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Interactive comment on "Bulk and Molecular-Level Characterization of Laboratory-Aged Biomass Burning Organic Aerosol from Oak Leaf and Heartwood Fuels" *by* Claire F. Fortenberry et al.

Anonymous Referee #2

Received and published: 12 August 2017

This paper describes experiments and analysis examining the composition of fresh and aged aerosol emissions from volatilization/combustion of oak wood and leaf matter using powerful and novel analytical methods. The paper describes repeated experiments heating the biomass in a combustion chamber and sampling it via a Potential Aerosol Mass (PAM) reactor into a Thermal desorption Aerosol Gas Chromatograph – Mass Spectrometer (TAG), High-Res AMS and a SMPS. Emissions were sampled unaged and under two different PAM aging conditions. TAG data were analyzed in a number of ways, including for specific eluted compounds, positive matrix factorization of chromatograms, and analysis of chemical fragments from thermal decomposition of particles. These analyses are compared to more 'standard' analyses of bulk aerosol

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composition from the AMS. The suite of different approaches taken to analyze these data leads to a number of interesting and potentially important conclusions that will be of interest to the broad community interested in emissions from biomass burning and how they evolve in the atmosphere. For example, the emission of aliphatic aldehydes from leaf coating volatilization is nicely supported. The emission and evolution of components contributing mass at m/z60 in both TAG and AMS spectra receives special attention and evidence for contribution from components formed during oxidation to mass at m/z 60 is given. It does an especially nice job of spanning levels of chemical detail from compound-specific determination using the TAG, to PMF of tag chromatograms to point to compound classes, to the AMS measurements of bulk fragments.

Overall, this is a very nicely written and clear paper that makes an important contribution to understanding of a complex and important source of atmospheric aerosol. Therefore, I find it to be suitable for publication in ACP once my concerns are addressed. I have identified a number of points that, when addressed, will help the paper better fit into the existing literature on the topic.

Major points: While the analytical methods applied here are unique and provide strong insights, I have a concern about how these results can be compared to other 'forms' of biomass combustion, and so I think that more effort should be made to qualify/compare the types of emissions that were sampled. The emphasis in emission generation was clearly on repeatability and consistency, rather than on representativeness, which makes sense for these experiments. However, it would be helpful to put the OA studied here a bit more clearly in the context of 'biomass burning OA (BBOA)', which typically refers to ambient observations of biomass burning emissions emitted from a range of different fuels/types/combustion conditions. In this case, the nature of the 'combustion' that was the source of the sampled aerosols is someone unclear to me. Very small portions of biomass (0.2-0.5 g) were 'combusted' in the chamber, but it is not clear to me if flame was involved, or strictly smoldering, and so how the results might be compared to what might come from a fire. For example, flame typically produces

black carbon, was any generated here? The experiments are called 'devolatilization and combustion', but is there any way to classify this combustion more broadly or put it in the context of biomass burning more generally? If not, can anything be said about the representativeness of the emissions from this setup relative to other studies? The relative change in f60 for the study of Ortega et al. is shown in Fig. 16, but the chemical character of the OA is not compared to that measured in that or other studies, even of the same type of fuel. Several studies have shown that combustion phase/type can have a substantial effect on OA emission properties (Weimer et al. 2008; Reece et al. 2017) and as you noted, observations of SOA production in lab and field studies have been found to be highly variable and distinct. Therefore, to the extent that you can include information about your combustion and the basic characteristics of your emissions, it will enable comparison with existing measurements and analysis.

In a similar vein, one of the motivations discussed for the use of the PAM was to understand SOA production, but this is never discussed in the paper, though some evidence is presented in Table S2 that there is SOA production for the wood experiments but not for leaf experiments. These outcomes are of interest in the context of the variability in SOA production discussed above, but also because they may influence interpretation of the 'relative to unaged' presentation of data that is used in a number of figures (e.g. Fig. 3, 16). For example, are changes in fragments/compounds due to 'dilution' of primary OA by SOA, or strictly due to gas-phase or heterogeneous oxidation? This is mentioned in the paper's final paragraph, but it seems at least some further evidence/data could be presented.

