

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) measurement/modeling analysis that enabled decoupling the effects of vapor-to-particle conversion 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 measurements. 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 extrapolating 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 $R_{coat-rBC} > 9$, while theory predicts the $MAC_{BC,781nm}$ should increase by this amount for individual particles when $R_{coat-rBC} > 1$ (Fuller et al., 1999).”

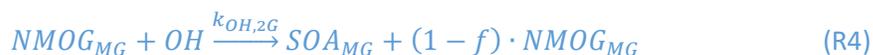
4) Figure 1: panel (g) is not described in the caption and the corresponding plots for individual burns are not given in the SI.

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 reaction be: $NMOG + OH \rightarrow SOA + NMOG_{MG}$, where $SOA = \alpha \cdot NMOG$ (since by definition, the yield is $SOA/NMOG$) and $NMOG_{MG} = (1 - \alpha) \cdot NMOG$?

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:



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,



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 (cm^{-1} should be s^{-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. Specifically:

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 propagate 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(\pm 9)% at 405 nm and 29(\pm 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 $MAC_{BC,pure} = 11.8 \text{ m}_2 \text{ g}^{-1}$ (405 nm), $8.8 \text{ m}_2 \text{ g}^{-1}$ (532 nm) and $5.5 \text{ m}_2 \text{ g}^{-1}$ (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_{BC} 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 $E_{\text{abs},781\text{nm}}$ at the very largest $R_{\text{coat-BC}}$ and $[\text{OA}]/[\text{rBC}]$ 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 $E_{\text{abs},781\text{nm}}$ and $[\text{OA}]/[\text{rBC}]$ than with $R_{\text{coat-BC}}$. 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 $[\text{OA}]/[\text{rBC}]$ 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 $\text{SSA}_{405\text{nm}}$; *the $\text{SSA}_{405\text{nm}}$ exhibited strong relationships with a variety of other intensive optical properties and with the $[\text{OA}]/[\text{rBC}]$ 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, $[\text{OA}]/[\text{rBC}]$ 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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1 **Biomass-burning-derived particles from a wide variety**
2 **of fuels: Part 2: Effects of photochemical aging on**
3 **particle optical and chemical properties**

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25 **KEY POINTS**

26 - Despite wide diversity in properties of primary particles produced from biomass
27 combustion, photochemical aging engenders generally consistent changes

28 - Photochemical aging alters the absorptivity of brown carbon (aka absorbing organic
29 aerosol) resulting from secondary organic aerosol production and heterogeneous oxidation

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ABSTRACT

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PLAIN LANGUAGE SUMMARY

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Particles in smoke emitted from biomass combustion have a large impact on global climate and urban air quality. There is limited understanding of how particle optical properties—especially the contributions of black carbon (BC) and brown carbon (BrC)—evolve with photochemical aging of smoke. We analyze the evolution of the optical properties and chemical composition of particles produced from combustion of a wide variety of biomass fuels, largely from the Western U.S.. The smoke is photochemically aged in a reaction chamber over atmospheric-equivalent timescales ranging from 0.25-8 days. Various aerosol optical properties (e.g., the single scatter albedo, the wavelength dependence of absorption, and the BC mass absorption coefficient (MAC_{BC})) evolved with photochemical aging, with the specific evolution dependent on the initial particle properties and conditions. The impact of coatings on BC absorption (the so-called lensing effect) was small, even after photochemical aging. The initial evolution of the BrC absorptivity (MAC_{BrC}) varied between individual burns, but decreased consistently at longer aging times; the wavelength-dependence of the BrC absorption generally increased with aging. The observed changes to BrC properties result from a combination of SOA production and heterogeneous oxidation of primary and secondary OA mass, with SOA production being the major driver of the changes. The SOA properties varied with time, reflecting both formation from precursors having a range of lifetimes with respect to OH and the evolving photochemical environment within the chamber. Although the absorptivity of BrC generally decreases with aging, the dilution-corrected absorption may actually increase from the production of SOA. These experimental results provide context for the interpretation of ambient observations of the evolution of particle optical properties in biomass combustion-derived smoke plumes.

Particles and gases from combustion of a wide range of biomass fuels (e.g. leaves, twigs, logs, peat, dung) were continuously photochemically aged in a small chamber up to eight days of equivalent atmospheric aging. The properties of the emitted particles and smoke depended on the fuel used and the combustion conditions. Upon aging, the particle chemical composition and ability to absorb sunlight changed as a result of conversion of gases into particulate material and

60 from conversion of emitted particulate material into a different chemical form. We developed a
61 model to explain the observations, and used this to derive insights into the aging of smoke in the
62 atmosphere.

63

64 **KEYWORDS**

65 0305 Aerosols and particles; 0325 Evolution of the atmosphere; 0345 Pollution: urban and
66 regional; 0360 Radiation: transmission and scattering

67 **1 Introduction**

68 Open and contained biomass combustion contributes substantial amounts of particulate matter
69 to the atmosphere (Bond et al., 2004). The emitted particles have a strong influence on global
70 climate by scattering and absorbing solar radiation and impacting cloud properties and
71 stratospheric water content (Penner et al., 1992; Sherwood, 2002; Jacobson, 2014). Biomass
72 burning-derived particles (BB particles, for short) also have substantial negative impacts on human
73 health globally (Lelieveld et al., 2015), especially when produced as a result of indoor combustion
74 associated with residential cooking and heating. In some parts of the world the frequency and
75 severity of uncontrolled fires is rising and projected to become worse in the future as a consequence
76 of climate change (Dale et al., 2001; Stephens et al., 2013) with effects already being seen in some
77 regions (McClure and Jaffe, 2018).

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78 Particles produced from biomass burning are primarily composed of organic material and black
79 carbon (Andreae and Merlet, 2001). The relative contribution of organic aerosol (OA) and black
80 carbon (BC) depends on the burn conditions, which is strongly related to the fuel type and other
81 environmental factors (McMeeking et al., 2009; McClure et al., 2020). The chemical, optical, and
82 physical properties of freshly emitted BB particles produced from burning of various biomass fuel
83 types under various conditions are reasonably well studied (e.g. Lewis et al., 2008; McMeeking et
84 al., 2009; Levin et al., 2010; Cheng et al., 2016; Fortner et al., 2018; McClure et al., 2020). Such
85 measurements have established that some fraction of the emitted OA is light absorbing, with the
86 absorptivity dependent upon the burn conditions (Saleh et al., 2014). Light absorbing OA is
87 commonly referred to as brown carbon (BrC). Compared to BC, brown carbon is generally less
88 absorbing and exhibits a much stronger wavelength dependence (Kirchstetter et al., 2004; Andreae

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93 and Gelencser, 2006). As such, the importance of BrC to light absorption tends to increase as
94 wavelength decreases.

