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The underappreciated role of nonvolatile cations on aerosol ammonium-sulfate molar ratios

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Abstract. Overprediction of fine particle ammonium-sulfate molar ratios (R) by thermodynamic models is suggested as evidence for an organic film that only inhibits the equilibration of gas phase ammonia (but not water or nitric acid) with aerosol sulfate and questions the equilibrium assumption long thought to apply for submicron aerosol. The ubiquity of such organic films implies significant impacts on aerosol chemistry. We test the organic film hypothesis by analyzing ambient observations with a thermodynamic model and find that R and ammonia partitioning can be accurately reproduced when small amounts of nonvolatile cations (NVC), consistent with observations, are considered in the thermodynamic analysis. Exclusion of NVCs results in predicted R consistently near 2. The error in R is positively correlated with NVC and not organic aerosol mass fraction or concentration. These results strongly challenge the postulated ability of organic films to perturb aerosol acidity or prevent ammonia from achieving gas-particle equilibrium for the conditions considered.

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1. Introduction

pH is a fundamental aerosol property that affects aerosol formation and composition through pH-sensitive reactions (Jang et al., 2002; Eddingsaas et al., 2010; Surratt et al., 2010) and gas-particle partitioning of semivolatile species (Guo et al., 2016; Guo et al., 2017a). Acidity also modulates aerosol toxicity and atmospheric nutrient supply to the oceans through changing solubility of transition metals (Meskhidze et al., 2003; Nenes et al., 2011; Longo et al., 2016; Fang et al., 2017). Despite its importance, the inability to directly measure fine mode particle pH (e.g. Rindelaub et al. (2016) presents an indirect method that infers particle H^+ activity for sizes above 10 µm and requires activity coefficient predicted by a thermodynamic modeling. This method reports the pH for a HSO_4^-/SO_4^{2-} aerosol system similar to the fine particle pH predicted by a thermodynamic modeling used in this study (Guo et al., 2015)) has led to the use of measurable aerosol properties as acidity proxies, such as aerosol ammonium-sulfate ratio or ion balances (e.g. (Paulot and Jacob, 2014; Wang et al., 2016; Silvern et al., 2017)). Recent work has shown that acidity proxies are not uniquely related to pH, which in turn strongly questions any conclusions derived from its use. There are numerous reasons why acidity proxies do not represent pH well; they do not capture the variability in particle water content, ion activity coefficients, or partial dissociation of species in the aerosol phase (Guo et al., 2015; Hennigan et al., 2015; Guo et al., 2016). The method that best constrains aerosol pH is comparison between a thermodynamic analysis and observations of gas-particle partitioning of semivolatile species that are sensitive to pH at the given environmental conditions (i.e., gas-particle concentration ratios near 1:1) (Guo et al., 2015; Guo et al., 2016; Weber et al., 2016; Guo et al., 2017a). NH_3-NH_4^+, HNO_3-NO_3^-, and HCl-Cl^- pairs often meet this condition. The method has been utilized for a range of meteorological conditions (RH, T) and gas/aerosol concentrations demonstrating that model predictions are often in agreement with observations.

It has been noted that thermodynamic models fail to accurately predict ammonium-sulfate molar ratios when just considering the NH_4^+-SO_4^{2-}-NO_3^- aerosol system in equilibrium with the corresponding gas species (Kim et al., 2015; Silvern et al., 2017). In the southeastern US, where total ammonium ($NH_x = NH_3 + NH_4^+$) is observed to be in large excess of particle sulfate and observed NH_4^+/SO_4^{2-} molar ratios are in the range of 1-2 (Hidy et al., 2014; Guo et al., 2015; Kim et al., 2015), thermodynamic models often predict very low pH (0.5 to 2) (Guo et al., 2015) and molar ratios close to 2 (Kim et al., 2015; Weber et al., 2016; Silvern et al., 2017). The molar ratio discrepancy has led to the hypothesis that thermodynamic predictions are incorrect, and particles are coated by organic films that inhibit the condensation of NH_3 from the gas phase and give rise to the molar ratio discrepancy (Silvern et al., 2017). Such kinetic limitations, if prevalent, opposes the validity of aerosol thermodynamic equilibrium and could significantly impact aerosol chemistry and acidity-mediated processes, given the large organic aerosol mass fractions worldwide (Zhang et al., 2007) and expected increasing organic mass fractions in the future due to changing emission, such as SO_2 emission reduction in the eastern US (Hand et al., 2012; Attwood et al., 2014; Hidy et al., 2014). The hypothesis of organic films, however, is in stark contrast to established literature showing that NH_3, water vapor, and HNO_3 equilibrate with organic-rich aerosols (Fountoukis et al., 2009; Guo et al., 2015; Guo et al., 2016; Guo et al., 2017a). Such a film, as proposed by Silvern et al. (2017), selectively limits NH_3, but not H_2O and HNO_3 molecules that are both larger than NH_3 hence more difficult to diffuse through media. At low temperature or low relative humidity, aerosols may be in semi-liquid or glassy state and have very low diffusivity of molecules throughout its volume (Tong et al., 2011; Bones et al., 2012). This may severely limit gas-particle mass transfer of all components and require much longer time scales to equilibrate. However, we have not observed such an effect for the conditions in the eastern US, as there is good agreement between observed and predicted particle water, and partitioning of NH_3-NH_4^+ and HNO_3-NO_3^- (the bias in NO_3^- prediction becomes progressively worse when RH drops below 40%, likely owning to glassy states during the wintertime) (Guo et al., 2015; Guo et al., 2016).

Other reasons that are unrelated to organic films may drive the molar ratio discrepancy. One is related to the variation of aerosol composition with size, which may translate to a large range of acidity, hence equilibrium composition (Keene et al., 1998; Nenes

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et al., 2011; Bougiatioti et al., 2016; Fang et al., 2017). Another related issue is the presence of soluble nonvolatile cations (NVC, such as Na^+, K^+, Ca^{2+}, Mg^{2+}), which are often neglected in thermodynamic calculations because of their relatively minor contribution to aerosol mass or are not routinely included in aerosol composition measurements (e.g., those made with an aerosol mass spectrometer). Here we show that ignoring even small amounts of NVC as inputs to the thermodynamic model results in predicted NH_4^+/SO_4^{2-} molar ratios close to 2 due to the model criteria of electrical neutrality, whereas including small levels of NVC brings model-predicted molar ratios into agreement with observed levels.

