We thank the referees and the editor for their thoughtful and constructive comments. We have addressed their comments (numbered, below), with referee comments in quotes and italics, and our responses in plain text.

Referee #1

1. "*One such issue that puzzles this reviewer is that another paper was just published in ACP ("Trends in particle-phase liquid water during the Southern Oxidant and Aerosol Study") discussing the same general topic, region, and campaign (SOAS) with figures that at times are showing similar things as in this paper. Based on the current form of this paper in review, I did not get a sense that it was sufficiently different to be comfortable. The methods will differ, but the general scientific nuggets presented after going through the details of the methods and uncertainties are aligned and at times redundant. For example, compare the current Figure 7 (for this paper in review) with their Figures 6-7. At times during my reading I felt that this paper was better suited for a methods-oriented venue such as AMTD. With all this being said, with significant revisions the authors need to make a much stronger effort to articulate and show how this manuscript is different than the other one and to make a case for why the science presented is of sufficient impact beyond those of the other paper*."

   We respectfully disagree with the referee on this comment. Our paper focuses mainly on particle pH and its wide implications. To calculate pH and associated uncertainties, a discussion of particle water is necessary since it is involved in the pH calculation. The Nguyen et al. (2014) paper does not include any discussion of particle pH and thus the assertion that the papers are largely similar is incorrect. Furthermore, we calculate water in a completely different method than that used by the Nguyen et al. (2014) paper and also proceed to an attribution of water from organics and inorganics, which is important for climate forcing of aerosols in the region. We do of course cite the Nguyen et al. (2014) paper and attempt to reconcile differences; we have reorganized the structure of this paper to make the discussion of particle pH rather than particle water stand out.

2. "*Together with this past comment, the authors should consider strongly that the current paper in review is quite heavy in discussion of methods and uncertainties and it is hard to extract the key scientific advancements due partly to the great effort required to digest and comprehend all of the content up until Section 4.4.*"

   We understand the analysis of LWC and pH uncertainty is rather detailed. We feel it is important enough to include in the manuscript, a view that reviewer #2 enthusiastically supported. We have however reorganized the sections for clarity and placed the LWC and pH uncertainty discussion in Section 4.2a.

3. "*What are the broader implications of this study to other regions and studies since it seems to be highly specific to the instrumentation/methods and sites examined by the investigators?*"

   The measurements are carried out at a site that is representative of the broader SE US over a period of a year, so the conclusions are both broad, numerous and very important. Firstly, it is shown that the pH is consistently low in the SE US, so that isoprene SOA may not be limited by availability of either water or acidity; the companion paper by Xu et al. (2015) published in PNAS confirm this. The implications for SOA formation is surprising and with important implications for isoprene SOA worldwide. Secondly, we demonstrate rather clearly that water associated with organics can be a considerable fraction of the total water content, which means the organic fraction has an important contribution to both aqueous phase chemistry and radiative forcing. We attempt to establish a method for obtaining liquid water content and pH (that is well evaluated against optical closure and NH_3 partitioning) with instrumentation that is readily available in many groups, and feel that this in itself is of interest to the community as a whole. Finally, demonstrating that ion balance and molar ratio consistently fails as a proxy of aerosol pH is another important finding that reveals a major weakness in previous studies using these acidity metrics.

4. "*Section 2.2: can the authors clarify more about whether they measured PM2.5 or PM1 and what the sampling strategy was. This seems like a key point since PILS is being compared to the AMS. Clarity is needed throughout the paper about the different size resolutions being compared between instruments and how differences impact results.*"

   It is stated on Page 27150 Line 19 that PILS-IC was operated with a URG $PM_{2.5}$ cyclone for the 1st half of field study (June 1 to June 22) and PM_1 cyclone for the latter half (June 23 to July 15). We have added the following sentences to clarify the cut size of AMS and CCNc: "A URG (Chapel Hill, NC) PM_1 cyclone was installed for both AMS and CCNc". Nephelometers measured $PM_{2.5}$ aerosol scattering coefficients as stated on Page 27151 Line 22. Because the major ions associated with predicting particle water and pH (e.g., sulfate and ammonium) were mostly associated with PM_1 and occasional dust events were excluded in our analysis, there was little difference in sulfate and ammonium loadings between PILS-IC PM_1 or $PM_{2.5}$ and AMS PM_1 whether a PM_1 or $PM_{2.5}$ cyclone was used (Figure 2). Based on this consistency, we argued that AMS data can be used to estimate $PM_{2.5}$ water and pH in southeast, if rare dust events are excluded.

