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Atmospheric Chemistry and Physics Discussions
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Interactive comment on "A critical evaluation of proxy methods used to estimate the acidity of atmospheric particles" *by* C. J. Hennigan et al.

Anonymous Referee #1

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General Comments

This manuscript reports an interesting analysis by a well-respected group of investigators that addresses an important topic relevant for publication in ACP. As the authors correctly point out, aerosol solution pH a fundamentally important property that influences the multiphase chemical evolution of the troposphere and associated atmosphere-biosphere interactions. However, aerosol pH is difficult to estimate with confidence and commonly used proxy methods often yield unreliable results. Hopefully, a critical evaluation of different methods such as that reported by the authors will bring some semblance of order to the research community interested in this issue.

That said, as detailed under Specific Comments below, I have numerous substantive concerns regarding aspects of the authors analysis as presented in the manuscript. These can be summarized as follows:

- Many important methodological details were omitted.

- Only calculated values were reported making it difficult to impossible for readers to interpret acidities in the context of either the underlying data from which they were derived or the broader ambient air quality.

- Some of the terminology was incorrect or potentially confusing.

- Some key underlying assumptions were not stated or explicitly.

- Several of the equations and/or corresponding units were incorrect.

- The importance of accumulated analytical uncertainties in constraining the reliability of H+ inferred from small differences between relatively large sums of anions and cations or from ratios of relatively large sums of cations versus anions was not evaluated explicitly.

- The importance of unmeasured (or ignored) ionic constituents in estimating acidity from ion-balance or ion-ratio approaches was not addressed quantitatively.

- The gas-aerosol phase partitionings of both NH3 and HNO3 were measured but pHs were inferred from only NH3. The inclusion of paired estimates based on HNO3 would provide useful and relevant perspective for this analysis.

-The potential importance of evaluating activities explicitly was treated rather superficially and the sensitivity of results to calculations based on concentrations versus activities was not evaluated.

Least these comments be viewed as overly critical, my primary motivation is to assist the authors in improving the manuscript. I applaud them for initiating this effort and am confident that a revised version that addresses the comments and recommendations herein will yield a valuable contribution to the literature.

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Specific Comments

Page 27,581, line 21. The impacts of aerosol pH on halogen-radical chemistry are not limited to coastal regions. For example, the cited investigation by Pszenny et al. (2004) evaluated influences of pH in open ocean air at Hawaii. Numerous other publications have reported results from measurement and modeling studies that characterized the pH-dependence of halogen activation over the open ocean.

Page 27,581, line 23. Thornton et al. (2010) speculated about the influence of aerosol pH on Cl-radical chemistry in continental regions but a subsequent investigation in which Thornton and colleagues were involved confirmed the importance of solution pH and the associated thermodynamics of HCl phase partitioning in sustaining ClNO2 production (Brown et al., 2013; Riedel et al., 2013; Young et al., 2013).

Page 27,582, lines 6-8. I know what the authors mean but the suggestion that “analysis procedures such as dilution in water prevent” characterization of aerosol solution pH is potentially misleading. As reported in several of the cited papers, direct measurements of H+ in dilute extracts of aerosol samples can be reliably extrapolated to the pH of concentrated aerosol solutions but clearly H+ concentrations do not scale proportionately with dilution. I encourage the authors to clarify this point.

Page 27,582, line 26. The term “strong acidity” is not synonymous with “free (or ionized) acidity” as suggested here. Strong acidity refers to H+ contributed by acids that are essentially completely dissociated at a given pH (i.e., with pKas « solution pH). For example, in a dilute solution at pH 4, strong acidity would correspond to that contributed by sulfuric, nitric, and hydrochloric acids. Weak acidity refers to H+ contributed by acids that are partially dissociated at a given pH (i.e., with pKas in the range of solution pH). Examples for a dilute solution at pH 4 include formic and acetic acids. Free acidity refers to ionized H+ at a given pH and total acidity refers to ionized H+ plus undissociated acids. The text should be clarified and, for the benefit of readers who may not be familiar with the term, “total acidity” should be defined.

