Below, we have addressed the reviewer comments that raise an issue. The reviewer comments are presented in quotes and italics, followed by our responses in plain text.

Responses to Reviewer 3

1. *"However, I agree with reviewer 2 that the data used by the authors to argue that all is well with thermodynamics are either unusual (high Na+) or misleading (inferred high Na+). The authors don't provide a satisfactory response in the revised text.*"

   We *do no*t argue that "all is well with thermodynamics", but *what we do* argue is that for major inorganic ions, like NH_4^+, the large discrepancy in predicted versus measured partitioning (expressed by the molar ratio) can be explained by careful attention to the presence of non-volatile cations (NVC), and a demonstrated large NH_4^+ sampling bias in the CSN data. Together with the observed strong correlation of molar ratio discrepancy with NVC and a lack of correlation with organic mass and mass fraction indicates that organics are unlikely associated with any inhibition in NH_3 uptake. The demonstrated equilibration of aerosol species (like water and nitrates) further excludes the presence of glassy aerosol or organic films that would strongly inhibit mass transfer.

   Furthermore:

   1. The Na^+ data used in our analysis is of good quality and not unusually high for the region. For the SOAS study, PILS-IC observed Na^+ was on average 0.07 μg m^{-3} and in good agreement with MARGA Na^+ (see Fig. S2 in the supplement, the last submitted version, hereafter referred as V1). Average Na^+ over a full year at various sites in the southeast are in the range of 0.05 to 0.1 μg m^{-3} (see new Supp material Table S1 and S2, which are also shown below).
   2. The analysis is consistent for Na^+ concentrations over the full Na^+ measurement range, including below our assigned Na^+ LOD. As an example, Fig. 4a shows that discrepancies in *R* vs. Na^+ apply over the complete range of the observed Na^+ data. Nothing changes through the LOD transition (vertical line in Fig. 4a) to lower concentrations. The comparison between ISORROPIA predicted and measured ammonium partitioning in Fig. 2a is also consistent for all data points, which includes data below the Na^+ LOD. We do agree that the time series plot of Fig. 1 tends to emphasize the higher Na^+ events, but this is only one component of the paper.
   3. The ion balance does not produce misleading Na^+ data, it is, however, highly uncertain due to subtracting large numbers of small difference (i.e., SO_4^{2-} and NH_4^+). We have discussed this in the text

(Line 27 Page 5 V1). The issue of not including H^+ in the ion balance, based on a full thermodynamic analysis, is discussed below. The statement that the inferred Na^+ is always consistently high is also incorrect; in SOAS this is true, but in the WINTER study it is consistently lower (Line 15 Page 8 V1).

2. *"I agree with reviewer 1 that the authors should not ignore the low values of R in the CSN data, and if they think that these values are biased they should say so and why."*

   In response to this, we have added a paragraph and table showing there is a substantial bias in CSN *R*. (Note, this was recognized by Silvern et al. (2017), but was used anyway to argue that a low *R* indicted problem with thermodynamic predictions, even if the bias by itself can account for the molar ratio discrepancy). The following is added on Page 4. "In addition to the SOAS and WINTER data sets, the Southeastern Aerosol Research and Characterization (SEARCH) CTR sampling site (the same as SOAS) historical data from year 1998 to 2013 is re-analyzed to show that thermodynamic model can reproduce the observed decreasing trend of R_{SO4} when NVCs are considered. Molar ratios determined from the Chemical Speciation Network (CSN), which were utilized and discussed by Silvern et al. (2017) and Pye et al. (2018), are not used in this work because of a significant low bias when compared to the SEARCH and SOAS data (see Table S1 and S2 in the supplement)". For example, during the 12-day SOAS study period investigated here (11-23 June 2013), the online measurements in SOAS (CTR) reported *R* values of 1.70 ± 0.23 for PILS and 1.78 ± 0.18 for MARGA. SEARCH filter-based measurements of *R* were similar at 1.57 ± 0.11 at CTR and 1.64 ± 0.14 at Birmingham (BHM). In contrast, the two closest CSN sampling sites near CTR reported much lower *R* of 0.70 ± 0.36 at BHM and 0.75 ± 0.42 at Montgomery (MTG). For the year of 2013, the CSN data at BHM showed a similar low bias compared to the SEARCH; SEARCH *R* of 2.05 ± 0.23 was significantly higher than CSN *R* of 1.26 ± 0.59. The discrepancy is likely due to the loss of semivolatile NH_4^+ collected on the CSN nylon filters, as noted by Silvern et al. (2017). Note that this bias is of the order of the discrepancy of *R* that is postulated to arise from organics. This fact alone should be sufficient for any reviewer to recognize as a critical issue in the Silvern et al. (2017) analysis. The two tables below are added to the supplemental material.

Table S1. Comparisons of observed $PM_{2.5}$ ions and molar ratio between SOAS, SEARCH, and CSN ground sampling sites for the 11-23 June 2013 period (Fig. 1 in the main text). Since CSN (Chemical Speciation Network) doesn't have a site at CTR to be directly compared to SOAS and SEARCH, the two closest sites at

Birmingham (BHM) and Montgomery (MTG) are used. The most direct comparison is between Birmingham, SEARCH and CSN data. Means are shown with standard deviations.

Network	SOAS	SOAS	SEARCH	SEARCH	CSN	CSN
Site location	CTR	CTR	CTR	BHM	BHM	MTG
Site coordinate	32.90289, −87.24968	32.90289, −87.24968	32.90289, −87.24968	33.55302, −86.81485	33.49972, −86.92417	32.41281, −86.26339
Method	PILS-IC	MARGA(-IC)	Teflon filter(-IC)	Teflon filter(-IC)	Nylon filter(-IC)	Nylon filter(-IC)
NH_4^+, µg m^{-3}	0.64 ± 0.22	0.79 ± 0.22	0.63 ± 0.13*	0.69 ± 0.20*	0.24 ± 0.14	0.25 ± 0.19
SO_4^{2-}, µg m^{-3}	2.06 ± 0.68	2.38 ± 0.66	2.16 ± 0.44	2.23 ± 0.51	1.69 ± 0.40	1.46 ± 0.84
Na^+, µg m^{-3}	0.07 ± 0.09	0.09 ± 0.10	0.06 ± 0.04	0.05 ± 0.04	0.13 ± 0.06	0.10 ± 0.04
R	**1.70 ± 0.23**	**1.78 ± 0.18**	**1.57 ± 0.11**	**1.64 ± 0.14**	**0.70 ± 0.36**	**0.75 ± 0.42**
Data points	229	229	13	4	5	3
Notes on data	Hourly data	Hourly data	Daily data; every day	Daily data; every three days (6/12-6/21)	Daily data; every three days (6/9-6/24)	Daily data; every six days (6/9-6/21)
Reference	(Guo et al., 2015)	(Allen et al., 2015)	(Edgerton et al., 2005; Hidy et al., 2014)		(Solomon et al., 2014)	

* SEARCH NH_4^+ was measured by automated colorimetry.

Table S2. Comparisons of observed $PM_{2.5}$ ions and molar ratio between SEARCH and CSN ground sampling sites for the year 2013.

Network	SEARCH	SEARCH	CSN	CSN
Site location	CTR	BHM	BHM	MTG
Site coordinate	32.90289, −87.24968	33.55302, −86.81485	33.49972, −86.92417	32.41281, −86.26339
Method	Teflon filter(-IC)	Teflon filter(-IC)	Nylon filter(-IC)	Nylon filter(-IC)
NH_4^+, µg m^{-3}	0.55 ± 0.28*	0.72 ± 0.31*	0.48 ± 0.34	0.41 ± 0.29
SO_4^{2-}, µg m^{-3}	1.71 ± 0.89	1.96 ± 0.90	1.91 ± 0.99	1.65 ± 0.89
Na^+, µg m^{-3}	0.05 ± 0.05	0.05 ± 0.05	0.13 ± 0.30	0.10 ± 0.08
R	**1.75 ± 0.28**	**2.05 ± 0.05**	**1.26 ± 0.59**	**1.24 ± 0.59**
Data points	154	111	93	61
Notes on data	Daily data; every three days	Daily data; every three days	Daily data; every three days	Daily data; every six days
Reference	(Edgerton et al., 2005; Hidy et al., 2014)		(Solomon et al., 2014)	

* SEARCH NH_4^+ was measured by automated colorimetry.

3. *“I also agree with reviewer 2 that the propensity of the authors to cite their own previous work as right and to misleadingly characterize the work of others as wrong borders on the embarrassing.*”

The point is well taken, and we have attempted to reduce our self-citations, where possible. As the manuscript stands now, there are 21 self-citations to papers involving Guo, Weber, and Nenes, compared to 151 citations to the work of other groups. If the reviewer was referring to the discussion of Rindelaub et al. (2016) in the introduction, it has been removed in the last submitted version as it was not highly relevant to this paper. This should resolve the issue reviewer 2 had pertaining to that discussion (see response to reviewer 2 below). We have also removed from the abstract the statement that the organic film proposed by Silvern et al. (2017) selectively inhibiting NH_3, but not water vapor and HNO_3.

There are three issues the reviewer may wish to also consider on this matter:

1) As stated in our response to reviewer 2, who brought this up, there is very little recent work on aerosol pH, other than our own, and so the number of available papers to cite is limited.
2) This paper is in part a rebuttal of the Silvern et al. (2017) paper that proposes a different explanation for trends in *R* over the last decade, in contrast to what we had proposed (Weber et al., 2016). Thus, it is natural to cite our work on this topic. We do cite other publications in the introduction which show that the organic film hypothesis that predicts lack of ammonia gas-particle equilibrium is in contrast to established literature showing that NH_3, water vapor, and HNO_3 equilibrate with organic-rich aerosols (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., 2017; Liu et al., 2017; Paulot et al., 2017) (V1). We have also added more citations from other research groups in this round of reviews. We note that to question hypotheses and then use well documented arguments for a revised picture of reality is exactly how science should progress, and is something that no one should be embarrassed of!
3) It might be worth noting that Reviewer 2, who made this self-citation comment, has requested throughout their reviews that we cite various other papers (there are 6 of them, which are listed at the end of this response). We have attempted to include all of these papers in our manuscript, where appropriate. It is worthy to note, that 5 of these 6 requested manuscripts also have a common author, giving the appearance that the reviewer’s main concern is that we cite their papers. The irony of this is not lost on us.

4. *"I don't think that the authors have satisfactorily addressed in the text the much lower R values found in the CSN data, which cannot be explained by the NVC hypothesis.*"

   We have addressed this question in bullet 2 above. The CSN data is biased so not considered in our analysis.

5. *"But isn't standard protocol to remove that sea-salt sulfate and just report non-sea-salt sulfate? Just checking, I know it's standard protocol in research data sets.*"

   The discussion was referring to particle mixing state and measurements of mixing state by single particle analysis, which of course cannot distinguish between sulfate from different sources. And it is not correct to do so either, because the thermodynamics is affected by all forms of sulfate, regardless of origin.

6. *"But then of course R would be less than 2. These are unusual conditions when NVCs are high.*"

   We have answered this question in bullet 1 above. Again, as an example, Fig. 4a shows, there is no discontinuity in the *R* discrepancy for Na^+ above and below the LOD. As we show, the NVC levels we report are not unusual.

7. *"I agree with the reviewer that inferred* Na^+ *is highly problematic and I don't see that the authors have addressed that concern in the revised text. A major problem is that the charge balance equation used to infer* Na^+ *doesn't include* H^+ *and thus forces* H^+ *to be low so R to be high resulting in a circular argument. The authors justify this by arguing that* H^+ *is very low compared to other cations but that is based on their thermodynamic calculation for* H^+ *assumed to be correct (note that in their example* $[NH_4^+] >> [H^+]$*, effectively meaning R close to 2), so it is self-fulfilling.*"

   The numbers prove that our statement holds and is not a circular argument. To show this, we have added a comparison (see plots below) between Na^+ predicted with H^+ in the ion balance and without H^+ in the ion balance, where H^+ is determined iteratively with the full thermodynamic model. The following has been added to the main text: "For the three data sets used in this study, the difference in Na^+ predicted from an ion balance without considering H^+ compared to including H^+ is less than 1% for SOAS and SEARCH CTR, and 6% for the WINTER study, (see Fig. S3 in the supplement). In the following, we have not included H^+ in the ion balance."

We also point out that it is much more reliable to get aerosol H^+ through a full thermodynamic analysis and have added a sentence in the summary, “Note that the ion charge balance on its own generally cannot be used to infer H^+ since the H^+ concentrations are generally very low, even at the low pH of the southeastern US aerosols, and the dissociation states of acids must be known (e.g., proportions of HSO_4^- and SO_4^{2-}), which requires a full thermodynamic analysis.”

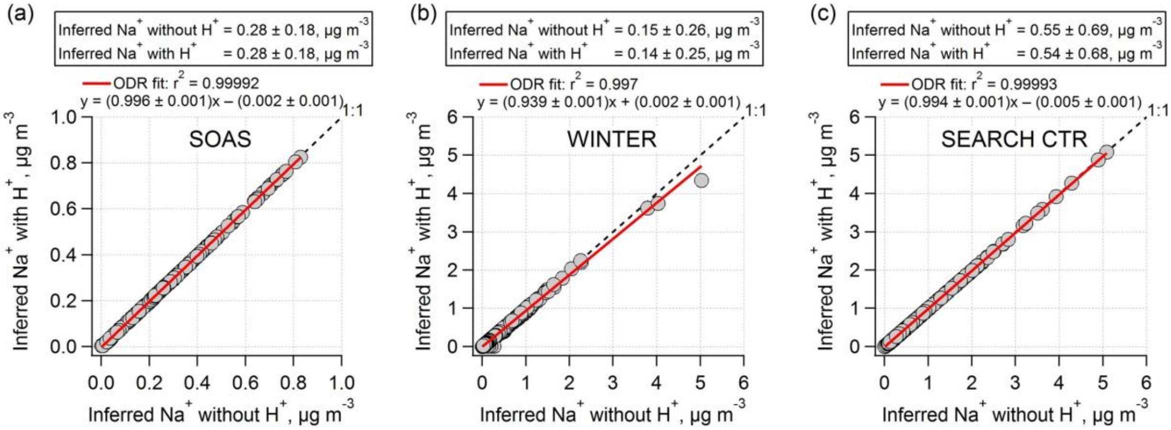

Fig. S3. Comparisons of ion charge balance inferred Na^+ including H^+ ($2SO_4^{2-} + NO_3^- + Cl^- - NH_4^+ - H^+$; y-axis) versus excluding H^+ ($2SO_4^{2-} + NO_3^- + Cl^- - NH_4^+$; x-axis) for three data sets used in the paper, (a) SOAS (Fig. 1), (b) WINTER (Fig. 5), and (c) SEARCH CTR (Fig. 6). The H^+ concentration was determined using ISORROPIA in an iterative approach. Na^+ is predicted from the ion balance is included with all other gas/particle species in the model, resulting in a predicted H^+. This H^+ is included in the ion balance to predict a new Na+, which is then used in a new model iteration. The procedure is repeated until the Na^+ concentration converges. The number of iterations for conversion are 1 for (a), 5 for (b), and 0 for (c), respectively, until inferred Na^+ converges. Orthogonal distance regression (ODR) fits are shown and uncertainties in the fits are one SD.

