inorganics similar in composition to that of Baltimore, conditions applied in this study, an increase of 25-50% of oxalic acid compared to the base case had an insignificant effect on aerosol pH when only one liquid phase was present. Pye et al. (2018) utilized data from the Southern Oxidant and Aerosol Study (SOAS) in ISORROPIA and AIOMFAC to investigate the gas-particle partitioning of ammonia, water, and organic compounds, and how liquid-liquid phase separation (LLPS) in particles can affect aerosol pH, predicting a 0.7 pH unit increase when the organic fraction and its diluting effect was considered. Generally, aerosol processes are not affected by a pH change of this magnitude, except in the regions on the thermodynamic sigmoid curves of semi-volatile species where partitioning is shown to vary greatly for small changes in pH (Nah et al., 2018; Guo et al., 2018b).

In this work, we explore the effects of WSOC on aerosol pH in a systematic way by utilizing inorganic data to construct combinations of single, aqueous phase particulate compositions, and utilizing aerosol thermodynamic models to investigate the effects of different WSOC species and concentrations on γ_{H+} and a_{H+}.

2. Methods

Data

Inorganic and meteorological data used for this study were reported in prior work. Briefly, data from Baltimore, MD were taken from (Battaglia et al., 2017), and include speciated inorganic $PM_{2.5}$ concentrations, meteorological data, and gas-phase NH_3 measurements. The data used as thermodynamic model inputs are summertime (July) averages based on 3- or 5-years of monitoring. All model inputs and outputs are available in the Supporting Information.

Aerosol inorganic composition, gas-phase NH_3 measurements, and meteorological parameters were obtained during a study of winter haze formation in Beijing, China in 2015 (Wang et al., 2016). These data represent a contrast with Baltimore due to different source contributions, differences in NH_3 concentrations, T, RH, and inorganic aerosol levels. The inorganic $PM_{2.5}$ concentrations, and averaged seasonal T and RH, along with NH_3 gas concentration values were obtained as model-ready inputs of the Beijing winter haze data from (Guo et al., 2018b), based on supplemental information from (Wang et al., 2016).

General Approach

The general approach to this study was to utilize the inorganic PM and NH_3 data described above, in combination with various additional WSOC constituents, as inputs to aerosol thermodynamic equilibrium models to investigate the effects on model-predicted aerosol pH and γ_{H+}. Inorganic data were modeled in either E-AIM IV or ISORROPIA-II to obtain equilibrium concentrations of aerosol liquid water (ALW) along with all inorganic aerosol ionic species. Organic constituents were then added to this invariant inorganic matrix (assuming the added organic mass was at equilibrium), at identical T and RH, and the resulting particle compositions were modeled in AIOMFAC to obtain aerosol H^+ ion activity (a_{H+} and γ_{H+}), and thus aerosol pH. The average inorganic composition, gas-phase NH_3, and meteorological conditions were held approximately constant for each location, while WSOC composition and concentrations were systematically varied. A matrix was constructed to examine multiple combinations of the selected organic component composition levels (factorial design), and their effects evaluated on the basis of organic-to-inorganic ratio (OIR) or organic mass fraction, both computed on a dry particle basis. This full factorial design consists of three factors for each acid or non-acid condition (the identity of each species), each with discrete possible values (air concentrations in $\mu g\ m^{-3}$), where the experiment incorporates all possible combinations of these values across all factors (Keppel, 1991). For each location, this resulted in a total of 7986 model simulations in total, with 1331 simulations run for both cases of organic compounds selected, and at each of three distinct RH level, as described below. A summary of the models run for each location is shown in **Table 1**. The RH in all simulations was fixed at either ~70%, ~80%, or ~90%, with inorganic system inputs calculated and invariant at each RH level based on the initial input data from either Baltimore or Beijing to ensure deliquescence of inorganic aerosol particles, to understand the sensitivity of the model-predicted aerosol pH to changes in RH (ALW), and to avoid liquid-liquid phase separation as a potential cause of organic-influenced aerosol pH changes (Pye et al., 2018). For all of the results presented in this analysis, aerosol pH was computed as the negative base-ten logarithm of the hydrogen ion activity taken from the E-AIM or AIOMFAC output ($pH = -\log_{10} a_{H+}$) on a molality basis.

Organic Constituents

Water-soluble organic compounds were selected by broadly classifying them as organic acids or non-acid organics. Within each category, three individual species were selected based on their detection in atmospheric particles and their availability in the predefined list of AIOMFAC organic species available on the AIOMFAC web interface, or the ability to reasonably construct them using the functional groups approach of AIOMFAC. In addition, non-acid organics were selected from three different primary moiety groups from among the AIOMFAC standard species. Oxalic acid ($C_2H_2O_4$ $pK_{a1} = 1.23$, $pK_{a2} = 4.19$) (Lide 1994) , glutaric acid ($C_5H_8O_4$, $pK_{a1} = 4.31$, $pK_{a2} = 5.41$) (Lide, 1994), and malonic acid ($C_3H_3O_4$, $pK_{a1} = 2.83$, $pK_{a2} = 5.69$) (Lide, 1994) were selected as the three dicarboxylic acid species. Levoglucosan ($C_6H_{10}O_5$), tetrahydrofuran ($(CH_2)_4O$), and 2-methyltetrol (1-methylbutane-1,2,3,4-tetrol, $C_5H_{12}O_4$), three organic species observed in ambient aerosols, were selected as the non-acid WSOC species. Concentration levels were not constrained by observations, but were instead selected to achieve similar organic to inorganic mass ratios for each of the two geographic regions being considered. For Beijing, typical organic mass fractions can be on the order of 50-70% of total aerosol mass (Zhou et al., 2018), and 20-60% of total aerosol mass for continental mid-latitude locations like Baltimore (Carlton et al., 2009). For each geographic region, 11 different concentrations were chosen for each WSOC compound (0-4 µg m^{-3} for Baltimore; 0-40 µg m^{-3} for Beijing), and combined in factorial fashion: each organic acid concentration level combination of the three organic acids were examined in combination with every other level of the remaining two, and vice-versa for the non-acid organic species. Combinations of organic acids and non-acid organic species were not explicitly considered here; only combinations of organic acids with organic acids, or combinations of non-acids with non-acids were examined experimentally. All model inputs and outputs are included in the Supporting Information.

