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Interactive comment on “Laboratory studies of the chemical composition and cloud condensation nuclei (CCN) activity of secondary organic aerosol (SOA) and oxidized primary organic aerosol (OPOA)” by A. T. Lambe et al.

Anonymous Referee #1

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Lambe et al. describe experiment results using a Potential Aerosol Mass flow tube reactor and very high oxidant concentrations to study the oxidation of organic gaseous precursors to form secondary organic aerosol, and oxidation of primary organic aerosol (POA) to produce oxidized POA. An Aerosol Mass Spectrometer was used to characterize the oxygen:carbon and hydrogen:carbon ratios of the resulting aerosol, and aerosol hygroscopicity was measured using CCN analysis. An extensive set of experiments were carefully performed using appropriate methods, which are well described. The results help to address an important outstanding question regarding the range of

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oxidation and hygroscopicity that can be produced in organic aerosol through oxidative processing. The manuscript is well written overall. However, caution is certainly warranted in the attempt to link these laboratory results to the properties of realistic atmospheric aerosol particles. These experiments were conducted using oxidant concentrations (OH) at least 10,000 times higher than tropospheric concentrations of hydroxyl radical. The oxidant exposure was also conducted over very short time scales of about 100 seconds. These two factors have the strong potential to produce aerosol whose chemical evolution and composition does not resemble that produced by realistic atmospheric processes. Furthermore, the reductionist approach to the aerosol compositional analysis by discussing it only in terms of O:C and H:C ratios and PMF factors further limits the applicability of these experiments to the understanding of atmospheric behavior and the interactions of particles with clouds, as the authors attempt to suggest. It is dangerous to assume that OA particles produced at 5 orders of magnitude higher oxidant concentrations will have similar composition and other properties to tropospheric OA just because they have similar elemental ratios. I was also disappointed by the lack of details provided regarding chemical information that could be gleaned from the aerosol mass spectra, as only elemental ratios were reported. Little attempt was made to identify possible reaction products and thus mechanisms. The manuscript must be revised to address these and other issues outlined below before it can be reconsidered for publication in ACP. The subject matter is well within the scope of ACP.

General Comments

The f44 vs. f43 results presented in several figures clearly suggest that unit-resolution f44 and f43 data cannot be used to reliably derive elemental ratios of the organic aerosol component. High-resolution MS measurements are required to separate the isobars at these two nominal m/z values and resolve the contributions from less and more oxidized ion fragments (e.g. $C_3H_7^+$ vs. $C_2H_3O^+$). This deserves further discussion and reference to previous reports that have evaluated the reliability of using

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unit-mass AMS measurements to derive elemental ratios.

On a related note, it was not discussed which experiments used the C-TOF-AMS instead of the HR-TOF-AMS. As only the HR measurements appear to be reliable for determining elemental ratios, due to the overlapping ion fragments at m/z 43 and 44, this is an important issue that needs addressing. The C-TOF measurements are not clearly discussed in the text or indicated in the Tables or Figures. Were elemental ratios derived from these measurements? If so how do they compare with the HR measurements? The elemental ratios from C-TOF measurements would seem quite unreliable based on the data presented here.

The manuscript offers zero discussion of mass spectral features other than f_{43} and f_{44} to get insights into the products produced and their mechanisms. Other groups have used similar methods to learn a great deal about the products that form during oxidation of OA [e.g. George et al., 2008; Greishop et al., 2009; Tobias et al., 2000]. It is disappointing to see so little effort given here in this manuscript. Surely the HR-AMS can provide more chemical insight than just elemental ratios and PMF factor comparison? I can understand the desire to look for general trends when comparing so many different systems, but the analysis presented here is overly simplistic.

It is also not clear what the lower limit of measurable κ was here. This is determined by the dry particle diameters selected, and the CCN supersaturation range scanned. I would like to see data presented from the unoxidized POA precursors (elemental ratios, and an upper limit to their presumably small κ values) to see if this data extends the trends reported here, prior to oxidation, or not. There is also no mention of the aerosol size distribution produced during these experiments, or what diameters were selected for CCN analysis.

Specific Comments

Pg 13620, line 5: Should also include references to Jon Abbatt's work here.

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Pg 13623, line 8: The activated carbon denuder would also alter gas-particle partitioning of OA components. This should be discussed later in the paper, along with the important roles that partitioning play in these experiments. These are not adequately discussed at present. It is not clear what mechanisms the authors believe dominate the production of SOA/OPOA. Gas-phase oxidation followed by nucleation/condensation? Dynamic evaporation-oxidation-condensation cycles? Heterogeneous oxidation?

Pg 13624, line 5: Should make it clear that particle size was held constant while supersaturation was stepped through. What size particles were selected by the DMA for CCN analysis? The size distributions of the SOA, POA, and OPOA are never mentioned, what were they?

Pg 13624, Eq 1: This equation used to derive kappa is an approximate expression, as stated in Petters & Kreidenweis (2007): "If kappa > 0.2, then kappa alternatively can be calculated from paired sc – Dd values from the following approximate expression: [your Eq. 1]".

As you derive kappa values that are typically significantly less than 0.2 this approximation is not valid. Kappa values should be re-calculated from your Sc – Dd data pairs. There are tools freely available for this available here: <http://www4.ncsu.edu/~mdpetter/code.html>, including a spreadsheet that can be used to calculate kappa easily.

