RESPONSES TO REVIEWER 1

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

Fortenberry et al. present a study that examines links between chemically speciated fresh and aged BBOA data to more bulk measurements of the AMS. They use PMF technique to pull out mass spectral trends in the speciated data and looked mass spectra from compounds that eluted during the thermal decomposition window of the TAG. Their results show 60 m/z, a traditionally used ion for the AMS to track biomass burning, depends on fuel type and aging of the aerosol particles. They also suggest that 44 m/z ion could be used as an estimate for aerosol particle's aging state. This manuscript is written clearly and contributes to the understanding of both the complexity of BBOA and interpreting results from the AMS. I recommend this paper be published in ACP with some minor revisions.

We thank the reviewer for his/her comments and insight. We address comments 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.

Minor Comments:

Line 38: parallel structure, change to "and impacts" or something along those lines

In line 36 (Section 1, Paragraph 1, Line 2), "…and can impact the global energy balance…" was changed to "… and impacts the global energy balance…"

Line 39: awkward sentence starting with "Organic aerosol. . ." In addition, aerosol refers to both the particle and gas phase. When the authors mean particle phase, please change aerosol to aerosol particle.

We reworded this sentence to improve clarity (lines 37-39; Section 1, Paragraph 1, Lines 7-9):

"Organic aerosol (OA) particles compose 20-90% of submicron PM (PM_1) and may consist of thousands of distinct organic compounds (Goldstein and Galbally, 2007; Ng et al., 2010; Zhang et al., 2007)."

In addition, we minimized our use of the word "aerosol" throughout the text, instead using "particles," "gases," and "emissions" where necessary.

Line 164: Traditionally, the radical dot of OH is left off, though the authors are technically correct. The dot just looks a bit strange when used, for example, in line 580.

To remain consistent with previous literature, we removed the radical dot from each reference to the hydroxyl radical.

Line 166: How well-mixed in the PAM reactor? Could large concentration gradients in aerosol particles affect the observed results?

Recent work demonstrates that the PAM reactor used in this study is approximately well mixed if sufficient time is given prior to sample collection to establish a well-mixed and near steady-state concentration throughout the combustion chamber and PAM chamber (Mitroo, 2017). We therefore do not expect concentration gradients within the PAM reactor to significantly impact observed results.

This question has been addressed in-text with the addition of the following sentence in lines 219-223 (Section 2.3, Paragraph 7):

"Flow field simulations and chemical tracer tests have demonstrated that the PAM reactor used in this study is approximately well mixed if sufficient time (at least 15 minutes) is given prior to sample collection to establish a well-mixed and near steady-state concentration throughout the combustion chamber and PAM chamber (Mitroo, 2017). The TAG therefore consistently collected 30 minutes after the biomass heat pulse to minimize particle concentration gradients within the reactor."

Line 180: add fuels after leaf

In line 188 (Section 2.3, Paragraph 2, Line 9), "For both heartwood and leaf, …" was changed to "For both heartwood and leaf fuels, …"

Line 210: What is the rate at which the cells are heated to 310ËŽC? There is some discussion that heating rate will affect which compounds desorb vs. thermal decompose. The authors do illustrate the ramping time in Figure 1, but it would be helpful to have it written down in the text.

In line 258 (Section 2.4.1, Paragraph 1, Line 2), a typical collection and thermal desorption heating rate of 50°C min^{-1} has been added to the text per the reviewer's suggestion.

Line 222: combustion chamber were clean

Here (now line 278; Section 2.4.1, Paragraph 3, Line 4), we clarified the language by replacing "… to ensure that the emissions and combustion chamber was clean prior to …" with "… to ensure that both the emissions chamber and the PAM reactor were clean prior to …"

Line 469: have specific standards been observed to decompose at these ions in this thermal decomposition window?

We thank the reviewer for this question. We have not observed these ions in any recent standard work, though this is an area of active research.

Developing satisfactory analytical standards for the TAG decomposition window has been particularly challenging. While we can tentatively identify the fragments eluting in the decomposition window using available mass spectral identification tools, we often cannot infer the source of the fragments, since they are products of compound thermal decomposition rather than volatilization. With that, many of the compounds undergoing decomposition during sample desorption are potentially too involatile for typical GC-MS analysis.