Thermodynamic Model Input Configuration and Equilibrium Model Evaluations

E-AIM Model IV provides thermodynamic equilibrium modeling of the H^+-NH_4^+-Na^+-SO_4^{2-}-NO_3^--Cl^--H_2O system at temperatures from 263.15 K to 330 K for subsaturated systems that contain NH_4^+ and Cl^-, or Na^+ in combination with other ions (Friese and Ebel, 2010). Data for Baltimore and Beijing were formatted for E-AIM input in the following ways: average inorganic species concentrations (µg m^{-3}) were converted to mol m^{-3}; the average daily temperature for the same period was used as the temperature input; the relative humidity of the system was fixed (at 70%, 80%, or 90%) both to ensure the inorganic system was in a deliquesced state and because of the RH restrictions (subsaturated solution requirements, RH > 0.6) on E-AIM Model IV inputs. In addition to fixing system RH at 70%, 80%, or 90%, the aerosol metastable (solid precipitate formation disabled) mode was enforced on the model by disabling the formation of all solids in the model input matrix, according to the analysis and recommendation of Guo et al.

(2018b; 2015). Crustal species (Ca^{2+}, Mg^{2+}, K^+) not supported by the model were not considered, and the persistent cation deficiency was corrected by the addition of H^+ to the system to ensure electroneutrality. The amount of H^+ added was a not-insignificant amount, comprising approximately 65% of the amount of NH_4^+ included in the model for Baltimore, but makes sense given the expected acidic nature of eastern US, sulfate-rich aerosols (Weber et al., 2016). For Beijing, a persistent anion deficiency was addressed by addition of OH^- to the system to ensure electroneutrality. The amount of OH^- added to the system for the Beijing case was one order of magnitude lower than the cation species, but on the same order of magnitude and 4-7 times lower than any other anion except Cl^-.

E-AIM offers support for certain organic acid species. For the Baltimore and Beijing simulations, the organic acid species were added directly to the E-AIM model inputs. In the case of organic acid model runs, factorial combinations of the organic acid species at 0.0, 0.01. 0.02, 0.04, 0.08, 0.16, 0.32, 0.5, 1, 2, and 4 μg m^{-3} (Baltimore) and 0.0, 1, 2, 5, 10, 15, 20, 25, 30, 35, and 40 μg m^{-3} (Beijing) and were converted to mol m^{-3} input. Formation of organic solids was also disabled as part of the metastable equilibrium condition. For the non-acid organics, the addition of the selected species to the E-AIM equilibrium calculation was not possible, and the model was run with the inorganic constituents only. E-AIM provides output of the aqueous species mole fractions and mole fraction-based activity coefficients; this mole fraction-based aerosol pH was converted to a molality-based aerosol pH utilizing known thermodynamic relations (Robinson and Stokes, 1965; Jia et al., 2018).

ISORROPIA-II Model Input Configuration and Equilibrium Model Evaluations

ISORROPIA-II provides thermodynamic equilibrium modeling for the H^+-NH_4^+-Na^+-SO_4^{2-}-NO_3^--Cl^--Ca^{2+}-Mg^{2+}-K^+- H_2O across a wide range of temperature and RH values without limitation based on the input composition (Fountoukis and Nenes, 2007). Data for Beijing were already formatted for use in ISORROPIA-II as described above (Guo et al., 2018b). The formation of solids in the model was disabled (leading to potential supersaturated aerosols, metastable mode operation), based on the justifications in previous studies (Guo et al., 2015; Guo et al., 2018b) and to maintain consistency with the E-AIM model conditions. An initial model run was performed to verify that identical model outputs were obtained using the inputs of Guo et al. (2018b). For the purposes of this investigation, the RH value was changed from the Beijing average ambient value of 56% to 70%, 80%, or 90%, consistent with the model input for the Baltimore data for the same reasons discussed above. The Beijing average ambient temperature of 274.05 K was used in the Beijing inorganic model calculations with the three RH values.

AIOMFAC Model Input Configuration and Equilibrium Model Evaluations

E-AIM was utilized to determine the equilibrium composition of the inorganic aerosol, including the NH_3 phase partitioning and the aerosol liquid water content. Outputs from E-AIM were then used as inputs into AIOMFAC to characterize the organic effects on aerosol H^+ activity, and γ_{H+} (**Figure 1**). The E-AIM outputs (AIOMFAC inputs) were also checked for consistency with ISORROPIA to ensure that the applied model assumptions (H^+ and OH^- as balancing species to achieve electroneutrality) provided reasonable results.

The particle-phase outputs from the E-AIM model runs were used as inputs to AIOMFAC; however, this required significant adjustments to the format to fit the AIOMFAC model. AIOMFAC requires inorganic species inputs to be entered as ionic *pairs* (whole molecular species entered as a cation and anion pair) in order to guarantee electroneutrality. Therefore, the ionic species outputs of E-AIM were converted to molecular species inputs by assigning pairs, and then performing a stoichiometric balance until all ions were accounted for (*i.e.* E-AIM H^+

and SO_4^{2-} being combined in stoichiometric fashion as H_2SO_4 with corresponding reductions in the 'pool' of E-AIM H^+ and SO_4^{2-}). In the Baltimore case for the pure inorganic input (all organic species modeled at 0.0 μg m^{-3} concentration), E-AIM Model IV provided particle-phase output for the following ions: H^+, NH_4^+, Na^+, HSO_4^-, SO_4^{2-}, NO_3^-, and OH^-. In order to format these concentrations for AIOMFAC-specific inputs (that is, to compute the necessary mole fraction format of molecular species in the aerosol), the ions were assigned in the following ways. First, all SO_4^{2-} was associated with H^+ for the H_2SO_4 pair in AIOMFAC. All NO_3^- was associated with Na^+ for the $NaNO_3$ pair. Remaining Na^+ was associated with SO_4^{2-}, then NH_4^+ with HSO_4^- and remaining NH_4^+ with the remaining SO_4^-. This allocation process proceeded similarly for the Beijing data. The selected species and order of allocation of the ionic species appears to be dependent solely on the user, and *a priori* knowledge of which molecular species are likely to exist in the aerosol particle as the dissociated ionic species. The selection of species is unlikely to affect model outcomes, as this is simply a way to account for the ionic species present in the AIOMFAC model inputs, which require matched cation-anion pairs, and are expected to be fully-dissociated in the aqueous phase during model evaluation. The end result is a mixture of inorganic molecular species containing the full concentration values generated by E-AIM assumed to be dissociated within the aerosol where each functional group can contribute to species activity based on the AIOMFAC model paradigm; assignment of molecular species pairings is performed only on the basis of formatting specifically for the AIOMFAC model. The inorganic inputs used in the AIOMFAC models for both Baltimore and Beijing simulations are given in **Table 2**.

An additional key step in formatting the E-AIM output for input to AIOMFAC is in the model treatment of the water associated with organic constituents, W_o. E-AIM provided output of W_o

as a part of the total aerosol liquid water (ALW; $W_i + W_o$) for the organic acid simulations, but provides no estimate of W_o for the non-acid simulations. RH is not an input to the AIOMFAC model runs. Rather, AIOMFAC requires the input of all species (inorganic and organic) in mole fractions, and assumes the difference between the total inputs and unity is contributed by water, the water activity of which is equal to the ambient relative humidity. Therefore, accounting for the water contributed by the organic species was an additional step in formatting the E-AIM outputs for AIOMFAC input as described below.

