



A critical evaluation of proxy methods used to estimate the acidity of atmospheric particles

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Abstract

Given significant challenges with available measurements of aerosol acidity, proxy methods are frequently used to estimate the acidity of atmospheric particles. In this study, four of the most common aerosol acidity proxies are evaluated and compared: (1) the ion balance method, (2) the molar ratio method, (3) thermodynamic equilibrium models, and (4) the phase partitioning of ammonia. All methods are evaluated against predictions of thermodynamic models and against direct observations of aerosol-gas equilibrium partitioning acquired in Mexico City during the MILAGRO study. The ion balance and molar ratio methods assume that any deficit in inorganic cations relative to anions is due to the presence of H^+ ; and that a higher H^+ loading and lower cation/anion ratio both correspond to increasingly acidic particles (i.e., lower pH). Based on the MILAGRO measurements, no correlation is observed between H^+ levels inferred with the ion balance and aerosol pH predicted by the thermodynamic models and ammonia–ammonium ($NH_3-NH_4^+$) partitioning. Similarly, no relationship is observed between the cation / anion molar ratio and predicted aerosol pH. Using only measured aerosol chemical composition as inputs without any constraint for the gas phase, the Extended Aerosol Inorganics Model (E-AIM) and ISORROPIA-II thermodynamic equilibrium models tend to predict aerosol pH levels that are inconsistent with the observed $NH_3-NH_4^+$ partitioning. The modeled pH values from both models run with gas + aerosol inputs agreed well with the aerosol pH predicted by the phase partitioning of ammonia. It appears that (1) thermodynamic models constrained by gas + aerosol measurements, and (2) the phase partitioning of ammonia provide the best available predictions of aerosol pH. Furthermore, neither the ion balance nor the molar ratio can be used as surrogates for aerosol pH, and published studies to date with conclusions based on such acidity proxies may need to be reevaluated. Given the significance of acidity for chemical processes in the atmosphere, the implications of this study are important and far reaching.

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1 Introduction

The acidity of atmospheric particles is a critical parameter that affects air quality and the health of aquatic and terrestrial ecosystems. Acute and chronic exposures to acidic particles have been linked to deleterious effects in people, although the underlying physiological mechanisms are unclear (Gwynn et al., 2000; Dockery et al., 1996). The deposition of acidic gases and particles has been known for decades to damage fresh-water and terrestrial ecosystems (Schindler, 1988; Johnson et al., 2008). While the trends in emissions are promising in the US and western Europe, ecosystem recovery from the effects of acid deposition is a slow process that can take decades (Likens et al., 1996; Stoddard et al., 1999). This may be a source of emerging environmental crisis in places such as China, where acid deposition is increasing due to rapid industrialization (Pan et al., 2013; Cao et al., 2013). Particle acidity also affects global biogeochemical cycles by controlling the solubility – and thus, bioavailability – of limiting nutrients that are delivered through atmospheric deposition in many marine environments (Meskhidze et al., 2005, 2003; Nenes et al., 2011). This has important implications for marine primary productivity, the carbon cycle, and even climate (Mahowald, 2011).

Particle acidity is also a critical factor that influences many chemical processes in the atmosphere. The oxidation of S(IV) to S(VI) in liquid water, the primary pathway of sulfate formation, is highly sensitive to pH (Chameides, 1984). Halogen chemistry is strongly influenced by particle acidity, which has direct implications for the oxidation of volatile organic compounds (VOCs) and ozone formation in coastal regions (e.g., Keene et al., 1998; Sander and Crutzen, 1996; Pszenny et al., 2004). Recent evidence suggests this effect may be important in continental locations, as well (Thornton et al., 2010). Further, aerosol acidity directly affects the deposition and lifetime of many compounds in the atmosphere through its influence on the gas-particle partitioning of semi-volatile species, including ammonia (NH₃), nitric acid (HNO₃), and organic acids (Ahrens et al., 2012; Keene et al., 2004). Aerosol acidity may affect secondary organic aerosol (SOA) formation, as well (e.g., Gaston et al., 2014; Surratt et al., 2007),

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although the atmospheric importance of this phenomenon remains highly uncertain (Peltier et al., 2007; Takahama et al., 2006; Tanner et al., 2009; Zhang et al., 2007).

Despite its significance, aerosol acidity remains very poorly constrained in the atmosphere (Keene et al., 1998). All direct measurements employ filter sampling (e.g., Jang et al., 2008; Keene et al., 2002; Koutrakis et al., 1988), which is both labor intensive and limited by poor time resolution. Measurements are also challenged by the non-conservative nature of H^+ : analysis procedures such as dilution in water prevent the direct translation of filter extract measurements to conditions within the particles. Certain methods are also susceptible to sampling artifacts, which can greatly increase the uncertainty of an inherently challenging measurement (Pathak et al., 2004). Due to these limitations, indirect methods are frequently employed to estimate the acidity of atmospheric particles. These methods include (1) the ion balance method, (2) the molar ratio, (3) thermodynamic equilibrium models, and (4) the phase-partitioning of semi-volatile species (HCl , NH_3 , HNO_3). The purpose of this study is to evaluate and compare the proxy methods most commonly used to estimate aerosol acidity.

2 Methods to infer pH

Before proceeding with this analysis, it is necessary to define the different physical quantities commonly described by the term “aerosol acidity”. First, it is used to represent the pH of an aerosol particle or distribution. The pH represents the hydrogen ion activity in an aqueous solution (Stumm and Morgan, 1996):

$$pH = -\log(\gamma \cdot x_{H^+}) \quad (1)$$

where γ is the hydrogen ion activity coefficient and x_{H^+} is the aqueous mole fraction of dissociated H^+ . The presence of aerosol water is implicit in this definition since free H^+ cannot exist in solid particles. Second, “aerosol acidity” is commonly used to describe the loading of protons in atmospheric particles, in units of $nmolm^{-3}$. This definition can take several forms, including aerosol strong acidity (H^+) or total acidity

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(H_{tot}), typically defined by the measurement approach (Keene et al., 2004; Lawrence and Koutrakis, 1996). The major difference between aerosol pH and the proton loading is that pH is a measurement relative to the liquid solvent volume (i.e., aerosol water) while the aerosol proton loading is the concentration in reference to an air volume. The true quantity, however, driving much of the processes described above is pH; H^+ is insufficient to truly distinguish the acidity as it scales with aerosol mass. This is a critical distinction that will be discussed in detail below, especially in relation to the appropriate use of each parameter for the analysis of chemical processes in the atmosphere.

2.1 Ion balance method

The ion balance method is commonly employed to estimate the proton loading in atmospheric particles. This method is based upon the principle of electroneutrality, and assumes that any deficit in measured cationic charge compared to measured anionic charge is due to the presence of protons, according to:

$$[H^+] = \sum (\text{anions}) + [OH^-] - \sum (\text{cations}) \quad (2)$$

where all concentrations are in milliequivalents to account for multiply charged species. If the sum of measured cations exceeds that of the measured anions, then the difference is attributed to hydroxide (OH^-). H^+ levels under an anion deficit are calculated from the inferred $[OH^-]$ using the water dissociation constant, K_w . Most applications of the ion balance use inorganic ions only, even though organic acids can be important to the interpretation of aerosol acidity in diverse locations (Lawrence and Koutrakis, 1996; Metzger et al., 2006; Trebs et al., 2005), especially at relatively low acidities where organic acids dissociate and contribute to the ion balance. Organic compounds can also form salt complexes with inorganic species (e.g., ammonium oxalate) (Reid et al., 1998), further indicating the importance of organic acids in the ion balance.