2. Methods

Molar ratios definition: Two ammonium-sulfate aerosol molar ratios are used in the following analysis,

$$R = \frac{\mathrm{NH_4^+}}{\mathrm{SO_4^{2-}}} \quad (1)$$

$$R_{\mathrm{SO_4}} = \frac{\mathrm{NH_4^+} - \mathrm{NO_3^-}}{\mathrm{SO_4^{2-}}} \quad (2)$$

both are based on inorganic mole concentrations in units of μmol m^{-3}. R_{SO4} is a more narrowly defined molar ratio that excludes NH_4^+ associated with NO_3^-, because ammonium sulfate and ammonium nitrate are typically associated with different sized particles (externally mixed) (Zhuang et al., 1999) and molar ratios are calculated based on bulk composition data ($PM_{2.5}$ or PM_1). The upper limit for R and R_{SO4} is 2 for a particle composition of pure $(NH_4)_2SO_4$, the lower limit is 0 for R when SO_4^{2-} is associated with other cations instead of NH_4^+ (e.g. Na_2SO_4) or if there is free H_2SO_4 in the aerosol. A negative R_{SO4} can occur for conditions of high NO_3^- and low NH_4^+, SO_4^{2-} concentrations (e.g., $NaNO_3$), but rare for ambient fine particles. R or R_{SO4} is typically observed in the range of 1 and 2 in the southeastern US (i.e., between NH_4HSO_4 and $(NH_4)_2SO_4$) (Hidy et al., 2014; Guo et al., 2015; Weber et al., 2016). In cases where NO_3^- levels are low relative to SO_4^{2-}, the two ratios, R_{SO4} and R, are equivalent, as is observed in the summertime southeastern US, where NO_3^- is typically ~0.2 μg m^{-3}, NH_4^+ ~1 μg m^{-3}, and SO_4^{2-} ~3 μg m^{-3} (Blanchard et al., 2013).

Observations: Two datasets are used for analysis, the Southern Oxidant and Aerosol Study (SOAS) and the Wintertime Investigation of Transport, Emissions, and Reactivity (WINTER). The SOAS study was conducted from 1 June to 15 July in the summer of 2013 at a rural ground site in Centreville (CTR), AL, representative of the southeastern US background atmosphere in summer. The WINTER data was produced from 13 research aircraft flights from 1 Feb to 15 Mar in 2015 mainly sampling over the northeastern US. Details of the campaigns and instruments, and calculations and verification of pH based on the observation datasets, have been described in Guo et al. (2015) and Guo et al. (2016), respectively. In the following analysis, we use R for summertime datasets with low NO_3^- and R_{SO4} for wintertime datasets with high NO_3^- concentration. Both datasets report highly acidic aerosols with average pH~1 (Guo et al., 2015; Guo et al., 2016). At these pH levels, aerosol sulfate can be in the partially deprotonated form of HSO_4^- instead of SO_4^{2-}. For example, 14% sulfate is predicted to be HSO_4^- and the rest as SO_4^{2-} in the winter dataset (Guo et al., 2016). Free form H_2SO_4, which requires even lower pH, is rare in the ambient aerosol. The SO_4^{2-} in this study refers to the sum of total aqueous aerosol sulfate (SO_4^{2-}, HSO_4^-, and H_2SO_4), the same definition (i.e., S(VI)) used in Silvern et al. (2017), since aerosol instruments normally report total aqueous sulfate as just SO_4^{2-}. The same applies to NH_4^+ and NO_3^-. The observation data are from two widely deployed aerosol instruments; a Particle-Into-Liquid-Sampler coupled with an Ion Chromatograph (PILS-IC) and a High-Resolution Time-of-Flight Aerosol Mass Spectrometer (hereafter referred to as AMS). The PILS-IC detects aerosol water-soluble anions and cations collected and diluted by deionized water to the extent of complete deprotonation of H_2SO_4 in the aqueous sample (Orsini et al., 2003). The AMS vaporizes aerosols and ionizes non-refractory

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species with a 70 eV electron impact ionization and cannot distinguish the dissociation states of inorganic ions (DeCarlo et al., 2006).

Thermodynamic analysis of observations: The thermodynamic model ISORROPIA-II (Fountoukis and Nenes, 2007) was used to determine the composition and phase state of an NH_4^+-SO_4^{2-}-NO_3^--Cl^--Na^+-Ca^{2+}-K^+-Mg^{2+}-water inorganic aerosol (or a subset therein) and its partitioning with corresponding gases. Using this model, we have developed a method for pH prediction that includes appropriate validation and uncertainty assessment (Guo et al., 2015) and applied the methods to several other locations (Bougiatioti et al., 2016; Guo et al., 2016; Weber et al., 2016; Guo et al., 2017a; Guo et al., 2017b). Here pH is defined following the same approach,

$$\mathrm{pH} = -\log_{10}\gamma_{\mathrm{H}^+}H^+_{aq} = -\log_{10}\frac{1000\gamma_{\mathrm{H}^+}H^+_{air}}{W_i + W_o} \cong -\log_{10}\frac{1000\gamma_{\mathrm{H}^+}H^+_{air}}{W_i} \quad (3)$$

where γ_{H^+} is the hydronium ion activity coefficient (assumed = 1), H^+_{aq} (mol L^{-1}) the hydronium ion concentration in particle liquid water, H^+_{air} (μg m^{-3}) the hydronium ion concentration per volume of air, and W_i, W_o (μg m^{-3}) are particle water concentrations associated with inorganic and organic species, respectively. pH predicted solely with W_i is fairly accurate; pH was 0.15-0.23 units systematically lower than and highly correlated to (r^2 = 0.97) pH predicted with total particle water (W_i + W_o) in the southeast, where W_o accounted for 35% of total particle water (Guo et al., 2015). For simplicity, we therefore use W_i for the following pH calculations.

ISORROPIA-II was run in "forward" mode to calculate gas-particle equilibrium concentrations based on the input of total concentration of various inorganic species (e.g., NH_3 + NH_4^+). The best agreement between model and observations were achieved assuming "metastable" particles with no solid precipitates (H^+ is not stable in an effloresced aerosol). We also assumed that the particles were internally mixed, and that pH did not vary with size (so that bulk properties represent the aerosols, including pH) and gas-particle partitioning was in thermodynamic equilibrium. For submicron aerosol (PM_1), equilibrium states are typically achieved within 30 minutes under ambient conditions (Dassios and Pandis, 1999; Cruz et al., 2000; Fountoukis et al., 2009). The prediction of gas-particle partitioning has been found to be in good agreement with observations when using particle bulk concentrations as model input (Guo et al., 2015; Guo et al., 2016; Guo et al., 2017a), although particle pH is size dependent. pH increases for particles above 1 μm as a result of NVC (Fang et al., 2017) resulting in particle mixing state becoming more important with increasing particle size (Guo et al., 2017a). ISORROPIA input data files for the analyses reported in this paper are provided with the supplementary material.

