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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~~. Measurements show that the deviation between *R* from a molar ratio of 2 is correlated with sodium (Na^+), a nonvolatile cation (NVC), with no correlation to organic aerosol mass concentration or mass fraction. *R* predicted by the thermodynamic model is very sensitive to concentrations of Na^+ or NVC in general. Both *R* and ammonia gas-particle partitioning can ~~be~~ accurately ~~reproduced~~reproduce observations when small amounts of nonvolatile cations (NVC~~), consistent with observations,~~) are ~~considered~~included in the thermodynamic analysis~~. Exclusion~~, whereas exclusion of NVCs results in predicted *R* consistently near 2. ~~The error in *R* is positively correlated with NVC~~ This happens because more NVCs shift pH higher, shifting NH_3-NH_4^+ equilibrium to favor the gas and resulting in less particle phase ammonium and lower *R*. When NVCs are present, but not ~~organic aerosol mass fraction or concentration.~~included in the thermodynamic model, the missing cation is replaced with ammonium in the model (NH_3-NH_4^+ equilibrium shifts to the particle), resulting in higher *R*. Thus, poor representation of NVCs in the thermodynamic model leads to higher *R* than observed. None of these effects are associated with interactions between inorganic and organic aerosol components. These analyses are based on bulk aerosol composition measurements and assuming all species are internally mixed, however, similar results are found even if NVCs and sulfate and ammonium are largely externally mixed, as long as a small fraction of the sulfate is mixed with the NVCs. These results strongly challenge the postulated ability of organic films to perturb aerosol acidity ~~or~~and prevent ammonia from achieving gas-particle equilibrium for the conditions considered. Furthermore, the results demonstrate the limitations of using molar ratios to infer aerosol properties or processes that depend on particle pH.

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)~~(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)~~(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 solubility ~~(Meskhidze et al., 2003; Nenes et al., 2011; Longo et al., 2016; Fang et al., 2017)~~(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~~. Despite its importance, challenges in measuring fine mode particle pH have 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)~~(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;~~ because 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)~~(Guo et al., 2015; Hennigan et al., 2015; Guo et al., 2016). ~~The~~A better 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)~~(Guo et al., 2015; Hennigan 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)~~(Kim et al., 2015; Weber et al., 2016; 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)~~(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)~~. Thermodynamic models 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)~~(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~~ because particles are coated by organic films that inhibit the condensation of NH_3 from the gas phase ~~and give~~, which gives rise to the molar ratio discrepancy ~~(Silvern et al., 2017).~~(Silvern et al., 2017). Such kinetic limitations, if prevalent, opposes the validity of aerosol thermodynamic equilibrium ~~and~~. This could significantly impact aerosol chemistry and acidity-mediated processes, given the large organic aerosol mass fractions worldwide ~~(Zhang et al., 2007)~~(Zhang et al., 2007) and expected increasing organic mass fractions in the future due to changing emission, ~~such~~ as seen with SO_2 emission ~~reduction~~reductions in the eastern US ~~(Hand et al., 2012; Attwood et al., 2014; Hidy et al., 2014)~~(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)~~(Ansari and Pandis, 2000; Moya et al., 2001; Morino et al., 2006; Fountoukis et al., 2009; Guo et al., 2015; Guo et al., 2016; Guo et al., 2017a; Liu et al.,

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2017; Paulot et al., 2017)~~. Such a film, as proposed by Silvern et al. (2017)~~. 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~~particles 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)~~(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 has not been observed 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~~is sufficiently high (greater than 40~~%,~~%) that the aerosol is likely ~~owning to glassy states during the wintertime)~~in a complete liquid state (~~Guo et al., 2015~~Guo et al., 2015; Guo et al., 2016).

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Other reasons that are unrelated to organic films may drive the molar ratio discrepancy. ~~One is related to the~~Most analyses of aerosol acidity, molar ratios and partitioning of semivolatile species do not consider variation of aerosol composition with size, which may translate to a large range of acidity~~,~~ and hence equilibrium composition ~~(Keene et al., 1998; Nenes et al., 2011; Bougiatioti et al., 2016; Fang et al., 2017)~~(Keene et al., 1998; Nenes et al., 2011; Young et al., 2013; Bougiatioti et al., 2016; Fang et al., 2017). ~~Another related issue is the~~The presence of soluble nonvolatile cations (~~NVC~~NVCs, 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~~and ion charge balance (e.g., (Kim et al., 2015; Silvern et al., 2017)), or because they are not routinely included in aerosol composition measurements (e.g., those made with an aerosol mass spectrometer~~). Here we show~~), or are not well quantified due to high measurement limit of detections (LODs) relative to anion species, can affect acidity and molar ratios. Here we show, based on a bulk $PM_{2.5}$ aerosol analysis 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~~them brings model-predicted molar ratios into agreement with observed levels. We also assess the implications of a bulk analysis by comparing those conclusions to aerosol that is externally mixed.

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2. Methods

Molar ratios definition: Two ammonium-sulfate aerosol molar ratios (mol mol^{-1}) are used in the following analysis,

$$R = \frac{NH_4^+}{SO_4^{2-}} \tag{1}$$

$$R_{SO_4} = \frac{NH_4^+ - NO_3^-}{SO_4^{2-}} \tag{2}$$

~~both~~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 some fractions of ammonium sulfate and ammonium nitrate ~~are typically~~can be associated with different sized particles ~~(externally mixed) (Zhuang et al., 1999)~~(Zhuang et al., 1999) and molar ratios are calculated based on bulk composition data ($PM_{2.5}$ or PM_1). This issue is discussed in more details below. The upper limit for R and R_{SO4} is 2 for a particle composition of pure (~~NH_4~~NH_4)$_2SO_4$, ~~the~~and a lower limit ~~is~~of 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 are rare for ambient fine particles~~.~~ (at least not seen in the two data sets studied in this paper). 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)~~(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).

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~~**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 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~~

Data: 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. $PM_{2.5}$ ions were determined with from Particle-Into-Liquid-Sampler coupled with an Ion Chromatograph (PILS-IC). 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). NH_3 was from chemical ionization mass spectrometer measurements (You et al., 2014). In the following, we only use $PM_{2.5}$ ion data from a 12-day period (11-23 June) of the SOAS campaign. This is only part of our SOAS data set, which involved measurement of $PM_{2.5}$ in the first half of the study and PM_1 in the second half. Periods of rainfall are not included in the analysis. The same data set was used to study pH sensitivity to sulfate and ammonia (Weber et al., 2016). $PM_{2.5}$ anion and cation data were also collected during SOAS, along with NH_3 and HNO_3 with a Monitor for AeRosols and GAses (MARGA) (Allen et al., 2015). These data support the PILS data analysis; the results are similar using either data set. The WINTER data was collected during 13 research aircraft flights from 1 February to 15 March 2015 mainly sampling over the northeastern US. We use PM_1 aerosol data collected with a High-Resolution Time-of-Flight Aerosol Mass Spectrometer (hereafter referred to as AMS), which have been extensively compared to the PILS anion measurements also made in that study (Guo et al., 2016). Details of the these two 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 focus on R for summertime data sets since NO_3^- was generally low, and R_{SO4} for wintertime data sets where higher NO_3^- concentrations were observed. 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, 10% of the total sulfate is predicted to be HSO_4^- for the SOAS condition (see Fig. S1 in the supplement). Free form H_2SO_4, which requires even lower pH, is rare. 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 report total aqueous sulfate as just SO_4^{2-}. The same applies to NH_4^+ and NO_3^-. The AMS vaporizes aerosols and ionizes non-refractory species with a 70 eV electron impact ionization and also cannot distinguish the dissociation states of inorganic ions (DeCarlo et al., 2006).

