To Date: 30th June 2018
Rob MacKenzie,
Co-editor,
Atmospheric Chemistry and Physics.

Sub: Submission of revised research article ACP-2018-85 for publication.

Dear Prof. MacKenzie,

First of all, I would like to thank you on behalf of my co-authors for kindly agreeing to extend the deadline for submission of our revised article. I am hereby submitting the revised version of our manuscript ACP-2018-85. We have revised the manuscript in accordance with the comments and suggestions made by the reviewers.

We have confirmed the mistakes in Eqs. 4 and 9 in the original manuscript as shown below (as we have communicated with Prof. Nenes before). The density of solvent was taken as the density of hygroscopic aerosol by mistake in the original manuscript as details shown in the table below.

Eq. #	Original (with mistake)	Corrected
4	$y_H = f_H \frac{\rho_{\mathrm{sln}}}{\rho_{\mathrm{sln}} + 0.001[M_s \Sigma c_i - \Sigma c_i M_i]}$	$y_H = f_H \frac{\rho_{solvent}}{\rho_{\mathrm{sln}} + 0.001[M_s \Sigma c_i - \Sigma c_i M_i]}$
9	$pH_x - pH_c = -\mathrm{lg}\frac{f_H x_H}{\mathrm{c_H} y_\mathrm{H}} = -\mathrm{lg}\frac{0.001Ms}{\rho_{\mathrm{sln}}} = 1.74 + \mathrm{lg}\rho_{\mathrm{sln}}$	$pH_x - pH_c = -\mathrm{lg}\frac{f_H x_H}{\mathrm{c_H} y_\mathrm{H}} = -\mathrm{lg}\frac{0.001Ms}{\rho_{solvent}} = 1.74 + \mathrm{lg}\rho_{solvent}$

However, as Dr. Zuend suggested to use more general equations (considering solvents other than water), the corrected equations do not directly appear in the revised manuscript. Instead they have been shown in a more general form as: $f_H = y_H 1000 \frac{dm^3}{m^3} \frac{M_w}{\rho_0} \frac{c_H}{x_H}$ (6) and $pH_x - pH_c = \log 10 \frac{1000 dm^3/m^3 M_s c^0}{\rho_0}$ (12) in the revised manuscript.

In the original manuscript, we had discussed the effect of the density of aerosol solution on the conversion between molality-based pH and molarity-based pH, which formed the major part of the *Results and Discussion* section. However, after correction, the conversion between molarity and molality-based pH actually does not depend on the density of the solution, but does so on the density of the pure solvent. Therefore the orignal discussion is only partially valid when the acitvity coefficent of H^+ is simplified as unity (e.g. by ISORROPIA-II). Consequently, we have revised the mansucript significantly. The major revisons include: (1) removing the original discussion regarding comparision between pHm and pHc; (2) incorporating the calculation of pH on differnet scales using multiple thermodynamic models; 3) using a gas+aerosol system instead of an aerosol only system to estimate pH; and (4) inclusion of a sub-section to discuss the general issues regarding aerosl acidity comparision across studies. We believe that the importance of our study and the major conclusion remain unaffected by the mistake although a significant revision has been done.

I am also submitting herewith itemized responses to each of the reviewers' comments. All changes made in the manuscript have been highlighted in red fonts.

I sincerely hope that the manuscript in its revised form will satisfy all queries of the reviewers.

With regards,

Wang Xuemei

Response to Dr. Zuend

Comments are in black, responses in blue and the revised text in red.

1 General comments

Acidity is an important characteristic of liquid aerosol particle phases, which often tend to be highly acidic, as expressed by a low pH value. This technical note addresses several issues arising from the existence of distinct ways to define "pH". The authors discuss the differences between pH defined on molality, molarity and mole fractions scales and the importance of using thermodynamically correct conversions among these scales when field data is compared. This scale-dependence of pH is an important point indeed. While this reviewer has been aware of the pH scale dependence and its potential pitfalls for a while, it is an issue appropriate for a "technical note" outlining the proper thermodynamic scale conversion (theory) and providing discussion of related practical issues in aerosol acidity evaluations from field data.

However, the present manuscript contains a number of flaws, several of which are further discussed under specific comments below.

The interactive comment by Simon Clegg (https://www.atmos-chem-phys-discuss.net/acp-2018-85/acp-2018-85-SC1.pdf) summarizes the main concerns shared by this reviewer. Major revisions are necessary to transform this manuscript into a paper that contains (i) a thorough discussion of the thermodynamic scale conversions as well as (ii) a discussion of the general issues with pH estimation of field aerosol samples.

While the latter point is not the focus of this technical note, mostly ignoring the issues of that point is not appropriate either. Errors from incorrect H^+ concentration estimations, e.g., by use of an ion charge balance, as done in this study (and others), may frequently be more substantial than the errors from pH value comparisons without proper pH scale conversion. Therefore, a discussion of issues with aerosol acidity determination and pH scale intercomparison must include both.

Response:

We thank Dr. Zuend for the constructive comments on our manuscript. We also thank him for agreeing with the importance of pH interconversion between different scales, which is the main focus of the current study.

First of all, we would like to apologize for the mistakes made in Eqs. 4 and 9 in the original manuscript that stem from errors originally made in the equation by van Boekel (2008) used in our reference. The density of solvent was taken as the density of hygroscopic aerosol by mistake in the original manuscript. Since the mistakes are not included in either of the reviewer's comments or in the short comments by Prof. Clegg, we clarify this issue first before responding to the reviewers' comments in detail. The details of the mistakes are shown in Table 1 below.

Table 1. Correction of Eqs. 4 and 9 in the original manuscript

Eq. #	Original (with mistake)	Corrected [a]
4	$y_H = f_H \frac{\rho_{\text{sln}}}{\rho_{\text{sln}} + 0.001[M_s \Sigma c_i - \Sigma c_i M_i]}$	$y_H = f_H \frac{\rho_{solvent}}{\rho_{\text{sln}} + 0.001[M_s \Sigma c_i - \Sigma c_i M_i]}$
9	$pH_x - pH_c = -\lg \frac{f_H x_H}{\mathrm{c_H} y_\mathrm{H}} = -\lg \frac{0.001Ms}{\rho_{\text{sln}}} = 1.74 + \lg\rho_{\text{sln}}$	$pH_x - pH_c = -\lg \frac{f_H x_H}{\mathrm{c_H} y_\mathrm{H}} = -\lg \frac{0.001Ms}{\rho_{solvent}} = 1.74 + \lg\rho_{solvent}$

[a] Since we have taken Dr. Zuend's suggestion to use more genearl equations (considering solvents other than water), the corrected equations do not direcely appear in the revised mansucript. Instead they have been shown in a more general form as: $f_H = y_H 1000 \frac{dm^3}{m^3} \frac{M_w}{\rho_0} \frac{c_H}{x_H}$ (6) and $pH_x - pH_c = \log 10 \frac{1000dm^3/m^3 M_s c^0}{\rho_0}$ (12) in the revised manuscript.

In the original manuscript, we discussed the effect of the density of aerosol solution on the conversion between molality pH and molarity-based pH, which formed the major part of the *Results and Discussion* section. However, after correction, the conversion between molality and molarity-based pH actually does not depend on the density of the solution but does so on the density of the pure solvent. Therefore the orignal discussion is only partially valid when the acitvity coefficent of H^+ is simplified as unity (e.g. by ISORROPIA-II). Consequently, we have revised the manscuript significantly. The major revisons include (1) removing the original discussion regarding comparision between pH_x and pH_c; (2) incorporating the calculation of pH on differnet scales using multiple thermodynamci models; 3) using a gas+aerosol system instead of an aerosol only system to estimate pH; 4) discussing the differnce between different scales for a generalized solvent system instead of only water and (5) inclusion of a sub-section to discuss the general issues regarding aerosl acidity comparision across studies. We believe that the importance of our study and the major conclusion remain unaffected by the mistake although a significant revision has been done. Below are our detailed responses to each of the comments.

Response to general comments:

We have addressed Prof. Simon Clegg's comments point by point. A major revision of the manuscript has been conducted according to all comments. Especially, we have now revised the method to estimate aerosol acidity using a gas + aerosol system instead of the aerosol only system utilized in original version. We have also added an entire section (Section 3.2) in the revised manuscript to summarize the general issues for pH comparison across studies. A detailed response to each of the Reviewer's comments is listed below:

2 Specific comments

1. Abstract, line 16: Stating that this issue is addressed "for the first time" is rather bold given that the theoretical framework for activity coefficient and pH scale con- versions has been known for decades (even though it may be true that it is a frequently ignored issue, therefore it is worthy of attention by the atmospheric chemistry community).

Response:

We agree that the description here is inappropriate. We have deleted the concerned phrase in the description (Page 1, Lines 15-18).

Revised text:

Such comparisons are however routinely performed in the atmospheric science community. This study attempts to address this issue by comparing $PM_{2.5}$ aerosol pH based on different scales (molarity, molality and mole fraction) on the basis of theoretical considerations followed with a set of field data from Guangzhou, China as an example.

2. Abstract, line 18: "Using hourly ionic species measurements in Guangzhou, China, it is observed that pH_X (mole fraction based) is always 1.74 pH unit higher than pH_m (molality based)". This is clearly misleading, since the pH unit difference is not truly based on observation. It is a circular argument also made at other places in the manuscript. The 1.74 pH unit difference is in fact coming from the application of such a theory-based difference and using the same thermodynamic model to compute the pH values in different scales based on H^+ activity coefficient prediction from the same samples.

