

Review of “Particle water and pH in the southeastern United States” by Guo et al.

Overall comment:

This paper discussed a method for inferring particle pH and aerosol water content, important properties that are challenging to measure directly, from a suite of more readily available measurements in conjunction with thermodynamic modeling. My only significant comment is that it appears to me that the major contribution is the method itself more so than the actual results for the SOAS campaign, and portions of the paper could be reworked a little to emphasize this.

Major comments:

A major conclusion of the paper, which occurs prominently in the abstract, is that the method used here is an improvement over the ion balance approach that is commonly used. However, there is only an indirect (?) comparison of the methods (Fig S1), and this occurs in the supplemental material. I strongly recommend that the main text include a scatterplot showing pH by their method and the ion balance method. In contrast, I think that some of the figures that occur in the main text are of secondary importance and could be moved to the supplemental section, but I will let the authors use their judgment on this.

Similarly, the results section could demonstrate more clearly **why** the proposed method is better than the ion balance approach. The paper suggests two explanations: 1) it accounts for variations in RH; 2) it accounts for incomplete dissociation of ions such as sulfate. Reading between the lines a little, it appears that diurnal variations in RH and water content are the larger problem for the ion balance approach. It would be helpful if the authors could quantify the relative errors associated with these two problems. Given the apparent importance of the diurnal cycle, it seems that the ion balance approach would systematically overestimate pH during the daytime and underestimate at night. This might be shown (e.g. in Figure 10).

It also appears that the ion balance would get the right average pH. Is this true?

p. 27146, lines 20-21: “A comparison between an ion balance-predicted H^+ air to that from the full analysis discussed below, for this data set, is shown in the Supplement.”

I assume this refers to Fig S1, which is really an indirect comparison since the y and x axes are not directly comparable? Or are they? Does the ion balance approach overestimate H^+ by a factor of 6-8 (the slope lines in that figure) compared to the more rigorous method? If there is a systematic bias in the ion balance approach, this should be clearly discussed in the main text of the paper. Again, it would be better to have a clear comparison of the methods and a quantitative discussion of the errors in the ion balance approach in the main text.

I agree with the other reviewers that a strength of the paper is the systematic uncertainty analysis. However, it is often difficult to follow the details, which are numerous and sort of occur throughout. A table of inputs, including their assumed uncertainties, would go a long way to clarifying the situation. Deleting these details from the text would probably streamline some of the denser sections as well. To the extent that the discussion of uncertainty can be consolidated, this would be helpful, but I'm not sure that much more can be done in this regard.

The conclusion section could emphasize more the methodological improvements developed here and the benefits compared to the ion balance method. There is the statement (p. 27165) that the diurnal pattern in pH is driven mainly by water dilution. I think it is worth putting this sort of thing in the conclusions to emphasize what the new method can deliver. The conclusion (p. 27167, lines 6-9) that precise information about organics is not necessary for reasonable pH estimates is an important conclusion about data requirements that should be mentioned in conclusions and perhaps abstract as well.

Minor comments:

Showing fits in the form of $y = a + bx$ (in several figures) is confusing to the reader since most people are familiar with $y = mx + b$ where b is the intercept rather than the slope. Therefore, when a casual reader glances at the fits, they are likely to misinterpret b as the intercept. Suggest to change to $y = mx + b$.

Intro. p. 27147, lines 14-18: "LWC plays a large role in secondary aerosol formation for inorganic and possibly organic species by providing a large aqueous surface for increased gas uptake and a liquid phase where aqueous phase chemical reactions can result in products of lower vapor pressures than the absorbed gases."

In fact, it is not clear to me that LWC is terribly important for secondary inorganic aerosol formation. Most sulfate oxidation occurs in cloud water rather than aerosol water, and most models entirely neglect sulfate oxidation in aerosol water. This statement should be deleted or revised or the authors should provide citations to indicate that I am mistaken.

Intro. p. 27147, lines 18-20: "In the eastern US, the potential for organic gases to partition to LWC is greater than the potential to partition to particle-phase organic matter (Carlton and Turpin, 2013)"

With due respect to the authors of the cited paper, I found the metrics used in that paper for “potential” to be confusing and was not entirely sure how to interpret the results. Therefore, I suggest softening the language to “it has been suggested that...” or similar. At the very least, the ability of organics to partition to water or OM must depend on what sort of organics we are talking about.

p. 27166, lines 13-15: “(Note, organic acids are not considered in our model, under these acidic conditions (pH= 1) their contributions to the ion balance (hence pH) are expected to be negligible.”

This seems reasonable to me, but this statement should occur in the methods section rather than as an aside buried in the results section. Also, it appears a closed parentheses is missing at the end.

Eqn 6 is essential to the method but is not entirely clear since it’s not equally clear how H_{+air} is calculated. I think what is happening is that an initial H_{+aq} value is computed from ISOROPPIA-II neglecting organic water uptake. Then this value is diluted by a factor of $W_i/(W_i+W_o)$ to account for water uptake? Please clarify mathematically what is going on.

Throughout the text, please refer to ions correctly, including the charges (i.e. NH_4^+ rather than NH_4 and similar for sulfate etc.)

p. 27166: “summer pH was lower due to higher ion (i.e., sulfate) concentrations”

Presumably, the seasonal cycle of ammonia plays a role here too?

p. 27166, line 22: “owning” should be “owing”

p. 27167, lines 17-19: “ W_o accounted for a significant fraction of total LWC, at a mean of 35% ($\pm 3\%$ SD) for SOAS and SCAPE field studies, indicating the importance of organic hygroscopic properties to aerosol scattering and direct radiative forcing.”

This statement might be read to be a global statement about water uptake due to organics, but the sites analyzed are unusual in that they are highly dominated by organics. Please clarify with a qualifier such as “in the SE US” or similar.