Thermodynamic analysis of observations: We have used the thermodynamic model ISORROPIA-II ~~(Bougiatioti et al., 2016; Guo et al., 2016; Weber et al., 2016; Guo et al., 2017a; Guo et al., 2017b)~~(Fountoukis and Nenes, 2007)~~. Here pH is defined following the same approach,~~ to determine the liquid water content and composition (including H^+) 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 in a number of different locations (Guo et al., 2015; Bougiatioti et al., 2016; Guo et al., 2016; Weber et al., 2016; Guo et al., 2017a; Guo et al., 2017b). As in all of these studies pH is defined as;

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

where γ_{H^+} is the hydronium ion activity coefficient (assumed = 1; note that the binary activity coefficients of ionic pairs, including H^+, is calculated in the model), H_{aq}^+ (mol L^{-1}) the hydronium ion concentration in particle liquid water, and H_{air}^+ (μg m^{-3}) the hydronium ion concentration per volume of air~~, and~~. W_i~~,~~ and W_o (μg m^{-3}) are particle water concentrations associated with inorganic and organic species, respectively. pH predicted solely with predicted W_i is fairly accurate~~;~~. We found the 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)~~measured total particle water ($W_i + W_o$) in the southeast (which includes the SOAS study), 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.~~$NH_3 + NH_4^+$). In all cases we also chose a "metastable" (not "stable") solution, which assumes inorganic ions are associated with the aerosol components that are completely aqueous and contain no solid precipitates (H^+_{aq} is meaningless in a completely effloresced aerosol) and so restrict the analysis to conditions where RH > 40%.

~~3.~~

Mixing State: Because the aerosol composition data is bulk PM_1 or $PM_{2.5}$, we also assumed that the particles were internally mixed and that pH did not vary with size. This assumes that bulk properties represent the aerosols, including pH, and that gas-particle partitioning was in thermodynamic equilibrium with one bulk mixture of inorganic ions. In the following, we perform the analysis of NVCs on molar ratios and pH under the totally internal mixture (bulk) assumption. Then in the discussion that follows, we consider how the results of this assumption affects our findings by assuming NVCs are largely externally mixed with sulfate. In the external mixing analysis, the bulk aerosol is split into two subgroups that can be viewed as species largely found in PM_1 (e.g., NH_4^+ and SO_4^{2-}) and species found in $PM_{1\text{-}2.5}$, which contains mostly the NVCs, NO_3^- and some SO_4^{2-} and NH_4^+. These two external mixtures are in equilibrium with the same gases, NH_3 and HNO_3, and so interact through these species (i.e., NH_4^+ and NO_3^- can move between the two subgroups). Nonvolatile species, such as SO_4^{2-} and NVCs (Na^+) remain in the original size class assumed at the start of the analysis. To determine the final composition of the two subgroups we iteratively solve for the equilibrium conditions for each subgroup, by sequentially performing the equilibrium for one subgroup than the other. The final solution is found when the composition of each group no longer changes and are in equilibrium with the same gas phase species (in this case, NH_3, HNO_3, and H_2O (water vapor)). Mass of each species (gas plus particle) is conserved at all times. The assumed starting fractions of the semivolatile species in the subgroups (i.e., NH_4^+ and NO_3^-) does not affect the final solution. Below we test how the extent of SO_4^{2-} mixing with the NVCs affects pH and *R* compared to the bulk analysis. Previous studies have shown that pH is size dependent and generally higher at larger size (Young et al., 2013; Bougiatioti et al., 2016; Fang et al., 2017). The pH of the two externally mixed group of particles differ, and may also differ from the bulk pH determined from the internally mixed case. For comparison to the bulk pH, the average pH of the external mixture can be determined by:

$$\mathrm{pH} = -\log_{10}\frac{1000\left(H^+_{air,subgroup\ 1}+H^+_{air,subgroup\ 2}\right)}{W_{i,subgroup\ 1}+W_{i,subgroup\ 2}} \qquad (4)$$

ISORROPIA input data files for the analyses reported in this paper are available in the supplemental files.

3. Results

3.1 NVCs cause discrepancy in molar ratios (*R*) prediction

The SOAS data set: We first investigate the issue of *R* discrepancy using PILS-IC $PM_{2.5}$ data from a 12-day period of the SOAS campaign. To test the sensitivity of ISORROPIA-II predictions to NVCs, we ran the model with three different Na^+ concentration inputs, with all other inputs (referred as the base case) remaining the same. Inputs for the base case included: total ammonium ($NH_x = NH_4^+ + NH_3$), SO_4^{2-}, NO_3^-, and Cl^-. Ca^{2+}, Mg^{2+}, K^+ inputs were set to zero as they were mostly below detection limits. Three different Na^+ input concentrations were tested: (1) Measured $PM_{2.5}$ Na^+ from PILS-IC, including data below the LOD; (2) Na^+ determined from an ion charge balance, $Na^+ = 2SO_4^{2-} + NO_3^- + Cl^- - NH_4^+$ (unit: nmol m^{-3}), hereafter as inferred Na^+; (3) $Na^+ = 0$.

The LOD of PILS-IC Na^+ was 0.07 μg m^{-3}, close to the average Na^+ concentration (determined including values below detection limits) that was measured during this period. In the following, Na^+ data below the LOD is used in the analysis to increase the size of the data set. Data below LOD are identified in the figures throughout. Na^+ data below LOD generally agree with independent MARGA measurements of Na^+, see Fig. S2a in the supplement. As all other NVC, such as K^+, Ca^{2+} and Mg^{2+}, were also generally below the ~~**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~~ LOD and set to zero in the ~~model input). The~~ analysis, 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~~ Inferred Na^+ has a high uncertainty due to error propagation of NH_4^+, SO_4^{2-}, NO_3^-, and Cl^- measurements (see Fig. S2b). Inferred Na^+ is generally above zero~~; for calculated values below zero (~~ indicating a cation deficiency, but 8 out of 229 points~~,~~ (3% of the data~~), due to combined measurement uncertainty~~) were slightly below zero. In these cases, a small positive value of 0.005 μg m^{-3} ~~is assigned.~~

was assigned to inferred Na^+. Including these data has no effect on the results because the observed *R* was ~2. The concentration of H^+ is ~~also~~ ignored in the ion charge balance calculation ~~as~~since 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~~35.4, SO_4^{2-} = ~~0.0211~~21.1, NO_3^- = ~~0.0037~~3.7, Na^+ = ~~0.0029~~2.9, and Cl^- = 0.~~00082 μmol~~82 nmol m^{-3}, compared to ISORROPIA-predicted H^+ = 0.31 nmol m^{-3}. Fig. ~~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}).~~1a shows that the inferred Na^+ was always higher than measured Na^+. This is due to overestimation of Na^+ by assuming total aqueous aerosol sulfate as SO_4^{2-} and contributions from other NVCs (K^+, Mg^{2+}, and Ca^{2+}). The inferred Na^+ from PILS and MARGA generally agree with each other and also agree with the total NVCs from MARGA measurements before June 18. The larger differences after June 18 are likely from difficulties in detecting NVCs in low concentrations and accumulation of systematic errors in various ionic species measured by one or both of these instruments.

The SOAS study period investigated here includes an episode of high Na^+ associated with a sea-salt (NaCl) aerosol event (Fig. 1a). This provided an opportunity to assess the role of NVCs on pH when concentrations were substantially above LOD. Periods when Na^+ was closer to typical background levels and near or below the LOD lead to similar conclusions in the following analysis. The observed Na^+ is mainly associated with NO_3^- (Fig. 1a), and to a lesser degree with Cl^-. These ions are highly correlated (Na^+-NO_3^- $r^2 = 0.82$ and Na^+-Cl^- $r^2 = 0.64$) and indicate some level of "chloride depletion" as the observed Cl^-/Na^+ ratio was 0.24 ± 0.16 (mol mol^{-1}) (mean ± SD), whereas fresh sea salts would have a molar ratio close to 1 (Tang et al., 1997). Chloride depletion occurs when an acid, such as HNO_3, is mixed with NaCl producing HCl that evaporates since higher volatility than HNO_3 (Fountoukis and Nenes, 2007), resulting in a loss of Cl^- and H^+ (increase in pH). Cl^- concentrations were sufficiently small (0.03 ± 0.04 μg m^{-3}, LOD = 0.01 μg m^{-3}) compared to the dominant and nonvolatile anion SO_4^{2-} and HCl was not included in the model input, so Cl^- had negligible effect on ISORROPIA predictions of pH and molar ratios.