95 The influence of atmospheric processing on the properties of biomass combustion smoke has
96 received less attention, especially in the context of how aging influences BB particle optical
97 properties. (Here, we use “smoke” to indicate the mixture of particles and gases emitted from
98 biomass combustion.) Understanding how BB particles evolve over time is key to establishing
99 their atmospheric impacts (Wang et al., 2018). Field observations of the effects of photochemical
100 aging on BB particle optical properties, and in particular light absorption, are sparse. Forrister et
101 al. (2015) observed that absolute absorption by water soluble BrC decreased over time within a
102 biomass-burning plume, with a decay time constant of about a day. Wang et al. (2016) observed
103 that the BrC absorptivity (as opposed to the absolute absorption) decreased with photochemical
104 age, with a similar time constant as reported by Forrister et al. (2015). However, both studies
105 suggest that there is some fraction of the BrC that is more persistent and less subject to
106 photochemical degradation, and Zhang et al. (2017) found no decrease in BrC absorption with age
107 for particles in convective outflow. Laboratory measurements can help provide mechanistic
108 understanding necessary to comprehensively interpret the field observations. Most laboratory
109 studies investigating photochemical aging effects on optical properties, and in particular light
110 absorption, of BB particles have done so for only a small number of individual fuel types or burn
111 conditions and often for particles alone rather than smoke (e.g., Saleh et al., 2013; Sumlin et al.,
112 2017; Tasoglou et al., 2017; Wong et al., 2017; Kumar et al., 2018). Thus, while these studies have
113 proven insightful, the limited number of fuels and conditions considered makes extending the
114 observations to the atmosphere thus far challenging.

115 In this study, we examine how the optical properties of BB particles evolve as a result of OH
116 radical dominated photochemical aging for smoke derived from combustion of a multitude of fuel
117 types and spanning a wide range of burn conditions. We characterize the influence of
118 photochemical aging on optical properties for a substantially greater number of fuel types than
119 have been reported previously in the literature, for burn conditions ranging from mostly flaming
120 to entirely smoldering. We access aging time scales ranging from a fraction of a day to many days
121 and characterize the continuous evolution of the particle properties. We show that the BB particle
122 optical properties evolve with photochemical oxidation, linked both to chemical evolution of the
123 primary particles and production of secondary organic aerosol. We characterize and quantify this

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125 behavior, developing a generalizable model for the evolution of brown carbon properties in
126 wildfire plumes.

127 **2 Methods**

128 **2.1 Campaign overview and sampling strategy**

129 The Fire Influence on Regional to Global Environments and Air Quality Experiment (FIREX-
130 AQ) lab campaign took place at the Missoula Fire Sciences Laboratory in November 2016
131 (NOAA, 2013). A full description of the sampling strategy and methods, including descriptions of
132 instruments used, for our study is provided in Lim et al. (2019) and [McClure et al. \(2020\)](#). Only a
133 short description is provided here. A wide-variety of fuels (**Table S1**) were combusted under
134 realistic conditions in a large combustion chamber (ca. 12 m x 12 m x 19 m). Fuels included bear
135 grass, rice straw, chaparral (chamise and manzanita), juniper, sagebrush, canopy, litter and mixed
136 components from [soft woods](#) (fir, pine, spruce), rotten logs, peat, dung. Data from the FIREX lab
137 study are available via the NOAA website (<https://www.esrl.noaa.gov/csd/projects/firex/firelab/>;
138 last access date 24 January 2020), with data specific to this work also archived as Cappa et al.
139 (2019a).

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140 The particle and gas emissions from individual [stack](#) burns were injected into a 0.15 m³
141 photochemical reaction chamber (the “mini chamber”). A burn typically lasted about 10-20
142 minutes. Smoke was transferred from the burn room to the adjacent room housing the mini
143 chamber and associated instrumentation through a 30 m long high-velocity community inlet. The
144 residence time in the community inlet was determined as <2 s. Smoke from the community inlet
145 was sub-sampled into the mini chamber through a PM₁ cyclone using an ejector diluter. There
146 were some losses of particles and gases during transfer. However, comparison between the VOC
147 concentrations measured prior to sampling through the community inlet and from the mini
148 chamber prior to photooxidation demonstrate losses were relatively minor (<8% per volatility bin,
149 across the entire measured VOC distribution) and should not substantially impact the results here
150 (Coggon et al., 2019; Lim et al., 2019).

153 2.2 The mini chamber

154 Prior to each burn, the chamber was flushed with clean air with RH ranging from 25-40%.
155 Smoke was sampled into the mini chamber across an entire burn or until shortly after the
156 concentration in the mini chamber reached maximum. An instrument suite continuously sampled
157 air from the mini chamber (see below). Clean make-up air added from a zero-air generator
158 (Teledyne 701H) ensured the total inflow (sample + make-up air) equaled the air being sampled
159 out of the chamber. The actual flowrate out of the chamber varied slightly between experiments
160 dependent upon the exact instrument suite. Given the mini chamber volume and the typical
161 flowrates, the net dilution from the community inlet was about a factor of seven.

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162 Details of the mini chamber and its operation are provided in Lim et al. (2019). The FIREX
163 mini chamber operated in semi-batch mode, where unoxidized smoke-laden air is first sampled
164 into the mini chamber. After the sampling period, a clean airflow replaces the sample flow,
165 maintaining the size of the bag over time. Oxidation is initiated by turning on one 254 nm UV
166 light. Externally generated ozone added at 50-100 ppb serves to initiate production of OH radicals
167 via generation of O(¹D). The concentrations of gases and particles continuously decreased owing
168 to dilution by clean air and wall losses. The observed decay rate of acetonitrile (ACN) provides
169 the dilution rate (see Section 2.3); gases that are substantially more sticky than ACN may be lost
170 at a faster rate. The ACN loss rate, characterized as $-\text{dlog}[\text{ACN}]/\text{dt}$, was around 0.024 min^{-1} ,
171 consistent with the gas flow rates. The particle loss rate was greater owing to additional losses of
172 particles to the walls of the chamber. The general particle mass loss rate was $-\text{dlog}[\text{particles}]/\text{dt} \sim$
173 0.038 min^{-1} . However, for BC-rich particles the loss rate was initially enhanced when the lights
174 were turned on, discussed further below. OH exposures were determined from the dilution-
175 corrected decay of deuterated n-butanol (D9). These are converted to an equivalent time-evolving
176 photochemical age (t_{OH}) assuming $[\text{OH}] = 1.5 \times 10^6 \text{ molecules cm}^{-3}$. The t_{OH} ranged from 0.25 to
177 about 8 days of equivalent aging. OH concentrations determined for real-world biomass burning
178 plumes may be higher than assumed here (Akagi et al., 2012) and thus aging may happen on shorter
179 timescales. For the model calculations in Section 3.2.1, the time-evolving OH exposures were
180 converted to equivalent OH concentrations based on the time since the lights were turned on. The
181 n-butanol (D9) measurements were available for only about half of the individual burn experiments
182 owing to data availability limitations of the VOC measurements. While there is some experiment-
183 to-experiment variability in the t_{OH} values accessed, the relationship between experiment time and