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Page 27,583, lines 2-6. The discussion here seems unnecessarily convoluted. For example, it is unclear what the authors mean by “. . .The true quantity, however, driving much of the processes described above is pH; H+ is insufficient to truly distinguish the acidity as it scales with aerosol mass.” What is a “true quantity” and how is it used to “truly distinguish” anything in the context of scaling “with aerosol mass.” As indicated in equation 1, solution pH is simply another way of expressing the aqueous H+ activity. Here and elsewhere, the authors should clearly distinguish between solution pH or H+ per unit volume of liquid water versus H+ per unit volume of air.

Page 27,583, lines 12-13 and Eq. 2. I encourage the authors to clearly state the complete underlying assumptions involved in the ion-balance approach and to evaluate results in the context of each.

Assumption 1. This approach is reliable if and only if all ionic species other than H+ are measured without bias. The approach yields biased results if (1) any ionic constituents other than H+ that contributed significantly to ion balances are not measured or (2) any of the measured ionic concentrations were inaccurate. In the context of discussing unmeasured organic anions later in the paragraph, the authors should point out that significant concentrations of unmeasured organic anions would introduce significant positive bias in H+ inferred from ion balances based on measured species.

Assumption 2. All ionic species other than H+ are measured at relatively high precision. For many types of aerosols, H+ is a minor ionic constituent of the aerosol and consequently H+ concentrations typically correspond to small differences between relatively large sums of anions and cations. In such cases, calculated H+ concentrations based on Eq. 2 will often fall within the range of accumulated analytical uncertainties for the many measured ions thereby yielding insignificant results.

Assumption 3. Reliable extrapolation of H+ concentrations inferred from ion imbalances in dilute analytical solutions (e.g., the PILS sampling medium or in water extracts of aerosols sampled on filters or impaction substrates) to the pH of concentrated

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aerosol solutions accounts for the large differences in liquid water volume, the buffering effects of the H+ + SO42- ↔ HSO4- equilibrium (e.g., Keene et al., 2002, 2004), and differences between concentrations and activities (Young et al., 2013).

In addition, most aerosol solution pHs that have been reliably characterized to date (including those reported by the authors in Fig. 12) yield pHs that are less than ∼5 in which chase OH- concentrations are trivial and can be ignored. Rather than complicate the presentation with unimportant details, I encourage the authors to drop OH- from the equation and to add a simple qualifier to the text noting the possibility of rare cases when explicit evaluation of OH- may be necessary. If the authors wish to consider aerosol solution pHs greater than about 5, contributions from carbonic acid must also be evaluated explicitly, which should be addressed in the manuscript.

Page 27,584, Section 2.2. The “molar ratio” approach and “ion-balance method” represent different variants for interpreting the same information to address the same issue and should be reported as such. For example, if the equivalent sum of all anions minus the sum of all cations in dilute analytical solutions equals 0.0 (implying no contributions from H+), then the corresponding equivalent ratio for sum all anions to sum all cations will equal 1.0 (implying “complete neutralization”). The underlying assumptions and limitations detailed above for the ion-balance approach apply equally to the molar ratio approach.

While concentrations in units of micromoles can be converted to and interpreted in units of microequivalents, equations 3, 4, and 5 as written correspond to equivalent ratios not molar ratios. The molar ratio does not equal the sum of anions divided by the sum of cations in units of microequivalents as indicated in Equation 3. In addition, the units for concentrations reported in equations 4 and 5 are in micromoles not microequivalents as stated in the text. The text and equations should be corrected.

