

RESPONSES TO REVIEWER 3

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

Fortenberry et al. present chemical composition measurements of photochemically aged laboratory biomass burning organic aerosols (BBOA). BBOA was generated from the combustion of oak leaves and oak wood samples in a burn chamber, then exposed to OH radicals in a Potential Aerosol Mass oxidation flow reactor. Ensemble aerosol mass spectra were obtained with an AMS, and GC-MS samples were obtained with a TAG. The authors used factor analysis to identify characteristic groups of GC effluent signals that behaved differently as a function of OH exposure. In my opinion, the manuscript presents an interesting experiment and application of the measurement techniques that were used to mimic aging of BBOA surrogates. Publication in ACP may be appropriate after consideration of my comments below.

We thank the reviewer for his/her insight and address each comment individually below. Where appropriate, approximate line numbers corresponding to the edited (with markup) manuscript provided, along with line numbers relative to the section/paragraph number.

General/Major Comments

1. *Given the goal of using TAG measurements to interpret ensemble/bulk techniques such as the AMS, and given the large number of oxygenated/polar compounds present in BBOA (and oxidized BBOA), it wasn't clear to me why the authors chose not to incorporate the online derivatization technique used in previous TAG measurements (Isaacman et al., 2014), which reports "complete derivatization of [...] alkanolic acids, polyols, diacids, sugars, and multifunctional compounds." In principle, derivatization should offer the following advantages:*
 - a. *improved recovery of methoxyphenols, levoglucosan, and other sugars and primary species that are measured in this work, along with potentially less significant matrix effects (see Comment #2).*
 - b. *recovery of oxidation products formed following OH exposure in the PAM reactor (e.g. dicarboxylic acids) that were not resolved here.*
 - c. *evaluation/supplementation of the thermal decomposition window because the TAG recovery and resolution of highly polar compounds is still low, as implied by discussion in L441-L454 (see Comment #16) and L493-L494. The authors should explain in the manuscript why they chose not to incorporate/adapt the TAG derivatization technique published by Isaacman et al.*

Although online derivatization would provide several advantages for measuring both primary and secondary BBOA components, the derivatization technique used in Isaacman et al., 2014 was not used in these experiments for multiple reasons. First, this derivatization technique was developed for a metal filter collection cell and has not been successfully adapted for the impaction CTD cell featured on our system. In fact, the thermal decomposition window is not available when derivatizing since the derivatization agent needs to be purged from the cell and derivatized molecules are refocused on a secondary trap. Through this process, any decomposing material is also purged. Additionally, derivatization may complicate the identification of unknown compounds by altering mass spectral fragmentation patterns. Finally, not all compounds derivatize with 100% efficiency, further complicating quantification efforts. Further study may incorporate evaluation of the metal filter cell and online derivatized measurements to complement decomposition window analysis.

As requested, we briefly address the lack of derivatization in the manuscript in lines 267-274 (Section 2.4.1, Paragraph 2):

“The TAG system developed by Isaacman et al. features an online derivatization technique designed to improve analysis of oxidized species, including methoxyphenols, levoglucosan, and other compounds unique to BBOA (Isaacman et al., 2014). Although this technique presents multiple analytical advantages, it was developed for a metal filter collection cell and is not suitable for the impactor-style CTD cell used in these experiments. We chose to use the impactor-style CTD cell to allow analysis of the thermal decomposition

window, since other collection cells purge this material when transferring to a secondary trap. Additionally, we were interested to identify new molecular marker compounds that could be associated with these source types. We therefore performed all experiments without sample derivatization prior to chromatographic analysis.”

