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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Particle water and pH in the southeastern United States" *by* H. Guo et al.

Anonymous Referee #2

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Guo et al. undertake a detailed calculation along with an uncertainty analysis to predict particle liquid water content (LWC) and pH based on comprehensive measurements made at several sites in the southeastern US. The authors conclude that LWC and pH calculations can be made if one knew the aerosol composition (measured via an AMS or a PILS-IC), relative humidity and temperature. Their analysis suggests that organic aerosol accounts for a substantial fraction of LWC and (despite the dilution from this additional water), accumulation mode aerosol in the southeast US is very acidic. The results from this work have strong implications for pH-driven processes (e.g., acid-catalyzed reactions of isoprene epoxydiol).

The analysis is well done and the paper is well written. I particularly admired the uncertainty analysis undertaken by the authors and hope that this paper will serve as a reference for future work that wants to estimate uncertainty in interpreted values from uncertainties in the raw measurement data. However, my biggest concern was how the authors failed to discuss the interaction of the organic and inorganic constituents in the condensed phase and the implication of that interaction on the conclusions from this work. The other two concerns pertain to a reorganization of the results section to elucidate the findings from this work and a nuanced discussion of how the methods in this work are different from the methods conventionally used in 3D models. Once these major (and some minor) concerns are addressed and the editor has had a chance to review them, I would recommend publication in ACP.

Major Comments

1. Organic-Inorganic Interactions

The authors assume a single organic-inorganic phase (Page 27154, line 11-13) and implicitly assume that there no chemical or thermodynamic interactions between the organic and inorganic constituents (e.g., enhanced solute effect, changes in the activity coefficient) in the condensed phase and that their independent contributions to particle water can be added to estimate total LWC. Clearly, the analysis in this manuscript and the interpretation of it depend critically on this assumption. Hence, I was surprised that this assumption was simply stated (without references) and not discussed in the manuscript along with recent literature in the field. Are the authors aware of relevant literature to suggest a single-phase with minimal organic-inorganic matrix effects? The following publications imply that, more often than not, organics and inorganics are phase-separated: (1) theoretical work from Andreas Zuend and coworkers (Zuend et al., 2010;Zuend and Seinfeld, 2012) where they model and discuss the implications of phase separation in mixed organic-inorganic aerosol, (2) experimental work from You and coworkers (You et al., 2013;You et al., 2012) where they suggest that ambient aerosol might have separate organic and inorganic phases.

If they had assumed separate organic and inorganic phases (as Zuend and You suggest), then the pH calculations would look very different. Separate phases (in the simplest case, the aerosol exists as a mixture of a pure organic and a pure inorganic phase) would mean that each phase would uptake different amounts of water and would be associated with different H+ concentrations and therefore different pH levels. The pH of the inorganic phase would now be lower than what the authors have calculated since the water in the organic phase would not “dilute” the H+. Further, the organic phase would now allow for some dissociation of acids and be acidic (although have a pH much higher than the inorganic phase). On a related note, Figure 7 suggests that a model based on separate water uptake by the organic and inorganic fractions can reproduce the observed levels of LWC. Doesn’t this hint at a separate organic and inorganic phase?

In its current form, the analysis provides a very simplistic treatment of the organic and inorganic constituents in the condensed phase. Are there ways the authors could improve on their analysis through a better model for organic-inorganic interactions. For example, the AIOMFAC model could be used to assess if the aerosol was phase-separated. At the very least, I expect the authors to mention that the current treatment of organic-inorganic interaction might be weak, discuss ways to model the interaction and speculate how, if at all, it would change the results from this work.

Having said that, it is likely that the water-soluble organic carbon and the highly soluble gases purported to form secondary organic aerosol (glyoxal and IEPOX) are going to disproportionately partition into the phase with more water and subsequently uptake more water. In that case, I would not expect the conclusions from this work to change substantially.

2. Reorganization

One of the goals of this paper (as I saw it) was to demonstrate the use of a set of tools (ISORROPIA, κ from CCN measurements) to calculate LWC and pH (and quantify the uncertainty in those estimates) if one knew the aerosol composition, temperature and relative humidity. The techniques were validated by comparing model-measurement

performance for LWC and ammonia partitioning at the CTR site and then applied to the SCAPE sites. However, this story was quite jumbled in the results section. For example, wasn’t Section 4.4 where they compared predictions of LWC against measurements a part of the model validation? Further, there wasn’t a clear delineation of the discussion of the results at the CTR site and the SCAPE sites. I would encourage the authors to state this goal more clearly in the abstract+conclusions and potentially reorganize the results section to differentiate the analysis for the CTR site (demonstrate validation) from that for the SCAPE sites (demonstrate application).