2.2 Molar ratio

While the ion balance method is used to estimate the absolute proton loading in atmospheric particles, the molar ratio is independent of absolute concentrations. The molar ratio is a ratio of the measured inorganic cations to the measured inorganic anions:

$$\text{Molar ratio} = \frac{\sum(\text{cations})}{\sum(\text{anions})} \quad (3)$$

where all concentrations are again in milliequivalents. The concept was first introduced in thermodynamic models to define major ions and composition domains (e.g., Pilinis and Seinfeld, 1987; Nenes et al., 1998; Kim et al., 1993; Fountoukis and Nenes, 2007), but never to infer the levels of acidity and pH. Thermodynamic models using the major species/composition domain approach (e.g., Fountoukis and Nenes, 2007) consider the possibility that aerosol species may volatilize enough to affect the ratio at equilibrium. Furthermore, the degree of dissociation of species such as $\text{H}_2\text{SO}_4/\text{HSO}_4^-/\text{SO}_4^{2-}$, $\text{HNO}_3/\text{NO}_3^-$, HCl/Cl^- , and $\text{NH}_3/\text{NH}_4^+$ can affect the value of the ratio. In subsequent studies, however, the molar ratio has been treated as a proxy for acidity, with lower ratios corresponding to particles with the highest levels of acidity (lowest pH) (Kerminen et al., 2001). Molar ratios of unity or greater are assumed for fully neutralized aerosol. Two common simplifications of the molar ratio approach are often applied when the concentrations of crustal elements are relatively low (e.g., Zhang et al., 2007):

$$\text{Molar ratio} = \frac{\text{NH}_4^+}{\left(\text{Cl}^- + \text{NO}_3^- + 2 \cdot \text{SO}_4^{2-}\right)} \quad (4)$$

and (e.g., Peltier et al., 2007; Tanner et al., 2009; Froyd et al., 2010):

$$\text{Molar ratio} = \frac{\text{NH}_4^+}{\left(2 \cdot \text{SO}_4^{2-}\right)}. \quad (5)$$

2.3 Thermodynamic equilibrium models

Several thermodynamic equilibrium models have been developed to predict the behavior – most commonly the phase partitioning, liquid water content, and chemical

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speciation – of inorganic aerosol precursors. Previous studies have performed detailed comparisons and have explored the causes of disagreement among different thermodynamic equilibrium models (Ansari and Pandis, 1999; Zhang et al., 2000). We do not attempt to repeat this exercise. Instead, thermodynamic models are considered as one method to estimate the acidity of atmospheric particles. Two models are used in the present analysis: ISORROPIA-II (Fountoukis and Nenes, 2007; Nenes et al., 1999) and the Extended Aerosol Inorganic Model (E-AIM) (Clegg et al., 1998, 2003; Wexler and Clegg, 2002). ISORROPIA-II was designed with high computational efficiency to facilitate its incorporation in large-scale models and has seen wide usage. E-AIM is computationally expensive but is considered the benchmark since it employs few assumptions in its calculation of aerosol inorganic behavior (Zaveri et al., 2008).

Two applications of each model are considered (Fountoukis et al., 2009): (a) “forward” (or “closed”) mode calculations, in which inputs to the model include temperature (T), relative humidity (RH) and the total (gas + aerosol) concentrations of aerosol precursors in the air parcel, and, (b) “reverse” (or “open”) calculations, in which inputs to the model include T , RH and the concentration of aerosol species. The output of both calculations is the concentration of species in the gas and aerosol (solid/liquid) phases, pH, and aerosol water. Highly time-resolved measurements of aerosol composition (e.g., via Particle-into-Liquid Sampler or Aerodyne Aerosol Mass Spectrometer) are frequently conducted without the corresponding gas-phase aerosol precursor measurements (HCl, HNO₃, NH₃). Under this condition, it is conceptually straightforward to run the thermodynamic models in “reverse” mode, and this approach is frequently applied to analyze ambient data. In this analysis, we consider aerosol acidity predictions using both methods.

2.4 Phase partitioning

Aerosol pH can also be estimated from the phase partitioning of certain semi-volatile compounds, such as HNO₃/NO₃⁻, NH₃/NH₄⁺, and HCl/Cl⁻ (e.g., Keene et al., 2004; Meskhidze et al., 2003). The H⁺ concentration in aqueous particles can be calculated

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assuming that the system is in equilibrium (using $\text{HNO}_3/\text{NO}_3^-$ as an example):



Under this approach, both the gas-phase and aerosol ionic components are measured, and the liquid H^+ concentration can be calculated after combining the equilibrium expressions from Reactions (R1) and (R2):

$$[\text{H}^+] = \frac{K_{\text{H}}K_{\text{a}}p\text{HNO}_3}{[\text{NO}_3^-]}, \quad (6)$$

where $[\text{H}^+]$ is the molar concentration of H^+ in atmospheric particles, K_{H} is the temperature-dependent Henry's law constant, K_{a} is the temperature-dependent acid dissociation constant, $p\text{HNO}_3$ is the gas-phase partial pressure of nitric acid, and $[\text{NO}_3^-]$ is the aqueous concentration of aerosol nitrate. Since aerosol components are measured in reference to their concentrations in air, the aerosol liquid water content is required to derive $[\text{NO}_3^-]$ (e.g., to convert from $\mu\text{g m}^{-3}$ to mol L^{-1}). This is most often calculated from thermodynamic equilibrium models (e.g., see Table 6 of Fountoukis and Nenes, 2007). The H^+ activity coefficient can also be calculated from thermodynamic equilibrium models in order to convert the molar H^+ concentration to pH (Eq. 1), although the simplifying assumption of $\gamma = 1$ is sometimes employed, with satisfactory results (Fountoukis and Nenes, 2007).

2.5 Evaluation dataset

We evaluate the above methods using ground-based data collected during the MLAGRO campaign at the T1 site in Mexico City (Molina et al., 2010). The measurements spanned 1–30 March 2006. Inorganic $\text{PM}_{2.5}$ composition was measured with a Particle-into-Liquid Sampler coupled to a dual ion chromatograph (Hennigan et al.,

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2008). Ammonia was measured with a quantum cascade laser spectrometer (Aerodyne Research, Inc.). Nitric acid was measured via thermal dissociation-laser induced fluorescence of nitrogen oxides (Day et al., 2002; Farmer et al., 2011). All chloride was assumed to reside in the particle phase (i.e., gas-phase HCl was effectively zero), which was determined to be a valid assumption given the high concentration of gas-phase NH_3 (Fountoukis et al., 2009).

The chemical measurements, along with ambient temperature and RH, were used as inputs into ISORROPIA-II and E-AIM. Fountoukis et al. (2009) evaluated the equilibrium partitioning of semi-volatile compounds at T1 using ISORROPIA-II. We do not duplicate that effort here: instead, we focus solely on particle acidity and the comparison across the different proxy methods described above. For the “reverse” model runs, aerosol concentrations only were used while the “forward” model runs used total gas + aerosol inputs. The forward model runs were only performed if all three measurements (NH_3 , HNO_3 , and $\text{PM}_{2.5}$ inorganics) were operational for a given sampling interval, explaining the difference in sample numbers between the forward and reverse simulations. ISORROPIA-II models runs were performed in “metastable” mode where the aerosol is only in the aqueous phase and can be supersaturated (<http://isorro피아.eas.gatech.edu/>). ISORROPIA treats the $\text{Na}^+ - \text{NH}_4^+ - \text{K}^+ - \text{Ca}^{2+} - \text{Mg}^{2+} - \text{Cl}^- - \text{NO}_3^- - \text{SO}_4^{2-}$ system. For conditions of excess cations, ISORROPIA-II assumes that bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) account for the deficit and a pH limit of 7 is imposed (as in Fig. 4). Model version AIM-IV was used for RH conditions greater than 60% and model version AIM-II was used for RH conditions between 40–60% (<http://www.aim.env.uea.ac.uk/aim/aim.php>). AIM-IV treats the $\text{Na}^+ - \text{NH}_4^+ - \text{Cl}^- - \text{NO}_3^- - \text{SO}_4^{2-}$ system while AIM-II treats $\text{NH}_4^+ - \text{NO}_3^- - \text{SO}_4^{2-}$. For AIM, measured cations not treated by the model were accounted for as equivalent sodium (Na^*) in AIM-IV and equivalent ammonium (NH_4^*) in AIM-II. Cl^- was accounted for as equivalent sulfate (SO_4^*) in AIM-II. E-AIM assumes that OH^- balances any excess cations, and thus has regions of higher predicted aerosol pH (e.g., Fig. 4).