2. *The TAG recovery of the selected tracers is potentially influenced by BBOA matrix effects, which could be either positive or negative in magnitude. Using a different TD-GC/MS system, Lavrich and Hays et al. (2007) showed that the thermal extraction of large PAHs from a soot matrix was hindered. Using a TAG system, Lambe et al. (2010) showed that the recovery of a C₃₀D₆₂ alkane internal standard in a lubricating oil matrix increased by a factor of 2-3 as a function of matrix loading. Matrix effects may be even more significant for the polar analytes measured in BBOA (e.g. methoxyphenols and sugars). Without application of representative internal standards for at least a subset of experiments, in my opinion the authors cannot unambiguously rule out the contribution of matrix effects. For example, in Fig. 3b, the authors show an increase in the abundance of vanillin, syringol, and syringaldehyde when the OH exposure in the PAM reactor is increased to 2-3.4 days. In the manuscript, a plausible formation mechanism for vanillin was provided (Figure S8). The increase in vanillin, other methoxyphenols, and other tracers (including the integrated m/z = 44 SIC) that display similar behavior could also be due to higher concentrations of desorbed primary or secondary organic aerosols that adsorbed onto active sites in the TAG sample transfer path, e.g. the effect observed in Lambe et al. (2010). At the least, the discussion should be revised to acknowledge that the above scenarios can plausibly explain the observed trends regarding increase and decrease in abundance as a function of OH exposure. A more convincing response – which may prove the above hypotheses incorrect – would be to repeat one or two of the combustion experiments, while manually spiking each collected TAG sample with an appropriate set of isotopically labeled standards. For example, there are sugars that are readily available with a range of levels of deuterium-substitution, and I also found suppliers of vanillin-5-d1 and isovanillin-2,5,6-d3.*

We thank the reviewer for this insight. While we acknowledge that the impacts of matrix effects cannot be unambiguously ruled out for our experiments, we do not think that the effects observed by Lambe et al. cited by the reviewer can adequately explain our findings.

Lambe et al. observed a two-fold increase in C₃₀D₆₂ TAG responses with motor oil co-injected over a range of 0-60 µg, possibly due to greater competition for active sites in the TAG sampling system with greater masses of organic matter (i.e. the motor oil). They also found that uncertainties in TAG responses were large throughout these experiments, and that the effect varied depending on the tracer compound (e.g. the size of the tracer molecule) tested. From SMPS estimated maximum mass concentrations (assuming a typical BBOA density of 1.2 g m⁻³; e.g. Li et al., 2015), we estimate that for each experiment, the TAG collected total particle masses ranging from 6-16 µg for leaf BBOA and 22-36 µg for wood BBOA.

Based on the high replicability of our TAG measurements between triplicate experiments within a fuel type and the small ranges of collected masses (relative to 0-60 µg motor oil), we do not expect the effect reported in Lambe et al. to explain the trends observed in our TAG data, especially the eight-fold increase in vanillin abundance. Additionally, based on the results from the previous work cited by the reviewer, we expect matrix effects to be more significant for components with very high molecular masses, e.g. large PAHs and long-chain alkanes, and less so for smaller compounds like syringol, syringaldehyde, and vanillin.

However, we do agree that the influence of matrix effects should be investigated further to rule out bias in future experiments. Unfortunately, due to time and resource constraints, we were not able to conduct the suggested tracer tests, but these will be incorporated into future combustion experiments. We have therefore added a brief discussion of potential matrix effects to the manuscript (lines 749-759; Section 4, Paragraph 4):

“Future work will focus on characterizing sources of bias to improve quantification of material in both the TAG compound and decomposition window. For example, particle matrix effects, whereby certain compounds exhibit enhanced or diminished recovery due to the presence of a particle matrix, have been reported to influence compound responses in previous work with the TAG and other thermal desorption GC systems, particularly for large molecular weight compounds (Lambe et al., 2009; Lavrich and Hays, 2007). Lambe et al. quantified this effect for the TAG by co-injecting a constant C₃₀ deuterated alkane standard with 0-60 µg motor oil and found that the presence of the motor oil matrix enhanced recovery of the standard by a factor of 2-3 (Lambe et al., 2009). In these experiments, the TAG collected estimated ranges of 6-16 µg particles for leaf BBOA and 22-36 µg particles for heartwood BBOA. Based on these mass ranges, we do not expect these matrix effects to contribute significantly to our results, especially for the lower molecular weight compounds. However, future work will incorporate an evaluation of matrix effects to minimize bias in TAG measurements.”