3. Discussion

The cause for discrepancy between modeled and measured molar ratios (R): We first investigate the issue of *R* discrepancy using PILS-IC $PM_{2.5}$ data from a 12-day period (11-23 June) of the SOAS campaign. The same period has been used to study pH sensitivity to sulfate and ammonia and shown to accurately predict NH_3-NH_4^+ partitioning compared to observations (Weber et al., 2016). To test the sensitivity of ISORROPIA-II predictions, we ran the model with the same input as Weber et al. (2016), (inputs include Na^+, (NH_4^++NH_3), SO_4^{2-}, NO_3^-, Cl^-, Ca^{2+}, Mg^{2+}, K^+, RH, T, where Ca^{2+}, Mg^{2+}, K^+ inputs were zero, NH_4^+, SO_4^{2-}, NO_3^-, Cl^- concentrations were from PILS-IC $PM_{2.5}$ observational data, NH_3 was from chemical ionization mass spectrometer measurements (You et al., 2014)) and tested three different Na^+ levels: (1) Na^+ determined from an ion charge balance by $Na^+ = 2SO_4^{2-} + NO_3^- + Cl^- - NH_4^+$ (unit: μmol m^{-3}); (2) measured $PM_{2.5}$ Na^+ from PILS-IC; (3) $Na^+ = 0$.

Different Na^+ concentrations were used to investigate the impact of Na^+ on model output. The inferred Na^+ was on average 0.28 ± 0.18 μg m^{-3}, higher than the measured level of 0.06 ± 0.09 μg m^{-3}. Note that, the limit of detection (LOD) of PILS-IC Na^+ in

this study was 0.07 μg m^{-3}, close to the reported average level. Unlike the standard procedure of reporting below LOD values as ½ LOD, we use the Na^+ concentrations directly from the instrument, including those below the LOD because, as will be shown, *R* is highly sensitive to trace levels of NVC. Also, we note that all other NVC, such as Ca^{2+} and Mg^{2+}, were generally below the PILS-IC LOD (therefore set to zero in the model input). The charge balance predicted Na^+ should then be viewed, for this data set, as the concentration of generic NVC concentrations with a valence of 1. The charge balance predicted Na^+ must be above zero; for calculated values below zero (8 out of 229 points, 3% of the data), due to combined measurement uncertainty, a small positive value of 0.005 μg m^{-3} is assigned.

The concentration of H^+ is also ignored in the ion charge balance calculation as it is 2-3 orders of magnitude smaller than the major inorganic ions, even at these low pH (between 0 and 2). For example, the average $PM_{2.5}$ mole concentrations per volume of air for the ions measured by the PILS-IC were NH_4^+ = 0.0354, SO_4^{2-} = 0.0211, NO_3^- = 0.0037, Na^+ = 0.0029, and Cl^- = 0.00082 μmol m^{-3}, compared to ISORROPIA-predicted H^+ = 0.00031 μmol m^{-3} for this period. The observed Na^+ appeared to be mainly associated with NO_3^-, and to a lesser degree with Cl^-, based on high linear correlations, r^2 = 0.82 and 0.64, respectively. A typical level of "chloride depletion" was observed as a Cl^-/Na^+ ratio of 0.24 ± 0.16 (mol mol^{-1}), due to higher volatility of HCl versus HNO_3 (Fountoukis and Nenes, 2007). In this case, Cl^- input to ISORROPIA is negligible as it does not affect the predictions of pH or molar ratios due to the measured Cl^- concentration being small, 0.03 ± 0.04 μg m^{-3} (LOD = 0.01 μg m^{-3}).

Fig. 1 shows the time series of various parameters for the SOAS 12-day period investigated. From these data, the effect of Na^+ (i.e., NVC) on ISORROPIA-predicted SO_4^{2-}, NH_4^+, NH_3, *R*, and pH is investigated. Fig. 1a and Fig. 1d show the overall behavior of total ammonium (NH_x = NH_3 + NH_4^+) and sulfate. SO_4^{2-} is nonvolatile so remains unchanged by the model, as does total ammonium and hence the NH_x/SO_4^2 molar ratio. Therefore, the discrepancy between modeled and measured *R* must result from the NH_4^+ prediction. It is noteworthy that NH_x/SO_4^{2-} is generally above 2, indicating excess NH_x compared to SO_4^{2-}. Under such conditions, it is often interpreted that NH_3 must completely neutralize SO_4^{2-} (Kim et al., 2015; Silvern et al., 2017). The thermodynamic model predicts otherwise; despite the excess NH_x, $PM_{2.5}$ is predicted to be highly acidic, with a pH range between 0 and 2 (Fig. 1h), resulting from NH_4^+ semivolatility and SO_4^{2-} being virtually nonvolatile at any atmospherically-relevant concentration and acidity (Weber et al., 2016).

The predicted time series of NH_3-NH_4^+ partitioning agrees most with observations when measured Na^+ (Fig. 2) is included in the model compared to model results with identical inputs, except with zero Na^+ or inferred Na^+ from ion charge balance (Fig. 1e, 1f, 1g, and Fig. 2). For ISORROPIA simulations with measured Na^+ as input, the orthogonal linear regression of ISORROPIA-predicted versus measured particle phase fractions of total ammonium, where $\varepsilon(NH_4^+) = NH_4^+/NH_x$, is: $\varepsilon(NH_4^+)_{predicted}$ = (1.00 ± 0.03) $\varepsilon(NH_4^+)_{observed}$ + (0.03 ± 0.02), with r^2 = 0.76 and "±" is one standard deviation (SD). Mean $\varepsilon(NH_4^+)_{observed}$ was 54 ± 13%, making the partitioning sensitive to pH (Guo et al., 2017a). As the nonvolatile Na^+ competes with semivolatile NH_4^+, predicted NH_4^+ decreases when higher levels of Na^+ are input to the model, whereas predicted gas phase NH_3 increases for conservation of input NH_x. Thus, since the ion charge balance inferred Na^+ is often higher than measured Na^+ (Fig. 1c), the lowest NH_4^+ and $\varepsilon(NH_4^+)$ are predicted with the input of inferred Na^+. In contrast, the highest NH_4^+ and $\varepsilon(NH_4^+)$ are predicted with zero Na^+ input, whereas the predicted values with measured Na^+ as model input are between these two. For the period in Fig. 1, measured Na^+ was 0.06 μg m^{-3} and the inferred value was 0.28 μg m^{-3}.

R also depends on the input Na^+ concentration. For the Fig. 1 period, predicted *R* was on average 1.43 ± 0.32 for an ISORROPIA input with inferred Na^+, 1.85 ± 0.17 for measured Na^+ input, and the highest *R* at 1.97 ± 0.02 when zero Na^+ was used as model input. The average measured *R* was 1.70 ± 0.23 by PILS-IC and 1.75 ± 0.20 by another $PM_{2.5}$ water-soluble ion measurement (Allen et al., 2015). Thus, model *R* with measure Na^+ input was closest to the measured *R*. Under the meteorological conditions of the southeast in summertime (T = 25 ± 5 °C, RH = 68 ± 18 %), the thermodynamic model predicts *R* always near or equal to

2, when input NVCs are set to zero and the only other particle composition inputs are SO_4^{2-}, NH_4^+, and NO_3^-, with paired gases NH_3 or HNO_3, indicating a particle composition of mainly $(NH_4)_2SO_4$; expected for electroneutrality of the aerosol aqueous phase. These are the model inputs when particle composition are from an AMS (e.g. (Kim et al., 2015; Silvern et al., 2017)) and explains why ISORROPIA-predicted *R* disagreed with measured values, which is a basis for the organic film hypothesis (Silvern et al., 2017).