For two of the four cases (Baltimore and Beijing inorganics plus non-acid organics), W_o was added to the system by the following process, a flow diagram of which is shown in **Figure 1**. For the first 11 points of the factorial design (representing the addition of only the first organic constituent at each concentration level) and the final 11 points of the factorial design (representing the 11 highest organic addition points, including the addition of all three organic species at their maximum selected concentration), total system moles were varied manually by increasing the inorganic model-predicted moles of aerosol water. AIOMFAC inputs (as mole fractions) were calculated using this adjusted total mole value. The 22 manually-adjusted points were modeled in AIOMFAC. If the option for liquid water is selected (as it was in all of our simulations), AIOMFAC assumes that water makes up the difference between the mole or mass fraction of all inputs summed together and unity. To achieve consistency with the inorganic model results, the total moles of the system were manually adjusted until the RH output generated by the AIOMFAC model was within ~5% of the RH value fixed for the inorganic systems. Once this close fit was achieved for the 22 selected points, they were used to generate polynomial fits of the total moles added to the system as W_o versus total organic mass (regardless of species). These polynomial fits were then applied to all model points to adjust the total system moles through the addition of liquid water associated with organic mass, resulting in AIOMFAC-predicted RH values within 5% of the E-AIM RH values of 70%, 80%, or 90%. This method of accounting for W_o is a strictly mathematical construct, and does not reflect the use of a species-dependent organic hygroscopicity parameter, which would have been prohibitive to apply for each point across all cases and RH levels. Additionally, following the introduction of the adjusted W_o to the system, the gas-phase was not allowed to re-equilibrate to the new water content contributed by the organic species. This provides a conservative (high) constraint on the effect of W_o (Guo et al., 2015).

Evaluation of LLPS and Accommodations for LLPS Scenarios

The O:C ratio is a key factor that determines whether LLPS occurs in organic-containing particles (Song et al., 2018a; Freedman, 2017). We followed the parameterization found experimentally by Bertram et al. (2011) to evaluate the presence of LLPS in our simulations. This method uses the overall mixture O:C ratio to determine the separation RH of the mixture. If the modeled (in this case, specified/enforced) system RH is lower than the parameterized separation RH (RH_{LLPS}), LLPS is likely to occur. This was performed for each of the non-acid mixtures for both Baltimore and Beijing data to verify the claim that LLPS was not anticipated to occur. For cases where the parameterized RH_{LLPS} was higher than the predicted system RH, LLPS was anticipated to occur, and the point was flagged and excluded from further analysis. Out of 1331 simulations, Baltimore had 55% (*n* = 732), 70% (*n* = 932), and 75% (*n* = 998) simulations that met the non-LLPS criteria at 70%, 80%, and 90% RH respectively. Beijing had 85% (*n* = 1131), 89% (*n* = 1185), and 93% (*n* = 1238) of simulations meet the non-LLPS conditions at 70%, 80%, and 90% RH respectively. Experimental work by (You et al., 2013) indicates that glutaric acid, malonic acid, oxalic acid, or their mixtures do not undergo LLPS at any of the RHs investigated.

3. Results and Discussion

Effects of WSOC on Aerosol γ_{H+}

AIOMFAC-predicted aerosol pH and γ_{H+} versus the organic dry mass fraction (total mass of organics/mass inorganics, excluding ALW), along with aerosol liquid water used in the model evaluations for the non-acid species runs in Baltimore and Beijing at al RH levels, are shown in Figures 2 and 3. For the case of non-acid WSOC compounds at 80% RH (Figs. 2d and 3d), ALW increases from 4.7×10^{-9} L m^{-3} to 9.7×10^{-9} L m^{-3} and from 9.6×10^{-8} L m^{-3} to 1.8×10^{-7} L m^{-3} for Baltimore and Beijing, respectively, as the organic mass fraction increases. Similar trends follow for the 70% and 90% RH scenarios in both cities. This behavior makes sense, because the inorganic species concentrations and RH were fixed, so adding increasing levels of water-soluble organics increases the ALW. Increasing the organic dry mass fraction increases the value of γ_{H+}, from initial values of 0.10 and 0.16 (80% RH) for Baltimore and Beijing under inorganic-only conditions, to 2.4 for Baltimore (Fig. 2d) and 1.6 for Beijing (Fig. 3d). The higher absolute ALW levels in the Beijing simulations are due to the significantly higher inorganic and organic aerosol loadings.

The results follow for the additional RH values studied. For the case of non-acid organics at 70% RH (Figs. 2 and 3) increasing the organic dry mass fraction increases the value of γ_{H+}, from initial values of 0.11 and 0.18 for Baltimore and Beijing under inorganic-only conditions, to 1.3 for Baltimore (at an organic dry mass fraction of 0.65) and 2.5 for Beijing (organic dry mass fraction of 0.67). ALW follows a similar trend at 70% RH as it does at 80% RH, but with lower absolute ALW levels. For the case of non-acid organics at 90% RH, increasing the organic dry mass fraction increases γ_{H+} from initial values of 0.12 and 0.20 for Baltimore and Beijing under inorganic-only conditions, to 1.2 for Baltimore (at an organic dry mass fraction of 0.79) and 0.78 for Beijing (organic dry mass fraction of 0.64). For these simulations, the ALW increases from 9.1×10^{-9} L m^{-3} to 2.4×10^{-8} L m^{-3} and from 2.1×10^{-7} L m^{-3} to 3.6×10^{-7} L m^{-3} for Baltimore and Beijing, respectively. In each case, the data plotted in Figures 1 and 2 are those that are determined not to have LLPS according to the parameterization of Bertram et al. (2011).

The plots of ALW display distinct behaviors attributable to the way in which the water content was derived for the model systems. For the organic acid simulations, the ALW was taken directly from the E-AIM Model IV output of aqueous phase water (mol m^{-3}) run with inorganic and organic acid inputs. For all non-acid organic cases, total ALW ($W_i + W_o$) was determined according to the manual AIOMFAC output fitting/polynomial fit correlation described in the methods section (Figure 1). This results in system water behavior described by polynomial fits of additional water versus organic dry mass fraction.

Effects of WSOC on Aerosol pH

The model-predicted effects of WSOC on aerosol pH are shown in Figures 2 - 5. As the dry organic mass fraction increases, ALW increases as well, since the RH and inorganics are held constant. This suggests a diluting effect, which would increase pH, in agreement with Guo et al. (2015). On the other hand, γ_{H+} also increases with increasing dry organic mass fraction, indicating that the addition of WSOC compounds increases the acidity (decreases pH).

