I was asked by the Editor to offer arbitration on the anonymous reviews to the Guo et al. paper and the authors' responses in revision. I do so below by commenting on the anonymous reviewers' comments and the authors' responses. My comments are in red. In summary:

- I think that the authors are making an important point in their paper that NVCs may not have been properly accounted for in thermodynamic calculations of the sulfate-nitrate-ammonium system and notably the ammonium-sulfate ratio *R*. This deserves publication.
- I agree with many of the authors' responses to the reviewers, and the addition in the revised paper of a thermodynamic calculation for externally mixed PM2.5 (in response to reviewer 2) is very nice in showing that external mixing does not matter so much.
- 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.
- 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.
- 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.

My recommendation to the Editor is to ask for a second round of revisions that addresses the last three bullet points above. See below in red for details.

Responses to Referee #1

We thank the referee for the thoughtful and constructive comments. Before a point-by-point response to the issues raised, we would like to articulate the main points of our work:

- Including NVCs in the thermodynamic model largely resolves the molar ratio discrepancy, based on our data set, which is representative of the southeast. Only small amounts of NVC are often required, therefore the practice of omitting NVCs from fine mode calculations (which may seem unavoidable for many datasets) induces important biases in molar ratios, which have to be considered in any relevant interpretations (especially on the role of organics).
- The bias in *R* (ISORROPIA predicted *R* with Na^+ minus ISORROPIA predicted *R* without Na^+, where $R = NH_4^+/SO_4^{2-}$, mole/mole) is highly correlated with measured Na^+ ($r^2 = 0.93$), but not correlated with OA mass or OA mass fraction. Furthermore, the difference in observed *R* from a ratio of 2 (*R* observed minus 2) is correlated with NVCs and not correlated with OA mass or OA mass fraction. Both results provide strong evidence for NVCs, and not OA, as the underlying driver of the molar ratio discrepancy.

We have addressed the comments (numbered, below), with referee comments in quotes and italics, and our responses in plain text.

1. *“To explain this discrepancy, mainly two hypothesis are proposed, namely the organic-film hypothesis (Pye et al., 2017) and the non-volatile cations (NVC) hypothesis (as shown in this manuscript). By including in the measured NVC, the authors could now decrease predicted R from 1.97 to 1.85, which is still higher than the corresponding observation of 1.7. The remaining difference could possibly be due to the presence of organic-film, or the size heterogeneity. Considering the large disagreement in observation data, neither of the above hypothesis could be fully validated.”*

   The above statistics are for the whole Fig. 1 period including many data points where we had to estimate Na^+ since the measured Na^+ was below our LOD. Focusing only on the periods with measured Na^+ above LOD (reliable NVC concentrations), there is no statistical difference between predicted and measured R (t- test $\alpha = 0.05$).

   See also our response to the comments from Daniel Jacob and Rachel Silvern (Figure I in that response), where we also discuss differences in R between model-predicted and observations and also point out that a significant fraction of the differences in R between some data sets (e.g., AMS PM_1 vs various $PM_{2.5}$ data) can be attributed to the differences in measured particle size ranges.

In summary, our NVC analysis can fully explain the discrepancy in molar ratio predictions for either $PM_{2.5}$ or PM_1 data sets.

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.

2. *"What's the average activity coefficient of NH3Â°uH2O(aq) and NH4+? Does that change with NVC levels? If so, how would the theoretical S-curve be influenced, or what's the potential range of S-curve in this study? In comparison, the S-curve range based on the activity coefficient of H+ as given in Pye et al. (2017) should also be indicated*"

The activity coefficient of dissolved NH_3, $\gamma(NH_3)$, has a negligible effect on the S curve and so not considered (Guo et al., 2017). For example, at 298 K, the acid dissociation constant of NH_4^+, K_a = 5.69×10^{-10} mole L^{-1} (Clegg et al., 1998), results in $\frac{K_a}{\gamma_{NH3}} \ll \frac{\gamma_{H^+}[H^+]}{\gamma_{NH4^+}}$ as long as the solution is not too basic. SOAS fine particles were very acidic with pH on average 0.94 ± 0.59 (SD). The measured Na^+ (above zero) for the SOAS study doesn't change $\frac{\gamma_{H^+}}{\gamma_{NH4^+}}$ significantly; including or excluding Na^+ gives the same $\frac{\gamma_{H^+}}{\gamma_{NH4^+}}$ of 1.38 ± 0.12 (no statistical difference as confirmed by t-test at α = 0.05).

