

Interactive comment on “On the link between hygroscopicity, volatility, and oxidation state of ambient and water-soluble aerosol in the Southeastern United States” by K. M. Cerully et al.

K. M. Cerully et al.

nenes@eas.gatech.edu

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General Comments

We thank the referee for the thoughtful and constructive comments. Following are the comments raised (in quotes and italics), and our responses in plain text.

“It is often tricky to understand to which aerosol the authors refer in the text. Please keep the convention that you introduced: ambient/PILS, denuded/ non-denuded. Most of the time in the text, the sampled aerosol have two characteristics (ambient/PILS) and (denuded/ non-denuded) but only one characteristic is given and it is up to the

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reader to find back what could be the other characteristic. Please correct through the text.”

The point raised is well taken. We have made changes to instances where the modifiers improved clarity; adding both characterizations at every instant of “aerosol”, however, made the text terse.

“I found hard to follow section 4.1 and 4.2, maybe a bit of rewriting or maybe a diagram to follow all the hypothesis would help the reader.”

Changes have been made to improve clarity.

Regarding the multiple requests to add references throughout the text: this manuscript is not a review of the extensive literature on the topic, and that is why “e.g.” is added in front of most of the references. The additional reference requested is often honored, but is done where we feel there is added value to the point made.

Minor comments:

“P30837: Line 4: “as well as acting as cloud condensation nuclei (CCN)”, you could add Rosenfeld et al., 2008, Science: Flood or Drought: How Do Aerosols Affect Precipitation? “

The IPCC chapters cited have many references that support these statements and we feel that this is sufficient. The sentences has been adjusted however to better reflect the intended reference.

“Line 16:” though numerous studies have focused on the link between two of these parameters” you could add Ristovski et al., 2010, ACP: “Sulphates and Organics in new particle formation” → paper using VHTDMA technic “

“Line 21: “Several studies have shown and proposed parameterizations for the relationship between organic hygroscopicity and degree of oxidation” you could add Duplissy et al., 2011, ACP “Relating hygroscopicity and composition of organic aerosol particu-

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late matter" → paper providing parameterization between mz/44 and GF."

References added.

"P30839: - *"The Southeastern United States presents itself as a particularly interesting location of study, as it has experienced an overall cooling trend in surface temperature, in contrast to the warming trend seen elsewhere in the United States (Goldstein et al., 2009; Portmann et al., 2009)." → for which period?"*

Time period added.

"P30840: Line 8: *"This study will primarily focus on comparing non-denuded and thermally-denuded measurements in order to investigate the relationship between hygroscopicity, volatility, and oxidation for both ambient and water-soluble ambient size-resolved and PM1.0 aerosol."* → *"In order to investigate the relationship between hygroscopicity, volatility and oxidation, this study will primarily focus on comparing non-denuded and thermally-denuded measurements of PM1.0 size-resolved aerosol for both ambient and water-soluble ambient"*

Sentence replaced with "These measurements are then used here to investigate the relationship between hygroscopicity, volatility, and oxidation state for the ambient and water-soluble fraction of the aerosol sampled."

"Line 17: *"aerosol were collected directly from ambient" → there it is confusing as it seems that aerosol is not passing through PM1.0 anymore."*

We have rewritten this section to clarify what was done.

"Line 19: *"The PILS liquid ..." → missing the debubbler (shown in figure 1) description in this sentence."*

Good point. Position of the debubbler added in the description sentence.

"Line 23: *"AMS" please write meaning of acronym and provide reference (for example Canagaratna et al. 2007) (this is the only instrument without references)"*

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Acronym and reference for the AMS was already explained in L6 of the same page.

"Line 25: *"To account for nebulizer efficiency and any losses in the PILS-nebulizer system, sulfate measured by the PILS-AMS system was compared to ambient AMS sulfate and used as a scaling factor."* → *You could say few words why sulfate is the chemical used for scaling."*

Good point. This is now done.

"P30841: Line 6: *"Temperature set points in the TD heating section were switched between 60, 80, or 100 C. In this setup, the TD was operated without a cooling section, as recondensation of vapors is minimal at low ambient mass loadings characteristic of the conditions during this study (e.g., Cerully et al., 2014; Saleh et al., 2011)." → Provide residence time of the TD as it is a crucial parameter. Although this TD is describe in another paper, please provide a bit more details of the TD in this paper as it is important for the understanding the volatility properties. Lot of the discussion is based on the TD result."*

Thank you for raising this important point. The flow rate used for these measurements was 1.5 LPM. That would correspond to an average residence time of ~7 seconds.