Page 27,584, lines 2-3. Both the ion balance and the molar ratio approaches can be applied to loadings in the atmosphere, loadings on filters, or concentrations in dilute solutions. As noted above, both involve the same underlying data. For example, both ion balances and ion ratios are often used in laboratories as QA diagnostics for measured aerosol loadings (i.e., in units of microequivalent per filter or impaction substrate or per liter of extract solution) before converting to concentrations per unit volume of air. Many labs also routinely employ both ion balances and ion ratios as QA diagnostics for measured ionic constituents in samples of precipitation and cloud water (in units of microequivalents per liter). There is nothing inherently different in these two approaches.

Page 27,584, equations 4 and 5. As indicated above, these equations define equivalent not molar ratios. The authors should point out here that ignoring other ionic constituents in samples introduces bias into the corresponding acidity inferred from such relationships. I encourage them use their own data to illustrate this important point explicitly.

Page 27,586, lines 1-10. The Henry's Law and dissociation constants and associated temperature corrections used in these calculations should be reported. Are these values the same as those used in E-AIM and ISORROPA? If not, what are the implications for interpreting results?

Page 27,586, Equation 6. The equation as written is incorrect. It should specify activities for H+ and NO3- not concentrations. If the distinction between activities and concentrations is ignored in these calculations, the assumption that concentrations are equal activities should be stated explicitly and the implications for results assessed, particularly in light of the fact that the thermodynamic model calculations with which these results are compared are based on activities not concentrations.

Why is the partitioning equation for HNO3 used as an example when no aerosol solution pHs based on this approach are reported in the manuscript? Only pHs based on NH3 partitioning are reported so it would seem appropriate to specify the equation for NH3 here. More generally, since the data for particulate NO3- and HNO3 are available,

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why are pHs not also calculated and interpreted based on the phase partitioning of HNO3? These results are directly relevant to the analysis and would provide another useful constraint on these approaches. These results may also fill in some of the large gaps in paired particulate- and gas-phase data suggested by the small numbers of estimated pHs reported in Figures 10, 11, and 12. I encourage the authors to report and interpret pHs inferred from the measured partitioning of HNO3.

Page 27,586, lines 15-18. The activity coefficients for the aqueous anions (NO3- and Cl-) and NH4+ employed in this approach also impact the calculated activity of H+, particularly at the relatively low RHs and high ionic strengths during this study, and should be considered explicitly for the most accurate results. Were the reported pHs inferred from the measured NH3 phase partition calculated based on activities or concentrations? If concentrations, what are the implications for results? It would be helpful to evaluate the sensitivity of results to use of activities versus concentrations. If activities were employed in the calculations, which estimates of activity coefficients were used? Two models were run in two modes each (reverse and forward) so, presumably, four discrete sets of estimates of activity coefficients were available for each sample.

The authors should also specify which estimates of liquid water contents were used in calculating pHs from the measured phase partitioning. Again, two models were run in two modes each so, presumably, four discrete estimates of liquid water content were available for each sample.

Pages 27,586-27,587, Section 2.5. The measurement frequency for each measurement technique should be specified and the approach used to create paired data for techniques that sampled at different frequencies should be described. For example, were the gas-phase data averaged over each aerosol sampling interval? In addition, the suit of ions that were characterized with the PILS and used in this analysis should be specified.

Page 27,586, lines 22-23. As described in several of the cited papers, aerosol composition (including pH) typically varies significantly as a function of particle size. Consequently, the compositions of PM2.5 sampled in bulk with the PILS (and the corresponding pH inferred from that composition) are not necessary representative of those for the size-resolved aerosol distributions with which NH3, HNO3, and HCl partitioned in ambient air. This is an important point that the authors should address in the context of this analysis. Their approach assumes implicitly that ambient aerosol composition and pH is invariant over particle sizes less than 2.5 micrometer diameter, which is almost certainly not the case. What are the implications for results?