   Response:

   We agree with the reviewer's point that the relationship between pH_x and pH_m is from theory. The field data shown in this study is only an example of the application of the theory. The text has been revised as below (Page 1, Lines 16-21).

   Revised text:

   This study attempts to address this issue by comparing $PM_{2.5}$ aerosol pH based on different scales (molarity, molality and mole fraction) on the basis of theoretical considerations followed with a set of field data from Guangzhou, China as an example. The three most widely used thermodynamic models (E-AIM-IV, ISORROPIA-II, and AIOMFAC) are employed for the comparison. It has been shown theoretically that the difference between pH_x (mole fraction based) and pH_m (molality based) is always a constant (1.74, when the solvent is water) within a thermodynamic model regardless of aerosol property.

3. Page 2, line 9: The authors state; "The acidity of aerosols can be quantified by parameters such as strong acidity, free acidity, cation-to-anion ratio and ammonium- to-sulfate ratio. However, these parameters neglect the effect of liquid water content or the dissociation of ions and acids (Pathak et al., 2004; Hennigan et al.,2015)." First, a definition of what strong acidity and free acidity represents is not given. Second, it is incorrect that free acidity neglects water content, as the partial dissociation of species like bisulfate is very much dependent on water content and therefore affects free acidity. Pathak et al. and Hennigan et al. do not seem to make such a point.

   Response:

   We agree that our original description was vague and inaccurate. In the revised manuscript, we have (1) added the definition of both strong and free acidity; and (2) specified the drawbacks of these parameters with proper citation (Page 2, Lines 17-26).

   Revised text:

The most accurate parameter to characterize aerosol acidity is considered to be pH. The other parameters often used as proxies of aerosol acidity do not offer information on how acidic the particles are when they are present as aqueous droplets (Pathak et al., 2004). For example, strong acidity (defined as nmol of total H^+ per m^3 of air measured in water extracts of particles using the USEPA Reference Method (USEPA, 1992)) and ion charge balance are unable to distinguish between free and undissociated H^+ (e.g., protons associated with bisulfate) (Pathak et al., 2004;Hennigan et al., 2015). Ammonium-to-sulfate ratio and cation-to-anion ratio are unable to provide any measure of the degree of aerosol acidity even qualitatively (Hennigan et al., 2015). And lastly, free acidity (defined as the actual concentration of free H^+ per m^3 of air, not including the H^+ released from bisulfate ions in aqueous extracts) represents the quantity of H^+ in a specific volume of air while neglecting the concentration of H^+ in liquid water (Pathak et al., 2004).

4. Equation (1): Define the meaning of "lg".

   Response:
   We have revised lg to log10 to make it clearer throughout the manuscript.

5. Equation (2): This equation and its description is flawed. (1) What are the terms of "1000" in the numerator and denominator? The authors likely use these for conversion from units of kg to g. If so, the mathematically correct way of writing this would be to write 1000 $\frac{g}{kg}$in the equation and it would be necessary to state that the molar masses are supposed to be used in units of $\frac{g}{mol}$ rather than the standard SI unit of $\frac{kg}{mol}$. Otherwise it is simply incorrect and a potential source of confusion. However, since the ACP recommendation is to use SI units whenever possible, there is not need for these unit conversion terms at all (they would be 1). (2) This expression is only correct for the special case where the only solvent for the ions is water. However, in the more general case, there may be other solvents, such as organic compounds mixed with water and the ions in a liquid phase. In that case, the distinct molar masses of the organics must be accounted for in the activity coefficient conversion expression. Hence, since this is a key part of the discussion about different thermodynamic composition scales and reference and standard states, it should be shown correctly for the general case. A rigorous derivation of such scale conversions is, e.g., shown in the PhD thesis by Zuend (2007) (page 45 – 47 there), which shows different versions of the scale conversion formula. One of which (useful here) is $\ln[\gamma_i] = \ln[f_i^*] + \ln[\frac{x_i}{m_i M_w}]$ and f^* the mole fraction scale activity coefficient, both with reference state of infinite dilution in pure water; x_i the ion mole fraction with respect to dissociated ions, m_i the ion molality and M_w the molar mass of water. Since solvents other than water are also included in both the mole fraction and molality expressions for ion "i", this is a general expression. From this scale conversion of ion activity coefficients, it is readily shown that the difference in pH values is generally given by $pH_x - pH_m = -\log10[m^0 M_w]$, where m° denotes unit molality (= 1 mol/kg) (similar to Eq. (8) in the manuscript, but note the difference in units, the given Eq. (8) is not dimensionless in the log).

   Response:
   We thank the Reviewer for pointing out this issue.
   1) The factor of 1000 in the original equation was for the conversion of kg to g. The unit of molecular mass was g/mol in the original manuscript. We have now revised the unit of

molecular mass to the SI unit of kg mol^{-1} as suggested. All other units in the manuscript are now SI units except molarity (mol dm^{-3}). So, $1000\frac{dm^3}{m^3}$ as a conversation factor is still shown when molarity of ion is involved.

2) We agree that the original Eq.2 is only valid when water is the only solvent. We have now cited Eq. 2.59 in the PhD thesis by Zünd (2007) and Robinson and Stokes (2002) to show the conversion (1) between γ_H and f_H (Eq. 4); (2) between γ_H and y_H (Eq. 5); and (3) between f_H and y_H (Eq. 6) in a more general form as below (Table 2).

Revised equations:

$$\gamma_H = f_H \frac{x_H}{m_H M_s} \quad (4)$$

$$\gamma_H = 1000 \frac{dm^3}{m^3} \frac{c_H y_H}{m_H \rho_0} \quad (5)$$

$$f_H = y_H 1000 \frac{dm^3}{m^3} \frac{M_w}{\rho_0} \frac{c_H}{x_H} \quad (6)$$

3) For the interconversion of concentrations in different scales, we have used the parameter M_s to represent the molar mass of the solvent (for single solvent) or the averaged molar mass for the scenario of multiple solvents in the system (Table 2).

Revised equations:

$$x_H = \frac{m_H}{\sum m_i + \frac{1}{M_s}} \quad (7)$$

$$c_H = \frac{m_H}{\frac{\sum m_i M_i + 1}{\rho_{sln}}} \quad (8)$$

$$x_H = \frac{M_s c_H}{M_s \sum c_i + 0.001 \frac{m^3}{dm^3} \rho_{sln} - \sum c_i M_i} \quad (9)$$

6. As pointed out in the comment by Simon Clegg, thermodynamic models differ in the way single-ion activity coefficients are calculated (since only mean cation/anion pair activity coefficients are measureable) and of course they also differ in the expressions, such that even with the correct conversion of activity coefficients or pH values between scales, different models may predict different pH$_m$ (or pH$_x$) values for the same input composition. Furthermore, only some models account for the influence of organic species in the mixture (e.g. AIOMFAC can be used for that, while ISORROPIA is only for inorganic aqueous mixtures) and differences in predicted pH may partially stem from organic interactions with ions and treatment of phase separation, see Pye et al (2018).

Response:

We agree with the Reviewer's point. This comment has been handled in combination with #10. We have now added Section 3.2 to discuss the general issues when comparing aerosol acidity across studies (including the difference in models, forward vs. reverse mode, stable vs. metastable mode, effect of non-volatile cations and effect of organic compounds) (Page 8, Line 12 to Page 9, Line 14).

Revised text:

3.2 General issues with pH comparison

It has been shown above that proper scale conversion has to be conducted when aerosol pH is compared. However, one should bear in mind that even with the same measured data and scale, pH calculated with different thermodynamic models or with different parameters may still not be comparable. Below, we briefly describe some of the general issues that need to be considered when aerosol acidity is compared across studies along with a summary of parameters used in the published studies in Table S1.

(1) Thermodynamic models like ISORROPIA-II and E-AIM can run in forward mode and reverse mode which result in significant difference (Song et al., 2018;Hennigan et al., 2015). It is recommended to use thermodynamic models in forward mode (gas plus aerosol as input) instead of reverse mode (aerosol only as input) which is highly sensitive to measurement uncertainties (Hennigan et al., 2015).

(2) Thermodynamic model can also be run in stable (liquid only) or metastable modes (both solid and liquid) which has not been specified in many studies (Table S1). Song et al. (2018) have shown that model calculations coupled with stable or metastable state assumptions can provide reasonable estimates of aerosol water and pH. However, as pointed by Song et al. (2018), the studies using standard ISORROPIA-II (without code correction) running in stable mode have predicted unrealistic pH values of around 7 and should be reevaluated.

(3) The effect of non-volatile cations such as Na^+, Ca^{2+}, Mg^{2+} and K^+ on aerosol pH may also not be ignored. Although the effect of non-volatile cations on pH may be only 0.2-0.5 pH units, their impact on predicted partitioning of a semi-volatile species can be significant due to the highly non-linear response of NH_3-NH_4^+ or HNO_3-NO_3^- partitioning to pH (Guo et al., 2017). Since E-AIM cannot explicitly treat Ca^{2+}, Mg^{2+} and K^+ (unlike ISORROPIA-II and AIOMFAC), pH estimated using E-AIM may ignore Ca^{2+}, Mg^{2+} and K^+ (as shown in Table S1) or treat them as equivalent sodium (e.g. (Hennigan et al., 2015)). Even if all non-volatile cations are treated as Na^+, the predicted thermodynamic states can be biased due to the strong non-ideality of divalent ions as well as variations in water uptake characteristics between Na^+ salts and its counterparts (e.g., Fountoukis et al., 2009).