I agree with the authors.

3. *"At high or low pH ranges, the partitioning fraction of NH3(g) can be extremely low or large, but can never reach 0% or 100%. What's the accuracy of the ISORROPIA model? Or, at what value would the model treat the ratio actually as 0% or 100%? Since the observation data can never be zero, what's the discrepancy of predicted NH3 and observation NH3 at those extreme conditions, for gas- and aerosol-phase respectively? Similarly, how about the HNO3-NO3- pair?"*

Theoretically, the partitioning fraction of NH_3 may never be 0 or 100%, but practically this is not an issue. We only use the semivolatile pairs with fractions close to 50% to constrain our pH predictions since this is the region of greatest sensitivity (e.g. (Guo et al., 2015)). Propagated uncertainty in the partitioning fraction can be determined from both gas and particle measurement uncertainties. The average propagated uncertainty in $\varepsilon(NH_4^+)$ is ~4% (absolute value, not percentage of $\varepsilon(NH_4^+)$) for SOAS, the pH prediction is accurate within 0.08 for $\varepsilon(NH_4^+)$ at 50% and 0.22 for $\varepsilon(NH_4^+)$ at 10%. A similar result is derived for HNO_3-NO_3^- partitioning (0.07 for $\varepsilon(NO_3^-)$ at 50% and 0.22 for $\varepsilon(NO_3^-)$ at 10%).

I agree with the authors.

4. *"Adding Fig. 3 in the authors' comment to Pye et al. (2017) would help improve the current manuscript. To my eye, the theoretical S-curve in that figure is to the right edges of the corresponding observation data. What if the aerosol water associated with organics are taken into account? That dilution effect would increase pH, shift the corresponding observation data points to the right and may result in better agreement. In addition, the authors claim that*

corresponding S-curve of Pye et al. (2017) can be derived by shift the S-curve of 0.8 pH units. This argument looks confusing and should be better described.”

To actually do this properly we need the Pye et al. (2017) data set, which is not yet available. Furthermore, this paper does not directly address the claims of Pye et al. (2017).

I don’t have any comment on this. It seemed to just be a suggestion by the reviewer.

5. *“The authors attributed the data with R over 2 to "measurement uncertainty and error propagation at low SO42- concentrations". However, based on data shown in Figure 1, these periods are not the periods with the lowest SO42- concentration (and thus largest uncertainty). Also, these periods correspond to periods with negative inferred Na+. The arbitrary exclusion of these data is problematic. Basically that is to say that ambient aerosols can never be neutral or basic. As mentioned in other papers (Allen et al., 2015), sometimes the sea-salt episodes can be observed. How could the authors prove that cation-abundant situations are wrong? Do those data have any common distinct features from others? The data can be discarded for better reasons, not just due to that they look abnormal.”*

The observed PILS-IC data points with *R* over 2 are within the measurement uncertainty range and are periods of lower sulfate concentrations than average. For example, lowest sulfate was record near June 19 midnight and *R* slightly above 2. We don’t find the *R* above 2 points distinctly different from other periods, e.g., enhanced Na^+ or NO_3^- was not simultaneously observed, indicating no significant change in aerosol composition (see Figure I below).

Similar results are found for other measurements of $PM_{2.5}$ ions during SOAS, e.g., MARGA data (Allen et al., 2015). The figure below shows good consistency between PILS and MARGA measured *R* and Na^+. MARGA and PILS sulfate and ammonium also agree well; ODR fits, MARGA SO_4^{2-} = (1.00 ± 0.01) PILS-IC SO_4^{2-} + (0.51 ± 0.02 μg m^{-3}), r^2 = 0.96; MARGA NH_4^+ = (1.04 ± 0.01) PILS-IC NH_4^+ + (0.21 ± 0.01 μg m^{-3}), r^2 = 0.91, see our comment to Pye et al. (2017) for a plot.)

