While the topic of this manuscript is certainly within the scope of ACP, I have significant concerns regarding some of the experimental methods used and how these are presented. Furthermore, several key pieces of experimental data are not included, and many of the results are not clearly discussed and explained. I found it difficult to under- stand many aspects of the paper. The SI is a spreadsheet of data with several figures that are not discussed. Many of these are important figures that should be presented and discussed in the main paper to understand the experiments (such as the aerosol size distributions). I do not think this submission meets the standards in terms of quality or clarity required for ACP and that it would be challenging to revise the paper to meet the standards of ACP. Many of my serious concerns and questions below were raised in pre-review for ACPD and were not addressed by the authors. Therefore, I am concerned that they are not taking the peer review processes seriously and am also significantly concerned with the reliability of many of their results. I conclude that it will be very challenging to substantially revise this manuscript to meet the standards of ACP and must recommend it be rejected.

Authors response
We do appreciate the concern of the reviewer and we would like the reviewer to know that we do take the review process very seriously and we will address all the concerns. The closing of labs due to COVID 19 and the relocation of the experimentalist who ran the chemical characterization experiments to Europe made it difficult to address all concerns in a timely manner earlier. However, the concern about the reliability of our results is somewhat biased and unfounded and insulting and we reject that concern. Our labs both at NCAT and UNC-Chapel Hill have maintained the highest ethical standards in our work and we stand by our results.

Most of the details of the experimental methods related to generation of biomass burning aerosols, burning conditions, details of the smog chamber used and the measurement of the optical properties is already described in Part I of this work (Smith et. al. 2020), and referenced in this paper. We have however provided enough and appropriated details in this paper. In response to the reviewer's concern we will have a separate supplemental document of figures that were placed in the spreadsheet. The discussion in the manuscript will refer to these figures in the revised manuscript. Additional figures and more details of the analysis will be provided in the revised manuscript to address all the concerns.

Reviewer Comment
The central issue is the experimental design seems poor. Very high aerosol mass concentrations are added to the chamber, and even after 12 hours of aging these only increase by half. This is a lot of time for semi-volatiles to partition to the walls which will cause additional "aging" that does not really simulate atmospheric aging processes; you will lose a lot of the semivolatile compounds that are strongly involved in atmospheric photooxidaton processes. There is a wide body of information on this specific to the dynamics of BBA and the key roles of dilution and evaporation such as from the FLAME experiments. It is also not clear how much aerosol is left in the chamber after 12 hours of aging, and the aerosol size distributions are not shown in the main paper. In the size distributions in the SI it appears there is substantial aerosol growth, but this is also not

discussed. The high aerosol chamber mass concentrations will result in a lot of semi-volatiles being partitioned to the aerosol phase which will affect how they respond to photochemical aging since this occurs quite differently in the gas phase versus in the aerosol phase.

Authors response

The authors are bound by the limitations of their (or anybody's) instrumentation. Insufficient particle concentrations, particularly after aging, would preclude any meaningful measurements. In addition, had the authors used smaller concentrations, the wall loss of semivolatiles would become more important. Therefore, researchers that study SOA formation, for instance, frequently use ammonium sulfate seed particles, but such seeding was neither necessary nor desirable in this work.

Reviewer Comment

A relationship between BrC components and volatility has been found and would play an important role here though this is never discussed here. See for example the recent work of Rawad Saleh. Many studies on chamber aging and the role of dilution and evaporation of BBA have been reported and need to be discussed and used to interpret these results. See the many papers from the 4 prior FLAME campaigns, such as the work of Andrew May and Allen Robinson, and the more recent papers from the FIREX lab studies. The chamber studies of BBA aging reported by Ahern et al. from FLAME-4 are especially relevant to this work. Jeff Pierce has also examined the key interplay between fire size, dilution, and the resulting gain or loss of OA with "aging".

Authors response

We agree with the reviewer that dilution driven evaporation of BBA could potentially impact some aspect of our result. However, we don't think that will have a major impact on our conclusion. We believe these issues are critical for the organic aerosol enhancement studies like Ahren et al. and many more FLAME and FIREX studies as mentioned by the reviewer. Furthermore, we agree with the reviewer that some of the highly volatile BrC could potentially evaporate during this dilution process but as shown in a recent paper by Hodshire et al. (2019), our case would have low dilution driven evaporation due to a relatively larger load of OA.

Reviewer Comment

ppm levels of a few VOCs also appear to be added to the chamber during the UV aging but the purpose of this is not explained. Thus, the aging consists of high mass concentrations with high amounts of a few VOCs added but no additional oxidants added, and UV photochemistry. What type of realistic atmospheric aging does this represent? The high aerosol mass concentrations represent in-plume concentrations while in the atmosphere most photochemical aging will occur under much more dilute conditions as the smoke entrains background air, and possible additional oxidants. Adding such high concentrations of VOCs is also odd as this would not occur as the smoke plume (a large source of VOCs itself) spreads and dilutes. Without a better handle on what specific type of aging is simulated here and how it represents atmospheric processes it is difficult to extrapolate these experiments to understand the real atmosphere. The focus is on understanding the sources, properties, and evolution of brown carbon.

Authors response

Some of the details of VOC addition is discussed in the first part of this paper (Smith, 2020). The purpose of adding the VOCs was to represent a polluted urban environment, where we used the emission inventory for urban environments from South Africa. This does not necessarily represent the east African emission inventory, but this serves as a baseline, since this is the only available data to us for the continent.

The concentration injected into the chamber was approximately 7 – 26 times more concentrated than values found from urban South African emissions and 6 – 18 times more concentrated than suburban values. The reason for these elevated levels was mostly due to sample preparation constraints, since the amounts needed for an exact match were too small for our scale to weigh appropriately. It is also plausible that the concentrations in east African emerging megacities can be that high since there are no regulations and many VOC sources. Concentrations in the chamber were intentionally higher than atmospheric conditions, to age the BB aerosol faster and accentuate the potential effect of SOA. No additional oxidants were added. This does not necessarily represent a realistic atmospheric aging environment but provides an insight for proper realistic experimental design. A limited number of fuel-specific comparisons can be made between the laboratory and field studies (Hodshire, 2019). Unlike field campaigns, laboratory campaigns keep chambers at an effectively fixed dilution ratio, so direct comparisons are not possible,

Despite the use of anthropogenic VOCs at concentrations larger than those average values found in urban and suburban regions of South Africa, no distinct effect was observed for SSA values of BBA produced during combustion at 500 °C. While it is possible that the relatively long aging time could obscure some of the effects due to the presence of VOCs, it is also possible that combustion products dominate molecular species and the effects of additional VOCs are insignificant. The latter would suggest that these added VOCs to represent urban pollution did not seem to affect the optical properties of BBA. A higher temporal resolution is needed to simulate the impact of the VOCs on aerosol SSA, where continuous or much more frequent measurements are needed. Since we size select particles in our work continuous measurements cannot be performed with our setup.