5. "*AMS description: Clarify assumptions about the collection efficiency and how results can be impacted by the uncertainty in this value.*"

   Following standard practice, a composition-dependent collection efficiency is applied to all AMS datasets based on the algorithm described in Middlebrook et al. (2012). The same collection efficiency is applied to all AMS-measured species. Collection efficiency affects predicted water because water uptake is proportional to concentrations of water-soluble ions, for a given RH and T. The influence of collection efficiency is less for pH because it is an intensive aerosol property, and the proportion of ions (hence LWC) is largely affected in the same way by CE (see Figure 1 below). The uncertainty associated with collection efficiency is included in the final AMS data uncertainty. AMS measurement uncertainty is 30% according to Bahreini et al. (2009).

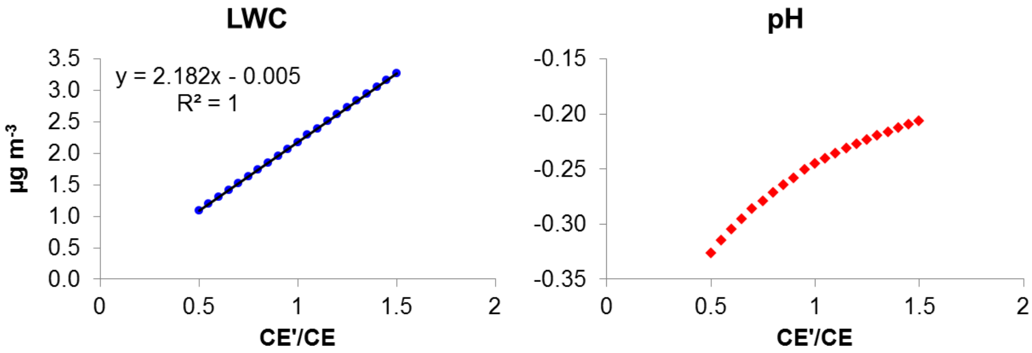

Figure 1. ISORROPIA input (excluding RH and T) was rescaled via the ratio of collection efficiency. Ammonia data was not included in the calculation. LWC output responded linearly to the variation. Note that the response of LWC to CE has a factor of 1 (Slope/base LWC level=1). pH varied in a very small range from -0.35 to -0.20.

6. “*Page 27153: write out what TEOM is.*”

TEOM stands for Tapered Element Oscillation Microbalance. We have revised the sentence on Page 27153 Line 9 to “For SOAS, dry PM$_{2.5}$ mass concentrations were measured continuously by a TEOM (tapered element oscillating microbalance, 1400a, Thermo Fisher Scientific Inc., operated by Atmospheric Research & Analysis Inc.).”

7. “*Figure S4: I would recommend starting the y-axis at a more reasonable lower limit than zero to show the variations better in the plotted points.*”

We have adjusted y-axis range to 1.4-1.6 to show diurnal variation of particle density.

8. “*Supplement Section 3 about nephelometers and in Section 2.3: A major assumption that seems highly problematic is that Q_wet and Q_dry are equivalent. Just looking at Figure S3 shows that some significant changes can be expected in Q based on particle size. For example, if a dry particle at 250 nm grows in a humid environment to 450 nm, the ratio of the Q values will be much larger than 1. Couldn’t refractive index change? and would this affect this Q_wet=Q_dry assumption? Careful discussion/analysis is needed here since this was not given adequate attention based on my reading.*”

