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 for the first time by providing a theoretical framework to compare and convert between aerosol pH values calculated based on molarity, molality and mole fractions. 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) and follow the same trend, regardless of aerosol property. The difference between pH_x and pH_c (molarity based), on the other hand, ranges from 1.74 to 1.89 depending on the density of hygroscopic aerosol. It is observed that application of this pH standardization protocol can significantly influence conclusions on aerosol acidity reported by past studies and is thus highly recommended.

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 NH_3 and

5   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 from volatile organic compounds

such as octanal, carbonyls, isoprene, limonene, and caryophyllene (Jang et al., 2002).

The acidity of aerosols can be quantified by parameters such as strong acidity, free acidity, cation-to-anion

10   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). The most accurate parameter to

characterize aerosol acidity is considered to be pH since the remaining parameters do not offer information on

how acidic the particles are when they are present as aqueous droplets (Pathak et al., 2004). However, the standard

definition of pH as per the International Union of Pure and Applied Chemistry (IUPAC) in 1984, i.e. the negative

15   log activity of hydrogen ions (Covington et al., 1985), can vary depending on the selected standard state of the

activity of hydrogen ions. The commonly used standard states include 1 mol $H^+ L^{-1}$ (molarity based), 1 mol H^+ kg^{-1}

water (molality based) (Covington et al., 1985) and pure H^+ (mole fraction based) (Zhang et al., 2007).

Molarity-based pH is the most commonly used scale in aquatic chemistry since the equilibrium constant is

often determined based on molarity (Squizzato et al., 2013); it is also the most widely used scale for characterizing

20   aerosol acidity (Cheng et al., 2011; Pathak et al., 2009; Yao et al., 2007; Yao et al., 2006, etc.). Mole fraction-

based pH has also been used to characterize the acidity of hygroscopic aerosols (Squizzato et al., 2013; Weber et

al., 2016; Zhang et al., 2007; Hennigan et al., 2015) as this approach is more convenient to describe solutions with

high concentrations (Rard et al., 2010). For most purposes in aqueous chemistry, the difference between molality-

and molarity-based pH can be ignored since the solution is dilute (Covington et al., 1985). However, ions in

25   hygroscopic aerosol can be very concentrated (Fountoukis and Nenes, 2007), and thus the difference between

molarity and molality based pH cannot be neglected. Although the IUPAC Gold Book defines pH based on

molality (McNaught and Wilkinson, 1997), this approach is rarely used in aerosol acidity characterization.

It therefore 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 (Huang et

al., 2011). In fact, pH based on different definitions has 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-based pH. Additionally, pH values obtained via different definitions are sometimes cross-compared, e.g., Squizzato et al. (2013) stated that pH of PM$_{2.5}$ in the

5 Po Valley, Italy (mole fraction-based) was much higher than those in megacities in China (Pathak et al., 2009) (molarity-based), which needs 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 define and compare, for the first time, the PM$_{2.5}$ aerosol pH based on different scales (molarity, molality and mole fraction). Further, in order to

10 enable other researchers to easily compare pH of different scales, an inter-scale conversion factor for pH has been developed.

2 Materials and Methods

2.1 Evaluation data set

A set of field data collected in Guangzhou, China was used to evaluate pH values calculated based on

15 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 and the total number of valid samples was 440.

20 ### 2.2 pH calculation

The Extended Aerosol Inorganic Model (E-AIM)-IV (http://www.aim.env.uea.ac.uk /aim/aim.php) (Friese and Ebel, 2010; Wexler and Clegg, 2002) was adopted to estimate pH of aerosols. The concentrations of Cl$^-$, SO$_4^{2-}$, NO$_3^-$, NH$_4^+$ and Na$^+$ in particulate phase were obtained from the hourly monitoring system described above; the concentrations of H$^+$ were calculated based on charge balance.

25 The E-AIM outputs used for pH calculation include mole fraction-based activity coefficient of hydrogen (f_H), mole fraction of hydrogen (x_H), molality of hydrogen (m_H), and density of the hygroscopic aerosol (ρ_{sln}). Detailed calculations of pH in different scales are described below. The reference state for the activity coefficients of

hydrogen ion is the solution of infinite dilution (with respect to water). Abbreviations used in this study are summarized in Table 1.

2.2.1 Mole fraction-based pH (pH_x)

Since both f_H and x_H are direct outputs from E-AIM, pH_x can be readily obtained using Eq. 1 below.