8. *“So a problem with this paper right now is that it pushes its argument either by presenting unusual situations where Na^+ is above LOD or by forcing the argument to be correct through the upper limit of inferred Na^+.”*

We have addressed these points above in Bullet 1. In a short summary, the above LOD Na^+ in the SOAS study is not unusually high compared to other co-collected data. Inferred Na^+ level is by nature an upper limit since it represents all the NVCs. A careful review of the data shows that the inferred Na^+ is no unrealistic. It is higher than SOAS measured Na^+ but lower than WINTER measured Na^+.

9. "*Page 4 Lines 33 - 36 and Page 5 lines 1 - 7: Of the three different Na^+ levels tested, option 1 infers that any lack of charge balance can be attributed to Na^+. On line 35 - 36, the authors then note that inferring the amount of Na^+ leads to a value more than 4 times higher than the measured value. There are a number of other possibilities that could explain these strongly different results and inferring shouldn't work as there is almost no Na^+ mixed with SOA particles. This is in fact supported by the fact that the reported values for Na^+ are below the limit of detection of the measurement (0.06 value when LOD is 0.07).*"

   This comment was made by reviewer 2, which we had addressed, and addressed again in Bullet 1 above. This reviewer seems satisfied with our added section addressing the mixing state issue. We further discuss it below in response to reviewer 2, who continues to raise the issue.

10. "*I agree with the reviewer and I don't think that the authors have addressed the issue satisfactorily. Conditions where Na^+ > LOD are unusual and conducive to their argument. Conditions where Na^+ < LOD should indeed not be used and the inferred Na+ seems misleading.*"

    We once more emphasize that the Na^+ data above LOD is not unusual. To clarify this, we have added one sentence justifying why we use Na^+ below the LOD on Page 6, "In the following, Na^+ data below the LOD is used in the analysis to increase the size of the data set, given that there is no obvious discontinuity in the results for data above and below the Na^+ LOD (see Fig. 4) and that Na^+ below the PILS LOD still roughly agrees with MARGA measurements of Na^+, which has a lower LOD (see Fig. S2a in the supplement)."

11. "*I agree with the reviewer and think that the authors make too much hay off this organic film hypothesis. It seems to have been suggested by Silvern et al. as a speculative explanation for the low R in the CSN and AMS data, but here the paper misleadingly characterizes Silvern et al. as being all about the organic film hypothesis and misses their main point which was to draw attention to the low R in the CSN data (a problem ignored by this paper).*"

We apologize if we gave the wrong impression. We have deemphasized the references to organic films (although still point out to why they are unlikely), and broadened the discussion at the level of "organic aerosol", because the main point is that the discrepancy between predicted and observed R is not correlated with organic mass or fraction.

We disagree that the main point of the Silvern et al. (2017) paper was to point to the CSN issue! The paper's title is "Inconsistency of ammonium–sulfate aerosol ratios with thermodynamic models in the eastern US: a possible role of organic aerosol". This paper discusses more than molar ratios in the southeast, it claims the low molar ratios are inconsistent with thermodynamic models and that an organic film that impedes NH_3 uptake could be an explanation. These assertions, if true, have large ramifications. Our point is that if one includes Na^+ data in the thermodynamic model (it is not included when using AMS data), and use high quality data (i.e., not CSN with a known NH_4^+ low bias, but SOAS study online data), there is no discrepancy in R and so no need for organic films or organics overall. We show this is true with an additional data sets (WINTER study and SEARCH CTR study). Finally, we have noted the molar ratio discrepancy in an earlier paper (Weber et al., 2016), where instead of focusing on molar ratios (R), we focused on pH. We show that there is no inconsistency with a trend of lower sulfate relative to ammonia, a constant pH and small drop in molar ratios. In fact, we showed the opposite of Silvern et al., that thermodynamic models actually explain the observations.

12. "*The authors again seem to make misleading claims to dismiss previous literature – here that they used R as an acidity proxy. They did not.*"

    There was a misunderstanding in the reference to the Rindelaub et al. (2016) paper in the first version of the manuscript. We intended to say that the lack of direct particle pH measurements contributes to the use of pH proxies. This issue was addressed in the first set of revisions; we have removed the sentence and the reference to Rindelaub and so the issue is resolved.

13. "*Again, the authors misleadingly describe Silvern et al. as claiming that the organic film limitation would apply to* NH_3 *but not to* H_2O *and* HNO_3*. They said nothing of the sort and instead pointed out that the organic film limitation hypothesis was problematic precisely because it would have to also apply to* H_2O *and* HNO_3*.*"

The reviewer is not correct here. Silvern et al. (2017) notes that "A mass transfer retardation of thermodynamic equilibrium may also have broader implications for the partitioning of semivolatile species and for hygroscopicity." We have added citations to papers showing that there is evidence for equilibrium of NH_3, H_2O, and HNO_3 in contrast to the organic film hypothesis. We have deemphasized the statements that the organic film proposed by Silvern et al. (2017) only selectively inhibits NH_3 in an attempt to be less confrontational (although it remains a critical point).

14. "*I agree with the reviewer that the authors' propensity to cite their own work and to dismiss others' borders on the embarrassing. I don't think that they fixed this in revision. The message one gets from the paper is that the authors are the only ones who understand particle thermodynamics and acidity, and everyone else doesn't know what they're doing; that doesn't come across very well.*"

    We have addressed the claimed self-citation issue above (as the manuscript stands now, there are 21 self-citations to papers involving Guo, Weber, and Nenes, compared to 151 citations to the work of other groups). We are certainly not the only group that understands thermodynamics, but we do think it is reasonable to point out in the published literature any flaws, statements that are in disagreement with quantitative data, or conclusions based on data with a demonstrated bias. The reviewer's final comment is a subjective and personal critique, which we will not respond to.

15. *Reviewer 2: "A constant throughout the manuscript is that strong statements are supported primarily by prior work from the authors of this study. It would strengthen the manuscript to either make less strong statements or cite work from other groups to support the claims being made."*
    Authors' response: "This point is well taken. We have cited more work from other groups. We believe that our statements are justified by our analysis."
    "*I agree with the reviewer and I don't think that the authors have significantly corrected that in revision*."

    We believe that we have presented strong arguments that are *supported by data* and by *thermodynamics*. An attempt to "tone down" the paper has been made as requested, but prefer not to make qualifying statements throughout the paper as it reduces the force of our arguments, which we believe are correct. How one choses to write is a question of *style*, and our preference is a direct straightforward approach for the sake of clarity.

At the end of the paper, we have added a text on limitations with this analysis: "Further assessments on possible effects of organic effects on semi-volatile partitioning of inorganic species however should be carried out, especially for regions that are chemically different from the eastern US conditions evaluated in this study."

Summary of papers reviewer 2 has suggested to cite:

1. Allen, H. M., Draper, D. C., Ayres, B. R., Ault, A., Bondy, A., Takahama, S., Modini, R. L., Baumann, K., Edgerton, E., Knote, C., Laskin, A., Wang, B., and Fry, J. L.: Influence of crustal dust and sea spray supermicron particle concentrations and acidity on inorganic NO3- aerosol during the 2013 Southern Oxidant and Aerosol Study, Atmos. Chem. Phys., 15, 10669-10685, doi: 10.5194/acp-15-10669-2015, 2015.
2. Bondy, A. L., Bonanno, D., Moffet, R. C., Wang, B., Laskin, A., and Ault, A. P.: Diverse Chemical Mixing States of Aerosol Particles in the Southeastern United States, Atmos. Chem. Phys. Disc., 1-37, doi: 10.5194/acp-2017-1222, 2018.
3. Craig, R. L., Nandy, L., Axson, J. L., Dutcher, C. S., and Ault, A. P.: Spectroscopic Determination of Aerosol pH from Acid-Base Equilibria in Inorganic, Organic, and Mixed Systems, J Phys Chem A, 121, 5690-5699, doi: 10.1021/acs.jpca.7b05261, 2017.
4. Reid, J. P., Bertram, A. K., Topping, D. O., Laskin, A., Martin, S. T., Petters, M. D., Pope, F. D., and Rovelli, G.: The viscosity of atmospherically relevant organic particles, Nat Commun, 9, 956, doi: 10.1038/s41467-018-03027-z, 2018.
5. Rindelaub, J. D., Craig, R. L., Nandy, L., Bondy, A. L., Dutcher, C. S., Shepson, P. B., and Ault, A. P.: Direct Measurement of pH in Individual Particles via Raman Microspectroscopy and Variation in Acidity with Relative Humidity, J Phys Chem A, 120, 911-917, doi: 10.1021/acs.jpca.5b12699, 2016.
6. Zhang, Y., Chen, Y., Lambe, A. T., Olson, N. E., Lei, Z., Craig, R. L., Zhang, Z., Gold, A., Onasch, T. B., Jayne, J. T., Worsnop, D. R., Gaston, C. J., Thornton, J. A., Vizuete, W., Ault, A. P., and Surratt, J. D.: Effect of the Aerosol-Phase State on Secondary Organic Aerosol Formation from the Reactive Uptake of Isoprene-Derived Epoxydiols (IEPOX), Environ. Sci. Technol. Lett., 5, 167-174, doi: 10.1021/acs.estlett.8b00044, 2018.

Responses to Reviewer 2

1. *"The authors have added a section considering mixing state, which is a helpful addition for considering that different sources of aerosols are present in the southeast U.S. Despite this addition, there are still concerns about the conclusion NVCs are driving this process and that mixing state is not impacted by a lack of NVCs the smaller OC - sulfate particles. The very strong arguments in the intro and remainder of the paper that organic coatings and viscous aerosols cannot have an effect on pH and partitioning are still too strong and should be weakened or acknowledged as at least potentially playing a role."*

   We address the concern of mixing state below. We have attempted to tone down our statements in the paper and we claim the effects of organics are minor or negligible based on our analysis, but could be more important in other regions not considered in this study. We have also added a few lines on the limitations of this study at the end of the paper.

2. *"The concern with this statement is that, even if including NVCs in the thermodynamic model resolves the discrepancy, if the NVCs are not in the particles this is referring to, then the correct answer is being obtained, but not for the correct reasons. Without evidence that NVCs are present in the SOA/sulfate particles that dominate in the SE US, I am still concerned about the overall finding of this manuscript. For SOAS, if ~5% of sulfate is mixed with sea salt or dust particles and ~95% of sulfate is mixed with SOA particles (simplifying here), but all of the NVCs are present in the salt/dust particles, then the NVCs likely do not play a large role in the ammonium - sulfate molar ratio. Hence, my overall concern that the title "underappreciated role" of NVCs could mislead readers if NVCs do not in fact have much effect on ammonium - sulfate ratios. Recently, we've seen other groups from SOAS point out in a paper under review for ACPD (Bondy et al. 2018) that NVC's are present in < 3% of SOA - dominated particles during SOAS. If >95% of SOA particles contain nearly all the sulfate, but contain no NVCs it is still not clear how the title reflects what is occurring in the aerosols. At a minimum, the authors should discuss that the Na+ concentrations measured are not in the majority of the accumulation more and qualify their results, accordingly."*

   In the added section, we show that for the data in which Na^+ is above LOD, on average 18% SO_4^{2-} by mass is needed in the $PM_{1-2.5}$ size range to obtain the same molar ratio as a complete internal mixture. This is an extreme case. For periods when Na^+ concentrations are lower, the Na^+ mass fraction required is lower. For example, as stated in the paper, 5% by mass of the sulfate needs to be mixed with Na^+ when the Na^+ is at the study mean concentration of 0.07 $\mu g\ m^{-3}$. Bondy et al. (2018) reports that NVCs are in less than 5% of the SOA/sulfate mixed particles, by particle number (the instrument does not provide a quantitative mass measurement). Our analysis is based on mass, so the stated percentages are not directly comparable. This is important because there is considerable uncertainty in going from a number mixing percent to a mass mixing percent (see Bondy et al. (2018)). One factor is that the average sulfate mixing is of <5% is for all sizes, and sulfate is mainly associated with PM_1 and Na^+ in $PM_{2.5}$, (as we assume in the mixing model), thus the mass fraction in the larger sizes where Na^+ is, will likely be larger (mass scales with D_p^3). Furthermore, Bondy et al. (2018) reports mixing for the complete SOAS study, we use only the first half of the study data when we measured $PM_{2.5}$ ionic species, a period when Na^+ was larger, thus for the whole study even less sulfate mixing % with Na^+ would be required as the Na^+ concentrations are lower. This all shows that the results of Bondy et al. are not contrary to our mixing assumptions.

In fact we feel Bondy et al. (2018) supports our findings based on their general statements. From the Abstract, Bondy et al. (2018) states "These results emphasize that neither external nor internal mixtures fully represent the mixing state of atmospheric aerosols, even in a rural, forested environment,…". From the conclusions, Bondy states "Although SOA/sulfate dominated the overall measured aerosol population, especially in the accumulation mode (0.2-1.0 μm), it was found to be present at supermicron sizes as well." We have noted these findings and cited Bondy et al. (2018) in the discussion of mixing state.

3. "*When considering mixing state, this argument is not as clear as it might appear. If dust or salts are introduced (Allen et al. 2015, Bondy et al. 2017), Na^+ will go up, but so will sulfate from sea salt, though it is likely a low fraction of overall sulfate (that is externally mixed from the most of the sulfate mixed with OC in submicron particles). The equilibration time scale between (as modeled now in the paper) is not well known in the atmosphere, though if the authors can define that it would be useful. Thus, the correlation here may be indicative of shifting concentrations of different populations and not particularly strong evidence that Na^+ is leading to changes in R (e.g. correlation equals not causation).*"

Based on a scaling analysis (see Equation (12.48) in Seinfeld and Pandis (2006)), for a 10 nm thick film a rough estimation gives the characteristic time scale of diffusion as 0.0001 sec for a typical diffusion coefficient of 10^{-12} m^2/s in solid, and 1×10^{-7} sec for a typical diffusion coefficient of 10^{-9} m^2/s in liquid (the diffusivity is cited from http://webserver.dmt.upm.es/~isidoro/dat1/Mass%20diffusivity%20data.pdf). The above characteristic times are miniscule relative to the equilibration time scales of approximately 30 min for NH_3-NH_4^+ in the ambient atmosphere (Dassios and Pandis, 1999; Cruz et al., 2000; Fountoukis et al., 2009). Therefore, the quantitative data suggests this is not an issue.

