

RESPONSES TO REVIEWER 2

Reviewer comments are italicized; author responses are in normal font.

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 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/z 60 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.

We thank the reviewer for his/her insight. We address each comment individually below (the reviewer’s major and minor points have been numbered for ease of reference). Where appropriate, approximate line numbers corresponding to the edited (with markup) manuscript provided, along with line numbers relative to the section/paragraph number.

Major points:

[1] *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 authors agree this point is important to clarify for future comparisons of lab and field observations. To provide better context for the type of emissions sampled here, we expanded the description of the devolatilization and combustion process in the Materials and Methods section. Specifically, while we had previously specified that smoldering combustion was observed only in the final minute of the heat ramp, we now also clarify that no flaming combustion occurred during any of the experiments (lines 153-154; Section 2.2, Paragraph 2, Lines 5-6)

We also provide a more thorough discussion of the influence of combustion conditions on the relevance of our measurements to real world systems. We provide more detailed discussion in the Conclusion section of the main text (lines 737-748; Section 4, Paragraph 3):

“Based on previous studies, combustion conditions are expected to significantly impact the chemical composition of both primary and secondary BBOA (Ortega et al., 2013; Reece et al., 2017; Weimer et al., 2008; see “AMS Chemical Characterization” in Supplemental Information). The resistive heating technique applied in these experiments allows for the isolation of devolatilization (pre-combustion) and low-temperature ($\leq 300^{\circ}\text{C}$) smoldering conditions, which is difficult to achieve in combustion chambers that require ignition of a flame. For example, Tian et al. designed a chamber that allows the user to control the relative contributions of smoldering and flaming combustion, though smoldering combustion is only achieved in this chamber following the introduction of a flame to the biomass fuel (Tian et al., 2015). The devolatilization and combustion procedure presented here is thus advantageous for investigating aerosol from small masses of biomass fuel under tightly controlled conditions. However, these results alone are likely not representative of many real-world fire systems, where smoldering combustion often occurs alongside flaming combustion. Our results may therefore serve to complement field measurements, where either smoldering or flaming combustion may dominate, as well as laboratory studies where combustion conditions are controlled.”

In addition, we have added a new section in Supplemental Information (“AMS Chemical Characterization”; see response to Major Comment #2) in which we compare AMS chemical composition to relevant data reported in literature.

[2] *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 addition to expanding the description of the devolatilization/combustion characteristics (see major comment #1), we have reviewed the recommended sources and now discuss them in our expanded analysis. To more thoroughly compare the chemical character of the OA produced here to previous measurements, we have added a section to the Supplemental Information titled “AMS Chemical Characterization.” This section includes the following figures:

- An average AMS mass spectrum for each fuel at each level of oxidation, as well as difference mass spectra (Figure S13)
- A van Krevelen plot for both heartwood and leaf BBOA (Figure S14)
- Total organics, potassium, and sulfate concentrations (Figure S15)

In this section, we discuss the impact of combustion techniques and conditions on the chemical composition of both aged and unaged oak BBOA, contextualizing our results with information from previous studies. We refer to this section in the manuscript in lines 336-339 (Section 3.1, Paragraph 2):

“According to AMS mass spectra, the BBOA measured in these experiments is chemically consistent with BBOA from similar oak fuel sources, though with key differences related to combustion conditions (Cubison et al., 2011; Ortega et al., 2013; Reece et al., 2017; Weimer et al., 2008). Detailed analysis and contextualization of the AMS chemical composition data is provided in Supplemental Information (Section: AMS Chemical Characterization).”

[3] *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.*

Decoupling effects of SOA formation from other processes occurring in the PAM reactor remains challenging and is the subject of ongoing study. However, we have added discussion of the potential relative contributions of other mechanisms (e.g. gas-particle partitioning and heterogeneous vs homogeneous reactions) for certain key species. We address each of these changes below:

- In lines 390-401 (Section 3.2.1, Paragraph 3), we use gas-phase reaction rate constants from literature (Kwok and Atkinson, 1995) to justify the assumption that gas-phase reactions contribute little to overall trends in oak leaf tracer compounds.
- Similarly, in lines 407-411 (Section 3.2.1, Paragraph 4, Lines 6-10), we use the literature-reported sinapaldehyde/OH gas phase reaction rate constant (Lauraguais et al., 2015) to justify the assumption that sinapaldehyde decay occurs primarily in the particle phase.
- We calculated approximate particle-phase partitioning fractions (Table S12) for levoglucosan in both heartwood and leaf BBOA and include an expanded discussion of levoglucosan phase partitioning in lines 680-694 (Section 3.4, Paragraph 8).
- We evaluated phase partitioning for syringol, syringaldehyde, and vanillin, species in the heartwood BBOA that increase in abundance with photochemical aging (e.g. those that may be formed through secondary processes). These calculations are discussed in lines 415-431 (Section 3.2.1, Paragraphs 5-6).