Contrasts between measured and predicted *R* for periods of differing model input Na^+ levels can be seen in Fig. 1. First, if the ambient Na^+ mass concentration was higher than the PILS-IC LOD, such as the period of 11-13 & 16 June, the predicted and measured *R* agree when measured Na^+ is input. Inferred Na^+ from the ion charge balance appears to be overestimated at these times, and this causes a noticeable bias in the prediction of *R*, NH_3, NH_4^+, and $\varepsilon(NH_4^+)$. The pH calculated based on the inferred Na^+ also differs compared to the pH calculated from the measured Na^+ for this period. During periods when ambient Na^+ mass concentration was below the measurement LOD but close to zero, no discrepancy in *R* is found since both values are near 2 (e.g., around the time of 16 June midnight). This results from negligible effects of NVC since concentrations are very low. When ambient Na^+ concentrations were below LOD but not zero, there is a discrepancy between predicted and observed *R* for ISORROPIA with input of measured Na^+ or zero Na^+, however, inferred Na^+ results in better agreement. For instance, during the period of 18-20 & 22-23 June, the predicted *R* with the inferred Na^+ input follows (but is slightly lower than) observations; this is consistent with an overestimation of Na^+ from the ion charge balance calculation. Overall, the time series analysis demonstrates how model-predicted molar ratios are affected by measurement accuracy and LODs of NVC and the sensitivity of ISORROPIA-predicted *R* to NVCs input concentrations. Note that a few measured *R* points were above 2 (e.g. midnight of 15 June), a result of measurement uncertainty and error propagation at low SO_4^{2-} concentrations.

Quantification of NVC effects on R and pH: We have shown that the discrepancy in *R* can be resolved for this data set by adding small amounts of Na^+, either measured (when near or above LOD) or inferred from an ion charge balance analysis when not measured or significantly below the measurement method LOD. However, due to propagation of SO_4^{2-}, NH_4^+, and NO_3^- measurement errors, the uncertainty in inferred Na^+ data may cause a noticeable bias in the prediction of *R* or pH, such as observed on 11-13 June (Fig. 1b). Because of this, quantifying the sensitivities of *R* and pH to Na^+, or any other NVC, is of interest. Here we use Na^+ as an example since it was the highest NVC concentration measured in this study; K^+ and Mg^{2+} have similar effects. Ca^{2+} behaves differently due to $CaSO_4$ solids precipitating out, shown as Fig. S1 in the supplement.

Differences in predicted *R* with and without measured Na^+ are plotted against Na^+ mass and organic aerosol mass fractions in Fig. 3a; ΔR is defined as ISORROPIA predicted *R* with Na^+ minus ISORROPIA predicted *R* without Na^+. Fig. 3a shows that ΔR is highly correlated with Na^+ ($r^2 = 0.93$). Based on an orthogonal linear regression $\Delta R = (-1.74 \pm 0.03)\ Na^+ + (0.001 \pm 0.003)$. From the regression slope, the average measured Na^+ level of 0.06 μg m^{-3}, a background level of $PM_{2.5}$ Na^+ in the southeast, causes a response of −0.10 in *R*. At a Na^+ level of only 0.3 μg m^{-3}, ΔR reaches −0.5, indicating a rapid decrease from $R = 2$ (no NVC) to $R = 1.5$ (with NVC) for these conditions. Thus, not only is ΔR highly correlated with Na^+, it is also highly sensitive to Na^+. This is not seen for the organic aerosol mass fraction, here used as a proxy for the thickness of a possible film because it constrains the organic volume per particle. (A similar plot based on organic aerosol mass concentration is shown in Fig. S2). In stark contrast to Na^+, Fig. 3a shows no correlation between ΔR and organic aerosol mass fraction. (There is also no correlation when ΔR is plotted against OA mass concentration for data points ΔR = measured $R - 2$, and an inverse correlation is observed for some points between ΔR and organic aerosol mass concentration for ΔR = predicted *R* (with Na^+) − predicted *R* (no Na^+), see Fig. S2 in the supplement). These results are inconsistent with the bias in *R* being linked to increases in mass fraction of organic species, as proposed by Silvern et al. (2017).

In comparison to *R*, pH is less sensitive to inclusion of Na^+, or other NVCs in general. ΔpH is only 0.07 for the average Na^+ level of 0.06 μg m^{-3}, and increases to 0.38 at 0.3 μg m^{-3} Na^+ (Fig. 3b). The magnitude of ΔpH is relatively small and consistent with our previous studies where we investigated the effects of sea-salt on pH (Guo et al., 2016; Weber et al., 2016). ΔpH would be higher in regions with more abundant NVC. For instance, a ΔpH of 0.8 unit was found in Pasadena, CA, where the average $PM_{2.5}$ Na^+ mass was 0.77 μg m^{-3} (Guo et al., 2017a). Differences in sensitivity of *R* and pH to Na^+ can be seen based on linear regressions. The magnitude of the Δ*R*-Na^+ slope is −1.74 compared to ΔpH-Na^+ slope of 1.27. Sensitivities of pH and *R* (or R_{SO4}) to Na^+ are discussed further below, next we investigate NVC effects on *R* and pH for a different data set.

NVC Effects on molar ratios and pH based on winter data: The above discussion is based on data collected at a ground site in summertime (SOAS), we expand the investigation of the *R* discrepancy to a larger geographical scale and for a different season by performing a similar analysis with the WINTER study data set collected in wintertime. In this study, NVCs were generally higher, especially when the aircraft sampled near coastlines (e.g. PM_1 Na^+ = 0.23 μg m^{-3}). Also, PM_1 nitrate was comparable to sulfate, largely owing to lower temperatures (NO_3^- 0.013 μmol m^{-3} vs. SO_4^{2-} 0.011 μmol m^{-3}) (Guo et al., 2016). Therefore, R_{SO4} was calculated instead of *R*. In this case the aerosol inorganic composition data input for ISORROPIA-II is from an AMS. Since the AMS does not efficiently detect ions associated with refractory species, such as Na^+ and associated Cl^- from NaCl, in our past analysis of the WINTER aerosol pH, we only included NH_4^+, SO_4^{2-}, and total nitrate (NO_3^- + HNO_3) as input for ISORROPIA-II. (NH_3 should be included, but was not measured, although in this case it was found to have a small effect on predicted pH: ~0.2 higher pH when including an NH_3 concentration of 0.10 μg m^{-3} determined from an iteration method). With these assumptions, we found good agreement between predicted and measured HNO_3-NO_3^- partitioning (average ε(NO_3^-) = 39%), especially when RH was above 60% (Guo et al., 2016). However, again Fig. 4a shows that the model overpredicted R_{SO4}. Also, when concentrations of NVC were low, predicted and measured R_{SO4} was generally 2. (Note that the predicted R_{SO4} should be biased low since NH_4^+ was underpredicted due to lack of NH_3 data, resulting in some fraction of input particle phase NH_4^+ repartitioned in the model to the gas phase). On average, predicted R_{SO4} was 1.68 ± 0.51 versus the measured value of 1.47 ± 0.43. In Fig 4a, the gray error bars show the propagated uncertainties for R_{SO4} based on a 35% AMS measurement uncertainty for NH_4^+, SO_4^{2-}, and NO_3^- (Bahreini et al., 2009).