4. “*The argument that mixing does not alter the conclusions of the original analysis is surprising and I am still unclear as to how this can be. Particularly as the authors now cite work showing the pH is predicted to be higher for particles > 1 micron than < 1 micron. The authors are correct to point out that not all sulfate is in SOA particles, but based on filter measurements and AMS measurements at SOA, it would be safe to say the vast majority of sulfate is present in submicron SOA - sulfate particles. The concern is that if no NVCs are present in > 95% of SOA - sulfate particles, it seems highly unlikely that the R is being controlled by NVCs. The authors have addressed the inverse concern (e.g. does having a small amount of sulfate with NVCs change the overall finding), but this is not the major concern. The concern is that NVCs are not present in the very acidic SOA - sulfate particles that are the focus of this paper. If the NVCs in the 2nd externally mixed population are driving acidity in the other population that is a very surprising result, though perhaps I’m misunderstanding the external mixing section.*”

   This has been addressed above. Again, the added plots show there is no significant difference between overall *R* assuming complete internal mixing (i.e., as Silvern did in their paper and we did in ours) if some fraction of the sulfate is mixed with NVCs (on average 18% for periods of Na^+ above the LOD, only 5% by mass when Na^+ is at the LOD, and lower % at lower Na^+). We refer the reviewer again to the revised paper Fig 7.

5. “*I am still uncomfortable with the extensive use of periods of data below LOD and inferred ion balance. LOD is admittedly arbitrarily defined, but it is an analytical standard, since as data approaches background noise, measurements are less reliable. I still have concerns that a higher concentration of “inferred” Na^+ is needed to make the model match the measurements, perhaps that means that Na^+ is not driving the R here? It is appreciated that the authors clearly define the time periods.*”

   This is discussed in our response to reviewer 3 above. As noted, there is nothing special about the choice of LOD, researchers define it different ways. Fig. 4a clearly demonstrates that there is no discontinuity in the model or the data in the molar ratio discrepancy as a function or Na^+ when moving below the Na^+ LOD, and it correlates very well with MARGA Na, which has a lower LOD. If those NVCs are not driving the molar ratio, we would not see the very good agreement between predicted and observed molar ratio for WINTER and SEARCH data sets, when inferred Na^+ is added to the model input.

6. “*More evidence continues to come out about diffusion limitations of viscous particles (see citations within (Reid et al., 2018)) and the role of coatings inhibiting partitioning that are not simply related to organic mass fraction (Zhang et al., 2018). Zhang et al. from the Surratt Group this year for example showed that*

even a 10 nm coating of oxidized monoterpene SOA, could decrease reactive uptake coefficients by a factor of 4 and that would decease isoprene SOA formation via IEPOX by 15 ‐ 20% in conditions representative of the SE US. Clearly, IEPOX is a much larger molecule than ammonia, but at the ionic strengths listed below it seems very plausible that a distinct organic phase that could inhibit water or ammonia uptake could be present. I think given the caveats of the author's own assumptions (e.g. inferring sodium concentrations), that the statement ruling out a role for organic coatings and glassy organics should be weakened."

As noted, the Zhang paper is not directly applicable to this work. Generalizations from laboratory experiments involving completely different chemical systems (with much larger molecular weight, hence less diffusive and more susceptible to kinetic limitations) to this work are not directly comparable. Finally, stating that delays are "up to a factor of 4" means that the gas-to-particle mass transfer rate is still is within the same order of magnitude; persistent disequilibrium in ammonia-ammonium partitioning requires considerably longer delays than that.

7. "*By the authors' standard of a direct measurement, would they consider a pH probe a direct measurement of H+ activity/pH? If not, then it is likely the direct measurements of H+ or pH are essentially impossible based on the standard the authors establish. pH probes and other measurements of pH have a long established history, even if there are a few assumptions needed since the activity of each ion is solution is not known precisely in many systems (including aerosols). Direct in this discussion was intended to refer to measuring both the acid and conjugate base concentrations directly, of which the Rindelaub measurement is the first of its kind. Arguments over the definition of "direct" aside, the authors misunderstand the Rindelaub paper, as it does not assume an ideal solution. Activity calculations are conducted for all species in solution (since it is a model system). The followup work in Craig et al., includes an entire figure on H+ activity coefficient versus ionic strength for inorganic, organic, and mixed system. Activity coefficients are calculated for all components in both Craig et al. and Rindelaub et al., so the non ‐ ideality is not being ignored, as the authors claim.*"

   There apparently is a misunderstanding here, we were not claiming that nonideality was being ignored. In any case, Rindelaub et al. (2016) reference and associated discussion was removed and so this is a comment on a comment, not an issue with what is in the latest version of the manuscript.

8. "*The authors note that the average ionic strength for this study is 29 mol/liters, which is quite high and brings about three questions:*
   1) At that concentration are there concerns about the limited water present and the impact on the thermodynamic calculations? How are the authors handling the fact that most thermodynamic models

struggle with non‐dilute solutions? This may be a lack of knowledge of ISORROPIA, but Debye‐Hückel breaks down above 0.1 M ionic strength I believe, does it not? How are the authors avoiding this, if so, it would be helpful to mention this high ionic strength and include a brief discussion."

ISORROPIA-II, like all atmospheric aerosol thermodynamic models, uses activity coefficients to calculate nonidealities. The model uses the mean activity coefficient models of Kusik and Missner for ion pairs and the multicomponent mixing rule of Bromely. This approach applies to high ionic strengths, at least 30 M (see relevant discussion in Fountoukis and Nenes, 2007). The ability to reproduce NH_3, NH_4^+, and liquid water in SOAS (Guo et al., 2015) for the range of relative humidity considered demonstrates that it captures nonidealities reasonably well up to very high ionic strengths.

"*2) How would this change if ISORROPIA accounted for organic components, a large mass fraction of the aerosols in question? My hunch is that it would lower the ionic strength, which would impact the figure shown below of shifting Ka (moving less to left), so it would be helpful if the authors could address this.*"

This is a good point. Vasilakos et al. (2018) and Song et al. (2018) added organic-inorganic interaction calculations in the soluble phase and found that the pH to be affected very little. Pye et al. (2018) considered liquid-liquid phase separation effects, and found a slightly larger impact on pH, but it was still within 0.7 units of assuming a single aqueous organic-inorganic phase. An important impact of organics is to contribute liquid water, and through this contribution affect the inorganic equilibria, and is something we already have discussed in the manuscript.

"*At such high ionic strengths and lower water activities, it seems likely that many of the inorganics would end up salting out of the organic component, leading to core‐shell liquid liquid phase separations. Despite the authors stating that the organics will not have an effect, it would seem this likely supports that these organic phases, possibly quite viscous, could impact partitioning and thus R. If the authors could address this it would be helpful.*"

We do not claim there is absolute no effect from organics on gas-particle partitioning, but the effects are minor in the SOAS or WINTER studies, as the partitioning of inorganic semivolatile species can be carried out without considering organics. Pye et al. (2018) confirms a secondary effect from organics by including organic species in thermodynamic modeling. The effect of semi-solid phases, would be to slow down partitioning of all species, including water, ammonia/ammonium; the data suggests this is not the case. Guo et al. (2015) provides a relevant discussion; in summary, the oxidation state and the relative humidity seen in the dataset suggests that viscous aerosol is unlikely.

9. "*Considering the challenging processes being studied by this paper and other papers focused on this topic, the authors would be well - served to acknowledge the possibility of other factors beyond their proposed explanation, which relies on its own assumptions.*"

   We are confident in our conclusions as they are well supported by observational data. Ammonium partitioning, see Fig 2a, would not be accurately predicted by an equilibrium models if an organic film inhibits NH_3 uptake to the point where equilibrium is never reached. We also point out that the organic effects of Silvern et al. (2017) are based on an inference that may be from a bias in the observed NH_4^+ concentration (i.e., use of CSN data). We feel that this, together with a lack of correlation of the R discrepancy with organic fraction further presents strong support for our hypothesis.

   Nevertheless, at the end of the paper, we have added text on limitations with this analysis: "Further assessments on possible effects of organic effects on semi-volatile partitioning of inorganic species however should be carried out, especially for regions that are chemically different from the Eastern US conditions evaluated in this study."

10. "*The authors make a fair point, presuming organic species do not lower the ionic strength significantly. How much would this then shift the* pK_a *of the bisulfate/sulfuric acid system, the authors noted in comment 13? Would that likely mean that it would be much lower than could be observed in ambient aerosols? Thus, sulfate and bisulfate are the only forms of sulfate that need to be addressed for aerosols? Some clarification would be helpful.*"

    This is indeed a good point. From the calculations (that consider ionic strength effects, hence shifts in the pK_a), if pH is larger than -1 then HSO_4^-/SO_4^{2-} are the only forms of sulfate that we need to consider in the thermodynamics.

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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~~interactions with organic ~~film~~constituents that ~~only inhibits~~inhibit 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~~This hypothesis ~~by analyzing ~~is tested through thermodynamic analysis of ambient observations~~ with a thermodynamic model.~~. Measurements show that the deviation between *R* from a molar ratio of 2 is strongly correlated with the concentration of sodium (Na^+), a nonvolatile cation (NVC), ~~with~~but exhibits no correlation to organic aerosol mass concentration or mass fraction. ~~*R* predicted by the~~It is shown that thermodynamic ~~model is very sensitive to concentrations of Na^+ or NVC in general. Both~~predictions of both *R* and ammonia gas-particle partitioning can accurately reproduce observations when small amounts of nonvolatile cations (NVC) are included in the ~~thermodynamic analysis~~calculations, whereas exclusion of NVCs results in predicted *R* consistently near 2. ~~This happens because more NVCs shift pH higher, shifting NH_3-NH_4^+ equilibrium~~The sensitivity of *R* to ~~favor the gas and resulting in less particle phase ammonium and lower *R*. When NVCs~~small amounts of NVCs arises because when the latter are present~~,~~ but not included in the thermodynamic ~~model~~calculations, the missing ~~cation is~~cations are 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~~*R* that is biased high. Results and conclusions based on bulk aerosol ~~composition measurements and assuming~~considerations that assume all species are internally mixed~~, however, similar results~~ are ~~found~~not changed even if NVCs and sulfate ~~and ammonium ~~are largely externally mixed~~, as long as a small fraction~~; fine particle pH is found to be much less sensitive to mixing state assumptions than molar ratios. We also show that the data used to support the "organic inhibition" of ~~the sulfate is mixed with ~~NH_3 from equilibrium, when compared against other network and field campaign data sets, displays a systematically and significantly lower NH_4^+ (thought to be from an evaporation bias), that is of the ~~NVCs. These results strongly challenge~~order of the effect postulated to be caused by organics. Altogether, these results question the postulated ability of organic ~~films~~compounds to considerably perturb aerosol acidity and prevent ammonia from achieving gas-particle equilibrium, at least for the ~~conditions~~locations 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 that involve the hydronium ion ~~(Jang et al., 2002; Eddingsaas et al., 2010; Surratt et al., 2010)~~(e.g., Jang et al., 2002; Eddingsaas et al., 2010; Surratt et al., 2010) and gas-particle partitioning of semivolatile ~~species~~ acids and bases ~~(Guo et al., 2016; Guo et al., 2017a)~~(e.g., Fridlind and Jacobson, 2000; Young et al., 2013; Guo et al., 2016; Guo et al., 2017). Acidity also modulates aerosol toxicity and atmospheric nutrient supply to the oceans ~~through changing~~ by augmenting the solubility of transition metals ~~solubility~~ and other nutrient species ~~(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; Stockdale et al., 2016; Fang et al., 2017). Despite its importance, challenges in measuring fine mode particle pH have led to the ~~use~~adoption of measurable aerosol properties as acidity proxies, such as aerosol ammonium-sulfate ratio or ion balances ~~(e.g.~~ with a priori assumed dissociation states (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~~such proxies are not uniquely related to pH because they do not capture ~~the~~ variability in particle water content, ion activity coefficients, or ~~partial~~ dissociation state of ~~species in the aerosol phase~~polyprotic acids and bases ~~(Guo et al., 2015; Hennigan et al., 2015; Guo et al., 2016)~~(Guo et al., 2015; Hennigan et al., 2015; Guo et al., 2016; Song et al., 2018). ~~A~~ An alternative approach that better ~~method that~~ constrains aerosol pH is ~~comparison between a~~ a thermodynamic analysis ~~and observations of gas-particle partitioning~~ of semivolatile ~~species that are~~acid (or base) measurements, whose partitioning is observably sensitive to ~~pH at the given environmental conditions (i.e.,~~ shifts in aerosol acidity (pH is optimally constrained when gas-particle concentration ratios ~~near~~approach 1:1~~)~~), and with the aerosol water content or phase state constrained as well ~~(Guo et al., 2015; Hennigan et al., 2015; Guo et al., 2016; Weber et al., 2016; Guo et al., 2017a)~~(Guo et al., 2015; Hennigan et al., 2015). NH_3-NH_4^+, HNO_3-NO_3^-, and HCl-Cl^- pairs often meet this condition~~.~~ for a wide range of atmospherically-relevant pH. 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~~.~~ (Bougiatioti et al., 2016; Guo et al., 2016; Guo et al., 2017; Liu et al., 2017; Murphy et al., 2017; Song et al., 2018).