(4) Most studies so far have estimated pH of aerosols with only inorganic compounds. However, it has been reported that pH can be affected by organic compounds in several ways. Guo et al., (2015) have shown that the pH can be increased by 0.15 to 0.23 units when aerosol water associated with organic compounds is considered. Omission of the contribution of organic acids to H^+ has been estimated to increase the pH by 0.07 ± 0.03 by Song et al. (2018) using E-AIM-IV. It has been shown recently that accounting for non-ideal mixing can modify the pH such that a fully interactive inorganic–organic system showed a pH roughly 0.7 units higher than that predicted using an inorganic only system by AIOMFAC (Pye et al., 2018).

7. Equation (4): Similar to above comment. A general expression should be shown, with proper use of units.

Response:

Thanks. Equation 4 has been revised accordingly (Eq. 6 in the revised manuscript).

Revised equations:

$$f_H = y_H 1000 \frac{dm^3}{m^3} \frac{M_w}{\rho_0} \frac{c_H}{x_H} \qquad (6)$$

8. Page 4, line 3: the last sentence there makes little sense. The pH values can be compared when the scale effect is accounted for; the point is that one should not expect the values to be equal.

   Response:
   We assume that the Reviewer actually meant page 5 in the original manuscript. This sentence has been deleted in the revised manuscript.

9. Page 4, line 13: “This is supported by our field data”. Again, this is a circular argument. The $\mathrm{pH}_x - \mathrm{pH}_m$ scale difference is used in the evaluation of the pH values, so of course it will show as consistent, but the measurements are no proof for that. Also, the fact that the difference should be a constant in pH units is clear from the theory, as long as the same thermodynamic model is used to compute the activity coefficients (which may not be the case when different studies are compared).

   Response:
   We assume the Reviewer actually meant page 5 in the original manuscript. We agree with the reviewer’s point and have revised the text accordingly. As we clarified in the beginning of our response, other revisions have also been made and the final revised text is as below (Page 6, Lines 24-27).

   Revised text:
   The difference of pH_x and pH_m is $\log 10 M_s m^0$ (according to Eq. (10)) which is only determined by the molecular weight of the solvent. When water is the only solvent in the system (molecular weight of 0.018 kg mol^{-1}), pH_x - pH_m is fixed at 1.74 within the model regardless of aerosol property or the model (as in this study).

10. Page 7, line 6: The discussion in this paragraph is not sufficient to address the other very important issues when aerosol acidity is attempted to be assessed from field measurements. It is also clear from theory and comparisons that organic compounds will affect aerosol acidity, maybe not dramatically but noticeably, since their interactions with water and H^+ions are affecting the activity of H^+. Last sentence in paragraph: “The relationship between pHx, pHc and pHm established in this study is valid regardless of the method selected to estimate aerosol acidity.” This is true only for the scale conversion, since it depends on proper application of thermodynamic theory only (which has been known for decades and is not a novelty of this study). However, when aerosol sample acidity is estimated in practice, different models are used for activity coefficients (e.g. ISORROPIA, E-AIM, AIOMFAC) or unit activity coefficients are assumed (not recommended). Moreover, different methods are applied to determine the approximate H+ amount, which is a critical problem in acidity evaluation, see Hennigan et al (2015). Therefore, the difference in reported pH values is not just due to the offsets between these different pH scales. The authors have failed to make this important point very clear.

Response:

We agree with the reviewer's point. This comment has been handled in combination with #6. We have now added Section 3.2 to discuss the general issues when comparing aerosol acidity across studies (including difference in models, forward vs. reverse mode, stable vs. metastable mode, effect of non-volatile cations and effect of organic compounds). The revised text is shown in the response to comment #6.

11. Table 1: The definitions include many mistakes and typos; e.g., pH$_m$ is not molarity based, the last two entries are confusing and not correctly described and reference states of activity coefficients are missing.

Response:

Table 1 has been revised thoroughly. The reference state of activity and activity coefficient have been added in the definition of activity. The revised Table 1 is shown below.

Revised table:

Table 1. List of abbreviations.

Abbreviation	Definition
ac_H	activity of hydrogen ions with standard state of the hypothetical ideal aqueous solution of unit molarity and reference state of infinite dilute solution (dimensionless)
am_H	activity of hydrogen ions with standard state of the hypothetical ideal aqueous solution of unit molality and reference state of infinite dilute solution (dimensionless)
ax_H	activity of hydrogen ions with standard state of the hypothetical pure H^+ solution and reference state of infinite dilute solution (dimensionless)
c^0	unit molarity (1 mol dm^{-3} solution)
c_H	molarity of hydrogen ion (mol dm^{-3} solution)
c_i	molarity of solute species i (in dissociated form) (mol dm^{-3} solution) [a]
f_H	mole fraction scale activity coefficient
m^0	unit molality (1 mol kg^{-1} solvent)
m_H	molality of hydrogen ions (mol kg^{-1} solvent)
m_i	molality of solute species i (in dissociated form) (mol kg^{-1} solvent) [a]
M_i	molar mass of solute species i (kg mol^{-1})
M_s	molar mass of single solvent or averaged molar mass for multiple solvents (kg mol^{-1})
pH_c	molarity based pH (dimensionless)
pH_m	molality based pH (dimensionless)
pH_x	mole fraction based pH (dimensionless)

x_H	mole fraction of hydrogen ions (dimensionless, mol H^+ in total moles)
y_H	molarity scale activity coefficient
γ_H	molality scale activity coefficient
ρ_0	density of pure solvent or averaged density for multiple solvents (kg m^{-3})
ρ_{sln}	density of hygroscopic aerosol solution (kg m^{-3})

Note: [a] The molarity and molality are expressed as species in dissociated ions for salt.

Reference

USEPA, 1992. Determination of strong acidity of atmospheric fine-particles (<2.5 μm) using annular denuder technology. Atmospheric Research and Exposure Assessment Laboratory, EPA Report No. EPA/600/R-93/037, Washington, DC.

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Song, S., Gao, M., Xu, W., Shao, J., Shi, G., Wang, S., Wang, Y., Sun, Y., and McElroy, M. B.: Fine-particle pH for Beijing winter haze as inferred from different thermodynamic equilibrium models, Atmos. Chem. Phys., 18, 7423-7438, 10.5194/acp-18-7423-2018, 2018.

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van Boekel, M. A. J. S.: Kinetic Modeling of Reactions In Foods, CRC Press, New York, 2008.

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Response to Anonymous Referee #2

Comments are in black, responses in blue and the revised text in red.

Particle acidity is an important property in terms of aerosol chemistry and its impact on health and climate. Due to the importance, there has been an increasing amount of publication investigating particle pH through thermodynamic models in recent years, which is a step forward compared to the problematic ion balance or molar ratio because of particle liquid water and non-ideality effect (activity coefficient). Without a consensus on the pH definition, it would be difficult to compare various studies, and this may lead to misunderstanding or misinterpretation of particle pH. Although some particle acidity studies state clearly the pH definition used in the analyses, there are some papers not talking about the definition at all. In the latter case, some studies probably take the approach of molality-based or molarity-based because they take a pH of 7 as neutral.

This paper shows the two pHs are very close and the minor difference is caused by particle density (for dilute water solution, no difference is expected from the two pHs). In general, this paper hits an important point (i.e., pH definition) that has not been paid enough attention to by the community and fits the scope of a technical note on ACP. However, some revisions are needed before considering a publication.

Response:
We thank the Reviewer for the helpful comments and suggestions, and also for agreeing with the importance of pH interconversion between different scales, which is the main focus of current study.

First of all, we would like to apologize for the mistakes made in Eqs. 4 and 9 in the original manuscript that stem from errors originally made in the equation by van Boekel (2008) used in our reference. The density of solvent was taken as the density of hygroscopic aerosol by mistake in the original manuscript. Since the mistakes are not included in either of the reviewer's comments or in the short comments by Prof. Clegg, we clarify this issue first before responding to the reviewers' comments in detail. The details of the mistakes are shown in Table 1 below.

Table 1. Correction of Eqs. 4 and 9 in the original manuscript

Eq. #	Original (with mistake)	Corrected [a]
4	$y_H = f_H \frac{\rho_{\mathrm{sln}}}{\rho_{\mathrm{sln}} + 0.001[M_s \sum c_i - \sum c_i M_i]}$	$y_H = f_H \frac{\rho_{solvent}}{\rho_{\mathrm{sln}} + 0.001[M_s \sum c_i - \sum c_i M_i]}$
9	$pH_x - pH_c = -\lg \frac{f_H x_H}{\mathrm{c_H} y_\mathrm{H}} = -\lg \frac{0.001Ms}{\rho_{\mathrm{sln}}} = 1.74 + \lg \rho_{\mathrm{sln}}$	$pH_x - pH_c = -\lg \frac{f_H x_H}{\mathrm{c_H} y_\mathrm{H}} = -\lg \frac{0.001Ms}{\rho_{solvent}} = 1.74 + \lg \rho_{solvent}$

[a] Since Dr. Zuend suggested to use more genearl equations (considering solvents other than water), the corrected equations do not direcely appear in the revised mansucript. Instead they have been shown in a more general form as: $f_H = y_H 1000 \frac{dm^3}{m^3} \frac{M_w}{\rho_0} \frac{c_H}{x_H}$ (6) and $pH_x - pH_c = \log 10 \frac{1000 dm^3/m^3 M_s c^0}{\rho_0}$ (12) in the revised manuscript.