Changes made in the Manuscript:
The following is added in section 2.
"Details of VOC addition is discussed in the first part of this paper (Smith, 2020). The purpose of adding the VOCs was to represent a polluted urban environment, where we used the emission inventory for urban environments from South Africa. This does not necessarily represent the east African emission inventory, but this serves as a baseline, since this is the only available data to us for the continent.

Reviewer Comment
Nitration of organics such as aromatics is known to play a prominent role in BrC production yet the role of nitrogen oxide chemistry is not discussed. 12 hours of photochemistry will likely deplete most of the NOx/NOy while this would not necessarily be the case under atmospheric conditions.

Authors response
It is unfortunate that NOx measurements were unavailable during these experiments, as the authors wish they could better address the primary emissions of NOx and its abundance over time

as the sample ages. We address the role of nitrogen oxide chemistry in a discussion of catechol, along with other nitro aromatics, in a reviewer response below.

Reviewer Comment

Allowing the biomass fuel to dry in a hood for a year will drive evaporative loss of a substantial fraction of the organic components that can be emitted or are combusted in biomass burning, thus substantially altering the composition of the BBA measured here compared to realistic biomass burning. This aspect needs to be discussed as it can significantly alter the composition of the resulting BBOA and SOA. See Ahern et al. for a discussion of this:

Ahern, A. T.; Robinson, E. S.; Tkacik, D. S.; Saleh, R.; Hatch,L. E.; Barsanti, K. C.; Stockwell, C. E.; Yokelson, R. J.; Presto, A. A.; Robinson, A. L.; et al. Production of Secondary Organic Aerosol During Aging of Biomass Burning Smoke From Fresh Fuels and Its Relationship to VOC Precursors. J. Geophys. Res. Atmos. 2019, 124 (6), 3583–3606.

Authors response

We agree with the reviewer that long term drying of fuels will drive evaporative loss of organic compounds. This is also true for most domestic use of biomass fuels in the region where this study is focused on. Dried eucalyptus and acacia biomass fuels are common domestic fuels in east Africa. The moisture content of the samples was 10%. The reviewer's comment is valid if we try to make comparisons with wildfires, but fresh, wet fuels would not be used for domestic heating and cooking. Additionally, there are transportation problems (i.e. rotting) when dealing with fresh wood samples. The method used here actually preserves semivolatiles better than other potential drying methods, such as drying in the sun or in an oven. This is because the yield of essential oil upon distillation of Artemisia nilagirica (clarke) pamp leaves (another species whose oil contains significant quantities of eucalyptol) was largest for shade-dried samples (Anjum, et al. 2015).
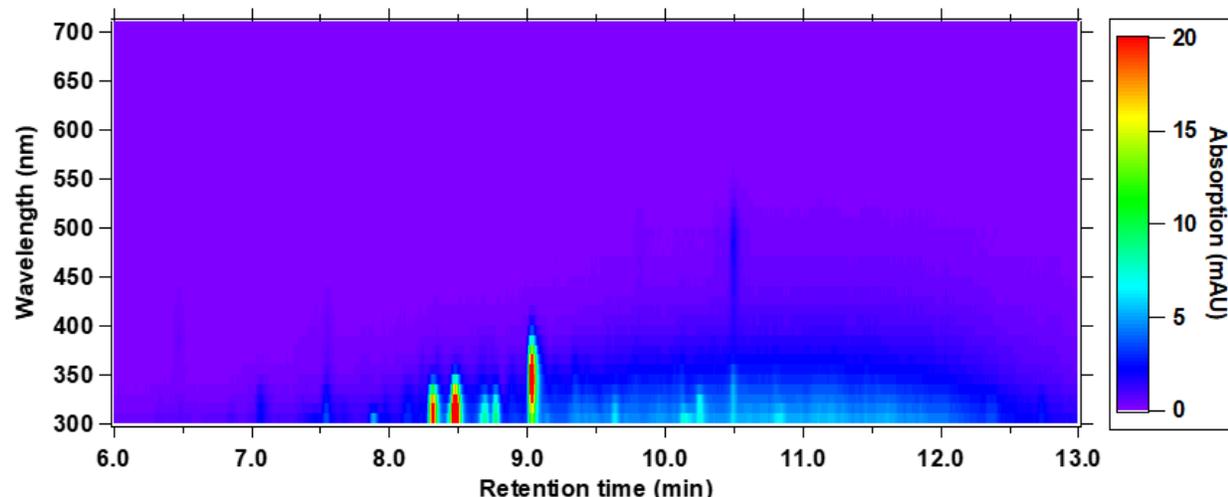
Reviewer Comment

UPLC is used to separate the methanol extract of the BBA filter samples, but no chromatograms are shown. This is critical as BBA is notoriously difficult to separate using a C18 or similar reverse-phase column, and these chromatograms are used here in much of the analysis.

Authors Response:

Chromatograms of m/z vs. retention time (RT) vs. abundance of ions from UPLC/DAD-ESI-HR-QTOFMS for all the experiments were shown in SI. Although it can be challenging to separate BBOA constituents using a C_{18} reverse-phase column with UPLC (Di Lorenzo et al., 2016), our UPLC method clearly resolved most of the most methanol-extracted BBOA constituents from RT=5 to 14 min using a C_{18} reverse-phase column. However, we acknowledge that our UPLC/DAD-ESI-HR-QTOFMS method has the following limitations: We only used ESI operated in the negative ion mode (which doesn't ionize all BrC components - mostly the acidic ones), we used only RPLC (which may not resolve the high-MW BrC components, like SEC columns do as shown in Cora Young's work, due to poor separation or permanent retention on the RPLC column). However, we are likely to detect freshly produced smaller MW species with our method that ionize in the negative ion mode. Please see below for more details.

– To demonstrate the utility of our method to detect and resolve some of the BrC components we have added new figures, such as Figure 6.

Chromatograms of UV/Visible absorption vs wavelength and retention time for each fuel, age, and burning condition have been included in the SI and are referenced within the paper. Here is one example, from freshly combusted Acacia at 500 °C:

Reviewer Comment

Cora Young has a series of papers, on the use of size exclusion chromatography that discusses issues in UPLC analysis of BBA that should be consulted and discussed, as well as what they have learned regarding the relationship between BrC and molecular weight. Showing the chromatograms, at least in the SI, is also important as there are some weird baseline correction issues mentioned in the paper. Throughout the paper the properties of BrC obtained from other studies, not on these same systems are extrapolated to also describe the BrC/OA in these experiments. This is not a safe assumption.

Di Lorenzo, R. A.; Place, B. K.; VandenBoer, T. C.; Young, C. J. Composition of Size- Resolved Aged Boreal Fire Aerosols: Brown Carbon, Biomass Burning Tracers, and Reduced Nitrogen. ACS Earth Sp. Chem. 2018, 2 (3).

Di Lorenzo, R. A.; Washenfelder, R. A.; Attwood, A. R.; Guo, H.; Xu, L.; Ng, N. L.; Weber, R. J.; Baumann, K.; Edgerton, E.; Young, C. J. Molecular-Size-Separated Brown Carbon Absorption for Biomass-Burning Aerosol at Multiple Field Sites. Environ. Sci. Technol. 2017, 51 (6).