~~It has been noted that~~Despite their skill and widespread use in regional and global models, aerosol thermodynamic models ~~fail to accurately~~can predict ammonium-sulfate molar ratios ~~(Kim et al., 2015; Weber et al., 2016; Silvern et al., 2017)~~(Kim et al., 2015; Weber et al., 2016; Silvern et al., 2017)~~.~~ that departs from observations in seemingly counterintuitive ways. In the southeastern US, where total ammonium ($NH_x = NH_3 + NH_4^+$) is ~~observed to be~~ in large excess of particle sulfate, 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 predict very low pH (0.5 to 2) ~~(Guo et al., 2015)~~(Guo et al., 2015) and molar ratios always 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 because particles are coated by organic films that inhibit the condensation of~~ ~~NH_3~~ ~~from the gas phase, which gives rise to the molar ratio discrepancy (Silvern et al., 2017). Such kinetic limitations, if prevalent, opposes the validity of aerosol thermodynamic equilibrium. This 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, as seen with~~ ~~SO_2~~ ~~emission reductions in the eastern US~~ . This predicted-observed molar ratio discrepancy has led to the hypothesis that thermodynamic predictions are incorrect because they do not consider interactions with organic species, either in the form of films that inhibit gas-to-particle mass transfer of NH_3 or other mechanisms that are not accounted for (Silvern et al., 2017). Such limitations, if prevalent, are suggested to oppose the validity of aerosol thermodynamic equilibrium with significant impacts on aerosol chemistry and acidity-mediated processes worldwide (Silvern et al., 2017), especially given the expected increasing organic mass fractions in the future due to reduced anthropogenic emissions, as seen with SO_2 emission 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 (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., 2017; Paulot 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, particles may be in semi-liquid or glassy state and have very low diffusivity of molecules throughout its volume~~ .

The effect of organic species on gas-particle equilibrium of inorganic species has been the subject of many past studies. Organic “films” are often hypothesized to act as barriers for gas-particle mass transfer, which given their ubiquity, means they require especial attention in studies. For example, Anttila et al. (2007) reports the formation of ~10 nm thick organic films in regions with monoterpene emissions, which is the largest source of summertime organic aerosol in the southeastern US (Zhang et al., 2018). Lab studies have shown that organic films may significantly slow down mass transfer of NH_3 from gas to particle at low relative humidity (less effect at higher RH, such as the southeastern US) ~~(Tong et al., 2011; Bones et al., 2012)~~(Daumer et al., 1992; Liggio et al., 2011)~~. This~~ but have little effect on water vapor uptake for a large RH range (Garland et al., 2005). Such films, as noted by Silvern et al. (2017), would have important implications for partitioning of NH_3 and other larger semivolatile molecules, such as H_2O, HNO_3 and organic acids. However, in contrast, numerous studies show that NH_3, water vapor, and HNO_3 equilibrate with organic-rich atmospheric aerosols (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., 2017; Liu et al., 2017; Murphy et al., 2017; Paulot et al., 2017), which suggest organic films, if present, do not impose considerable delays in mass transfer and gas-particle equilibration.

At low temperature and low relative humidity, particles may ~~severely limit~~be in a semi-liquid or glassy state characterized by a very low molecular diffusivity throughout its volume (e.g., Zobrist et al., 2008; Bertram et al., 2011; Tong et al., 2011; Zobrist et al., 2011; Bones et al., 2012; Reid et al., 2018). When in this state, gas-particle mass transfer of all semi-volatile components may be severely limited and require much longer time scales to equilibrate~~.~~ than the ~20 minutes typically thought to apply for PM_1. However, 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^-~~ when~~, especially in cases where RH is sufficiently high (greater than 40%) ~~that~~to maintain the aerosol ~~is likely~~ in a ~~complete~~deliquesced (completely liquid) state ~~(Guo et al., 2015; Guo et al., 2016)~~(Guo et al., 2015; Guo et al., 2016).

Other reasons~~ that are~~, unrelated to the presence of organic ~~films~~aerosol, may drive the observed molar ratio discrepancy. ~~Most analyses~~Analyses of aerosol acidity, molar ratios, and partitioning of semivolatile species~~ do not consider variation of aerosol~~ , often neglect the variations of composition with size, ~~which may translate to a large range of~~especially in the PM_1 to $PM_{2.5}$ range (Keene et al., 1998; Fridlind and Jacobson, 2000; Nenes et al., 2011; Young et al., 2013; Bougiatioti et al., 2016; Fang et al., 2017). If acidity ~~and hence~~across size changes sufficiently, average equilibrium composition ~~(Keene et al., 1998; Nenes et al., 2011; Young et al., 2013; Bougiatioti et al., 2016; Fang et al., 2017). The presence of soluble~~(including molar ratios) may deviate considerably against observations owing to the nonlinear dependence of partitioning with acidity (e.g., Guo et al., 2015). Soluble nonvolatile cations (NVCs, such as Na^+, K^+, Ca^{2+}, Mg^{2+}), ~~which are often neglected in~~potentially present in large quantities in $PM_{2.5}$ and to a lesser extent in PM_1, can strongly modulate acidity and molar ratios. NVCs are often omitted from thermodynamic calculations because of their relatively minor contribution to aerosol mass and ion charge balance~~ (e.g., (Kim et al., 2015; Silvern et al., 2017)), or because they are~~; for similar reasons, NVCs are not routinely included in aerosol composition measurements~~ (e.g., those made with an aerosol mass spectrometer), or are not well quantified due to high measurement limit of detections (LODs) relative to anion species, can affect acidity and molar ratios. ~~; when they are, proximity to level of detection (LOD) often increases their concentration uncertainty. Here we show, based on ~~a bulk $PM_{2.5}$ aerosol ~~analysis ~~that ignoring~~of observational aerosol and gas data sets, that excluding even small amounts of NVC ~~as inputs to the~~in thermodynamic ~~model~~analyses results in predicted NH_4^+/SO_4^{2-} molar ratios close to 2, whereas including them brings model-predicted molar ratios into agreement with observed levels. We also assess the implications of ~~a bulk~~using specific datasets on R, and the impact of adopting a size-averaged ("bulk") thermodynamic analysis ~~by comparing those conclusions to aerosol that is externally mixed~~against one that considers the incomplete mixing (size-dependent composition) of ambient aerosols.

2. Methods

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

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

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

Both are based on 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 can be associated with different sized particles ~~(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~~detail below. The upper limit for R and R_{SO4} is 2 for a particle composition of pure $(NH_4)_2SO_4$, and a lower limit 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 ~~(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).

Data: Two datasets are mainly 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~~a 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~~(Orsini et al., 2003). NH_3 was obtained from chemical ionization mass spectrometer measurements ~~(You et al., 2014)~~(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~~ (PILS PM_1 data ~~set, which involved measurement of $PM_{2.5}$~~were collected in the ~~first~~second half of the study and ~~PM_1 in the second half.~~are not used here).

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Periods of rainfall are not included in the analysis, as equilibrium does not apply. 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)~~(Weber et al., 2016). $PM_{2.5}$ anion and cation data along with NH_3 and HNO_3 were also collected with a Monitor for AeRosols and GAses (MARGA) during SOAS ~~(Allen et al., 2015). These data support the PILS data analysis; the results are similar using either data set.~~(Allen et al., 2015). 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)~~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~~Thermodynamic analysis of both datasets ~~report~~indicate highly acidic aerosols with average pH~1 ~~(Guo et al., 2015; Guo et al., 2016)~~(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~~To avoid any confusion, what SO_4^{2-} refers to in this study ~~refers to~~regards 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~~). Similarly, NH_4^+ refers to the sum of total aqueous ~~sulfate as just SO_4^{2-}. The same applies to NH_4^+~~ ammonium (NH_4^+, NH_3) and NO_3^-~~.~~ refers to the sum of total nitrate (NO_3^-, HNO_3) in aqueous aerosols. SO_4^{2-}, NH_4^+, and NO_3^- are reported by PILS-IC. However, PILS-IC cannot distinguish the in-situ aerosol ion forms for collecting aerosols in diluted deionized water (i.e., the ionic strength is changed) (Orsini et al., 2003). 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).

In addition to the SOAS and WINTER data sets, the Southeastern Aerosol Research and Characterization (SEARCH) CTR sampling site (the same as SOAS) historical data from year 1998 to 2013 is re-analyzed to show that thermodynamic model can reproduce the observed decreasing trend of R_{SO4} when NVCs are considered. Molar ratios determined from the Chemical Speciation Network (CSN), which were utilized and discussed by Silvern et al. (2017) and Pye et al. (2018), are not used in this work because of a significant low bias when compared to the SEARCH and SOAS data (see Table S1 and S2 in the supplement). The discrepancy is likely due to the loss of semivolatile NH_4^+ collected on the CSN nylon filters (Yu et al., 2006; Silvern et al., 2017), and can result in an underestimation in R, compared to online measurements by as much as 1 unit (Table S1).

Thermodynamic analysis of observations: We have used the thermodynamic model ISORROPIA-II ~~(Fountoukis and Nenes, 2007)~~(Fountoukis and Nenes, 2007) 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;~~. A molarity-based definition of pH is used:

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

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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}) and H^+_{air} (µg m^{-3}) are the hydronium ion concentration in particle liquid water~~, and H^+_{air} (µg m^{-3}) the hydronium ion concentration per~~ and volume of air, respectively. 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~~by 0.15-0.23 units but highly correlated ~~to~~ (r^2 = 0.97) to pH predicted with measured total particle water (W_i + W_o) ~~in~~for the southeast US (which includes the SOAS study), where W_o accounted for 35% of total particle water ~~(Guo et al., 2015)~~(Guo et al., 2015). For simplicity, we therefore use only 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^+). 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 form other than $CaSO_4$ (H^+_{aq} is meaningless in a completely effloresced aerosol~~) and so~~). Given this phase state requirement, we restrict the analysis to conditions where RH > 40%.

~~***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.~~***Mixing State:*** Because up to now the aerosol composition data is bulk PM$_1$ or PM$_{2.5}$, and used as input to ISORROPIA-II, the thermodynamic analysis implicitly assumes that all particle species were internally mixed, so that one value of pH represents the aerosols and governs the gas-particle partitioning. The existence of externally mixed particles may quantitatively and qualitatively affect the bulk thermodynamic analysis, so their impact needs to be assessed. For this, we begin from the bulk analysis, then repeat the same calculation, augmenting each time the degree of external mixture of NVC with sulfate. Direct measurements of aerosol mixing state during SOAS suggests that ambient particles indeed exhibit a range of mixing states (Bondy et al., 2018). 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,~~gaseous 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, by sequentially calling ISORROPIA for each subgroup~~, by sequentially performing the equilibrium for one subgroup than the other. The final~~. The solution is found when the composition of each group no longer changes with iteration and both 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~~, and constrained by 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~~observations. Given that pH is size dependent and generally higher at larger ~~size~~sizes ~~(Young et al., 2013; Bougiatioti et al., 2016; Fang et al., 2017)~~(Fridlind and Jacobson, 2000; 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~~, bulk pH is compared against an aerosol liquid water-weighted pH:

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

~~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~~ratio (*R*) ~~prediction~~predictions

~~***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 the level of 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:~~, including 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~~sets of 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~~$^+$;~~$^+$”, and, (3) $Na^+ = 0$~~.~~, which corresponds to ignoring NVCs all together.

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~~for the whole observation time-series. 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 PILS-IC LOD and set to zero in the analysis, the charge balance predicted Na^+ should be viewed as the concentration of generic NVC concentrations with a valence of 1. 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~~, given that there is no obvious discontinuity in the results for data above and below the Na^+ LOD (see Fig. 4) and that Na^+ below the PILS LOD still roughly agrees with MARGA measurements of Na^+, which has a lower LOD (see Fig. S2a in the supplement). The inferred Na^+, determined from the charge balance, provides an upper limit of the NVC equivalents that can affect aerosol pH and satisfies solution electroneutrality. 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, may not be 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). Inferred Na^+ has an expected high uncertainty due to error propagation of NH_4^+, SO_4^{2-}, NO_3^-, and Cl^- measurements (see Fig. S2b), and uncertainties in the dissociation state of sulfate (see Fig. S1 for the pH-dependence). The concentration of H^+ is ignored in the ion charge balance calculation for inferred Na^+, since H^+ is at least an order of magnitude less than the NVC ion equivalents, even for these very low pH data points (between 0 and 2). To demonstrate this, the average ion molar concentrations in $PM_{2.5}$ were $NH_4^+ = 35.4$, $SO_4^{2-} = 21.1$, $NO_3^- = 3.7$, $Na^+ = 2.9$, and $Cl^- = 0.82$ nmol m^{-3} by PILS-IC, compared to ISORROPIA-predicted $H^+ = 0.31$ nmol m^{-3}. For the three data sets used in this study, the difference in Na^+ predicted from an ion balance without considering H^+ compared to including H^+ is less than 1% for SOAS and SEARCH CTR, and 6% for the WINTER study (see Fig. S3 in the supplement). In the following, we have not included H^+ in the ion balance. In SOAS, inferred Na^+ is generally above zero indicating a cation deficiency, but 8 out of 229 points (3% of the data) were slightly below zero. In these cases, a small positive value of 0.005 µg m^{-3} 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 ignored in the ion charge balance calculation 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 $NH_4^+ = 35.4$, $SO_4^{2-} = 21.1$, $NO_3^- = 3.7$, $Na^+ = 2.9$, and $Cl^- = 0.82$ nmol m^{-3}, compared~~

~~to ISORROPIA-predicted $H^+ = 0.31$ nmol m^{-3}. Fig. 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+}).~~Fig. 1a shows that the inferred Na^+ was always higher than measured Na^+. 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~~.~~, suggesting that the magnitude of inferred Na^+ is not unreasonable (see Fig. S2). 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).~~(Tang et al., 1997). Chloride depletion occurs when an acid, such as HNO_3, is mixed with NaCl producing HCl that evaporates ~~since~~owing to its higher volatility ~~than~~relative to HNO_3 ~~(Fountoukis and Nenes, 2007)~~(e.g., Katoshevski et al., 1999; Fountoukis and Nenes, 2007)~~, resulting in a loss of Cl^- and H^+ (increase in pH).~~, resulting in a loss of aerosol Cl^-. The chloride depletion in sea-salt aerosols during the SOAS study was discussed in detail by Bondy et al. (2017). 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. Periods where Na^+ was closer to typical background levels and near or below the LOD lead to similar conclusions in the following analysis.