In the original manuscript, we discussed the effect of the density of aerosol solution on the conversion between molality-based pH and molarity-based pH, which formed the major part of the *Results and Discussion* section. However, after correction, the conversion between molarity and molality-based pH actually does not depend on the density of the solution but does so on the density of the pure solvent. Therefore the orignal discussion is only partially valid when the acitvity coefficent of H^+ is simplified as unity (e.g. by ISORROPIA-II). Consequently, we have revised the mansucript significantly. The major revisons include (1) removing the original discussion regarding comparision between pH_m and pH_c; (2) incorporating the calculation of pH on differnet scales using multiple thermodynamci models; 3) using a gas+aerosol system instead of an aerosol only system to estimate pH; 4) discussing the differnce between different scales for a generalized solvent system instead of only water and (5) inclusion of a sub-section to discuss the general issues regarding aerosl acidity comparision across studies. We believe that the importance of our study and the major conclusion remain unaffected by the mistake although a significant revision has been done. Below are our detailed responses to each of the comments.

1. There are several “circular” statements as pointed out by the other reviewer Andreas Zuend. The differences between pHx, pHc, pHm are all expected from their definitions. This is the key point of this paper: the difference between pHc and pHm is small (within 0.2 pH units, caused by particle density), but pHx is significantly higher than pHc and pHm (pHx – pHm = 1.74). The E-AIM (or any other model) predicted pHs are supposed to be consistent with the rule, if one model is used consistently in this analysis. Therefore, it is not a real support by field data (used as E-AIM input) as claimed on line 13 Page 5. Relating to this, the author should consider changing the saying of “observed” (Line 18 Page 1) in the abstract. The presented result is all based on a thermodynamic model prediction of pH but not measured pH.

   Response:
   We agree with the Reviewer’s point. The differences between *pHx*, *pHc* and *pHm* are expected from their definitions. The field data shown in this study is actually an example to show the conversion between different scales. The following revision has been done in the revised manuscript (Page 1, Lines 16-18).

   Revised text

   This study attempts to address this issue by comparing $PM_{2.5}$ aerosol pH based on different scales (molarity, molality and mole fraction) on the basis of theoretical considerations followed with a set of field data from Guangzhou, China as an example.

2. From a boarder view of an application, this paper could be more beneficial by showing the default pH scales given by widely used thermodynamic models. The E-AIM model has been discussed in detail, however, ISORROPIA or AIOMFAC or any other model is not mentioned. For example, ISORROPIA gives pH in the model output and the pH scale is molality-based (Fountoukis et al., 2009; Guo et al., 2015). If a literature doesn’t specify the pH scale, this piece of info could be very helpful to readers.

Response:

We agree with the Reviewer's point.

(1) We have addressed this issue in the *Introduction* section (Page 3, Lines 17-21).

Revised text:

It appears that the selection of the standard state of activity is arbitrary for aerosol acidity studies, and is not always defined in published articles when pH is used to characterize the acidity of aerosol (8 out of 32 studies as shown in Table S1). This may not be problematic in the case of ISORROPIA-II where the default output pH is always molality-based; however, confusion is possible when E-AIM or AIOMFAC are used since these models provide both molality- and mole fraction-based concentrations as output.

(2) Following the reviewer's suggestion, we have now shown the calculations with all the 3 models. We have also described the parameters that can be obtained from the model outputs as well as how other parameters are estimated. The revised text is shown below (Table S2).

Revised text:

Table S2. A summary of estimation methods of parameters for pH calculation based on different standard states.

Parameters	E-AIM-IV	ISORROPIA-II	AIOMFAC
Mole fraction			
x_H	output	Eq. (7)	output
f_H	output	1[a]	Eq. (4)
Molality			
m_H	output	output	output
γ_H	Eq. (4)	1[a]	output
Molarity			
c_H	Eq. (8) [b]	Eq. (8) [b]	Eq. (8) [b]
y_H	Eq. (6)	1[a]	Eq. (6)

Note: [a] activity coefficient is assumed to be 1; [b] the density of aerosol solution is based on the result from E-AIM-IV.

3. The section 3.3 is problematic without discussion of uncertainty, especially considering that the presented pH in this study is solely based on particle data (no gas data used to constrain pH). The predicted pH uncertainty is propagated from the particle ionic composition data (6% reported by Chen et al. (2016)) and RH, T. It is not easy to estimate particle pH uncertainty. Guo et al. (2015) estimated a pH uncertainty of 13% using another model, ISORROPIA, and in forward model for their dataset. Even though the two data points (S-I and S-II) are selected for the largest deviation from the1:1 line, small differences (7% or 8%) in hydrogen ion activity are found, which seem to be within uncertainty range. Hennigan et al. (2015) and other papers have pointed out that forward mode is superior over reverse mode in terms of particle pH prediction accuracy. For one reason, reverse mode is more sensitive to particle measurement uncertainty (likely the cause for occasionally very high pH seen in Figure 1). For the other reason, particle pH is sensitive to gas-particle partitioning of semivolatile species (e.g., NH4+, NO3-, and Cl-), as long as the species is not totally in gas phase or particle

phase. The forward mode predicted pH can then be validated if predicted and observed gas-particle partitioning agree. In contrast, the reverse mode predicted pH could not be verified in the same way. The Line 7 on Page 7 seems to suggest there is no advantage of using forward mode calculation and this is misleading to potential users.

Response:

We thank the reviewer for pointing out this important issue.

(1) We have revised the method to calculate aerosol pH from the forward mode, which is of lower uncertainty, instead of reverse mode.

(2) We acknowledge that the difference between pH_m and pH_c may not be large compared with uncertainties from measurement errors. Therefore, to address the limitation of our finding, we have added the following text in the discussion (Page 7, Line 29 to Page 8, Line 5).

Revised text:

Given that the uncertainty of pH calculation due to measurement errors can be as high as 14% (Guo et al., 2015), the difference of pH_c and pH_m can simply fall within the range of measurement errors. However, the bias between pH_c and pH_m can be considered to be a systematic one, which needs to be addressed for the sake of comprehensiveness in theoretical analysis. Moreover, even small biases in pH may imply substantial partitioning errors for semivolatile species like ammonium, nitrate, chloride, and even organic acids (Guo et al., 2017).

4. As Andreas Zuend points out, it would be nice to mention the possible differences be- tween predicted pH via different models at the end of section 3.4. Even if the same inputs are given to models, 100% agreement in pH is not expected due to differences in assumptions and approaches. There are a number of studies comparing thermodynamic models and exploring the differences (Hennigan et al., 2015; Liu et al., 2017; Pye et al., 2018; Song et al., 2018)

Response:

We agree with the Reviewer's point. We have addressed this issue in the revised manuscript.

(1) Following the reviewer's suggestion, we have shown the comparison of pH calculated using different thermodynamic models in the revised manuscript as below followed by a comparison of the three models (Table 3 and Page 6, Lines 2 to 18).

Table 3. Calculated concentrations, activity coefficient of H^+ and pH for the three thermodynamic models. [a]

	E-AIM-IV	ISORROPIA-II	AIOMFAC
Molar fraction			
x_H	$1.07\times10^{-4}\pm1.28\times10^{-4}$ $(2.17\times10^{-5}–9.49\times10^{-4})$	$3.49\times10^{-5}\pm4.80\times10^{-5}$ $(4.59\times10^{-6}–3.69\times10^{-4})$	$2.71\times10^{-4}\pm3.36\times10^{-4}$ $(4.56\times10^{-5}–2.46\times10^{-3})$
f_H	0.74±0.25 (0.43–1.97)	1 [b]	0.27±0.10 (0.15–0.79)
pH_x	4.26±0.28 (3.16–4.82)	4.63±0.36 (3.43–5.34)	4.31±0.27 (3.24–4.86)
Molality			
m_H	$7.80\times10^{-3}\pm9.52\times10^{-3}$ $(1.50\times10^{-3}–7.03\times10^{-2})$	$2.60\times10^{-3}\pm3.64\times10^{-3}$ $(3.18\times10^{-4}–2.80\times10^{-2})$	$1.98\times10^{-2}\pm2.50\times10^{-2}$ $(3.14\times10^{-3}–1.82\times10^{-1})$
γ_H	0.57±0.19 (0.35–1.54)	1 [b]	0.21±0.08 (0.12–0.62)
pH_m	2.52±0.28 (1.41–3.07)	2.77±0.36 (1.55–3.50)	2.56±0.27 (1.50–3.11)
Molarity			
c_H	$5.56\times10^{-3}\pm6.59\times10^{-3}$ $(1.14\times10^{-3}–4.89\times10^{-2})$	$1.73\times10^{-3}\pm2.35\times10^{-3}$ $(2.38\times10^{-4}–1.80\times10^{-2})$	$1.43\times10^{-2}\pm1.76\times10^{-2}$ $(2.48\times10^{-3}–1.30\times10^{-1})$
y_H	0.79±0.26 (0.45–2.04)	1 [b]	0.28±0.10 (0.16–0.75)
pH_c	2.52±0.28 (1.41–3.07)	2.94±0.35 (1.75–3.62)	2.56±0.27 (1.50–3.11)

Notes: [a] All parameters are shown as average ± standard deviation with the range in bracket except for [b] activity coefficient of ISORROPIA-II which is assumed to be 1.

