Response to Reviewer #1

We thank the reviewer for this careful review. The reviewer comments are shown below in **black** and our responses in **blue**. New text is indicated in *italics*.

This manuscript by Cappa et al. presents results of the evolution of biomass-burning smoke due to photochemical aging in a mini chamber. The study features a wide range of fuel types and combustion conditions and derives general trends / conclusions from averaging different burns grouped into 6 categories based on combustion conditions and consequent aerosol optical properties. The averaged experimental results are then used to develop a model for SOA formation and processing and the associated evolution of brown carbon optical properties. The major strengths of this manuscript are the 1) analysis of averages of large data sets which enables the derivation of general trends based on the average behavior (this is not possible to achieve from a small number of burns due to the high variability in combustion conditions), and 2) measure- ment/modeling analysis that enabled decoupling the effects of vapor-to-particle con- version versus heterogeneous oxidation on the evolution of optical properties (granted by using some simplifying assumptions, which is justified given the high complexity of the problem).

I believe this paper presents interesting and very useful insights on the evolution of biomass-burning smoke, and the data analysis and presentation are of high quality. I have only a few minor comments.

1) Section 3.3: The discrepancy in observed evolution in BrC absorptivity between the experiments here and ambient observations is interesting. One possible explanation is related to the molecular-size dependence of absorptivity, solubility, and susceptibility to photobleaching (Saleh [1] and references within). Wong et al. [2] showed that larger BrC molecules are less susceptible to photobleaching. These larger BrC molecules are more absorptive [3,4] and less soluble in water/methanol [5]. It is plausible that the ambient studies referenced in Section 3.3 (that used solvents) overestimated the effect of photobleaching compared to this study, which relies on airborne particle measure- ments. I suggest including a discussion along these lines in Section 3.3.

This is an interesting hypothesis regarding the potential origin of the lab/ambient discrepancy here. We have added brief discussion along these lines in Section 3.3.

> *There is also evidence that the larger molecules comprising OA from biomass burning, which are often more absorbing yet less soluble than small molecules (Di Lorenzo et al., 2017;Saleh et al., 2018), are less susceptible to photobleaching (Wong et al., 2017;Wong et al., 2019). This could lead to absorption measurements from solvent extracts overestimating the effects of photobleaching. Nonetheless, the suggestion that the measurement method contributes to the lab-field difference* remains speculative as direct, quantitative comparisons between BrC absorption measured for suspended particles versus from solution extracts are limited; we suggest that targeted comparisons between absorption measurement methods would be informative.

Section 3.2.6: It is not clear that the analysis in Line 766-786 is useful for the discussion of the results. The authors argue that the May et al. volatility distributions are not expected to provide good predictions for the concentrations in their experiments, so why do the calculations / comparison to begin with? I suggest taking this part out.

We appreciate the reviewers point here. However, we disagree that it is not necessarily “expected” that the May et al. distributions should provide good predictions at our concentration range. The derived volatility distributions from May et al. have been used by others to predict the influence of dilution on BBOA concentrations to low concentrations; the May et al. paper has been cited over 100 times. Given this, we think it is important that we present the evidence we have that there is limited/negligible influence of dilution observed to very low concentrations and over very large dilution factors. Per the reviewers point, we have considered moving this to the supplemental material. However we concluded that we did not want this observation to get buried/lost in the supplemental (which far fewer people read).

Line 95: Feng et al. 2013 and Wang et al. 2014 are not appropriate here, as these studies did not address BB evolution / photochemical aging.

We have removed these references.

Line 218-223: in McClure et al., MAC_BC_pure values were obtained by extrapolat- ing MAC vs OA/BC fits to zero. This should be mentioned here.

We have added mention of this.

3) Line 227-229: Can this statement be more quantitative?

We have made this statement more quantitative: “The $MAC_{BC,781nm}$ only increases notably (by more than 10%) when $R_{coat\text{-}rBC} > 9$, *while theory predicts the* $MAC_{BC,781nm}$ *should increase by this amount for individual particles when* $R_{coat\text{-}rBC} > 1$ (Fuller et al., 1999).”

4) Figure 1: panel (g) is not described in the caption and the corresponding plots for individual burns are not given in the SI.

We have updated the caption and added a figure to the supplemental (new Fig. S9)

5) Line 455 (Reaction scheme): I might be missing something, but shouldn’t the reac- tion be: NMOG + OH –> SOA + NMOG_MG, where SOA = alpha * NMOG (since by definition, the yield is SOA/NMOG) and NMOG_MG = (1- alpha) * NMOG?

Indeed, these reactions need to be written in the manner indicated by the reviewer. We have updated the reaction scheme.