3. *Aerosol loadings corresponding to primary BBOA, oxidized BBOA, and/or SOA formed from oxidation of VOCs/IVOCs in the PAM reactor are not presented. In my opinion this data should be added to provide information about (1) the magnitude of SOA formation and corresponding SOA-to-BBOA ratio (2) phase partitioning of the selected biomass burning tracers. For example:*
 - a. *C23, C25, C29 alkane signals decrease ~60%, ~70%, and ~75% following 9.8 days aging time (Fig. 3a). At an OH exposure of ~1.1E12 molec/cm³ /sec (8.5 days), Smith et al. (2009) observed ~70% decay of squalane particles subjected to heterogenous oxidation by OH. Thus, the observed C23, C25, & C29 decay rates are broadly consistent with heterogenous oxidation in the condensed phase. On the other hand, if the same compounds were oxidized in the gas phase, the observed decay rates should be much faster because the reaction is no longer rate-limited by diffusion of OH to the particle surface. Applying estimated gasphase OH rate constants of 2.9E-11, 3.2E-11, and 3.8E-11 cm³/molec/sec, for C23, C25, C29 alkanes (Kwok and Atkinson, 1995) suggests that ~100% of the alkanes should be reacted at only 3.4 days' OH exposure if the reaction occurs in the gas phase. Information about the experimental partitioning of this tracers would provide context for interpreting the observed decay rates.*

We are grateful to the reviewer for providing this insight. We agree with the reviewer's analysis of C23, C25, and C29 partitioning, though using the information provided in Kwok and Atkinson, 1995, we obtained slightly different gas-phase OH reaction constants. Still, we found the overall conclusion to be the same: if these compounds were reacting in the gas phase only, they would be entirely depleted at 3 days of equivalent aging. Using parameters from Kwok and Atkinson's work, we also performed a similar analysis to evaluate the gas-phase kinetics of the long-chain aldehydes identified in the leaf BBOA. These findings have been summarized in the manuscript in lines 390-401 (Section 3.2.1, Paragraph 3):

“Literature information available for hydrocarbon particle- and gas-phase OH kinetics indicates that the trends observed in leaf BBOA alkanes and aldehydes with OH_{exp} are consistent with heterogeneous OH oxidation. For example, Smith et al. report approximately 70% decay of squalane (a C₃₀ branched alkane) particles when exposed to an OH_{exp} of 1.1×10^{12} molec cm⁻³ s⁻¹ (8.5 days of equivalent aging; Smith et al., 2009), a figure approximately consistent with the observed C₂₉ alkane decay of 75% at 6-10 days of equivalent aging. Additionally, based on parameters provided by Kwok and Atkinson, gas-phase OH reaction rate constants at 298K are estimated to be 2.5×10^{-11} , 2.7×10^{-11} , and 3.1×10^{-11} cm³ molec⁻¹ s⁻¹ for C₂₃, C₂₅, and C₂₉ alkanes, respectively (Kwok and Atkinson, 1995). Taking these rate constants into account, if purely gas-phase chemistry is assumed, all three alkanes would react nearly 100% before 1-3 days of equivalent aging. A similar analysis on relevant aldehydes gave estimated gas-rate constants of 2.5×10^{-11} , 2.8×10^{-11} , and 3.0×10^{-11} cm³ molec⁻¹ s⁻¹ for C₂₄, C₂₆, and C₂₈ aldehydes, respectively (Kwok and Atkinson, 1995), which in all cases would lead to complete depletion by 3.4 days of equivalent aging if gas-phase chemistry is assumed.”

- b. *Levoglucosan signal decreases ~80% following 9.8 days aging time (Fig. 16). The authors reference literature rate constants of $3.09E-13$ cm³/molec/sec and $1.1E-11$ cm³/molec/sec. The levoglucosan decay rate reported in this paper is somewhere in between the referenced literature values. Is it possible that some of the discrepancy is related to phase partitioning? This is alluded to near the end of the paper (L558-L571), but it wasn't clear to me why the authors didn't explore this further by calculating the levoglucosan phase partitioning in the oak leaf and 3 oak wood experiments and comparing to phase partitioning in the literature studies.*

We thank the reviewer for this insight. Per the reviewer's suggestion, particle-phase fractions for levoglucosan were calculated based on AMS total organic concentrations (C_{OA} , $\mu\text{g m}^{-3}$) and levoglucosan effective saturation concentrations (C_{LG} , $\mu\text{g m}^{-3}$) based on previous work (Donahue et al., 2006). The equation used to calculate partitioning is now included as equation 1 in the main text. We discuss these calculations and the relative contribution of phase partitioning to our results in lines 680-694:

“While levoglucosan decays rapidly in the leaf BBOA with increasing OH_{exp} , levoglucosan in the wood BBOA is depleted more slowly. Levoglucosan is classified as semivolatile (at 25°C, $p_L^\circ \sim 1.81 \times 10^{-7}$ torr; ACD/Labs, 2017) and is therefore expected to partition between the gas and particle phases. To approximate phase partitioning, particle-phase fractions for levoglucosan (ξ_{LG}) were calculated based on AMS total organic concentrations and effective saturation concentrations (C_{LG}^* , $\mu\text{g m}^{-3}$) using equation 1. The resulting values and relevant parameters are reported in Table S12. For each fuel, little variance is expected in levoglucosan particle-phase fraction between oxidation conditions, so we conclude that phase partitioning is unlikely to be driving trends in levoglucosan abundances observed in these experiments. Based on the partitioning approximations, the leaf BBOA is expected to contain a higher percentage of levoglucosan in the particle phase than the heartwood BBOA ($91.1 \pm 1.65\%$ vs $77.8\% \pm 2.26\%$), though in both cases, gas-phase levoglucosan concentrations are likely to remain low. The prevalence of levoglucosan in the particle phase during photochemical aging is consistent with previous laboratory measurements of aged levoglucosan particles (Kessler et al., 2010). Considering that heartwood BBOA exhibited lower total organic concentrations than the leaf BBOA, the slower depletion of levoglucosan in the heartwood samples is perhaps consistent with OH suppression effects, wherein OH experiences increased reactivity with gas-phase species at the particle surface.”

- c. *Increased condensed-phase partitioning of vanillin and other methoxyphenols following potentially significant SOA formation after ~3.4 days aging time ($\sim 4.4e11$ molec/cm³*sec) might explain their increase in concentration from 0 to 3.4 days' oxidation. At this approximate OH exposure, the “peak” SOA yield from oxidation of a specific precursor has been observed in previous studies, e.g. Lambe et al. (2012), Ortega et al. (2016). Although vanillin is relatively volatile, without knowing the aerosol loadings and ensuing partitioning, one can hypothesize plausible scenarios to explain some or all of the effect observed in Figure 3b. I encourage the authors to expand their discussion to analyze the observed tracer decay rates in the context of the expected phase partitioning. They already report calculated C^* 's, which, together with the aerosol loadings provided by AMS, facilitate this discussion. While I don't view it as the authors' responsibility to resolve the discrepancy in reported levoglucosan decay rates, it would certainly increase the impact of the paper if a plausible explanation is possible (L533-L549).*

In addition to expanding discussion on levoglucosan phase partitioning (see above comment), we evaluated phase partitioning of relevant methoxyphenols (syringol, syringaldehyde, and vanillin) using AMS total organic concentrations and effective saturation concentrations. In doing so, we determined that under standard conditions, all three methoxyphenols are expected to exist almost exclusively in the gas phase (Table S12). We therefore agree with the reviewer's suggestion that increased SOA formation with oxidation may be driving these compounds into the particle phase.

The following discussion has been added to the main text (lines 420-431; Section 3.2.1, Paragraphs 6-7):

“To examine the potential impacts of phase partitioning for these compounds, particle-phase fractions for syringol, syringaldehyde, and vanillin (ξ_i) were calculated based on AMS total organic concentrations (C_{OA} , $\mu\text{g m}^{-3}$) and effective saturation concentrations (C_i^* , $\mu\text{g m}^{-3}$) using the basic partitioning equation (Donahue et al., 2006):

$$\xi_i = \left(1 + \frac{C_i^*}{C_{OA}}\right)^{-1} \quad (1)$$

Resulting particle-phase fractions are tabulated in supplemental information (Table S12). Based on these approximations, syringol, syringaldehyde, and vanillin are expected to partition primarily to the gas phase. For these compounds, the increase in abundances at low-mid levels of oxidation could therefore result from increased SOA formation driving these compounds into the particle phase. This observation is consistent with previous measurements where maximum SOA concentrations were observed at similar levels of OH_{exp} for aerosol generated from oxidation of a single precursor (Lambe et al., 2012; Ortega et al., 2016).”

