Response to reviewers for the paper "Photochemical aging of biomass burning smoke: Secondary organic aerosol formation and primary organic aerosol oxidation in a flow reactor during FLAME-3."
A.M. Ortega, J.L. Jimenez, et al. *ACPD*, doi:10.5194/acpd-13-13799-2013

Firstly, we would like to thank the reviewers for their comments on our paper. Second, to guide the review process we have copied the all reviewer comments *in black italics*, and our responses follow each comment in regular blue font. Lastly, changes to our paper are **in bold blue text**.

Anonymous Referee #1
R1.0. This paper presents measurements primarily from the high resolution AMS on several burns from the Missoula Fire Lab using the Potential Aerosol Mass flow Chamber. An important finding from this study is that the enhancement ratio for wildfire smoke decreases with increasing POA concentrations, providing an explanation for the variety of recent field observations of OA from wildfire plumes. This paper characterizes wildfire smoke using current AMS analysis techniques (elemental analysis, f44 vs f43, and f44 vs f60 plots) and provides a technique for correcting the AMS unit mass resolution fragmentation table for instances when organic mass is high and sulfate mass is low. Using the PAM chamber provides an upper limit of SOA mass expected from wildfire smoke, and thus these results will constrain how SOA from wildfire sources in models is evaluated. After the comments below are addressed, I recommend this paper for publication in ACP.

We thank the reviewer for the useful summary and positive evaluation of our paper.

Comments:
R1.1. Page 13801, Line 14: "This study confirms that the net SOA to POA ratio of biomass burning smoke is far lower on average than that observed for urban emissions." To this I would add the discussion that the ratio of net SOA to CO can be similar for both sources, as noted on page 13826, Line 14, since this ratio is what is often reported.

Unfortunately there were no high-quality CO measurements during FLAME-3, and thus we could not study the ratio of net SOA to CO for this experiment. A previous publication in which our group collaborated (Jolleys et al., ES&T 2012; their Fig. 2) have already compared this ratio between urban and fire emissions. Thus we do not think it is needed to add that result to the abstract of this paper, since it is not a result of this study, and it has already been previously reported in the literature. We have kept the text on page 13826 that makes the comparison within the body of the paper.

R1.2. Page 13808, Line28: "Although the AMS samples particles 10^7 times more efficiently than gases: : :" please provide reference.

We have added "**(Cubison et al., 2011; Canagaratna et al., 2007)**" as a reference for this statement.

R1.3. Page 13809, Line 23: Why not consider using Argon at m/z 40 as ion for the airbeam correction? Was there organic interference at m/z 40 also?

We examined the possibility of using *m/z* 40 (Ar^+) for airbeam correction in this study, and this has been done in some previous studies. However, due to the high organic loadings in this study, all 'air' *m/z* had substantial signal from organic ions present. In addition to Ar^+ at *m/z* 40, C_2O^+, $C_2H_2N^+$, and $C_3H_4^+$ were present. Therefore, *m/z* 40 had a similar degree of interference as *m/z* 28, and separating out Ar^+ required the same high-resolution fitting as fitting N_2^+. *m/z* 32 (O_2^+) was also investigated and shows similar issues.

We added the following text, **"We examined the potential of using other *m/z* for tracking changes in AMS sensitivity (*m/z* 40 for Ar^+ and *m/z* 32 for O_2^+); however, due to high organic loadings in this study, all air *m/z* had substantial signal from organic ions present."**

R1.4. Page 13810, Line 7: This comment is regarding the choice of CE of 1. For the concentrations of POA up to 10^4 ug/m3, it seems unlikely that the AMS could accurately quantify all of the aerosol. For the times during the high organic loadings (say for 1,000 ug/m3), does the closed signal go to zero? Do the filament and/or heater properties inside the AMS change?

In terms of quantification problems induced by high concentrations, these could be due to saturation of the detector or the data acquisition board, or to large increases of the background signal. Because in this study we only used the W ion path mode of the high-resolution TOFMS, and this mode had low ion currents, saturation of the detector or board are not expected until signal levels 10-100 times larger than observed here.