Di Lorenzo, R. A.; Young, C. J. Size Separation Method for Absorption Characterization in Brown Carbon: Application to an Aged Biomass Burning Sample. Geophys. Res. Lett. 2016, 43 (1), 458–465.

Authors response

As shown below in the responses, the BrC constituents are detected by RPLC since we interfaced it to the DAD and ESI-HR-QTOFMS detectors, assuming they ionize in the negative ion mode. We acknowledge that some of these light-absorbing compounds shown in Figure 6 may not ionize in the negative ESI mode. However, the elemental composition determined from the accurate mass measurements tells us something about the molecular composition, and thus, the double bond equivalents(DBEs). Prior work, such as in Lin et al. (2014, ES&T) showed that RPLC interfaced to DAD and ESI-HR-QTOFMS could resolve BrC components that eluted at the same retention

times in the DAD and the ESI-HR-QTOFMS chromatograms; specifically, the structures chemically characterized by the ESI-HR-QTOFMS had the highest DBEs and likely explained the light-absorbing properties from IEPOX-derived SOA. In addition, this same method has been applied to urban aerosols (Zhang et al., 2013, ES&T) and BBAs derived from the combustion of Indonesian biomass (Budisulistiorini et al., 2017, ES&T). Notably, BrC components derived from Indonesian biomass was only characterized in the negative ion mode in the Budisulistiorini et al. (2017, ES&T) study. In addition to these studies, there is a lot of literature showing that as the organic component increases in DBEs the more likely it will absorb light. However, if the retention time in the ESI-HR-QTOFMS doesn't provide a formula that supports it would absorb in the BrC region (as measured by the DAD), then it is likely we missed it due to ESI operated in the negative ion mode. Other studies (including some of our own work with IEPOX SOA) have also used ESI in the positive ion mode since some BrC components preferentially ionize in that ion mode of ESI. However, even ESI can be blind to some BrC features seen in DAD, as explained by several papers from Prof. Alex Laskin's group. Prof. Laskin's group has shown that APPI is another ionization source that might help to better determine some of the BrC features seen in LC/DAD data.

The RPLC/DAD are powerful and show the light-absorbing aerosol components, but we must be careful in assuming that ESI operated in negative ion mode characterizes all of these. ESI operated in negative ion mode is very good at measuring acidic species, especially things like nitro-aromatics (e.g., nitrocatechols) (Zhang et al., 2013, ES&T). Although, one limitation of the RPLC/DAD method is that we might be biased to certain molecular weights of BrC components. Prof. Cora Young's papers showed (especially Di Lorenzo et al., 2016, GRL) that SEC-UV is very good at resolving large molecular weight (MW) species, especially greater than 500 Da. Thus, we are biased to smaller MW species due to the use of RPLC. However, we can measure freshly-generated BrC components in the lower MW range and likely are missing the detection of larger species (especially > 1000 Da) either since they don't ionize or possibly were retained permanently by the PRLC column. With that said, we can still explore relative changes between fuel types and conditions with the compounds we report.

Reviewer Comment

In the non-targeted analysis, the use of retention time is not clear to me. Is it used to help propose a chemical formula for a given ion peak? Or page 7 it says similar m/z with difference were combined.

Authors response

The purpose of the non-targeted analysis is to efficiently reveal the differences between two spectra (e.g., "fresh" vs. "aged"). The BBOA constituents, as the detected/resolved ions shown in the SI section, were then carefully examined in the MassHunter with their exact m/z values, retention times (RTs), and peak areas. When examined by MassHunter, some chromatographic peaks had similar m/z values (usually within ±0.001 Da), resulting in the exact same molecular ion compositions. This indicated that these chromatographic peaks were likely isomers of each other, and thus, their peak areas were summed together in order to see how this molecular ion composition varied as a function of BB aerosol generation conditions. These data are recorded in the six tables of the SI (spreadsheet) Section. The chemical formulas were suggested based on the exact masses measured by the ESI-HR-QTOFMS. RTs reported in these tables from the RPLC

separations provide information on hydrophobicity, where the later eluting components are more methanol soluble than water soluble. As noted earlier for the gradient elution method, components eluting in the first 2 minutes of the RPLC run are mostly water soluble since the mobile phase is solely composed of the aqueous eluent.

Changes made in the manuscript
To clarify the statement on page 7 the following will be added:

"When examined by MassHunter, the chromatographic peaks with similar *m/z* values (usually within ±0.001 Da) were found to have the same molecular formulas. This indicated that these chromatographic peaks were likely isomers of each other."

Reviewer Comment
Also, were any standard run to determine the expected retention time?

Authors response
As described in Section 2.4, seven external (2-nitrophenol, 4-nitro-1-naphthol, 4-methyl-5-nitrocatechol, vanillin, vanillic acid, coniferaldehyde, and benzoic acid) commercially-available authentic standards were prepared for 6-point calibration curves from 0.004 –10 µg mL^{-1}, in order to obtain their retention times, as well and response factors and potential MS/MS fragments if needed. While this statement was in the context of previous studies, these standard were also run during these experiments. In addition, commercially-available authentic samples of 4-nitro-o-cresol and sinapinic acid were also run as external standards.

The suggested names were listed in the six tables in SI (spreadsheet) are examples corresponding to the previously identified BBOA molecular formulas in the literature. For example, two isomers of m/z 161.0244 corresponding to C$_9$H$_6$O$_3$ (RT=8.32, 8.45) were suggested to be umbelliferone (Fleming et al. 2020) or hydroxycoumarin (Budisulistiorini et al. 2017). For compounds that were identified based on their high-resolution m/z *and retention time, these assignments have been denoted in the tables with a dagger (†) and their corresponding retention times in SI have been bolded. Descriptive text pertaining to this has been added to the table captions.*

Reviewer Comment
Or is a standard C18 elution program being used and a database of retention times being referenced?

Authors response
A standard elution program was used, as described in Section 2.3, but a database of retention times was not used. Retention times were used to determine the number of isomers present, but were not used explicitly for structural identification. Accurate mass analysis, previous observations in the literature, and lignin structural motifs were used to make suggested identifications shown in SI Tables. (spread sheet)

No database of retention times is being referenced here; however, compounds can be unequivocally identified to one of our 9 external standards.

Reviewer Comment

The UV/vis absorption spectra in Fig 5. These very flat featureless spectra do not make sense or provide any information. Even black carbon does not have such a flat wavelength spectrum. It seems that the UV/Vis absorption spectrum is averaged over the entire chromatogram. Why? This is throwing away valuable information, and likely explains why the spectra in Fig. 5 are so featureless. If you examine the absorption spectra for specific chromatographic peaks you can then relate the light absorption properties and potential chromophores to the ions observed at that same retention time. This provides molecular-level understanding of the specific compounds that are light absorbing, their sources, and their alteration by aging.

Authors response

UV/Vis absorption spectrum was averaged over the entire chromatogram, as described in Section 2.6.

The reviewer brings up a very good point. Considering this, a discussion of this has been added in the form of Section 3.4, the conclusion, and SI, as stated below. This includes figures such as Figure 6, where we demonstrate that we can chromatographically resolve some individual BrC components in the RPLC/DAD.