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186 t_{OH} is reasonably consistent. Thus, we use the average behavior to estimate the photochemical ages
187 for experiments lacking direct measurement.

188 As discussed in Coggon et al. (2019), the conditions of the mini chamber do not perfectly
189 represent the photochemical conditions of the atmosphere. The use of the 254 nm UV lights
190 enhances photolysis of a small number of select non-methane organic gases (NMOG), especially
191 furfural. In contrast, photolysis of NO_2 is likely substantially slower than in the atmosphere. This
192 impacts the time-evolution of the NO/NO_2 ratio, and consequently radical reactions (e.g. $RO_2 +$
193 NO) and NO_x loss processes. The influence of photobleaching of BrC is likely underestimated
194 relative to the atmosphere as the actual exposure time (tens of minutes) is much shorter than the
195 equivalent photochemical age (many days). Overall, the photochemical environment in the mini
196 chamber emphasizes OH-driven oxidation under initially high- NO_x conditions that rapidly shift
197 towards low- NO_x conditions (Coggon et al., 2019).

198 2.3 Instrumentation

199 The suite of instruments sampling from the mini chamber are listed in **Table S2** and further
200 details of instrument operation and uncertainties are provided in [McClure et al. \(2020\)](#), Lim et al.
201 (2019), and Coggon et al. (2019). In brief, particle-phase instruments sampled alternately
202 through a two-stage thermodenuder that operated at 150°C and 250 °C with a residence time of ~5
203 seconds. The cycle rate between ambient and thermodenuder sampling was 2 minutes. The ambient
204 (“bypass”) line on the thermodenuder was lined with charcoal cloth to remove excess NMOG, O_3 ,
205 and NO_2 that might otherwise interfere with the measurements. [Light absorption and extinction](#)
206 [coefficients \(\$b_{abs}\$ and \$b_{ext}\$, respectively\) were measured at 405 nm and 532 nm using the UC Davis](#)
207 [cavity ringdown-photoacoustic spectrometer \(CRD-PAS\) and at 781 nm using a DMT](#)
208 [photoacoustic soot spectrometer \(PASS-3\). Estimated uncertainties for the absorption](#)
209 [measurements were 8%, 5%, and 10% at 405 nm, 532 nm, and 781 nm, respectively.](#) Particle size
210 distributions were measured using a scanning electrical mobility spectrometer (SEMS; Model
211 2002, Brechtel Mfg., Inc.). The overall concentration and composition of sub-micron non-
212 refractory particulate matter (NR- PM_{10}) were measured using a high-resolution time-of-flight
213 aerosol mass spectrometer (HR-AMS; Aerodyne Research, Inc.). The concentration and
214 composition of refractory BC-containing particles was characterized using a soot particle aerosol
215 mass spectrometer (SP-AMS; Aerodyne Research, Inc.); the SP-AMS was operated with only

Deleted: McClure et al. (2019)

217 laser-vaporization of particles such that it was sensitive to only those particles containing
 218 refractory black carbon (rBC). Refractory black carbon concentrations and size distributions for
 219 volume-equivalent diameters from 90-350 nm were quantitatively measured using a single particle
 220 soot photometer (SP2; DMT). Refractory BC outside of this size window was accounted for
 221 through multi-modal fitting of the observed mass-weighted size distributions. The estimated
 222 uncertainty in the rBC concentration is 30%. Gas-phase instruments sampled directly from the
 223 mini chamber through Teflon sampling lines. These included: a proton-transfer-reaction time-of-
 224 flight mass spectrometer (PTR-ToF-MS) to characterize primary organic gases (Yuan et al., 2017);
 225 an I chemical ionization mass spectrometer to characterize various gas-phase organic oxidation
 226 products; an ozone monitor (2B Technologies, Model 202); a CO monitor (Teledyne, Model
 227 T300), and a CO₂ monitor (LI-COR, LI-840A).

228 2.4 Brown carbon, coatings, and particle classification

229 Mass absorption coefficients, referenced to BC, are calculated as:

$$230 \quad MAC_{BC} = \frac{b_{abs}}{[BC]}, \quad (1.)$$

231 where b_{abs} is the absorption coefficient (Mm^{-1}) and $[BC]$ is the concentration of refractory black
 232 carbon ($\mu g m^{-3}$). The observed MAC_{BC} may include contributions to absorption from both the BrC
 233 (the BrC enhancement, $E_{abs,BrC}$) and from the so-called lensing effect that can occur when non-
 234 absorbing coatings mix with BC (the coating-induced enhancement, $E_{abs,coat}$) (Cappa et al.,
 235 2012; Lack et al., 2012). The observable absorption enhancement is characterized as:

$$236 \quad E_{abs} = \frac{MAC_{BC,obs}}{MAC_{BC,pure}}; \quad (2.)$$

237 where $MAC_{BC,obs}$ is the observed value and $MAC_{BC,pure}$ is a reference value for pure, uncoated BC.
 238 The reference $MAC_{BC,pure}$ can be established from the literature or from the observations; we take
 239 the latter approach here, using wavelength-specific $MAC_{BC,pure}$ values determined by McClure et
 240 al. (2020) for this data set by extrapolation of the observed $MAC_{BC,obs}$ versus $[OA]/[BC]$
 241 relationship to zero $[OA]/[BC]$. The $MAC_{BC,pure} = 11.8 \pm 1.2 m^2 g^{-1}$ (405 nm), $8.8 \pm 0.9 m^2 g^{-1}$ (532
 242 nm), and $5.5 \pm 0.6 m^2 g^{-1}$ (781 nm). We assume these reference values are applicable to all burns,
 243 consistent with the negligible dependence of the primary particle $MAC_{BC,781nm}$ on the coating-to-
 244 BC mass ratio ($R_{coat-rBC}$) (McClure et al., 2020) and the lack of size dependence of the $MAC_{BC,pure}$

Deleted: $\frac{MAC_{BC,obs}}{MAC_{BC,ref}}$

Deleted: McClure et al. (2019) for this data set. 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).