The overall reaction scheme is summarized below:

$$NMOG_{fast} + OH \xrightarrow{k_{OH,fast}} SOA_{fast} + NMOG_{MG} \qquad \text{(R1)}$$

$$NMOG_{slow} + OH \xrightarrow{k_{OH,slow}} SOA_{slow} + NMOG_{MG} \qquad \text{(R2)}$$

$$NMOG_{VS} + OH \xrightarrow{k_{OH,VS}} SOA_{VS} + NMOG_{MG} \qquad \text{(R3)}$$

$$NMOG_{MG} + OH \xrightarrow{k_{OH,2G}} SOA_{MG} + (1-f) \cdot NMOG_{MG} \qquad \text{(R4)}$$

Reactions 1-4 represent oxidation of gas-phase species and SOA formation, where $SOA_i = \alpha_i \cdot NMOG_i$ *and for a given reaction* $NMOG_{MG} = (1 - \alpha_i) \cdot NMOG_i$*; the subscript i indicates which NMOG type reacted. Also,*

$$SOA_i + OH \xrightarrow{k_{OH,het}} (1 - f_{het}) \cdot SOA_{het} \quad \text{(R5)}$$

$$POA + OH \xrightarrow{k_{OH,het}} (1 - f_{het}) \cdot POA_{het} \quad \text{(R6)}$$

$$SOA_{het} \text{ or } POA_{het} + OH \xrightarrow{k_{OH,het}} volatile\ products \quad \text{(R7)}$$

6) Line 546: specify wavelength for MAC.

We have added 405 nm.

7) Line 768-771: This part is a bit confusing. Are you saying that using May et al. volatility distribution, OA/BC decreases from 19.2 to 11.2 assuming a dilution factor of 33 (i.e. assuming the particles on the walls do not contribute to particle-gas equilibrium) and to 10.5 with a dilution factor of 21? One should expect lower dilution ratio to result in less decrease in OA/BC, no?

Indeed. The calculations at a dilution of factor of 21 accidentally had set a different temperature (warmer), leading to excess dilution. This has been corrected. The correct value is 12.1 rather than 10.5 for a factor of 21 dilution.

Some typos:

Line 68: particulate.

Line 217: in equation 2, MAC_BC_ref is inconsistent with the text (MAC_BC_pure).

Line 437: units of rate coefficient (cmˆ-1 should be sˆ-1).

Line 450: delete “occurs”

These have been corrected.

Response to Reviewer #2

We thank the reviewer for this careful and thoughtful review. The reviewer comments are shown below in **black** and our responses in **blue**. New text is indicated in *italics*.

Clarification is needed in Section 2.3 about the instrumentation. Specif- ically:

The description of the CRD-PAS instrument with measurements of light absorption is missing (already mentioned in a note from the authors).

Consistent with McClure et al. (2020), we have added the following sentence: "*Light absorption and extinction coefficients were measured at 405 nm and 532 nm using the UC Davis cavity ringdown-photoacoustic spectrometer (CRD-PAS) and at 781 nm using a DMT photoacoustic soot spectrometer (PASS-3).*"

How was BrC absorption derived from the CRD-PAS measurement of total absorption? By comparison of denuded and undenuded absorption, or by wavelength-dependence of absorption at three wavelengths?

Absorption by BrC is described by Eqn. 3 (now on line 256).

$$b_{abs,BrC} = b_{abs,obs} - MAC_{BC,pure} \cdot [rBC] \cdot E_{abs,coat} \quad (3)$$

In words, the BrC absorption is determined by difference between the observed absorption and the absorption expected from the measured [rBC] based on the wavelength-specific and campaign-specific MAC_{BC}, with an adjustment for the observed "lensing" based absorption enhancement.

In Eqn 1, what are the uncertainties in b_abs and [BC]? How do these uncertainties propogate through Eqns 2 and 3, and the determination of b_abs_BrC?

We have added uncertainty estimates for these parameters, and also note that "further details of instrument operation and uncertainties are provided in McClure et al. (2020), Lim et al. (2019), and Coggon et al. (2019)."

"*Estimated uncertainties for the absorption measurements were 8%, 5%, and 10% at 405 nm, 532 nm, and 781 nm, respectively.*"

"*The estimated uncertainty in the rBC concentration is 30%.*"

The uncertainty in the $b_{abs,BrC}$ was estimated from error propagation. We have modified the language when $b_{abs,BrC}$ and MAC_{BrC} are introduced to note this. "The uncertainties in $b_{abs,BrC}$ and the derived MAC_{BrC} are estimated by error propagation and scale inversely with the [OA]/[rBC] ratio as the OA contribution to the total absorption decreases (McClure et al., 2020)."

Line 168: How was the [OH] concentration calculated?