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E-AIM model runs were performed in solid + liquid mode where salts precipitate once the aqueous solution becomes saturated. Overall, strong similarities between E-AIM and ISORROPIA suggest that the choice of metastable vs. stable (solid + liquid) mode did not appreciably affect the predicted aerosol pH levels. Given the importance of aerosol liquid water, data below 40 % RH were excluded from the analysis. During the MILAGRO study, this was approximately 50 % of the total measurement period. Further, points with modeled aerosol liquid water content of zero were excluded from the analysis since a pH cannot be derived for these samples.

3 Results and discussion

3.1 Ion balance vs. aerosol pH

Figure 1a shows a frequency distribution for the ion balance during MILAGRO. Approximately 75 % of the paired cation-anion measurements had a cation deficit and would thus be inferred as acidic according to the ion balance. Figure 1b shows the aerosol pH predicted by E-AIM corresponding to the inorganic ion balance. The data follow the traditional titration curve shape, with those points having a negative ion balance (anions > cations) all having predicted pH below 3.0 and points having a positive ion balance (cations > anions) all having predicted pH above 7.8.

The ion balance is frequently treated as a proxy for aerosol pH. That is, conditions of high aerosol H⁺ loading (in nmol m⁻³) are assumed to produce similar effects to conditions in which an aerosol distribution has a low (acidic) pH (e.g., Guo et al., 2012; Feng et al., 2012). Figure 2 shows the relationship between predicted aerosol pH and the H⁺ concentration inferred from the ion balance. An anion deficit in the ion balance is assumed to be due to OH⁻ (Eq. 2) – implying extremely low H⁺ levels – so we only considered the data with a negative ion balance ($n = 340$). Figure 2 shows no correlation between the H⁺ loading and the predicted aerosol pH. The black horizontal bars represent the median aerosol pH for the lowest 25th percentile of H⁺ loadings (blue

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diamonds), the 25th–75th percentile of H^+ loadings (green circles), and the highest 25th percentile of H^+ loadings (orange squares). In all three cases, the aerosol is predicted to be highly acidic, and the differences are small between the groups. Numerous points in the lowest H^+ quartile have pH levels below the median pH of the upper H^+ quartile. Similarly, for a given H^+ loading, a wide pH range of ~ 2 – 3 pH units is typically predicted. This wide pH range is observed across all H^+ loadings, even at the high and low ends, because aerosol liquid water content and the H^+ activity coefficient can differ dramatically for a given H^+ level. The ion balance method is insensitive to either of these factors that are critical in determining aerosol pH (Eq. 1). Pathak et al. (2009) found a similar disconnect between H^+ inferred from the ion balance and predicted aerosol pH for measurements in four cities across China.

A further problem with the ion balance is that it is unable to distinguish between free and undissociated H^+ (e.g., protons associated with bisulfate (HSO_4^-)) (Keene et al., 2004). This limitation becomes very important when the solution pH approaches the pK_a of any major ion that is associated with acidity, including HNO_3 , HCl, and NH_3 . The pK_a of HSO_4^- is 1.99 (Stumm and Morgan, 1996), and at pH levels below 3 (i.e., all of the data in Fig. 2), the bisulfate/sulfate equilibrium begins to shift appreciably towards the protonated form, implying that the ion balance overestimates H^+ . This is illustrated in Fig. 3a and b, which show the H^+ level inferred from the ion balance compared to the H^+ loading predicted by E-AIM and ISORROPIA (both run in reverse mode), respectively. Although the thermodynamic models use electroneutrality to derive H^+ , they account for partial dissociation, which explains why the ion balance gives H^+ levels that are ~ 45 – 65 % higher than the models.

These results strongly suggest that the ion balance is inadequate to represent the pH of atmospheric particles. The ion balance may provide a qualitative indication of acidic conditions, but, even then, cannot qualitatively distinguish alkaline particles from mildly acidic particles due to uncertainties in the aerosol composition measurements. This recommendation against the use of the ion balance as a surrogate for aerosol pH is supported by prior work (Keene and Savoie, 1998; Winkler, 1986). The H^+ con-

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centration derived from the ion balance is often just a surrogate for sulfate, especially in environments where sulfate is the dominant inorganic species (Pathak et al., 2009; Zhang et al., 2007). It is possible – likely even – to simultaneously have particles with a low concentration of H^+ (in nmol m^{-3}) that are highly acidic (low pH). Studies that infer the effects of particle acidity on atmospheric chemical processes using the inorganic ion balance are likely flawed. For example, correlations between SOA and aerosol H^+ concentrations (from the ion balance) have been interpreted as evidence for acid-catalyzed SOA formation (Feng et al., 2012; Guo et al., 2012; Budisulistiorini et al., 2013; Pathak et al., 2011). These studies have likely mistaken correlation for causation in their data, since H^+ is likely a surrogate for sulfate and many factors lead to correlations between sulfate and SOA in regional pollution (Sun et al., 2011).

3.2 Molar ratio vs. pH

Similar to applications of the ion balance, the molar ratio is frequently used as a proxy for aerosol pH. Molar ratios near unity are assumed to represent neutral or near-neutral aerosol, with a decreasing ratio assumed to represent decreasing aerosol pH (He et al., 2012). Figure 4a shows the aerosol pH predicted by both ISORROPIA-II and E-AIM vs. the $\text{NH}_4^+ / (\text{Cl}^- + \text{NO}_3^- + 2 \cdot \text{SO}_4^{2-})$ molar ratio. Figure 4 brings to light several important revelations regarding the molar ratio. The molar ratio appears to correctly indicate the occurrence of alkaline particles, since all points with a molar ratio > 1 have a predicted $\text{pH} > 7$ ($n = 56$). The molar ratio also appears to correctly indicate the presence of strongly acidic particles, as all samples with a molar ratio < 0.75 have a predicted $\text{pH} < 1$ ($n = 258$). However, the molar ratio appears to have significant problems with the particles with molar ratios in the range of 0.75–1.0. Accounting for roughly one third of the data ($n = 151$), the molar ratio suggests that these particles are mildly acidic. However, for this subset of the data, both models predict that approximately 50 % of these points are alkaline. This discrepancy is strongly tied to the presence of crustal species (Ca^{2+} , K^+ , and Na^+) since they were at times present in Mexico City at high concentrations but are not included in the calculation of the molar ratio. If the majority

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of inorganic species are accounted for, then the molar ratio is able to distinguish acidic particles from alkaline or neutral particles with good reliability. Figure 4b shows aerosol pH vs. the molar ratio for the samples in which the sum of $(\text{NH}_4^+ + \text{Cl}^- + \text{NO}_3^- + \text{SO}_4^{2-})$ accounts for greater than 95 % of the measured inorganic aerosol mass. For this subset of the data, fewer than 10 % of the samples (15 of 178) differ in their prediction as acidic or alkaline by the molar ratio and thermodynamic equilibrium models (points to the left of the grey line but above pH 7). These results strongly support numerous studies that have also demonstrated the importance of including crustal elements in the analysis of particle acidity (Cao et al., 2013; Jacobson, 1999; Trebs et al., 2005; Ziemba et al., 2007; Moya et al., 2002).