248 measured for uncoated BC particles produced from a laboratory flame (Forestieri et al., 2018). The
 249 use of a campaign-specific value helps to mitigate instrumental uncertainties in determining E_{abs}
 250 (Cappa et al., 2019b).

251 We observe limited change in the $E_{abs,781nm}$ with photochemical aging here, with $E_{abs,781nm}$ for
 252 aged particles averaging 1.19 for $R_{coat-rBC} < 9$ (Figure S2). The $E_{abs,781nm}$ (and $MAC_{BC,781nm}$) only
 253 increases notably (by more than 10%) when $R_{coat-rBC} > 9$, while theory predicts the $MAC_{BC,781nm}$
 254 should increase by this amount for individual particles when $R_{coat-rBC} > 1$ (Fuller et al., 1999).

255 Other laboratory experiments, often performed using mono-disperse BC seed particles, have
 256 observed substantial coating-induced enhancements and a dependence on the $R_{coat-rBC}$ (e.g. Cross
 257 et al., 2010; Shiraiwa et al., 2010; Cappa et al., 2012; Metcalf et al., 2013; Peng et al., 2016a; You et
 258 al., 2016). We suggest that the small $E_{abs,coat}$ for photochemically aged biomass combustion
 259 particles results from three phenomena: (i) condensation occurring onto a polydisperse rBC
 260 distribution, leading to some particles having very thick coatings and some quite thin, yielding a
 261 large average $R_{coat-rBC}$ yet small enhancement (Fierce et al., 2016; Fierce et al., 2020); (ii) the coated
 262 biomass burning-derived rBC particles not having a core-shell morphology and reduced $E_{abs,coat}$
 263 (Helgestad, 2016; Liu et al., 2017); and, (iii) weak absorption by BrC at 781 nm by both internally
 264 and externally mixed BrC that becomes notable only when the total [OA] greatly exceeds [BC]
 265 (McClure et al., 2020). This is supported by the comparably much stronger relationship for
 266 photochemically aged particles between $MAC_{BC,781nm}$ and the [OA]/[rBC] ratio than with the
 267 $R_{coat-rBC}$ (Figure S2). This suggests that the majority of the variability in the $MAC_{BC,781nm}$ derives
 268 from varying contributions of BrC, rather than in $E_{abs,coat}$, and that $E_{abs,coat}$ is near unity.

269 The wavelength-specific BrC absorption ($b_{abs,BrC}$) is estimated as:

$$270 \quad b_{abs,BrC} = b_{abs,obs} - MAC_{BC,pure} \cdot [rBC] \cdot E_{abs,coat} \quad (3.)$$

271 Given the above discussion and the complementary discussion in McClure et al. (2020), we assume
 272 $E_{abs,coat}$ is unity, with the derived $b_{abs,BrC}$ an upper limit. A lower limit for $b_{abs,BrC}$ can be obtained
 273 using an empirical $E_{abs,coat}$ versus $R_{BC-coat}$ relationship. For the aged particles, the average upper-
 274 limit $b_{abs,BrC}$ values exceed the lower limit $b_{abs,BrC}$ values by 11(±9)% at 405 nm and 29(±16)% at
 275 532 nm. The brown carbon-specific mass absorption coefficient (MAC_{BrC}) is:

$$276 \quad MAC_{BrC} = \frac{b_{abs,BrC}}{[OA]} \quad (4.)$$

Deleted: The $E_{abs,781nm}$ observed for primary particles was near unity with a negligible dependence on the coating-to-BC mass ratio ($R_{coat-rBC}$) (McClure et al., 2019).

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Deleted: uncertainties in $b_{abs,BrC}$ and the derived

Deleted: scale inversely with the [OA]/[rBC] ratio, where MAC_{BrC}

290 The MAC_{BrC} values are bulk-average values and do not account for different molecules and classes
291 of molecules likely having different absorptivities. Uncertainty in the estimated $MAC_{BC,pure}$ and
292 measured b_{abs} , and [rBC] also contribute to uncertainty in the estimated ~~$b_{abs,BrC}$ and MAC_{BrC} . The~~
293 ~~uncertainties in $b_{abs,BrC}$ and the derived MAC_{BrC} are estimated by error propagation and scale~~
294 ~~inversely with the [OA]/[rBC] ratio as the OA contribution to the total absorption decreases~~
295 ~~(McClure et al., 2020).~~

Deleted: MAC_{BrC} .

296 The Ångström absorption exponent (AAE) characterizes the wavelength dependence of
297 absorption:

$$298 \quad AAE_{\lambda_1-\lambda_2} = -\log\left(\frac{b_{abs,\lambda_1}}{b_{abs,\lambda_2}}\right) / \log\left(\frac{\lambda_1}{\lambda_2}\right); \quad (5.)$$

299 where λ_1 and λ_2 indicate two different measurement wavelengths. The AAE can be calculated
300 based on the total absorption or just for BrC, with the latter designated as AAE_{BrC} . The single-
301 scatter albedo (SSA) characterizes the fraction of light extinction attributable to scattering:

$$302 \quad SSA_{\lambda} = \frac{b_{ext}-b_{abs}}{b_{ext}} = \frac{b_{sca}}{b_{ext}} \quad (6.)$$

303 ~~McClure et al. (2020) classified individual experiments into six classes dependent on the primary~~
304 ~~particles SSA_{405nm} ; the SSA_{405nm} exhibited strong relationships with a variety of other intensive~~
305 ~~optical properties and with the [OA]/[rBC] mass ratio.~~ We use these same classifications, ranging
306 from class 1—primary particles having low SSA_{405nm} values (0.22 - 0.38) and small [OA]/[rBC]
307 (0.3 - 2.6)—to class 6—primary particles having high SSA_{405nm} values (0.94 to 0.96) and very large
308 [OA]/[rBC] (400 to 1×10^5)—to interpret the influence of photochemical aging. **Table S3** provides
309 the general relationship between fuel type, SSA, and $\log([OA]/[BC])$. As noted by ~~McClure et al.~~
310 ~~(2020)~~, the classifications relate somewhat to the burn-average modified combustion efficiency
311 (MCE), which characterizes the burn efficiency, with class 1 generally deriving from more
312 efficient, flaming burns having higher MCE and class 6 from more less efficient, smoldering burns
313 having lower MCE. The average dependence of the various aerosol properties on photochemical
314 age is determined for each SSA class. Grouping experiments by SSA classification is justified
315 given the substantial variability in the primary particle properties between individual burns. The
316 focus on average behavior increases robustness of the resulting interpretation as sensitivity to
317 experiment-by-experiment differences (e.g., length of experiment, initial concentration, amount of
318 fuel consumed) is reduced.