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

2.2.2 Molality-based pH (pHm)

Since the molality-based activity coefficient (γ_H) was not directly available as output from the AIM model, γ_H needs to be obtained with Eq. 2 (Clegg et al., 1998).

$$\gamma_H = f_H \frac{1000}{Ms \sum m_i + 1000} \tag{2}$$

pH_m can be accordingly calculated using Eq. 3.

$$pH_m = -\lg(a_{m_H}) = -\lg(\frac{\gamma_H m_H}{\text{mol/kg water}}) \tag{3}$$

2.2.3 Molarity-based pH (pH_c)

Neither the molarity of hydrogen (c_H) nor the molarity-based activity coefficient of hydrogen (y_H) is direct output from the AIM model. y_H can therefore be obtained with Eq. 4 (van Boekel, 2008).

$$y_H = f_H \frac{\rho_{\text{sln}}}{\rho_{\text{sln}} + 0.001[M_s \sum c_i - \sum c_i M_i]} \tag{4}$$

The relationship between x_H and c_H can be described as Eq.5 according to the definition of x_H.

$$x_H = \frac{c_H}{\dfrac{1000\rho_{\text{sln}} - \sum c_i M_i}{Ms} + \sum c_i} \tag{5}$$

pH_c can be consequently calculated using Eq. 6.

$$pH_c = -\lg(a_{c_H}) = -\lg(\frac{y_H c_H}{\text{mol/dm}^3}) \tag{6}$$

3 Results and Discussion

3.1 Scale comparison of pH_x, pH_c and pH_m

To evaluate pH results obtained from different scales, the temporal trends of pH_x, pH_m and pH_c for

atmospheric PM$_{2.5}$ are represented in Fig. 1. It is apparent that pH_x, pH_m and pH_c are different among scales; while most pH_m and pH_c values are negative, pH_x values are mostly positive. pH_x is the highest among the three scales and pH_c is slightly higher than pH_m. These results clearly indicate that pH_x, pH_m and pH_c cannot be compared.

3.2 Interconversion of pH_x, pH_c and pH_m

5   In order to cross-compare pH from different scales, an interconversion of pH_x, pH_m and pH_c needs to be conducted as discussed below.

3.2.1 Interconversion of pH_x and pH_m

Based on the definition of x_H, the relationship between x_H and m_H can be described as Eq. 7.

$$x_H = \frac{m_H}{\frac{1000}{M_s} + \sum m_i} \tag{7}$$

10   Combining Eqs. 1-3 and 7, the relationship between pH_x and pH_m can be obtained as Eq. 8.

$$pH_x - pH_m = -\lg \frac{f_H x_H}{\gamma_H m_H} = -\lg \frac{Ms}{1000} = 1.74 \tag{8}$$

Therefore, the conversation of pH_x and pH_m can be readily conducted through Eq. 8, and the difference between pH_x and pH_m is fixed at 1.74 pH units regardless of aerosol properties. This is supported by our field data (shown in Fig. 1 and Fig. S1 of Supplement) with a constant difference of 1.74 between pH_x and pH_m.

15   **3.2.2 Interconversion of pH_x and pH_c**

Combining Eqs. 1 and 4-6, the relationship between pH_x and pH_c can be obtained as Eq. 9 below.

$$pH_x - pH_c = -\lg \frac{f_H x_H}{c_H y_H} = -\lg \frac{0.001 Ms}{\rho_{sln}} = 1.74 + \lg \rho_{sln} \tag{9}$$

It can be concluded from Eq. 9 that the difference between pH_x and pH_c depends on the density of the hygroscopic aerosol. In order to obtain the range of the difference between pH_x and pH_c, the lower and upper

20   bounds of the density of hygroscopic aerosol need to be considered. The density of pure water (1 kg dm^{-3}) is taken as the lower bound for hygroscopic aerosol since all disolved salts in aerosol have higher densities than that of pure water. Considering that ammonium and sulfate are generally the most abundant ionic species in aerosol, the density of hygroscopic aerosol with the highest concentraion of ammonium sulfate (under its efflorescence relative humidity (ERH) 38%) is taken as the upper bound (1.4 kg dm^{-3}, calculated using AIM). In this case, the

corresponding lower bound and upper bound of pH_x-pH_c are obtained as 1.74 and 1.89, respectively. It is worthwhile to note that the difference between the lower and upper bounds of pH_x - pH_c is only 0.15 pH unit (1.74 to 1.89) due to the influence of aerosol density; however, it could not be neglected as the H^+ concentration can change significantly by up to 41% corresponding to a change of 0.15 pH unit.