[4] *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 type 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.*

This is an excellent comment, and the authors have considered thoroughly the best way to handle this point. To better constrain the equivalent aging times characteristic of our system, we conducted additional experiments to estimate total gas-phase OHR_{ext} . A full description of these experiments is provided in Supplemental Information (“Methods: PAM Calibrations and Equivalent Aging Estimations, “Estimation of External OH Reactivity (OHR_{ext})”). In the main text, we discuss these experiments briefly in lines 191-218 (Section 2.3, Paragraphs 3-6).

In these experiments the burn procedure was repeated for both leaf and heartwood fuels, and CO was measured using a trace-level CO monitor. Aerosol was sampled alternately through the PAM reactor and through a bypass line to obtain CO measurements for aged and unaged emissions. During these experiments, the PAM light settings corresponded to approximately 3 equivalent days of aging according to the most recent offline calibration.

With this method, we found that in both types of BBOA, aged and unaged CO concentrations exhibited little variation, giving OHR_{ext} values of 0.56 and 0.52 s^{-1} , respectively. To estimate total OHR_{ext} , we took the reviewer’s suggestion and estimated typical emissions by scaling published VOC profiles from laboratory studies of oak forest emissions (Burling et al., 2010) to our measured CO concentrations. Using rate constants from the NIST Chemical Kinetics Database, we obtained OHR_{ext} for each relevant species, and, taking the sum of all calculated species-specific OHR_{ext} , obtain a total OHR_{ext} of 2.21 s^{-1} and 2.17 s^{-1} . We therefore use 2.2 s^{-1} in subsequent estimations of OH_{exp} and equivalent aging time ranges.

In addition, to better inform our use of the Oxidation Flow Reactor Exposure Estimator tool, we measured reactor-produced O_3 with no external O_3 addition and report the measurements in the supplemental information (Table S1). Based on these data, and assuming an OHR_{ext} of 2.2 s^{-1} , we obtain a lower limit for equivalent aging times at each level of oxidation, which we provide in Table 1. We retain the OH_{exp} values calculated from the offline SO_2 calibration as the upper limits for each oxidation condition, but we reduce the significant figures in the corresponding equivalent aging times from two to one.

Specific points

[5] 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.

To better qualify our experimental setup and approach, we have added expanded discussion of the combustion characteristics of our procedure, contextualizing our results with data from previous studies (see Major Comment #1)

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

Yes, the level of external O₃ injection was consistent. In all experiments, we passed 0.4 L min⁻¹ of oxygen through the lamps, which were held at a constant intensity (lines 171; Section 2.3, Paragraph 1, Line 7).

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

We thank the reviewer for this suggestion and believe we have addressed his/her concerns above (see Major Comment #4.)

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?

We used SMPS volumes rather than AMS total OA concentrations because we did not obtain satisfactory AMS data during the first set of TAG experiments (lines 509-521; Section 3.3, Paragraph 2). We do agree that normalizing to AMS total organic concentrations would otherwise be more appropriate, and we plan to do so where possible in all future experiments.

We have provided a table in supplemental information (Table S3) with total organic concentrations alongside co-measured SMPS volume concentrations.

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

As suggested, we have modified the sentence to specify that this is a relative abundance (lines 376-377; Section 3.2.1, Paragraph 2, Lines 4-5):

"Nearly all compounds identified after 35 minutes decrease in relative abundance with photochemical aging."

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

As requested, we have added this information into the main text (now lines 368-371; Section 3.2.1, Paragraph 1, Lines 9-10):

"Based on even-numbered alkane standard injections, compounds eluting after minute 35 exhibit approximate saturation vapor pressures not exceeding that of docosane (approximately 2.73×10^{-5} torr at 25°C), which corresponds approximately to $\log_{10}(C^*) = 2.76$ "

We also include saturation concentration values in our discussion of oak heartwood compound volatilities (lines 403-405; Section 3.2.1, Paragraph 4, Lines 2-4):

“Based on even alkane standard injections, compounds eluting within this time window exhibit approximate vapor pressures within 4.52×10^{-3} - 2.73×10^{-5} torr at 25°C ($\log_{10}(C^*) \approx 4.85$ - 2.76 ; Table S4 in Supplemental Information; ACD/Labs, 2017).”