Deleted: McClure et al. (2019) classified individual experiments into six classes dependent on the primary particles SSA_{405nm} .

Deleted: McClure et al. (2019)

323 3 Results and Discussion

324 3.1 Observations of the influence of photochemical aging on optical properties

325 3.1.1 Total particles (black + brown carbon)

326 The suite of intensive optical (e.g. SSA, MAC, AAE) and chemical and physical properties (e.g.
327 [OA]/[rBC], $R_{\text{coat-rBC}}$) vary with photochemical aging; the average behavior for each particle class
328 is shown in **Figure 1** and the experiment-specific behavior within each class in **Figure S3** through
329 **Figure S8**. The majority of the mass formed is OA, with minor contributions from inorganic
330 species. A detailed assessment of SOA formation is provided by Lim et al. (2019).

331 The changes observed for the lower number (more BC-rich) particle classes are typically more
332 pronounced than for the higher number (more OA-rich) particle classes. For example, the class 1
333 $\text{SSA}_{405\text{nm}}$ increases from 0.3 to 0.7 and the $\text{AAE}_{405-532}$ from 1.4 to 3.5 with aging, while the class
334 6 $\text{SSA}_{405\text{nm}}$ remains near constant at 0.94 and the $\text{AAE}_{405-532}$ decreases slightly from ca. 7 to 5.
335 Notably, the $\text{AAE}_{405-532}$ converge towards a common value, around 4, with aging. While there
336 remain some class specific differences, this indicates that the SOA that is forming has similar
337 optical properties independent of the initial burn conditions.

338 Also, the [OA]/[BC] for class 1 increases by a factor of nearly 70 while the increase for class
339 6 is ten times smaller, and the particle class 1 $R_{\text{coat-rBC}}$ increases by a factor of 11 while there is
340 negligible change for particle class 6. Generally, the most rapid changes occur when the equivalent
341 aging time is less than a day, with slower changes after this. Some of the observed changes, in
342 particular for class 1 and class 2 particles, results from enhanced loss of BC-rich particles when
343 the lights are turned on, although this alone cannot explain the differing extents of change and
344 would not directly impact the $R_{\text{coat-rBC}}$ (Section 3.2.1). These observations indicate substantial
345 formation of secondary OA and a net increase in the overall (dilution-corrected) OA, consistent
346 with Lim et al. (2019). If secondary OA formation were offset by evaporation of primary OA then
347 the SSA would not have increased, nor would the [OA]/[rBC] or $R_{\text{coat-rBC}}$ ratios have increased.

348 Additionally, the OA O:C atomic ratio increases and the AMS f_{60} (a marker for primary
349 biomass burning OA attributed to levoglucosan and similar species) decreases rapidly with
350 photochemical aging (**Figure 1**). However, unlike the above properties, the O:C and f_{60} evolution

351 are generally similar between SSA classes, despite some variability in the primary particle
352 properties (McClure et al., 2020). The changes in both O:C and f_{60} occur more rapidly than can be
353 explained by heterogeneous oxidation, implying rapid photochemical production of secondary OA
354 (Lim et al., 2019). The O:C increases rapidly at $t_{OH} < 1$ day with continual increases with further
355 aging. The f_{60} values decline rapidly at $t_{OH} < 1$ day to around $f_{60} = 0.008$, changing negligibly with
356 continued aging. It is noteworthy that the f_{60} plateaus around 0.008 upon aging, rather than at
357 0.003, the value denoted by Cubison et al. (2011) as the nominal background outside of biomass
358 burning influenced areas. This suggests that observation of f_{60} values much smaller than 0.008 in
359 ambient measurements indicate an influence of OA from non-biomass combustion sources (both
360 POA + SOA).

Deleted: (McClure et al., 2019).

361 3.1.2 Brown Carbon

362 **Observations:** The class-average $MAC_{BrC,405}$ and the $AAE_{BrC,405-532}$ evolve with photochemical
363 aging (Figure 2). Results for individual experiments are shown in Figure S10 and Figure S11.
364 Overall, the $MAC_{BrC,405}$ values decrease from the primary values with aging. However, for the
365 initially less absorbing BrC, corresponding to the higher SSA classes (i.e., class 5 and 6), the
366 $MAC_{BrC,405}$ first increase at $t_{OH} < 1$ day before decreasing. This behavior suggests rapid formation
367 of SOA more absorbing than the primary OA for these classes, with production of less absorbing
368 SOA or conversion of POA or SOA via heterogeneous oxidation into less absorbing forms at later
369 times (discussed further in Section 3.2.2). The $MAC_{BrC,532}$ behave similarly (Figure S12). The
370 class-average $MAC_{BrC,405}$ values all converge around $0.2 \text{ m}^2 \text{ g}^{-1}$ after many days (~ 5) of equivalent
371 aging. The class-average $AAE_{BrC,405-532}$ converge towards $AAE_{BrC,405-532} \sim 5$ after many days of
372 equivalent aging, with the exact behavior dependent on the initial $AAE_{BrC,405-532}$.

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373 **Comparison with literature:** Our observations can be compared with various literature
374 observations, where we use reported SSA or AAE values to infer the equivalent particle class
375 (Table S4). Martinsson et al. (2015) observed that the 370 nm OA absorptivity of class 1 particles
376 decreased after rapidly aging for $t_{OH} = 8.3$ days. Saleh et al. (2013) reported the AAE for class 1
377 particles produced from oak combustion changed negligibly (1.38 to 1.42) while the AAE for
378 particles from pine combustion increased slightly (1.48 to 1.73) after photochemically aging
379 smoke for t_{OH} of a few hours; the extent of aging was likely greater for the pine than oak. The AAE
380 for class 1 particles during FIREX increased to a greater extent (1.4 to 2.2) after similar aging (t_{OH}

385 ~ 6 h). Saleh et al. (2013) also report smaller SOA absorptivity compared to POA at 550 nm,
386 qualitatively consistent with our observations. Zhong and Jang (2014a) observed the 550 nm
387 absorptivity of class 5 particles initially increased over ~2 h, but then gradually declined upon
388 photochemical aging of smoke from smoldering combustion. This general behavior is consistent
389 with the behavior of the class 5 and 6 particles here, for which the MAC_{BrC} increased slightly in
390 the first few hours of equivalent aging followed by a continuous decline.