Fig. 1 shows the effect of Na^+ ~~(i.e., NVCs in general)~~ on ISORROPIA-predicted SO_4^{2-}, NH_4^+, NH_3, *R*, and pH. Fig. 1b and Fig. 1e show that measured and predicted ~~sulfate (~~SO_4^{2-}~~)~~ and ~~total ammonium (~~NH_x ~~$= NH_3 + NH_4^+$)~~ are always identical. SO_4^{2-} ~~is nonvolatile and so remains unchanged by~~completely resides in the ~~model (output = input).~~aerosol phase in all calculations. 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 model prediction of NH_x partitioning~~, i.e., the predicted NH_4^+ concentration.~~. It is noteworthy that NH_x/SO_4^{2-} is practically always above 2, indicating excess NH_x compared to SO_4^{2-}. Under such conditions, ~~it is sometimes interpreted~~conventional thought suggests that NH_3 must completely neutralize sulfate so that it can be in the form of SO_4^{2-} ~~(Kim et al., 2015; Silvern et al., 2017)~~(Kim et al., 2015; Silvern et al., 2017)~~, but the~~ ; this view however neglects the large difference in volatility between SO_4^{2-} and NH_x, which thermodynamic ~~model predicts~~models consider. Because of this, $PM_{2.5}$ ~~to be~~can remain highly acidic, with a pH between 0 and 2 (Fig. ~~1h). This results from NH_4^+ being semivolatile and SO_4^{2-} being virtually nonvolatile at any atmospherically-relevant concentration and acidity~~1h), even if there is a large amount of excess NH_x (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~~sensitivity to ~~various Na^+~~NVC input concentrations. Fig. 1g and Fig. ~~2~~2a shows very good agreement between measured and observed NH_3-NH_4^+ partitioning when measured Na^+ is used in the model. ~~However,~~Using inferred Na^+ generally ~~under-predicts~~ results in an underestimation of $\varepsilon(NH_4$~~$^+$), possibly because for this data set it over-predicts~~$^+$). This is consistent with using overestimated NVC levels~~,~~ – as the resulting ~~in higher~~ pH is overestimated (Fig.

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1h), ~~and a higher pH~~which in turn shifts a fraction of the NH_4^+ to gas phase NH_3~~.~~ and biases ε(NH_4^+) low. Zero Na^+ shows the opposite behavior (Fig. 1g and Fig. ~~2~~2c); ε(NH_4^+) is over-predicted because ~~predicted pH is too low for no~~neglecting NVCs ~~in the model but actually present in the aerosol. A lower pH partitions~~biases pH low, driving more NH_3 to the particle phase ~~(ε~~(and biasing ε(NH_4^+)~~ is too~~ high~~).~~.

From the above it is clear that *R* ~~also~~strongly depends on ~~the input Na^+ concentration.~~how NVCs are considered in the thermodynamic analysis. 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* using measured Na^+ was on average 1.85 ± 0.17. ~~Predicted~~As expected, predicted *R* was significantly lower ~~by~~when inferred Na^+ ~~at a ~~was used (mean, ~~of~~*R* = 1.43 ± 0.32~~,~~), and ~~the ~~highest ~~*R* at~~for zero NVC (average *R* = 1.97 ± 0.02~~ was found when zero Na^+ was used as model input~~) in the thermodynamic analysis (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~~-derived *R* is very similar~~. For example, MARGA~~, with 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~~(see Figs. S4 and S5 in the supplement). Note that CSN data used by other investigators (Silvern et al., 2017; Pye et al., 2018) have much lower *R* (Table S1 and S2) due to a known ammonium sampling artifact (Yu et al., 2006) that cannot be accounted for, and so the ~~supplement. (Fig. S4 ~~dataset cannot be used in this analysis. Together, the analysis shows ~~a scatter plot of these comparisons for the three Na^+ cases). Overall, these results show:~~that (1) when NVCs are ~~most accurately measured (above LOD), ISORROPIA~~well constrained by measurements, predicted *R* is in close agreement with measured *R* (*t*-~~-~~test at α = 0.05 confirms no statistical difference); (2) using inferred Na^+ ~~is overestimated for this data set~~overestimates NVC and ~~has higher uncertainty, resulting~~biases *R* low; however, the trend in ~~a lower ~~predicted *R* ~~than~~generally follows measured *R* (see Fig. 1f), which argues that inferred Na^+ can be a useful upper limit in NVC concentrations, when not constrained by measurements; (3) when ~~$Na^+ = 0$ is input~~NVC levels are zero, ISORROPIA ~~always ~~predicts $R \sim 2$, a consequence of ~~electroneutrality of~~having the maximum possible condensation of NH_3 to the aerosol. Even if $R \sim 2$, however, the aerosol ~~aqueous phase~~continues to remain strongly acidic.

~~***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*.~~***Sensitivity of R and pH to NVCs and organic species:*** The

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results until now have clearly shown that the difference between predicted and observed R for this dataset is affected by the levels of NVC. However, it is very important to assess whether organic species are associated with changes in the partitioning of semivolatile inorganics and aerosol acidity (Pye et al., 2018) or other unaccounted effects that drive the discrepancy between observed and predicted R. To avoid any cross correlations between organics and NVC variations, we examine how the discrepancy between observed R and its theoretical limit of 2 (corresponding to when NVC=0) correlates with organic aerosol. The results, presented in Fig. 4, clearly suggest that $\Delta R = R_{measured} - 2$ increases with measured Na^+ but does not depend on OA mass fraction (gray points) or OA concentration (see Fig. S6 in the supplement). This suggests that ΔR is not driven by organic aerosol effects, but a poor representation of NVCs in the thermodynamic model. 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 is ~~highly~~remarkably correlated with Na^+ 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 the gas phase NH_3~~ (supplemental Fig. S8a),~~, resulting in lower NH_4^+ and lower R.

From the regression slope, for the SOAS measurement period analyzed, an average measured Na^+ level of 0.~~06~~07 μg m^{-3} ~~causes~~(which is a ~~decrease in R~~ tiny amount of ~~0.10. At~~NVC) decreases R by 0.12 units. For a Na^+ level of 0.3 μg m^{-3}, ~~ΔR reaches~~R decreases by 0.5~~, indicating a rapid decrease~~ units, 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~~ΔR is ~~ΔR~~ highly correlated ~~with Na^+, it is also highly~~and sensitive to Na~~+. This~~$^+$, both of which is not seen for the organic aerosol mass fraction~~, here~~. Mass fraction can be used as a proxy for ~~the~~organic film thickness ~~of a~~too, given that the maximum possible ~~film as it constrains the~~ thickness (and delay) associated for an organic film scales with (organic volume~~ per particle~~)$^{1/3}$ or (organic mass)$^{1/3}$.

In comparison to R, pH is less sensitive to inclusion of Na^+, or other NVCs in general. ΔpH is only 0.~~07~~09 for the average Na^+ level of 0.~~06~~07 μg m^{-3}~~,~~ and increases to 0.38 at 0.3 μg m^{-3} Na^+ (Fig. 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 also be seen based on linear regressions. The magnitude of the ΔR-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~~(Guo et al., 2017). Differences in sensitivity of R and pH to Na^+, being 1.74 for the ΔR-Na^+ slope, and, 1.2 for the ΔpH-Na^+ slope is expressed by their linear regressions (Fig. 4c). NVC effects on R and pH are next studied for a very different aerosol data set.

~~The~~ ***WINTER data set:*** The R discrepancy is investigated for a different season and a larger ~~geographical scale, different region~~ and different ~~season~~region by ~~performing a similar~~repeating the SOAS analysis, with~~ the~~ WINTER study data set collected from the NSF C-130 research aircraft during wintertime. ~~In this case the~~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^- 13 nmol m^{-3} vs. SO_4^{2-} 11 nmol m^{-3}) ~~(Guo et al., 2016)~~(Guo et al., 2016). Therefore, R_{SO4} was calculated instead of R.

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The base case input to ISORROPIA-II in this analysis included NH_4^+, SO_4^{2-}, and total nitrate (NO_3^- + HNO_3). (NH_3 should be included to determine NH_x for input~~,~~ but was not measured. 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~~typical of the Eastern US levels, and estimated from an order-of-magnitude iteration method ~~(Guo et al., 2016)~~(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 ~~NVCs determined from an ion charge balance get smaller.~~ inferred Na^+ is smaller. Again, NVC concentrations were determined as NVCs = Na^+ = $2SO_4^{2-}$ + NO_3^- − NH_4^+ (unit: nmol m^{-3}) where all NVC are assumed to be Na^+. (Note that the predicted R_{SO4} should be biased low since NH_4^+ was 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~~R_{SO4} 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~~Interestingly, as predicted NVCs increase, predicted and measured R_{SO4} ~~become closer and~~ converge to ~~a molar ratio of~~ zero, because NVC progressively dominate the cations, and force NH_4^+ ~~approaches zero (NVC have replaced NH_4^+).~~to evaporate. On average, predicted R_{SO4} was 1.68 ± 0.51 versus the measured value of 1.47 ± 0.43~~ and average predicted Na^+ concentration was 0.15 μg m^{-3} (which is comparable to the offline PILS fraction collector IC-measured PM_1 Na^+ of 0.23 μg m^{-3}).~~ .

In contrast to ISORROPIA-predicted R_{SO4} without NVCs, including NVCs (inferred Na^+) brings predicted and measured ammonium-sulfate molar ratios into agreement ~~throughout the range in charge balance (relating to inferred NVCs) (Fig.~~(Fig. 5b). ~~Again, NVC concentrations were determined as NVCs = Na^+ = $2SO_4^{2-}$ + NO_3^- − NH_4^+ (unit: nmol m^{-3}) where all NVC are assumed to be~~ Including or excluding H^+ in the Na~~$^+$. (Results~~$^+$ calculation produces similar results (Fig. S7). Findings based on other NVCs are shown in supplemental Fig. ~~S6~~S8. 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,~~. For 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)). The~~ linear regression result is $R_{SO4,predicted}$ = (1.~~05~~089 ± 0.~~01~~001) $R_{SO4,measured}$ ~~+ (=~~– (0.~~12~~166 ± 0.~~01~~002), r^2 = 0.~~99~~996. As found for the SOAS data set, again, the molar ratio bias from the thermodynamic model ~~is simply a matter of~~appears to result from 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 PM_1 Na^+ from the ion charge balance was 0.15 μg m^{-3}, 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) (In comparison, inferred Na^+ is higher than measured Na^+ in the SOAS case). 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 given the analytical sampling method used in this study~~.~~ (i.e., offline analysis).

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~~increase 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).~~). For example, as shown in supplemental Fig. ~~S7~~S9, a 0.3 unit pH bias in SOAS campaign could cause ~ 20% bias in $\varepsilon(NH_4^+)$ 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 study, a 0.5 pH bias causes up to 30% bias in $\varepsilon(NH_4^+)$ or $\varepsilon(NO_3^-)$. 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 southeastern US (Vasilakos et al., ~~2017~~2018).

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~~Effect of NVCs in trends in pH and R in the southeastern US:~~ ~~One curious observation that the organic film hypothesis (Silvern et al, 2017) attempted to address was~~***Effect of NVCs in trends in pH and R in the southeastern US:*** The organic aerosol impacts on NH_3 equilibration (Silvern et al., 2017) was postulated to address the decreasing trend in *R* in the southeastern US despite the substantial drop in sulfate. Weber et al., (2016) also noted this and proposed that it could be explained by NH_4^+ volatility. However, the thermodynamic 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} was applied to all historical data. With ~~a~~this constant ~~ISORROPIA Na~~~~$^+$~~ input of 0.03 μg m^{-3}, predicted R_{SO4} was nearly constant at ~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).~~Weber et al., (2016)). 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 ISORROPIA-predicted R_{SO4} (Fig. 6 & Fig. ~~S8~~S10). It also ~~results in ISORROPIA-predicted~~predicts a 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~~Hidy et al. (2014) for the 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. 6b), but as expected the pH was slightly higher with higher input Na^+ concentrations. 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~~can be accounted for~~.~~ only with including NVC effects and NH_4^+ volatility. 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.

4. Discussion

Internal vs External Mixtures: ~~This~~Our thermodynamic analysis up to this point 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, (Seinfeld and Pandis, 2016), aerosol near their source regions tend to be externally mixed. Typical ambient conditions can be expected to exist somewhere between these two extreme cases~~.~~ (Bondy et al., 2018) owing to chemistry, coagulation, cloud processing, dilution, and gas-to-particle mas transfer (Zaveri et al., 2010). 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).~~

PM$_{2.5}$ Na^+, K^+, Ca^{2+}, and Mg^{2+} from sea-salt (or dust) are often not well mixed with ammonium and sulfate because of their different sources and sizes. NVC from sea-salt and dust are largely produced by mechanical means and so are mainly in the coarse mode, with a tail extending into the fine mode (Whitby, 1978). Biomass burning and biogenic K^+ is emitted into the fine mode (Bougiatioti et al., In review), however, ammonium and sulfate are formed through gas-phase processes and mostly reside in the accumulation mode (e.g., Whitby, 1978; Seinfeld and Pandis, 2016). 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 (e.g., Katoshevski et al., 1997; Seinfeld and Pandis, 2016). 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), and subsequent evaporation of HCl.

NVCs can also be associated with 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)~~(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)~~(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)~~(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)~~; McInnes et al., 1994; Murphy et al., 1998; Laskin et al., 2002; Bondy et al., 2018). 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$_{1-2.5}$ (particles with sizes 1-2.5 µm).~~, Na^+ with associated anions (NO_3^- and Cl^-) and at least small amounts of NH_4^+ and SO_4^{2-} are associated in PM$_{1-2.5}$ (particles with sizes 1-2.5 µm). This is consistent with the single particle mixing state observations by Bondy et al. (2018) from the SOAS study. 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~~increases 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~~S9), 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*~~.~~ for the data sets we analyzed. But the bulk analysis is only an approximation of the actual aerosol mixing state. ~~Can~~We next test if assuming an internal mixture will 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~~)~~ at the timescale of aerosol lifetime (Zaveri et al., 2010)) 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)~~(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,~~where all NH_4^+ is predicted to be in PM_1, and all NO_3^- is predicted to be in $PM_{1\text{-}2.5}$.

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For more realistic mixing cases where some fraction of the sulfate is mixed with NVCs~~,~~ (Bondy et al., 2018), 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~~S11). 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 on 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~~From this analysis, 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% (by mass) 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)~~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~~the SOAS 12-day Na^+ ~~at the LOD~~average level of 0.07 µg m^{-3} ~~(for the PILS-IC operated during SOAS),~~, only 5% of the SO_4^{2-} (by mass) when mixed with Na^+ produces the same results as the bulk totally internal mixture ~~analyses~~case (see supplemental Fig. ~~S10).~~

S12). 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)~~(Zdanovskii, 1936; Stokes and Robinson, 1966). The PM_1 liquid water dominates over $PM_{1-2.5}$, 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~~.~~ (see Fig. 7c).

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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.~~sets. (We have not utilized the CSN data set as other researchers have due to a large low bias in R.) 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~~.~~ observed in the southeastern US.