If I may, the reorganization could look like:

1. Summary of meteorology and PM composition

2. LWC and pH at CTR 2a. Base estimates, diurnal and seasonal trends 2b. Uncertainty 2c. Validation using LWC and ammonia partitioning

3. LWC and pH at SCAPE sites

4. Conclusions 4a. Brief summary 4b. What do the LWC and corresponding pH levels mean for tropospheric processes? 4c. Discussion about big assumptions (organic-inorganic interactions) 4d. Application to other parts of the world (e.g., California where fine aerosol is dominated by ammonium nitrate).

3. Traditional Calculations of LWC and pH

At several points in the manuscript (e.g., Page 27145, line 13-15), it seemed to me that the authors were suggesting that earlier efforts (e.g., references on Page 27146, line 15-16) to quantify LWC and pH were unsatisfactory. However, based on the conclusions of this work, I would argue that the methodology used (with one small difference) is consistent with how LWC and pH are actually calculated in 3D models. To my knowledge, most 3D air quality models (e.g. CMAQ) and many global climate models (e.g., GISS-TOMAS) use thermodynamic models like ISORROPIA or AIM to model H+ concentrations and water uptake by inorganic aerosol. Since the work by Petters and

Kreidenweis (2007), several 3D models have started using the hygroscopicity parameter κ to model water uptake by OA. However, I am unaware whether these models use both the organic+inorganic water to calculate pH like the suggestion made by the authors of this manuscript. In the revised manuscript, I would like to see a more balanced discussion of how earlier work has attempted to calculate LWC and pH and how this manuscript provides a path forward to improve those calculations. What recommendations do the authors make to experimentalists, modelers and regulators in calculating aerosol LWC and pH?

Minor Comments

1. Page 27145, line 3-5: Isn't the model validated using with model versus measured LWC? See above for reorganization with respect to the validation versus application sections in the manuscript. The authors say so on Page 27148, line 23-25 but do not mention it in the abstract or conclusions.

2. Page 27145, line 25-26: "Weak dependence of pH on organics" - I could not find where the authors show this in the manuscript.

3. Page 27146, line 10: What do you mean by "...measuring pH is not conserved..."? The sentence seems to suggest that dilution during the measurement process does not conserve pH and hence cannot be readily measured. I recommend rewording the sentence. On a related note, it might be worth mentioning the literature in microfluidics where pH levels are measured using nanoliters of sample volume and how that could be useful to measure pH of ambient aerosol.

4. Page 27147, line 14-18: Provide references for role of LWC in SOA formation. IEPOX- and glyoxal papers?

5. Page 27148, line 1: The authors mention that the "relationship of organics to LWC is not well characterized, and it requires a parameterized approach". But there were neither references to support that statement nor a discussion of the relevant literature

(small organic acids are very hygroscopic (Koehler et al., 2009), water uptake can be parameterized using the hygroscopicity parameter κ (Petters and Kreidenweis, 2007), κ can correlate with degree-of-oxygenation of organic aerosol (Jimenez et al., 2009) or it may not (Cerully et al., 2014;Hildebrandt Ruiz et al., 2014), organics depress deliquescence (Marcolli et al., 2004)). Moreover, I had expected a longer conversation in the introduction about the role of organics on LWC given that one of the major conclusions was that organics account for a substantial fraction of the water uptake.

6. Page 27148, lines 2-3: I agree that LWC is not routinely measured but that does not mean, "ambient particle total mass concentration is not well characterized". Ambient dry particle mass is very well characterized by air quality monitoring networks (STN, IMPROVE, etc). Further, if one were to accept the conclusions from this work that suggests that ISORROPIA along with parameterized kappa values can accurately predict LWC, air quality models can offer a realistic assessment of the mass and composition of "ambient particle total mass concentration". I suspect what the authors mean here is that in some cases LWC and its effect on pH can drive processes that could potentially change the mass and composition of ambient aerosol and it is this change that is not well characterized.

7. Page 27149, line 7: The abbreviation VOC was used for the first time. Expand.

8. Page 27150, line 5-9: The intent is described here (validation at CTR followed by application at SCAPE sites) but not executed in the description of the results.

9. Page 27155, Section 3.3: "3.3 pH prediction" does not need to be under the Section "3.1 LWC prediction from aerosol composition". Recommend separation.

10. Page 27156, line 16: "whom" should be "both of whom".

11. Page 27158, line 13-15: Long and confusing sentence. Consider breaking it into two.

12. Page 27158, line 15-18: The point was already made in the earlier section. Also, I

did not understand its purpose in the "LWC uncertainty" section.

13. Page 27161, line 18: "have" instead of "having" and line 19: "higher pH" instead of "pH higher"?

14. Page 27165, line 7-10: Could you instead use the NH3(g)/NH4 ratio at the CTR site and apply it to the SCAPE sites to determine total gas+particle ammonia for use with ISORROPIA-II?

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