The authors rightly point out that the operation of the PAM during experiments was not fully constrained by the SO2 calibration of integrated OH exposure, but then in the paper use quite tightly constrained values (3.4 and 9.8 days) of equivalent oxidation to describe the aging under the two operation conditions. The fact that there are repeated experiments and repeatable results is great (and difficult to do for biomass burning) and suggests that aging within an experiment tyep should be consistent. However,

your 'sensitivity' analysis (Table S1) shows that actual OH exposure estimates for your experiments may vary by a factor of 5 to 10 given the assumed range of external OH reactivities. Therefore, it seems strange to specify your aging conditions to such a precise degree. I would feel more comfortable if a range of days were reported or if you can find a way to estimate OH reactivity during your experiments (e.g. using published VOC profiles and a tracer ratio?) to better constrain this. At the very least, uncertainty in this value should be clearly stated when it is discussed (e.g. in the context of Table 1), so that the values given are not over-interpreted.

Specific points

Page 4; Line 138 - Initially it was unclear to me whether this heading referred to separate experiments or one type. As noted above, more of an effort should be made to describe/qualify the approach taken and how the resultant emissions compare to what might come from a fire. In addition, it would make sense to be clear and consistent when using 'BBOA' in the context of your experiments.

Page 5; Line 165 - Was level of external O3 injection always the same?

Page 6; Line 194-195 - As noted above, this uncertainty should be reflected in estimated atmospheric ages used throughout paper.

Page 7; Line 234-235 - Also related to combustion emission properties. Why are SMPS volumes used and not AMS OA concentrations? For example, if there is a contribution from BC, this will both effect the determination of OA mass by adding to volume, and also potentially affecting DMA sizing. This may not be an issue, but could at least compare AMS OA to SMPS volume?

Page 9; Line 298 - Need to be clear that this is referring to relative abundance - important if SOA production is 'diluting' primary species.

Page 9; Line 296 - I noted this included in Supplemental tables, but it might be helpful to translate to effective saturation concentration.

Page 9; Line 299 - Where possible (e.g. Fig 3),would be best to include error bars to show inter-test variability. You have done this in some places, but would be good to see it here.

Page 10; Line 323-324 - These don't seem to be fully depleted -seems to be 50-100% of relative abundance at the start?

Page 12; Line 412-413 - A useful comparison to quantify inter-test variability might be to do this calculation on repeated experiments at same loading. E.g., what are dot products between repeated tests at same conditions that are averaged together for other analyses?

Page 13; Line 425 - Isn't really clear if this is indicating an increase in the presence of material containing mz44 that can thermally decompose or an increase in thermal decomposition?

Page 13; Line 431 - As noted above, to be most useful, this should be placed in the context of other BBOA measured by AMS. How do these numbers compare to those measured in other studies - e.g. Ortega et al, 2013, Reece et al, 2017

Page 13; Line 433-436 - Significant figures not justified (or, really, linear regression advised) for 3 data points unless there is a very strong argument for there being a linear relationship

Page 13; Line 439 - It seems as or more plausible that fragmentation leads to move volatile species that aren't captured by the TAG?

Page 15; Line 504-505 - This is a good point, but here the distinction may be as much type of emission/combustion as type of biomass, as it appears that at least some OA is from volatilized leaf coating so is not 'burned' (for leaf e.g. Fig. S7)

Page 15; Line 511-513 - If possible, it would be helpful to quantify (even approximately) the relative amount of material contributing m/z 60 in the compound window vs decom-position window. I take it there is more in the former? The AMS will presumably see a

weighted average of the two?

Page 17; Line 563 - OH suppression will likely be dominated by what is in the gas phase and total OHR may be very different for two types (see above comment about uncertainty in actual OH exposure.

Page 18; Line 608-609 - No mention of relative enhancement of OA and so how much condensation versus oxidation drives changes in relative contribution from different components.

Minor points

Page 7; Line 219 - data were, not data was

Page 14; Line 461 - I think I know what 'triplicate averages' is meant to say, but can be said more clearly.

Page 15; Line 508 - I think 'distinct' would work better than 'unique'.

Page 15; Line 506-507 - Would be good to point to Fig. 16 here.

Page 17; Line 578-579 - Not sure if a species can be called a 'tracer' (for a primary source) if it is increasing w/ atmospheric processing. At the very least, it's not a tracer of a unique source.

References

Reece, S. M., Sinha, A., and Grieshop, A. P. (2017). "Primary and photochemically aged aerosol emissions from biomass cookstoves: chemical and physical characterization." Environmental Science & Technology. DOI: 10.1021/acs.est.7b01881

Weimer, S., Alfarra, M. R., Schreiber, D., Mohr, M., Prévôt, A. S. H., and Baltensperger, U. (2008). "Organic aerosol mass spectral signatures from wood-burning emissions: Influence of burning conditions and wood type." Journal of Geophysical Research: Atmospheres, 113(D10), D10304.

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