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Excluding minor amounts of fine mode NVC in thermodynamic calculations results in predicted 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. 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)~~(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, under certain conditions. Because NVCs are often minor constituents of fine particles, especially for submicron particles, implying low ambient concentrations and high measurement uncertainties, assessing thermodynamic model predictions through molar ratios is problematic. If NVCs were not measured or significantly below the measurement LOD, an ion charge balance could be used to ~~inferred~~infer an upper limit on NVC concentrations, but addition of measurement uncertainties can lead to uncertain results. Note that the ion charge balance on its own generally cannot be used to infer H^+ since the H^+ concentrations are generally very low, even at the low pH of the southeastern US aerosols, and the dissociation states of acids must be known (e.g., proportions of HSO_4^- and SO_4^{2-}), which requires a full thermodynamic analysis.

A motivation for the organic effects on ammonia partitioning ~~(Silvern et al., 2017)~~(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~~does not 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~~lead to agreement with the observed R_{SO4} decreasing trend. ~~Finally, although~~Although the analysis was performed assuming ~~total~~ internal mixtures of aerosol ~~components~~constituents, 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, with the requirement that small amounts of sulfate are mixed with the NVC-rich particle, which is qualitatively consistent with the particle mixing state measured for the SOAS study reported by Bondy et al. (2018). In contrast to molar ratio, the average pH for externally mixed aerosol is not sensitive to the mixing fraction of SO_4^{2-} and Na^+. 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~~carried out with caution, and certainly not by neglecting their effects, even if their concentration is close or below the LOD. Moreover, 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)~~(Guo et al., 2015; Hennigan et al., 2015; Guo et al., 2016; Song et al., 2018).

Based on our analysis, the presence of organic species does not seem to correlate with discrepancies in predicted *R* or inhibit NH_3 equilibration. Sampling artifacts (in the CSN data sets), however, together with underappreciated effects of NVC can explain for the discrepancies between predicted and observed *R*. Further assessments on possible effects of organic effects on semi-volatile partitioning of inorganic species however should be carried out, especially for regions that are chemically different from the eastern US conditions evaluated in this study.

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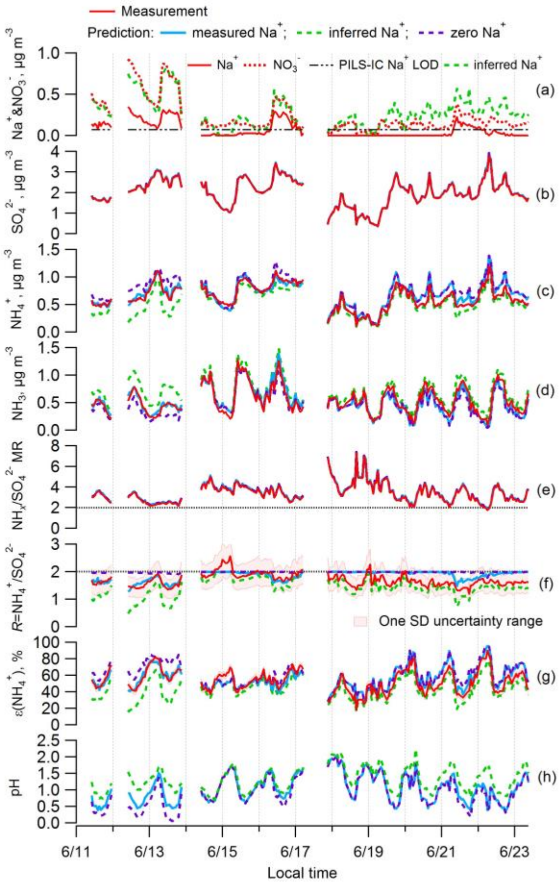

Figure 1. Time series of various measured and ISORROPIA-predicted parameters and $PM_{2.5}$ component concentrations for the SOAS study. Specific plots are as follows: (a) Na^+ and NO_3^-, (b) SO_4^{2-}, (c) NH_4^+, (d) NH_3, (e) total ammonium ($NH_x = NH_4^+ + NH_3$) to sulfate molar ratio (NH_x/SO_4^{2-}), (f) ammonium-sulfate ratio ($R = NH_4^+/SO_4^{2-}$), (g) particle-phase fractions of total ammonium, ε(NH_4^+), and (h) particle pH. 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.

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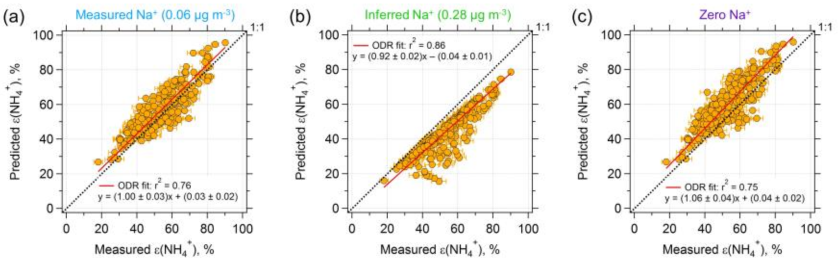


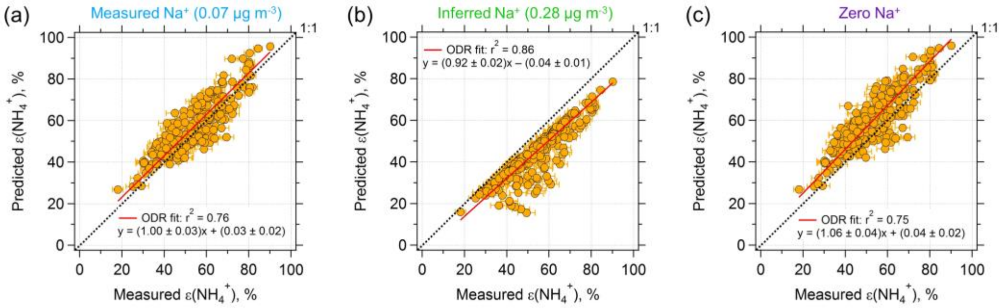


Figure 2. Comparisons of predicted and measured particle phase fractions of total ammonium, ε(NH_4^+) = NH_4^+/NH_x. (a) The model prediction is based on an ISORROPIA input of measured Na^+, NH_x, SO_4^{2-}, NO_3^-, Cl^-. (b) Same model input, but Na^+ is inferred from an ion charge balance and (c) Na^+ 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.

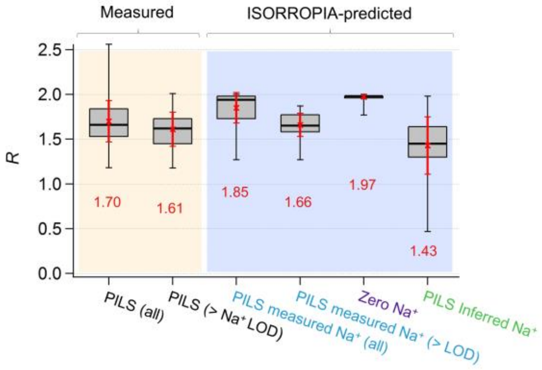


Figure 3. Comparisons of $PM_{2.5}$ ammonium-sulfate molar ratios (*R*) between measurements and ISORROPIA-predictions for the base case but with differing Na^+ inputs. Data are from the SOAS study. Red numbers are the means and red error bars are one SD. Standard box-whisker plots are shown, with 100% 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.

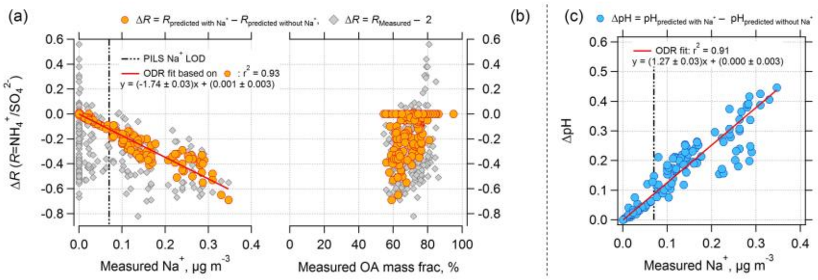
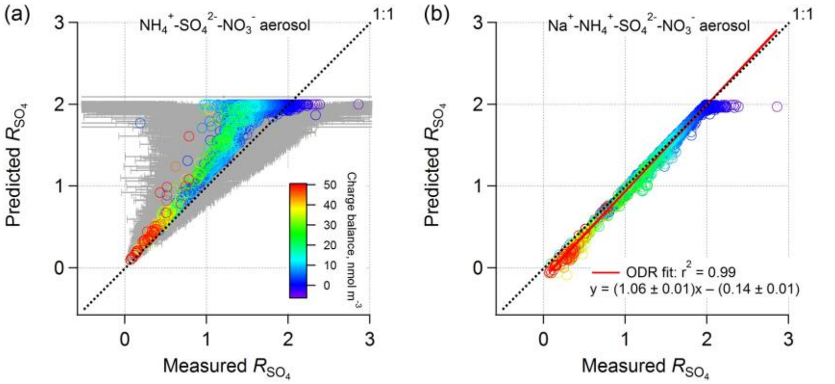


Figure 4. Effect of nonvolatile cations (NVC) on the $PM_{2.5}$ ammonium-sulfate molar ratios (R) and pH as a function of measured Na^+ concentration and organic aerosol (OA) mass fractions for the SOAS data set studied. Plot (a) is ΔR versus measured Na^+, (b) ΔR versus measured OA mass fraction (OA mass divided total particle mass reported from AMS), and (c) ΔpH versus measured Na^+. Grey diamonds in plots (a) and (b) are for ΔR equal to the measured R minus 2. Orange circular points 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. ΔR 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 (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. ~~S5~~S6. The vertical dotted line is the Na^+ LOD of 0.07 µg/m^3.



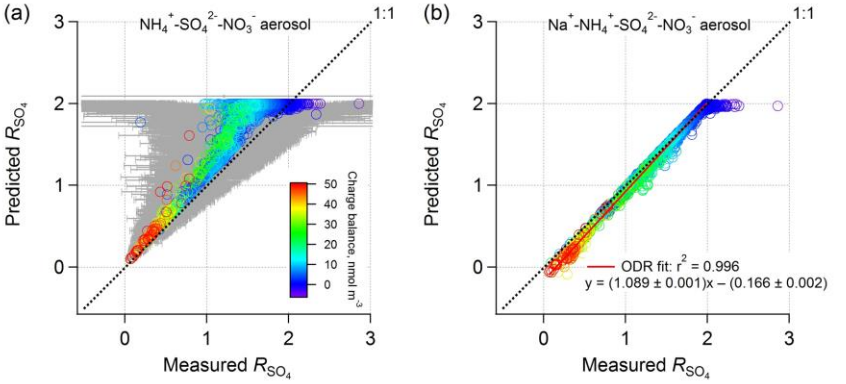


Figure 5. Comparison between PM_1 ISORROPIA-predicted R_{SO4} and AMS-measured R_{SO4} ($R_{SO4} = (NH_4^+ - NO_3^-)/SO_4^{2-}$) (mol mol^{-1}), where the ISORROPIA-prediction is based on (a) NH_4^+, SO_4^{2-}, NO_3^- aerosol and (b) Na^+, NH_4^+, SO_4^{2-}, NO_3^- aerosol, and both include HNO_3 to calculate total nitrate for the model input. All measurement data are from the WINTER study. NVCs were determined by an ion charge balance with the predicted molar concentration shown by symbol color. Error bars 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).~~(Bahreini et al., 2009). Error bars are larger at higher ratios due to subtraction of higher concentrations of nitrate and so subject to greater measurement error. Data points with low SO_4^{2-} levels (<0.2 μg m^{-3}; 9% of the total points) were excluded due to high uncertainties.

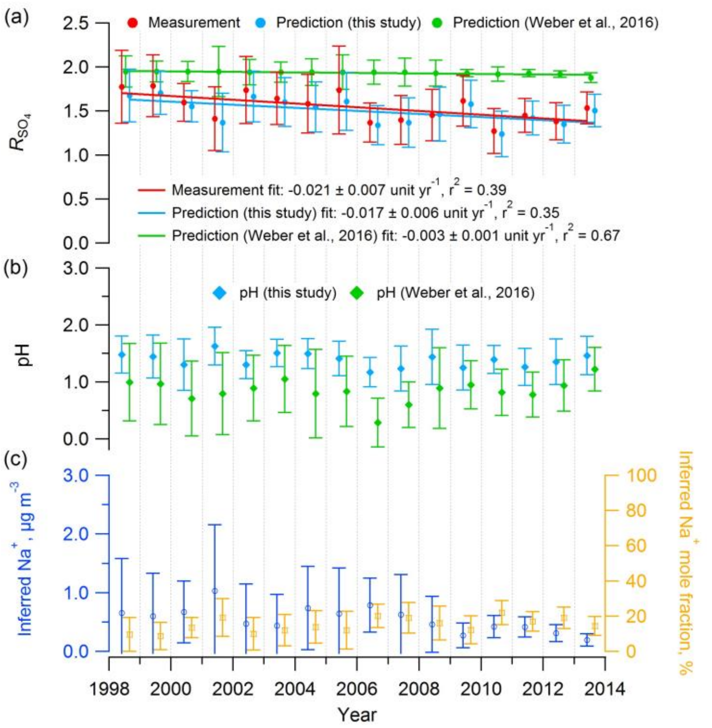


Figure 6. Mean summer (June–August) trends in (a) measured and predicted R_{SO4}, (b) predicted PM$_{2.5}$ pH, and (c) inferred Na$^+$ concentration and mole fraction at the SEARCH-CTR site. Na$^+$ was inferred from an ion charge balance of Na$^+$-NH$_4^+$-SO$_4^{2-}$-NO$_3^-$. ISORROPIA inputs include 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)~~(Blanchard et al., 2013) and 0.23 ± 0.14 µg m^{-3} (2008-2013) ~~(Weber et al., 2016).~~(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}).

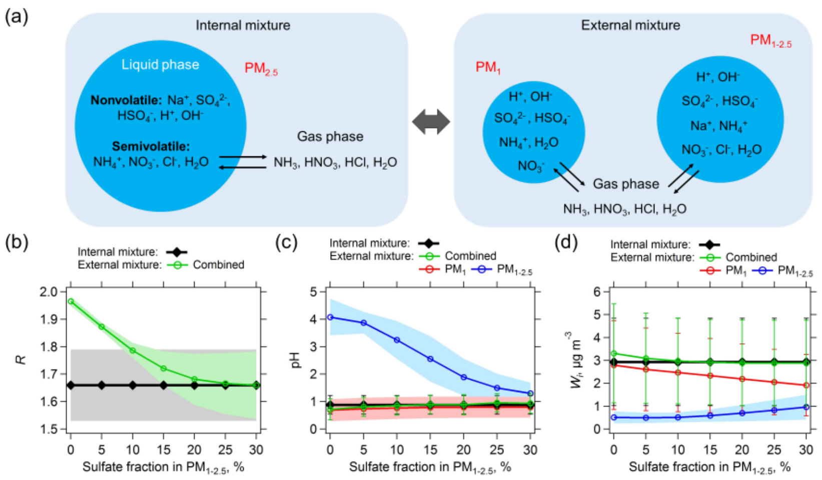


Figure 7. (a) Schematic of assumed internally and externally mixed aerosols. NVCs (here represented by Na$^+$) are all assumed in PM$_{1-2.5}$ for the external mixing case. The two externally mixed aerosol groups (PM$_1$ and PM$_{1-2.5}$) are in equilibrium with the same gases. The internal mixed case 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 (mass) 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.

