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

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.

*Authors: 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).*

Reviewer Comment: 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.

*Authors: The bias in R (ISORROPIA predicted R with Na+ minus ISORROPIA predicted R without Na+, where R = NH4+/SO42-, mole/mole) is highly correlated with measured Na+ (r2 = 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.*

Reviewer Comment: 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).

*Authors: 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% SO42-/Na+ mass ratio) (DOE, 1994),* *apart from any secondary non-sea-salt sulfate or subsequent effects from aerosol aging processes. 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.*

Reviewer Comment: 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.

*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 α = 0.05). 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 PM1 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+, Mg2+, and Ca2+ (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+, Mg2+, and Ca2+ 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).*

Review Comment: 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.

*Authors: 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 NH3 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 NH3, etc.) unless if a specific mechanism can be proposed to support it.*

Reviewer Comment: 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.

*Author Comment: We clearly have a different understanding of "direct" pH measurement than the reviewer. We cited the method of Rindelaub et al. (2016) as an indirect (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 HSO4-/SO42- 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 HSO4- and SO42- cannot be determined simply by HSO4- and SO42- concentrations because the non-ideal effects are caused by interactions of all water-soluble ions in aqueous aerosols, such as NH4+ and NO3-. 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.*

Reviewer comment: 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.

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.
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 $K_a$ (moving less to left), so it would be helpful if the authors could address this.
3) 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.

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.

*Author Comment: 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, HSO4- 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, SO42- is the dominant form at pH of 1. Therefore, our statement is consistent with the basic acid dissociation rules. Instead of citing 14% as HSO4- from WINTER study, the Figure II has been added to supplemental material to explain how activity coefficients affect the relative fractions of SO42- and HSO4-.*

Review comment: 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.

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, 2018.

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 Aerosol-Phase State on Secondary Organic Aerosol Formation from the Reactive Uptake of Isoprene-Derived Epoxydiols (IEPOX), Env. Sci. Tech. Lett., doi: 10.1021/acs.estlett.8b00044, 2018. 2018.