The larger problem illustrated by Fig. 4 is that the molar ratio does not scale with predicted aerosol pH. Figure 4 shows that for samples with a molar ratio less than 1, aerosol pH does not decrease with decreasing molar ratio. Even for the subset of samples with (1) a low contribution of crustal species (< 5 % of inorganic aerosol mass) and (2) molar ratios less than 0.75, there is no relationship between molar ratio and predicted aerosol pH (Fig. 5). If a relationship between the molar ratio and aerosol pH were to exist, this subset of the data is most likely where it would be observed. We use the $\text{NH}_4^+ / (\text{Cl}^- + \text{NO}_3^- + 2 \cdot \text{SO}_4^{2-})$ ratio in this analysis since this method is so frequently employed. However, for other common forms of the molar ratio (e.g., $\text{NH}_4^+ / \text{SO}_4^{2-}$ and $\sum(\text{cations}) / \sum(\text{anions})$), there was no relationship observed between the molar ratio and predicted aerosol pH. Instead, the molar ratio is actually correlated with the inorganic ion balance ($R^2 = 0.58$, Fig. 6). Thus, some of the same limitations of the ion balance apply to the molar ratio method as well. Like the ion balance, the molar ratio does not account for variations in aerosol liquid water content or the partial dissociation of protonated compounds. Zhang et al. (2007) demonstrated similar problems translating the molar ratio into aerosol pH for an ambient study in Pittsburgh, PA (see Fig. S1d in the Supplement in Zhang et al., 2007).

These results indicate that caution should be used when employing the molar ratio to infer the acidity of atmospheric particles. When the majority of inorganic species

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($> 95\%$) are accounted for, the molar ratio is able to distinguish alkaline particles from acidic particles with good reliability; however, it is unable to provide any measure – even qualitative – of the degree of aerosol acidity. The lack of relationship between the molar ratio and predicted aerosol pH strongly suggests problems with studies that have used the molar ratio as a proxy for pH. For example, studies that have attempted to characterize the occurrence of acid-catalyzed SOA formation in the atmosphere may have incorrectly interpreted the aerosol acidity using a molar ratio approach (e.g., Tanner et al., 2009; Peltier et al., 2007; Zhang et al., 2007; Froyd et al., 2010).

3.3 Thermodynamic equilibrium models

Thermodynamic equilibrium models are frequently used to estimate aerosol acidity (as in Fig. 1–5). Prior studies have observed and discussed large differences in aerosol acidity predicted by different models (Ansari and Pandis, 1999); we do not revisit this analysis, but instead seek to understand some of the limitations and uncertainties of using thermodynamic equilibrium models to predict aerosol pH. Figure 7 shows that a large source of uncertainty is tied to the availability of gas-phase data and whether the model is run in the forward (gas + aerosol inputs) or reverse (aerosol inputs only) mode. Note that the number of forward mode predictions was less than the reverse mode predictions due to availability of gas-phase measurements. For ISORROPIA and E-AIM, the median differences between the models run in forward and reverse modes were 3.5 and 3.1 pH units, respectively. Other parameters, such as aerosol liquid water, have much closer agreement between the forward and reverse modes (not shown), given that it is largely driven by total aerosol mass and thus, is much less sensitive to errors in specific ions.

The large differences in the forward-reverse mode predictions of aerosol pH seen in Fig. 7 come about for several reasons. Upon specification of the aerosol species and surrounding RH, T , thermodynamic models first determine the aerosol pH and liquid water content (assuming that a liquid phase can exist), followed by computing the concentration of gas-phase semivolatile compounds in equilibrium with the aerosol

(e.g., NH_3 , HNO_3 and HCl). The aerosol pH is largely driven by electroneutrality in the aqueous phase, as any imbalance between charges from cations and anions needs to be balanced by H^+ and OH^- :

$$[\text{H}^+] + \sum_{n^+} [\text{X}^+] = [\text{OH}^-] + \sum_{n^-} [\text{Y}^-], \text{ or } [\text{H}^+] + I_b - [\text{OH}^-] = 0 \quad (7)$$

5 where $I_b = \sum_{n^+} [\text{X}^+] - \sum_{n^-} [\text{Y}^-]$, is the ion balance parameter, n^+ and n^- are the number of positively and negatively charged ionic species, respectively, and $[\text{X}^+]$ is the concentration of a species in the aqueous phase, in gram equivalents (geq). In the case where the aerosol is acidic (i.e., $\text{pH} < 7$ or $I_b < -\sqrt{K_w}$, with $K_w = [\text{OH}^-][\text{H}^+]$) then $[\text{OH}^-]$ contributes negligibly to I_b , and $[\text{H}^+] \cong -I_b$. Similarly, when the aerosol is alkaline (i.e., $\text{pH} > 7$ or $I_b > \sqrt{K_w}$) then $[\text{H}^+]$ contributes negligibly to I_b , $[\text{OH}^-] \cong I_b$ and $[\text{H}^+] = K_w/[\text{OH}^-]$.

Given the above, one can construct a diagram that relates aerosol pH to I_b ; this is shown in Fig. 8. It is noteworthy that pH changes considerably over a narrow range of I_b , when the value of the parameter is close to zero. For acidic and very alkaline aerosol, uncertainty in I_b – shown as the (a) and (c) regions of Fig. 8 – may introduce a 0.5–1.0 bias in predicted pH. In region (b) however, a small uncertainty in I_b leads to shifts in pH that spans effectively 10 pH units (or more). This uncertainty may come from either uncertainty in the measurements, themselves, or from approximations such as the exclusion of minor species (e.g., crustal elements) from the analysis.

20 The data used in Fig. 8 are hypothetical – values of I_b ranging from -1 to 1 at a constant aerosol loading were input under conditions of constant T and RH to generate the predicted pH. However, Fig. 9 shows that for the MILAGRO dataset, the predicted aerosol pH is extremely sensitive to minor uncertainties in the measurement inputs, and thus, to uncertainties in I_b . Figure 9 shows the sensitivity in predicted aerosol pH under the reverse mode calculation to $\pm 10\%$ changes in the aerosol NH_4^+ concentration. The aerosol pH differed by more than 1.0 pH units for 18% of the data when NH_4^+ increased by 10%. Likewise, aerosol pH differed by more than 1.0 pH units for 12%

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of the data when NH_4^+ decreased by 10%. Similar sensitivities were also observed for $\pm 10\%$ changes in aerosol NO_3^- and SO_4^{2-} inputs. This behavior is not unique to the Mexico City aerosol, as similar model sensitivities have been observed in diverse locations, as well. Using gas + aerosol inputs strongly constrains the effects of measurement errors and therefore is thought to give a more accurate representation of aerosol partitioning and composition (Guo et al., 2014; Fountoukis et al., 2009).