Fig. ~~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~~1 shows the effect of Na^+ (i.e., NVCs in general) on ISORROPIA-predicted SO_4^{2-}, NH_4^+, NH_3, *R*, and pH ~~is investigated.~~. Fig. ~~1a~~1b and Fig. ~~1d~~1e show ~~the overall behavior of~~that measured and predicted sulfate (SO_4^{2-}) and total ammonium ($NH_x = NH_3 + NH_4^+$) ~~and sulfate.~~are always identical. SO_4^{2-} is nonvolatile and so remains unchanged by the model~~, as does total ammonium and hence~~ (output = input). The model predicts the gas-particle partitioning by conserving NH_x, so the NH_x/SO_4^{2-} molar ratio is also always accurately predicted. Therefore, the discrepancy between modeled and measured *R* must result from variation in the ~~NH_4^+~~model prediction of NH_x partitioning, i.e., the predicted NH_4^+ concentration. It is noteworthy that NH_x/SO_4^{2-} is ~~generally~~ practically always above 2, indicating excess NH_x compared to SO_4^{2-}. Under such conditions, it is ~~often~~sometimes interpreted that NH_3 must completely neutralize SO_4^{2-} ~~(Kim et al., 2015; Silvern et al., 2017)~~(Kim et al., 2015; Silvern et al., 2017)~~. The~~, but 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~~). This results from NH_4^+ ~~semivolatility~~being semivolatile and SO_4^{2-} being virtually nonvolatile at any atmospherically-relevant concentration and acidity (Weber et al., 2016).

Comparing measured to ISORROPIA-predicted NH_3-NH_4^+ partitioning (particle phase fraction of total ammonium, $\varepsilon(NH_4^+) = NH_4^+/NH_x$) can be used to test the model output to various Na^+ input concentrations. Fig. 1g and Fig. 2 shows very good agreement between measured and observed NH_3-NH_4^+ partitioning when measured Na^+ is used in the model. However, inferred Na^+ generally under-predicts $\varepsilon(NH_4^+)$, possibly because for this data set it over-predicts NVC levels, resulting in higher pH (Fig. 1h), and a higher pH shifts a fraction of the NH_4^+ to gas phase NH_3. Zero Na^+ shows the opposite (Fig. 1g and Fig. 2): $\varepsilon(NH_4^+)$ is over-predicted because predicted pH is too low for no NVCs in the model but actually present in the aerosol. A lower pH partitions more NH_3 to the particle phase ($\varepsilon(NH_4^+)$ is too high).

R also depends on the input Na^+ concentration. ~~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: $\varepsilon(NH_4^+)_{predicted} = (1.00 \pm 0.03)\ \varepsilon(NH_4^+)_{observed} + (0.03 \pm 0.02)$, 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,~~

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~~the highest NH_4^+ and ε(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. 1f shows the time series comparison between *R* for various Na^+ levels included in the ISORROPIA input. Fig. 3 shows the summary statistics for various comparisons of *R*. For the SOAS analyzed time period, for an ISORROPIA input of the base case and measured Na^+, the predicted *R* was on average 1.85 ± 0.17. Predicted *R* was significantly lower by inferred Na^+ at a mean of 1.43 ± 0.32, and the highest *R* at 1.97 ± 0.02 was found when zero Na^+ was used as model input (see Figs. 1f and 3). The average measured *R* was 1.70 ± 0.23 for all PILS data and 1.61 ± 0.19 excluding the points with Na^+ below LOD. The MARGA measurement of *R* is very similar. For example, MARGA measured *R* was 1.78 ± 0.18 for all data and 1.65 ± 0.15 for periods when PILS Na^+ was above LOD (Allen et al., 2015), see Fig. S3 in the supplement. (Fig. S4 shows a scatter plot of these comparisons for the three Na^+ cases). Overall, these results show: (1) when NVCs are most accurately measured (above LOD), ISORROPIA predicted *R* is in close agreement with measured *R* (t- test at α = 0.05 confirms no statistical difference); (2) inferred Na^+ is overestimated for this data set and has higher uncertainty, resulting in a lower predicted *R* than measured *R*; (3) when $Na^+ = 0$ is input, ISORROPIA always predicts *R* ~ 2, a consequence of electroneutrality of the aerosol aqueous phase.

Sensitivity of R and pH to NVCs: The sensitivities of *R* and pH to Na^+, or any other NVC, is of interest. The discrepancy in *R* has been shown to 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. In the SOAS case, inferred Na^+ resulted in too low predicted *R* (Fig. 3), likely because of propagation of SO_4^{2-}, NH_4^+, and NO_3^- measurement errors, indicating that thermodynamic model prediction of *R* is sensitive to the model input concentrations of NVCs. Also, to assess a possible role of organic species in general (Pye et al., 2017) or organic films (Silvern et al., 2017) on *R* and pH, the sensitivity of *R* and pH to $PM_{2.5}$ NVC (i.e., Na^+) and organic aerosol (OA) mass fraction or total OA, is compared. 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 of solution.

Fig. 4 shows that differences in measured *R* from a value of 2 (i.e., $\Delta R = R_{measured} - 2$) increases with measured Na^+, but does not depend on OA mass fraction (gray points) or OA concentration (see Fig. S5 in the supplement). These results are consistent with the bias in *R* being associated with poor representation (or lack of inclusion) of NVCs in the thermodynamic model, but inconsistent with expectations if OA had a significant effect on *R*. Fig. 4 also shows that ISORROPIA-predicted *R* also depends on Na^+. Predicted *R* with Na^+ in the model input minus predicted *R* without Na^+ decreases with increasing measured Na^+ and~~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~~ concentration (orthogonal linear regression, $\Delta R = (-1.74 \pm 0.03)\ Na^+ + (0.001 \pm 0.003$~~) .~~), $r^2 = 0.93$). The decreasing trend in R with increasing Na^+ can be explained simply by the pH increasing with Na^+, as shown in Fig. 4c. With increasing pH, some NH_4^+ shifts to gas phase NH_3 (supplemental Fig. S8a), resulting in lower NH_4^+ and lower R.

From the regression slope, ~~the~~for the SOAS measurement period analyzed, an 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 =~~ causes a decrease in R of 0.10~~ in R~~. At a Na^+ level of ~~only~~ 0.3 µg m^{-3}, ΔR reaches ~~=~~decreases by 0.5, indicating a rapid decrease from $R = 2$ (no NVC) to $R = 1.5$ (with NVC) for these conditions~~.~~ (i.e., it depends on the base case). 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~~as 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~~4b). 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)~~(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.~~(Guo et al., 2017a). Differences in sensitivity of *R* and pH to Na^+ can also 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 (Fig. 4). 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 very 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~~ **WINTER data set:** The *R* discrepancy ~~to~~is investigated for a larger geographical scale, different region and~~ for a~~ different season by performing a similar analysis with the WINTER study data set collected ~~in~~from the NSF C-130 research aircraft during wintertime. In this case the aerosol inorganic composition data used in the analysis is from an AMS and is PM_1. In this study, NVCs were generally higher than those measured during SOAS, 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~~13 nmol m^{-3} vs. SO_4^{2-} ~~0.011 µmol~~11 nmol m^{-3}) ~~(Guo et al., 2016).~~(Guo et al., 2016). Therefore, R_{SO4} was calculated instead of *R*.~~ In this case the aerosol inorganic composition data~~

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The base case input ~~for~~to 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~~in this analysis included NH_4^+, SO_4^{2-}, and total nitrate (NO_3^- + HNO_3~~) as input for ISORROPIA-II.~~). (NH_3 should be included to determine NH_x for input, but was not measured~~, although in this case it~~. It was found to have a small effect on predicted pH~~:~~; e.g., ~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,~~ (Guo et al., 2016)). Fig. 5a shows that ISORROPIA over-predicted R_{SO4} for the base case (i.e., when cations are not included) and that this deviation increases as molar ratios approach 2 when ~~concentrations of NVC were low, predicted and measured R_{SO4} was generally 2.~~NVCs determined from an ion charge balance get smaller. (Note that the predicted R_{SO4} should be biased low since NH_4^+ was ~~underpredicted~~under-predicted 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, thus the deviation is even worse than shown). Fig. ~~).~~5a shows that *R* is highly sensitive to lack of inclusion of NVCs when their concentrations are very low. However, when concentrations of NVC reach zero, predicted and measured R_{SO4} converge to the expected value of 2 (dark blue symbols in Fig. 5a). At the other extreme, as predicted NVCs increase, predicted and measured R_{SO4} become closer and converge to a molar ratio of zero because NH_4^+ approaches zero (NVC have replaced NH_4^+). 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~~ and average predicted Na^+ concentration was 0.15 µg m^{-3} (which is comparable to 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).~~offline PILS fraction collector IC-measured PM_1 Na^+ of 0.23 µg m^{-3}).