In terms of the background signal, it has been observed in previous studies with similar transient concentrations of OA (i.e. when sampling rapidly changing concentrated aircraft exhaust, or when flying through biomass burning plumes in aircraft sampling studies) that longer-term contamination of the AMS background is not a problem, and it goes away quickly after the high concentrations cease. This is not the case for some low-volatility metals, and in that case we have demonstrated a method to quantify them from the background signals (Salcedo et al. ACP 2010; Salcedo et al., AST 2012), but metals were minor contributors of the particle mass in this study. In this study, we observe that the closed signal is always less than 10% of the open signal, which is typical of general AMS operation (Huffman et al., 2009).

We observed a slight decrease in filament emission during the highest loadings of each burn. Taking into consideration all burn experiments across the campaign, the majority of burns showed ~5% or less decrease, and one burn had a ~10% filament emission decrease. Given that the AMS filament emission is known to fluctuate within 10% during normal operating conditions and that such variations are routinely corrected by using the air beam signal, we used the N_2^+-only airbeam correction to account for any changes in ionization efficiency during each burn experiment due to filament emission variations or any other reasons.

We have added the following text to the paper to clarify these points:

"The high levels of OA sampled in some of the burns are not thought to cause significant non-linearity or other detection problems for the AMS, due to the low ion currents measured with the W-mode and the short lifetime of the AMS OA background signal."

R1.5. Page 13810, Line 18: Why not also include Na+?

We have not added Na^+ to our cation balance as the Na concentration is typically much lower than K in biomass burning emissions. As reported in a previous FLAME study using very similar fuels and burning conditions, using IC analysis of $PM_{2.5}$ filters, McMeeking et al. (2009) reports an average Na^+/K^+ ratio of ~10% across many burns, with a range of 0-37%. In our study, we see Na^+/K^+ ratio of the same order. Additionally, Na^+ tends to be more difficult to detect with the AMS compared to IC analysis, as in some cases it can be dominated or have a substantial contribution of surface ionization. Unlike, K^+, we are not aware of any AMS papers that have reported or attempted to quantify Na^+ signals, other than using the specific $NaCl^+$ ion as a marker for sea salt aerosol (Ovadnevaite et al., 2012), but this ion was not detected in this study. Although the similarity of the ratio between the AMS and the previous IC is intriguing, a more detailed evaluation would be necessary to explore these signals (including analyzing the ion shape for all burns) and their impact on the AMS ion balance would be minor anyway. Future work should explore that quantification of Na^+ by the AMS. We have added the following text to the paper to clarify this point:

“Na^+ was not included due to substantially lower concentrations than K^+ in biomass burning smoke (McMeeking et al., 2009), as well as the difficulty of quantifying this ion with the AMS.”

R1.6. Page 13816, Line 18: “: : :that leads to evaporation of particle-phase species: : :” it would be nice if a future paper incorporated size resolved data to confirm evaporation of the particle distribution. With such high loadings, processing of particle time-of-flight AMS data would seem possible. It is not necessary for the scope of this paper.

We acknowledge the interest of further investigating these size distribution measurements, but the coverage of size distribution data for this campaign is intermittent, due to the use of W mode in which the signal-to-noise in PToF (size distribution mode) is not high despite the high concentrations, and the need to maintain high time resolution for the 1 min reactor vs unprocessed smoke switching. In addition their interpretation would be complex as several processes are likely acting at the same time (e.g. some condensation of SOA species formed in the gas phase, at the same time that there is some evaporation due to heterogeneous chemistry and also some due to partitioning). Given that there are hundreds of size distributions, one for each *m/z* (and even high-resolution ions), this would require an in depth study similar to that of Ulbrich et al. (AMT 2012). Thus we agree with the reviewer that this is not within the scope of this paper but we will consider examining it in future work, if time permits.