As in the SOAS data set, including NVCs also brings predicted and measured ammonium-sulfate molar ratios into agreement (Fig. 4b). Here, the amounts of NVC needed for an ion charge balance involving NVC-NH_4^+-SO_4^{2-}-NO_3^- aerosols were calculated based solely on NVC assumed to be Na^+ (the thermodynamic results based on other NVCs are shown in the supplemental material in Fig. S3. K^+ and Mg^{2+} work similarly to Na^+, while Ca^{2+} can precipitate sulfate in the form of $CaSO_4$). Overall, Na^+ is chosen as a proxy NVC in our dataset because it constitutes most of the NVC mass and does not precipitate out of solution. The choice of Na^+ as a NVC proxy, although appropriate here, is not generally applicable; in regions with considerable dust contributions, treating NVC as "equivalent Na^+" in the thermodynamic calculations can result in large prediction errors (e.g., (Fountoukis et al., 2009)). As done before, in this analysis, when the ion charge balance predicts negative Na^+ concentrations (137 data points out of 3226, 4%), a small positive value of 0.005 μg m^{-3} is assigned. It is clear in Fig. 4b that with the added NVC, the predicted R_{SO4} is in good agreement with the observation, with regression result $R_{SO4,predicted}$ = (1.05 ± 0.01) $R_{SO4,observed}$ + (−0.12 ± 0.01), r^2 = 0.99. Again, the molar ratio bias from the thermodynamic model is simply a matter of not including small amounts of NVC (e.g. 0.15 μg m^{-3} Na^+ or 0.26 μg m^{-3} K^+). The average amount of inferred Na^+ from the ion charge balance in this case is smaller than what was measured offline during the study; PM_1 Na^+ of 0.23 μg m^{-3} (Guo et al., 2016). The analysis using measured PM_1 Na^+ results in highly scattered data due to the high sensitivities of R_{SO4} to NVC and the significant Na^+ measurement uncertainty at these low levels and the analytical method used in this study.

Because molar ratios are sensitive to NVCs and NVC concentrations are often very low, use of molar ratios to test the thermodynamic model should be done with caution, but actually not recommended. Since NVC associated with sea-salt and crustal materials are normally very small fractions of the PM_1 inorganic mass, it is typically reasonable to ignore these species when determining PM_1 NH_4^+ and NO_3^- partitioning, or pH, using ISORROPIA-II, as we have shown (Guo et al., 2016; Guo et al., 2017a). Since the molar ratio is a pH proxy that is highly sensitive to small mass concentrations of NVCs, as well as measurement errors, and only provides limited insights on pH and its effects (see discussion in the Introduction), we view this as a minor issue since pH should be used instead (Guo et al., 2017a). Alternatively, if accurate NVC data is not available, NVC can be estimated through an ion charge balance calculation with the measured NH_4^+-SO_4^{2-}-NO_3^- data and include the resulting inferred NVC in the ISORROPIA input, which will produce a better estimate of *R* than setting NVC to zero in the model input.

Effects of not fully considering NVC of pH: The molar ratios and pH reported for SOAS (Guo et al., 2015) and WINTER (Guo et al., 2016) may exhibit biases since NVCs were not fully considered. This was because the NVC (Na^+, K^+, Ca^{2+}, Mg^{2+}) concentrations were low, often close to or below the PILS-IC LOD during the SOAS study (the 1st half period measuring $PM_{2.5}$ and the 2nd half period measuring PM_1 with even lower NVC) and not measured by an AMS during the WINTER study. We have discussed the effect of NVC on *R* and R_{SO4} above, here we focus on the effect on pH and the implications.

In our datasets, ion charge balance inferred Na^+ (or K^+, Mg^{2+}) is an upper limit (for assuming complete dissociation; e.g., all sulfate is in the form of SO_4^{2-}) on soluble NVC based on the observed NH_4^+-SO_4^{2-}-NO_3^- data, and satisfies the criterion of aerosol electrical neutrality. As shown above, H^+ is negligible in ion charge balance calculation even at such low pH of 1. Using an inferred Na^+ as a reference value, a worst case of zero NVC in the input results in an underestimation of pH by 0.32 for SOAS and 0.49 for WINTER, and overestimation of molar ratios by 0.58 for SOAS (*R*) and 0.62 for WINTER (R_{SO4}), respectively. Using measured Na^+ as input instead of zero NVC results in a difference in pH of −0.26 and 0.22, and in molar ratio of 0.46 (*R*) and −0.33 (R_{SO4}), for SOAS and WINTER, respectively. (See Section 4 in the supplemental material). NVCs are seen to have a larger effect on molar ratios than pH based on the regression slopes (see Fig. 3), and the effect is even more pronounced considering observed ranges in molar ratios (*R* or R_{SO4} from 0 to 2) are less than pH (from -1 to 3) (see Fig. S5) (Guo et al., 2015; Guo et al., 2016).

As noted, NVC concentrations may be uncertain due to low concentrations, measurement uncertainties or not measured at all. Comparing observed and predicted partitioning of NH_3-NH_4^+ or HNO_3-NO_3^- provides insights on the accuracies of NVC concentrations used in the thermodynamic analysis. For example, as discussed above for the 11-13 June period in Fig. 1, the model fairly accurately predicts NH_3-NH_4^+ partitioning with input of measured Na^+, whereas inclusion of inferred Na^+ does not produce as good a result. Overall, our previously reported pH for SOAS and WINTER studies appears sufficiently accurate for the majority of the data since the pH and predicted partitioning was in reasonable agreement with observed partitioning of NH_3-NH_4^+ or HNO_3-NO_3^- without ion charge balance inferred NVC as input. (For example, see the 12-day SOAS data (Fig. 2) and the WINTER data for periods of 60-95% RH (Guo et al., 2016)). However, during periods when a bias is observed between measured and predicted partitioning, including or slightly adjusting NVC concentrations can be tested as a possible cause (note that increasing NVCs always increases the pH).