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~~As in the SOAS data set~~

In contrast to ISORROPIA-predicted R_{SO4} without NVCs, including NVCs ~~also~~ brings predicted and measured ammonium-sulfate molar ratios into agreement ~~(~~throughout the range in charge balance (relating to inferred NVCs) (Fig. 5b). Again, NVC concentrations were determined as NVCs = $Na^+ = 2SO_4^{2-} + NO_3^- - NH_4^+$ (unit: nmol m^{-3}) where all~~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~~ are assumed to be Na~~$^+$ (the thermodynamic results~~$^+$. (Results based on other NVCs are shown in~~ the~~ supplemental ~~material in~~ Fig. ~~S3~~S6. K^+ and Mg^{2+} work similarly to Na^+, while Ca^{2+} can precipitate sulfate in the form of $CaSO_4$~~).~~ and so cannot be used). Overall, Na^+ is chosen as a proxy NVC in our dataset because in this case 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~~;~~, such as 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)~~(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~~The linear regression result is $R_{SO4,predicted}$ = (1.05 ± 0.01) $R_{SO4,}$~~$_{observed}$~~$_{measured}$ + (−0.12 ± 0.01), $r^2 = 0.99$. ~~Again~~As found for the SOAS data set, again, the molar ratio bias from the thermodynamic model is simply a matter of not including small amounts of NVC (e.g~~.~~., in this case on average 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).~~(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~~given 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)~~

3.2 Implications of not including NVC on predicting gas-particle partitioning and historical trends in molar ratios

Sensitivity of semi-volatile species partitioning to NVCs: In our datasets, inferred Na^+ (or K^+, Mg^{2+}) from an ion charge balance that groups all NVCs into one species is an upper limit of the NVCs because it assumes complete dissociation of all dissolved ionic species. Additional errors can occur if other ions are also missing, but this approach satisfies electroneutrality. Comparing ISORROPIA predictions that includes the other major species, but with an inferred Na^+ input versus $Na^+ = 0$ input results in an average difference in pH by 0.32 for SOAS and 0.49 for WINTER, respectively. Even though the effect of NVC on pH may appear relatively small, 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)~~(Guo et al., 2016; Guo et al., 2017a). For example, ~~for SOAS average conditions~~as shown in supplemental Fig. S7, a 0.3 unit pH bias ~~(i.e., as noted above) results in~~ in SOAS campaign could cause ~ 20% bias in ~~prediction of~~ $\varepsilon(NH_4^+)$ or $\varepsilon(NO_3^-)$ prediction 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~~study, 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~~southeastern US (Vasilakos et al., 2017).

~~In our past studies, we also investigated~~

Effect of NVCs in trends in pH and ~~molar ratios over time periods of changing emissions. Our interest~~***R in the southeastern US:*** One curious observation that the organic film hypothesis (Silvern et al, 2017) attempted to address was ~~on~~ the ~~lack of change~~decreasing trend in ~~pH over~~*R* in the ~~past 15 years of~~southeastern US despite ~~a 70% reduction~~the substantial drop in sulfate ~~aerosol (~~. Weber et al., (2016) noted this and proposed that it could be explained by NH_4^+ volatility. However, the ~~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~~model predictions of R_{SO4} in that study did not find a comparable decreasing R_{SO4} rate with time (see Fig. 6a), since the SOAS study mean PILS-IC Na^+ concentration of 0.03 μg m^{-3} ~~from the SOAS study~~ was 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~~

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~~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).~~2 for the input $SO_4^{2=}$ range (Fig. 6a) and would only rapidly decrease below 1 µg m^{-3} SO_4^{2-} (See Fig. 2b in the paper). 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 in the historical data set, 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).~~(Fig. 6 & Fig. S8). It also results in ISORROPIA-predicted decreasing R_{SO4} rate of –0.017 yr^{-1}, fairly close to the measured rate at the SOAS site (Centerville, AL) of -0.021 yr^{-1} (see Fig. 6a), and in the range of the R_{SO4} trend of –0.01 to –0.03 yr^{-1} reported by Hidy et al. (2014) for SEARCH sites throughout the southeast. 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~~6b), but as expected the pH was slightly higher with higher input Na^+ concentrations ~~(i.e., from ion charge balance).~~. Thus, including daily estimates of NVC in ISORROPIA, the conclusion that $PM_{2.5}$ pH has remained largely constant over the last 15 years remains, but the unexpected decreasing R_{SO4} trend appears to be accounted for. These observations can all be explained by volatility of NH_4^+, as discussed in Weber et al. (2016), without need to invoke organic effects on the ammonia partitioning.

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4. Discussion

Internal vs External Mixtures: This analysis has been based on the assumption that all ions were internally mixed (e.g., bulk $PM_{2.5}$ or PM_1). Although over time, gas-particle and particle-particle interactions will lead to complete internally mixed systems, aerosol near their source regions tend to be externally mixed. Typical ambient conditions can be expected to exist somewhere between these two extreme cases. We address this here by studying how the conclusions described above are affected by the degree of mixing of NVCs with ammonium and sulfate – as the other species, being semi-volatile, quickly equilibrate.

$PM_{2.5}$ sea salts (or other NVCs) are often not well mixed with ammonium and sulfate because of their different sources. NVCs are largely produced by mechanical means and so mainly in the coarse mode, with a tail extending into the fine mode (Whitby, 1978). In contrast, ammonium and sulfate are mostly formed through gas-phase processes and mostly reside in the accumulation mode (e.g., (Whitby, 1978; Zhuang et al., 1999; Fang et al., 2017)). For the SOAS PILS-IC data set, NH_4^+ and SO_4^{2-} were highly correlated ($r^2 = 0.88$), but NH_4^+ and Na^+ ($r^2 = 0.07$) or SO_4^{2-} and Na^+ ($r^2 = 0.17$) were not. In contrast, $PM_{2.5}$ Na^+ and NO_3^- ($r^2 = 0.82$) or Na^+ and Cl^- ($r^2 = 0.64$) were highly correlated, consistent with internal mixing of most Na^+, NO_3^-, and Cl^- ions, leading to depletion of some Cl^- through evaporation of HCl. Rapid scavenging of HNO_3 by sea salt aerosols is well established (Hanisch and Crowley, 2001; Meskhidze et al., 2005), with equilibrating time scales 3-10 hours for HNO_3 uptake by 1-3 µm sea spray aerosols (Meng and Seinfeld, 1996; Fridlind and Jacobson, 2000).

NVCs can also be associated small amounts of sulfate. For example, sea salt aerosols are largely composed of NaCl but also include sulfate found in sea water, approximately 8% (g g^{-1}) of all ions (~25% SO_4^{2-}/Na^+ mass ratio) (sea water salinity of 35 psu) (DOE, 1994). In addition, sulfur enrichment and chloride depletion in aged sea salt aerosols are possible by uptake of H_2SO_4 or oxidation of dissolved SO_2 by O_3 (McInnes et al., 1994; O'Dowd et al., 1997). These secondary produced sulfates are normally referred as non-sea-salt sulfates, to be distinguished from sea-salt sulfate that is naturally in sea waters (Tang et al., 1997). Many studies have reported sulfate-containing sea salt aerosols with some degrees of internal mixing (Andreae et al., 1986; McInnes et al., 1994; Murphy et al., 1998; Laskin et al., 2002). In summary, a realistic external mixing state of the SOAS fine particles is that most of NH_4^+ and SO_4^{2-} are in PM_1 and Na^+ with associated anions (NO_3^- and Cl^-) and at least small amounts of NH_4^+ and SO_4^{2-} in $PM_{1\text{-}2.5}$ (particles with sizes 1-2.5 µm). This is illustrated in Fig. 7a. Particle size distributions measured in the southeast US also support these types of particle mixing state (Fang et al., 2017).