The discrepancy in pH predicted by the forward and reverse mode thermodynamic calculations also implies large differences in the predicted aerosol H^+ loadings. Figure 10 shows H^+ levels inferred from the ion balance compared to H^+ levels predicted by E-AIM and ISORROPIA, both run in forward mode. The forward mode thermodynamic calculations predict H^+ levels that are orders of magnitude lower than either the ion balance or reverse mode calculations, similar to the large differences in predicted pH (Fig. 7). This finding is consistent with large discrepancies in H^+ levels in Pittsburgh, PA predicted by forward (Takahama et al., 2006) and reverse (Zhang et al., 2007) thermodynamic equilibrium model simulations. Although the measurement periods for these studies did not overlap, the similar NH_4^+ and SO_4^{2-} concentrations suggest that the large differences in aerosol H^+ were likely due to differences in the forward and reverse model simulations, not in the actual pH levels of the aerosol.

Using gas + aerosol inputs strongly constrains the effects of measurement errors and therefore is thought to give a more accurate representation of aerosol partitioning and composition (Fountoukis et al., 2009). Our results support this thought, and indicate that reverse mode calculations of aerosol H^+ and pH should likely be avoided for the interpretation of experimental data. The exception to this recommendation would be a system that contains very low concentrations of semi-volatiles. Without accompanying gas-phase data to constrain the thermodynamic models, an alternate approach that may yield a more accurate representation of aerosol pH is the use of aerosol concentrations as input in forward mode calculations. In the southeastern US, Guo et al. (2014) report that this approach led to biases in aerosol pH of ~ 1 pH unit, which

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is considerably lower than the bias observed in Fig. 7, if we assume that the forward mode predictions are accurate.

The recommendation that neither the ion balance nor the molar ratio should be used as a proxy for aerosol pH was based upon the results of reverse model simulations (Figs. 1–4). This is a straightforward method of applying thermodynamic models and ambient studies frequently employ reverse modeling to predict aerosol acidity. However, this leads to the following question: if there are significant limitations to reverse model predictions of aerosol pH, how valid are the conclusions that the ion balance and molar ratio are poor proxies for aerosol pH? Figure 11 shows the relationship between forward-mode aerosol pH and the $\text{NH}_4^+ / (\text{Cl}^- + \text{NO}_3^- + 2 \cdot \text{SO}_4^{2-})$ molar ratio. Although there are major differences in the pH predicted by the forward and reverse models (Fig. 7), Fig. 11 shows no relationship at all between aerosol pH and the molar ratio. Similarly, no relationship was observed between aerosol pH under the forward model runs and the ion balance (not shown). Thus, the conclusions that the ion balance and molar ratio methods are unsuitable to be used as proxies for aerosol pH are unchanged.

3.4 Phase partitioning

Figure 12 shows aerosol pH predicted by ammonia phase partitioning vs. aerosol pH predicted by E-AIM and ISORROPIA run in forward and reverse modes. The best agreement between the phase partitioning approach and the models was found for both forward model applications (Fig. 12a and c). A slope of 0.98 and high R^2 value (0.80) indicate excellent agreement between E-AIM and the phase partitioning approach (Fig. 12a). The median difference between these methods was only 0.4 pH units. Likewise, a slope of 0.98 and high R^2 (0.47) demonstrate good agreement between ISORROPIA-II in forward mode and the phase partitioning pH (Fig. 12c).

The above results were contrasted by very poor agreement between the reverse models and phase partitioning predictions of aerosol pH (Fig. 12b and d). The median difference between aerosol pH predicted by NH_3 phase partitioning and E-AIM run in reverse mode was 3.5 pH units ($n = 72$). Similarly, the median difference be-

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tween aerosol pH predicted by NH_3 phase partitioning and ISORROPIA-II run in reverse mode was 3.1 pH units ($n = 72$). These large differences are consistent with the large differences observed between the forward and reverse predictions of pH (Fig. 7). These results are also consistent with very large discrepancies (of order 1–4 pH units) in aerosol pH between E-AIM run in reverse mode and the phase partitioning approach for a study in Hong Kong (Yao et al., 2006). As discussed above, gas + aerosol inputs constrain the effects of measurement uncertainty on thermodynamic models, and thus, the large differences observed in Fig. 12b and d provide further support that the reverse model applications are challenged to accurately predict aerosol pH. For the MILAGRO data set, approximately half of all reverse model runs predicted pH values less than 0 (44 % for E-AIM, 51 % for ISORROPIA). This is inconsistent with the observed aerosol ammonium fraction ($\text{NH}_4^+ / (\text{NH}_3 + \text{NH}_4^+)$), which was only 0.2, on average, over the study period.

These results suggest that the two best proxy methods for estimating aerosol pH are: (1) thermodynamic equilibrium models run using gas + aerosol inputs, and (2) the phase partitioning of ammonia. Prior studies suggest that the phase partitioning of $\text{HNO}_3/\text{NO}_3^-$ gives similar results to that of ammonia (Young et al., 2013), so this is another feasible approach. It should be noted that Young et al. (2013) caution against the use of HCl/Cl^- partitioning to estimate pH on the basis of large (order of magnitude) uncertainty in the Henry's law constant for HCl. Other limitations of the phase partitioning approach should be considered, depending on the environment. This includes long equilibration timescales for coarse particles, and the presence of insoluble or partially soluble salts (Jacobson, 1999; Fridlind and Jacobson, 2000; Meng and Seinfeld, 1996).

4 Conclusions

We have carried out an analysis of proxy methods used to estimate the pH of atmospheric particles. The ion balance method, which is used to infer the aerosol H^+ loading, showed no correlation with aerosol pH predicted by multiple independent metrics.

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This indicates that conditions of increasing H^+ loading do not necessarily correspond to decreasing (i.e., more acidic) aerosol pH. Likewise, the cation/anion molar ratio (and related metrics) showed no relationship with different predictions of aerosol pH. When species accounting for greater than 95 % of inorganic aerosol mass were included in the analysis, the molar ratio appears to reliably distinguish acidic from alkaline particles; however, the molar ratio should not be treated as a surrogate for aerosol pH. The molar ratio actually showed a strong relationship with the ion balance. A major reason for the inability of these methods to represent aerosol pH is that both neglect the effects of aerosol water and partial dissolution of ions and acids on pH, in accordance with previously published studies (Keene and Savoie, 1998; Winkler, 1986). These results strongly discourage the use of the ion balance or molar ratio for pH or H^+ inference.

These results also suggest that thermodynamic equilibrium models require both gas + aerosol inputs for accurate predictions of H^+ and pH. Two independent models – E-AIM and ISORROPIA – performed similarly and predict much lower pH (more acidic particles) in the reverse modes (aerosol inputs only). The aerosol pH levels predicted by both reverse models do not agree with either the pH predictions using gas + aerosol inputs or the phase partitioning of ammonia. The models in reverse mode predict highly acidic particles for extended periods of time (i.e., pH < 0), despite the availability of excess ammonia. Further, the models in reverse mode are highly sensitive to uncertainty in the measurement inputs, as small deviations in major aerosol species can induce changes in predicted pH that exceed 10 pH units. This finding is also consistent with other studies that show much better model performance when aerosol + gas inputs are used (Fountoukis et al., 2009; Guo et al., 2014).