Changes to the Text

The following has been added following Section 3.3:

3.4 Chromatographic analysis of potential chromophores in the visible

In addition to examining the integrated spectrum, we can also focus on potential chromophores that absorb in the 500 – 570 nm region of the spectrum. Considering that flaming-dominated combustion shows little in the way of absorbing species and the abundance of these species decreases upon aging, only fresh emissions from combustion at 500 °C will be examined. Figure 6 shows the extracted wavelength chromatogram for the 500 – 510 nm region, where absorption would be most intense over this range, for Eucalyptus and Acacia combusted at 500 °C. This chromatogram has been background subtracted by the filter blank and, given that the amount of aerosol deposited on these filters was not measured, no scaling was applied. Remarkably, only a few peaks dominate the chromatogram, though there are likely several low abundance and indistinct peaks 11 – 13 minutes. The UV/visible absorption spectra for each designated peak in Figure 6 are given in Figure S4. As can be seen in Figure 6, several of these species have similar retention times. A comparison was made between these peaks, with respect to elution time. Peak A and H, despite coming from different fuels, show similar retention times and UV spectra, as can be seen in Figure S5. The same can be said for peaks B, C, I, and J, which have well separated peaks at ~340 and ~485 nm with a gradual decrease to 600 nm. Peaks D, E, and K also have the same general appearance, and may be related to B, C, I and J, but are somewhat broader and peak at slightly shorter wavelengths (332 and ~480 nm).
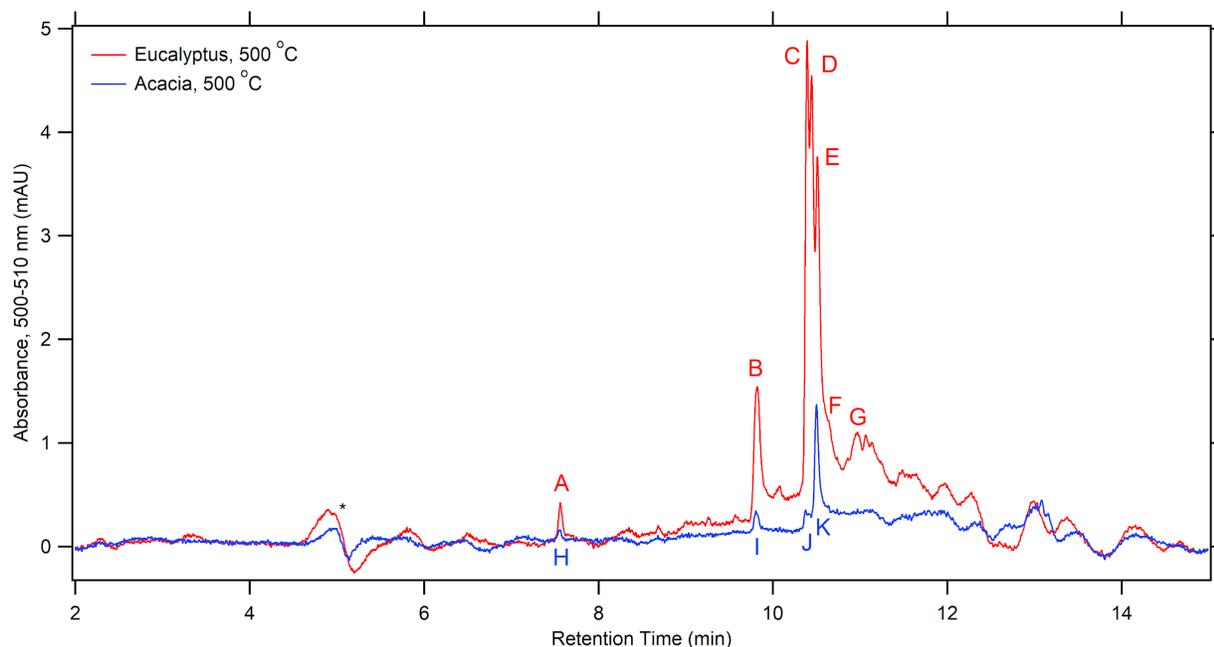
Figure 6. The extracted wavelength chromatogram for the 500 – 510 nm region for each fuel freshly combusted at 500 °C. The peak with the asterisk is an artifact from background subtraction.

To determine which species produced the absorption features shown in Figure 6, mass spectra at the absorption maxima were examined and assessed based on the peak height in the mass spectra, how well the retention times of extracted ion chromatograms matched the extracted visible wavelength chromatogram, and if a compound can be reasonably thought to absorb in the 500-510 nm region. Assignments using this method are tenuous, given that species detected by the DAD may not be seen by negative-mode ESI-MS. Additionally, many of the species described below have additional peaks outside those described, suggesting that not all isomers corresponding to a given formula absorb in this region. The extracted ion and visible chromatograms (shown in Figure 6) are in Figure S6a for Eucalyptus. Peak A is either $C_9H_{10}O_3$ (*m/z* 165.0559), tentatively assigned earlier, and/or $C_9H_{12}O_4$ (*m/z* 183.0658), which could be an isomer of trimethoxyphenol or dimethoxy methyl catechol. Several isomers of $C_9H_{10}O_3$ are known to only absorb below 240 nm, though veratraldehyde and caffeyl alcohol UV/visible spectra have not been measured, nor has trimethoxyphenol or dimethoxy methyl catechol for $C_9H_{12}O_4$. A $C_9H_{10}O_3$ isomer may also contribute to peak B and, while $C_8H_{10}O_2$ (*m/z* 137.0612) is more abundant at peak B and previously identified as several isomers in this work, none would absorb in this region. Likewise, $C_{10}H_{10}O_2$ (*m/z* 161.0604) elutes with peak B, which may be methoxycinnamaldehyde, methylcinnamic acid, or methylhydrocoumarin. While the spectra of those compounds have not been previously measured, it is unlikely that they would absorb in this region either. One compound that could weakly absorb in the visible and elutes at peak B is hydroxycoumarin ($C_9H_6O_3$, *m/z* 161.0244). One such compound, umbelliferone, absorbs to ~420 nm (Abu-Eittah and El-Tawil, 1985), though several isomers are present which may have somewhat different spectra.