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.

We thank the reviewer for the suggestion. We initially tried including error bars in this figure, but found that it made the figure difficult to read. For this reason, we included raw chromatographic abundances and errors in the supplemental information (Tables S6 and S7). We now refer the reader to these tables in the caption of figure 3.

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

We have changed “fully depleted” to “depleted” in this sentence (line 417; Section 3.2.1, Paragraph 5, Line 3).

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?

We thank the reviewer for the suggestion. We have repeated the procedure and provide the results in supplemental information (Table S9).

Page 13; Line 425 - Isn't really clear if this is indicating an increase in the presence of material containing m/z44 that can thermally decompose or an increase in thermal decomposition?

While this is an interesting question, the temperature cycle is consistent from run to run and any change in this signal would be due to a combination of the type of material present and the associated thermal decomposition potential of that material. It has been shown in past work that this signal correlates best with oxygenated OA concentrations (Williams et al. 2016). With the lack of adequate standards, we do not know the relative decomposition potential of all types of OA, and include this point in our discussion of the need for standard calibrations in the Conclusions section of the manuscript (lines 766-774; Section 4, Paragraph 6).

The text has been updated to reflect this point (lines 534-538; Section 3.3.1, Paragraph 1, Lines 12-16):

“For both types of BBOA, the decomposition m/z 44 integrated signal increases overall from 0 days to 6-10 days of equivalent aging, indicating an increase in OA material that can thermally decompose with increased PAM oxidation. This trend is consistent with relative increased decomposition of highly oxidized aerosol within the PAM reactor, as was also indicated in previous ambient aerosol observations (Williams et al., 2016).”

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

We thank the reviewer for this suggestion and believe that we have addressed his/her concerns (see Major Comment #3).

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

In general, we agree with the reviewer, and we reduce the number of significant figures in our regressions to 1. We retain the linear regression because we feel that it serves as a useful comparison between trends in leaf and heartwood BBOA m/z 44 signals.

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

Implicit in this explanation is that the TAG does not capture the highly volatile products of fragmentation. We have modified the sentence to clarify this point (lines 547-551; Section 3.3.1, Paragraph 2, Lines 6-10):

“The non-linear trend in TAG decomposition m/z 44 for leaf BBOA may indicate a shift in the dominant oxidation mechanisms between moderate and high levels of OH within the PAM chamber; at the highest OH_{exp}, primary gas and/or particle-phase components may undergo increased fragmentation, leading to a net decrease in production of the aged OA that thermally decomposes during TAG analysis, along with an increase in highly volatile fragmentation products that are not 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)

We have modified this point to acknowledge the role that combustion characteristics play in measured m/z 60 (lines 621-623; Section 3.4, Paragraph 2, Lines 10-12):

“Additionally, the presence of m/z 60 is likely dependent on the combustion characteristics, as combustion processes can influence the emission and phase of different compounds.”

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 decomposition window. I take it there is more in the former? The AMS will presumably see a weighted average of the two?

We thank the reviewer for this suggestion. We have quantified relative m/z 60 abundances as percentages for both compound and decomposition window signals and provide them in a separate supplemental table (Table S11). Based on these calculations, the AMS likely does measure an approximately weighted average of the two signals, which is displayed in figure 12 (was figure 16 previously).

Minor points

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

“Data was” has been changed to “data were” in this sentence (line 275; Section 2.4.1, Paragraph 3, Line 1) and in subsequent occurrences.

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

We have modified this sentence for clarity (Lines 524-526; Section 3.3.1, Paragraph 1, Lines 2-4):

“At each oxidation condition, SICs from the triplicate chromatograms were blank subtracted, normalized to maximum volume concentrations, and averaged to obtain the displayed trace.”

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

As suggested, “unique” has been replaced with “distinct” in this sentence (line 627; Section 3.4, Paragraph 3, Line 4).

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

We now reference figures 11 and 12 (figure 12 was figure 16 previously) in line 626 (Section 3.4, Paragraph 3, Line 3).

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.

We have replaced “tracers” with “components present in freshly-emitted BBOA” in this sentence (line 723; Section 4, Paragraph 1, Line 6).

Literature Cited:

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