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Atmospheric Chemistry and Physics
Discussions

# *Interactive comment on* "Incomplete sulfate aerosol neutralization despite excess ammonia in the eastern US: a possible role of organic aerosol" *by* Rachel F. Silvern et al.

**Anonymous Referee #1**

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The crux of the puzzle being addressed in this paper is stated on page 2, lines 15 and 16, which states: [There appears to be a mechanism that maintains the neutralization ratio at a low value even as the SO2/NH3 emission ratio decreases.] Ignoring for the moment the ambiguity of the term neutralization ratio (discussed below), this very issue was identified in a recent paper [Weber et al., 2016] where it was shown that a thermodynamic model predicts this precise drop in neutralization ratio (ie, molar ratio) with decreasing SO4= and steady NH3 levels. The cause was identified to be due to the semi-volatile nature of ammonia and the insensitivity of the system to gas phase NH3 concentrations. Equilibrium partitioning of ammonia predicts lower ammonium-sulfate molar ratios as sulfate concentrations drop. The model was verified by comparison to observations [Guo et al., 2016; Guo et al., 2015]; the thermodynamic model predictions of the partitioning (gas- particle concentration ratios) of semi-volatile species, such as ammonia and nitric acid, are consistent with observations. Furthermore, the paper explained why little nitrate aerosol has been observed despite large reductions in sulfate.

In this paper, the authors propose a different cause for acidity (actually a NH4+/2SO4= molar ratios less than 1) despite the presence of gas phase ammonia. They suggest that impedance of gas phase ammonia uptake by fine aqueous particles due to an outer organic film is the cause. Simply put, since sulfate is nonvolatile, this increases the time to equilibrium, results in an average (I guess) predicted lower particle ammonium concentration, which lowers the molar ratio. There is no discussion on what happens when equilibrium is reached; presumably this model cannot explain the molar ratios at that point. A question is, why the different conclusions. One explanation may be due to the different analysis approach taken. One group has focused on pH predictions, and then using the predicted pH to assess it's affects on verifiable processes (comparing predicted and measured partitioning of various species), whereas in this work, the question is framed around observed vs predicted ammonium/sulfate molar ratios and using them to interpret ambient data (referred to here as MR). No other verification is provided (ie, comparison of some pH dependent process or species concentration to observations, such as nitrate aerosol).

First off, do the authors have a possible explanation why simply ammonia volatility is insufficient to explain these observations? It would seem prudent to least include a brief discussion stating that an alternative explanation to what they are proposing has been offered, briefly describe it and state why an alterative explanation is necessary. The logic used here seems odd. The authors use E-AIM or ISORROPIA in the analysis (and seem to accept that they largely agree with each other), but adjust the NH3 uptake to get these model predicted MR to agree with observations. But it has been shown that the same model (ISORROPIA) explains these observations. I conclude the issue is that MRs are not a robust nor reliable way to assess model predicted aerosol pH nor it's effects, and this is the fundamental cause for the different views.

Why do the authors use MRs when investigating particle pH? Although commonly used in many different forms (e.g., ion balances, gas ratios, etc) it has been shown that MR do not provide quantitative insight on pH [Guo et al., 2016; Guo et al., 2015; Hennigan et al., 2015; Weber et al., 2016], but instead can lead to confusion and imprecise conclusions (see a list of them in specific comments below). Given this, it is not clear what their utility is. The author's show that the particle MR is not related to pH in any straightforward way (see fig 1) and that pH remains very low despite MR near or approaching 1. Given that pH is what controls aerosol processes related to acidity, such as partitioning of semi-volatile acids, acid catalyzed reactions, etc, and not MR, the use of MR to infer acidity is problematic.