Several species show peaks in the mass chromatogram that correspond to peaks B-F, including $C_{10}H_8O_3$ (*m/z* 175.0405), $C_{11}H_8O_3$ (*m/z* 187.0401), and $C_{11}H_{10}O_3$ (*m/z* 189.0565). The species corresponding to $C_{10}H_8O_3$ could be methoxycoumarin or methylhydroxycoumarin, though

9

these species mainly absorb below ~450 nm (Abu-Eittah and El-Tawil, 1985) and may only absorb very weakly above 500 nm if at all. Naphthalenetriol is a much more likely candidate for $C_{10}H_8O_3$, given its extended and functionalized aromatic system, though a spectrum for any of its isomers has not been measured. The less functionalized 1,4-naphthalenediol absorbs to ~680 nm (Linstrom and Mallard, 2020). The structures attributable to $C_{11}H_8O_3$ could be hydroxynaphthoic acid, acetylcoumarin, or methylcoumarinaldehyde, but none of these compounds absorb above 410 nm (Donovalová et al., 2012). Still, several of these compounds are yellow solids in their pure forms according to their SDS sheets, suggesting they have some interaction with visible light. Similarly, an indistinct number of peaks associated with $C_{11}H_{10}O_3$ are found within these retention times, which may be isomers of methylmethoxycoumarin or dimethylhydroxycoumarin; none of which have previously measured spectra. Peaks in the vicinity of peaks F and G correspond to $C_{12}H_{10}O_3$ (*m/z* 201.0554) methoxynaphthoic acid or methoxyhydroxynaphthaldehyde. No UV/visible spectra are available for these compound and, while some spectra are available for related compounds such as 1- and 2-naphthoic acid (Linstrom and Mallard, 2020), these spectra seem truncated at ~350 nm. More telling is the SDS descriptions for these substituted naphthaldehydes and naphthoic acids, which are light yellow, yellow, and light brown. This suggest that their absorption extends into the visible and possibly into the 500 nm region.

One set of isomers in the vicinity of peaks C through F correspond to the formula of $C_{11}H_6O_3$ (*m/z* 185.0256). Given the high degree of unsaturation (DBE = 9), these can only be furanocoumarins, which have a fused furan and benzene ring. Two common isomers of these species are psoralen and angelicin. While these species do not absorb in this region of this visible, they are strong absorbers below 370 nm (Rutan et al., 2018) and have not been previously identified as BrC species in BB aerosol. The peaks for nitroguaiacol, discussed earlier in this work, do not align well with peaks in Figure 6.

Fresh Acacia combusted at 500 °C underwent a similar analysis, as shown in Figure S6b. All the previously mentioned extracted ion chromatograms appear very similar for Acacia, with the main difference being that the ion abundance for Acacia was smaller by a factor or 2-4. Most ions had similar temporal profiles as Eucalyptus except for $C_{11}H_{10}O_3$ (*m/z* 189.0565), which only matched peak K and onwards. Given this, it is very likely that peaks with similar DAD retention times are produced by the same species, and peak A corresponds with peak H, B with I, C with J, and E with K.

The following has been added to the Conclusion section:

"An attempt was also made to identify which species produce absorption at wavelengths longer than 500 nm. An extracted wavelength chromatogram from 500 – 510 nm shows only a few peaks dominate the absorption from fresh emissions of combustion at 500 °C. Both Acacia and Eucalyptus have common absorbing species, as shown by peaks with common retention times, similar UV/Visible spectra, and extracted ion chromatograms. By comparing the retention times of extracted ion and wavelength chromatograms, several species were tentatively suggested for contributing to absorption in this wavelength range. This includes functionalized courmarin species (hydroxy-, methoxy- methylhydroxy-, methylmethoxy-, etc.), naphthalenetriol, and methoxyhydroxynaphthaldehyde or methoxynaphthoic acid. UV spectra available from the literature for several of these species and/or related compounds seem truncated and are very likely

to extend into this visible region of the spectrum, which highlights the need for broadband UV/Visible spectral measurements of these compounds. While not important for absorption in this visible region, a novel set of compounds were found that could be strong BrC species – furanocoumarins."

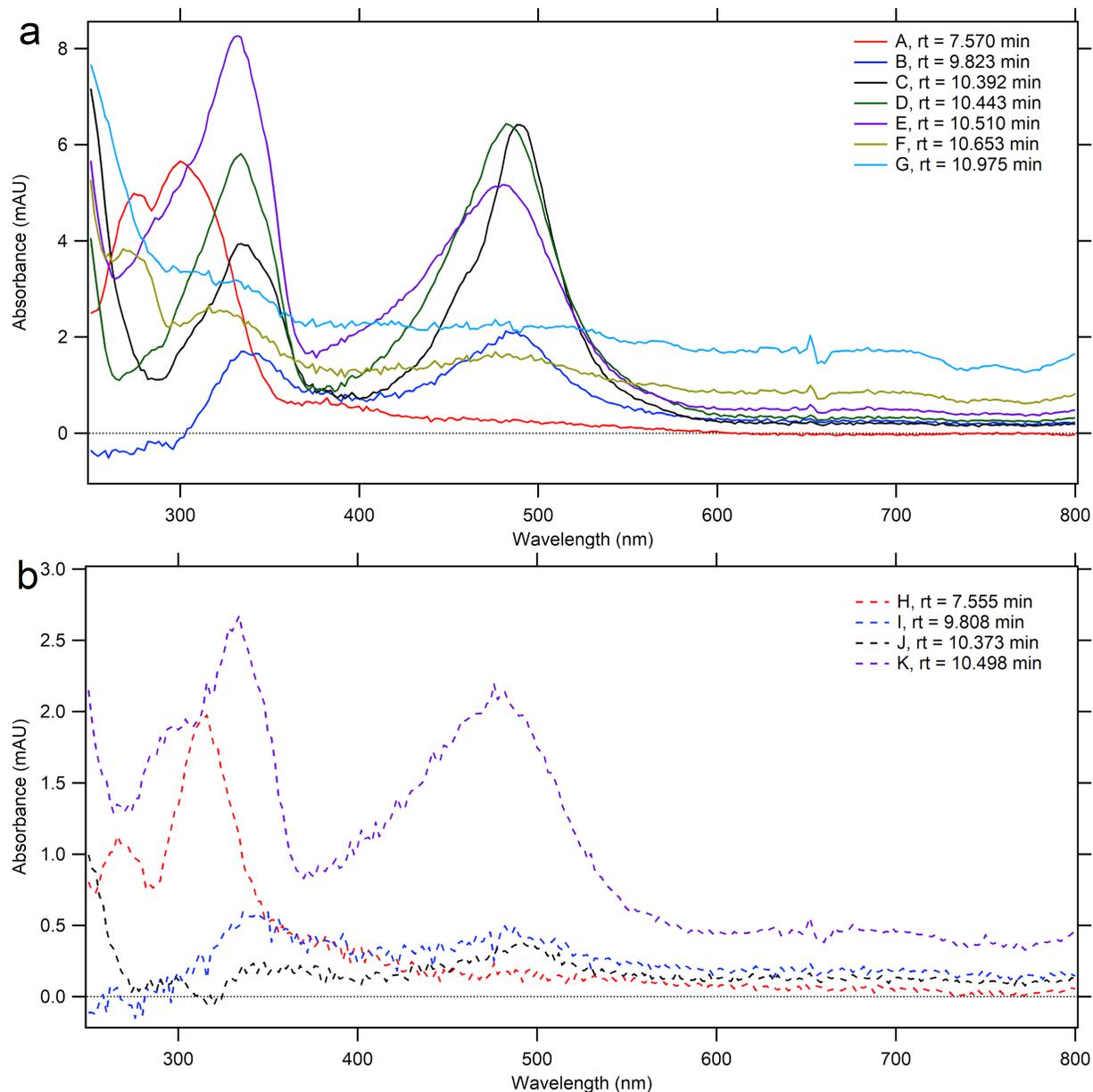*The following Figures have been added to the Supplemental Information:*