"P30841: Line 5: *"The resulting CCN concentrations were compared with activation spectra predicted by applying Köhler theory (Köhler, 1936) to SMPS-measured concentrations under the assumption that the distributions had a kappa of approximately 0.2–0.3, a general estimate of an aerosol population composed of organics and ammonium sulfate with equal volume fractions 10 or slightly higher organic volume fraction than ammonium sulfate (see Sect. 3.3), as a filter to help identify irregularities in the data."* → *From this sentence, it seems that data with kappa different that 0.2-0.3 were removed from the data set, which is hopefully not the case as show in figure 3."*

The points in discussion typically had very high or very low hygroscopicities (<0.005 or >0.6) and were inconsistent with their observed composition. The filter mentioned

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was not used to remove the data, but rather used to identify data for which a closer look was required. The data was removed from the analysis when it corresponded to transient behavior in the instrumentation (e.g., during a supersaturation change in the instrument).

"P30847: Line 26: "than the non denuded PILS aerosol"

Changed to "non-denuded PILS aerosol"

"Line 28: denuded ambient aerosol "

Changed to "denuded ambient aerosol"

"Line 26 to 28: From the figure 4, I cannot see what the authors are claiming. I would rather say that for ambient aerosol, these aerosol can be either more hygroscopic or less hygroscopic after the denuder, showing that the aerosol composition show different behavior at different time of the campaign. I would suggest something like this: "Through the full campaign, the average denuded PILS aerosol show slightly higher hygroscopicity than the nondenuded PILS aerosol, though these changes in kappa are within 10 %. Average thermally-denuded ambient aerosol, on the other hand, displays hygroscopicity similar to that of the non denuded ambient aerosol. However, the scatter of the data shows that the aerosol composition have different hygroscopicity/volatility behaviors at different time of the campaign." Maybe adding the organic to inorganic ratio in Figure 4 as color coded could help to understand this scatter."

This is a good point. As noted in the figure caption "All points shown are for periods where non-denuded measurements are directly followed by denuded measurements and vice versa"; therefore compositional variability with respect to particle size is a prime candidate for the scatter. In light of this we rephrase the sentence as: "Through the full campaign, the average denuded PILS aerosol displays slightly higher hygroscopicity than the non-denuded PILS aerosol, though these changes in kappa are within 10 %. Average thermally-denuded ambient aerosol, on the other hand, displays

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hygroscopicity similar to that of the non-denuded ambient aerosol, with some scatter that could be from the size-dependent variability of composition that is not present in the PILS aerosol."

"P30848: Line 21: "at four unique ambient environments." : please list them."

Done.

"P30847-30850: Section 4.1 Authors could also discuss the effect of cooking the organic in the TD which could affect or not the kappa."

This is an excellent point. A subsequent study in preparation focuses on applying PMF on the TD aerosol of the SOAS dataset, and confirms that the PMF factor spectra remain largely unaltered by the volatilization. As a consequence, the hygroscopicities are not expected to be affected by the volatilization process either. We mention this point briefly in the text.

"P30850: Line 24: Meyer et al. 2009"

Reference added.

P30851: Line 1 : Possible other reference about oligomer and volatility "Dommen et al. 2006, Laboratory observation of oligomers in the aerosol from isoprene/NOx photooxidation"

Done.

P30851: It is often tricky to understand to which aerosol the authors refer in the text. Please keep the convention that you introduced: ambient/PILS, denuded/ non-denuded. Most of the time in the text, the sampled aerosol have two characteristics (ambient/PILS) and (denuded/ non-denuded) but only one characteristic is given and up to the reader to find back what could be the other characteristic. Please correct through the text.

Please see our response when the point was made in the general comments.

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Line 27: "left panel" Line 13: "Centerville". I m a bit lost. First time Centerville is mention in the text. Is it the name of the measurement site?

Centerville as the sampling site has already been mentioned in the Introduction, P30839 L18.

P30852. Line 8: than at lower temperature

Clarification added "denuded ambient aerosol" and "...at other temperatures..." replaced by "...at lower temperature...".

P30857: Line 21: looking at figure 8, it is hard to see any diurnal variation of the total korg, which is rather flat line at kappa=0.14. In the conclusion/outlook, it would be good to mention that HTDMA analysis (sub-saturated) should be done as well using the 3 PMF.

We have modified the text to better reflect these points.

Fig 5: "...the average for while..."

Caption updated to read better.

Fig 6: It is missing the small colored dots in the two right panels.

The figures were deliberately made that way, as the left panel indicates all the dots relevant.

Fig 8: -"korg" not "kor" -panel b: what is the left axis? I understood that it is the "contribution of PMF factor to Korg", but at the same time is it a way to read the general korg value? It is a bit confusing. Please correct.

Good point. The k_{org} trace presents the value of the parameter as a function of time of day. A secondary axis is added to the right to clarify this. Typos are also corrected.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 30835, 2014.

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