We have expanded our conclusion to include a discussion of the challenges of interpreting thermal decomposition window data (now lines 766-774; Section 4, Paragraph 6):

"The utility of the thermal decomposition window is limited by a lack of adequate analytical standards, particularly for organic components. Although ammonium sulfate and ammonium nitrate standards have been used to quantify sulfate and nitrate particles in previous work (Williams et al., 2016), the development of satisfactory standards for decomposing organics remains difficult for several reasons. While fragments eluting in the decomposition window may be tentatively identified using available mass spectral identification tools, we often cannot infer the source of the fragments, since they are products of compound thermal decomposition rather than volatilization. Many of the compounds undergoing decomposition during sample desorption are therefore too thermally labile for typical GC-MS analysis, and the original molecular structure remains undetermined. Despite these challenges, analytical standards composed of complex organic mixtures are currently under development to aid interpretation of decomposition window results based on molecular functionality."

Line 534 (though may happen earlier): No comma after Kessler. This comma is not needed as Kessler and others (in English) requires no comma even when used in line. Please remove comma in previous+subsequent usages.

We thank the reviewer for pointing out this mistake. The unnecessary commas have been eliminated from in-line references throughout the text.

Figure 2 (a): The three types of green are very difficult to distinguish. I understand the authors were aiming for green=leaf and warm colors for heartwood, but greens all look the same. Maybe cool colors for leaf and warm colors for heartwood?

The colors in Figure 2(a) have been changed to teal, purple, and pink to improve figure readability. Subsequent leaf BBOA plots have been changed to match this color scheme.

Figure 3 (b): Why are syringol, syringaldehyde, and vanillin dotted lines? Is it because they are observed to increase with aging time? If so, please mention that in the caption.

These compounds were indicated with the dotted lines to visually distinguish that unlike the rest of the compounds, they do not directly decrease abundance with equivalent aging. The following sentence has been added at the end of the figure caption:

"Compounds that decrease in abundance are indicated with solid lines, while compounds that deviate from this trend are displayed with dotted lines."

Figure 8 (a): The greens are hard to distinguish.

As with figure 2(a), the colors were changed to teal, purple, and pink to improve figure readability.

Figure 10 (a): The green color gradient is not great and implies there was a near continuous gradient of samples collected for that range of aging time. There were only three sampled times, so a gradient seems a bit misleading. Also, the colored right-hand and top axes are a bit confusing because the reader is trying to match the green points to the green axis instead of TAG to green. Also, the caption says the dotted lines are guidelines for where the points tend to be concentrated. This doesn't seem to be the case for the green AMS points. The blue dotted line for these points would look more like a rectangle covering the bottom half of the graph then a downward pointing cone. Is there greater meaning behind this cone?

We agree with the reviewer that the continuous color gradient may be misleading. In both figure 10(a) and 10(b), we have changed the legend to reflect the three distinct aging times for each fuel type. We have also changed the color scheme in figure 10(a) to match the colors used in figure 2(a).

The triangle formed by the dotted lines provides a visual guideline for the evolution of OA chemical composition in f43/f44 space. The apex of the triangle formed by the lines indicates the direction of increasing photochemical oxidation. These triangles have been used as visual aids in previous presentations of AMS f43 and f44 data (Ng et al., 2010) and are provided by default by the AMS Squirrel analysis software. We agree that in the case of our leaf BBOA AMS data, the points do not fit well within the confines of the dotted lines, so we have modified the position of the triangle to better fit our AMS data points. In addition, we have clarified the functionality of the triangle in the figure caption (what is now Figure 8) by modifying the last sentence:

"The triangles formed by the blue dotted lines provide visual guidelines for the evolution of OA chemical composition across f_{44} vs f_{43} space; the apex of the triangle indicates the direction of photochemical oxidation for AMS measurements (Ng et al., 2010)"

Figure 15 (A): same comment about the green.

As with figure 2(a), the colors were changed to teal, purple, and pink to improve figure readability.

Even more minor comments for the SI:

Figure S4: the TAG collection 1 blue shaded region does not look to start at 30 minutes after start of heat pulse as the caption indicates.

Now Figure S5, the location of the shaded region has been fixed to start at 30 minutes after the heat pulse.

Table S5-6: The raw SIC integration numbers have too many significant digits (and is difficult to read). Maybe consider limiting it to 2-3 with scientific notation.

The raw SIC integrations have been fixed as suggested: the values now have 3 significant digits and are presented in scientific notation.

Literature Cited:

Goldstein, A. H. and Galbally, I. E.: Known and Unexplored Organic Constituents in the Earth's Atmosphere, Environ. Sci. Technol., 41(5), 1514–1521, doi:10.1021/es072476p, 2007.

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