Page 27,587, lines 3-6. The assumption that “HCl was effectively zero” is inconsistent with the reported measurements, the associated thermodynamics of the system, and some of the cited literature. As is the case for HNO3 (equation 6), the gas-aerosol phase partitioning of HCl is controlled by aerosol liquid water content and solution pH not by “high concentrations of gas phase NH3.” For example, the authors cite Young et al. (2013) who reported significant aerosol acidities and mixing ratios of gaseous HCl in the presence of high concentrations of gas phase NH3. The solubility of NH3 decreases with increasing pH. In addition, HNO3 is infinitely soluble in alkaline solution so the presence of significant HNO3 vapor clearly indicates that the aerosols with which it equilibrated were acidic. Indeed, all reported estimates of aerosol pH that the authors consider to be reliable range from about 2 to 5 (e.g., Fig. 12). Applying the thermodynamic expression reported by the authors (equation 6) to HCl partitioning in the presence of acidic aerosol would yield significant gas phase concentrations, consistent with the cited literature. The text should be corrected.

Page 27,587, lines 19-28. It would be helpful if the authors evaluated the sensitivity of results to these approaches for forcing the required ion balances. For example, the authors’ analysis suggests that pHs predicted by the thermodynamic models run in the “reverse” mode are highly sensitive to NH4+ concentrations (e.g., Fig. 9 and associated text) and yet, for E-AIM, they add NH4+ to balance “missing” cations that are not considered in the model. What are the implications for results if missing cations were balanced by adding H+ rather than NH4+?

It would also be helpful for the authors to comment on how the E-AIM models II and IV compared at RHs above 60%. Do they yield comparable results and, if not, what are the implications for results?

Note that Figure 4 is cited out of sequence.

Page 27,588, line 6. In this regard, it would be helpful to specify the numbers or percentages of samples evaluated with E-AIM II (i.e., at RHs between 40% and 60%) versus E-AIM IV (i.e., at RHs greater than 60%). The authors should also point out that eliminating all data for periods when RH was less than 40% presumably eliminated a disproportionately large fraction of daytime samples.

Page 27,588, Section 3. Although the underlying measurements may have been reported elsewhere, only calculated values based on unspecified subsets of those measurements are presented in the manuscript. Without digging into the cited literature, this prevents interpretation of results in terms of either the measurements from which they were derived or ambient air quality. It would be helpful for readers if the authors included time series plots (or at minimum summary statistics) for the major chemical and physical properties of the system on which the analysis was based. In preceding sections the authors describe some data qualitatively (e.g., high concentrations of gas phase NH3) but not quantitatively. This begs the question of how high is high?

Page 27,588, lines 11-14 and Figure 1. The species included in the ion-balance calculations should be specified. To minimize the potential for confusion, I also suggest that the authors employ consistent terminology when describing the model modes used for the calculations. Here they refer to "…E-AIM corresponding to the inorganic ion balance …" whereas elsewhere (including the cited figure) they refer to "… E-AIM in the reverse mode."

Figures 1b, 2, 3a,b, 4a,b, 5. Major conclusions of this analysis include the following:

“These results suggest that the two best proxy methods for estimating aerosol pH are: (1) thermodynamic equilibrium models run using gas+aerosol inputs, and (2) the phase partitioning of ammonia.”

“The aerosol pH levels predicted by both reverse models do not agree with either the pH predictions using gas+aerosol inputs or the phase partitioning of ammonia.”

Based on the above, it is unclear why the authors focus much of the analysis on the presentation (as depicted in the above mentioned figures) and interpretation of unreliable acidities inferred from ion balances and molar ratios versus unreliable pHs predicted by the reverse models. If these three approaches are all considered unreliable, how can the primary cause(s) for variability be ascertained by comparing paired sets of corresponding results? If pHs based on the forward models and measured phase partitioning are considered the most reliable estimates, then it would seem appropriated to use one or the other or both as the primary reference(s) for these interpretations. In this regard, the authors may wish to consider the merit of reorganizing the manuscript to present the reliable approaches first and then to employ results for these approaches to illustrate the nature of problems with the other approaches.