R1.7. Page 13817, Line 15: “Most ER were reproducible within: : :although a few showed more variability.” Can you make a hypothesis as to why there was variability?

We have added the following text to the paper to address this point:

“The observed variability is thought to be due to variability in the burning process dynamics, which was observed visually for some fuels. This may include the fraction of the combustion time (fraction of the fuel burned) in flaming and smoldering fire phases. The burn-to-burn variability we observed was also recorded using other aging methods (Hennigan et al. 2011) at this same study, as well as in other laboratory and field biomass burning studies (Grieshop et al. 2009; McMeeking et al. 2009; Cubison et al. 2011; Akagi et al. 2012).”

R1.8. Section 3.2: Why is the concentration of initial POA higher for some burns rather than others? Perhaps the modified combustion efficiency was different? Does the initial CO (g) trend with initial POA level? If you plot 8b versus initial CO instead of initial POA does it show the same trend?

POA for some burns was higher than others due to the very different emissions of different fuels, as has been reported previously. Fuel weight was chosen in order to partially compensate for the different emission strengths of different fuels, to that less different PM concentrations were achieved in each burn experiment. As mentioned above, no high-quality CO measurements are available for FLAME-3. Using those CO measurements that were available to calculate MCE and OA/ΔCO produced results that did not seem meaningful or support previous publications of MCE from similar fuels in previously reported studies at the FSL. We believe this discrepancy is due to instrument technical issues on the part of CO measurements and thus chose not to use those measurements in this manuscript.

R1.9. Figure 4: There is an overlap in the axis for b.) and c.)

We thank the reviewer for this catch. An updated plot with axis separated will be uploaded.

R1.10. Figure 5: Please check the legend for part a.). It looks like the aged and unprocessed have been mis-labeled in the legend.

We thank the reviewer for this catch. An updated plot had already been uploaded as a comment in the public discussion of this paper, and we will update the paper figures with this new version.

R1.11. Figure 9: The axis is overlapping on the Ponderosa Pine data

We thank the reviewer for this catch. An updated plot with axis separated will be uploaded.

Supplemental Material Comments
R1.12. Page 1 Line 22: Please reference Figure S3 for the C4+ to SO+ ratio as a function of organic mass loading.

We have modified the text, the last three sentences of supplemental text, Page 1 lines 21-24: **"To accomplish this, *m/z* 48 was used as the basis for estimating the sulfate contribution. As seen in Fig. S3, the ratio of dominant ions at *m/z* 48, C_4^+ and SO^+, were plotted as a function of OA mass to show that this ratio asymptotes to a constant value with increasing OA mass. See Table S1 for the modified fragmentation table."**

R1.13. Figure S5. Is some of the CO+ possibly from gas-phase CO? The correction for CO2+ gas-phase interference is discussed in section 2.3, but what about for gas-phase CO?

No. As discussed for example by Cubison et al. (ACP 2011, 2nd paragraph of Methods section), due to the AMS sampling aerosols 10^7 times more efficiently than particles, the gas-phase concentrations needed to create a detectable signal in the AMS are quite high, at least several tens of ppm of the gas phase, and more so at CO^+ due to the proximity of the very intense N_2^+ ion. Since CO(g) is present in smoke at levels typically 20 times lower than CO_2(g), the interference from CO(g) is not detectable for this study. I.e. for a typical max CO(g) concentration of 5 ppm (~ 5 x 10^6 ng m^{-3} of actual concentration) during this study, the signal produced at CO^+ (after accounting for the 10^7 discrimination against gases) would be similar to that produced by 0.5 ng m^{-3} of aerosol. The detection limit for the CO^+ ion is of the order of ~100 ng m^{-3}, and thus the gas-phase signal due to CO(g) is about a hundred times smaller than what we could detect. We have added the following text to the caption of Fig. S5 for clarity:

“Note that the contribution of CO^+ from CO(g) is negligible due to the strong discrimination against gases (by 10^7) by the AMS inlet.”