As an example, what do the authors mean by their commonly used term, sulfate neutralization? Or sometimes, the term is just, aerosol neutralization, such as in the figures and in the text (pg 5 line 32). It is also in the title of the paper. Strictly, is one to interpret this to mean that the MR is 1 or greater? However, it also seems to be used to imply (or at least it gives the impression) that the authors are referring to overall particle acidity (i.e., pH), such that a MR of 1 implies a neutral aerosol. Example, page 8 line 7 and 8 states: quote [The aerosol in the standard model is fully neutralized throughout the eastern US (mean f = 1.00), at odds with observations.], end quote. But than Fig 1 shows that the pH is nowhere near neutral as f approaches 1; a contradiction. Including with their Fig 1, a plot of specifically f vs pH, would be very insightful, I believe. There are many instances in this paper of similar ambiguous statements (discussed more below).

In any case, molar ratios are used in this work. The author's point is that the molar ratio predicted by the thermodynamic model is higher than what is observed, and so there is either an issue with the thermodynamic model or with the assumptions the model is based on. This paper proposes the latter, that NH3 mass transport limitations due to organic films are the cause and that it takes over a day for equilibrium to be established, thus the strict use of thermodynamic models, which assume equilibrium, give incorrect results. However, maybe other causes for the discrepancy are possible, eg, relating to oversimplification when using the model, such as lack of size dependent composition and the mixing state of the aerosol. What if one simply adds a small amount of other non-volatile cations, such as mineral dust, to the model; a reasonable thing to do since the data are PM2.5. This should lower the predicted MRs. Considering the likely small amount of other cations needed to significantly alter the MR, and measurement uncertainties (discussed more below), it is not clear how the authors can outright concluded that other cations play no role (ie, reference to Kim 2015 and Liao 2015). More details, provided in this paper, such as including sensitivity tests with various amounts of other cations could be very insightful.

Another issue that is not clear is the extensive comparisons of parameters, such as aerosol composition and MRs, between measurements of wet deposition versus fine particles. In the abstract it is used to infer that gas phase ammonia is in excess (meaning, presumably, not equal to zero). Fig 3 compares wet deposition neutralization ratios to those of fine particles. Generally the authors find that the wet deposition trends for sulfate and ammonium follow SO2 and NH3 emission trends and that the neutralization ratios (ie, MRs) are close to 1, as expected for excess NH3, whereas neither is true for fine particles. Are the authors inferring this provides evidence for some additional process affecting the fine particles? It is actually thermodynamically consistent and is due to the vastly different concentrations of liquid water (many orders of magnitude) associated with these systems. It is not clear how differences in MRs between fine haze particles and fog/cloud particles support the hypothesis of this manuscript and needs to be clarified? Maybe that was not the intent, but the use of wet deposition is confusing and should be clarified.

Overall, this paper proposes an explanation for the persistent particle acidity despite reductions in SO2 emissions in the eastern US. Understanding the cause is clearly

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Discussion paper

of great importance. In my view, the proposed explanation is speculative and largely unsupported because the use of MRs in their analysis is highly suspect. Furthermore, a much simpler explanation exists. I do believe the authors could test their hypothesis further; say by predicting concentrations of semi-volatile aerosol components that depend on pH, in different settings. I am not against publishing this paper, but believe that significant clarifications are needed throughout prior to publication. More specific detailed questions are provided below.

Specific comments (in the following [ . . . ] indicates a quote from the manuscript)

How was the pH in Fig 1 calculated? Is it the equilibrium predicted pH, (ie, no kinetic limitation due to organic layer), or avg pH in the overall system that includes predicted pH before equilibrium is reached?

It is often not clear exactly what data were used for gas phase ammonia in the thermodynamic models. Was the wet deposition data used under the assumption that it represents the total sulfur and ammonia, and thus as model input? This is likely reasonable, but leads to much higher uncertainty than using direct measurements of the species involved (sulfate, ammonium, ammonia). Granted the wet deposition data is more widely available then NH3, but still analysis for studies where all the data exists would greatly support the hypothesis of this work.

If this organic film inhibits uptake of NH3, how it is likely to influence other semi-volatile species (nitric acid, HCl) and how will this impact the partitioning of these compounds. Will the model be able to accurately predict partitioning of these other species? Why not use this as a means of testing the hypothesis?