We determined the OH concentrations from the observed OH exposures by dividing by time since the lights were turned on. We now note this: "*For the model calculations in Section 3.2.1, the time-evolving OH exposures were converted to equivalent OH concentrations based on the time since the lights were turned on.*"

Lines 224-243: E_abs is reported to be close to 1. Does this affect prior published conclusions about lensing?

This adds to the literature results that show observed E_{abs} values vary over a wide range depending on the nature of the particles sampled. It affects prior published results only in-so-much as they assumed that "lensing" enhancements for primary biomass burning particles are large. We would point the interested reader to the work of (Fierce et al., 2020) and (Liu et al., 2017) for further discussion of some of the reasons for E_{abs} values being low in some studies but not others.

Lines 248-249: This sentence is unclear.

We have worked to rephrase this. "*For the aged particles, the average upper-limit $b_{abs,BrC}$ values exceed the lower limit $b_{abs,BrC}$ values by 11(±9)% at 405 nm and 29(±16)% at 532 nm.*"

Section 3.1.2 Comparison with Literature. A large list of comparisons are given in the text, and only partially summarized in Table S4. The paper would be stronger if the literature comparison were more completely and quantitatively summarized in a table.

We have added the missing references to Table S4 and added additional, albeit brief, notes regarding what was observed in each study to the Table.

Section 3.2: It would be useful to give an overview of the model here. What is the time step? How frequently is the model constrained to the measurements, and which measurements provide constraints?

The model is constrained via minimization of the difference from the observations of [OA]/[rBC] and MAC_{BrC} using the Global Fit package in Igor v.8.03 (see L502-504 in the original manuscript, now L563-565). The model timestep is two mins, as this is the time over which observations were averaged (given the cycling between ambient and thermodenuded states). We now note the model time step (L573).

Conclusions: Which conclusions are derived directly from the measurements, and which are from the model?

The information in the first paragraph derives from the measurements and in the second from the model application to the measurements. We have modified the first sentence of the second paragraph to make this clearer. "The evolution of the BrC absorptivity was shown *via application of a mechanistic model* to be consistent with a combination of production of strongly absorbing and much more weakly absorbing secondary OA,…"

Uncertainties and error bars are missing in the paper. These are important in Tables 1 and 2. The range of values measured could be shown as a shaded background for the lines in Figures 1, 2, 3, and 5. This would show the variability of the repeated measurements, and the uniqueness (or not) of the six classes.

We show the measurements associated with every burn in a series of supplemental figures. These allow for assessment of the burn-to-burn variability for the different classes. We have experimented with addition of shaded backgrounds per the reviewers suggestion but find that it is, at times, difficult to distinguish between all of the different shades as there are periods when more than two overlap. The figures in the supplemental allows for both comparison between particle class and visualization of the individual burns. We have therefore not updated the figures in the main text to use shaded backgrounds.

Minor Comments:

Line 86: "...absorptivity dependent upon on..."

Line 149: "An instruments suite..."

We have corrected these typos.

Response to comment by Dr. Radney

We thank Dr. Radney for the comments. Our responses follow:

The authors refer significantly to the 6 SSA classes and the corresponding particle optical properties. However, they do not make any reference to the underlying particle size distributions as if these optical values should be taken as some size-independent constant. The authors allude to their assumption that these properties are size independent on Line 280 – "suite of intensive optical (e.g. SSA, MAC, AAE)" – which is physically unreasonable. They again treat these properties as size independent in their conclusions. Significant discussion of the underlying particle sizes and their contributions to the observed optics is warranted.

While we appreciate Dr. Radney's concern regarding particle size, we did not anywhere assume a size-independence. We measured what we measured, which is for the size distributions that were observed; the companion paper by McClure et al. (2020) discusses the particle size distributions for the primary particles extensively. We show there that, while there is some burn-to-burn variability, the volume-weighted average size distributions are similar between the different classes. Thus, we expect that, in general, the particles begin from a similar state. The intensive properties we measured are, indeed, intensive; it is not clear how us stating that these are intensive necessarily implies that we assume they are size independent. Dr. Radney's criticism here could apply to 1000's of papers characterizing ambient particle SSA and AAE; we have used the terminology consistently with the common usage in the scientific literature on this topic.

2. Page 8, Line 221: "The $MAC_{BC,pure}$ = 11.8 m_2 g_{-1} (405 nm), 8.8 m_2 g_{-1} (532 nm) and 5.5 m_2 g_{-1} (781 nm)." What are the uncertainties associated with these values? Also, by using a campaign-specific average, the authors are suggesting that the MAC_{BC} is a constant (and hence the particle monomer dimensions, etc.) for all the different fuel-stocks involved? The authors should provide a justification or say that it is necessary due to data limitations especially considering that MAC_{BrC} is dependent upon these values. The authors allude to this on Line 254, but never provide values or an estimation of this dependence.