More generally, it would also be helpful to compare results based on the same unit conventions. For example, in Figure 2, the pH values calculated with E-AIM could be converted to and plotted as H+ in units of nmol m-3 (as in Figures 3 and 10). Conversely, the H+ values inferred from the ion balances could be extrapolated to aerosol liquid water contents and expressed as pHs.

Page 27,588, line 26 and Figure 2. Suggest adding the definition of the horizontal black lines to the figure caption.

Page 27,589, line 27. I encourage the authors to elaborate on the impact of analytical uncertainties on the reliability of results based on the ion-balance approach, ideally with reference to specific quantitative examples based on their measurements. If the underlying assumptions detailed above (comment regarding page 27,583, lines

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12-13 and Eq. 2) are valid, H+ concentrations in dilute analytical solutions can be reliably estimated from ion imbalances and then extrapolated to aerosol solution pHs with reasonable confidence using the same approach as used by others to extrapolate direct measurements of H+ in dilute analytical solutions to aerosol pH (e.g., Keene et al., 2002, 2004). As noted above, however, H+ concentrations inferred from ion imbalances often fall within the accumulated analytical uncertainties for the measured aerosol constituents and, thus, correspond to noise. This is the real Achilles heel of the approach when applied to many types of aerosol samples and should be emphasized in an analysis such as this. Readers would benefit if the authors employed their data to compare the relative magnitudes of H+ inferred from ion imbalances versus the corresponding estimated detection limits for H+ based on accumulated analytical uncertainties for the many measured ions. More generally, it would be helpful is the authors clearly differentiated between the reliability of H+ concentrations inferred from this approach versus the reliability of interpreting these results in the context of aerosol acidity.

Figure 3. Here and elsewhere, I suggest that the lines be defined on the figure captions. In addition, the technique used to calculate linear regressions should also be specified. For regressing paired data each of which are subject to significant uncertainty, the Reduced Major Axis procedure is the most appropriate method.

Pages 27,590-27,592, Section 3.2. As indicated above, the molar ratio approach is simply a different way of interpreting ion-balance relationships. As such, this section could be shorted considerably by referring to the same set of underlying issues raised in the preceding section. This component of the analysis may warrant a paragraph or two of text and perhaps one figure but it does not justify two pages of text along with three two-panel figures.

Page 27,590, line 16. Here and elsewhere, the authors should specify whether they are referring to predictions based on the reverse or forward models.

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Page 27,591, lines 7-9. The implicit assumption that acidity can be reliably inferred from relative concentrations of NH4+ versus (Cl- + NO3- + SO42-) is not valid. The authors could use their own data to illustrate this important point quantitatively and in a more direct manner than employed for Figure 6, which depicts a plot of equivalent ratios versus equivalent imbalances. Specifically, they could directly compare the equivalent ratios of NH4+ / (Cl- + NO3- + SO42-) versus the corresponding equivalent ratios for the sum of all cations divided by the sum of all anions versus (i.e., a plot of ratios versus ratios in the same units). Alternatively, they could compare the equivalent imbalances for NH4+ - (Cl- + NO3- + SO42-) versus the equivalent imbalances for sum anions minus sum cations in units of nmol m-3.

Figure 4. Suggest specifying numbers of samples depicted in panel a. What is meant by “low crustals” in panel b? Since a distinct definition for this subset is specified in the caption, I suggest that the characterization of “low crustals” be dropped from the figure.

Page 27,591, line 14. Here and elsewhere, to what “crustal species” are the authors referring and what is the rationale for characterizing them as “crustal” as opposed to, for example, biomass-burning products?