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Supporting Information for

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

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Table S1-S2

Figures S1-~~S10~~S12

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1. Differences in molar ratio (*R*) observations between SOAS, SEAECH, and CSN

Table S1. Comparisons of observed $PM_{2.5}$ ions and molar ratio between SOAS, SEARCH, and CSN ground sampling sites for the 11-23 June 2013 period (Fig. 1 in the main text). Since CSN (Chemical Speciation Network) doesn't have a site at CTR to be directly compared to SOAS and SEARCH, the two closest sites at Birmingham (BHM) and Montgomery (MTG) are used. The most direct comparison is between Birmingham SEARCH and CSN data. Means are shown with standard deviations.

Network	SOAS	SOAS	SEARCH	SEARCH	CSN	CSN
Site location	CTR	CTR	CTR	BHM	BHM	MTG
Site coordinate	32.90289, −87.24968	32.90289, −87.24968	32.90289, −87.24968	33.55302, −86.81485	33.49972, −86.92417	32.41281, −86.26339
Method	PILS-IC	MARGA(-IC)	Teflon filter(-IC)	Teflon filter(-IC)	Nylon filter(-IC)	Nylon filter(-IC)
NH_4^+, μg m^{-3}	0.64 ± 0.22	0.79 ± 0.22	0.63 ± 0.13*	0.69 ± 0.20*	0.24 ± 0.14	0.25 ± 0.19
SO_4^{2-}, μg m^{-3}	2.06 ± 0.68	2.38 ± 0.66	2.16 ± 0.44	2.23 ± 0.51	1.69 ± 0.40	1.46 ± 0.84
Na^+, μg m^{-3}	0.07 ± 0.09	0.09 ± 0.10	0.06 ± 0.04	0.05 ± 0.04	0.13 ± 0.06	0.10 ± 0.04
R	**1.70 ± 0.23**	**1.78 ± 0.18**	**1.57 ± 0.11**	**1.64 ± 0.14**	**0.70 ± 0.36**	**0.75 ± 0.42**
Data points	229	229	13	4	5	3
Notes on data	Hourly data	Hourly data	Daily data; every day	Daily data; every three days (6/12-6/21)	Daily data; every three days (6/9-6/24)	Daily data; every six days (6/9-6/21)
Reference	(Guo et al., 2015)	(Allen et al., 2015)	(Edgerton et al., 2005; Hidy et al., 2014)		(Solomon et al., 2014)	

* SEARCH NH_4^+ was measured by automated colorimetry.

Table S2. Comparisons of observed $PM_{2.5}$ ions and molar ratio between SEARCH and CSN ground sampling sites for the year of 2013.

Network	SEARCH	SEARCH	CSN	CSN
Site location	CTR	BHM	BHM	MTG
Site coordinate	32.90289, −87.24968	33.55302, −86.81485	33.49972, −86.92417	32.41281, −86.26339
Method	Teflon filter(-IC)	Teflon filter(-IC)	Nylon filter(-IC)	Nylon filter(-IC)
NH_4^+, μg m^{-3}	0.55 ± 0.28*	0.72 ± 0.31*	0.48 ± 0.34	0.41 ± 0.29
SO_4^{2-}, μg m^{-3}	1.71 ± 0.89	1.96 ± 0.90	1.91 ± 0.99	1.65 ± 0.89
Na^+, μg m^{-3}	0.05 ± 0.05	0.05 ± 0.05	0.13 ± 0.30	0.10 ± 0.08
R	**1.75 ± 0.28**	**2.05 ± 0.05**	**1.26 ± 0.59**	**1.24 ± 0.59**
Data points	154	111	93	61
Notes on data	Daily data; every three days	Daily data; every three days	Daily data; every three days	Daily data; every six days
Reference	(Edgerton et al., 2005; Hidy et al., 2014)		(Solomon et al., 2014)	

* SEARCH NH_4^+ was measured by automated colorimetry.

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~~1.~~2. Relative fractions of SO_4^{2-} and HSO_4^- for SOAS fine particles

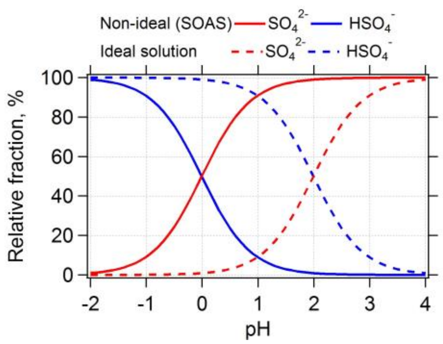

Fig. S1. Relative fractions of SO_4^{2-} (red) and HSO_4^- (blue) calculated based on ideal solutions (all activity coefficients equal one) and the SOAS non-ideal conditions. The average activity coefficients of ~~$\gamma_{SO_4^{2-}}/\gamma_{HSO_4^-} = 0.01$~~ $\gamma_{SO_4^{2-}}/\gamma_{HSO_4^-} = 0.01$ are predicted by ISORROPIA for the SOAS fine particles. ~~$\gamma_{H^+} = 1$~~ $\gamma_{H^+} = 1$ is assumed; a smaller ~~γ_{H^+}~~ γ_{H^+} shifts the red and blue curves towards the left, increasing SO_4^{2-} relative fraction at a given pH. The dissociation constant of HSO_4^- is 1.015×10^{-2} mol kg^{-1} at 298.15 K ~~(Fountoukis and Nenes, 2007)~~(Fountoukis and Nenes, 2007).

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~~2.~~3. Comparison of PILS NVCs to MARGA NVCs

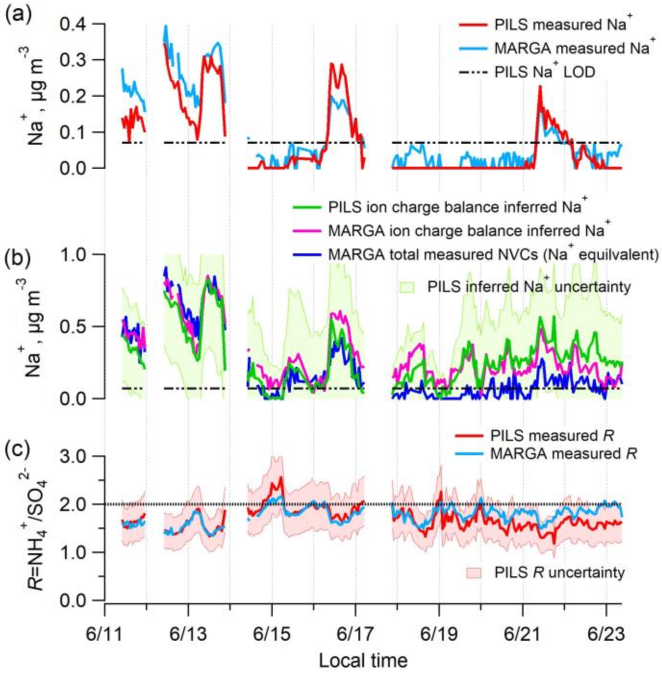

Fig. S2. (a) Comparison of $PM_{2.5}$ PILS and MARGA Na^+. (b) Comparison of inferred Na^+ (from ion charge balance; $Na^+ = 2SO_4^{2-} + NO_3^- + Cl^- - NH_4^+$, nmol m^{-3}) by PILS and MARGA to total measured NVCs by MARGA (represented by Na^+), and (c) comparison of PILS and MARGA ammonium-sulfate molar ratios (R). Data are from the SOAS study.

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4. Comparison of ion charge balance inferred Na$^+$ including H$^+$ versus excluding H$^+$

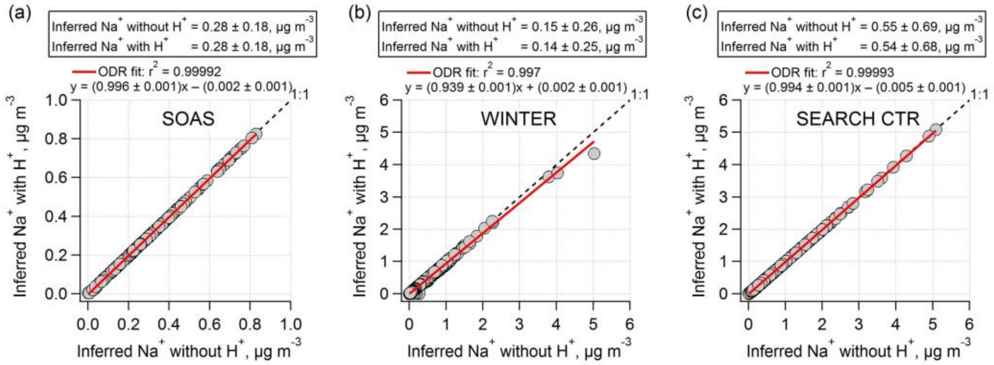

Fig. S3. Comparisons of ion charge balance inferred Na$^+$ including H$^+$ (2SO$_4^{2-}$ + NO$_3^-$ + Cl$^-$ − NH$_4^+$ − H$^+$; y-axis) versus excluding H$^+$ (2SO$_4^{2-}$ + NO$_3^-$ + Cl$^-$ − NH$_4^+$; x-axis) for three data sets used in the paper, (a) SOAS (Fig. 1), (b) WINTER (Fig. 5), and (c) SEARCH CTR (Fig. 6). The H$^+$ concentration was determined using ISORROPIA in an iterative approach. Na$^+$ is predicted from the ion balance is included with all other gas/particle species in the model, resulting in a predicted H$^+$. This H$^+$ is included in the ion balance to predict a new Na+, which is then used in a new model iteration. The procedure is repeated until the Na$^+$ concentration converges. The number of iterations for conversion are 1 for (a), 5 for (b), and 0 for (c), respectively, until inferred Na$^+$ converges. Orthogonal distance regression (ODR) fits are shown and uncertainties in the fits are one SD.

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~~3.~~5. Comparison of measured and ISORROPIA-predicted ammonium-sulfate molar ratios.

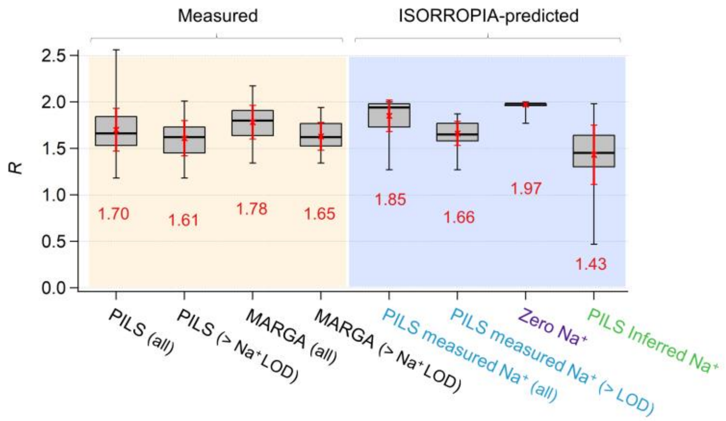

Fig. ~~S3~~S4. Comparisons of $PM_{2.5}$ ammonium-sulfate molar ratios (*R*) between measurements and ISORROPIA-predictions for the base case but with differing Na^+ inputs. Data are from the SOAS study. Red numbers are the means and red error bars are one SD. Standard box-whisker plots are shown, with 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 contrast all data and periods when measured Na^+ > PILS LOD of 0.07 μg/m^3. Inferred Na^+ is the value calculated from an ion charge balance representing NVCs.

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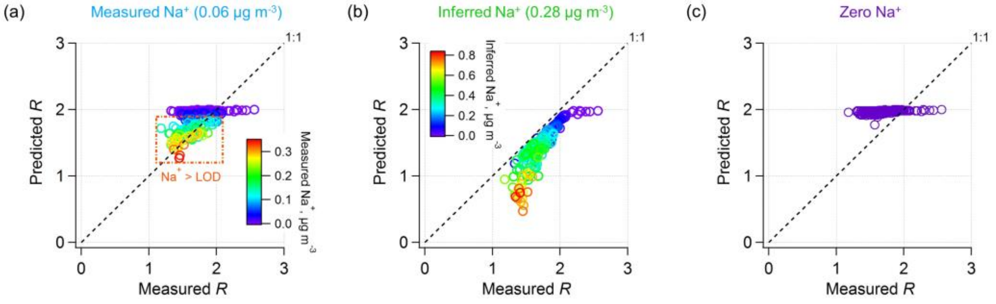

Fig. ~~S4~~S5. Comparisons of $PM_{2.5}$ ammonium-sulfate molar ratios (*R*) between measured and ISORROPIA-predictions for differing Na^+ inputs for SOAS data. ISORROPIA was run with base case inputs and differing Na^+ inputs: (a) all Na^+ measured by the PILS, (b) NVCs (i.e., Na^+) inferred from an ion balance, and (c) Na^+ (NVCs) set to zero.

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~~4.~~6. The relationships between errors in molar ratio and organic aerosol mass

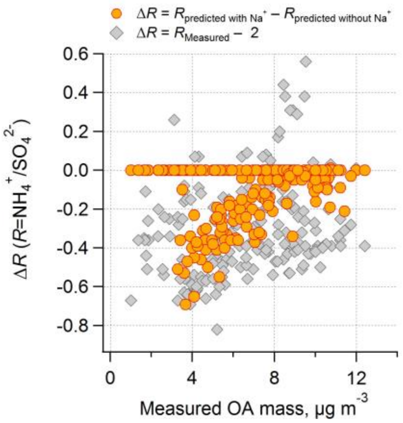

Fig. ~~S5~~S6. Effect of nonvolatile cations (NVC) on the $PM_{2.5}$ ammonium-sulfate molar ratio (*R*) as a function of measured organic aerosol (OA) concentrations based on AMS data (SOAS). The orange circular points denote Δ*R* calculated from ISORROPIA predicted *R* with measured Na^+ included in the model input minus ISORROPIA predicted *R* without Na^+ in the model input. Grey diamonds are for Δ*R* equal to measured *R* minus 2. Note that Δ*R* 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).