4. *Photobleaching of biomass burning particles has reported in previous literatures studies, e.g. Zhao et al., ACP, 2015; Wong et al., ES&T, 2017. The authors should discuss the potential role of 254 nm photolysis in these experiments, especially in regard to degradation of condensed-phase aromatic species that strongly absorb 254 nm radiation and react relatively slowly with OH due to diffusion limitations. Were control experiments conducted with 254 nm radiation (no 185 nm radiation) and no ozone addition to investigate whether photolysis induces changes in BBOA composition?*

We did not perform control experiments with only 254 nm radiation, but will do so in future experiments. We agree with the reviewer that more attention should be given to the potential contribution of 254 photolysis and diffusional effects. We therefore provide further discussion to contextualize our results (lines 224-230; Section 2.3, Paragraph 8):

“Photobleaching of BBOA, particularly at 254 nm, has been reported in previous literature (e.g. Sumlin et al., 2017; Wong et al., 2017; Zhao et al., 2015) and therefore should be considered when estimating oxidative aging. With the spreadsheet provided by Peng et al., we estimate 254 and 185 nm exposure ratios (ratio of photon flux, photons cm^{-2} , to OH_{exp} ; Peng et al., 2016) to be $1.2 \times 10^5 \text{ cm s}^{-1}$ and $8.1 \times 10^2 \text{ cm s}^{-1}$, respectively, at a measured internally-generated O_3 concentration of 1.7 ppm (at the highest PAM UV lamp intensity), a water mixing ratio of 1% (RH = 30%), and assuming a maximum OHR_{ext} value of 1 (Peng et al., 2016). Using Figures 1 and 2 of Peng et al., 2016 to interpret these values, we find that photolysis at both 185 nm and 254 nm is likely less than 10% in both cases.”

5. *To the extent possible, I recommend that the authors make additional effort to simplify, consolidate, and streamline the results that are presented, so that the reader is not overwhelmed – especially with the PMF results (see Comment #21).*

We thank the reviewer for the suggestions for improvement. To improve the readability of our results, we made many of the changes suggested by the reviewer in the technical/minor comments, which we address individually.

Technical/Minor Comments

6. *L139: Out of curiosity, what factor(s) led to the use of oak leaves and oak wood as opposed to, for example, a soft wood fuel that might have generated a much different range of tracers? Please briefly explain why the chosen systems were studied.*

We chose oak leaves and wood because these fuels are of interest to us in Missouri, which is characterized by oak deciduous forests, and the different fuel fractions represent different types of wildfire or controlled combustion. Ongoing experiments seek to characterize BBOA from various other relevant fuels.

We address our chosen system in lines 139-142 (Section 2.2, Paragraph 1, Lines 1-4):

“White oak (*Q. alba*) heartwood and leaves were chosen for these studies due to their high abundance in Missouri and the southeastern U.S. While comparing different tree species is also of interest, two different plant fractions of the same species are studied here to investigate different types of wildfire or controlled combustion processes, some of which may only impact leaf litter-fall and others would have wood available as a fuel.”

7. *L163: Clarify that the chromate coating increases the electrical conductivity of the chamber, which decreases charge buildup, and consequently loss of charged particles to the walls of the reactor.*

We have modified the description of the chromate coating to provide the appropriate clarification (lines 166-168; Section 2.2, Paragraph 1, Lines 2-4):

“The reactor consists of a 13 L cylindrical aluminum chamber coated internally with Iridite 14-2 (MacDermid, Inc., Waterbury, CT), a chromate conversion film designed to decrease charge buildup and thereby inhibit losses of charged particles to the walls of the reactor.”

8. *L164-L166: State here the range of ozone mixing ratios that were added to the reactor via the ozone chamber, and the range of ozone mixing ratios that were generated inside the reactor via 185 nm irradiance of O₂.*

As requested, we have included the externally added ozone mixing ratio (4 ppm, line 172; Section 2.3, Paragraph 1, Line 8) and the internally produced ozone mixing ratios (0.3-1.7 ppm, line 212; Section 2.3, Paragraph 6, Line 1). Internally produced ozone is also tabulated in supplemental information (Table S1).