Page 27,592, line 18. It would be helpful to include a table summarizing the data subsets that were generated and used in the analysis (e.g., (1) the total number of aerosol samples characterized, (2) the subset of (1) at RH greater than 40%, (3) the subsets of (2) with simulated liquid water contents greater than 0 for each model, and (4) the subsets of (3) with paired gas-phase data). For example, Figure 9 depicts 89 results based on ISORROPIA but only 39 based on E-AIM. Why the large difference? In addition, according to section 2.5, aerosol composition was characterized with the PILS (presumably at about 5-minute intervals) over about 30 days, which would have yielded about 8640 individual measurements. The authors indicated that half of these measurements ($\sim$4320) corresponded to RHs less than 40% and were not exclude from the analysis. What are the primary causes for the large differences between the presumed numbers of aerosol observations at RHs greater than 40% and the corresponding numbers of inferred pHs?

Page 27,592, line 20-23. What were the differences in estimated aerosol liquid water contents between the reverse versus forward models and which values were used to infer pH from the phase partitioning of NH3? This issue is directly relevant to the analysis.

Figure 8, caption. Ion imbalances in range ‘a’ are less than those in range ‘b’. The end of the caption should read, “. . .demonstrate the extreme sensitivity of aerosol pH at Ib values near 0.0 (region “b”).”

Page 27,594, line 3. Suggest citing examples to support the statement that “. . .similar model sensitivities have been observed in diverse locations, as well.”

Page 27,584, lines 7-10 and Figure 10. I suggest that scale on the X axes in Figure 10a,b be expanded so that relative variability in H+ predicted by the two approaches is evident. A notation in the caption indicating that the scales on the two axes differ coupled with a 1:1 line on the figure would suffice to alert readers to these differences. Alternatively, the data could be plotted on log scales.

Page 27,596, lines 9-13. The expected relationship between the pH values predicted by the reverse models and the corresponding ratio of NH4+ to NH4+ + NH3 is unclear. If retained, it would be helpful to specify the range in the ratio of NH4+ to NH4+ + NH3 predicted by thermodynamics at pH values in the range of 0.0. However, as questioned above, what is the rationale for interpreting paired sets of data both of which are considered unreliable?

Page 27,596, lines 16-18. While Young et al. (2013) reported good agreement between aerosol pHs inferred from the phase partitioning of NH3 and HNO3, Keene et al. (2004) reported significant divergence between results based on the same approach. This inconsistency should be mentioned. Differences between results from these two studies may reflect the fact that activity coefficients were evaluated explicitly by Young

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et al. whereas results reported by Keene et al. were based on concentrations. As indicated above, it would be useful and relevant to evaluate the sensitivity to pHs inferred from phase partitioning based on concentrations versus activities.

Page 27,597, lines 7-10. As noted above, an Achilles heel of both approaches is the generally small H+ signal relative to the noise associated with the overall analytical uncertainties. If signal-to-noise was high (and all ionic constituents were measured without bias), H+ in dilute solutions solutions can be reliably inferred from ion imbalances and extrapolated to ambient liquid water contents with reasonable confidence. This is an important distinction that should be clarified.

Page 27,597, lines 18-19. What is meant by “excess ammonia”?

Page 27,597, lines 19-21. If, as suggested by the authors, results based the reverse models are extremely sensitive to the initial inputs, then the approaches used to force ion balances for both models should be evaluated explicitly with respect to the corresponding sensitivity of results.

Page 27,598, line 25. Suggest adding that the equilibration times for sub-micron-diameter particles reported by Meng and Seinfeld (1996) are on the order of seconds to minutes, which is consistent with results from other studies.

Page 27,599, lines 4-5. It is unclear what the authors mean by a “gold standard.” As indicated in the manuscript, the cited papers by Keene et al. (2002, 2004) report aerosol pHs extrapolated from a “direct measurement method.” The 2004 paper by that group indicates that pHs extrapolated from direct measurements were reasonably consistent with corresponding estimates based on the thermodynamics of HCl and HNO3 phase partitioning but not with those based on NH3 phase partitioning.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 27579, 2014.