391 Similar to our observations, Kumar et al. (2018) observed $AAE_{370-660}$ values for class 1
392 particles increased from around 1.4 to 2 for photochemically aged beechwood smoke over $t_{OH} \sim 1$
393 day. They report that the primary OA is more absorbing than the SOA formed. We interpolate their
394 results to estimate MAC_{405} values for BC ($12.4 \text{ m}^2 \text{ g}^{-1} \pm 1.1$), primary BrC ($4.0 \text{ m}^2 \text{ g}^{-1} \pm 1.3$), and
395 secondary BrC ($1.6 \text{ m}^2 \text{ g}^{-1} \pm 1.4$). The $MAC_{BC,405}$ value agrees well with our estimate of 11.8 m^2
396 g^{-1} . However, their primary $MAC_{BrC,405}$ substantially exceeds our class 1 average ($2.25 \text{ m}^2 \text{ g}^{-1} \pm$
397 1.0) as does their primary BrC AAE (4.6 versus 2.2 ± 1.1 , respectively), while their AAE for SOA
398 is similar to that observed here at longer aging times (5.5 versus ~5, respectively). Over their ~1
399 day of equivalent aging they find little variability in the MAC_{BrC} for SOA. Cappa et al. (2019b)
400 reported $MAC_{BrC,405}$ and $AAE_{405-532}$ for relatively fresh biomass burning derived organic aerosol in
401 the ambient atmosphere, reporting values ($0.84 \text{ m}^2 \text{ g}^{-1}$ and 3.02, respectively) similar to those for
402 class 2 particles here.

403 Sumlin et al. (2017) heterogeneously aged class 6 particles with OH and observed negligible
404 changes in the absorptivity and SSA_{405} at 1 and 3.5 days of equivalent aging, but then a sudden
405 change at 4.5 days of equivalent aging. This differs substantially from our observations, where
406 changes occurred continuously; the reasons for this difference are unclear, although a
407 discontinuous change with increasing exposure is unexpected. Browne et al. (2019) also
408 heterogeneously aged class 6 particles with OH, but observed a continuous decrease in the
409 absorptivity with OH oxidation, consistent with the long-time behavior observed here. Wong et al.
410 (2017) photolytically aged (at 300-400 nm) water-soluble and water-insoluble solution extracts of
411 particles from smoldering combustion and observed that the particle absorptivity initially increased
412 over the course of about a day, peaked, and then declined over longer times to below the initial
413 value. While this general behavior is consistent with the evolution of our class 5 and 6 particles,
414 the photon flux here was likely too low for direct photolytic aging to contribute substantially (Peng
415 et al., 2016b), especially given the short absolute aging timescale in the mini chamber (tens of

416 minutes). Lee et al. (2014) photolytically aged water-soluble extracts of secondary BrC produced
417 from photooxidation of naphthalene and observed a continuous decrease in the absorptivity, but
418 again with a time constant that was likely too long to have influenced our experiments. Fleming et
419 al. (2020) photolytically aged particles from 12 of the FIREX burns that were collected on Teflon
420 filters. They observed a wide diversity of equivalent lifetimes (referenced to the time-averaged
421 photon flux in Los Angeles, CA) for different BrC chromophores, some of which were quite short
422 (<1 day). However, the equivalent lifetime of the total absorption was >10 days for all samples,
423 and with a recalcitrant component making up ca. 30% of the total absorption.

424 Overall, our results combined with the literature indicate that differences in starting conditions
425 (i.e., particle class) are important to consider when comparing between different photochemical
426 aging experiments on biomass combustion-derived particles. Additionally, it is important consider
427 whether a given experiment is likely to favor one process over another, e.g., SOA formation,
428 heterogeneous oxidation, or photolysis.

429 **3.2 Understanding and modeling the photochemical evolution of smoke**

430 **3.2.1 Chamber photochemical model description**

431 **Overview:** We observe that a wide range of particle properties evolve as the smoke from all
432 SSA classes is photochemically aged. To facilitate interpretation, we have developed a simplified
433 model of photooxidation that accounts for SOA formation from oxidation of gas-phase species,
434 heterogeneous oxidation, differential losses of particle types and dilution in the mini chamber. We
435 aim to simulate the evolution of the brown carbon absorptivity (i.e., MAC_{BrC}), specifically, using
436 the initial primary particle properties, gas-phase species, and evolution of the $[OA]/[rBC]$, $O:C$,
437 and AMS f_{60} as constraints or guides as to the reasonableness of the general model formulation.
438 Model parameters are constrained as possible by the observations or tuned to provide for good
439 agreement with the observations for all particle classes (**Table 1** and **Table 2**). Our modeling
440 approach complements the analysis of Lim et al. (2019), who show that the amount of SOA formed
441 is directly related to the total amount of precursor non-methane organic gases (NMOG) in the
442 chamber and that the effective SOA mass yield increases with aging. Here, we take a more
443 mechanistic approach to understanding SOA formation in these experiments and focus on the

444 influence of SOA formation on the observed optical properties. The model framework, constraints,
445 and assumptions are described below.