Even though the effect of NVC on pH may appear relatively small (e.g., difference of 0.2 to 0.5 pH units) the impact on predicted partitioning of a semivolatile species can be significant due to the highly non-linear response of NH_3-NH_4^+ or HNO_3-NO_3^- partitioning to pH (i.e., S curve) (Guo et al., 2016; Guo et al., 2017a). For example, for SOAS average conditions, a 0.3 unit pH bias (i.e., as noted above) results in ~ 20% bias in prediction of $\varepsilon(NH_4^+)$ or $\varepsilon(NO_3^-)$ when $\varepsilon(NH_4^+)$ or $\varepsilon(NO_3^-)$ = 50%, or no bias at all when the species are completely in one phase, $\varepsilon(NH_4^+)$ or $\varepsilon(NO_3^-)$ = 0% or 100%. For the WINTER data set, a 0.5 (see above) unit pH bias causes up to 30% bias in $\varepsilon(NH_4^+)$ or $\varepsilon(NO_3^-)$ (illustrated in Fig. S5). These partitioning biases may constitute

a significant source of bias for aerosol nitrate formation, especially if the total nitrate present in the gas-aerosol system is significant. In fact, the bias from the NVC may completely change the predicted response of nitrate to aerosol emissions and lead to errors in the predicted vs. observed trends in pH, such as was seen in the SE US (Vasilakos et al., 2017).

In our past studies, we also investigated trends in pH and molar ratios over time periods of changing emissions. Our interest was on the lack of change in pH over the past 15 years of despite a 70% reduction in sulfate aerosol (Fig. 5) (Weber et al., 2016). For example, Weber et al. (2016) reported thermodynamic calculations based on an average $PM_{2.5}$ and PM_1 PILS-IC Na^+ concentration of 0.03 μg m^{-3} from the SOAS study applied to all historical data (Fig. 2 in that paper). The Na^+ concentration was uncertain due to being significantly below the Na^+ measurement LOD (0.07 μg m^{-3}) and substantially lower than period average Na^+ of 0.28 μg m^{-3} calculated from a charge balance. This simplification did not consider historical Na^+ trends (although there was no trend in Na^+ mole fraction, see Fig. 5). With a constant ISORROPIA Na^+ input of 0.03 μg m^{-3}, predicted R_{SO4} does not follow the widespread observed trend of R_{SO4} decreasing from 1998 to end of 2013 in the southeastern US, but instead was nearly constant at ~1.9 (Fig. 5). Repeating the calculations using Na^+ inferred from the ion charge balance of Na^+-NH_4^+-SO_4^{2-}-NO_3^-, determined for each daily data point, results in good agreement between observed and predicted R_{SO4}; ISORROPIA-predicted R_{SO4} now reproduces the observed decrease R_{SO4} trend (Fig. 5 & Fig. S6 in the supplement). In contrast, using these different Na^+ input concentrations did not change the trends in ISORROPIA-predicted pH, in both cases it remained relatively constant (Fig. S6), but as expected the pH was slightly higher with higher input Na^+ concentrations (i.e., from ion charge balance).

4. Summary

Excluding minor amounts of submicron NVC in thermodynamic calculations results in predicted ammonium-sulfate molar ratios (R) near 2, which is generally higher than observed values. This results from the model criteria for aerosol electrical neutrality. Less absolute discrepancy is associated with predicted particle pH with or without NVC because pH is on a logarithmic scale of H_{aq}^+ and the range of pH is larger than that of R (or R_{SO4}) in the eastern US. However, neglecting NVC can induce pH biases that imply important partitioning errors for semivolatile species like ammonium, nitrate, chloride, and even organic acids. An important finding is that including small amounts of NVCs in the thermodynamic model brings predicted and measured R into agreement. Because NVCs are often minor constituents of fine particles, especially for PM_1, implying low ambient concentrations and high measurement uncertainties, assessing thermodynamic model predictions through molar ratios is problematic. For the eastern US, good agreement between ISORROPIA-predicted (with measured NVCs in SOAS $PM_{2.5}$ input and no NVC in WINTER PM_1 input; no consideration of organic compounds) and measured partitioning of NH_3-NH_4^+ (Guo et al., 2015; Weber et al., 2016), HNO_3-NO_3^- (> 40% RH in Guo et al. (2016)) and water vapor-aerosol liquid water (Guo et al., 2015), together with a lack of correlation of the bias with organic fraction discounts any influence of organic films and validates the thermodynamic equilibrium assumption for submicron aerosol. If organic films were limiting mass transfer, the discrepancy in R should worsen as the films become thicker. We find the opposite, the discrepancy in R is positively correlated with NVC and not correlated with the organic mass fraction or mass concentration. If NVCs were not measured, or significantly below the measurement LOD, for the data sets investigated here, an ion charge balance could be used to infer NVCs. Comparing measured and thermodynamic model predicted partitioning of semivolatile species provides insights on the importance of NVCs in the model predictions. Fully considering NVC doesn't change the finding of nearly constant fine particle pH in the southeastern U.S. (summertime) despite a large sulfate reduction, the result supported by predicting a R_{SO4} decreasing trend agreeable to the 15

years' observations. Overall, we find that the unique and non-intuitive behavior of pH reported in our past studies can be simply and consistently explained by thermodynamics without the need for organic films with selective ion transport properties.

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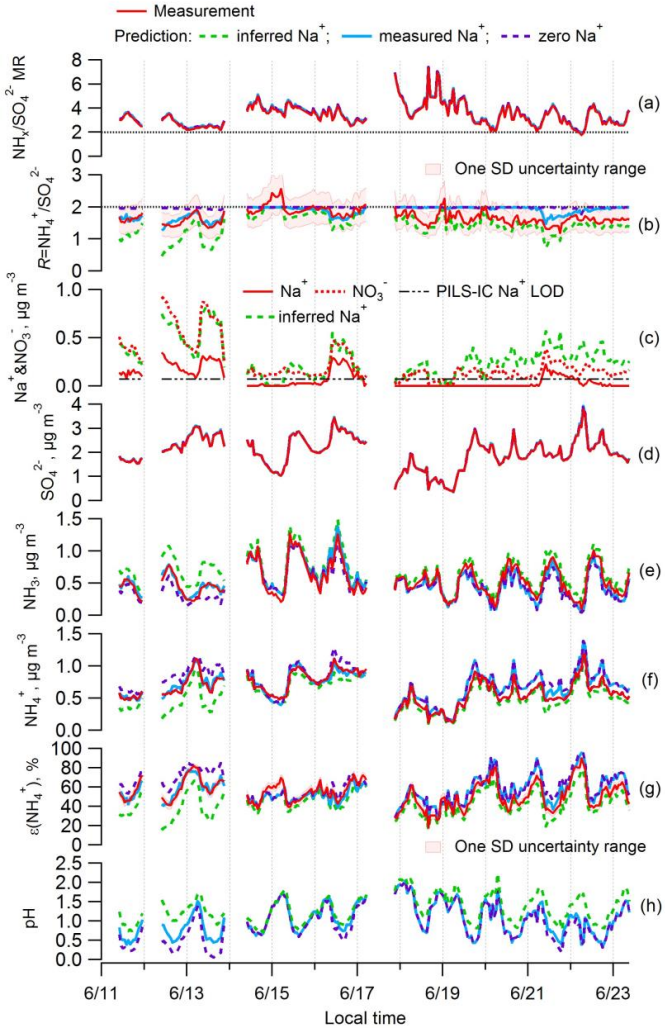