Explanation for role of NVCs on R based on bulk (internal mixture) analysis: Assuming the ions are all internally mixed, the observations relating *R* to NVCs, and deviations in *R* between models and observations can be readily explained. First, when NVC such as Na^+ are present in the ambient aerosol and not included in the thermodynamic model and some fraction of the associated anion pair is, the thermodynamic model will predict higher NH_4^+ than observed because the model will partition greater levels of available semivolatile cations (i.e., NH_3) to the particle phase (NH_4^+) to conserve NH_x and make up for the missing NVCs. This leads to a predicted *R* near 2. The trends in measured *R* with measured Na^+ are also expected. As noted before, measured *R* becomes increasingly less than 2 as measured Na^+ increase because at higher Na^+ bulk aerosol pH increases (Fig. 3c), resulting in lower $\varepsilon(NH_4^+)$ (see NH_4^+ S curve in supplemental Fig. S7), shifting NH_4^+ to gas phase NH_3. Other NVCs have similar effects as Na^+, as long as soluble forms of the salts are observed (e.g., $NaNO_3$, Na_2SO_4, KNO_3, K_2SO_4, $Ca(NO_3)_2$, $Mg(NO_3)_2$). We have shown with this bulk analysis that accurately including NVCs in the thermodynamic analysis appears to largely resolves the disparity in predicted and measured *R*. But the bulk analysis is only an approximation of the actual aerosol mixing state. Can assuming an internal mixture roughly represent the behavior of externally mixed aerosols in terms of the effect of NVCs on *R*, pH, and partitioning of semivolatile species? To assess this, we consider the behavior of external mixing cases.

Explanation for the role of NVCs on R based on external mixture analysis: An extreme (and unrealistic) external mixture is where PM_1 is composed of all the measured NH_4^+, SO_4^{2-} and $PM_{1\text{-}2.5}$ is composed of all the measured Na^+ (all NVCs), NO_3^-, and Cl^-. NH_3, HNO_3, HCl, and H_2O (water vapor) can still equilibrate between these externally mixed particle types (see Fig. 7a), given the relatively short equilibrating time scales for these sizes of particles (Dassios and Pandis, 1999; Cruz et al., 2000; Fountoukis et al., 2009). As Fig. 7b shows, for the extreme external mixing case (i.e. 0% sulfate in $PM_{1\text{-}2.5}$), predicted *R*, combined from PM_1 and $PM_{1\text{-}2.5}$, is close to 2, deviating from the lower predicted *R* of 1.66 ± 0.13 from the internal mixture. This is due to the vastly different pH of PM_1 (0.6) and $PM_{1\text{-}2.5}$ (4.1) (Fig. 7c), so, all NH_4^+ is predicted to be in PM_1, and all NO_3^- is predicted to be in $PM_{1\text{-}2.5}$.

For more realistic mixing cases where some fraction of the sulfate is mixed with NVCs, the combined *R* of the external mixture decreases rapidly as more SO_4^{2-} is mixed with Na^+ in $PM_{1\text{-}2.5}$. Higher Na^+ concentrations generally require more SO_4^{2-} to obtain agreement in *R* between external and internal mixtures (scatter plots are shown as supplemental Fig. S9). At 20% SO_4^{2-} fraction in $PM_{1\text{-}2.5}$, the average levels of predicted *R* start to converge between external and internal mixtures (Fig. 7b). The difference in pH between PM_1 and $PM_{1\text{-}2.5}$ is also reduced to within one pH unit (Fig. 7c). With these small differences in pH, NH_4^+ can condense both externally-mixed aerosol groups. For example, PM_1 and $PM_{1\text{-}2.5}$ NH_4^+ are predicted to be 0.67 µg m^{-3} and 0.04 µg m^{-3}, respectively (equal to the sum of the measured $PM_{2.5}$ NH_4^+ of 0.71 µg m^{-3}). For the external mixed cases, not including Na^+ in the model input causes an *R* overprediction the same way as we have explained for the internal mixture. From this analysis, which is based only on data when Na^+ was above the LOD, predicted *R* for the bulk and external mixture are the same when on average 18 ± 7% of the $PM_{2.5}$ SO_4^{2-} is in the $PM_{1\text{-}2.5}$ size range (i.e., mixed with Na^+). This is comparable to inferences of mixing based on size-resolved aerosol measurements in the southeast (e.g., Fang et al. (2017) shows ~30% $PM_{2.5}$ SO_4^{2-} mass in $PM_{1\text{-}2.5}$). Less internal mixing of SO_4^{2-} with Na^+ is needed when Na^+ concentrations are lower. For example, for Na^+ at the LOD of 0.07

µg m^{-3} (for the PILS-IC operated during SOAS), only 5% of the SO_4^{2-} mixed with Na^+ produces the same results as the bulk totally internal mixture analyses (see supplemental Fig. S10).

The difference between the internally and externally mixed system is not as great as may be expected, especially for particle pH and liquid water (W_i) (Fig. 7c and Fig. 7d). Since liquid water levels are determined as the sum of the water associated with the various salts, the bulk liquid water generally equals the sum of the two externally mixed liquid water concentrations, based on the Zdanovskii–Stokes–Robinson (ZSR) relationship (Zdanovskii, 1936; Stokes and Robinson, 1966). The PM_1 liquid water dominates over $PM_{1\text{-}2.5}$, making the combined pH of the external mixture nearly identical to PM_1 pH (see Equation 4 for combined pH calculation). The combined pH of the external mixture is also similar to that of internal mixture, regardless of the SO_4^{2-} fractions.

5. Summary

Including NVCs in the thermodynamic model largely resolves the ammonium-sulfate molar ratio ($R = NH_4^+/SO_4^{2-}$) discrepancy, based on our data set, which is representative of the southeastern US. Since only small amounts of NVC can significantly affect R, measurement limitations (high NVC LODs or not measured at all) can lead to substantial differences in observed and thermodynamic model predicted R. We show that this bias in R (ISORROPIA-predicted R with Na^+ minus ISORROPIA-predicted R without Na^+) is correlated with and highly sensitive to measured Na^+, but not correlated with organic aerosol mass or mass fraction. Furthermore, the difference in measured R from a ratio of 2 (2 minus observed R) is correlated to measured Na^+ (NVCs) and not correlated with organic aerosol mass or mass fraction. If organic films were limiting mass transfer, the discrepancy in R should worsen as the films become thicker. We find the opposite. These results provide strong evidence for the role of NVCs but not bulk organic aerosol species or organic films in the molar ratio discrepancy.

Excluding minor amounts of ~~submicron~~fine mode 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~~.~~ and semivolatile NH_4^+ has to be increased to compensate the missing NVCs. 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~~For example, the observed ranges in molar ratios (R or R_{SO4} from 0 to 2) are less than those of pH (from -1 to 3) in the two data sets investigated in this study (Guo et al., 2015; Guo et al., 2016). However, neglecting NVC can induce pH biases that could result in significant 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.~~, under certain conditions. Because NVCs are often minor constituents of fine particles, especially for ~~PM_1~~submicron particles, 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 NVCs were not measured or significantly below the measurement LOD, an ion charge balance could be used to inferred an upper limit on NVC concentrations, but addition of measurement uncertainties can lead to uncertain results.

A motivation for the organic effects on ammonia partitioning (Silvern et al., 2017) was the observed R_{SO4} decreasing trend over the past 15 years in the southeastern US. Fully considering NVCs doesn't change the finding of nearly constant fine particle pH in the southeast (summertime) despite the large sulfate reductions in the past 15 years, but it does now produce agreement with the observed R_{SO4} decreasing trend. Finally, although the analysis was performed assuming total internal mixtures of aerosol components, since only bulk $PM_{2.5}$ composition data were available, we show that external mixtures of NVCs and sulfate produce similar results, with the only requirement that small amounts of sulfate are mixed with the NVC-rich particles. As a final note, because molar ratios are sensitive to NVCs, and NVC concentrations are often very low and can be highly uncertain, use of molar ratios to test the thermodynamic model should be done with caution. Molar ratios are also poor pH proxies and not recommended to evaluate aerosol acidity (Guo et al., 2015; Hennigan et al., 2015; Guo et al., 2016).