Figure S4. The UV/Visible absorption spectra corresponding to peaks in Figure 6, with those associated with Eucalyptus plotted with solid lines and those associated with Acacia with dashed lines. Peaks were background subtracted against nearby "off-peak" retention times; specifically, 7.62 min for peak A, 9.717 min for peak B, 10.312 min for peaks C-G, 7.483 min for peak H, 9.726 min for peak I, and 10.323 min for peaks J and K. As can be seen in Figure 6, a nearby

retention time free of absorbers in the 500-510 region was not always readily available, so caution should be used when utilizing these spectra.
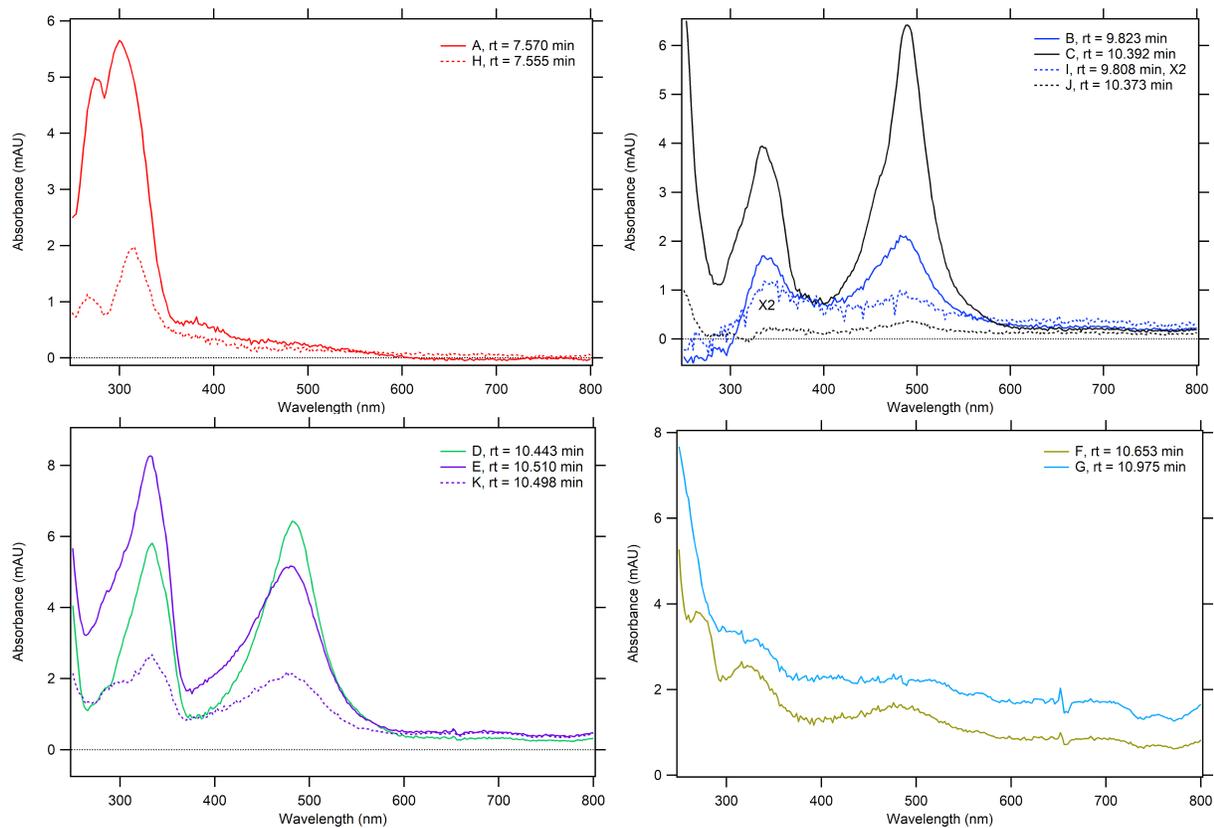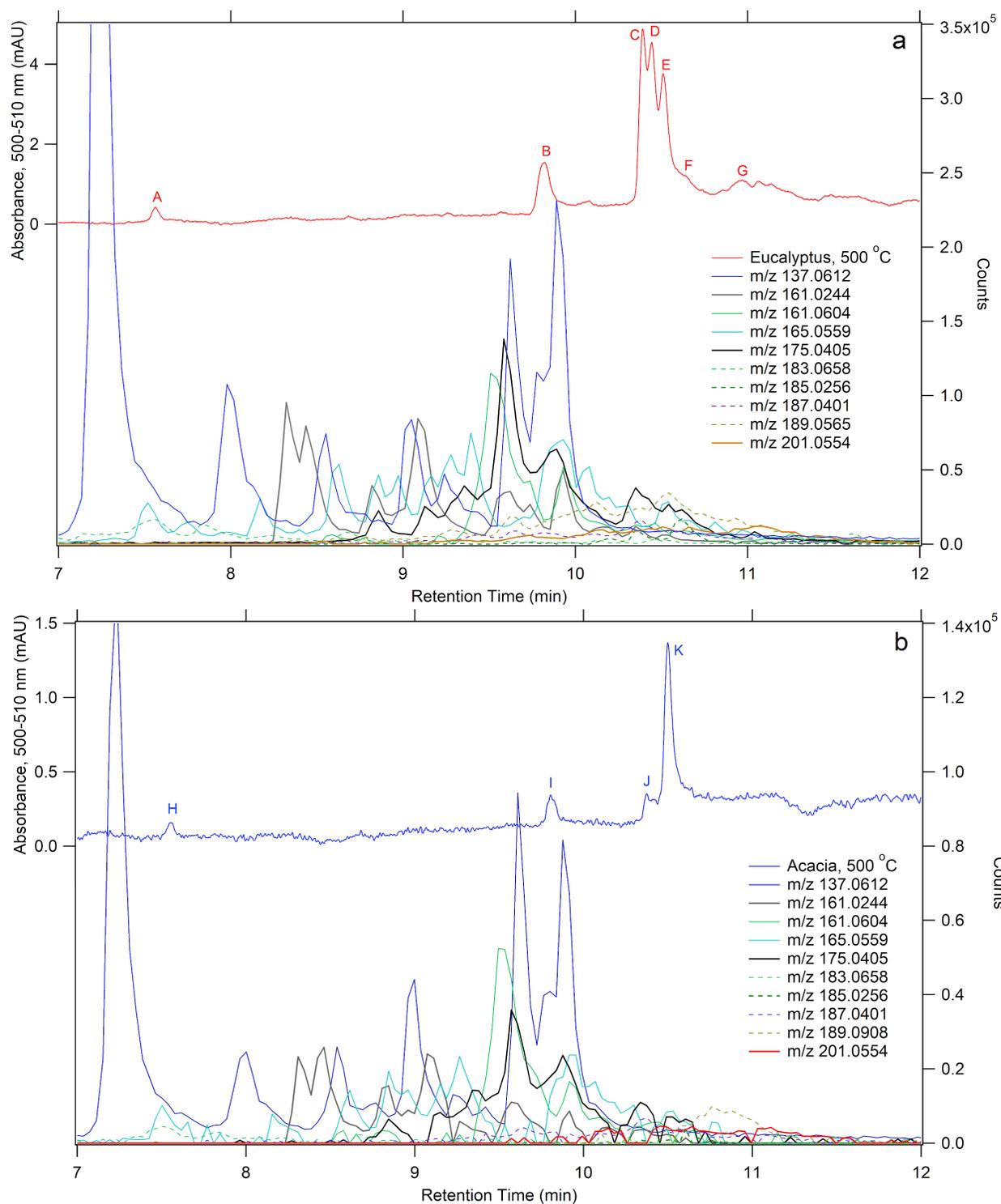

Figure S5. Similar to Figure S4, only with a pairwise comparison of species with similar retention times between the Acacia and Eucalyptus sample when combusted at 500 °C.