9. *L172: Here, and elsewhere, please be more precise with statements such as “The role of RH in OH· formation...”. Changing [H₂O] does change the rate of OH formation, and from the text, it appears that the authors did manipulate [H₂O]. Changing RH by itself, however – for example, changing the temperature inside the reactor – does not change the rate of OH production.*

We altered the wording as suggested to provide clarity (lines 177-179; Section 2.3, Paragraph 1, Lines 13-15):

“The reactor water concentration, and therefore RH, was altered by controlling N₂ flow through a Nafion membrane humidifier (Perma Pure LLC, Lakewood, NJ). The role of water concentration in OH formation is discussed in detail in Supplemental Information (Method: PAM Calibrations and Figure S3).”

10. *L183-L195: It wasn't clear why the authors didn't simply add SO₂ during a “representative” combustion experiment to conduct an online OH exposure calibration in the presence of (I)VOCs that might have suppressed OH. I would certainly encourage this, if practical, as this approach should introduce less uncertainty than attempting to apply the OH exposure estimator when the OH reactivity of the biomass smoke emissions is not known.*

We did not add SO₂ during a representative experiment for several reasons. First, we had concerns about the impacts of SO₂ on the chemical pathways occurring during atmospheric aging. Previous work demonstrates that addition of SO₂ can accelerate heterogeneous reactions of OH with organic aerosol by reacting with peroxy radicals to produce alkoxy radicals, propagating a chain reaction (Richards-Henderson et al., 2016). Additionally, long-chain aliphatics, particularly alkenes and fatty acids, have been observed to react with SO₂ to create long-chain organosulfate molecules (Passananti et al., 2016). Second, the sulfuric acid created

in the PAM reactor tends to damage inert coatings on the equipment used in these experiments (Williams et al., 2016).

With additional CO measurements (described in Supplemental Information: Methods: PAM Calibrations and Equivalent Aging Estimations, “Estimation of External OH Reactivity (OHR_{ext})”), we have attempted to better constrain the calibration. However, in future experiments, we hope to directly measure both total VOCs and concentrations of specific VOCs to obtain a more quantitative calibration.

11. L282: I suggest replacing “determined” with “inferred” or similar.

As suggested, “determined” has been replaced with “inferred” in this sentence (now line 356; Section 3.2, Paragraph 2, Line 8).

12. L309: This wording is confusing. Were oak leaves placed in a solvent to extract compounds on the surface of the leaves, and was this extract then injected into the TAG CTD? If so, please rewrite the sentence to clarify. What solvent(s) were used?

The wording here was altered for clarity (lines 385-389; Section 3.2.1, Paragraph 2, Lines 13-17):

“To confirm the presence of aldehydes in the leaf waxes, solvent extractions were performed on oak leaves and were manually injected onto the TAG CTD cell (Method: Oak Leaf Solvent Extractions and Figure S8 in Supplemental Information). Analysis of these extractions confirm that the aldehydes are present in the leaf wax prior to devolatilization and combustion.”

All details regarding oak leaf solvent extractions are provided in Supplemental Information in the section titled “Method: Oak leaf solvent extractions.”

13. L316-L318: It's true that sinapaldehyde signal decays more quickly than other tracers (e.g. alkanes), but ~70% decay over 3.4 days' aging is still slow in the context of gas phase oxidation rates – this corresponds to an effective rate constant of $\sim 2.7\text{E-}12 \text{ cm}^3 / \text{molec}/\text{sec}$, whereas, for example, the gas-phase OH rate constant of syringol is $8.5\text{E-}11 \text{ cm}^3 / \text{molec}/\text{sec}$ (Lauraguais et al., 2015).

We have modified the manuscript to include relative information on the reaction rate constants of sinapaldehyde (lines 407-411; Section 3.2.1, Paragraph 4, Lines 6-10):

“Of the compounds examined, sinapaldehyde decays most rapidly in the PAM reactor, with the normalized average integrated peak area decreasing by approximately 70% from 0 days to 2-3 days of equivalent aging (Figure 3b). Based on a rapid gas-phase OH reaction rate constant of $2.7 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ (Lauraguais et al., 2015), the observed sinapaldehyde decay is likely occurring in the particle phase.”

14. L387-L395: This paragraph seems out of place here, I would consider paraphrasing and moving to Conclusions.

As suggested, this paragraph has been moved to the Conclusions section (now lines 728-736; Section 4, Paragraph 2).