For the case of non-acid WSOC additions (Figs. 2and 3), increasing the organic mass fraction decreases the predicted aerosol pH from the initial inorganic-only values from 1.64 to a max of

1.94 (Baltimore) and from 4.29 to a max of 4.38 (Beijing) at 80% RH. For the 70% RH simulations, the model predicted pH changes from 1.49 to a max of 1.88 for Baltimore, and from 4.10 to a max of 4.33 for Beijing. For the 90% RH case, the model predicted pH changes from 1.85 to a max of 2.09 for Baltimore, and from 4.52 to a max of 4.56 for Beijing. The transition in the pH plots are smooth, where the contour lines reflect individual levels of the factorial design and highlight the overall trend: as non-acidic WSOC is added, AIOMFAC-predicted aerosol pH increases for both the Baltimore and Beijing conditions. Since the WSOC leads to ALW uptake (diluting acidity), the increase in pH comes about due to the increase ALW having a stronger effect than the increase in γ_{H+}.

For the case of organic acids, increasing the organic mass fraction results in only slight changes in the predicted aerosol pH for Baltimore (Figure 4), but more pronounced changes for Beijing (Figure 5). At 80% RH, the predicted pH ranges from an initial (inorganic-only) value of 1.49 (Baltimore) and 4.2 (Beijing) to 1.34 and 2.6, respectively (total range = 0.4 and 1.68 pH units respectively). Similarly, there is a change from 1.33 to 1.22 (range = 0.34 pH units) for Baltimore and a change from 4.06 to 2.52 (range=1.58 pH units) for the Beijing simulations at 70% RH. Finally, there is a change from 1.75 to 1.54 (range = 0.47) for Baltimore and a change from 4.44 to 2.68 (range = 1.78) for Beijing at 90% RH. The ranges represent the total range spread from highest to lowest model-predicted pH. For Baltimore, organic acids are predicted to have only a slight effect on aerosol pH. Under the highly acidic conditions typical of the eastern U.S. (inorganic-only pH ~1), pH changes are always < 0.5 pH units, even when the dry organic aerosol mass fraction exceeds 60% (corresponding to total aerosol organic acid concentrations up to 12 μg m^{-3}). This is likely due to the pH being sufficiently acidic that the organic acid dissociation is largely inhibited. The undissociated organic acids still contribute ALW and affect

γ_{H+}, but the combined effects produce very minor modifications to pH. For Beijing, aerosol pH changes are predicted to be me more substantial with the addition of organic acids, due to the initially-higher aerosol pH. As organic acids are added, they can dissociate and contribute free H^+. However, pH changes in excess of 1 pH unit only occur at dry organic mass fractions > 0.5. Given the high inorganic aerosol concentrations in Beijing, such pH changes in excess of 1 pH unit correspond to unrealistically-high aerosol organic acid mass concentrations (> 35 µg m^{-3}). The relatively minor effect of organic acids on aerosol pH in Beijing is partly due to the high concentrations of ammonia (Tot-NHx in Beijing = 32.8 µg m^{-3}), which also contribute to the much higher "inorganics-only" pH compared to the eastern U.S. conditions.

The effect of organic acids on pH is closely tied to acid strength (i.e., pK_a value). Figure 6 shows that organic acids affect pH in the order of their pK_a values, with oxalic acid (pK_{a1} = 1.23) > malonic acid (pK_{a1} = 2.83) > glutaric acid (pK_{a1} = 4.31) (Lide, 1994). The simulations with a single organic acid demonstrate this effect most clearly: addition of 40 µg m^{-3} oxalic, malonic, and glutaric acid produce pH changes of -1.3, -0.5, and -0.2 pH units, respectively. The pH changes are all negative, indicating that the organic acids have increased particle acidity (H^+). Note that although the molar amounts added are not equivalent, the observed pH changes represent log-scale changes to the H^+ activity and the effect does proceed in the order of acid strength.

The magnitudes of these observed pH changes, with the exception of the Beijing organic acids case at high organic mass fractions (> 35 µg m^{-3} acids concentration) is not expected to significantly alter particle conditions or lead to substantial changes in particle chemistry. For example, ~0.5 pH unit changes should not significantly alter IEPOX uptake (Xu et al., 2015) or metal dissolution (Fang et al., 2017), two processes affected by particle acidity. An exception would be conditions where the pH is close to the point where a given species is almost equally partitioned between the gas and particle phases (*i.e.* on the center/vertical portion of the titration-style sigmoid curves). This effect is demonstrated in the work of (Guo et al., 2018b; Vasilakos et al., 2018): when the pH lays on or near the inflection point of the sigmoid curve, a change of 0.5 pH units can have significant effect on species partitioning; however, when the pH is in the flatter regions of the curve above or below the rapid transitional region, a change of 0.5 pH units will have negligible effect on partitioning, and thus particle chemistry.

Taken together, these results indicate that, despite organic mass fractions greater than 60% (dry particle mass basis), the combined effects of WSOC species on model-predicted aerosol pH is only about 0.5 pH units, maximum, with most pH changes < 0.2 pH units. This result is observed for non-acidic WSOC species and realistic concentrations of organic acids, and for simulations with a single organic compound added or for mixtures (**Table 2**). This suggests that the overall effect of WSOC on aerosol pH is quite minimal in conditions where LLPS does not occur. This finding holds only for systems in which there is no LLPS and the solvent is H_2O. For systems in which LLPS does occur, a condition expected in systems with O:C ratio of the organic material ≤ 0.5, or RH $< 60\%$ with organic:sulfate mass ratio < 1 (Bertram et al., 2011; You et al., 2013), the situation becomes more complicated. As LLPS scenarios still require equilibrium between both predominantly-aqueous and predominately-organic phases, there is both water and inorganic ions (including H^+) in the organic phase, and organics in the inorganic-rich aqueous phase (Zuend and Seinfeld, 2012; Pye et al., 2018). Thus the IUPAC definition of pH could be applied to either phase so long as H^+ activity could be defined, necessitating an understanding of if and when LLPS occurs, and the phase for which pH is being reported.

This work stands apart from, but connects to related works. (Pye et al., 2018) specifically examined the effects of LLPS, but the present study examines a different particle regime altogether (single aqueous phase with water, inorganics, and organics); instances where LLPS were predicted to occur were excluded from the analysis for this reason.