Thermodynamic equilibrium models in forward mode had very good agreement with pH predicted by the phase partitioning of ammonia. These methods are largely, but not completely independent, as the aerosol liquid water required for the phase partitioning calculation is obtained from the same thermodynamic models. Thermodynamic equilibrium models are generally quite skilled in predicting aerosol liquid water (Khlystov et al., 2005), so this likely introduces minimal uncertainty to the present analysis. In

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regions where organics are high, their contribution to aerosol liquid water (and hence, pH) should be investigated (Guo et al., 2014). The fact that these largely independent methods agreed so closely provides the basis for the recommendation of their use to estimate the pH of atmospheric particles. As with the application of thermodynamic equilibrium models, the phase partitioning approach makes the implicit assumption that the gas/particle system is at equilibrium. This appears to be a good assumption for the Mexico City data set (Fountoukis et al., 2009), but it can be a poor assumption when coarse particles are abundant, such as in the marine environment (Fridlind and Jacobson, 2000). The phase partitioning approach is also likely limited in ammonia-poor environments where all or most of the ammonia resides in the aerosol phase. In such environments, the phase partitioning of nitric acid may be a good alternative if both nitric acid and aerosol nitrate concentrations are high enough (Young et al., 2013; Meskhidze et al., 2003). Uncertainty in the Henry's law constant of other compounds, especially HCl, may limit the application of the phase partitioning approach beyond $\text{NH}_3/\text{NH}_4^+$ and $\text{HNO}_3/\text{NO}_3^-$ (Young et al., 2013).

Our recommendation for the use of the phase partitioning approach and forward equilibrium model calculations to best predict aerosol pH contradicts the recommendations in a similar study (Yao et al., 2006). Both our study (from Mexico City) and the Yao et al. (2006) study (Hong Kong) agree that E-AIM run in reverse mode yields predicted aerosol pH levels significantly lower than the phase partitioning or forward model predictions. We differ on our interpretation of the results: Yao et al. (2006) conclude that the phase partitioning approach and forward model calculations erroneously assume that the gas-aerosol system has reached equilibrium, even though their analysis is based upon 12 and 24 h $\text{PM}_{2.5}$ measurements. This sampling time should far-exceed the equilibration time for small particles (Meng and Seinfeld, 1996). In addition, our comparisons in Fig. 12a and c only include the subset of data where RH exceeds 60 %, a region in which the thermodynamic predictions – and assumption of equilibrium – become more accurate (Moya et al., 2002). Fountoukis et al. (2009) examined the equilibrium assumption for $\text{PM}_{2.5}$ during MILAGRO and found it to be valid. Thus,

we believe that the forward thermodynamic models and phase partitioning approach are far more accurate in their predictions of pH than the reverse models run in closed (aerosol inputs only) mode.

As a “gold standard” measurement method against which the proxies can be compared is lacking, these recommendations should be evaluated in other environments with different chemical characteristics and meteorology than was observed during MI-LAGRO. Despite their uncertainties, thermodynamic models and phase partitioning provide the best methods to estimate the pH of fine atmospheric particles. Other widely used metrics – ion balance and ion ratios – are misleading and should be avoided beyond the establishment of general alkalinity or acidity. Hence, conclusions that are sensitive to aerosol pH but that are based upon the ion balance or molar ratio may need revision.

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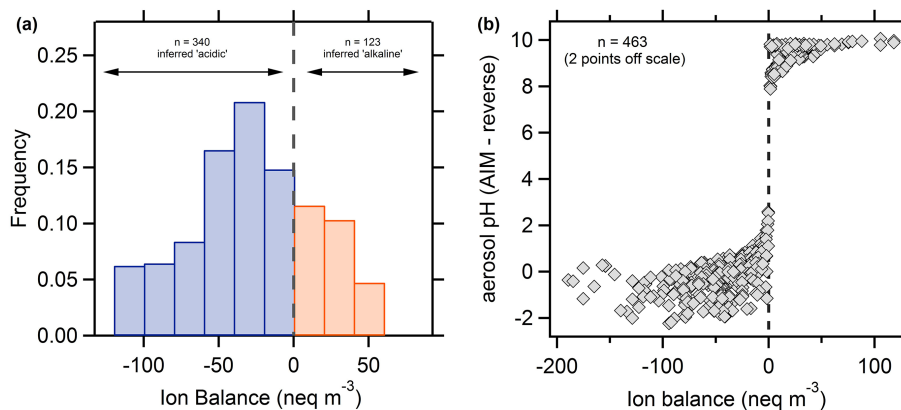


Figure 1. (a) Frequency distribution of the aerosol ion balance during MILAGRO, and (b) aerosol pH predicted by E-AIM in the reverse mode vs. the ion balance.

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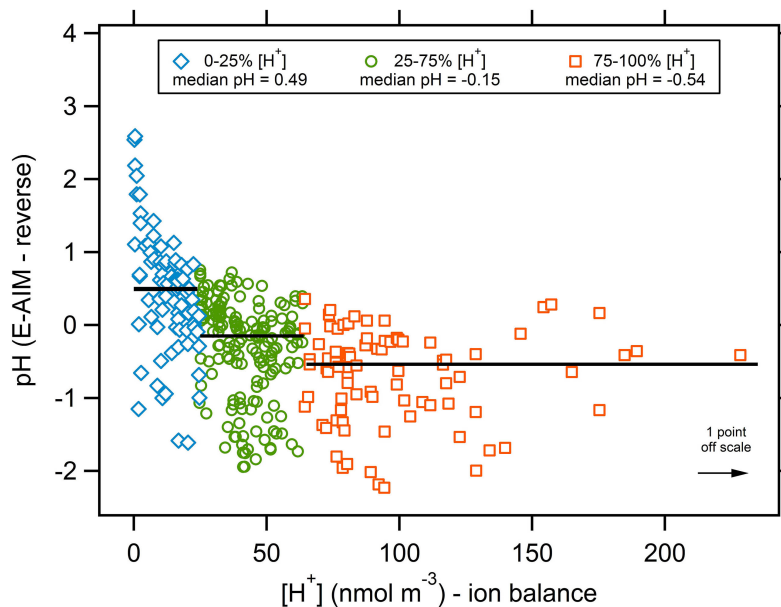


Figure 2. Predicted aerosol pH vs. the aerosol H⁺ loading inferred from the ion balance. Only points in which anions > cations are included in the analysis.

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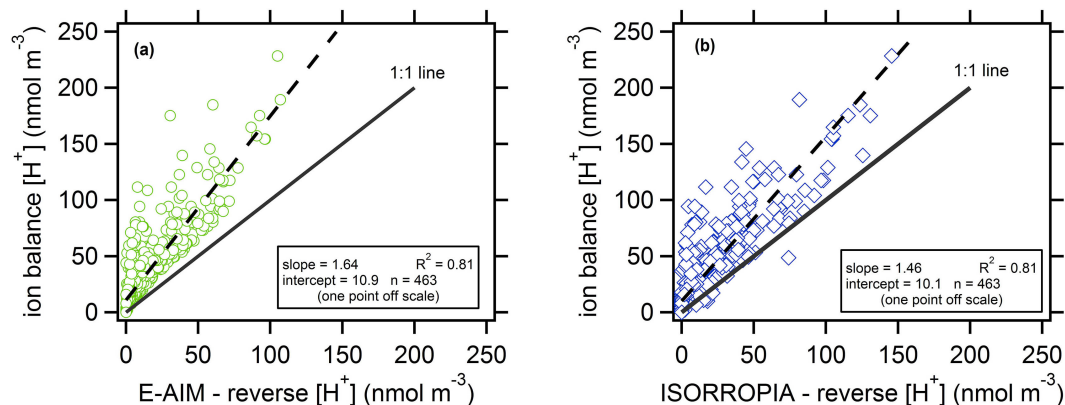


Figure 3. H⁺ levels inferred from the ion balance compared to H⁺ levels predicted by **(a)** E-AIM (reverse mode), and **(b)** ISORROPIA (reverse mode).