The sea-salt episodes mentioned by Allen et al. (2015) are included in our studies. Consistently low pH was predicted despite the occasionally enhanced Na^+ level. In response to reviewer 2 question of mixing state, we have added more details on the topic to the manuscript. Finally, including or removing the data when *R* is over 2 does not change the findings of the paper.

I agree with the authors.

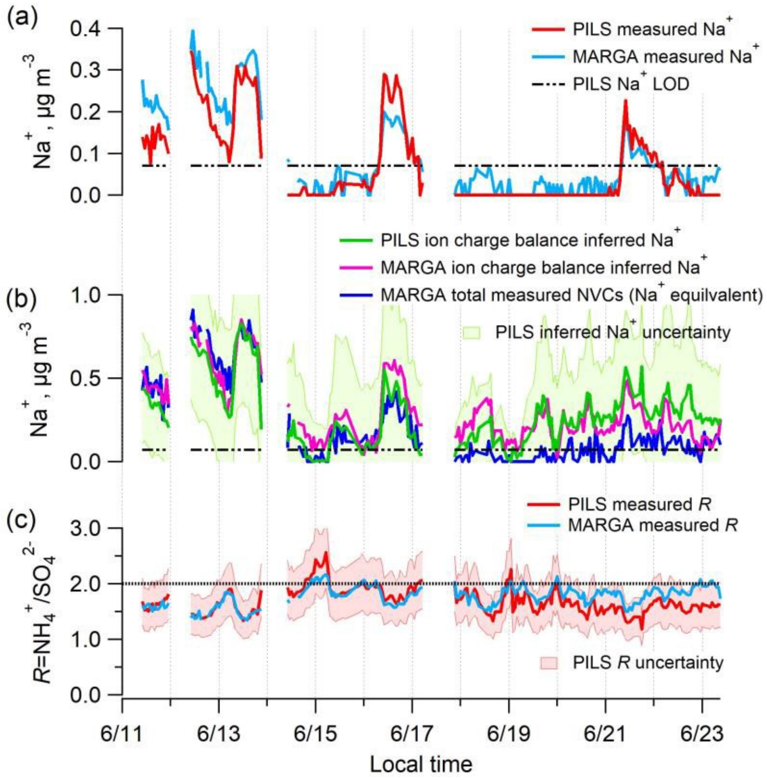

Figure I. (a) Comparison of $PM_{2.5}$ PILS and MARGA Na^+. (b) Comparison of inferred Na^+ (from ion charge balance; $Na^+ = 2SO_4^{2-} + NO_3^- + Cl^- - NH_4^+$, nmol m^{-3}) by PILS and MARGA to total measured NVCs by MARGA (represented by Na^+), and (c) comparison of PILS and MARGA ammonium-sulfate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

References:

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. Responses to Referee #2

We thank the referee for the thoughtful and constructive comments. Before a point-by-point response to the issues raised, we would like to articulate the main points of our work:

- Including NVCs in the thermodynamic model largely resolves the molar ratio discrepancy, based on our data set, which is representative of the southeast. Only small amounts of NVC are often required, therefore the practice of omitting NVCs from fine mode calculations (which may seem unavoidable for many datasets) induces important biases in molar ratios, which have to be considered in any relevant interpretations (especially on the role of organics).
- The bias in *R* (ISORROPIA predicted *R* with Na^+ minus ISORROPIA predicted *R* without Na^+, where $R = NH_4^+/SO_4^{2-}$, mole/mole) is highly correlated with measured Na^+ ($r^2 = 0.93$), but not correlated with OA mass or OA mass fraction. Furthermore, the difference in observed *R* from a ratio of 2 (*R* observed minus 2) is correlated with NVCs and not correlated with OA mass or OA mass fraction. Both results provide strong evidence for NVCs, and not OA, as the underlying driver of the molar ratio discrepancy.

We have addressed the comments (numbered, below), with referee comments in quotes and italics, and our responses in plain text.