R1.14. It would be nice to see a plot of O:C vs f44 for all of the burns with regressions to see if the different fuels produce difference regressions.

We thank the reviewer for this useful suggestion. We have made the suggested plot for all burns, with four burns highlighted (the same four used as examples elsewhere in the paper) and added it to the revised paper as Fig. 13 (old Fig. 13 became current Fig. 14). The following text has been added to section 3.4:

“The relationship between O/C and f_{44} can be useful since many AMS instruments can only produce unit-resolution data, as well as for quick-look analysis of high-resolution data during data acquisition. Examining the relationship of O/C and f_{44} (Fig. 13), aged and unprocessed smoke from different fuels follow relatively similar slopes, with the exception of Ponderosa Pine. Using ambient ground and aircraft AMS measurements near Mexico City, Aiken et al.(2008) reported an O/C vs. f_{44} slope of 3.82, while the slope of all burns in this study is 3.83. Although the lines are nearly parallel, there is a vertical offset for smoke data that results in higher O/C for the same f_{44} compared to the ambient data. Additionally, BBOA-only data from Aiken et al. (2008)’s field measurements are plotted in Fig. 13, and show a similar offset as the data from this study. Thus, it seems for both biomass-burning POA and SOA, f_{44} is a reasonable surrogate for O/C if high-resolution data is not available, but the difference in the offsets should be kept in mind.”

Figure 13.