Our findings are supported by the work of (Song et al., 2018b), who utilized E-AIM Model IV and ISORROPIA to model the same Beijing winter haze conditions, and found that addition of oxalic acid (set at 20% of the sulfate concentration) to their model in E-AIM produced reductions in pH of only 0.07 pH units. Our results are also consistent with those of (Vasilakos et al., 2018), who observed a similarly minor effect of oxalate addition on aerosol pH in the Eastern U.S., and(Nah et al., 2018) where oxalic acid/oxalate gas-particle partitioning predicted without considering organic species in the thermodynamic analysis was in reasonable agreement with measurements. Our results indicate that additions of weaker organic acids, even at higher concentrations, would have even less of an effect on pH.

A limitation of this study is that the model simulations were only run at three RH levels (70%, 80%, and 90%), with metastable conditions enforced at all times. However, aerosol particles progress through a wider RH range in the atmosphere, with concomitant effects on aerosol liquid water and phase transitions. Future work would need to expand on the RH range in order to elucidate the behavior as the system transitions from the LLPS condition to the fully mixed aqueous condition, and the contribution of changing ALW. Additionally, the use of E-AIM Model IV imposes composition limitations on the inputs (i.e., no support for Ca^{2+}, Mg^{2+}, or K^+; limited support for Na^+ in the presence of NH_4^+ and Cl^-), necessitating the use of equivalent cations to maintain electroneutrality in the model inputs. Combined with the use of metastable calculations, there exists a potential source of error in the solution activity if these species are considered and allowed to precipitate out in the thermodynamic model calculations (e.g., $CaSO_4$). As AIOMFAC relies on specific, uniquely-defined functional group interactions in the composition of activity coefficients, the exchange of a non-supported cation in E-AIM for a charge-equivalent cation may have effects on the output unknown to us carried through to the calculation of the species activity coefficients in AIOMFAC; this is a limitation of thermodynamic models that has been previously discussed (Jacobson, 1999; Kim and Seinfeld, 1995).

Another limitation of this study is consideration of only six WSOC species, despite hundreds or thousands being present in atmospheric particles. This is a limitation we acknowledge, but is based on the significant number of model runs given the factorial design paradigm, and the decision to utilize only compounds predefined in the thermodynamic models (particularly the AIOMFAC model, which allows users to create organic molecules by combining subgroups). Because the compounds selected here have relatively low molecular weight (MW), is it possible that higher MW compounds, such as humic-like substances (HULIS), may impart a different effect. However, given the consistent results found here for both Baltimore and Beijing conditions across the 70-90% RH range, and at organic dry mass fractions that range from 0 - 60% utilizing WSOC containing four moieties, we feel our results do represent conditions in atmospheric particles. Future studies would be necessary to expand the selection of WSOC compounds, and thus broaden the results reported here. Because we have forced the metastable mode on our use of the models, the system mixing state becomes another potentially significant source of error. Here we have considered only internally mixed aerosol particles without LLPS, a case that may not exist given the concentration of organic species utilized in the model study; formation of solid precipitates may occur, which has the potential to drastically alter the aqueous phase activity values. The most significant restriction of this study is the lack of observational data for comparison. Direct measurements of particle pH have so far been restricted to simple laboratory particles of specific super-micron sizes and compositions (Rindelaub et al., 2016).

4. Conclusions and Implications

In this work, the effects of WSOC on model-predicted aerosol pH were evaluated. Different inorganic datasets from Baltimore and Beijing winter haze conditions representing distinct inorganic composition regimes were first modeled in aerosol thermodynamic equilibrium models (E-AIM or ISORROPIA), then combined with six different organic species in AIOMFAC to determine the effects on aqueous-phase γ_{H+} and a_{H+}. We find that the effects of non-acid WSOC species to each of the regions has only a modest effect on aerosol pH (< 0.5 pH units, with most < 0.2 pH units). These small effects on pH were predicted even up to organic dry mass in excess of 60%. Organic acids are predicted to have a similarly small effect on pH in the eastern U.S. In Beijing, organic acids can have larger effects on pH (in excess of 2 pH units), but require stronger organic acids (pK_a values lower than the inorganic-only pH) present at high concentrations, on the same order of molar concentration as the dissociating inorganic species. The magnitude of these changes to aerosol pH are consistent with the results predicted by previous studies that considered only inorganic aerosol components combined with *a priori* knowledge of organic mass, organic water contribution, and organic species hygroscopicity (Guo et al., 2015; Bougiatioti et al., 2016).

The results of this study have important implications for the aerosol modeling community as well as for experimental studies that utilize phase partitioning data to constrain aerosol pH. Previous studies have postulated on the effect of organic species while ignoring their inclusion, or included them in order to elucidate the effects of LLPS, but this study demonstrates that in the case of single-phase systems, including these species may only contribute unnecessary complexity to the model runs. As their effects are predominantly < 0.5 pH units, it is not expected that the inclusion of organics will cause the pH of the system to reach any significant transitions unless the organic components have already driven the system to a sensitive portion of the species partitioning sigmoid curves, or aerosols in which there is significant phase separation. This work demonstrates that inclusion of large quantities of organic components does not appear to have a significant effect on model-predicted aerosol pH, consistent with the findings of (Guo et al., 2018a) and Vasilakos et al. (2018). Based on the species and concentrations of the organics studied here, future aerosol modeling studies carried out under conditions where LLPS is not occurring may be justified in the use of inorganic-only aerosol thermodynamic equilibrium models to predict aerosol pH without the direct inclusion of organic species.

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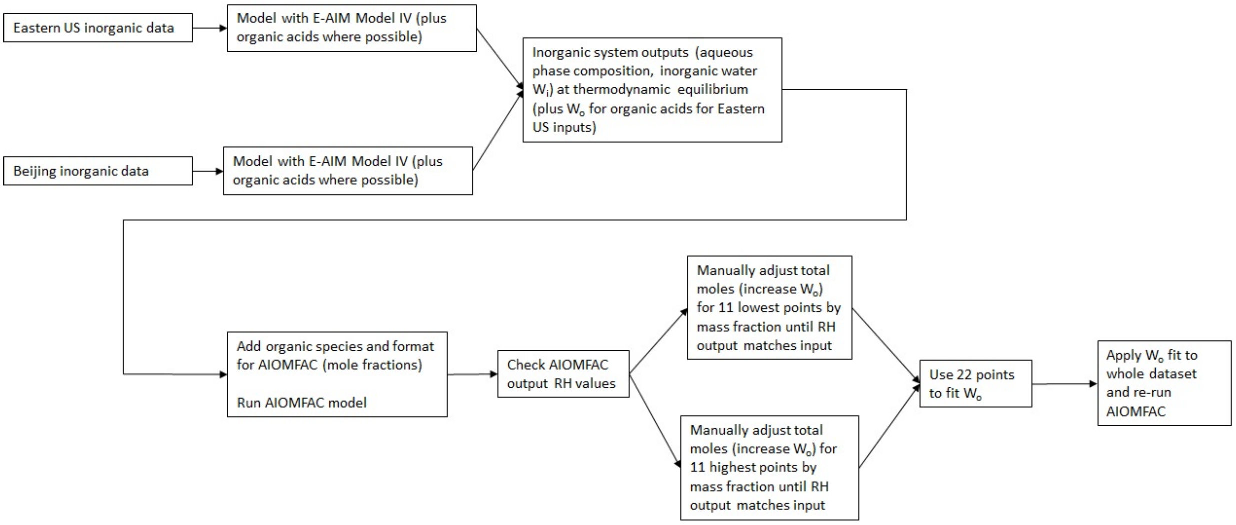

