

Summary

This manuscript describes the potential role of nonvolatile cations, such as sodium (or magnesium, potassium, or calcium, if soluble), on ammonium to sulfate ratios. Further the data presented is used as evidence that organic films do not form on particles, which could inhibit partitioning between the particle and the gas phase. A positive of the work is that it considers species beyond the “traditional” non-refractory species measured by AMS, which are often excluded from discussions of submicron aerosols. However, there are a number of severe shortcomings that constitute fundamental flaws to the logic of the article and it should not be published in its present form.

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 concern 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^+ . Overall, the topic is important and interesting, but the conclusions drawn from the manuscript overreach the data, the main result is fundamentally flawed and as a result the conclusions drawn (that NVCs are important in SOA) are not supported. The authors are clear leaders in the topic of aerosol acidity and thermodynamic modeling, but there is considerable concern is that if the manuscript is published with the current results and conclusions, this could spread the misconception that SOA contains sufficient NVCs to impact the sulfate-ammonium ratio, which is not the case.

Major Comments

- Page 4 Line 18: “We also assumed that the particles were internally mixed, and that pH did not vary with size”... and gas-particle partitioning was at thermodynamic equilibrium.” The use of the non-volatile cations (Na^+ , Mg^{2+} , etc.) without consideration of mixing state is very likely to lead to incorrect results, and numerous studies with different methods from Atlanta and the southeast have shown this over the past 20 years. Single particle mass spectrometry, such as ATOFMS is extremely sensitive to Na^+ and K^+ due to their ionization energies and can be detected even when well under 0.1% of the particle. Citations are discussed below, but briefly, there is essentially no sodium, magnesium, potassium, or calcium in SOA particles in the southeast US. Measurements are not as readily available in the northeast, but the expectation is that they would not be present mixed with SOA there either. There are NVCs present in the atmosphere at the same time, but they are present in other types of particles (industrial, biomass burning, sea salt, etc.) and thus NVCs cannot explain the discrepancies in R that this manuscript attributes the discrepancies to. Despite the interesting premise and analysis, the fundamental fact that NVCs are not in SOA renders many of the conclusions invalid.

- 2003 JGR Middlebrook et al. (2003) compared multiple single particle mass spectrometers. The PALMS (Murphy) organic/sulfate class of particles does not have an sodium peak, but the Na/K sulfate (likely SSA) and mineral dust do (though not labeled in dust, it is present in the spectrum). The ATOFMS spectra also shows no Na⁺ in organic/sulfate particles. The same lack of Na⁺ is also seen with RSMS-II (Johnston).
- 2003 JGR-A Liu et al. (2003) showed EC/OC and OC particles and the individual mass spectra did not contain Na⁺ (Figure 3). In Wenzel et al a missing particle type was identified (Wenzel et al., 2003). This missing type corresponds to ammonium sulfate mixed with organic carbon, which have low 266 nm cross sections. If Na was present in these particles, they would have been more likely to be ionized by the 266 laser and not been a “missing” type.
- 2011a&b ES&T Hatch et al. shows 41000 organic carbon particles from Atlanta during ANARChE, which showed no Na⁺ with the OC (Figure 1). That paper also showed for ANARChE and a study in 2008 (AMIGAS) that particles containing organosulfates (likely many OC-sulfate particles) have different sources than particles without organosulfates (Figure 3, 4, 5) (Hatch et al., 2011a; Hatch et al., 2011b).
- Future work (unpublished) from SOAS will show that Na is present is at levels > 1% of dry particle mass (thus excluding water), in less than 2% of SOA particles. That manuscript will show that Na is present in 5 other types of particles, which account for almost all sodium present.
- 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).
- 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.
- 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.
- 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.
- 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.

- 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).

Minor Comments

- 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.
- 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 $\text{HSO}_4^-/\text{SO}_4^{2-}$ aerosol system similar to the fine particle pH predicted by a thermodynamic modeling used in this study (Guo et al., 2015)) has led to the use of measurable aerosol properties as acidity proxies, such as aerosol ammonium sulfate ratio or ion balances (e.g. (Paulot and Jacob, 2014; Wang et al., 2016; Silvern et al., 2017)). Recent work has shown that acidity proxies are not uniquely related to pH, which in turn strongly questions any conclusions derived from its use. There are numerous reasons why acidity proxies do not represent pH well; they do not capture the variability in particle water content, ion activity coefficients, or partial dissociation of species in the aerosol phase (Guo et al., 2015; Hennigan et al., 2015; Guo et al., 2016).”
 - There are a number of problems with this section that need to be addressed.
 - 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).
 - 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 non-ideal 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.
 - 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).
- 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 Havalala Pye’s modeling paper from earlier this year.
- 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 $\text{pH} = 1$, 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.

- Page 2 Line 9: I believe the word “and” is missing after (Guo et al., 2015)). Also the second parenthesis is not needed.
- 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.
- Page 3 Line 14: missing the word “are”, should be “, but are rare for”
- Page 5 Line 39: “mode R with measure Na⁺ input”, should be “measured”
- 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.

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