5   As shown in Fig. S2 (Supplement), pH_x and pH_c are highly correlated (r=0.9998). A linear equation can be defined between pH_x and pH_c with intercept of -1.84 pH units, which indiates that the difference between pH_x and pH_c (pH_x - pH_c) is 1.84±0.02 (n=440). The small standard devation (1%) of pH_x - pH_c is due to the small fluctuation (relative standard deviation < 4%) in the density of hygroscopic aerosol (1.25±0.05 kg dm⁻³). Since the density of aerosol may not be always reported in published articles, Eq. 10 could be used as an empirical equation for the

10   interconversion between pH_x and pH_c as an approximation when the density of aerosol is not available.

$$pH_x - pH_c = 1.84 \tag{10}$$

As mentioned previous study by Squizzato et al. (2013), it showed that the pH of PM$_{2.5}$ in megacities in China (pH_c, ranging from -0.38 to 0.61) are much lower than that in the Po Valley, Italy (pH_x, ranging from 2.0 to 2.5). Now we have known that pH_c and pH_x could not be directly compared. As a demonstration of the applicability

15   of Eq. 10 developed here, pH data from Squizzato et al. (2013) could be converted from pH_x to pH_c scales using Eq. 10. Upon transformation, it is noteworthy to observe that the pH_x of PM$_{2.5}$ in some cities in China could actually be higher than that of the PM$_{2.5}$ particles in some regions in Italy. For example, pH_c in Guangzhou, China (pH_c = 0.61) is actually higher than the pH_c in the industrial areas in the Veneto region (pH_c = 0.16).

3.3 Trend comparision of pH_x, pH_c and pH_m

20   Figure 1 shows that although pH_x and pH_m are in different scales, their overall trends are in good agreement. This is expected as the interconversion between pH_x and pH_m does not rely on the property of aerosol. However, the interconversion between pH_x and pH_c is dependent on the density of aerosol, which in turn varies with relative humidity, chemical properties etc., thus affecting the trends. To investigate the trend comparison between pH_x and pH_c, their ranks (n = 440, in desending order) are plotted in Fig. 2. The points deviating from 1:1 line indicate

25   samples possessing different ranks according to pH_x 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. 2). As shown in Table 2, S-I is more acidic than S-II upon comparison of pH_x and pH_m values. However, in terms of pH_c, S-I is less acidic than S-II. Although ΔpH_m

(0.04) is only 0.07 pH unit higher than ΔpH_c (-0.03), the difference in H$^+$ concentration cannot be neglected. The hydrogen activity of S-II is 0.65 (mol kg^{-1} water) (6.7%) higher than that of S-I based on molality of hydrogen ion, however the hydrogen activity of S-II is even 0.64 (mol dm^{-3}) (7.8%) lower than that of S-I based on molarity of hydrogen ion. Therefore, while evaluating aerosol acidity (especially, trend analysis), considering the pH scale

5   is of utmost importance.

We acknowledge here that uncertainties exist for the methods used to calculate aerosol acidity. For example, the choice of forward or backward mode of the therodynamic model to estimate acidity is debatable (Hennigan et al., 2015; Yao et al., 2006). In addition, the role of organic compounds in affecting aerosol acidity is still being discussed (Pye et al., 2018). However, it should be noted that the method to calculate aerosol acidity is not the

10   focus of current study. The relationship between pH_x, pH_c and pH_m established in this study is valid regardless of the method selected to estimate aerosol acidity.

4 Conclusions

This study compares pHs (pH_x, pH_m and pH_c) of aerosol based on three different standard states and the corresponding interconversion between the three pHs. It is established that pH_x is always 1.74 pH unit higher than

15   pH_m regardless of aerosol property. The difference between pH_x and pH_m ranges from 1.74 to 1.98 depending on the density of hygroscopic aerosol. The trend of pH_x and pH_m are always the same, however the trend of pH_x and pH_c could be different due to the influence of aerosol density. It is recommended that the standard state of hydrogen activity should be defined clearly when pH value is used to characterize the acidity of aerosol, and it is very critical that pH has to be converted to the same scales prior to the comparison of acidity. Additionally, the scale for

20   investigating the trend of the aerosol acidity must be considered.

Data availability

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

Acknowledgements

The authors thank Dr. Krishnan Padmaja for her helpful comments and discussion during the preparation of

25   the manuscript. This work has been funded by the (1) National Key Research and Development Program of China under 2017YFC0210105, (2) National Science Fund for Distinguished Young Scholars under 41425020, (3)

Science and Technology Planning Project of Guangdong Province, China under 2016B050502005 and (4)
Guangdong Natural Science Foundation under 2017A030313234.