Figure 1: Flow diagram for adjusting total moles in the organic/inorganic mixed system inputs for the AIOMFAC model. Total moles were adjusted (representing increased W_o) of the first 11 and last 11 model points until the AIOMFAC-output RH was within 5% of the fixed model input value (70%, 80%, or 90%). These 22 points were then used to fit a polynomial function to correct the total system moles for the remaining 1309 data points.

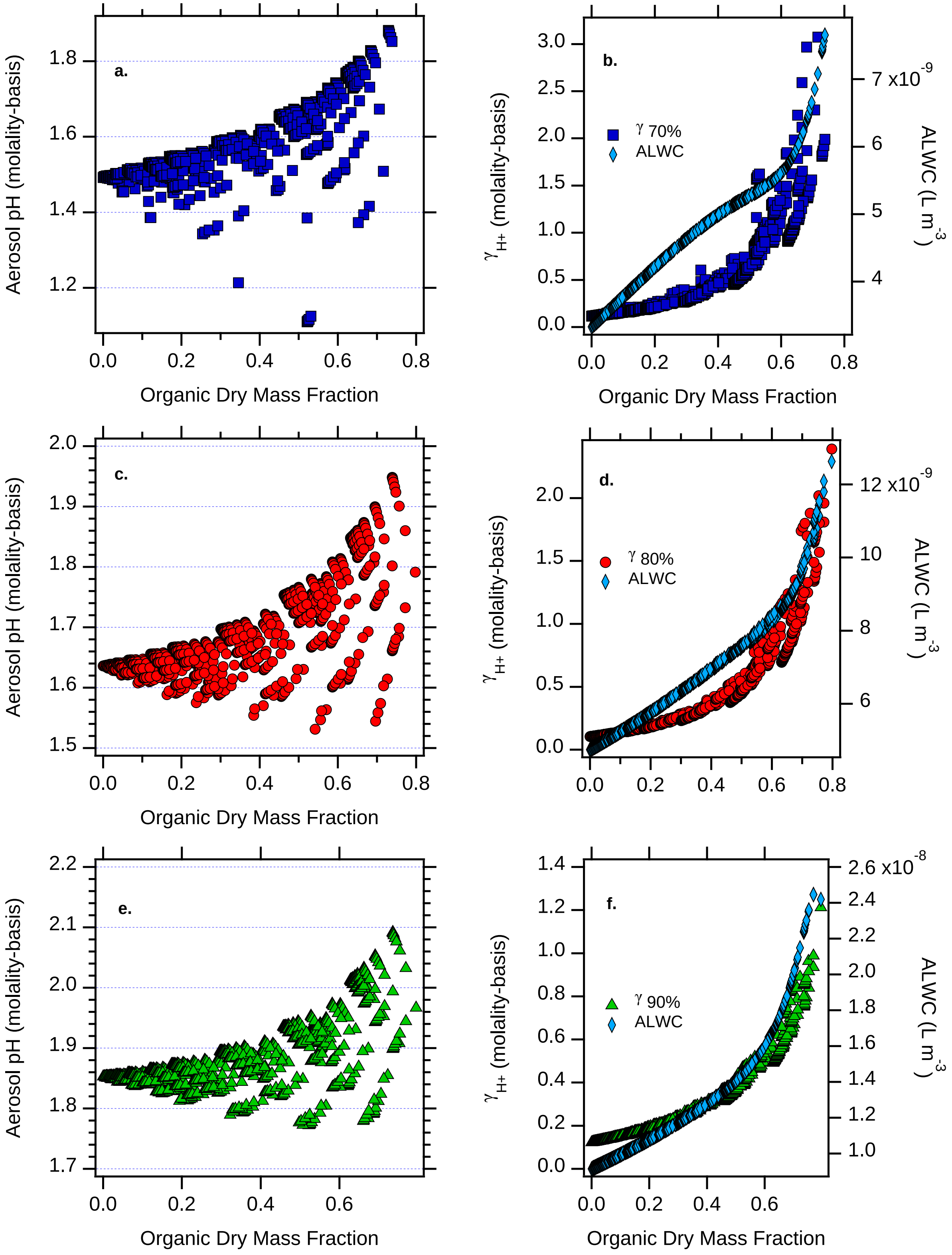
a.
Aerosol pH (molality-basis)
1.2
1.4
1.6
1.8
0.0
0.2
0.4
0.6
0.8
Organic Dry Mass Fraction
b.
γ 70%
ALWC
γ_{H+} (molality-basis)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
ALWC (L m^{-3})
4
5
6
7 x10^{-9}
0.0
0.2
0.4
0.6
0.8
Organic Dry Mass Fraction
c.
Aerosol pH (molality-basis)
1.5
1.6
1.7
1.8
1.9
2.0
0.0
0.2
0.4
0.6
0.8
Organic Dry Mass Fraction
d.
γ 80%
ALWC
γ_{H+} (molality-basis)
0.0
0.5
1.0
1.5
2.0
ALWC (L m^{-3})
6
8
10
12 x10^{-9}
0.0
0.2
0.4
0.6
0.8
e.
Aerosol pH (molality-basis)
1.7
1.8
1.9
2.0
2.1
2.2
0.0
0.2
0.4
0.6
Organic Dry Mass Fraction
f.
γ 90%
ALWC
γ_{H+} (molality-basis)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
ALWC (L m^{-3})
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6 x10^{-8}
0.0
0.2
0.4
0.6
Organic Dry Mass Fraction

Figure 2: AIOMFAC-modeled aerosol pH (molality basis) versus organic dry mass fraction with the factorial addition of non-acid organic species and AIOMFAC-modeled γ_{H+} (molality basis) and aerosol liquid water (ALW, polynomial fit to AIOMFAC output) versus organic dry mass fraction (right panel) for Baltimore at a) and b)70% RH, c) and d) 80% RH, and e) and f) 90% RH.

