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.

**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 [...] alkanoic 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.

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 C_{30}D_{62} 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
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-d$_1$ and isovanillin-2,5,6-d$_3$.

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/cm$^3$/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 gas-phase OH rate constants of 2.9E-11, 3.2E-11, and 3.8E-11 cm$^3$/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.

b. Levoglucosan signal decreases ~80% following 9.8 days aging time (Fig. 16). The authors reference literature rate constants of 3.09E-13 cm$^3$/molec/sec and 1.1E-11 cm$^3$/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
oak wood experiments and comparing to phase partitioning in the literature studies.

c. Increased condensed-phase partitioning of vanillin and other methoxyphenols following potentially significant SOA formation after ~3.4 days aging time (~4.4e11 molec/cm$^3$*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).

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?

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).

**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.

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.
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.

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.

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.

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

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?

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 ~2.7E-12 cm³/molec/sec, whereas, for example, the gas-phase OH rate constant of syringol is 8.5E-11 cm³/molec/sec (Lauraguais et al., 2015).

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

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 CO₂ backgrounds compared to the background + sample m/z = 44 SIC’s? This might be useful information to add to the Supplement.

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 f₄₃ and f₄₄ 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.

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

18. **L539-L549**: In my opinion, Lai et al.’s explanation for discrepancy in levoglucosan oxidation kinetics requires two unlikely scenarios:
a. using mz144 rather than mz162 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 first-order 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.

**Figures**

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.

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.

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:

- reduce the number of “PMF figures” from 8 to 4
- remove the number of subpanels in Figs. 4, 6, 11, 13 by 3x
- 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.

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?

References