1. *"The largest issue is that a fully internal mixture (with all species present in each particle at their bulk atmospheric concentrations) is assumed, meaning that any Na+ is assumed to be present in the same particles that have ammonium, sulfate, and nitrate. Literature from co‐located sampling over the same time period shows that in fact most Na+ present during SOAS was not mixed with SOA, but was present in sea spray aerosol or other mechanically generated particles, such as mineral dust (Allen et al., 2015; Bondy et al., 2017). Thus Na+ cannot explain the values of R that the manuscript is using Na+ to explain. The concept of "inferred‐sodium" is particularly worrisome, as it is not necessarily supported even by bulk measurements and Na+. Another serious concerns is that values of Na+ are reported that are below LOD, which is not appropriate and that the measured Na+ is below the LOD when "inferred Na+" is >4 times higher than a value which is unreliable. Studies going back almost 20 years in Atlanta and the southeast U.S. have shown that NVCs are not present in SOA, particularly with single particle mass spectrometry, which is extremely sensitive to Na+ and K+."*

   Mixing state of NVCs with ammonium, sulfate, and nitrate is a valid concern that we had not addressed in the original study. The assertion that there is *absolutely no mixing* of Na^+ with sulfate is incorrect. Na^+, which is largely from sea salt (as noted by the reviewer), will contain some fraction of sulfate since it is well known that there is sulfate in sea water (~25% SO_4^{2-}/Na^+ mass ratio) (DOE, 1994), apart from any secondary non-sea-salt sulfate or subsequent effects from aerosol aging processes.

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.

Nevertheless, we have now considered the impact of incomplete mixing of the non-volatile inorganic species (sulfate, sodium and other NVC) on *R* and pH in a separate section in the main text. The analysis shows that with a small fraction of sulfate internally mixed with Na^+-rich particles gives acidity and partitioning levels consistent with that of complete internal mixing. The issue of mixing state of NVCs with SOA does not affect our conclusions as well, especially given that the molar ratio discrepancies (one of the main points in our paper) can be explained by inorganic species without any consideration of organic effects. Therefore, effects from incomplete mixing of particles do not alter our conclusions obtained in the original analysis.

I agree with the authors that internal vs. external mixing shouldn't have a large effect on *R* and pH. That calculation is a nice addition to the paper.

The use of data below LOD is justified as the LOD is simply an estimate (i.e. three times of field blanks standard deviation). We note throughout the text when we are using data that is below the LOD. Below we show that the use of inferred Na^+ is reasonable as an upper limit of NVCs through comparisons with measurements by other instruments at the SOAS study. Here we show that when measured NVC > measurement LOD (i.e., reliable NVC concentrations, admittedly a small fraction of the study period) there is good agreement between measured and ISORROPIA-predicted *R* (updated Fig. 1f and Fig. 3, and associated text; no difference at a significance level of $\alpha = 0.05$).

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

Issues arise (which is not surprising) when the NVC concentrations are below or near LOD and they have to be estimated. Most defensible conclusions can be made for periods with the most reliable data (NVCs above LODs). Assessments and critiques that focus solely on only periods of the least reliable data sets (NVCs below LODs) are weak. However, even periods with NVCs below LODs, often provide consistent results. For example:

- For SOAS, when measured Na^+ was below LOD (0.07 μg m^{-3}), a Na^+ of 0.1-0.3 μg m^{-3} was needed to bring measured and predicted *R* into agreement, which is near the detection limit and so difficult to measure. Despite this, the trends are the same and the predicted *R* is generally smaller than the observed, and so including the estimated NVCs in this case overcompensates.
- For WINTER data, inferred NVC results in agreement in *R* prediction with the observation, but inferred Na^+ is smaller than observed PM_1 Na^+, 0.15 vs. 0.23 μg m^{-3}, stated in the caption of Figure 4. Again, the results are uncertain since measurements of NVC were not measured online in that study.