446 **Reactive gases:** Biomass burning releases a wide variety of NMOG (Koss et al.,
447 2018; Sekimoto et al., 2018; and references therein). Upon oxidation, these NMOG can form SOA.
448 In general, higher molecular weight NMOG have a higher propensity to form SOA (Cappa and
449 Wilson, 2012). We consider the suite of gas-phase compounds measured by PTR-ToF-MS (Koss
450 et al., 2018) having molecular weights greater than 50 amu as potential SOA precursor compounds.
451 (Consideration of all species measured, including those with MW < 50 amu does not change the
452 results, consistent with Lim et al. (2019).) These 107 identified gas-phase compounds have been
453 binned according to their OH reaction rate coefficients reported by Koss et al. (2018) (**Figure S13**
454 and **Figure S14**). The OH rate coefficients range from $3 \times 10^{-10} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ (for
455 sesquiterpenes) to 1.4×10^{-13} (for nitrobenzene); most compounds have k_{OH} values greater than 4
456 $\times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$. Based on these observations, we make a simplifying assumption that
457 there are three general classes of SOA precursor molecules: those that react fast ($3 \times 10^{-10} \geq k_{\text{OH}} >$
458 3×10^{-11}); those that react slowly ($3 \times 10^{-11} \geq k_{\text{OH}} \geq 2 \times 10^{-12}$); and those that react very slowly (k_{OH}
459 $< 2 \times 10^{-12}$). The corresponding SOA type-specific k_{OH} values we use in the model are: $k_{\text{OH,fast}} = 4$
460 $\times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ ($\tau_{\text{OH,fast}} = 0.19$ days), $k_{\text{OH,slow}} = 9 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ ($\tau_{\text{OH,slow}} =$
461 0.86 days), and $k_{\text{OH,VS}} = 7 \times 10^{-13} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ ($\tau_{\text{OH,VS}} = 11$ days) (**Table 1** and **Figure S13**).
462 (The time constants given correspond to $[\text{OH}] = 1.5 \times 10^6 \text{ molecules cm}^{-3}$.) The dividing lines
463 between the NMOG classes are somewhat arbitrary, but capture the general overall behavior and
464 are consistent with variable observed formation timescales of secondary NMOG (Coggon et al.,
465 2019). Loss of primary species due to photolysis is not considered; Coggon et al. (2019) show that
466 rapid photolysis dominates loss for a small number of primary species, notably furfural. These
467 species tend to be fast reacting, and thus are incorporated in the fast NMOG group, although their
468 actual loss rate is likely underestimated.

469 The initial total NMOG concentration is specified relative to the initial [OA], consistent with
470 Lim et al. (2019). The observed average ratio between the total carbon mass concentration
471 measured by the PTR-ToF-MS and the initial [OA] carbon mass is 7 ± 3 . SSA class-specific initial
472 [NMOG]/[OA] values are specified in the model, constrained to fall around this range (**Table 2**).
473 This initial gas-phase mass is apportioned between the fast, slow, and very slow NMOG. The PTR-

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477 TOF-MS measurements indicate that the relative abundances of fast, slow, and very slow reacting
478 NMOG average approximately 0.5:0.4:0.1 on a mass basis. We specify the very slow NMOG
479 fraction as a constant and allow the relative abundances of fast and slow reacting NMOG to vary
480 between the particle classes, with specific values determined from fitting to the observations; the
481 derived values are in general agreement with the observed range (**Table 2**). Allowing for some
482 variability is reasonable, given that the NMOG composition varied between experiments and with
483 burn type (Sekimoto et al., 2018).

484 The influence of multi-generation chemistry is accounted for by assuming all gas-phase
485 products from reaction of primary precursors are reactive towards OH radicals. This multi-
486 generational (MG) chemistry is simplified by assuming that all MG species react identically,
487 independent of the actual generation number (i.e., number of times reacted) or precursor identity.
488 This allows for a substantial reduction in the number of species tracked relative to more explicit
489 methods (Aumont et al., 2005; Cappa and Wilson, 2012). The assumed multi-generational oxidation
490 OH reaction rate coefficient, $k_{\text{OH,MG}}$, is set to $5 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ ($\tau_{\text{OH,MG}} = 1.54 \text{ days}$).
491 The $k_{\text{OH,MG}}$ falls between the fast and slow species. MG species are assumed to fragment upon
492 reaction, with a fragmentation probability (f) of 15%, serving to limit the maximum SOA
493 formation; assuming a constant f is a simplification over more detailed approaches (Cappa and
494 Wilson, 2012).

495 **SOA formation and processing:** SOA forms upon reaction of the primary NMOG types and
496 MG species, referred to here as SOA_{fast} , SOA_{slow} , SOA_{vs} , and SOA_{MG} . SOA formation occurs here
497 with fixed yields (α) assuming both instantaneous and irreversible (i.e., non-volatile)
498 condensation, simplifications over more detailed approaches. The influence of vapor wall losses
499 (Zhang et al., 2014) is not explicitly considered, and thus reflected in the derived α values. SOA
500 and POA also react heterogeneously with OH, producing oxidized OA that can also react with OH.
501 We assume an OH reactive uptake coefficient (γ_{OH}) of unity for all OA types. Upon oxidation,
502 15% of the POA and SOA mass is assumed lost owing to fragmentation and volatilization of the
503 products (i.e., $f_{\text{het,x}} = 0.15$). Heterogeneous oxidation of oxidized OA leads only to fragmentation
504 reflecting the greater propensity for more oxidized species to fragment upon reaction (Kroll et al.,
505 2015). The $k_{\text{OH,het}}$ values are calculated using the $[\text{OH}]$ with the observed surface-weighted particle
506 diameters and appropriate mass-transfer corrections (Smith et al., 2009).

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509 The overall reaction scheme is summarized below:



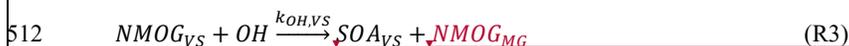
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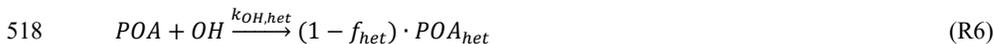
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514 Reactions 1-4 represent oxidation of gas-phase species and SOA formation, where $SOA_i = \alpha_i \cdot$
 515 $NMOG_i$ and for a given reaction $NMOG_{MG} = (1 - \alpha_i) \cdot NMOG_i$; the subscript i indicates which
 516 $NMOG$ type reacted. Also,



520 Reaction 5 represents the heterogeneous oxidation of fast, slow, very slow or multi-generation
 521 SOA and conversion to an oxidized SOA product, while Reaction 6 represents heterogeneous
 522 oxidation of POA to an oxidized product. Reaction 7 indicates that reaction of oxidized OA only
 523 produces volatile products.