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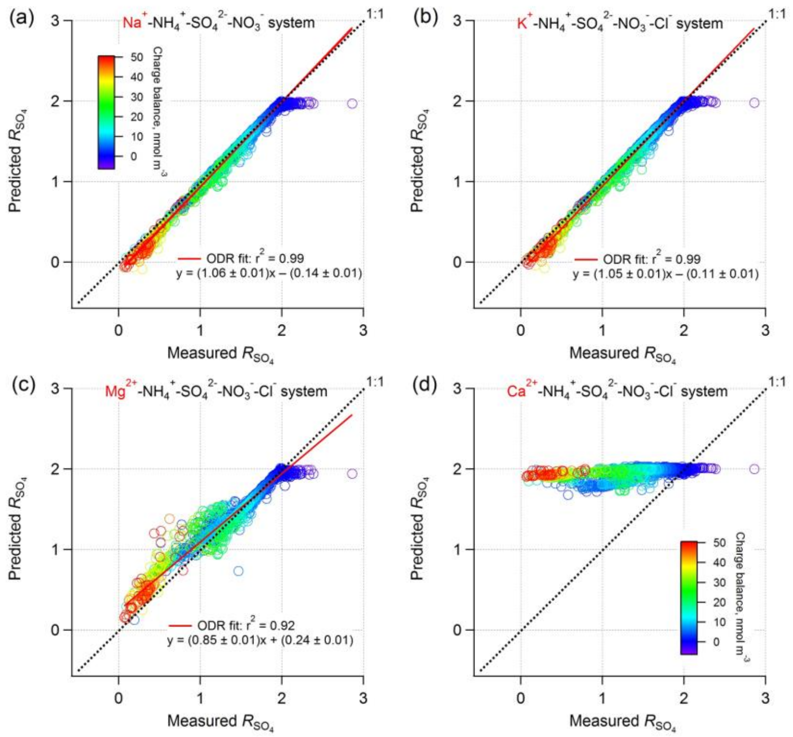
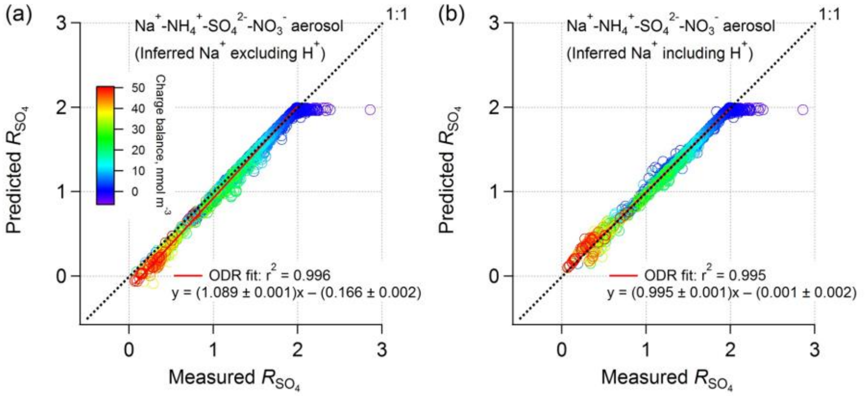
~~5.~~7. Comparison of predicted and measured R_{SO4} by adding NVC





~~Fig. S6.~~

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Fig. S7. Comparison between PM_1 AMS-measured R_{SO4} and ISORROPIA-predicted R_{SO4}, which is based on (a) inferred Na^+ excluding H^+ (see Fig. S3 x-axis) and (b) inferred Na^+ including H^+ (see Fig. S3 y-axis). The color wave indicates an ion charge balance, ($2SO_4^{2-} + NO_3^- - NH_4^+$) in units of nmol m^{-3}. The figure (a) is the same as Fig. 5b in the main text. The two results, (a) and (b) are very close, and the inferred Na^+ including H^+ produces slightly better result for a closer slope to one. ODR fits are shown and uncertainties in the fits are one SD.

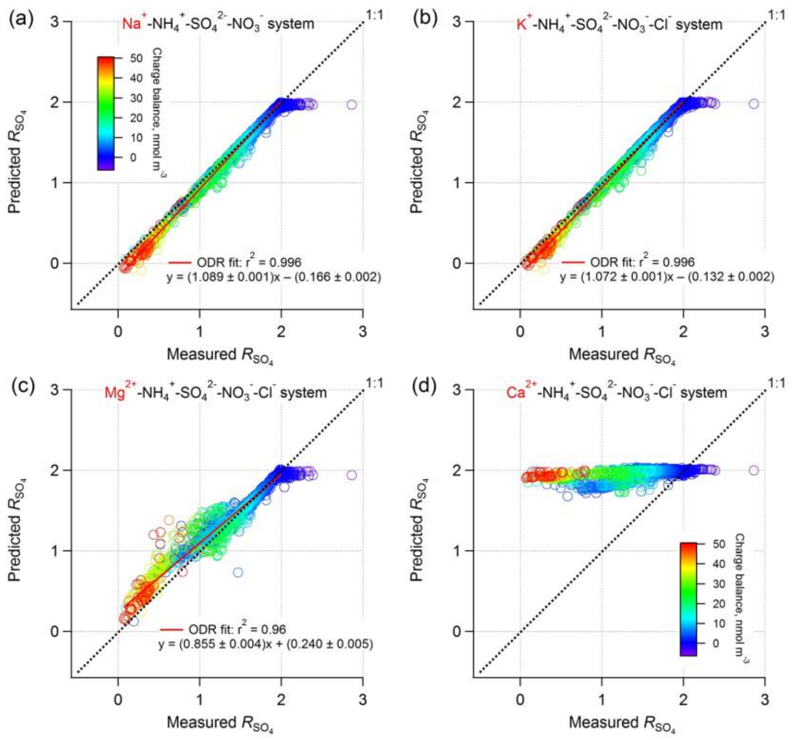

Fig. S8. Comparison between ISORROPIA-predicted and AMS-measured PM_1 R_{SO4} ($R_{SO4} = (NH_4^+ - NO_3^-)/SO_4^{2-}$, mol mol^{-1}), where the model predictions are based on NVC-NH_4^+-SO_4^{2-}-NO_3^-(-Cl^-) system for the WINTER study. NVC (nonvolatile cation) was determined by an ion charge balance (color wave), that is, ($2SO_4^{2-} + NO_3^- - NH_4^+$) in units of nmol m^{-3}. This results in 200% mole-equivalent concentrations of Na^+ and K^+ compared to Ca^{2+} and Mg^{2+} due to +1 versus +2 charges. NH_4^+, SO_4^{2-}, NO_3^- are observed AMS mass concentrations. For each graph, NVC is set to be a single species, including (a) Na^+, (b) K^+, (c) Ca^{2+}, (d) Mg^{2+}. For K^+, Ca^{2+}, and Mg^{2+}, a trace amount of total chloride (0.01 μg m^{-3}; a negligible level of Cl^-, 0.0012 μg m^{-3}, is predicted) is assumed to eliminate potential model errors but doesn't perturb the calculation of pH or HNO_3-NO_3^- partitioning. (Note that, Cl^- is only utilized as an input

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to ISORROPIA and is not included in the charge balance calculation.) Adding Na^+ and K^+ results in predicted R_{SO4} agreeing with measured R_{SO4}. Mg^{2+} also results in closer agreement, although some points deviate. Ca^{2+} doesn't work at all as it precipitates out from the aqueous phase as $CaSO_4$. The solubility of $CaSO_4$ is only 0.2 g per 100 mL water at 20 °C. An approximate calculation on $CaSO_4$ solubility shows that the average predicted particle liquid water ~~W_i~~W_i (2.0 μg m^{-3}) could only dissolve 0.004 μg m^{-3} Ca^{2+}, a tenfold lower amount than the inferred Ca^{2+} of 0.13 μg m^{-3} from an ion charge calculation. ODR fits are shown and uncertainties in the fits are one SD.

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~~6.~~8. The nonlinear response of NH_3-NH_4^+ or HNO_3-NO_3^- partitioning to pH (S curve)

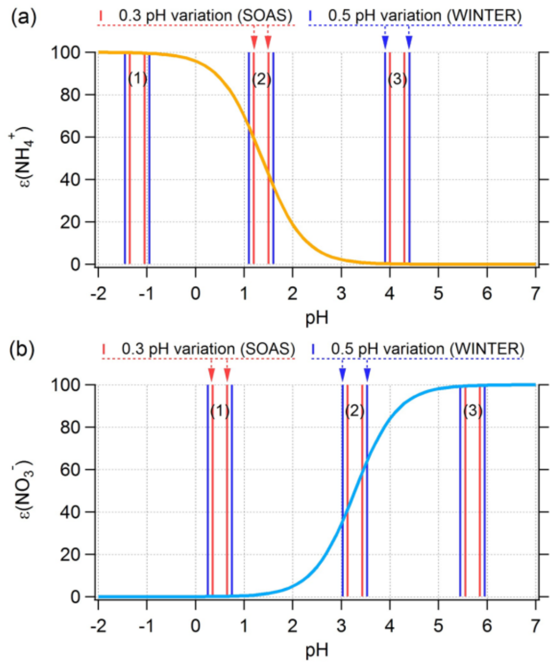

Fig. ~~S7~~S9. S curves illustrate the nonlinear response in particle phase fraction, ε(NH_4^+) or ε(NO_3^-), to variation in pH: (a) ε(NH_4^+) and (b) ε(NO_3^-) plotted vs. pH. The two S curves are calculated based on T = 20 °C, particle liquid water level = 5 µg m^{-3}, and ideal solution (i.e. ~~γ = 1). The S curve equations can be found at Guo et al. (2017)~~γ = 1). The S curve equations can be found at Guo et al. (2017). Non-ideality only shifts the S curves but does not change the shapes. The 0.3 unit pH (SOAS) and 0.5 unit pH (WINTER) variations (biases) are the upper limit values based on the difference between zero and inferred Na^+ inputs and indicated by paired red and blue sticks, respectively. The response of ε(NH_4^+) or ε(NO_3^-) to pH reaches maximum at 50% ε(NH_4^+) or ε(NO_3^-) (i.e., position (2), 0.3 unit pH change causes ~20% or 0.5 unit pH change causes ~30% shift in the particle phase fraction), but down to nearly zero when 100% or 0% ε(NH_4^+) or ε(NO_3^-) (e.g. position (1) or (3)).

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~~7.~~9. Thermodynamic predictions of the 15 years' summertime molar ratio at CTR site (Centreville, AL)

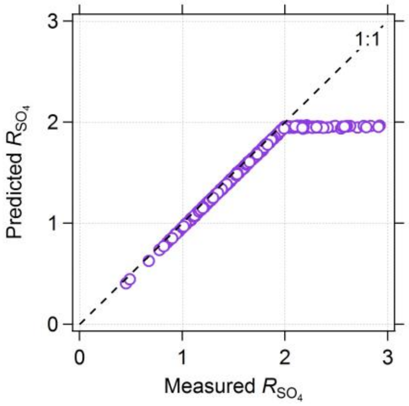

Fig. ~~S8~~S10. Comparison of the measured and predicted R_{SO4} (with inferred Na^+ as input), summer means at CTR, as shown in the Figure 6 in the main text. The upper limit of R_{SO4} is 2 for a composition of $(NH_4)_2SO_4$ in ambient aerosols. A few observed points above 2 are results of measurement uncertainties.

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~~8.~~10. Internal vs. external mixture: the effect on molar ratio prediction

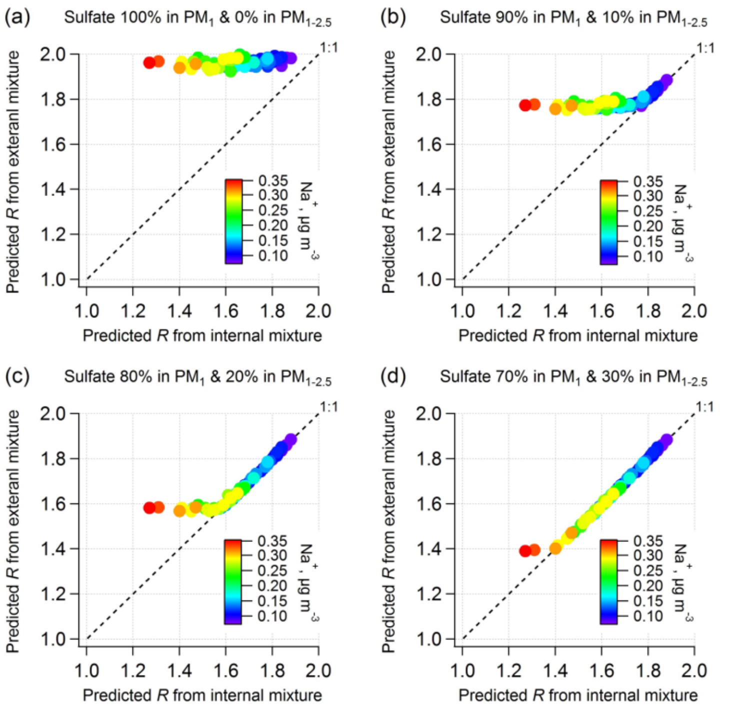

Fig. ~~S9~~S11. Comparison of predicted *R* between internally and externally mixed aerosols, as shown in Figure 7 in the main text. NVCs (here represented by Na^+) are all assumed in $PM_{1\text{-}2.5}$ for the external mixing case, while (a) 0%, (b) 10%, (c) 20%, and (d) 30% (mass) fractions of $PM_{2.5}$ sulfate is assumed to be mixed with Na^+, as shown above each figure. The two points with the highest Na^+ concentrations require 40% sulfate in $PM_{1\text{-}2.5}$ to reach agreement (i.e. on 1:1 line).

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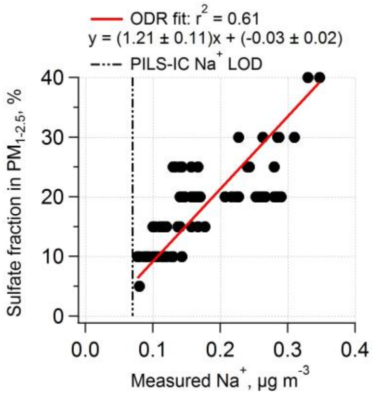

Fig. ~~S10~~S12. Minimum sulfate fraction in $PM_{1\text{-}2.5}$ to obtain agreeable ammonium-sulfate molar ratio (*R*) between the internally and externally mixed aerosols (as shown in Fig. S9) versus measured Na^+ concentrations.

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