The reviewer criticizes the inferred Na^+ from ion charge balance to be worrisome and much higher than measured Na^+. The inferred Na^+ represents an upper limit of NVCs, including K^+, Mg^{2+}, and Ca^{2+} (if soluble), that could be present in the aqueous aerosols based on charge neutrality of the solution. Therefore, it is supposed to be higher than a single measurement of NVC, such as Na^+. We have results from the WINTER study showing the inferred Na^+ is comparable to the offline measurement. Also, in Figure I (b), we show a comparison between inferred Na^+ from PILS-IC data and MARGA data and measured Na^+-equivalent NVCs (K^+, Mg^{2+}, and Ca^{2+} are represented by Na^+) from MARGA for the SOAS study (Allen et al., 2015). Before June 18, the three Na^+ levels are similar, indicating the inferred Na^+ level is reasonable. After June 18, the two inferred Na^+ levels are higher than MARGA total measured NVCs, but the differences are within uncertainties (propagated from PILS-IC ammonium, sulfate, nitrate, and chloride measurements).

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.

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^+.

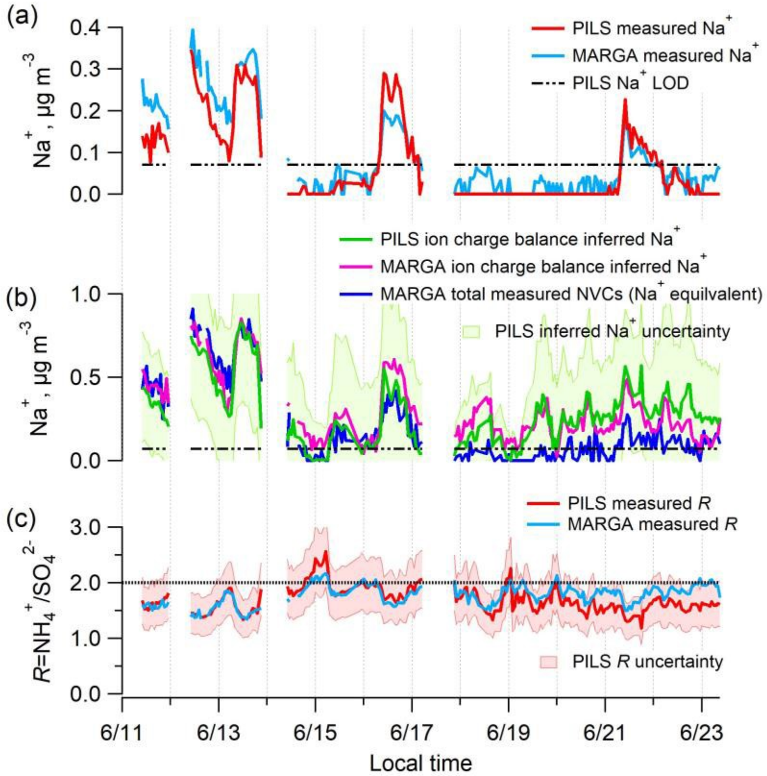

Figure I. (a) Comparison of $PM_{2.5}$ PILS and MARGA Na^+. (b) Comparison of inferred Na^+ (from ion charge balance; $Na^+ = 2SO_4^{2-} + NO_3^- + Cl^- - NH_4^+$, nmol m^{-3}) by PILS and MARGA to total measured NVCs by MARGA (represented by Na^+), and (c) comparison of PILS and MARGA ammonium-sulfate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

2. *“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)”*

   We have addressed this question above. The inferred Na^+ is at reasonable levels in both SOAS and WINTER studies.

I don’t see that the authors have addressed that issue in the revised text.

3. *"Page 5 Lines 2 ‐ 3: The authors choose to use values for Na+ below LOD for the rest of the study, even though they are below LOD. This is a substantial issue and values below LOD should not published or used as the basis for the main analysis over the remainder of the paper."*

   We believe there is a slight misinterpretation of results here. First of all, our PILS-IC measurement of Na^+ is believed to be accurate; it is in agreement with MARGA data, as showed in Figure I (a) above (this figure has also been added to the supplemental material as Fig. S2). The periods of below Na^+ LOD are intended to show that when close to zero Na^+ and is included in the thermodynamic model, a near 2 molar ratio (R) is predicted. We focus on the periods, where Na^+ is above the LOD for added confidence. For these periods, as noted before, we find good agreement between predicted and measured R (no statistical difference at $\alpha = 0.05$). The roles of NVCs and organics on molar ratio are based mainly based on observed data above LOD (Fig. 4). We have added more details on the comparisons of measured and predicted R for various Na^+ levels (see added Fig. 3), and included a comparison with MARGA data in the supplemental material (Fig. S2 and S3).