We have added the following statements in Supplementary Material Section 2 to support this assumption: “As part of this study Nguyen et al. (2014) (Table 2 and Figure 5) measured very similar size distributions between unperturbed and dry particles (their unperturbed particles are equivalent to our ambient particles; the same for dry particles). Two-mode lognormal distributions were identified. The number mean sizes decreased by only 13% for both modes from unperturbed to dry particles (Nguyen et al. (2014) Table 2 shows that the number mean diameters of mode 1 and 2 lognormal distributions both decreased by 13% after drying). An accurate estimation of the change in Q_s is done by Equation 5 using the study average (SOAS) unperturbed and dry size distribution data from Nguyen et al. (2014). Particles ranging from 6nm to 1 µm were binned to 60 groups. The uncertainty associated with assuming $Q_{s,wet}/Q_{s,dry}$=1 is calculated to be 40% ($\overline{Q_{s,wet}}/\overline{Q_{s,dry}} = 1.40$). Although discrepancy occurred between Nguyen et al. (2014) and our RH measurements, a slope of 0.91 between Nguyen's water and $f(RH)$_water suggests that the two measured water were comparable at the same magnitude. Therefore, it is reasonable to apply Nguyen's size distributions to estimate the uncertainty with Q_s. Note that the SMPS doesn't scan up to 2.5µm and particles in the size range between 1 µm and 2.5 µm have similar Q_s (around 2) and contribute to particle scattering. In summary, at region (0-1 µm) where Q_s changes significantly, particle size distributions don't vary significantly after drying; for region (1 µm-2.5 µm) where Q_s is nearly constant, particle size decreases due to drying, but doesn't have much effect on Q_s. Considering the above reasons, 40% is the uncertainty upper limit. Size distribution smooths out specific size influences on Q_s.

$$\frac{\overline{Q_{s,wet}}}{\overline{Q_{s,dry}}} = \frac{\sum_{i=1} \frac{\pi}{4} Q_{s,wet,i} D_{p,wet,i}^2 \, \Delta N_{wet,i} / \sum_{i=1} \frac{\pi}{4} D_{p,wet,i}^2 \, \Delta N_{wet,i}}{\sum_{i=1} \frac{\pi}{4} Q_{s,dry,i} D_{p,dry,i}^2 \, \Delta N_{dry,i} / \sum_{i=1} \frac{\pi}{4} D_{p,dry,i}^2 \, \Delta N_{dry,i}} \qquad (1)”$$

9. “*Since measurements are done for ambient RH, how would the RH change in the sampling lines up to the point of measurement? Also, how would the presence of coarse aerosol affect the nephelometer measurements, and overall study results, and what length did the authors go through the remove cases of coarse aerosol in their study using size distribution data? Presumably in the region there may be sources of such larger particles. Discussion/analysis to address these points is needed.*”

As noted, to accurately measure ambient scattering for the liquid water calculation, it was critical that the instrument was at the same RH and T as ambient. Therefore, the nephelometer was situated outside in a small white 3-sided shelter (one side covered by a loose tarp). The shelter was designed to be well vented. The inlet line was less than 1m to minimize particle losses in the sampling line. A URG $PM_{2.5}$ cyclone was installed, which removed coarse particles. All of these components were situated outside.

10. “*The authors should discuss (via analysis) if volatilization of vulnerable species (e.g. ammonium) in instrumentation (including sampling lines) affects the results in way and how this was accounted for.*”

Overall, evaporation of ammonium is not expected to be an issue. The aerosol was acidic, so ammonium nitrate is not a significant fraction of the aerosol, and practically all ammonium was associated with non-volatile sulfate, consistent with many studies conducted in the SE during summer and the results of our thermodynamic modeling. The sample lines located in sampling buildings were generally at similar or lower temperatures than ambient. Indoor temperature was 25 ℃ to minimize condensation of water in sample lines. Sample lines were thermally insulated and kept as short as possible; for example, the PILS-IC was situated such that the indoor portion of the sample line was less than 1m long.

11. “*The authors focus quite a lot on sulfate and ammonium in terms of PILS species in their calculation of pH uncertainty, but what about other species that the PILS is capable of examining?*”

Sulfate and ammonium are by far the dominant water-soluble species in $PM_{2.5}$ in the southeast. During SOAS, very low levels of other inorganic soluble species (e.g. nitrate and sodium), were observed. Therefore, the contributions of these species to water and pH are generally small, although included in the thermodynamic modeling calculations. Focusing on sulfate and ammonium gives us an overview of the main species that drive particle water and pH in the southeast. Occasional dust events are excluded in our discussion, so crustal species (Ca, K, Mg) are mostly below the IC detection limit.

12. "*Figure 3-5: A general comment that these figures may confuse other readers unless the captions become more descriptive of what is being shown.*"

    We have added more details in the captions to explain Figures 3-5 (renamed as Figures 6-8).