Figure S6. Extracted ion chromatograms for (a) Eucalyptus and (b) Acacia, which have chromatographic features matching the UV/Visible chromatogram for 500-510 nm. Ion chromatograms in bold are likely strong absorbers according to our analysis.

Reviewer Comment
Throughout the paper brown carbon (BrC) is discussed as though it is a distinct component, but it is just the organic carbon that has a significant molar absorptivity or real refractive index in the UV/vis wavelengths of interest. There is plenty of evidence from prior studies that BrC cannot be separated or easily distinguished from the rest of the organic aerosol. It really exists as a spectrum. See for example Rawad Saleh's work on this topic.

Authors response
Several studies have shown that BrC cannot be separated or easily distinguished from the rest of the organic aerosol. The optical properties of primary and secondary BrC span a wide range of values, inherent to broad variability in its chemical composition, mixing states of individual particles and their dynamic transformations resulting from atmospheric aging. Therefore, unraveling the relationship between the light-absorbing properties of BrC and its composition requires the use of a variety of complementary analytical techniques to determine both bulk and molecular-specific BrC properties [1-6]. But for biomass burning emissions, for lower MCE (< 0.9), the fraction of BC is very low (below 10% or so), whereas for higher MCE (>0.98), the fraction of BC is significantly higher. So, we still think we can say that less BC is produced during smoldering combustion, whereas more BC is produced during flaming combustion as in previous studies [7-11]. Indeed, Saleh classified BrC into four optical regions as a continuum associated with a continuum of physicochemical properties, including molecular sizes, volatility, and solubility [12, 13]. We will state these facts and the current understanding to indicate the very narrow definition of the use of the word BrC used in this paper. The language used in this work about BrC was mainly to contrast it with BC, which is decidedly a different component of aerosol, even if inextricably mixed in BBA. However, we disagree with the reviewer's statement "There is plenty of evidence from prior studies that BrC cannot be separated or easily distinguished from the rest of the organic aerosol" as our analysis shown in Figure 6 above we can resolve constituents that are BrC.

Changes Made in the Manuscript
The following is added

"Several recent studies have shown that BrC cannot be separated or easily distinguished from the rest of the organic aerosol (Saleh, 2020). BrC is classified into four optical regions as a continuum associated with a continuum of physicochemical properties, including molecular sizes, volatility, and solubility(Saleh et al., 2018;Saleh, 2020) . The language used in this work for BrC was mainly to contrast it with BC, based on the combustion temperature, which is decidedly a different component of aerosol, even if inextricably mixed in BBA."

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Reviewer Comment

The role of catechol is mentioned and there has been much recent work on the role of nitration of catechol as well as other aqueous chemistry in producing BrC. This needs to be discussed and in order to do so a solid understanding of the NOx/NOy chemistry in the fresh and aged BBA must be determined and presented. Biomass burning typically emits substantial NOx, and NOy such as HONO.

Authors response
The focus of this work has been on determining which species are most affected by aging and how the changes in molecular constituents alter the optical properties of aerosol. Given the complexity of the system, we have addressed the mechanistic aspects of production and removal in only a limited sense. However, given the abundance of catechol and how significantly it changes upon aging, we agree with the reviewer that a more in-depth discussion of this and related compounds is warranted.

Changes to Manuscript
The following has been added to the end of Section 3.2:

"Given that one isomer of dihydroxybenzene undergoes the greatest change upon aging, it is worth examining potential chemical transformations further. While resorcinol is a potential identity, catechol has gained significant attention due to its involvement as a precursor to a strong chromophore. Catechol can react in the atmosphere to form 4-nitrocatechol ($C_6H_5NO_4$) through photochemical and dark processes in the gas and aqueous phase through a number of mechanisms (Finewax et al., 2018; Kroflič et al., 2018; Vidovic et al., 2018; Wang et al., 2019). Given the dryness of our chamber and the presence of UV irradiation, this mechanism would proceed through hydrogen abstraction from the hydroxyl by OH to produce a *β*-hydroxyphenoxy/*o*-semiquinone radical, followed by radical-radical combination with NO_2 (Finewax et al., 2018). Both fresh and aged spectra for 500 °C combustion were examined for nitrocatechol ((M-H)⁻ at *m/z* 154.0140), and it was found at a rt of 8.39-8.55 min in both fresh and aged Acacia and Eucalyptus. There was a greater abundance in the aged samples, despite the mass loading on the filter being lower, suggesting a small amount from primary emission, but mainly a product of secondary formation for both fuels.

Smoldering-dominated burns were also examined for other nitroaromatic species. Methyl nitrocatechol, which has been identified as a tracer for BB SOA (Iinuma et al., 2010), and nitroguaiacol both have the formula of $C_7H_7NO_4$ and would have an (M-H)⁻ peak at *m/z* 168.0297. Fresh Eucalyptus had two peaks at retention times of 7.71 and 9.31 min, while Acacia only had a single peak at 9.30 min. Using the exact mass and the rt, this peak at 9.30 min has been identified as 4-methyl-5-nitrocatechol, so the 7.71 min peak must be another isomer produced in fresh combustion. Since this compound must be more polar to elute earlier, it may be the 4-, 5-, or 6-isomer of nitroguaiacol (Bluvshtein et al., 2017; Kitanovski et al., 2012a). Upon aging, both fuels had two peaks with smaller absolute abundances at 9.5-9.6 and 10.0 min. The 9.5-9.6 min peak is likely a slightly shifted 4-methyl-5-nitrocatechol, suggesting both a primary and secondary source of the compound. Based on previous observations of BB aerosol, the 10.0 min peak is either 3-methyl-6-nitrocatechol, 3-methyl-5-nitrocatechol, or 4-nitroguaiacol, whose sensitivity can be altered for it to elute either before or after 4-methyl-5-nitrocatechol (Bluvshtein et al., 2017;Kitanovski et al., 2012a). Nitrophenol ($C_6H_5NO_3$, (M-H)⁻ at *m/z* 138.0191) and nitrocresol ($C_7H_7NO_3$, (M-H)⁻ at *m/z* 152.0348) are secondary products of phenol and cresol, respectively. Neither was observed for fresh Eucalyptus and Acacia. There are at least two forms of methyl

nitrophenol in aged Acacia (rt of 10.15 and 10.46 min) and only one (rt 10.47 min) in aged Eucalyptus. Several isomers have been observed in BB aerosol in previous studies, including 3-methyl-4-, 2-methyl-4-, and 2-methyl-6-nitrophenol (Bluvshtein et al., 2017; Kitanovski et al., 2012a). The peak with a rt of ~10.46 was likely a slightly shifted 4-nitro-o--cresol, which was a standard compound run during the analysis of fresh BB aerosol and had a rt of 10.30 min. One nitrophenol peak at 9.37 min was observed in aged Acacia, while aged Eucalyptus did not exhibit any nitrophenol. This had a different rt than the 2-nitrophenol standard, which had a rt of 10.05 min, suggesting it was some other isomer. Nitronaphthol ($C_{10}H_7NO_3$, $(M-H)^-$ at m/z 188.0348) was not observed in any spectra."