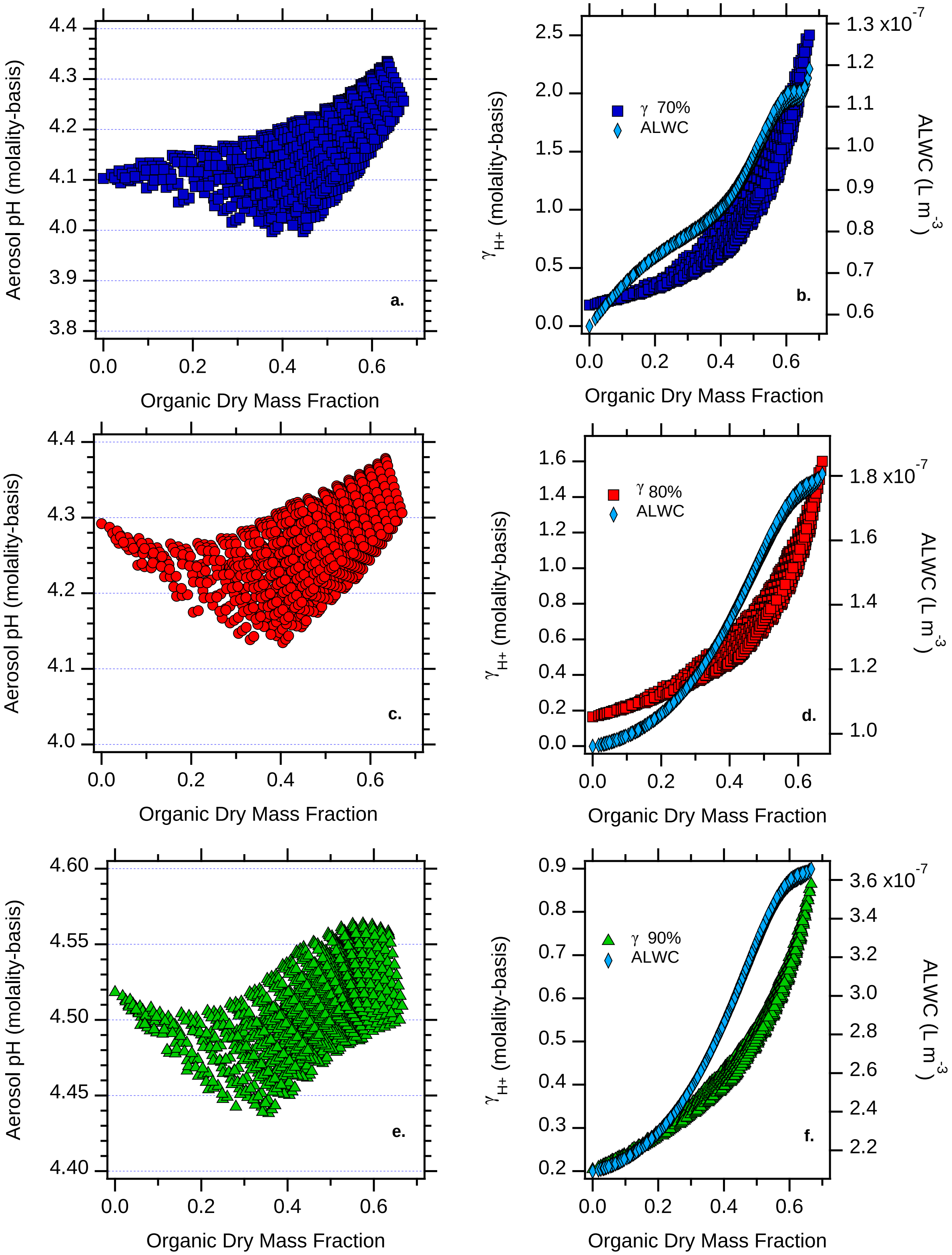
Aerosol pH (molality-basis)
4.4
4.3
4.2
4.1
4.0
3.9
3.8
0.0
0.2
0.4
0.6
Organic Dry Mass Fraction
a.
γ_{H+} (molality-basis)
2.5
2.0
1.5
1.0
0.5
0.0
γ 70%
ALWC
1.3 x10-7
1.2
1.1
1.0
0.9
0.8
0.7
0.6
ALWC (L m-3)
b.
Organic Dry Mass Fraction
Aerosol pH (molality-basis)
4.4
4.3
4.2
4.1
4.0
c.
Organic Dry Mass Fraction
γ_{H+} (molality-basis)
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
γ 80%
ALWC
1.8 x10-7
1.6
1.4
1.2
1.0
ALWC (L m-3)
d.
Organic Dry Mass Fraction
Aerosol pH (molality-basis)
4.60
4.55
4.50
4.45
4.40
e.
Organic Dry Mass Fraction
γ_{H+} (molality-basis)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
γ 90%
ALWC
3.6 x10-7
3.4
3.2
3.0
2.8
2.6
2.4
2.2
ALWC (L m-3)
f.
Organic Dry Mass Fraction

Figure 3: AIOMFAC-modeled aerosol pH (molality basis) versus organic dry mass fraction with the factorial addition of non-acid organic species and AIOMFAC-modeled γ_{H+} (molality basis) and aerosol liquid water (ALW, polynomial fit to AIOMFAC output) versus organic dry mass fraction (right panel) for Beijing at a) and b) 70% RH, c) and d) 80% RH, and e) and f) 90% RH.

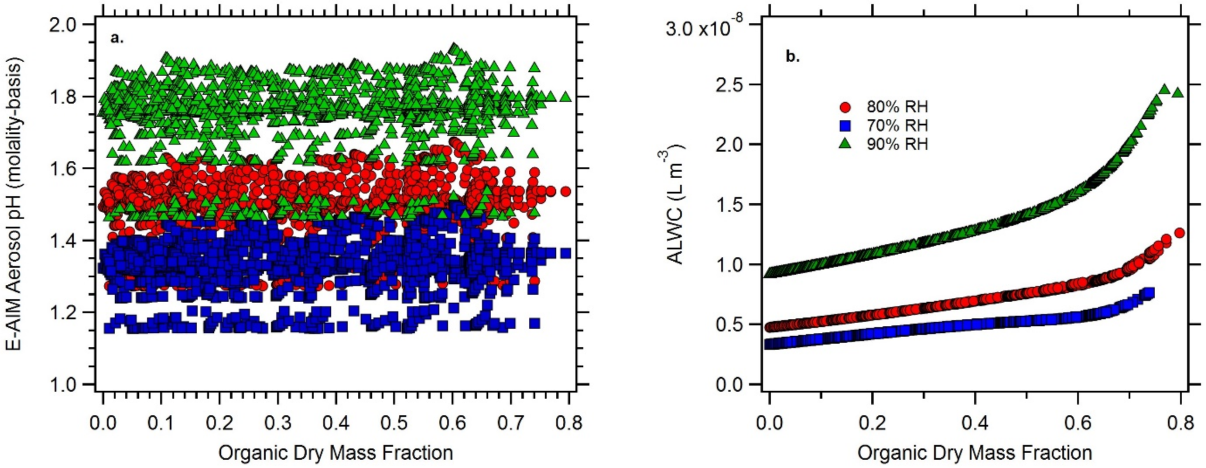

Figure 4: E-AIM-modeled (a) aerosol pH (molality basis) and (b) ALW at 70% (blue), 80% (red), and 90% RH (green) levels for the Baltimore simulations with organic acids.