   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.

4. *"Page 5 Lines 9 ‐ 15: Most Na+ at SOAS is present from sea spray aerosol (SSA), which has been shown in multiple papers (Allen et al., 2015; Bondy et al., 2017). This authors' observation that Cl ‐ and NO3 ‐ have high R2 values with Na+ and agrees with the papers showing that Na+ is from other sources than SOA, which further highlights that Na+ is not present in SOA particles. It is also worth noting that June 10 ‐ 13 at SOAS (during the period Guo et al focus on) there was a large contribution of sea spray aerosol at Centreville (Bondy et al., 2017). This includes the submicron where 20 ‐ 40% of particles between 200 ‐ 1000 nm were not SOA ‐ dominant particles and are likely where nearly all of the Na+ was located."*

   We have addressed this question above.

5. *"Page 6 Lines 7 ‐ 10: The paper here discusses June 11 ‐ 13, which was a high sea salt time period, leading to a more externally mixed aerosol and the Na+ was not present in SOA particles."*

   We have addressed this question above. Also note that a higher concentration of sea salt doesn't necessarily indicate a more externally mixed aerosol; the latter depends on the age of the aerosol and the processes that act upon it from emission.

6. *"Page 6 Last Paragraph: While Na+ somewhat tracks with delta R, since Na+ is not in the same particles the*

paragraph comes to close to attributing causation to a correlation. The wording in this section needs to be weakened. Also, the presumption that organic mass should be correlated with organic film thickness is overstated. Composition, viscosity, etc. all matter when a film might form and OA mass fractions would not provide meaningful estimates of this.”

We don't agree. Our results from assuming an external mixture are consistent with bulk analysis (internal mixture), see added section on internal vs. external mixture. It is true that we have no data on organic film thickness, but if the organic film is sufficient to impede NH_3 uptake it *has* to comprise a reasonable fraction of the overall OA (a timescale analysis easily shows this), and concurrently impede equilibration of water and nitrate with the gas phase. We show that neither OA mass or mass fraction is related to observed bias in *R*. If the argument is that an organic film has a widespread effect throughout the southeast, it can't be argued that it is some unique property of the OA (i.e. unique composition, unique viscosity, selectivity with respect to NH_3, etc.) unless if a specific mechanism can be proposed to support it.

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).

7. *"Page 7 Lines 10 ‑ 13: The authors mention higher Na+ near coastlines, which is again likely from sea spray and would not be mixed with SOA in the same particles in all likelihood (unfortunately there is not single particle data to provide information on mixing state from that study to my knowledge)."*

   We have answered this question above.

8. *"The clarity of the writing, particularly in the introduction, could be improved as there are numerous long sentences and confusing wording that could be improved. Also there numerous missing words, incorrect plural versus singular, and conjugation throughout the manuscript, which needs to be cleaned up"*

   We thank the reviewer for pointing this out. The paper has been edited for clarity.

9. *"Page 2 Lines 7 ‑ 11: "Despite its importance, the inability to directly measure fine mode particle pH (e.g. Rindelaub et al. (2016) presents an indirect method that infers particle H+ activity for sizes above 10 μm and requires activity coefficient predicted by a thermodynamic modeling. This method reports the pH for a HSO4 ‑ /SO42 ‑ aerosol system similar to the fine particle pH predicted by a thermodynamic modeling used in this study (Guo et al., 2015)) has led to the use of measurable aerosol properties as acidity proxies, such as aerosol ammonium sulfate ratio or ion balances (e.g. (Paulot and Jacob, 2014; Wang et al., 2016; Silvern et al., 2017)). Recent work has shown that acidity proxies are not uniquely related to pH, which in turn strongly questions any conclusions derived from its use. There are numerous reasons why acidity proxies do not represent pH well; they do not capture the variability in particle water content, ion activity coefficients, or partial dissociation of species in the aerosol phase (Guo et al., 2015; Hennigan et al., 2015; Guo et al., 2016)." o There are a number of problems with this section that need to be addressed. o It is not fair to state that the use of the sulfate/bisulfate ratio in Rindelaub et al. led to the use of molar ratios or ion balances, since those have been used for decades and Rindelaub came out in 2016 (Rindelaub et al., 2016). o Secondly, the use of the bisulfate ‑*