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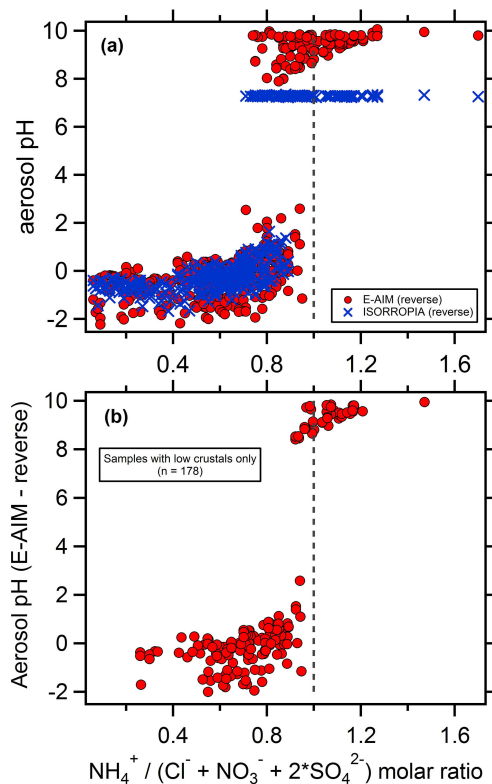


Figure 4. Predicted aerosol pH vs. the $\text{NH}_4^+ / (\text{Cl}^- + \text{NO}_3^- + 2 \cdot \text{SO}_4^{2-})$ molar ratio for **(a)** the entire MILAGRO data set and **(b)** the subset of data in which $\sum(\text{NH}_4^+ + \text{Cl}^- + \text{NO}_3^- + \text{SO}_4^{2-})$ accounts for greater than 95 % of measured inorganic aerosol mass.

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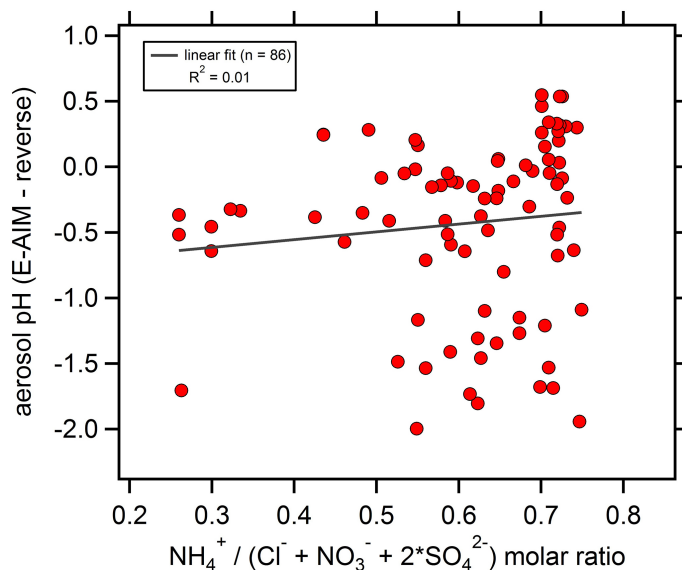


Figure 5. Predicted aerosol pH vs. the $\text{NH}_4^+ / (\text{Cl}^- + \text{NO}_3^- + 2 \cdot \text{SO}_4^{2-})$ molar ratio, using only data where the ratio is less than 0.75 and where $\sum(\text{NH}_4^+ + \text{Cl}^- + \text{NO}_3^- + \text{SO}_4^{2-})$ accounts for greater than 95 % of measured inorganic aerosol mass.

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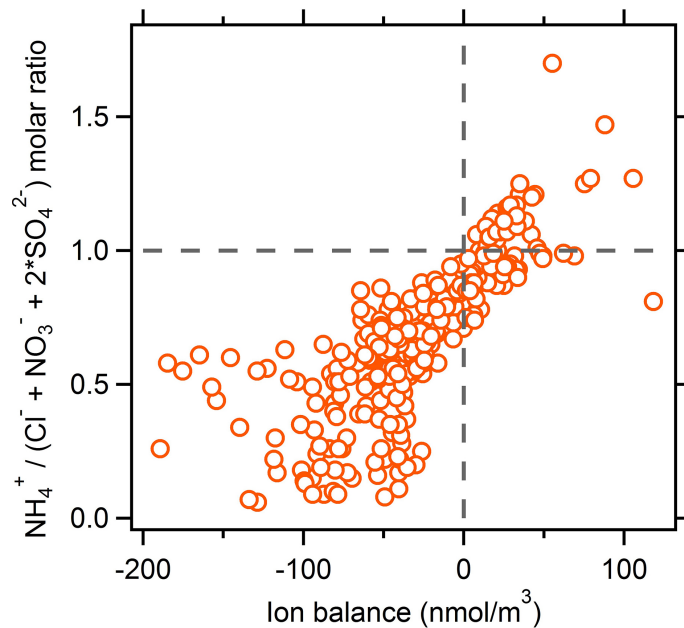


Figure 6. Relationship between the $\text{NH}_4^+ / (\text{Cl}^- + \text{NO}_3^- + 2 \cdot \text{SO}_4^{2-})$ molar ratio and the ion balance.

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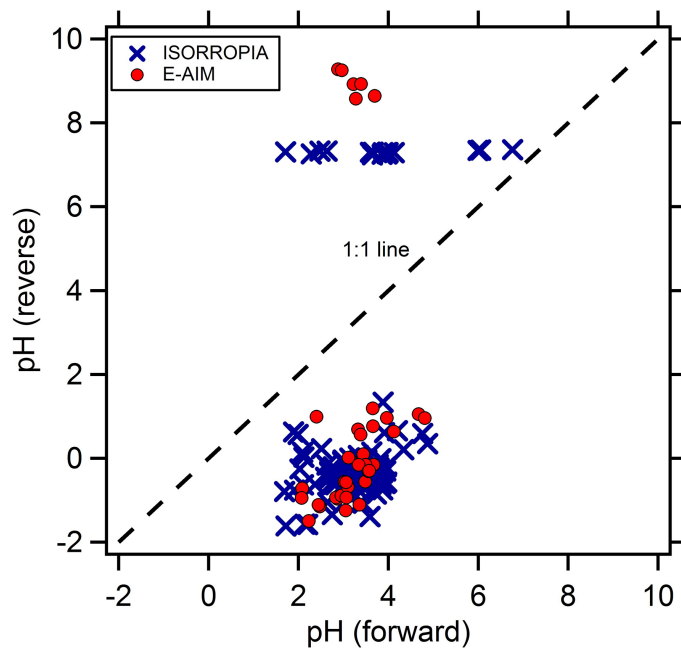


Figure 7. Comparison of pH predicted using the reverse and forward modes of ISORROPIA and E-AIM.

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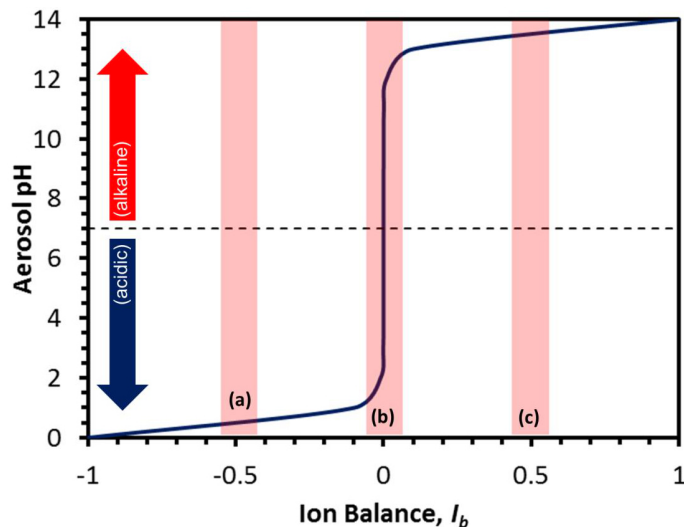


Figure 8. Aerosol pH as a function of the parameter I_b (see Eq. 7 for explanation). The data used here are hypothetical – values of I_b ranging from -1 to 1 at a constant aerosol loading were input under conditions of constant T and RH to demonstrate the extreme sensitivity of aerosol pH at low I_b values (region “b”).