The uncertainties are provided in McClure et al. (2020), which we cited as the source for these values; they are estimated as +/-10%. We now include these explicitly. Yes, we assume that the MAC_{BC} is a constant. The 781 nm measurements in McClure et al. (2020) are consistent with this assumption. And separate work from our group has shown that for uncoated soot produced from a laboratory flame that the MAC is size independent, most likely because absorption is dominated by the spherules and the MAC_{BC} is, theoretically, quite constant in the size range over which spherule sizes vary (10-50 nm) (Forestieri et al., 2018). We now state this assumption explicitly.

> *"We assume these reference values are applicable to all burns, consistent with the negligible dependence of the primary particle $MAC_{BC,781nm}$ on the coating-to-BC mass ratio ($R_{coat-rBC}$) (McClure et al., 2020) and the lack of size dependence of the $MAC_{BC,pure}$ measured for uncoated BC particles produced from a laboratory flame (Forestieri et al., 2018)."*

3. Page 9, Line 241: "This suggests that the majority of the variability in the $MAC_{BC,781nm}$ derives from varying contributions of BrC, rather than in $E_{abs,coat}$, and that $E_{abs,coat}$ is near unity."
While this statement may be true, considering the arguments that the authors have provided, it seems more accurate to say that the individual contributions cannot be separated and therefore it is assumed that $E_{abs,coat}$ is near unity.

We disagree. The changes in the $E_{abs,781nm}$ at the very largest $R_{coat\text{-}BC}$ and [OA]/[rBC] values are substantially higher than any lensing effect might be. Also, as we show in Fig. S2 and consistent with McClure et al. (2020), there is a much stronger relationship between $E_{abs,781nm}$ and [OA]/[rBC] than with $R_{coat\text{-}BC}$. This is stated in the sentence just prior to the one quoted by Dr. Radney. This observation provides evidence that BrC absorption is driving the behavior rather than the lensing effect.

4. Page 10, Line 273: "Grouping experiments by SSA classification is justified given the substantial variability in the primary particle properties between individual burns."
I agree that there is substantial variability between individual burns, but from the data presented in the SI it seems that these ranges are assigned solely to agree with those from McClure et al. (2019) and otherwise appear somewhat arbitrary. My point being, if we were to include uncertainties on some of these derived parameters, e.g. MAC_{BrC}, with what level of statistical certainty are these values actually different? Further, how are these parameters affected by the measured size distributions?

We disagree that these classifications are assigned solely to agree with those from McClure et al. (2020) and that they are "arbitrary." The work in McClure et al. shows very clearly that there is a strong relationship between many particle properties and the [OA]/[rBC] ratio, with SSA exhibiting an especially strong, very clear relationship. This suggests some commonality between burns of a given class. If we had used the modified combustion efficiency (MCE), a commonly used parameter with biomass burning studies, we think this would be more arbitrary than the classification scheme used here because there is only a weak relationship between MCE and many of the optical and chemical properties for the primary particles. We have modified the text to clarify that the classifications is based on/justified by the strong relationships observed between many different particle properties. "McClure et al. (2020) classified individual experiments into six classes dependent on the primary particles SSA_{405nm}*; the* SSA_{405nm} *exhibited strong relationships with a variety of other intensive optical properties and with the [OA]/[rBC] mass ratio*."

Regarding uncertainties, in McClure et al., the MAC_{BrC} values for the primary particles are shown with uncertainties (c.f. their Fig. 5). The uncertainty in the MAC_{BrC} is larger for the class 1 particles (those for which BC dominates absorption) than it is for the class 6 particles (those for which OA dominates the absorption). Differences in properties such as SSA, O:C, [OA]/[rBC] are clearly different between classes and well outside measurement uncertainties. For the MAC_{BrC}, we have now calculated p-values for each pair of classes using a one-way ANOVA test to determine which are distinguishable from each other at a statistically significant ($p < 0.05$) level. (Specifically, we have used the STATSANOVA1Test in Igor to carry out this comparison). A table summarizing the results is below (green = $p < 0.05$). The results demonstrate that most of the classes are statistically distinguishable from each other. The two exceptions are Class 3 vs. Class 4 and Class 4 vs. Class 5.

	Class 1	Class 2	Class 3	Class 4	Class 5	Class 6
Class 1		0.007305	4.55E-05	4.89E-05	9.59E-05	0.000479
Class 2	0.007305		0.000857	0.003682	0.000425	0.000105
Class 3	4.55E-05	0.000857		0.600462	0.036525	1.32E-05
Class 4	4.89E-05	0.003682	0.600462		0.304464	0.015077
Class 5	9.59E-05	0.000425	0.036525	0.304464		0.037135
Class 6	0.000479	0.000105	1.32E-05	0.015077	0.037135	

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