~~. 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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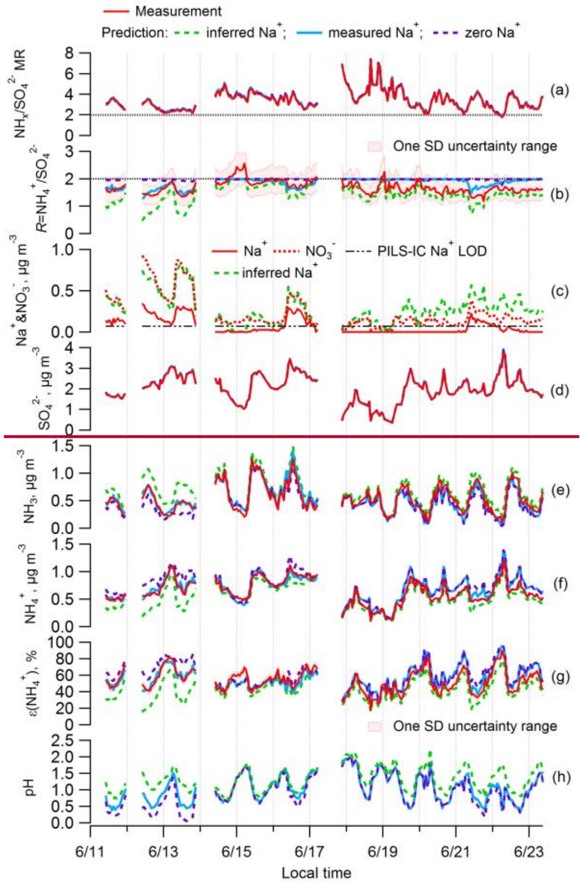
Measurement
Prediction: inferred Na$^+$; measured Na$^+$; zero Na$^+$
NH$_x$/SO$_4^{2-}$ MR
(a)
One SD uncertainty range
R=NH$_4^+$/SO$_4^{2-}$
(b)
Na$^+$ NO$_3^-$ PILS-IC Na$^+$ LOD
inferred Na$^+$
Na$^+$&NO$_3^-$, µg m^{-3}
(c)
SO$_4^{2-}$, µg m^{-3}
(d)
NH$_3$, µg m^{-3}
(e)
NH$_4^+$, µg m^{-3}
(f)
ε(NH$_4^+$), %
(g)
One SD uncertainty range
pH
(h)
6/11
6/13
6/15
6/17
6/19
6/21
6/23
Local time

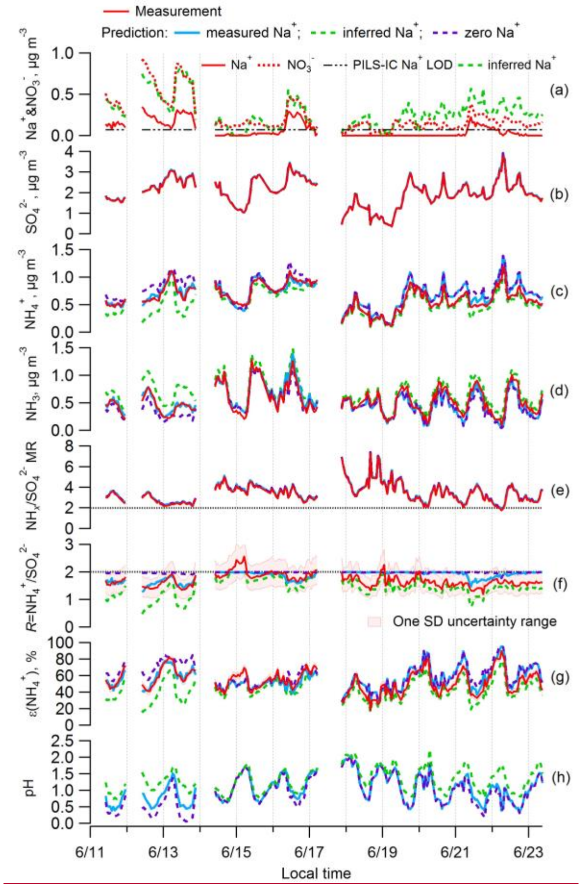

Figure 1. Time series of various measured and ISORROPIA-predicted parameters and $PM_{2.5}$ component concentrations for ~~a select period of~~ the SOAS study~~, with periods of rainfall removed. Three ISORROPIA-predicted results are shown at different Na^+ levels; calculated Na^+ needed for ion charge 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) Na^+ and NO_3^-, (b) SO_4^{2-}, (c) NH_4^+, (d) NH_3, (e) total ammonium (NH_x = $NH_4^+ + NH_3$) to sulfate molar ratio (NH_x/SO_4^{2-}), (~~b) aerosol~~f) ammonium-sulfate ~~ratios~~ratio ($R = NH_4^+/SO_4^{2-}$), (~~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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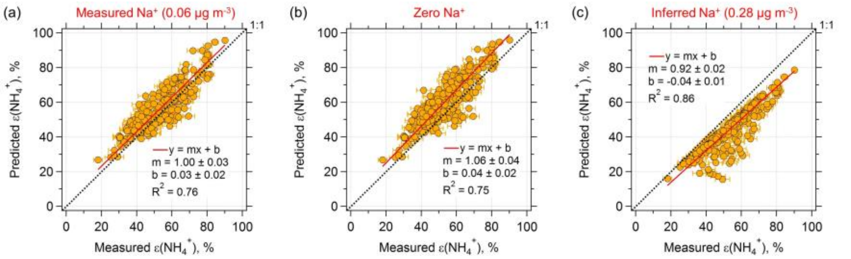
ISORROPIA-predicted results for the base case and three different Na^+ inputs are shown: measured Na^+ in blue, Na^+ from an ion charge balance ($Na^+ = 2SO_4^{2-} + NO_3^- + Cl^- - NH_4^+$, μmol m^{-3}) in green representing generic nonvolatile cation (NVC) concentrations, and zero Na^+ in purple.



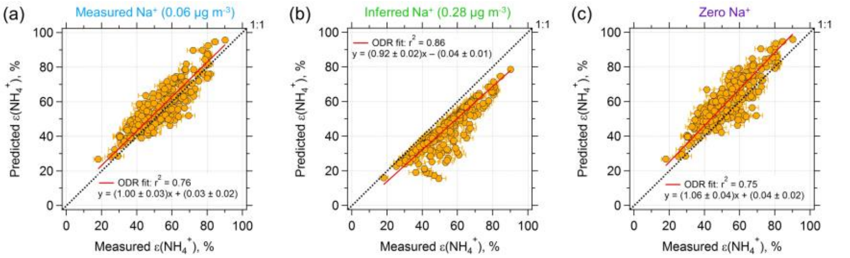
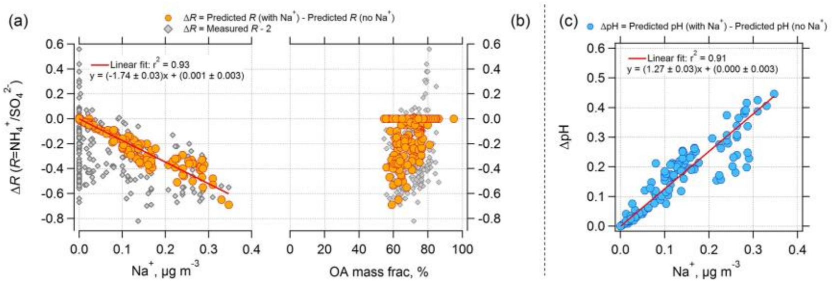


Figure 2. Comparisons of predicted and measured particle phase fractions of total ammonium, ε(NH_4^+) = NH_4~~$^+$/(NH_3 + NH_4^+), for a 12-day period data from the SOAS study. NH_4^+ was measured with a PILS-IC ($PM_{2.5}$ cut size) and NH_3 from a CIMS.~~$^+$/NH_x. (a) The model prediction is based on an ISORROPIA input of measured Na^+, ~~(NH_4^+ + NH_3),~~NH_x, SO_4^{2-}, NO_3^-, Cl^-~~; (b) Model input is identical to (a), except that Na^+ is set to zero; (c~~. (b) Same model input, but Na^+ is inferred from an ion charge balance and (c) Na^+ is set to zero. Orthogonal distance regression (ODR) fits are shown and uncertainties in the fits are one standard deviation (SD). Uncertainty of measured ε(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.~~