Pg 13625, line 29: I was surprised that the OH exposure was only varied by a factor of 20. In other work using the PAM the OH exposure has been one order of magnitude lower, $\sim 1E10$ molecules/cc. Why was a lower OH exposure not also tested here?

Pg 13626, line 2: You plot oxalic acid as an end point, do you detect ion fragments (Larger than m/z 44) indicative of oxalic acid or other carboxylic acids?

Pg 13627, line 12: A 50/50 mixture of α -pinene/naphthalene is hardly complex. Why weren't other, more complex mixtures explored? This would help to determine how

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atmospherically relevant these experiments are.

Page 13631, line 7: This explanation is confusing. A change in slope in Van Krevelen space indicates a change in reaction mechanism. If the same mechanism continues to replace one functional group with another then the slope would remain constant. From the data the former appears to be occurring – a change in reaction mechanism and products. This is an interesting finding that warrants much more detailed discussion.

Page 13632, line 13: More discussion of kappa values for the low O:C systems is warranted. For example, what is the kappa of unoxidized POA (such as lubricating oil)? Is it truly 0? Was is the lowest kappa value you could measure using your methods (dry diameter and CCN supersaturation range)?

Page 13632, line 19: It is true that HTDMA measurements tend to produce smaller kappa values than CCN measurements, and this is usually attributed to solubility arguments. If $k(\text{org})$ is larger for CCN measurements than HTDMA, and Jimenez et al. used HTDMA data while CCN data is used here, why is their slope of $k(\text{org})$ vs. O:C (0.37) more than double that presented here (0.17)?

Figure 7 warrants much greater discussion in general, particularly in terms of the low O:C measurements that lie well off the trend line. I am highly skeptical of a fundamental relationship existing between O:C and hygroscopicity. If you compare measured kappa for a variety of pure organics with similar O:C ratios you get a large spread in kappa. You can see this using the data in the Supplementary Information of Petters et al. (2009) which you have cited. For example, at O:C \sim 1.0, aspartic acid has kappa \sim 0.29 while xylitol has kappa \sim 0.16.

Page 13632, line 27: Only if the inorganics are soluble, which is not always the case.

Page 13633, line 5: The mixed glyoxal/ammonium sulfate experiments are confusing. A 50/50 mixed particle was oxidized by OH, which increased O:C but dramatically decreased the organic fraction? Please explain this more clearly.

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Page 13634, line 2: “Because ambient OOA contains organics from multiple precursors, the corresponding f44–f43 composition may provide information about OOA contributions from specific precursors.” I find this very hard to believe. In fact, Russell et al. (2011) recently reported that O:C ratios alone were not sufficient to characterize particle sources.

Page 13634, line 18: “the position of OOA in Van Krevelen diagrams may provide information about contributions from specific precursors.” While this would be nice I again find this highly doubtful as the analysis is overly simplistic and not supported by the presented data. This should be removed.

Page 13634, line 20: “The work presented here provides the most extensive evidence that κ_{org} depends on chemical composition.” This is an over-exaggeration and not strictly correct. First, chemical composition of the oxidized OA was not determined here. Only elemental ratios, which say nothing about structure or actual composition, were determined. Second, this is not the most extensive evidence. Petters et al. (2009) summarize hygroscopicity data from a wide variety of organic systems, for example. It is true that this work likely represents the most extensive set of hygroscopicity experiments on oxidized organic precursors (OOA & OPOA). The text should be clarified to reflect these issues.

Page 13634, line 23: I have significant problems with the parameterization of κ_{org} vs. O:C. First it treats particle properties as state functions, where only the final state (here O:C) matters, not the (reaction) pathway that was taken to reach the final state. I again question the atmospheric relevance of simulating oxidation of organic aerosol at more than five orders of magnitude higher OH concentrations, and very short exposure times. Second, the linear fit of κ_{org} vs. O:C has a significant amount of scatter, and data for low O:C systems fall well off the trend line. It is premature to claim that this fit can be extrapolated to realistically represent atmospheric aerosol hygroscopicity. While O:C may reflect the polarity of the organic compounds, it says nothing about structure or carbon chain length, which are also important param-

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eters in controlling organic component hygroscopicity.

Page 13634, line 25: “average molar volume” is a poor predictor of $\kappa(\text{org})$, as demonstrated by Petters et al. (2009).

Table 1: Please include data for unoxidized POA (BES, lubricating oil, and diesel fuel if this produced stable particles). κ for these systems is likely too low to determine; what is the lower limit of κ that can be derived using your method? This should be used to report an upper limit for κ for the POA (e.g. $\kappa(\text{org}) < x$).

Fig.6 : The y-axis scale should be narrowed so differences in the data can be seen more clearly. Hard to distinguish the open symbols. Figures are too small.

Fig. 7: Please explain what the grey box represents in the figure caption. Unoxidized POA should be included here as well to test if it follows the trend or not, even if a $\kappa(\text{org}) < \text{value}$ can only be estimated for those systems.

Fig. 8: Please list the $\kappa(\text{org})$ values used for O:C = 0.3 and 1.0 in the legend.

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