Referee #2

13. "*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.*"

We appreciate the above points made by the reviewer. The high RH and highly oxidized state of the organics favor a single phase in the aerosol. We have added the following sentences in the Section 3.4 Assumptions: "…Particulate organic and inorganic species are assumed to be internally mixed in the liquid phase due to the high RH (73.8 ± 16.1%) typical of this study and because a large fraction of the ambient aerosol organic component is from isoprene SOA (Xu et al., 2015), which are liquids at RH $\geq$ 60% (Song et al., 2015). Particle liquid phase separations are not considered, although they have been measured in bulk extracts of aerosols from the southeast (You et al., 2012). It is reported that liquid-liquid phase separation can occur when O:C ratio of the organic material is $\leq$ 0.5. More experiments showed that it is possible to have phase separation for organic O:C $\leq$ 0.7, but not for O:C $\geq$ 0.8 (Bertram et al., 2011;Song et al., 2012;You et al., 2013). SOAS O:C=0.75 ± 0.12 is in the transition region. According to Figure 2 in Bertram et al. (2011), at RH typically > 60% and organic:sulfate mass ratio >1, it is not possible to have phase separation, which is the case for our sampling sites. Based on our basic assumption of no liquid-liquid phase separation, pH is considered to be homogeneous in a single particle."

We also added the following sentences in the Section 3.4 Assumptions explaining the consequences of assuming liquid-liquid phase separation on the water and pH calculation. "However, separated phases would likely have different pHs if liquid-liquid phase separation occurs. In that case, pH should be calculated based on the amounts of water and H^+ in each phase. Thus, the pH of the inorganic phase could be lower (decrease by 0.15 to 0.23, mentioned in Section 4.3b) and pH of the organic phase possibly much higher, allowing dissociation of organic acids. Gas-particle phase partitioning will change accordingly, due to these separated phases. There are models that are set up to calculate these thermodynamics (e.g., AIOMFAC), but none is yet able to address the compositional complexity of ambient SOA. (Zuend et al., 2010;Zuend and Seinfeld, 2012)"

The reviewer implies that additivity of organic and inorganic water implies the phases are separated. This is not true. Even in a single phase, partial additivity of liquid water from each component at the same water activity (or RH) is the basis of the Zdanovskii-Stokes-Robinson (ZSR) relationship, which is what is assumed here. ISORROPIA-II also applies the same rule for calculating W_i from individual salts in the solution.

14. "*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).”

We have reorganized the discussion to address the issues raised.

15. “*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?”*

    We strongly recommend calculating both W_i and W_o to estimate particle water, since W_o was found to be 29%-39% of total LWC. To calculate W_o, parameterized κ_{org} is needed. In terms of pH, we revised Section 4.3b as follows to state that it is more important to include NH_3 than W_o in the pH calculations. “The effect of aerosol sources of particle water on pH can also be delineated. pH calculated just by W_i alone will be affected by an underestimation of particle water, resulting in a slightly lower pH (Figure 13). W_o is on average 29% to 39% of total water at all sites, as a result pH increases by 0.15 to 0.23 units when W_o is included. Independent of the pH range, a 29% to 39% W_o fraction always increases pH by 0.15 to 0.23 due to the logarithmic nature of pH. The effect of W_o on pH can be simply denoted as $\log_{10}(1-\varepsilon_{W_o})$. For example, when ε_{W_o} is 90%, it shifts pH up by 1 unit. pH based on W_i is highly correlated with pH for total water ($W_i + W_o$) ($R^2 = 0.97$). This indicates that if organic mass and κ_{org} are not available, ISORROPIA-II run with only ion data will give a reasonable estimate of pH, since both H^+_{air} and W_i are outputs of ISORROPIA-II, while W_o is predicted based on organic mass and κ_{org}. Accurate temperature and RH are still necessary inputs, especially when RH is high.”

16. “*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.”*

We have revised the abstract to “A comprehensive uncertainty analysis is included and the model is validated… Thermodynamic calculations based on measured ion concentrations can predict both pH and liquid water but may be biased since contributions of organic species to liquid water are not considered. In this study, contributions of both the inorganic and organic fractions to aerosol liquid water were considered and predictions were in good agreement with measured liquid water based on differences in ambient and dry light scattering coefficients (prediction vs measurement: slope = 0.91, intercept = 0.46 µg m^{-3}, $R^2 = 0.75$)”. We also added the following sentence in the conclusion: “The model was validated through comparing predicted to measured liquid water (W_i+W_o to *f(RH)*_water) and predicted to measured ammonia concentrations.”

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

   This is explained in detail in Section 4.3b The role of W_o. W_o is on average 29% to 39% of total water at all sites. However, pH increases by just 0.15 to 0.23 units when W_o is included.