The following has been added to the conclusion section:
"The removal of dihydroxybenzene was investigated by examining spectra for a known reaction product, dihydroxynitrobenzene (e.g. nitrocatechol). Results for both fuels suggest a small amount was produced by primary emissions, but it was mainly a product of secondary formation… Focusing on nitroaromatic species, one isomer of nitrophenol was produced during the aging of Acacia combusted at 500 °C, while none was produced for Eucalyptus. Despite being thought of as a tracer for BB SOA (Iinuma et al., 2010), there is evidence for both primary emission and secondary production of 4-methyl-5-nitrocatechol."

Reviewer Comment
There are several inappropriate and unsupported statements made regarding particle morphology and its role in the light absorption properties. For example, on page 2 "BrC aerosols are spherical in morphology", and on line 513: "Such an increase in SSA resulting from morphology changes is implausible". Aging can drive the condensation of secondary components that change morphology (how well coated the BC is, for example) that can absolutely alter SSA.

Authors response
Below are TEM images of particles produced from Eucalyptus for 500 °C and at 800 °C. combustion. They appear spherical, or nearly so, as at 500 °C (image B) as opposed to the images at 800 °C (image A)
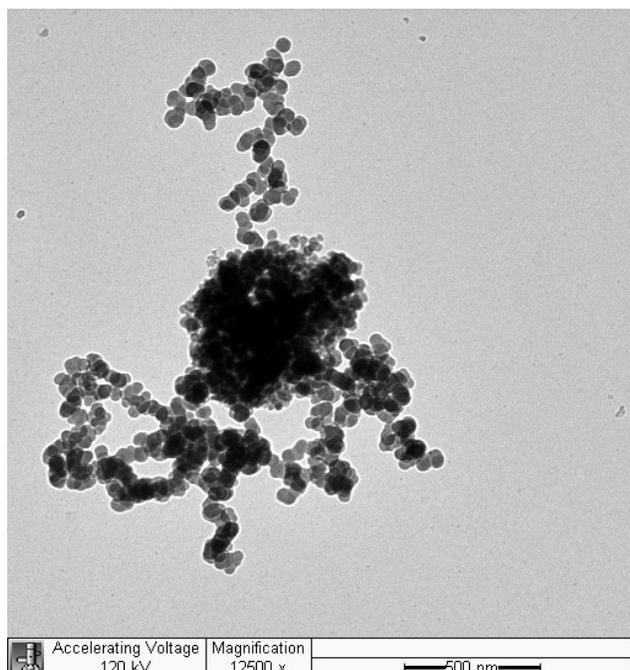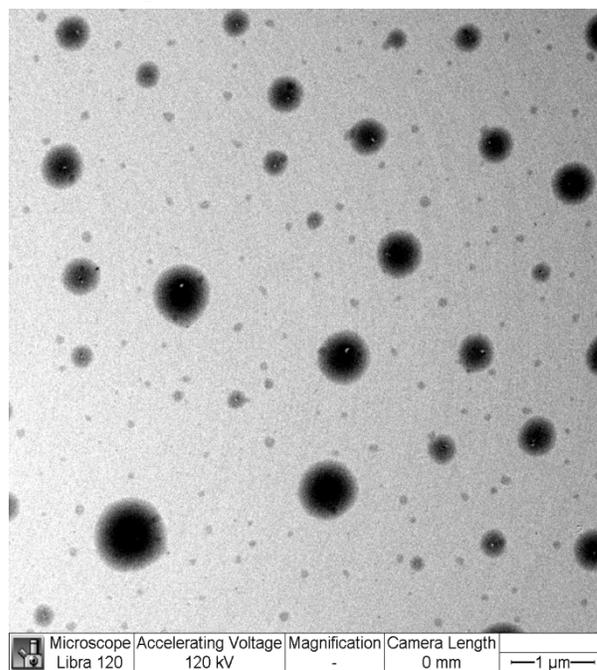
Image A   *Image B*

Accelerating Voltage	Magnification	
120 kV	12500 x	━━━500 nm━━━

Microscope	Accelerating Voltage	Magnification	Camera Length	
Libra 120	120 kV	-	0 mm	━1 μm━

The authors agree that condensation can drive morphology changes, as has been demonstrated in numerous studies. Unlike previous work, however, the size-resolved measurements in this work mean that it is smaller particles that must gain secondary components. We make the "implausible" statement because it is very unlikely that only morphology changes can produce SSA changes of 0.3.

Changes to Manuscript
Line 515 now states that "Such an increase in SSA resulting from morphology changes <u>alone</u> seems implausible…"

Reviewer Comment
More details on the type of TEM grid and how the sample was collected on it are required. Is it coated with formvar or similar, or a bare metal grid?

Authors response
The authors apologize, as it seems another digit was put into the part number. This has been corrected and detail added.

Changes to Manuscript
The text now reads "BB aerosols were collected onto 47-mm Teflon filters (Tisch Environmental, SF18040) for chemical analysis and tunneling electron microscope (TEM) grids (Ted Pella, 01844, carbon film on 400 mesh copper) for image analysis."

Reviewer Comment
Flaming-phase combustion also increases the mass fraction of inorganic components present, and nitrogen oxides and chloride can play a role in BrC chemistry (line 331). Were the inorganic components measured and quantified?

Authors response
No.

Reviewer Comment
Line 573: What mass fraction of eucalyptol would have to be present to explain the observations? Is this reasonable?

Authors response
The reason the authors hypothesize its presence is that it can make up a large, if not the majority, of distillation products. While we understand the importance of the reviewer's request and the refractive index has been measured near this region (Monerie, et al. 1985), there are several reasons we are hesitant to make this assessment. First, it was not directly measured, so its presence is conjectural. Secondly, while we have done Mie and RDG calculations in the past, we are not currently set up to do core-shell calculations, which would be needed to properly address this comment. In short, the authors are not comfortable making such an assessment based on its conjectured presence. In order to bolster the statement in the paper, the text will be accentuated.

Changes to Manuscript
The following has been added to line 359, where eucalyptol is first mentioned:
"When extracting essential oil from Eucalyptus leaves by water-steam distillation, an oil yield of 0.3 – 2.0% (dry wt.) was produced of which 7 – 75% was eucalyptol, depending on the species (Masamba et al., 2001; Subramanian et al., 2012)."

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