Figure 1. Time series of various measured and ISORROPIA-predicted parameters and $PM_{2.5}$ component concentrations for a select period of the SOAS study, with periods of rainfall removed. Three ISORROPIA-predicted results are shown at different Na^+ levels; calculated Na^+ needed for ion charge balance ($Na^+ = 2SO_4^{2-} + NO_3^- + Cl^- - NH_4^+$, μmol m^{-3}; mean value of 0.28 ± 0.18 μg m^{-3}) in green, measured Na^+ blue, and zero Na^+ in purple. All other inputs were the same. Na^+ represents generic non-volatile cations (NVC). Specific plots are as follows: (a) total ammonium ($NH_x = NH_4^+ + NH_3$) to sulfate molar ratio (NH_x/SO_4^{2-}), (b) aerosol ammonium-sulfate ratios ($R = NH_4^+/SO_4^{2-}$), (c) Na^+ and NO_3^-, (d) SO_4^{2-}, (e) NH_3, (f) NH_4^+, (g) particle-phase fractions of total ammonium, $\varepsilon(NH_4^+)$, and (h) particle pH.

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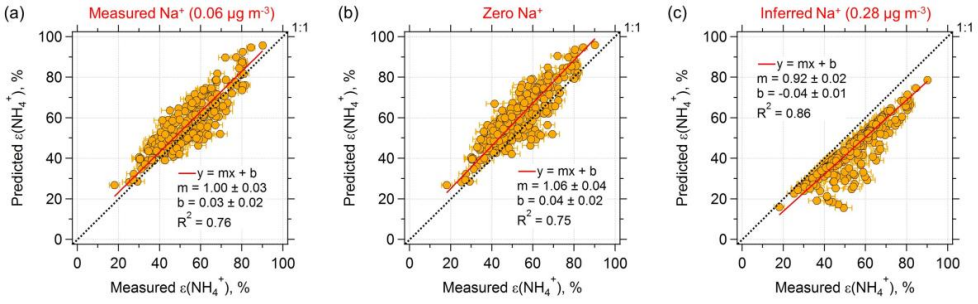

Figure 2. Comparisons of predicted and measured particle phase fractions of total ammonium, $\varepsilon(NH_4^+) = NH_4^+/(NH_3 + NH_4^+)$, for a 12-day period data from the SOAS study. NH_4^+ was measured with a PILS-IC ($PM_{2.5}$ cut size) and NH_3 from a CIMS. (a) The model prediction is based on an ISORROPIA input of measured Na^+, ($NH_4^+ + NH_3$), SO_4^{2-}, NO_3^-, Cl^-; (b) Model input is identical to (a), except that Na^+ is set to zero; (c) Same model input, but Na^+ is inferred from an ion charge balance. Orthogonal distance regression (ODR) fits are shown and uncertainties in the fits are one standard deviation (SD). Uncertainty of measured $\varepsilon(NH_4^+)$ is derived from error propagation of NH_4^+ (20%) and NH_3 (6.8%) measurements. Best agreement is achieved by using measured Na^+ as input. In general, very good prediction of NH_3-NH_4^+ partitioning was achieved by a thermodynamic model without including organic species.

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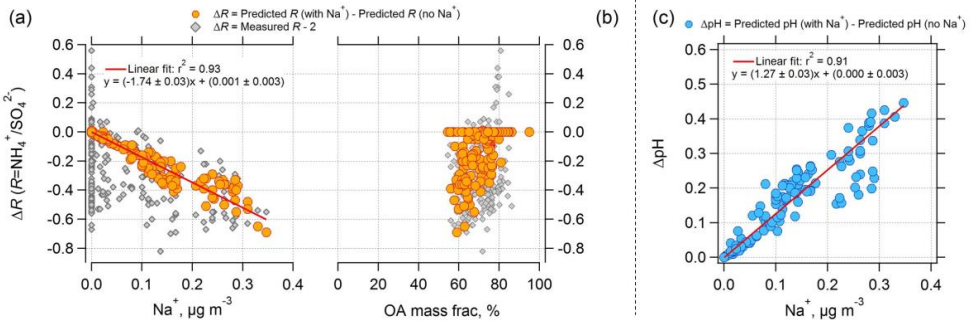

Figure 3. Effect of nonvolatile cations (NVC) on the $PM_{2.5}$ ammonium-sulfate molar ratio (R) and pH as a function of measured Na^+ concentration and organic aerosol (OA) mass fractions. The orange circular points in plots (a) and (b) are for ΔR equal to ISORROPIA predicted R with measured Na^+ included in the model input minus ISORROPIA predicted R without Na^+ in the model input. ΔpH in plot (c) is determined in a similar way. The grey diamonds in plots (a) and (b) are for ΔR equal to the actual measured R minus 2. Note that ΔR should be negative since including Na^+ in the thermodynamic model results in R lower than 2, whereas not including Na^+ results in an R close to 2 (on average R predicted without Na^+ is 1.97 ± 0.02), a measured R is generally less than 2. Plot (a) is ΔR versus measured Na^+, (b) ΔR versus measured OA mass fraction, and (c) ΔpH versus measured Na^+. Orthogonal distance regression (ODR) fits are shown and uncertainties in the fits are one standard deviation. A plot similar to (b), but versus OA mass concentration can be found as Fig. S2 in the supplemental material.

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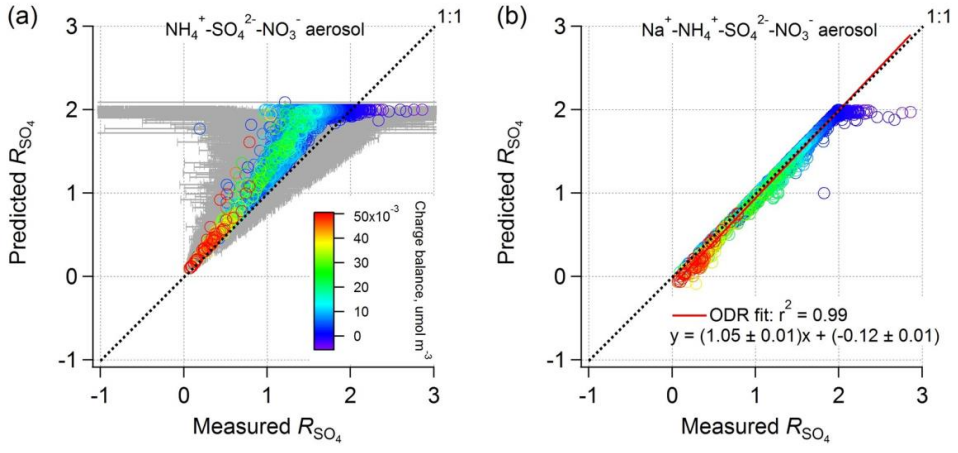