(a)
ΔR = Predicted R (with Na+) - Predicted R (no Na+)
ΔR = Measured R - 2
Linear fit: r2 = 0.93
y = (-1.74 ± 0.03)x + (0.001 ± 0.003)
ΔR (R=NH4+/SO42-)
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
0.0
0.1
0.2
0.3
0.4
Na+, μg m-3
(b)
0
20
40
60
80
100
OA mass frac, %
(c)
ΔpH = Predicted pH (with Na+) - Predicted pH (no Na+)
Linear fit: r2 = 0.91
y = (1.27 ± 0.03)x + (0.000 ± 0.003)
ΔpH
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0.0
0.1
0.2
0.3
0.4
Na+, μg m-3

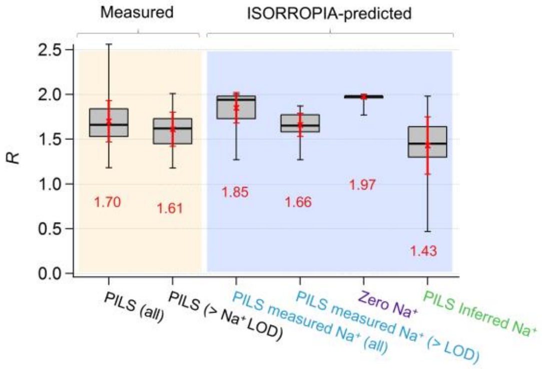


Figure 3. Comparisons of $PM_{2.5}$ ammonium-sulfate molar ratios (*R*) between measurements and ISORROPIA-predictions for the base case but with differing Na^+ inputs. Data are from the SOAS study. Red numbers are the means and red error bars are one SD. Standard box-whisker plots are shown, with 100% and 0% data indicated by black error bars. Top and bottom of box are the interquartile ranges (75% and 25%) centered around the median value (50%). Comparisons include all data and periods when measured Na^+ > LOD of 0.07 µg/m^3. Inferred Na^+ is calculated from an ion charge balance with no other NVC included.

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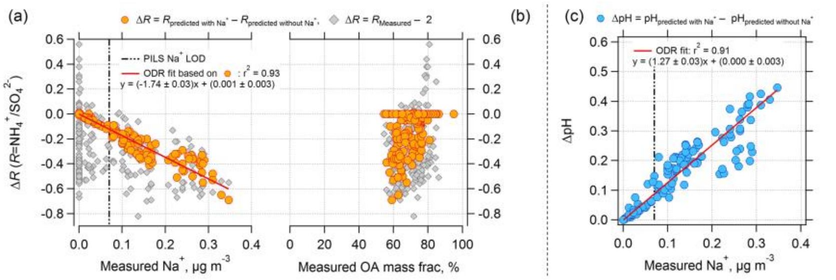

Figure 4. Effect of nonvolatile cations (NVC) on the $PM_{2.5}$ ammonium-sulfate molar ~~ratio~~ratios (*R*) and pH as a function of measured Na^+ concentration and organic aerosol (OA) mass fractions~~. The orange~~ for the SOAS data set studied. Plot (a) is Δ*R* versus measured Na^+, (b) Δ*R* versus measured OA mass fraction (OA mass divided total particle mass reported from AMS), and (c) ΔpH versus measured Na^+. Grey diamonds in plots (a) and (b) are for Δ*R* equal to the measured *R* minus 2. Orange circular points ~~in plots (a) and (b)~~ are for Δ*R* 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 Δ*R* equal to the actual measured *R* minus 2. Note that Δ*R* should be~~Δ*R* is 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 Δ*R* versus measured Na^+, (b) Δ*R* versus measured OA mass fraction, and (c) ΔpH versus measured Na^+. Orthogonal distance regression (ODR)~~see Fig. 3). 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~~S5. The vertical dotted line is the Na^+ LOD of 0.07 μg/m^3.

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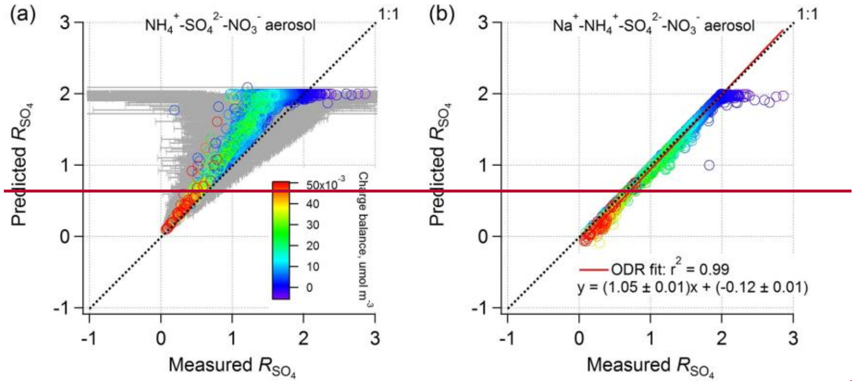

(a)
NH_4^+-SO_4^{2-}-NO_3^- aerosol
1:1
Predicted R_{SO_4}
Measured R_{SO_4}
50x10^{-3}
40
30
20
10
0
Charge balance, umol m^{-3}
(b)
Na^+-NH_4^+-SO_4^{2-}-NO_3^- aerosol
1:1
Predicted R_{SO_4}
Measured R_{SO_4}
ODR fit: r^2 = 0.99
y = (1.05 ± 0.01)x + (-0.12 ± 0.01)
-1
0
1
2
3

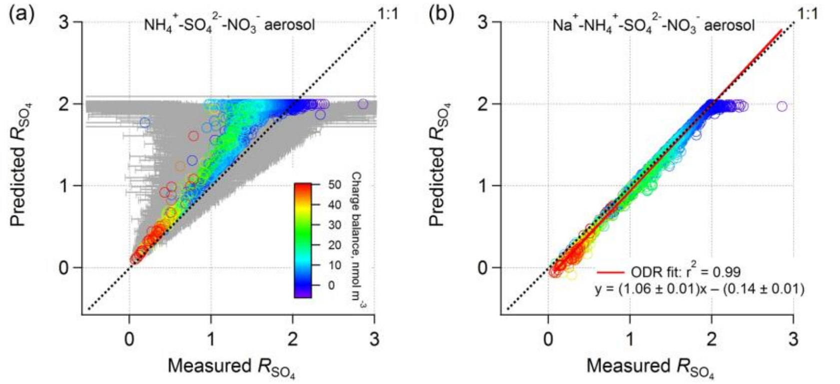
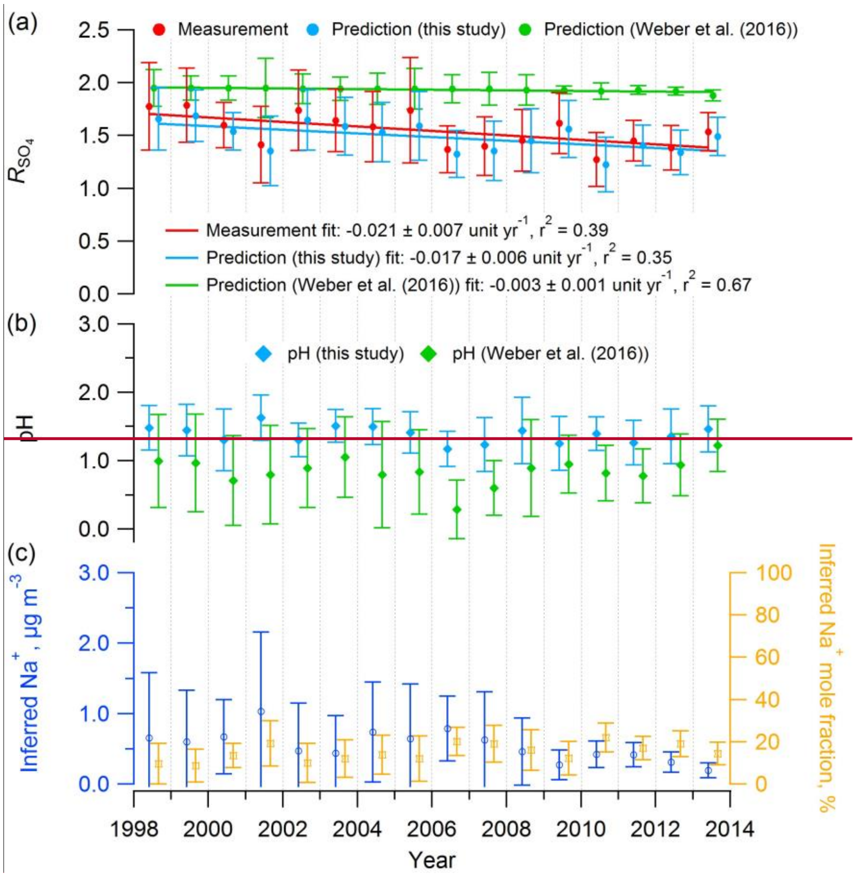