15. L417: What is the signal-to-noise ratio for the $m/z = 44$ decomposition SICs? I understand that the SIC's presented are background corrected – how large are gas-phase CO_2 + backgrounds compared to the background + sample $m/z = 44$ SIC's? This might be useful information to add to the Supplement.

We thank the reviewer for this suggestion. We have incorporated raw m/z 44 background signals and example decomposition m/z 44 SICs for each fuel type into a new supplemental figure (Figure S16).

16. L441-L454 and Figure 10: *Implicit in this discussion is the observation that TAG recovery of highly oxidized/oxygenated species is low (even with inclusion of the thermal decomposition window). One or two sentences should be added that states this explicitly. Another point that should be made is that this attempt at a direct f_{43} and f_{44} comparison assumes AMS flash vaporization at $T = 600$ deg C and TAG thermal decomposition at $T < 310$ deg C produce the same $m/z = 43$ and $m/z = 44$ ion signals. It's not clear to me that this assumption is justified, but at the least, this assumption should also be stated explicitly.*

The purpose of this figure is to suggest that inclusion of the thermal decomposition window facilitates more thorough TAG analysis of oxidized OA. We provide AMS f_{43} and f_{44} for comparison because this is a well-established technique for interpreting OA oxidative evolution.

Implicit in the interpretation of this figure is that the m/z 43 and m/z 44 detected by the TAG and the AMS are similar enough to merit some form of comparison, at least in how the signals trend with oxidative aging. However, we wish to clarify that this comparison does not entail that f_{43} and f_{44} measurements are the same between the two instruments (hence the distinct axes for both TAG and AMS f_{43} and f_{44}).

The reviewer's comments have been considered, and lines 564-570 (Section 3.3.1, Paragraph 3, Lines 11-17) now read:

"In general, the TAG fractions tend to fall to the left of AMS f_{44} vs f_{43} data points, indicating that the TAG excels at throughput of less-oxygenated hydrocarbon OA and struggles with throughput of oxidized species in the compound window. However, the increase in TAG f_{44} with inclusion of decomposition window material shows a clearer oxidation trend that is in greater agreement with the AMS oxidation trend. This interpretation implies that the m/z 43 and m/z 44 signals obtained in the TAG decomposition window from sample thermal desorption at 310°C is similar in nature to material flash-vaporized at 600°C in the AMS."

17. L483-L489: *Consider also moving this to Conclusions.*

This paragraph has been removed in favor of a more thorough discussion of thermal decomposition window analysis in the conclusion section (lines 766-774; Section 4, Paragraph 6).

18. L539-L549: *In my opinion, Lai et al.'s explanation for discrepancy in levoglucosan oxidation kinetics requires two unlikely scenarios: 5 a. using m/z 144 rather than m/z 162 would bias $k_{LG} \sim 30x$ too low -- Fortenberry et al.'s measurements are not subject to mass spectra interference either, and their levoglucosan decay rate is much closer to Kessler et al. than than Hennigan/Lai et al. (L564). A calculated levoglucosan + OH rate constant of $2.21E-13$ $cm^3/molec/sec$ (Bai et al., 2013), which is based on a theoretical study, may help put the different results in context. OR b. oxidation kinetics of OH + levoglucosan (or other model organics) are not firstorder with respect to OH. Previous studies suggest otherwise (e.g. Renbaum and Smith, 2011). I don't think it benefits the discussion in this paper to cite someone else's (in my opinion) incomplete explanation. I would consider removing it.*

We thank the reviewer for this insight. In the heartwood BBOA, the kinetics do agree best with those presented by Kessler et al., but in the leaf BBOA, the kinetics are most similar to those of Hennigan et al./Lai et al. Because we do not believe we have an adequate explanation for this discrepancy, the goal of this discussion was to investigate all potential explanations currently available in the literature. Therefore, we retain the explanation provided in Lai et al. because we believe it provides additional context for discrepancies in literature-reported levoglucosan kinetics, though we clarify that our chromatographic methods are not subject to the same mass spectral interferences (lines 673-674; Section , Paragraph 7, Lines 14-15):

“However, our chromatographic methods are not subject to this mass spectral interference, and in the case of the heartwood BBOA, the TAG-measured levoglucosan decay matches the decay predicted by Kessler et al.”