to $^-$ sulfate ratio to determine pH is not indirect and is in fact more direct than thermodynamic modeling of gas particle partitioning, as both species are in the aerosol phase where pH is being determined and the effects of coatings or other nonideal behavior is avoided. The method does use a thermodynamic model to determine activity coefficients, but the fact this is combined with multiple concentrations directly measured in the aerosol phase makes it very different than ion balance or molar ratio methods. o The manuscript states that Rindelaub only used particles above 10 microns, but *fails to mention Craig et al. from this summer, which showed this direct method working down to 2 – 3 microns for a range of systems (Craig et al., 2017).”*

We have edited the sentence citing Rindelaub et al. (2016) to minimize any confusion.

We clearly have a different understanding of “direct” pH measurement than the reviewer. We cited the method of Rindelaub et al. (2016) as an <u>indirect</u> (but clearly particle-level) measurement of aerosol pH because it doesn’t quantify the hydronium ion aqueous phase activity directly. Instead, it infers the H^+ concentration by HSO_4^-/SO_4^{2-} ratio, equilibrium constant, and activity coefficients. Deliquesced ambient fine particles are very concentrated liquids. The average ionic strength was 29 mol L^{-1} for this study. Therefore, non-ideality cannot be ignored and avoided by the method of Rindelaub et al. (2016) as the reviewer claims. Furthermore, the activity coefficients of HSO_4^- and SO_4^{2-} cannot be determined simply by HSO_4^- and SO_4^{2-} concentrations because the non-ideal effects are caused by interactions of all water-soluble ions in aqueous aerosols, such as NH_4^+ and NO_3^-. In terms of determining activity coefficients, a thermodynamic model with an input of all measured inorganic ions should be more accurate than one with only a fraction of the ions input.

We thank the reviewer from bringing attention on Craig et al. (2017) and this paper will be cited in future work.

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

10. *“Page 2, 2nd Paragraph: The authors go to great lengths to make clear that organic coatings or glassy particles which inhibit equilibrium between gases and particles are not possible based on “established literature”, but most of that literature is from the groups who authored this manuscript. If there are limitations to the thermodynamic model approach used in those studies, citing their prior work does not invalidate the other work suggesting films might be important, such as Havala Pye’s modeling paper from earlier this year.”*

We agree that we mainly cite our past work, because there are very few other detailed assessments of pH predictions by thermodynamic models using in-situ observations. What is meant by “established literature” is that assumption of equilibrium between gas and particle phases is widely used and agrees with observations. Take water vapor for example; LWC is predicted based on the equilibrium assumption and there is a rich body of published literature (spanning decades) comparing predicted and measured LWC. As noted in the paper, given their similar molecular weights and particle uptake properties, it is hard to argue that NH_3 and H_2O could interact completely differently with a hypothesized organic film so that equilibrium is not established for one species but established for another. (This is all articulated in the 2nd paragraph of the Introduction).

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.

As for our reported results, we have always tested the thermodynamic predictions in our past studies. We use gas-particle partitioning of semivolatile species that are sensitive to pH, to predict particle pH and compare predicted vs.

measured partitioning, based on the equilibrium assumption, to evaluate pH accuracy. At least in our past analysis, these comparisons show that results based on the equilibrium assumption agree with observations, when RH is sufficiently high (e.g. > 40% or higher) and particles are completely deliquesced. We have cited more papers from other groups (Ansari and Pandis, 2000; Moya et al., 2001; Morino et al., 2006; Liu et al., 2017; Paulot et al., 2017), to strengthen our point, but it nevertheless remains the same.