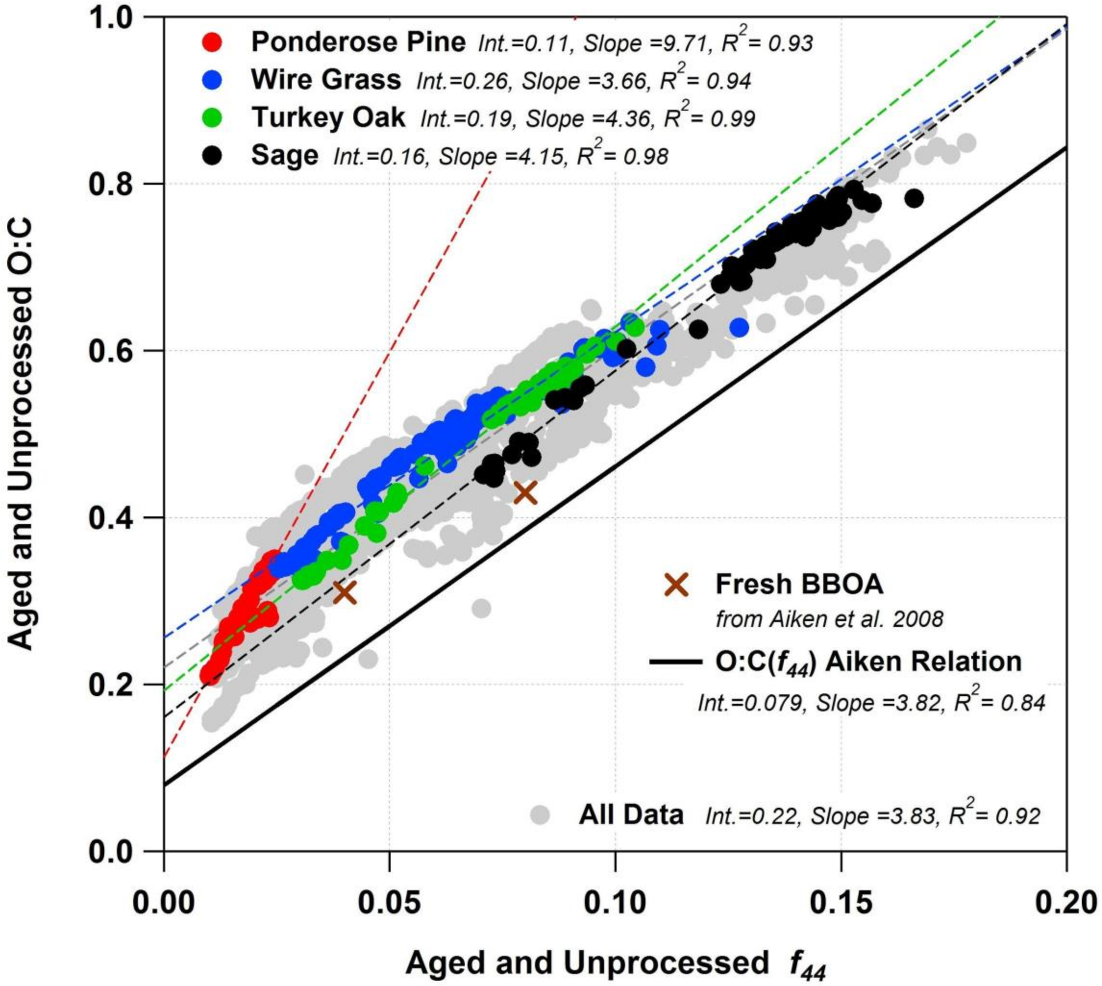

Fig. 13. Aged and unprocessed smoke O/C as a function of f_{44} for all burns with four fuels highlighted (ponderosa pine, burn 40; wire grass, burn 42; turkey oak, burn 45; and sage, burn 49). Each highlighted burn, as well as all data, is fitted with a linear ODR fit. Aiken et al.(2008)'s fit of O/C vs. f_{44} for ambient Mexico City measurements is plotted with BBOA-only data from that study highlighted for reference.

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Anonymous Referee #2

The paper by Ortega et al. summarizes results from measurements of organic aerosol (OA) formed in biomass burning of different fuels. Primary OA (POA) was measured using a high-resolution aerosol mass spectrometer by sampling burn emissions without exposing the smoke to oxidants while secondary OA (SOA) was measured by exposing the primary smoke to elevated OH and O3 in a PAM reactor flow tube. Gas phase characterization of the unprocessed and oxidized smoke was also performed by using a PIT-MS. The paper discusses in detail amount and characteristics of SOA formed in different burns and under different OH exposure limits. In general, results are very unique in that the conditions in the oxidation experiments reach levels beyond what is typically achieved in a smog chamber set up, and therefore the result extend what has previously been studied in smog chamber oxidation of biomass burning smoke. Conclusions of this work are still consistent with previous research and confirm the variability in SOA formation potential of different fuels. The paper is very well written and has a strong technical backbone. I recommend publishing the paper after the following comments are addressed:

We thank the reviewer for his/her review and this useful summary of the paper.

We also thank him/her for reminding us that our study extends the oxidation levels observed in smog chambers in previous studies, something we had not sufficiently highlighted. We have modified the abstract to summarize this point as follows:

"Hydroxyl (OH) radical concentrations in the reactor reached up to ~1000 times average tropospheric levels, producing effective OH exposures equivalent to up to 5 days aging in the atmosphere, and allowing us to extend the investigation of smoke aging beyond the oxidation levels achieved in traditional smog chambers."

R2.1. A general comment I have is regarding the design of the sampling by PAM. Of course the burns themselves are quite dynamic and I believe gas phase (and possible POA) emissions throughout a burn were not constant. Now if different OH exposure levels were tested out at different stages of a burn, doesn't that introduce another angle of variability on the data? How can these two effects be separated in the results presented here? An explanation of this is needed in the paper.

The combustion of each fuel took about ~5 minutes. We waited 15 minutes for the smoke to mix in the smoke chamber (with the help of large fans) before analyzing the enhancements due to photochemical processing. We believe by the end of combustion (allowing the fuel to naturally extinguish itself) and after mixing, the composition of the smoke was constant, with only relatively small changes due to evaporation as the smoke slowly diluted over the 3 hour containment period. This is discussed in the manuscript in section 2.1.