19. *Figure 2 and related text: It is hard to distinguish the multiple shades of green in Fig. 2a, and for some compounds it is hard to distinguish changes in relative abundance between chromatograms representing “3.4 days” and “9.8 days”. Please consider changing the colors in Fig. 2a. Additionally, consider removing the “3.4 days” TIC from Figs. 2a and 2b – this figure seems to be a general, “big picture” type of plot, so this would simplify the chromatogram without changing the take-home points.*

The color scheme has been changed to teal, purple, and pink in all leaf BBOA figures. Because we want to demonstrate visually that a select few compounds may increase in abundance with photochemical aging, we retain the trace for low-mid level of oxidation in the figure. However, we believe the change in color scheme greatly improves figure readability for the leaf BBOA data.

20. *Figure 3 and related text: Please add a subpanel plotting the concentrations of organics and any relevant inorganic species (e.g. K⁺) measured by AMS following OH exposure in the PAM reactor.*

Since the focus of this figure was intended to be solely on trends in TAG species, and because AMS total organics are presented in later figures (e.g. Figure 12), we did not include these species in Figure 3a and 3b. However, we have incorporated total organics, potassium (K⁺), and sulfate (SO₄⁺) concentrations, which were the most abundant species in our samples, in a supplemental plot (Figure S15).

21. *Figures 4-5, Figures 6-7, Figures 11-12, Figures 13-14: I find these figures to be complex and overwhelming. I found it difficult to quickly “match up” 37 sets of chromatograms and mass spectra (15 + 18 + 4) for each PMF factor across separate figures as is currently presented. In my opinion, reorganizing these figures to put the mass spectra next to their corresponding chromatograms would improve their clarity and usefulness.*

Here is one idea for consideration:

Figs. 4, 6, 11, 13: Put each factor “TIC” for 0, 3.4 days, 9.8 days on the same x-axis, (as was done in Fig. 2). Choose a three colors, one each for 0, 3.4, 9.8 days, that are shared across all factors. Then place the corresponding mass spectra shown in Figs. 5, 7, 12, 14 to the right of the TICs. This modification would: (i) reduce the number of “PMF figures” from 8 to 4 (ii) remove the number of subpanels in Figs. 4, 6, 11, 13 by 3x (iii) allow enough room to put the mass spectra from Figs. 5, 7, 12, 14 to the right of their chromatograms (iv) make it unnecessary to use unique colors for each factor in attempt to match up the chromatograms and mass spectra across figures. If this is not agreeable, the authors might consider just labeling the factors in Figs. 4, 6, 11, 13 and moving the mass spectral figures (5, 7, 12, 14) to the Supplement. This would save space/publication costs in the main part of the manuscript without making it any more difficult to “match up” the chromatograms and spectra.

To improve readability, we modified all PMF figures according to the reviewers first suggestion: time series and mass spectra for each factor are now presented side-by-side. This change has allowed for consolidation of PMF mass spectra and time series figures into one figure (Figures 4, 5, 9, and 10).

22. *Figure S13: The caption states 15 micrograms of levoglucosan and 5 micrograms of quinic acid were injected. That seems like a very large analyte mass for a single compound injection – is there any chance this is a typo, and that the injected quantities were actually 15 and 5 nanograms?*

This mass was not a typo. We experienced difficult single-component throughput of the injected levoglucosan and quinic acid standards, necessitating much larger injected masses. The mass injected here is much larger than found in the samples of interest, and the signal is larger than would be necessary as seen with peak “fronting” that appears in these chromatograms, a sign that excess mass was injected. While significantly

lower concentrations can be observed, poor transfer of highly oxidized standard compounds from the CTD cell to the column has been reported as a persistent problem in previous TAG literature (Williams et al., 2006), spurring the development of *in situ* derivatization methods (Isaacman et al., 2014), as discussed previously. We expect that, as reported for previous TAG measurements, a particle matrix improves throughput of these oxidized compounds compared to liquid standard injections (Lambe et al., 2009). Thus, while the standards presented here are sufficient for identification of compound retention time, they are not adequate for mass calibration of levoglucosan or quinic acid. Ongoing work focuses on better characterizing particle matrix effects for BBOA compounds of interest and improving TAG mass calibration methods.

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