Supplement

Figures showing comparison between pH_x, pH_m and pH_c are provided.

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Table 1. Abbreviations.

Abbreviation	Definition
x_H	mole fraction of hydrogen ions (dimensionless, mol in total moles)
f_H	activity coefficient of hydrogen ions based on mole fraction of hydrogen ions (dimensionless)
ρ_{sln}	density of hygroscopic particle (g cm^{-3})
m_H	molality of hydrogen ions (mol kg^{-1} water)
pH_x	mole fraction based pH (dimensionless)
pH_m	molarity based pH (dimensionless)
γ_H	activity coefficient of hydrogen ions based on molality of hydrogen of hydrogen ions (dimensionless)
Ms	molecular mass of water (18 g mol^{-1})
m_i	molality of solute species i (mol kg^{-1} water)
M_i	molecular mass of solute species i (g mol^{-1})
c_i	molarity of solute species i (mol dm^{-3})
c_H	molarity of hydrogen ion (mol dm^{-3})
y_H	activity coefficient of hydrogen ions based on molarity of hydrogen ion (dimensionless)
pH_c	molarity based pH
ax_H	activity of hydrogen ion based mole fraction of hydrogen ions
ac_H	activity of hydrogen ion based molarity of hydrogen ions
am_H	activity of hydrogen ion based molality of hydrogen ions

Table 2. Comparison of acidity of selected samples based on different scales.

#[a]	pH_x	ax_H	pH_m	am_H	pH_c	ac_H	density (g cm⁻³)
S-I	0.83	0.15	-0.91	8.18	-0.99	9.74	1.19
S-II	0.87	0.14	-0.87	7.54	-1.02	10.39	1.38
Difference (Δ)	0.04	-0.01	0.04	-0.64	-0.03	0.65	0.19

[a]S-I was collected during 4-5 pm on 25th Jul., 2013 and S-II was collected during 7-8 pm on 27th Jul., 2013.
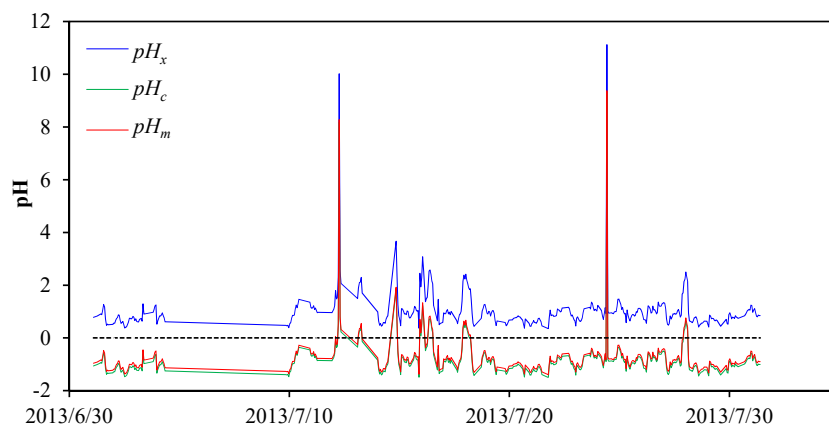
Figure 1. Temporal trend of pH_x, pH_c and pH_m
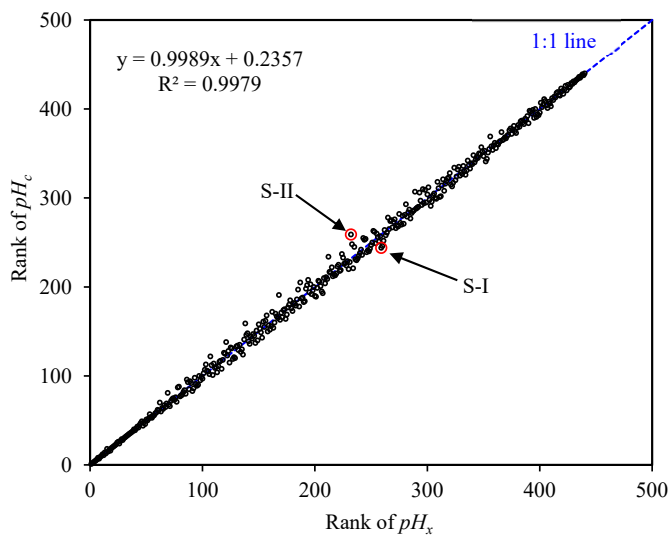
Figure 2. Comparison of the rank of pH_x and pH_c