Thus in the experimental configuration of “chamber burns” used in this paper we do not have information about OH exposure levels to smoke from individual stages of a burn (e.g. flaming vs. smoldering). That type of separation is a focus of the “stack” burn configuration of the FSL chamber as reported in previous literature (McMeeking et al. 2009; Sullivan et al 2008; Lee et al 2010). We agree that such information for flowtube oxidation of smoke would be very interesting and useful. We have added the following text to the manuscript to address this point:

“The use of the “chamber burn” configuration in the FSL fire chamber prohibited distinguishing between flaming- and smoldering-phases of combustion.”

R2.2. The variability in the observed OA mass and characteristics have been discussed only in the context of different fuel types; what is the role of burning condition in the observed variability? Some discussion based on the gas phase measurements (CO, CO2, NOx, O3 etc) is warranted.

Traditionally, modified combustion efficiency (MCE) is used as a measurement of flaming- and smoldering-phases of combustion contribution to the total emissions, determined by the fire-integrated excess mixing ratios of CO and CO_2. Unfortunately high-quality CO measurements are not available for FLAME-3, and unfortunately we cannot address this point. We have added the following text to address this point in the manuscript:

“Modified combustion efficiency (MCE) and dilution/emission ratios to CO are not presented here due to lack high-quality CO measurements in this study. We also examined the relationship between organic aerosol enhancement and NO_x concentrations, but found no significant correlation.”

O3 in the containment chamber was low or zero due to titration by NO, and thus correlating it with our results is not meaningful. CO2 is just a measure of the amount of fuel burned, which was kept relatively constant across burns, in an attempt to compensate for the known variability of PM emissions across fuels (i.e. more fuel mass was burned for fuels with low emissions and viceversa).

R2.3. In Fig. S4, authors compare the OA mass calculated from UMR analysis of full spectra with OA mass from HR resolution of spectra for m/z <100. Why isn’t the UMR-based mass or HR-based mass compared together for different lengths of spectra? (i.e., *full UMR-based mass vs. UMR-based mass for m/z <100, etc.) Related to this, why isn't HR analysis used for estimating mass at larger fragments? These are details that most probably would not change the conclusions of the paper since OA mass beyond m/z 100 is expected to be small, but still more clarification on the approach is needed.*

HR ions were not fit above *m/z* 100 because of the difficulty of obtaining high quality information above this *m/z* range, due to the presence of many different ions at each *m/z* and the limited resolution of the HR-AMS. The practice of using HR ions for lower *m/z* and UMR ions at higher *m/z* is quite common in the AMS community for this reason, see. e.g. Aiken et al. (ACP 2009).

When only UMR information is used for the higher *m/z*, the assumption needs to be made that parameters calculated from the HR data such as O/C and H/C are the same on average for all masses above vs. below the cutoff *m/z.* If the amount of OA mass accounted for by the UMR-only *m/z*'s is large, then the potential error for this reason would be large. The main point of showing Fig. S4 in the paper is indeed to show that the amount of mass is a smaller fraction of the total, and thus this potential error is not large. We have modified the text to address this point as:

"OA mass concentrations reported in this study are the combined mass of HR data up to *m/z* 100 and UMR above *m/z* 100, due to the difficulty of obtaining accurate information from the high-resolution fits at higher m/z, from the increasing number of different ions at each m/z and the limited resolution of the mass spectrometer."

and:

"Elemental analysis was applied to AMS OA measurements to yield ratios of oxygen-to-carbon (O/C) and hydrogen-to-carbon (H/C) (Aiken et al., 2008). This calculation was performed with HR ion fits up to m/z 100, and implicitly assumes that the elemental composition of larger ions is similar to that of the ions below *m/z* 100."

The fraction of the signal present at *m/z* > 100 in biomass burning smoke is higher compared to typical ambient OA spectra with low influence of biomass burning smoke, as has been reported previously (e.g. DeCarlo et al., ACP 2008). We have added this reference to the manuscript.