Figure 4. Comparison between PM_1 ISORROPIA-predicted R_{SO4} and AMS-measured R_{SO4} ($R_{SO4} = (NH_4^+ - NO_3^-)/SO_4^{2-}$) (mol mol^{-1}), where the ISORROPIA-prediction is based on (a) NH_4^+-SO_4^{2-}-NO_3^- aerosol and (b) Na^+-NH_4^+-SO_4^{2-}-NO_3^- aerosol both constrained by HNO_3. All measurement data are from the WINTER study. NVC was determined by an ion charge balance with the molar concentration shown as the color wave. For this data, the average predicted Na^+ concentration is 0.15 μg m^{-3}, comparable to the offline PILS fraction collector IC-measured PM_1 Na^+ of 0.23 μg m^{-3}. The one SD uncertainty range for the measured R_{SO4} is shown as gray error bars. The data points with low SO_4^{2-} levels (<0.2 μg m^{-3}; 9% of the total points) were excluded for high uncertainties. In both plots, the molar ratios are zero when concentrations of NH_4^+ are near zero and NVC concentrations highest. In plot (a), as molar ratios approach 2, predicted NVC levels drop, but the effect of not including them in the thermodynamic model results in larger deviations in predicted versus measured R_{SO4}. Error bars also increase due to subtraction of higher concentrations of nitrate and thus more subject to measurement error. As with the SOAS data, including NVC in the model results in agreement between predicted and measured ammonium-sulfate molar ratios.

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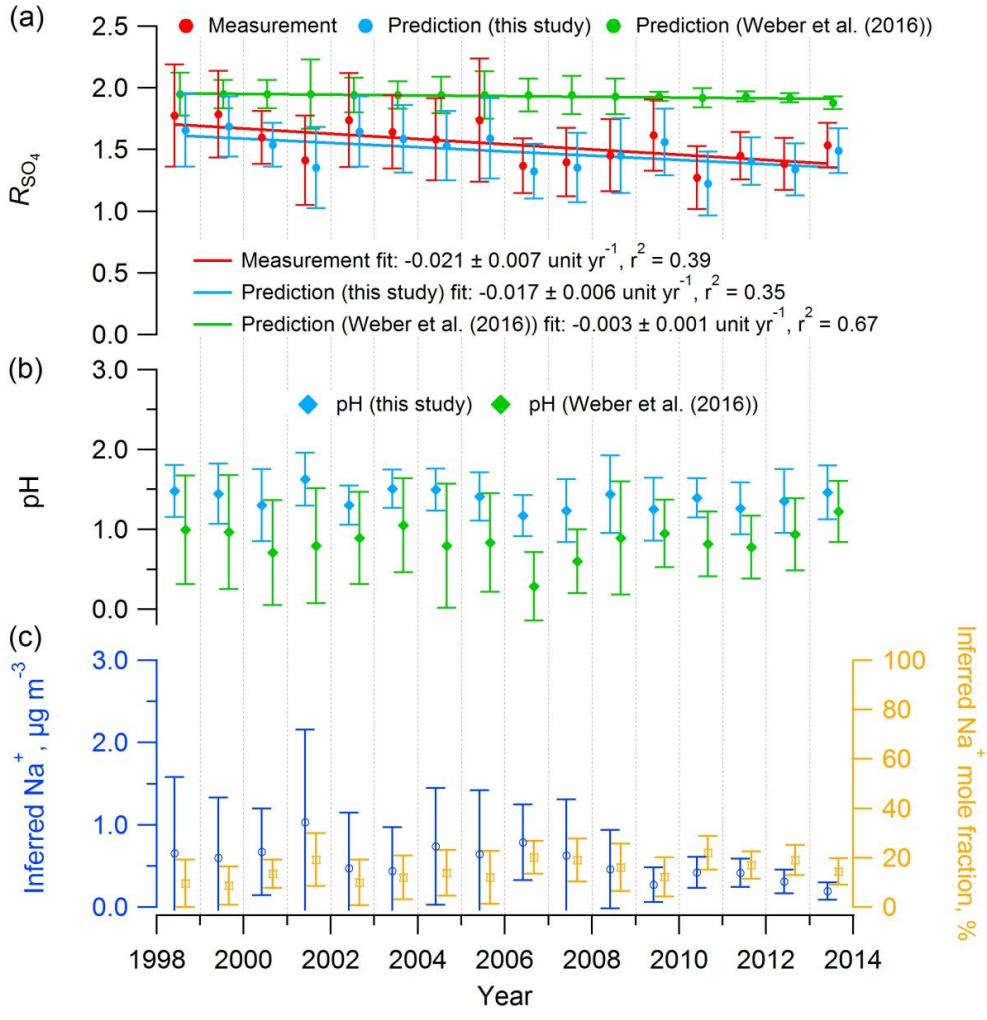

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Figure 5. Mean summer (June–August) trends in (a) measured and predicted R_{SO4}, (b) predicted $PM_{2.5}$ pH, and (c) inferred Na^+ (from ion charge balance of Na^+-NH_4^+-SO_4^{2-}-NO_3^- aerosols) concentration and mole fraction at the SEARCH-CTR site. Model input includes the observational $PM_{2.5}$ composition data (NH_4^+, SO_4^{2-}, NO_3^-) and meteorological data (RH, T) at CTR. R_{SO4} and pH were estimated with ISORROPIA-II run in forward mode with an assumed NH_3 level of 0.36 μg m^{-3}, the mean concentration from the SOAS study (CTR site, summer 2013), due to limited NH_3 data before 2008. Historical NH_3 mean summer concentration at CTR were 0.2 μg m^{-3} (2004-2007) (Blanchard et al., 2013) and 0.23 ± 0.14 μg m^{-3} (2008-2013) (Weber et al., 2016). 41 out of the total 609 (7%) daily mean R_{SO4} were observed above 3 due to measurement error, above the upper limit of R_{SO4} = 2, therefore, excluded in the model input. Error bars represent daily data ranges (SD). Linear regression fits are shown and uncertainties in the fits are one SD. In (a), based on regression slope, the observed R_{SO4} trend was –0.021 ± 0.007 at CTR versus a predicted value of –0.017 ± 0.006 unit yr^{-1} for ISORROPIA run with Na^+ from the charge balance, and –0.003 ± 0.001 unit yr^{-1} for a constant Na^+ of 0.03 μg m^{-3}, used by Weber et al. (2016). These results are consistent with the reported R_{SO4} trend of –0.01 to –0.03 yr^{-1} reported by Hidy et al. (2014) for SEARCH data set. In (b), the pH predictions with inferred Na^+ or with limited Na^+ of 0.03 μg m^{-3} shows a fairly stable $PM_{2.5}$ pH in the last 15 years. In (c), the inferred Na^+ shows a general decreasing trend while the inferred Na^+ mole fraction stays relatively stable around 15% (± 4%).