18. “*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.”*

   We have revised the sentence to “Measurement of pH is highly challenging and so indirect proxies are often used to represent particle acidity”. It is possible to measure particle pH by collecting particles into a solution. However, the H^+ in the solution is not correlated to the H^+ in the particle, because the dissociation states of ions have changed due to different amount of water and other reasons discussed in Hennigan et al. (2014).

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

   We have added several references, such as Ervens et al. (2011) and Nguyen et al. (2013).

20. “*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 _ (Petters and Kreidenweis, 2007), 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.”*

We have revised the paragraph to "In contrast, due to its chemical complexity that evolves with atmospheric aging, the relationship of organics to LWC is not well characterized and requires a parameterized approach (Petters and Kreidenweis, 2007). Relationships between volatility, oxidation level and hygroscopicity are not always straightforward and still remains to be fully understood (Frosch et al., 2011;Villani et al., 2013;Cerully et al., 2014;Hildebrandt Ruiz et al., 2014)."

21. "*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."*

    We have revised the sentence to "Thus typically, particle total mass concentration (that includes liquid water) is often not characterized."

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

    We have added "volatile organic compound".

23. "*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."*

    We have reorganized the results to follow this order.

24. "*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."*

    The title of Section 3 has been revised to "Modeling Methods: Predicting LWC and pH from aerosol composition".

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

    The text has been changed accordingly.

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

    We have revised the sentence to "These combined uncertainties lead to an W_i uncertainty of 25% (Figure 6), which is the same as the SO_4 uncertainty. SO_4, one of the most hygroscopic ions (Petters and Kreidenweis, 2007), controls W_i uptake."

27. "*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.*"

    We have deleted the sentences.

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

    We have reworded accordingly.

29. "*Page 27165, line 7-10: Could you instead use the $NH_{3(g)}/NH_4$ ratio at the CTR site and apply it to the SCAPE sites to determine total gas+particle ammonia for use with ISORROPIA-II?*"

    We have added the following sentences in the text that "Assuming the average $NH_{3(g)}/NH_4^+$ ratio from CTR applies to all SCAPE sites to estimate $NH_{3(g)}$, along with measured particle composition at each site, we got pH increases ranging from 0.87 to 1.38. In the following, all pHs reported for SCAPE are corrected for this bias (i.e., pHs are increased by 1 to simplify the correction)."

Editor

30. "*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.*
    *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).*

    We thank the editor for these suggestions! We have adopted them as follows in the text: "In part, because of the diurnal variation of LWC, a simple ion balance or NH_4^+/SO_4^{2-} molar ratio or per volume air concentration of aerosol hydronium ion (H_{air}^+) alone cannot be used as a proxy for pH in the particle. Figure 5a shows a weak inverse correlation (R^2=0.36) between ion balance and pH. An ion balance of an aerosol is usually calculated as follows (in unit of nmol equivalence m^{-3}), for a NH_4^+-SO_4^{2-}-NO_3^--Cl^--Na^+-water inorganic aerosol.

$$Ion\ Balance = \frac{[SO_4^{2-}]}{48} + \frac{[NO_3^-]}{62} + \frac{[Cl^-]}{35.5} - \frac{[NH_4^+]}{18} - \frac{[Na^+]}{23} \quad (7)$$

    where $[SO_4^{2-}]$, $[NO_3^-]$, $[Cl^-]$, $[NH_4^+]$, and $[Na^+]$ are concentrations of these ions in units of g m^{-3}. An ion balance is also a bad indicator of pH because it poorly predicts the aerosol concentration of H_{air}^+. An ion balance assumes all ions are completely dissociated, but multiple forms are possible, depending on pH (e.g., sulfate can be in the form, of H_2SO_4, HSO_4^-, or SO_4^{2-}). For example, if aerosol sulfate remains in the free form of H_2SO_4, it doesn't add protons. Thus, an ion balance usually overestimates protons and are only moderately correlated with H^+_{air} (Figure 5b)." We added Figure 5 to show the scatter plots between ion balance and pH, H^+_{air}. We also added the diurnal profiles of the ion balance and NH_4^+/SO_4^{2-} molar ratios to Figure 10. The molar ratio trend doesn't follow pH diurnal variation.

31. "*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."