3.1.1 Comparison of pH calculated by different models

The results of pH calculated based on different standard states with the three thermodynamic models are shown in Table 3. Overall, there are slight difference between pH calculated using different models. Taking pH_m as an example, the averaged pH_m calculated by ISORROPIA-II (2.77±0.36) is 0.25 pH unit higher than that calculated by E-AIM-IV (2.52±0.28), which is consistent with the result reported by Song et al. (2018) and Liu et al. (2017). The pH_m calculated by AIOMFAC (2.56±0.27) is closer to that calculated with E-AIM-IV (2.52±0.28). It is worthwhile to note that the activity coefficient of H^+ calculated by E-AIM-IV (0.57±0.19) is 2.7 times higher than that calculated by AIOMFAC (0.21±0.08) while the molality of H^+ calculated using AIOMFAC ($1.98\times10^{-2}\pm2.50\times10^{-2}$) is 2.5 times higher than that calculated by E-AIM-IV ($7.80\times10^{-3}\pm9.52\times10^{-3}$) although the resultant pH_m is similar.

The difference in the calculated pH between different models is due to differences in both concentration and activity coefficient. For example, a unity activity coefficient of H^+ is assumed for ISORROPIA-II for pH calculation even though the non-ideal interaction of H^+ with all other ions in solution is explicitly considered by the Kusik-Meisner and Bromely formulations in ISORROPIA-II (Fountoukis and Nenes, 2007). The exact factors contributing to the difference in pH remains unclear, and is not the focus of current study. The models may differ in many ways such as their methods for calculating the activity coefficients for H^+ and other ionic species, and in estimating aerosol water contents (Song et al., 2018).

(2) We have added a full section to discuss the general issue in pH comparison between different studies in the revised manuscript (Page 8, Line 12 to Page 9, Line 14).

Revised text:

3.2 General issues with pH comparison

It has been shown above that proper scale conversion has to be conducted when aerosol pH is compared. However, one should bear in mind that even with the same measured data and scale, pH calculated with different thermodynamic models or with different parameters may still not be comparable. Below, we briefly describe some of the general issues that need to be considered when aerosol acidity is compared across studies along with a summary of parameters used in the published studies in Table S1.

(1) Thermodynamic models like ISORROPIA-II and E-AIM can run in forward mode and reverse mode which result in significant difference (Song et al., 2018;Hennigan et al., 2015). It is recommended to use thermodynamic models in forward mode (gas plus aerosol as input) instead of reverse mode (aerosol only as input) which is highly sensitive to measurement uncertainties (Hennigan et al., 2015).

(2) Thermodynamic model can also be run in stable (liquid only) or metastable modes (both solid and liquid) which has not been specified in many studies (Table S1). Song et al. (2018) have shown that model calculations coupled with stable or metastable state assumptions can provide reasonable estimates of aerosol water and pH. However, as pointed by Song et al. (2018), the studies using standard ISORROPIA-II (without code correction) running in stable mode have predicted unrealistic pH values of around 7 and should be reevaluated.

(3) The effect of non-volatile cations such as Na^+, Ca^{2+}, Mg^{2+} and K^+ on aerosol pH may also not be ignored. Although the effect of non-volatile cations on pH may be only 0.2-0.5 pH units, their impact on predicted partitioning of a semi-volatile species can be significant due to the highly non-linear response of NH_3-NH_4^+ or HNO_3-NO_3^- partitioning to pH (Guo et al., 2017). Since E-AIM cannot explicitly treat Ca^{2+}, Mg^{2+} and K^+ (unlike ISORROPIA-II and AIOMFAC), pH estimated using E-AIM may ignore Ca^{2+}, Mg^{2+} and K^+ (as shown in Table S1) or treat them as equivalent sodium (e.g. (Hennigan et al., 2015)). Even if all non-volatile cations are treated as Na^+, the predicted thermodynamic states can be biased due to the strong non-ideality of divalent ions as well as variations in water uptake characteristics between Na^+ salts and its counterparts (e.g., Fountoukis et al., 2009).

(4) Most studies so far have estimated pH of aerosols with only inorganic compounds. However, it has been reported that pH can be affected by organic compounds in several ways. Guo et al., (2015) have shown that the pH can be increased by 0.15 to 0.23 units when aerosol water associated with organic compounds is considered. Omission of the contribution of organic acids to H^+ has been estimated to increase the pH by 0.07±0.03 by Song et al. (2018) using E-AIM-IV. It has been shown recently that accounting for non-ideal mixing can modify the pH such that a fully interactive inorganic–organic system showed a pH roughly 0.7 units higher than that predicted using an inorganic only system

by AIOMFAC (Pye et al., 2018).

Minor comments:

1. Toning down the statement of "for the first time" is suggested. Thermodynamic specialists must have known the difference between pH scales. The elucidation in the paper is based on established equations on textbooks and doesn't sound to me like a groundbreaking finding. The paper is of value to minimize the gaps in the current understanding of pH definitions.

Response:
Thanks for pointing out the issue. We have deleted the concerned phrase in the description and elsewhere in the revised manuscript (Page 1, Lines 16-18).

Revised text:
This study attempts to address this issue by comparing $PM_{2.5}$ aerosol pH based on different scales (molarity, molality and mole fraction) on the basis of theoretical considerations followed with a set of field data from Guangzhou, China as an example.

2. The units in Equation (3) (mol/kg water) and (6) (mol/dm3) look redundant. However, more explanations in the text are needed. Equation (3) is defined based on the mass of water, while Equation (6) is defined based on the volume of particle, which includes the volumes of water (solvent) and other solutes. If Equation (6) is defined solely on the volume of particle water, there would not be any difference with Equation (3). This is not clear in the text.

Response:
We thank the reviewer pointing out the issue. The two equations have been changed accordingly (Page 5, Lines 16-17). We have also explained that molarity means mol dm^{-3} solution while molality means mol kg^{-1} solvent in Table 1.

Revise equations:

$$pH_c = -\log 10(a_{c_H}) = -\log 10(\frac{\gamma_H c_H}{c^o}) \quad (2)$$

$$pH_m = -\log 10(a_{m_H}) = -\log 10(\frac{\gamma_H m_H}{m^o}) \quad (3)$$

Explanation of parameters (in Table 1):

m_H	molality of hydrogen ions (mol kg^{-1} solvent)
c_H	molarity of hydrogen ion (mol dm^{-3} solution)

3. Proper reference as suggested by Simon Clegg.

Response:
We have now added the sources of all equations as suggested by Prof. Simon Clegg in Table 2.

Revised text:

Table 2. Summary of equations for the interconversion of concertation and activity coefficient based on different standard states.

Parameter	pH_x vs. pH_m	pH_m vs. pH_c	pH_x vs. pH_c
Activity coefficient [a]	$\gamma_H = f_H \frac{x_H}{m_H M_s}$ (4)	$\gamma_H = 1000 \frac{dm^3}{m^3} \frac{c_H y_H}{m_H \rho_0}$ (5)	$f_H = y_H 1000 \frac{dm^3}{m^3} \frac{M_s}{\rho_0} \frac{c_H}{x_H}$ (6)
Concentration [b]	$x_H = \frac{m_H}{\sum m_i + \frac{1}{M_s}}$ (7)	$c_H = \frac{m_H}{\frac{\sum m_i M_i + 1}{\rho_{sln}}}$ (8)	$x_H = \frac{M_s c_H}{M_s \sum c_i + 0.001 \frac{m^3}{dm^3} \rho_{sln} - \sum c_i M_i}$ (9)
pH [c]	$pH_x - pH_m = -\log10[M_s m^0]$ (10)	$pH_m - pH_c = -\log10 \frac{c^0 1000 dm^3/m^3}{m^0 \rho_0}$ (11)	$pH_x - pH_c = \log10 \frac{1000 dm^3/m^3 M_s c^0}{\rho_0}$ (12)

Note: [a] The source of Eqs. (4)-(5) are Robinson and Stokes (2002) and the source of Eq. (6) is Zünd (2007). The details of derivation of Eqs. (4)-(6) are shown in Robinson and Stokes (2002) and (Zünd (2007)). [b] Eqs. (7)-(9) are based on the definition of each parameter. [c] Eqs. (10)-(12) are derived from Eqs (4)-(6) and (7)-(9) for each standard state.

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Technical note: Comparison and interconversion of pH based on different standard states for aerosol acidity characterization

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Abstract. Aerosol pH is often calculated based on different standard states thus making it inappropriate to compare aerosol acidity parameters derived thereby. Such comparisons are however routinely performed in the atmospheric science community. This study attempts to address this issue by comparing $PM_{2.5}$ aerosol pH based on different scales (molarity, molality and mole fraction) on the basis of theoretical considerations followed with a set of field data from Guangzhou, China as an example. The three most widely used thermodynamic models (E-AIM-IV, ISORROPIA-II, and AIOMFAC) are employed for the comparison. It has been shown theoretically that the difference between pH_x (mole fraction based) and pH_m (molality based) is always a constant (1.74, when the solvent is water) within a thermodynamic model regardless of aerosol property. On the other hand, pH_m and pH_c (molarity based) are almost identical with a minor effect from temperature and pressure. However, when the activity coefficient is simplified as unity by thermodynamic models, the difference between pH_m and pH_c ranges from 0.11 to 0.25 pH units, depending on the chemical composition and the density of hygroscopic aerosol. Therefore, while evaluating aerosol acidity (especially, trend analysis) when the activity coefficient is simplified as 1, considering the pH scale is important. The application of this pH standardization protocol might influence some conclusions on aerosol acidity reported by past studies, and thus a clear definition of pH and a precise

statement of thermodynamic model parameters are recommended to avoid bias when pH comparisons are made across studies.