One might expect this proposed process to be highly important in biomass burning plumes where the organic aerosol fraction is very high. Thermodynamic models appear to also work well in these cases [Bougiatioti et al., 2016]. Based on the arguments in this work one may expect them not to. The authors could investigate if there is other published work on thermodynamic predictions in smoke plumes that support their hypothesis.

In the Abstract it states: [. . .sulfate aerosol is not fully neutralized even in the presence of excess ammonia, at odds with thermodynamic equilibrium models]. Is it ever shown in this paper that this statement is true? There is only a general reference to Seinfeld and Pandis. A thermodynamic calculation that supports this statement is needed. Also from the Abstract, last line states: [If sulfate aerosol becomes more acidic as OA/sulfate ratios increase, then controlling SO2 emissions to decrease sulfate aerosol will not have the co-benefit of suppressing acid-catalyzed secondary organic aerosol (SOA) formation.] This requires knowing how this proposed process specifically affects pH, which I don't believe is ever discussed. That is, what is the effect of this organic coating on aerosol pH?

Page 3, line 2-6 states: [Nitrate partitions into the aerosol only when ammonia is in excess of sulfate neutralization, limited by the supply of excess ammonia and dependent on temperature.] Can one provide a thermodynamic analysis proving this is true? Fig A above, suggests otherwise.

Page 3 last sentence states: [In any case, sufficient ammonia is emitted in the eastern US to fully neutralize the sulfate contributed by SO2 emissions.] Again, can this statement be shown to be true based on a thermodynamic calculation?

Page 4 it states: [ alkaline cations other than ammonium do not contribute significantly to the neutralization (Kim et al., 2015),...] A few lines explicitly stating how this is shown in Kim would be very useful (as noted above).

Page 4 gives f(N) from various studies, including AMS data from SOAS and SEAC4RS. Is the reported +/- the standard deviation of the data or the uncertainty in f(N). If not uncertainty, what is the uncertainty? (As an example, AMS uncertainty of 35% is often reported, which would lead to an uncertainty of about 50% for f(N). Also, in side by side comparisons, such as in SOAS and WINTER studies, systematic differences in AMS and PILS measurements of sulfate, nitrate and ammonium can easily by 20%. I suspect similar levels apply to network data. It seems that measurement uncertainty alone, both random and systematic (the latter more important here), makes asserting that there is a difference between measured and model predicted f(N) tenuous.

Page 5 Lines 29 to 31 it states: [We see that the observed aerosol neutralization does not follow thermodynamic predictions. . .] A similar statement is made in the last line on page 5. Specifically, what thermodynamic predictions are being referred to? Was a full thermodynamic model run to verify this? Please provide specific evidence to support this statement.

Page 6 it states: [. . .the sulfate aerosol is far from neutralized, and one would expect under these conditions that the aerosol neutralization ratio should increase as the supply of sulfate decreases. But this is not observed.] What does, [one would expect], mean? Again, can these statements be proven with a thermodynamic calculation?

The proposed mechanism to bring model predictions closer to observed MRs is to lower the NH3 uptake. This results in the equilibrium time scales increasing to roughly a day or more. Presumably this will also affect fine particle nitric acid equilibrium time scales. Even ignoring any effect this film may have on nitric acid uptake. This could have a large impact on predicted fine particle nitrate concentrations, given that in many locations there is a significant mass of cations in the coarse mode (Na+, Ca2+, . . .) that can form non-volatile forms of nitrate, if given sufficient time. Thus, it would seem the viability of this proposed mechanism could be tested by predicting nitrate aerosol levels and comparing to observations, for example during cooler periods when more nitrate partitions to fine particles. It has been noted in a number of publications that ISORROPIA can accurately predict nitrate (without this proposed mechanism). How do the authors explain this if by their mechanism the aerosol is not in equilibrium?

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