    An ion balance is different from ISORROPIA-II calculated H^+_{air}, because it corresponds to very different LWC conditions; however studies utilizing ion balance treat it as if the two quantities are equivalent. The updated Figure 4 and 5 make this point clearly we feel. We have followed the editors suggestion to clarify all this; Supplemental material (section 1) was moved to the Section 4.2a of the main text, and it is shown (in Figure 4 and Figure 5b) that the ion balance overestimated H^+_{air} by a factor of ~8.

32. "*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.*"

    We have added the following sentences in the abstract: "However, not including contributions of organic water had a minor effect on pH (changes pH by 0.15 to 0.23 units), suggesting that predicted pH without consideration of organic water could be sufficient for the purposes of aqueous SOA chemistry…Particle ion balances or molar ratios, often used to infer pH, do not consider the dissociation state of individual ions or particle liquid water levels and so do not necessarily correlate with particle pH." We have also added some sentences in the conclusion like: "Particle pH is important and difficult to measure directly. However, the commonly used pH proxies of ion balances and NH_4^+/SO_4^{2-} molar ratios don't necessarily correlate with pH. Therefore, predicting pH is the best method to analyze particle acidity. However, the pH prediction is not highly sensitive to W_o, unless its mass fraction to the total particle water is close to 1. Thus, in most cases particle pH can be predicted fairly accurately with just measurements of inorganic species and ISORROPIA."

33. "*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.*"

    The graphs have been revised to the format of "y = mx+b".

34. "*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."

    Indeed, most sulfate is produced in clouds. However, partitioning of semi-volatile inorganic species is shifted to the aerosol phase in the presence of liquid water (or high RH); this is routinely captured by aerosol thermodynamic models used in almost every thermodynamic model today. There is no doubt that the aqueous phase enhances SOA as well. We have added several references, such as Ervens et al. (2011) and Nguyen et al. (2013).

35. "*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.*"

    We have added "it has been suggested that…".

36. "*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.*"

    We prefer not to change the location of this sentence. This sentence is meant to show that although the model doesn't consider organic acids, the predicted pH is still accurate at low pH ranges. The dissociation of organic acids is expected to be very small. We have added the following sentences in the conclusion: "ISORROPIA does not consider organic acids, but at the low pHs of this study, they do not contribute protons (Bacarella et al., 1955). However, for pH approaches 7, the dissociation of organic acids cannot be neglected."

37. "*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 ISORROPIA-II neglecting organic water uptake. Then this value is diluted by a factor of Wi/(Wi+Wo) to account for water uptake? Please clarify mathematically what is going on.*"

    H^+_{air} and W_i are the output of ISORROPIA based on input of water soluble ions and RH, T. H^+_{aq} is the ratio of H^+_{air} to LWC. So, W_o makes H^+_{aq} diluted by a factor of $W_i/(W_i+W_o)$.

38. "*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?*"

    Both ammonia and ammonium peak at summer (Heald et al., 2012;Hidy et al., 2014). It is probably that the seasonal cycle of ammonia plays a role in pH but the effect remains to be investigated. It is the NH_3/NH_4^+ ratio (ammonia partitioning) that matters to constrain pH. Since ammonia data is not available at SCAPE sites to support the statement, we applied a consistent pH correction of 1 unit at all SCAPE sites. Please refer to Question #29 for more info on our assumption. If NH_3/NH_4^+ ratio doesn't change significantly seasonally, our predicted pH in winter should be accurate within uncertainties. We have added the following sentences in the text to explain the weakness of our seasonal pH predictions. Section 4.2c: "At CTR ammonia partitioning has been included in all model runs, but as no $NH_{3(g)}$ was available for SCAPE. Assuming the average $NH_{3(g)}/NH_4^+$ ratio from CTR applies to all SCAPE sites to estimate $NH_{3(g)}$, along with measured particle composition at each site, we got pH increases ranging from 0.87 to 1.38. In the following, all pHs reported for SCAPE are corrected for this bias (i.e., pHs are increased by 1 to simplify the correction)."

39. "*p. 27167, lines 17-19: "Wo accounted for a significant fraction of total LWC, at a mean of 35% (±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.*"

    We have revised the sentence to "On average, for the SOAS and SCAPE field studies, particle water associated with the $PM_{2.5}$ organic species (W_o) accounted for a significant fraction of total LWC, with a mean of 35% (±3% STD) indicating the importance of organic hygroscopic properties to aqueous phase chemistry and radiative forcing in the southeast US."

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