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Atmospheric Chemistry and Physics Discussions

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.

Anonymous Referee #1

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Review "On the link between hygroscopicity, volatility, and oxidation state of ambient and water-soluble aerosol in the Southeastern United States" by Cerully et al.

The manuscript reports the volatility (using thermodenuder at 60C, 80C and 100C), hygroscopicity (using CCN), and oxidation state (using AMS) of ambient aerosol and water-soluble ambient aerosol (aerosol processes via a PILS) for aerosol collected in a rural site in the Southeastern United States during the SOAS field campaign. The main results are: - PILS aerosols are representative of the PM1 average ambient aerosols composition. - The hygroscopicity of the organic fraction remaining in the aerosol after volatilization is found to decrease slightly. This could be attributed to the presence of

oligomers in the aerosol that dissociate into more volatile and more hygroscopic fragments upon heating. - The least volatile aerosol did appear to be the most oxidized. - The use of OSc is clearly shown as a preferred indicator for oxidation compare to O:C. Here correlation was only observed with OSc, while no clear correlation was seen between O:C with volatility or hygroscopicity. -Results of AMS 3-factor PMF analysis were used with more oxidized OOA (MO-OOA), Less-oxidized OOA (LO-OOA) and isoprene derived OA. The hygroscopicity properties of these 3 factor were evaluated and found to be Kappa_mo-ooa= 0.16; Kappa_lo-ooa=0.08 and Kappa_isoprene_OA=0.2.

I recommend the publication of the manuscript after correction of the following comments:

General comments:

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

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? 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 particulate matter”→paper

ACPD
14, C12302–C12307, 2015

providing parameterization between mz/44 and GF.

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?

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”

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

Line 19: “The PILS liquid. . .”→missing the debubbler (shown in figure 1) description in this 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)

Line 25: “To account for nebulizer e_ciency 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.

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

ACPD
14, C12302–C12307, 2015

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.

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.

P30847: Line 26: “than the non denuded PILS aerosol” Line 28: denuted 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 scater.

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

P30847-30850: Section 4.1 Authors could also discuss the effect of cooking the organic

ACPD
14, C12302–C12307, 2015

in the TD which could affect or not the kappa.

P30850: Line 24: Meyer et al. 2009

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”

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.

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?

P30852. Line 8: than 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.

Fig 5: “. . .the average for while. . .” Fig 6: It is missing the small colored dots in the two right panels. 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.

Suggested references: -Rosenfeld et al: Science 2008: Vol. 321 no. 5894 pp. 1309-1313 DOI: 10.1126/science.1160606 -Ristovski et al: Atmos. Chem. Phys., 10, 2919–2926, 2010, www.atmos-chem-phys.net/10/2919/2010/ -Duplissy et al, Atmos. Chem. Phys., 11, 1155–1165, 2011 www.atmos-chem-phys.net/11/1155/2011/

ACPD

14, C12302–C12307, 2015

doi:10.5194/acp-11-1155-2011 -Canagaratna et al. Chemical and microphysical characterization of ambient aerosols with the aerodyne aerosol mass spectrometer. Mass Spectrom. Rev. 2007, 26 (2), 185–222. - Dommen et al. 2006, GRL, doi:10.1029/2006GL026523, Laboratory observation of oligomers in the aerosol from isoprene/NOx photooxidation

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