(a)
NH_4^+-SO_4^{2-}-NO_3^- aerosol
1:1
Predicted R_{SO_4}
Measured R_{SO_4}
50
40
30
20
10
0
Charge balance, nmol m^{-3}
(b)
Na^+-NH_4^+-SO_4^{2-}-NO_3^- aerosol
1:1
Predicted R_{SO_4}
Measured R_{SO_4}
ODR fit: r^2 = 0.99
y = (1.06 ± 0.01)x – (0.14 ± 0.01)
0
1
2
3

Figure ~~4~~5. 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, and both ~~constrained by~~include HNO_3~~.~~ to calculate total nitrate for the model input. All measurement data are from the WINTER study. ~~NVC was~~NVCs were determined by an ion charge balance with the predicted molar concentration shown ~~as the~~by symbol 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 ~~were determined by 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). Error bars are larger at higher ratios due to subtraction of higher concentrations of nitrate and ~~thus more~~so subject to greater measurement error. ~~As~~Data points with low SO_4^{2-} levels (<0.2 μg m^{-3}; 9% of the ~~SOAS data, including NVC in the model results in agreement between predicted and measured ammonium-sulfate molar ratios.~~total points) were excluded due to high uncertainties.


(a)
Measurement
Prediction (this study)
Prediction (Weber et al. (2016))
R_{SO_4}
2.5
2.0
1.5
1.0
0.5
0.0
Measurement fit: -0.021 ± 0.007 unit yr^{-1}, r^2 = 0.39
Prediction (this study) fit: -0.017 ± 0.006 unit yr^{-1}, r^2 = 0.35
Prediction (Weber et al. (2016)) fit: -0.003 ± 0.001 unit yr^{-1}, r^2 = 0.67
(b)
pH (this study)
pH (Weber et al. (2016))
pH
3.0
2.0
1.0
0.0
(c)
Inferred Na$^+$, µg m^{-3}
3.0
2.0
1.0
0.0
Inferred Na$^+$ mole fraction, %
100
80
60
40
20
0
1998
2000
2002
2004
2006
2008
2010
2012
2014
Year

~~**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%).~~

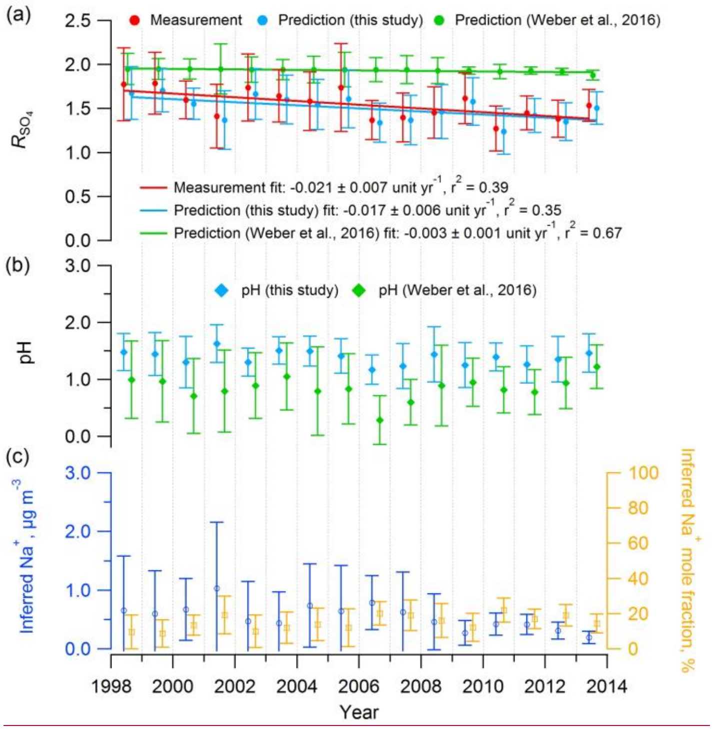


Figure 6. Mean summer (June–August) trends in (a) measured and predicted R_{SO4}, (b) predicted $PM_{2.5}$ pH, and (c) inferred Na^+ concentration and mole fraction at the SEARCH-CTR site. Na^+ was inferred from an ion charge balance of Na^+-NH_4^+-SO_4^{2-}-NO_3^-. ISORROPIA inputs include the measured $PM_{2.5}$ composition (NH_4^+, SO_4^{2-}, NO_3^-) and meteorological data (RH, T) at CTR. In all cases, 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 concentrations 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). Error bars represent daily data ranges (SD). Linear regression fits are shown and uncertainties in the fits are one SD. 41 data points out of 609 (7%) with observed daily mean R_{SO4} above 3 were considered outliers and not shown (if included the fit slope is −0.023 ± 0.008 unit yr^{-1}).

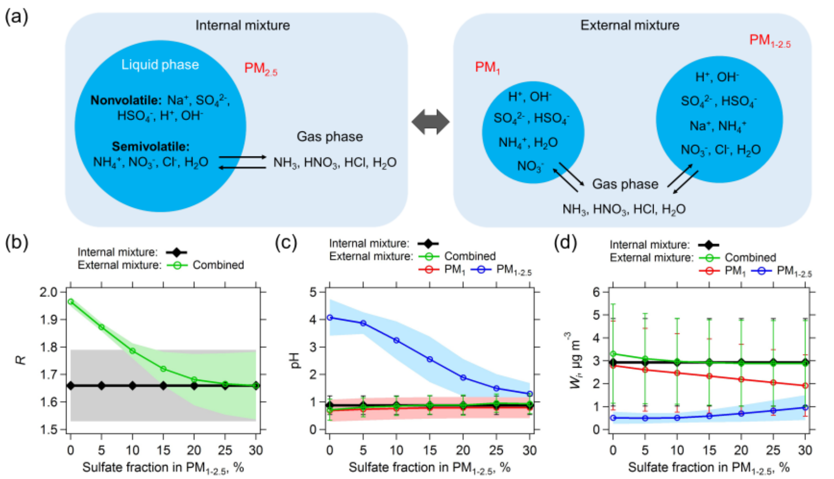


Figure 7. (a) Schematic of assumed internally and externally mixed aerosols. NVCs (here represented by Na^+) are all assumed in $PM_{1-2.5}$ for the external mixing case. The two externally mixed aerosol groups (PM_1 and $PM_{1-2.5}$) are in equilibrium with the same gases. The internal mixed case has bulk $PM_{2.5}$ composition (PM_1 + $PM_{1-2.5}$) together with gases as model input. The predicted molar ratio (*R*), pH, and liquid water ($\boldsymbol{W_i}$) of the internally and externally mixed aerosols are summarized in (b), (c), and (d), respectively. The x-axis is the sulfate fraction assumed in $PM_{1-2.5}$, with the remaining sulfate in PM_1. For the analysis shown here only data for which measured Na^+ was above the LOD are utilized. Lower Na^+ concentrations require smaller fractions of SO_4^{2-} in the $PM_{1-2.5}$ range for agreement with the bulk analysis (e.g., 5% for PILS-IC Na^+ LOD of 0.07 µg m^{-3}). Standard deviations of the data are shown as error bars or shaded zones.