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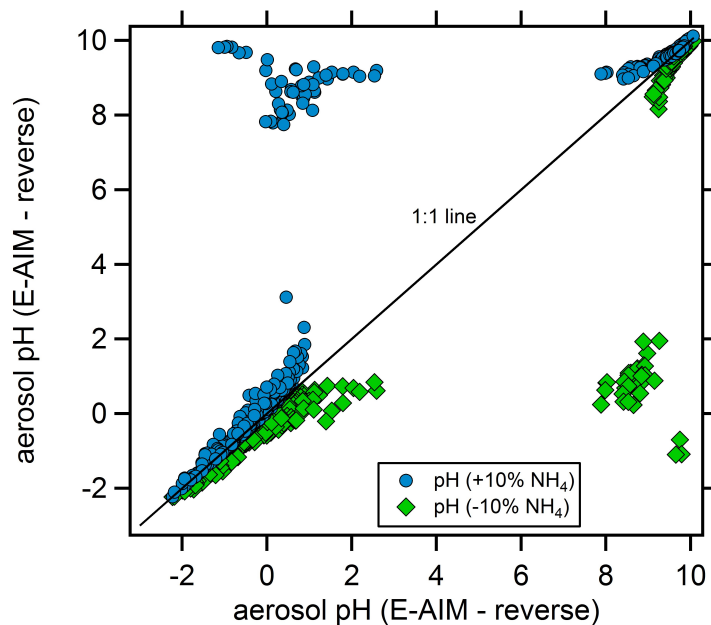


Figure 9. Sensitivity of aerosol pH predicted with E-AIM (reverse mode) to small changes in the input aerosol NH_4^+ concentration.

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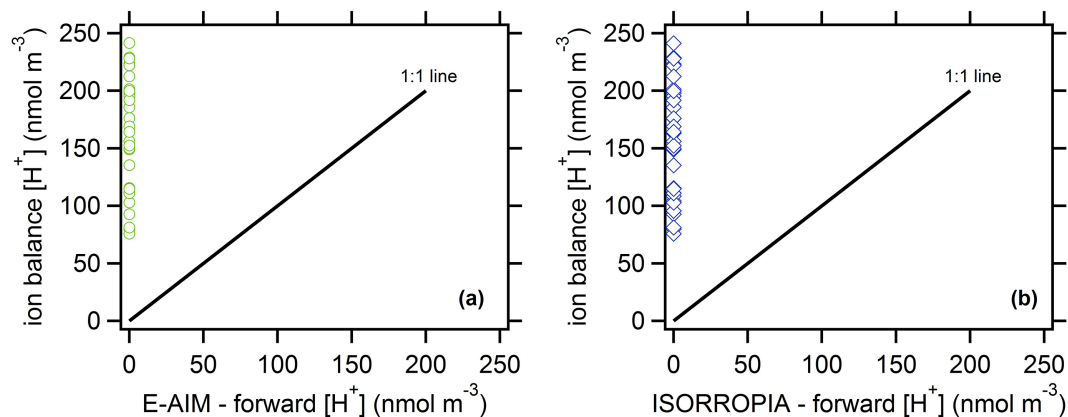


Figure 10. H⁺ levels inferred from the ion balance compared to H⁺ levels predicted by (a) E-AIM (forward mode), and (b) ISORROPIA (forward mode).

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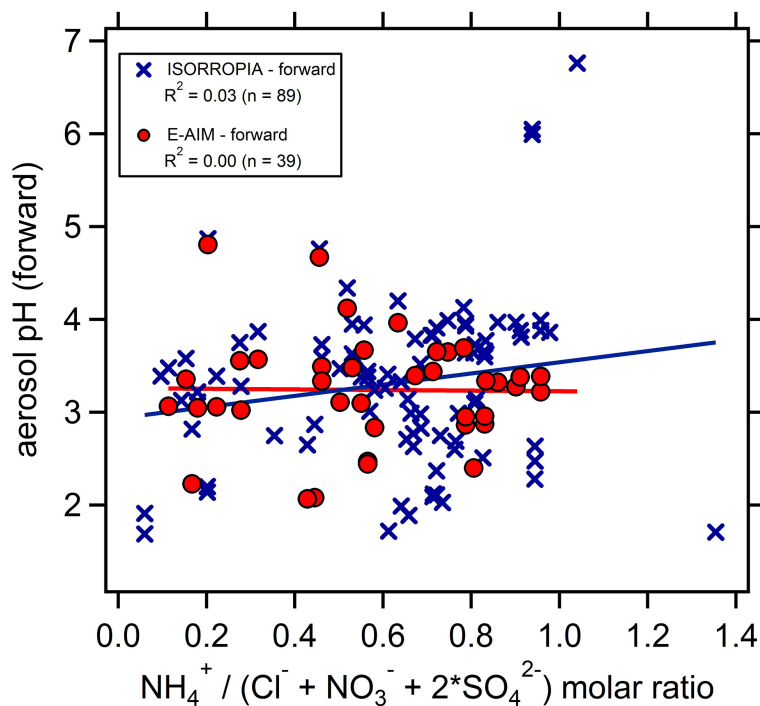


Figure 11. Aerosol pH predicted by the forward mode equilibrium models compared to the $\text{NH}_4^+ / (\text{Cl}^- + \text{NO}_3^- + 2 \cdot \text{SO}_4^{2-})$ molar ratio.

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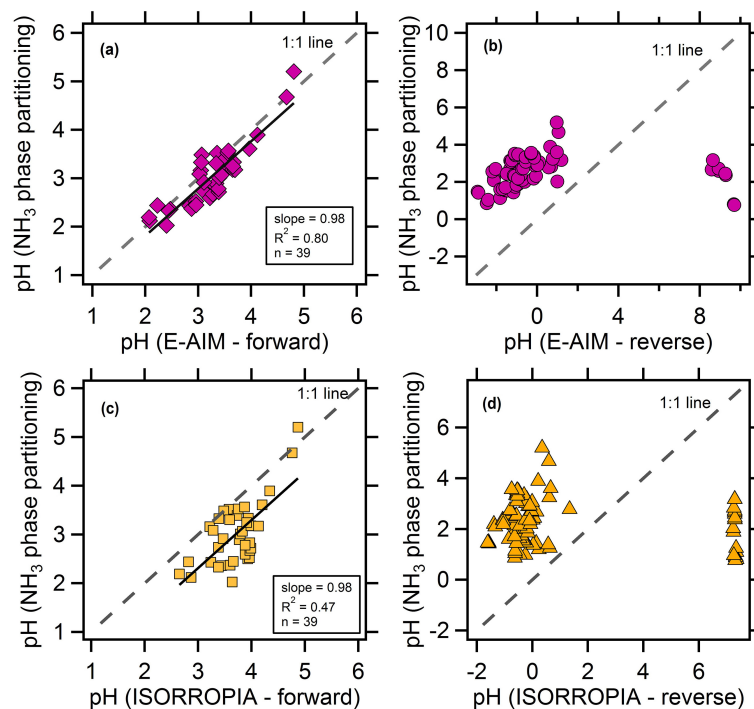


Figure 12. Aerosol pH predicted by the phase partitioning of ammonia compared to predictions of thermodynamic equilibrium models run in forward and reverse mode.

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