Pye et al. (2017) is still in review, therefore we do not address the issues raised in that paper. Nevertheless it is important to note it is an equilibrium model study, so kinetic limitations from hypothetical organic films are not important in that study as well.

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.

11. *“Page 3 Line 26: The authors state that “14% of “sulfate” is predicted to be* HSO_4^- *and the rest as* SO_4^{2-} *in the winter dataset.” Based on a simple acid dissociation constant calculation at pH =1, bisulfate should be >80% of the combination of sulfate and bisulfate. Some explanation should be included to explain why this does not follow basic acid dissociation rules. Is it related to activity coefficients somehow? This need to be addressed in a revised manuscript. Also it is confusing to refer to sulfate, bisulfate, and sulfuric acid together as “total sulfate”, as they are each distinct species. Total S(VI) sulfur could work or some other nomenclature.”*

The simple calculation as referred by the reviewer is likely based on ideal solutions, where all activity coefficients are treated as one. In this case, HSO_4^- is the dominant form at pH of 1 (shown as dash lines in Figure II). After taking into account of the activity coefficients predicted by ISORROPIA, the curves move left by 2 units (comparing solid vs. dash lines in Figure b). As a result, SO_4^{2-} is the dominant form at pH of 1. Therefore, our statement is consistent with the basic acid dissociation rules. Instead of citing 14% as HSO_4^- from WINTER study, the Figure II has been added to supplemental material to explain how activity coefficients affect the relative fractions of SO_4^{2-} and HSO_4^-.

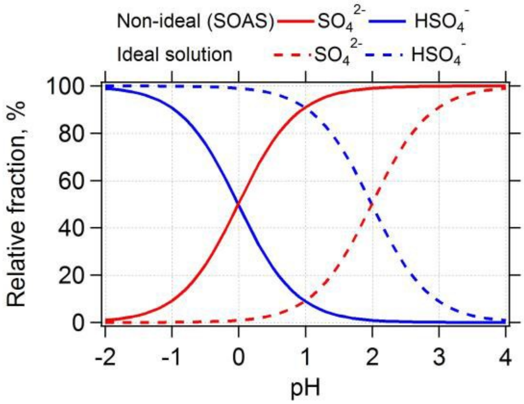
Non-ideal (SOAS)
SO4 2-
HSO4 -
Ideal solution
SO4 2-
HSO4 -
Relative fraction, %
100
80
60
40
20
0
-2
-1
0
1
2
3
4
pH

Figure II. 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 $\gamma_{SO_4^{2-}}/\gamma_{HSO_4^-} = 0.01$ are predicted by ISORROPIA for the SOAS fine particles. $\gamma_{H^+} = 1$ is assumed; a smaller 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).

12. *"Page 2 Line 9: I believe the word "and" is missing after (Guo et al., 2015)). Also the second parenthesis is not needed."*

This has been edited.

13. *"Page 3 Line 13: "or if there is free H2SO4 in the aerosol". For the pH values in this manuscript and others using this method, the aerosol acidity is never sufficient for any H2SO4 to exist. Below pH = 2, sulfate will transition to bisulfate, but not sulfuric acid."*

We agree that at on average pH ~ 1 in this study, free from of H_2SO_4 doesn't exist. The sentence in the text aims to explain the theoretical possibilities causing *R* = 0. For example, NH_4HSO_4 cannot give *R* = 0. We have revised the sentence to "the lower limit is 0 for *R* when SO_4^{2-} is associated with other cations instead of NH_4^+ (e.g. Na_2SO_4) or if there is free H_2SO_4 in the aerosol (in theory but not the reason at pH ~ 1 in this study)". Below pH of 2, sulfate transforms to bisulfate; but below pH of -2, bisulfate transforms to sulfuric acid.

14. *"Page 3 Line 14: missing the word "are", should be ", but are rare for"."*

We have revised accordingly.

15. *"Page 5 Line 39: "mode R with measure Na+ input", should be "measured"."*

We have revised accordingly.

16. *"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."*

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.