1 Introduction

Aerosol acidity is of great scientific interest due to its effects on human health and atmospheric chemical processes (Amdur and Chen, 1989;Xue et al., 2011). Acidic aerosols are found to correlate with health effects including asthma, bronchitis, and others respiratory diseases along with reduced lung function (Amdur and Chen, 1989;Ricciardolo et al., 2004;Longo and Yang, 2008). Acidic aerosols can also contribute to the bioavailability of iron and phosphorus in open oceans (Nenes et al., 2011;Zhu et al., 1992) and acidic sea salts have the potential to catalyze halogens to deplete tropospheric ozone (O_3) (Keene et al., 1998;Pszenny et al., 2003;Simpson et al., 2007). Moreover, aerosol acidity plays a key role in the gas-particle partitioning of species such as HCl/Cl^-, HNO_3/NO_3^- and NH_3/NH_4^+, and is therefore vital for predicting lifetimes of gaseous compounds such as HCl, NH_3 and HNO_3 in the atmosphere (Nemitz et al., 2004;Oss et al., 1998). Further, aerosol acidity is known to affect the formation of secondary organic aerosols (SOA); e.g., experimental studies show that seed aerosols with acidic surfaces can enhance the formation of organosulphate SOA upon reaction with volatile organic compounds such as octanal, carbonyls, isoprene, limonene, and caryophyllene (Jang et al., 2002).

The most accurate parameter to characterize aerosol acidity is considered to be pH. The other parameters often used as proxies of aerosol acidity do not offer information on how acidic the particles are when they are present as aqueous droplets (Pathak et al., 2004). For example, strong acidity (defined as nmol of total H^+ per m^3 of air measured in water extracts of particles using the USEPA Reference Method (USEPA, 1992)) and ion charge balance are unable to distinguish between free and undissociated H^+ (e.g., protons associated with bisulfate) (Pathak et al., 2004;Hennigan et al., 2015). Ammonium-to-sulfate ratio and cation-to-anion ratio are unable to provide any measure of the degree of aerosol acidity even qualitatively (Hennigan et al., 2015). And lastly, free acidity (defined as the actual concentration of free H^+ per m^3 of air, not including the H^+ released from bisulfate ions in aqueous extracts) represents the quantity of H^+ in a specific volume of air while neglecting the concentration of H^+ in liquid water (Pathak et al., 2004).

As per the International Union of Pure and Applied Chemistry (IUPAC), pH is defined as the negative log activity of hydrogen ions (https://goldbook.iupac.org/html/P/P04524.html). It is immeasurable because its definition involves a single ion quantity, the hydrogen ion activity (Baucke, 2002). Therefore, the value of pH is not an absolute one but depends on either how it is measured or the model used to calculate it. Especially, for aerosol pH, a commonly accepted measurement method is lacking despite some recent developments (Rindelaub et al., 2016), and it is usually calculated from thermodynamic models in practice.

One issue in comparing aerosol pH across studies even when calculated using the same model in actual practice is that different standard states can be used while defining the activity of H^+ ions. Although it is recommended that pH be defined based on the standard state of 1 mol H^+ kg^{-1} solvent (molality based) (https://goldbook.iupac.org/html/P/P04524.html), other standard states such as1 mol H^+ dm^{-1} solution (molarity based) and a hypothetical pure H^+ solution (mole fraction based) are also often used when quantifying aerosol acidity. Table S1 provides a brief summary of studies reporting aerosol pH calculated using thermodynamic models with different definition of pH. Molality based pH, as suggested by IUPAC, is used in 12 out of 32 studies. Molarity-based pH is the most commonly used scale in aquatic chemistry since the equilibrium constant is often determined based on molarity (Stumm and Morgan, 1996); it is also widely used for characterizing aerosol acidity (7 out of 32 studies). Mole fraction-based pH has also been used to characterize the acidity of hygroscopic aerosols (5 out of 32 studies) as this approach is more convenient to describe solutions with high concentrations (Rard et al., 2010).

It appears that the selection of the standard state of activity is arbitrary for aerosol acidity studies, and is not always defined in published articles when pH is used to characterize the acidity of aerosol (8 out of 32 studies as shown in Table S1). This may not be problematic in the case of ISORROPIA-II where the default output pH is always molality-based; however, confusion is possible when E-AIM or AIOMFAC are used since these models provide both molality- and mole fraction-based concentrations as output. In fact, pH based on different definitions have sometimes been used in the same study; e.g., Hennigan et al. (2015) defined pH based on the mole fraction of hydrogen; however, the authors used pH=7 as the critical point when $[H^+] = [OH^-]$, which actually is an elaboration of molarity (or molality) based pH. Some studies have employed molarity and molality of H^+ interchangeably in terms of defining and calculating pH (defined as mol dm^{-3} of H^+ but calculated as mol kg^{-1} of H^+ e.g.(Guo et al., 2016)), which is not ideal for the sake of consistency even though the resultant estimates are comparable. Additionally, pH values obtained via different definitions are sometimes cross-compared, e.g., Squizzato et al. (2013) observed that pH of $PM_{2.5}$ in the Po Valley, Italy (mole fraction-based) was much higher than those in megacities in China (Pathak et al., 2009) (molarity-based). Such comparisons need to be reevaluated given the different definitions of pH adopted in these studies.

Despite apparent incongruities in such cross-comparisons, this issue has not yet been addressed by the atmospheric science community. The main objective of this study is therefore to compare $PM_{2.5}$ aerosol pH based on different scales (molarity, molality and mole fraction) on the basis of theoretical considerations followed with a set of field data as an example. Further, in order to enable other researchers to easily compare pH based on different scales, the use of an inter-scale conversion factor has been demonstrated for the three most commonly used thermodynamic models, i.e., E-AIM-IV, ISORROPIA-II, and AIOMFAC.

2 Materials and Methods

2.1 Evaluation data set

A set of field data collected in Guangzhou, China was used to demonstrate the interconversion of pH based on different scales. The sampling site was located at the rooftop of a building, 15 m above the ground, in the Guangzhou Environmental Monitoring Center (23º07′59″N, 113º15′35″E) (refer to Chen et al. (2016b) for details). Hourly ionic species of $PM_{2.5}$ were measured using an AIM-IC 9000D (URG, Chapel Hill, NC) (refer to Chen et al. (2016a) for details). The sampling duration was from 1–31 July, 2013.

2.2 Thermodynamic models

The three most widely used thermodynamic models including E-AIM-IV (http://www.aim.env.uea.ac.uk /aim/aim.php) (Friese and Ebel, 2010;Wexler and Clegg, 2002), ISORROPIA-II (http://isorropia.eas.gatech.edu/index.php) (Fountoukis and Nenes, 2007) and AIOMFAC (http://www.aiomfac.caltech.edu) (Zuend et al., 2008) were selected to demonstrate the interconversion of pH between different scales. E-AIM is usually considered to be a benchmark model (Seinfeld and Pandis, 2016), while ISORROPIA is preferred for use in large-scale atmospheric models since it employs various simplifications to enhance computational efficiency (Fountoukis and Nenes, 2007). AIOMFAC can be used to calculate inorganic-organic interaction (Pye et al., 2018).

E-AIM-IV and ISORROPIA-II were run in forward mode (closed system). The compounds included in the calculation were Cl^-, SO_4^{2-}, NO_3^-, NH_4^+ and Na^+ in the particulate phase and NH_3, HNO_3 and HCl in the gaseous phase. Other inorganic ions such as K^+, Ca^{2+} and Mg^{2+}, and organic compounds were not included in the calculation in order to keep the consistency of the three models since K^+, Ca^{2+}, Mg^{2+} are not included in the system of E-AIM-IV while organic compounds are not included in ISORROPIA-II. This might induce some uncertainty in the estimated pH; however, this is not further discussed since the method to calculate aerosol acidity is not the focus of current study. The current online version of AIOMFAC is not capable of calculating gas-aerosol equilibrium, and therefore the output of aerosol compounds from E-AIM-IV were used as input in AIOMFAC to obtain aerosol properties in the reverse mode (open system). A stable particle phase state (solid plus liquid) was assumed for E-AIM-IV and ISORROPIA-II. Compounds in the aqueous phase of the output of E-AIM-IV were used as input to AIOMFAC. That way, AIOMFAC can be considered to be consistent with E-AIM-IV and ISORROPIA-II. According to Song et al. (2018), SORROPIA-II calculations with resultant pH of close to neutral (in stable mode) may not be accurate; hence, these samples (303 out of 440) were excluded from the calculation for all 3 models.

2.3 pH calculation and interconversion.

We provide below parameterizations of pH based on different standard states (molar fraction, molarity and molality). The reference state for the activity coefficients of H^+ ion is the infinite dilute solution in a reference solvent. Abbreviations used in this study are summarized in Table 1.

$$pH_x = -\log10(a_{x_H}) = -\log10(f_H x_H) \tag{1}$$

$$pH_c = -\log10(a_{c_H}) = -\log10(\frac{\gamma_H c_H}{c^o}) \tag{2}$$

$$pH_m = -\log10(a_{m_H}) = -\log10(\frac{\gamma_H m_H}{m^o}) \tag{3}$$

The equations for interconversion of H^+ concentrations and corresponding activity coefficients based on different standard states are listed in Table 2.