R2.4. Line 22, p. 13810: clarify that substantial organonitrate or organosulfate mass concentrations may lead to higher estimates of inorganic nitrate or sulfate and therefore misleading the measured ionic balance.

This is what the sentence is saying already, although we gather that not clearly enough. We have reworded it for clarity to:

“The most likely explanation for apparent cation deficit observed is inefficient detection by the AMS of K^+ or other mineral cations present in the smoke. It could also possibly have a contribution from organonitrates and/or organosulfates present in the smoke particles, that would lead to too high estimates of inorganic nitrate or sulfate. However we are not aware of reports of organonitrates or organosulfates in biomass burning aerosols, so that possible explanation remains speculative. Another possible reason for the observed cation deficit would be the presence of H^+ if the aerosols are acidic, since H^+ cannot be quantified directly by the AMS due to limitations of the time-of-flight mass spectrometer.”

R2.5. Line 15, p. 13815: Clarify which tracers ‘these’ refer to.

Modified the text to read, **“Tracers *m/z* 44 and *m/z* 60 show similar temporal trends as OA ...”**

R2.6. Editorial corrections: line 3, p. 13820 should read “: : :would be a near flat line : : :” and last sentence should be “: : : to other burns where EROA is >1.”.

We thank the reviewer for reporting these mistakes and have updated the manuscript accordingly.

R2.7. It’s stated on lines 10-15, p. 13820 that signal at m/z 44 for aged ponderosa pine smoke is dominated by CO2+ and not C2H4O+, but the opposite is mentioned on lines 8-9, p. 13815. Doesn’t Figure S7 indicate comparable signals at CO2+ and C2H4O+?

The first reference (in Section 3.1.2) to ions at *m/z* 44 is a general statement referring to the presence of both ions at *m/z* 44 for both fuel examples and in both aged and unprocessed measurements. An more detailed discussion on the intensity of these two ions is presented later, at the end of Section 3.3.1. Figure S7 indicates $C_2H_4O^+$ dominates *m/z* 44 for unprocessed smoke, but is depleted in aged smoke as CO_2^+ increases. In aged smoke both ions have comparable signals.

To clarify, we have added the following text to the end of Section 3.3.1, **“... as seen for Ponderosa Pine in Fig. S7 these two ions have comparable signals after aging.”**

R2.8. Line 11, p. 13821: Please clarify why would higher partitioning of SVOCs at higher OA concentration to the particle phase result in less gas phase oxidation?!

Because if more of the SVOCs are in the particle phase, there are less SVOCs in the gas phase where oxidation is much faster for kinetic reasons (e.g. May et al., 2012). We have modified that sentence to clarify this point as:

"We speculate the observations in Fig. 10a are due to greater fractional partitioning of SVOCs to the particles at higher OA concentrations. Since the oxidation kinetics of SVOCs are substantially slower in the particle phase compared to the gas-phase (e.g. May et al., 2012), such partitioning would result in less gas-phase oxidation and thus less of an increase in f_{44} for the fuels with higher initial POA concentrations."

R2.9. Line 3-4, p. 13825: increased O/C factor should be 3.27

We thank the reviewer for the catch and have updated the manuscript text to read, **"... the maximum O/C of the added SOA increased by <u>3.27</u> units. Since the intercept is near zero, the max O/C of the added SOA is approximately <u>3.27</u> times the O/C of the unprocessed POA."**

R2.10. Line 28, p. 13826: ": : : as the smoke from each: : :"

We thank the reviewer for the catch and have updated the manuscript text.

R2.11. Fig. 9: Why not show the sticks in the top mass spectra as % and indicate the average mass for the unprocessed and aged cases? This way it would be easier to see how the composition changes with aging.

We had an extensive internal debate about the format of this figure before submission of the paper to ACPD, including the format suggested by the reviewer and at least 3 other formats. We examined them together and concluded that each version had advantages and disadvantages, and agreed that the version currently in the manuscript is the most effective at communicating the transformations that the smoke has undergone.

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