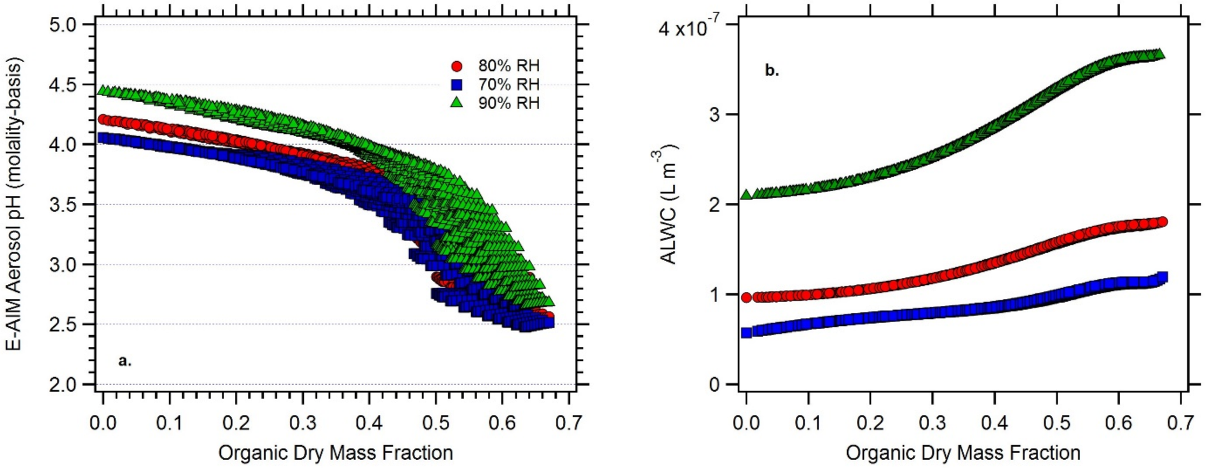

Figure 5: E-AIM-modeled (a) aerosol pH (molality basis) and (b) ALW at 70% (blue), 80% (red), and 90% RH (green) levels for the Beijing simulations with organic acids.

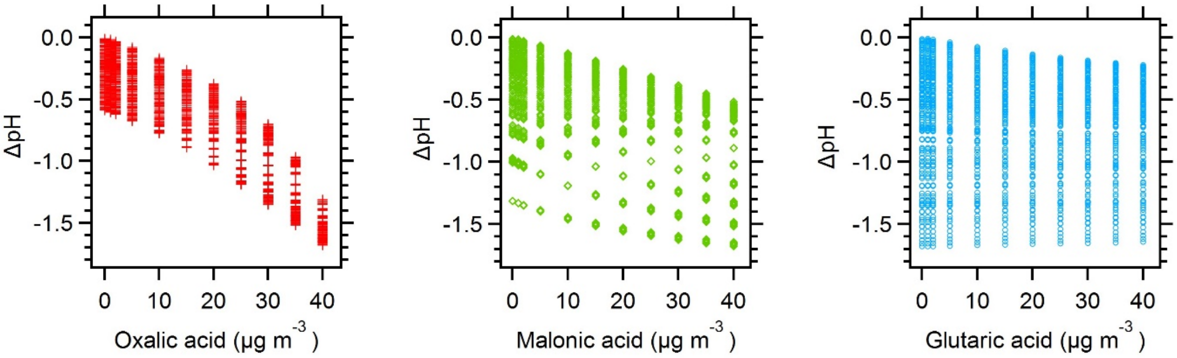

Figure 6: ΔpH vs. discrete organic acid levels for the organic acid pH calculations carried out in E-AIM for Baltimore and Beijing. ΔpH represents the difference between the initial ‘inorganic-only’ pH prediction and all other model evaluations where organic acids were present.

Table 1: Summary of model runs performed for the study. Inorganic composition is invariant and taken from the sources provided. Organic components were added in factorial fashion.

Location	Inorganic Data	Inorganic Equilibrium Model	Organic components	# of Points
Baltimore	Battaglia et al. 2017	E-AIM Model IV	Organic Acids	1331
Baltimore	Battaglia et al. 2017	E-AIM Model IV	Non-acid organics	1331
Beijing	Guo et al. 2018b	ISORROPIA 2.3 E-AIM Model IV	Organic acids	1331
Beijing	Guo et al. 2018b	ISORROPIA 2.3 E-AIM Model IV	Non-acid organics	1331

Table 2: Whole species inorganic inputs used in AIOMFAC modeling at 70%, 80%, or 90% RH. Inorganic equilibrium outputs were used to assign anions to cations to form whole species, represented here. Entries marked with a dash represent components not used for the given location as a result of anion or cation not being present in the composition data (species not measured).

Component	**Baltimore Conc. (mol m^{-3}) 70% RH**	**Baltimore Conc. (mol m^{-3}) 80% RH**	**Baltimore Conc. (mol m^{-3}) 90% RH**	**Beijing Conc. (mol m^{-3}) 70% RH**	**Beijing Conc. (mol m^{-3}) 80% RH**	**Beijing Conc. (mol m^{-3}) 90% RH**
H_2SO_4	1.488×10^{-10}	2.418×10^{-10}	3.326×10^{-10}	3.13×10^{-12}	6.273×10^{-12}	1.010×10^{-11}
NH_4HSO_4	3.460×10^{-9}	2.612×10^{-9}	1.899×10^{-9}	4.057×10^{-11}	3.173×10^{-11}	2.307×10^{-11}
$(NH_4)_2SO_4$	2.395×10^{-8}	2.318×10^{-8}	2.425×10^{-8}	2.710×10^{-7}	2.710×10^{-7}	2.710×10^{-7}
$NaNO_3$	6.425×10^{-11}	1.207×10^{-10}	3.573×10^{-10}	-	-	-
Na_2SO_4	1.403×10^{-9}	1.375×10^{-9}	1.257×10^{-9}	-	-	-
NH_4Cl	-	-	-	4.793×10^{-8}	4.797×10^{-8}	4.799×10^{-8}
NH_4NO_3	-	-	-	4.189×10^{-7}	4.189×10^{-7}	4.190×10^{-7}