A number of parameters needed to estimate aerosol pH cannot be obtained directly from the three models, and calculations and/or assumptions are therefore necessary. The details of the approach to obtain specific parameters are shown in Table S2, and pH of different scales are calculated based on their definitions (Eqs. (1)–(3)). It is worthwhile to note that the molality based activity coefficient of H^+ in ISORROPIA-II is assumed to be 1; consequently, the activity coefficient of H^+ based on molarity and mole-fraction scale cannot be obtained and was also assumed to be 1. Moreover, the density of aerosol is not calculated by ISORROPIA-II or AIOMFAC, and therefore the density output by E-AIM-IV were used for all the three models.

3 Results and Discussion

3.1 Comparison of pH_x, pH_c and pH_m

3.1.1 Comparison of pH calculated by different models

The results of pH calculated based on different standard states with the three thermodynamic models are shown in Table 3. Overall, there are slight difference between pH calculated using different models. Taking pH_m as an example, the averaged pH_m calculated by ISORROPIA-II (2.77±0.36) is 0.25 pH unit higher than that calculated by E-AIM-IV (2.52±0.28), which is consistent with the result reported by Song et al. (2018) and Liu et al. (2017). The pH_m calculated by AIOMFAC (2.56±0.27) is closer to that calculated with E-AIM-IV (2.52±0.28). It is worthwhile to note that the activity coefficient of H^+ calculated by E-AIM-IV (0.57±0.19) is 2.7 times higher than that calculated by AIOMFAC (0.21±0.08) while the molality of H^+ calculated using AIOMFAC ($1.98\times10^{-2}\pm2.50\times10^{-2}$) is 2.5 times higher than that calculated by E-AIM-IV ($7.80\times10^{-3}\pm9.52\times10^{-3}$) although the resultant pH_m is similar.

The difference in the calculated pH between different models is due to differences in both concentration and activity coefficient. For example, a unity activity coefficient of H^+ is assumed for ISORROPIA-II for pH calculation even though the non-ideal interaction of H^+ with all other ions in solution is explicitly considered by the Kusik-Meisner and Bromely formulations in ISORROPIA-II (Fountoukis and Nenes, 2007). The exact factors contributing to the difference in pH remains unclear, and is not the focus of current study. The models may differ in many ways such as their methods for calculating the activity coefficients for H^+ and other ionic species, and in estimating aerosol water contents (Song et al., 2018).

3.1.2 Comparison of pH based on different scales

Since ISORROPIA-II simplifies the calculation with the assumption of the activity coefficient as unity while E-AIM and AIOMFAC calculate the activity coefficients in practice, ISORROPIA-II is discussed separately from the other two models in the following text.

For E-AIM-IV and AIOMFAC, the interconversion of pH based on different standard states can be conducted based on the theory (Eqs. (10)-(12)) since all parameters are available. The difference of pH_x and pH_m is $\log 10 M_s m^0$ (according to Eq. (10)) which is only determined by the molecular weight of the solvent. When water is the only solvent in the system (molecular weight of 0.018 kg mol^{-1}), $pH_x - pH_m$ is fixed at 1.74 within the model regardless of aerosol property or the model (as in this study). As shown in Table S1, water is taken as the only solvent in aerosol solution in almost all studies. The only study that considers organic compounds as one of the solvent is Pye et al. (2018).

On the other hand, the difference between pH_c and pH_m, $\log 10(1000 \frac{dm^3}{m^3} \frac{c^0}{m^0 \rho_0})$, is related to the density of the pure solvent (Eq.(11)) while the difference between pH_x and pH_c, $\frac{1000 dm^3/m^3 M_s c^0}{\rho_0}$, is determined by both the molecular weight and the density of the pure solvent (Eq.(12)). Since standard states are defined at the same temperature and pressure as the solution (Robinson and Stokes, 2002), the density of a pure solvent can vary at standard state for different solutions based on corresponding temperature and pressure. However, the density of water (the major solvent in atmospheric aerosols) does not vary significantly with temperature and pressure. The variation of water density is only 4% within a temperature ranging from 0-100 ºC (Kell, 1975) (corresponding change of pH is only 0.02 pH unit). The change of water density due to pressure variation is even smaller. When pressure ranges from 0.1MPa to 10 MPa at 25 ºC, the density change is only 0.004% (Wagner and Pruß, 2002) (corresponding pH change is 1.9×10^{-4}). Therefore, the difference can be neglected for water at ambient temperature and pressure. While the temperature ranges from 24.55 to 31.55ºC in the current study, the water density varies from 9.952×10^{4} Pa to 9.972×10^{4} Pa, with the corresponding pH change being less than 0.001 pH unit.

However, for ISORROPIA-II, the activity coefficient is assumed to be unity for the molality scale. If the same assumption is made for the other scales, the conversion factor deviates somewhat from theory. As shown in Table 3, the averaged pH_m (2.77) is 0.15 pH unit (ranging from 0.11 to 0.25) lower than pH_c (2.94) due to the simplification of both activity coefficients as unity. This effect is of a similar magnitude to that of organic-associated water to aerosol pH (0.15 to 0.23 pH unit) (Guo et al., 2015). Based on Eq. (8), the difference between pH_m and pH_c is not only related to the concentration of other species, but is also affected by the density of the solution (Eq. (8)). The density of the solution in turn varies with relative humidity and chemical properties of the samples (Clegg and Wexler, 2011), thus leading to potential variations in the trend of pH_m and pH_c. To investigate the trend comparison between pH_m and pH_c, their ranks (in desending order) are plotted in Fig. 1. The points deviating from the 1:1 line indicate samples possessing different ranks according to pH_m compared to that of pH_c. To illustrate how pH trends could change with different scales, two samples which deviate most from the 1:1 line are selected as examples (marked S-I and S-II in Fig. 1). As shown in Table 4, S-I is more acidic than S-II upon comparison of pH_m values. However, in terms of pH_c, S-I is less acidic than S-II. Although ΔpH_m (-0.05) is only 0.1 pH unit lower than ΔpH_c (0.05), the difference in H^+ concentration may not be neglected. The molality of H^+ ions of S-I (2.01×10^{-3} mol kg^{-1} water) is 11.7% higher than that of S-II (1.80×10^{-3} mol kg^{-1} water); however, the molarity of S-I (1.21×10^{-3} mol dm^{-3} solution) is 10.7% lower than that of S-II (1.34×10^{-3} mol dm^{-3} solution). Given that the uncertainty of pH calculation due to measurement errors can be as high as 14% (Guo et al., 2015), the difference of pH_c and pH_m can simply fall within the range of measurement errors. However, the bias between pH_c and pH_m can be considered to be a systematic one, which needs to be addressed for the sake of comprehensiveness in theoretical analysis. Moreover, even small biases in pH may imply substantial partitioning errors for semivolatile species like ammonium, nitrate, chloride, and even organic acids (Guo et al., 2017). Therefore, while evaluating aerosol acidity (especially, trend analysis) when the activity coefficient is simplified as 1, considering the pH scale is important. For the conversion between pH_x and pH_m, when the solvent is fixed as water, the difference is affected by the molality of H^+ and other electrolyte species in liquid water (according to Eq. (7)). In the current study, the pH_x - pH_m ranges from 1.83 to 1.87 which is 0.09 to 0.13 pH units higher than that based on theory (1.74). The trends of pH_x and pH_m can also be different but with a smaller difference compared with that between pH_x and pH_m as shown in Fig. S1.

3.2 General issues with pH comparison

It has been shown above that proper scale conversion has to be conducted when aerosol pH is compared. However, one should bear in mind that even with the same measured data and scale, pH calculated with different thermodynamic models or with different parameters may still not be comparable. Below, we briefly describe some of the general issues that need to be considered when aerosol acidity is compared across studies along with a summary of parameters used in the published studies in Table S1.

(1) Thermodynamic models like ISORROPIA-II and E-AIM can run in forward mode and reverse mode which result in significant difference (Song et al., 2018;Hennigan et al., 2015). It is recommended to use thermodynamic models in forward mode (gas plus aerosol as input) instead of reverse mode (aerosol only as input) which is highly sensitive to measurement uncertainties (Hennigan et al., 2015).

(2) Thermodynamic model can also be run in stable (liquid only) or metastable modes (both solid and liquid) which has not been specified in many studies (Table S1). Song et al. (2018) have shown that model calculations coupled with stable or metastable state assumptions can provide reasonable estimates of aerosol water and pH. However, as pointed by Song et al. (2018), the studies using standard ISORROPIA-II (without code correction) running in stable mode have predicted unrealistic pH values of around 7 and should be reevaluated.

(3) The effect of non-volatile cations such as Na^+, Ca^{2+}, Mg^{2+} and K^+ on aerosol pH may also not be ignored. Although the effect of non-volatile cations on pH may be only 0.2-0.5 pH units, their impact on predicted

partitioning of a semi-volatile species can be significant due to the highly non-linear response of NH_3-NH_4^+ or HNO_3-NO_3^- partitioning to pH (Guo et al., 2017). Since E-AIM cannot explicitly treat Ca^{2+}, Mg^{2+} and K^+ (unlike ISORROPIA-II and AIOMFAC), pH estimated using E-AIM may ignore Ca^{2+}, Mg^{2+} and K^+ (as shown in Table S1) or treat them as equivalent sodium (e.g. (Hennigan et al., 2015)). Even if all non-volatile cations are treated as Na^+, the predicted thermodynamic states can be biased due to the strong non-ideality of divalent ions as well as variations in water uptake characteristics between Na^+ salts and its counterparts (Fountoukis et al., 2009).

(4) Most studies so far have estimated pH of aerosols with only inorganic compounds. However, it has been reported that pH can be affected by organic compounds in several ways. Guo et al., (2015) have shown that the pH can be increased by 0.15 to 0.23 units when aerosol water associated with organic compounds is considered. Omission of the contribution of organic acids to H^+ has been estimated to increase the pH by 0.07±0.03 by Song et al. (2018) using E-AIM-IV. It has been shown recently that accounting for non-ideal mixing can modify the pH such that a fully interactive inorganic–organic system showed a pH roughly 0.7 units higher than that predicted using an inorganic only system by AIOMFAC (Pye et al., 2018).

4 Conclusions

This study compares aerosol pH based on three different standard states (pH_x, pH_m and pH_c) and the corresponding interconversion. It has been shown theoretically that the difference between pH_x (mole fraction based) and pH_m (molality based) is always a constant within a thermodynamic model (1.74, when the solvent is water) regardless of aerosol property. On the other hand, pH_m and pH_c (molarity based) are almost identical with a minor effect from temperature and pressure. However, when the activity coefficient is simplified as unity by thermodynamic models, the difference between pH_m and pH_c ranges from 0.11 to 0.25 pH units, depending on the chemical composition and density of hygroscopic aerosol. Therefore, while evaluating aerosol acidity (especially, trend analysis) when the activity coefficient is simplified as 1, considering the pH scale is important. Overall, we recommend that the standard state of hydrogen activity be defined clearly when pH values are used to characterize the acidity of aerosol, and that pH values are converted to the same scale prior to comparison of acidity. As suggested by (Nenes, 2018), maintaining consistency in terms of pH calculation method and the thermodynamic model used is vital to ensure comparability of aerosol acidity between models and/or observations.

Data availability

Data for this paper are available from the corresponding authors upon request.

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Table 1. List of abbreviations.

Abbreviation	Definition
ac_H	activity of hydrogen ions with standard state of the hypothetical ideal aqueous solution of unit molarity and reference state of infinite dilute solution (dimensionless)
am_H	activity of hydrogen ions with standard state of the hypothetical ideal aqueous solution of unit molality and reference state of infinite dilute solution (dimensionless)
ax_H	activity of hydrogen ions with standard state of the hypothetical pure H^+ solution and reference state of infinite dilute solution (dimensionless)
c^0	unit molarity (1 mol dm^{-3} solution)
c_H	molarity of hydrogen ion (mol dm^{-3} solution)
c_i	molarity of solute species i [a] (mol dm^{-3} solution)
f_H	mole fraction scale activity coefficient
m^0	unit molality (1 mol kg^{-1} solvent)
m_H	molality of hydrogen ions (mol kg^{-1} solvent)
m_i	molality of solute species i [a] (mol kg^{-1} solvent)
M_i	molar mass of solute species i [a] (kg mol^{-1})
M_s	molar mass of single solvent or averaged molar mass for multiple solvents (kg mol^{-1})
pH_c	molarity based pH (dimensionless)
pH_m	molality based pH (dimensionless)
pH_x	mole fraction based pH (dimensionless)
x_H	mole fraction of hydrogen ions (dimensionless, mol H^+ in total moles)
y_H	molarity scale activity coefficient
γ_H	molality scale activity coefficient
ρ_0	density of pure solvent or averaged density for multiple solvents (kg m^{-3})
ρ_{sln}	density of hygroscopic aerosol solution (kg m^{-3})

Note: [a] Solute species i is expressed as dissociated ion for salt.

Table 2. Summary of equations for the interconversion of concertation and activity coefficient based on different standard states.

Parameter	pH_x vs. pH_m	pH_m vs. pH_c	pH_x vs. pH_c
Activity coefficient [a]	$\gamma_H = f_H \frac{x_H}{m_H M_s}$ (4)	$\gamma_\mathrm{H} = 1000 \frac{dm^3}{m^3} \frac{c_H y_\mathrm{H}}{m_H \rho_0}$ (5)	$f_H = y_H 1000 \frac{dm^3}{m^3} \frac{M_s}{\rho_0} \frac{c_H}{x_H}$ (6)
Concentration [b]	$x_H = \frac{m_H}{\sum m_\mathrm{i} + \frac{1}{M_s}}$ (7)	$c_H = \frac{m_H}{\frac{\sum m_i M_i + 1}{\rho_{sln}}}$ (8)	$x_H = \frac{M_s c_H}{M_s \sum c_i + 0.001 \frac{m^3}{dm^3} \rho_{sln} - \sum c_i M_i}$ (9)
pH [c]	$pH_x - pH_m = -\log 10[M_s m^0]$ (10)	$pH_m - pH_c = -\log 10 \frac{c^0 1000 dm^3/m^3}{m^0 \rho_0}$ (11)	$pH_x - pH_c = \log 10 \frac{1000 dm^3/m^3 M_s c^0}{\rho_0}$ (12)

Note: [a] The source of Eqs. (4)-(5) are Robinson and Stokes (2002) and the source of Eq. (6) is Zünd (2007). The details of derivation of Eqs. (4)-(6) are shown in Robinson and Stokes (2002) and Zünd (2007). [b] Eqs. (7)-(9) are based on the definition of each parameter. [c] Eqs. (10)-(12) are derived from Eqs (4)-(6) and (7)-(9) for each standard state.

Table 3. Calculated concentrations, activity coefficient of H^+ and pH for the three thermodynamic models. [a]

	E-AIM-IV	ISORROPIA-II	AIOMFAC
Molar fraction			
x_H	$1.07\times10^{-4}\pm1.28\times10^{-4}$ $(2.17\times10^{-5}–9.49\times10^{-4})$	$3.49\times10^{-5}\pm4.80\times10^{-5}$ $(4.59\times10^{-6}–3.69\times10^{-4})$	$2.71\times10^{-4}\pm3.36\times10^{-4}$ $(4.56\times10^{-5}–2.46\times10^{-3})$
f_H	0.74±0.25 (0.43–1.97)	1 [b]	0.27±0.10 (0.15–0.79)
pH_x	4.26±0.28 (3.16–4.82)	4.63±0.36 (3.43–5.34)	4.31±0.27 (3.24–4.86)
Molality			
m_H	$7.80\times10^{-3}\pm9.52\times10^{-3}$ $(1.50\times10^{-3}–7.03\times10^{-2})$	$2.60\times10^{-3}\pm3.64\times10^{-3}$ $(3.18\times10^{-4}–2.80\times10^{-2})$	$1.98\times10^{-2}\pm2.50\times10^{-2}$ $(3.14\times10^{-3}–1.82\times10^{-1})$
γ_H	0.57±0.19 (0.35–1.54)	1 [b]	0.21±0.08 (0.12–0.62)
pH_m	2.52±0.28 (1.41–3.07)	2.77±0.36 (1.55–3.50)	2.56±0.27 (1.50–3.11)
Molarity			
c_H	$5.56\times10^{-3}\pm6.59\times10^{-3}$ $(1.14\times10^{-3}–4.89\times10^{-2})$	$1.73\times10^{-3}\pm2.35\times10^{-3}$ $(2.38\times10^{-4}–1.80\times10^{-2})$	$1.43\times10^{-2}\pm1.76\times10^{-2}$ $(2.48\times10^{-3}–1.30\times10^{-1})$
y_H	0.79±0.26 (0.45–2.04)	1 [b]	0.28±0.10 (0.16–0.75)
pH_c	2.52±0.28 (1.41–3.07)	2.94±0.35 (1.75–3.62)	2.56±0.27 (1.50–3.11)

Note: [a] All parameters are shown as average ± standard deviation with the range in bracket except for [b] activity coefficient of ISORROPIA-II which is assumed to be 1.

Table 4. Comparison of acidity of selected samples based on different scales.

#	pH_m	m_H	pH_c	c_H
S-I	2.70	2.01×10^{-3}	2.92	1.21×10^{-3}
S-II	2.75	1.80×10^{-3}	2.87	1.34×10^{-3}
Difference (Δ)	-0.05	2.0×10^{-4}	0.05	-1.3×10^{-4}

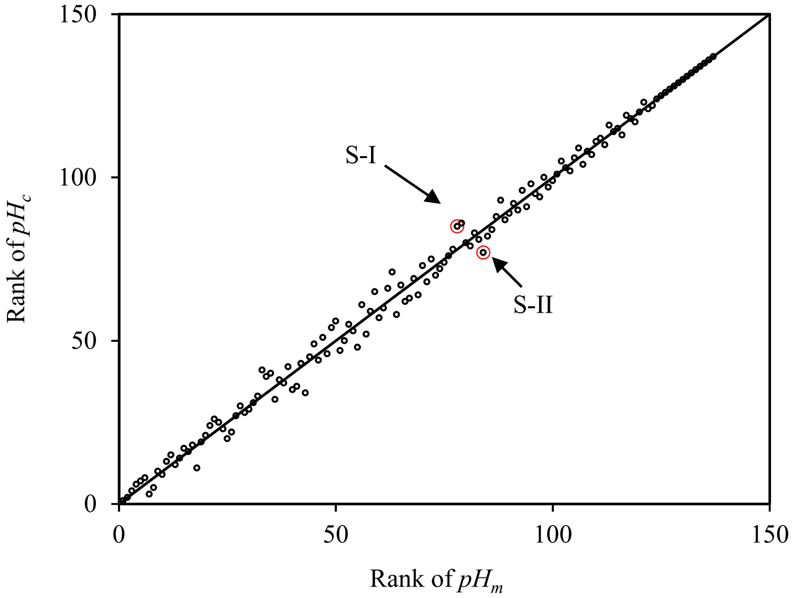

Figure 1. Comparison of the rank of pH_m and pH_c