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524 **Dilution and particle wall losses:** Given the semi-batch operation method for the mini
 525 chamber, the concentration of particles and gases all decreased over time owing to dilution and
 526 losses to the chamber walls. The non-OH loss rate of gases was assumed constant in the model,
 527 consistent with observations during an experiment where the lights were left off. However, we
 528 observed that the overall decay of BC particles containing little coating material (e.g. class 1 and
 529 class 2) was enhanced when the lights were turned on, while it was not for particles having thicker
 530 initial coating amounts (**Figure S15** and **Figure S16**). This enhanced loss was unique to BB
 531 particles, as no such behavior was observed for either atomized fullerene soot (highly absorbing)
 532 or ammonium sulfate (non-absorbing). That enhanced decay occurs for the BC-rich particles
 533 suggests that this phenomenon is related to the amount of coating material, since the class 1 and 2
 534 particles have substantially smaller initial $R_{coat,BC}$ values compared to the other classes (**Figure 1**

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547 and [McClure et al. \(2020\)](#). We speculate that the enhanced loss of BC-rich particles results from
548 their having a greater propensity towards photoelectric charging with the 254 nm light, as
549 photoelectric charging is highly sensitive to the state of the particle surface (Burtcher, 1992). We
550 determined an empirical relationship between the observed time-varying rBC decay rate and the
551 coating amount for use in the model ([Figure S17](#)). The decay rate slows as particles become more
552 coated (i.e., have larger $R_{\text{coat,rBC}}$), eventually reaching a plateau. We also account for the mixing
553 state of the particles when determining particle loss rates, as [McClure et al. \(2020\)](#) showed that the
554 fraction of total OA that is internally mixed with BC decreases as $[\text{OA}]/[\text{rBC}]$ increases. We
555 assume that the population of particles containing BC exhibit faster loss than the population that
556 does not. Independent of the enhanced decay for BC-rich particles, particle decay is faster than for
557 dilution-driven decay of gases because the particles are more subject to wall losses. The reference
558 decay rates for particles and gases were determined from experiments conducted using atomized
559 ammonium sulfate, atomized fullerene soot, and a “dark” smoke experiment. It is assumed that
560 POA does not evaporate upon dilution in the chamber, and thus does not contribute further to the
561 available NMOG, discussed further in Section 3.2.6.

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562 **SOA properties and model fitting:** The different types of SOA in the model, which form
563 from different NMOG, can have different properties. The properties that are allowed to differ
564 between SOA types and heterogeneous oxidation products, besides k_{OH} , are the MAC_{BC} , SOA
565 yields, O:C, and the f_{60} ([Table 1](#) and [Table 2](#)). While allowed to vary between SOA type, these
566 parameters are assumed to be independent of the SSA class. In this manner, we aim to find an
567 overall solution that allows for one set of SOA-type specific parameters that gives good model-
568 measurement agreement for all of the SSA classes. The choice of SOA yields influences all model
569 outputs, while the choice of the other parameters influence only that parameter output. The type-
570 specific MAC_{BC} and SOA yields (α) are determined by fitting the model to the observations,
571 specifically to the evolution of $[\text{OA}]/[\text{rBC}]$ and MAC_{BC} with the OH exposure ([Table 1](#)). The
572 Global Fit package in Igor v.8.03 (Wavemetrics) allowed for simultaneous fitting of the observed
573 $[\text{OA}]/[\text{rBC}]$ and MAC_{BC} for all particle classes. Thus, the retrieved MAC_{BC} and α values are those
574 that minimize the model-observation difference across all of the particle classes. After determining
575 the best-fit, type-specific MAC_{BC} and SOA yields, separate global fits were performed to the
576 observed O:C and f_{60} to determine the type-specific O:C and f_{60} ([Table 1](#)). The model time step
577 was 2 mins as this matched the averaging time for the observations.

581 Our analysis focuses on the evolution of the particle optical properties, and specifically the
582 BrC absorptivity. Section 3.2.2 provides a detailed discussion of the evolution of the MAC_{BrC} with
583 oxidation and the associated determination of SOA-type specific MAC_{BrC} values. Values for the
584 other parameters (SOA yields, O:C and the f_{60}) are briefly discussed here. The tuned SOA yields
585 were $\alpha_{fast} = 0.43$, $\alpha_{slow} = 0.15$, $\alpha_{VS} = 0.05$, and $\alpha_{MG} = 0.45$. These are effective yields averaged
586 across all NMOG of a given type. The derived average SOA yields are within the range of SOA
587 yields expected for the individual precursor species (Bruns et al., 2016).

588 Tuned values for the O:C for the SOA types are consistent with expected physical behavior,
589 guided by single-component studies (Chhabra et al., 2011). The fit O:C atomic ratios of the first-
590 generation SOA formed are 0.73 (fast), 0.59 (slow), and 0.59 (very slow, assumed the same as
591 slow). The O:C of multi-generation SOA and heterogeneously oxidized POA and SOA vary with
592 time, with the model fit indicating 1.22 oxygen atoms added per oxidation reaction, generally
593 consistent with expectations (Kroll et al., 2015). The observed AMS f_{60} rapidly falls to 0.008. To
594 match the observed behavior the fit $f_{60,fast} = 0.008$, $f_{60,slow} = f_{60,VS} = 0.003$, $f_{60,MG} = 0.006$, and the
595 f_{60} for products of heterogeneous oxidation dependent on whether SOA ($f_{60,het} = 0.01$), externally
596 mixed POA ($f_{60,het} = 0.003$), or internally mixed POA ($f_{60,het} = 0.008$) reacts. We note that similar
597 results are obtained if $f_{C_2H_4O_2^+}$ values are used instead of f_{60} . ($f_{C_2H_4O_2^+}$ is the high-resolution ion at
598 $m/z = 60$ that most corresponds to levoglucosan.)

599 3.2.2 Model-measurement comparison

600 The optimized model does a good job (reduced chi-square = 0.4) of describing the evolution
601 of MAC_{BrC} , $[OA]/[rBC]$, O:C atomic ratio, and AMS f_{60} (**Figure 3**). The reasonable agreement for
602 $[OA]/[rBC]$ indicates the appropriateness of the empirical correction for enhanced decay of rBC-
603 containing particles, the specified SOA yields and initial $[NMOG]/[OA]$ ratio, and the
604 apportionment between the different NMOG types. The model-measurement agreement improves
605 if the unknown model parameters are allowed to vary somewhat between particle classes; again,
606 some variability is expected given the burn-to-burn variability in the mix of NMOG species
607 (Sekimoto et al., 2018). However, that use of class-independent parameters provides for a
608 generally good description across classes demonstrates an overall general nature of the
609 photochemical evolution.

610 The evolution of the MAC_{BrC} , $[OA]/[rBC]$, O:C atomic ratio, and AMS f_{60} derive from changes
611 in the OA composition. Examples of the simulated time-dependent variation in OA composition
612 for particle class 1 and class 6 are shown in **Figure 4**. The observations demonstrate the importance
613 of SOA formation, with the predicted fractional contribution of POA decreasing over time. For
614 class 1, the MAC_{BrC} decays rapidly owing to a large fraction of the POA being internally mixed
615 with BC and therefore subject to enhanced decay in our experiments. Importantly, simulations
616 with heterogeneous oxidation only (i.e., no SOA formation is allowed) show much too small
617 increases in $[OA]/[rBC]$ values and too slow decay of the AMS f_{60} and rise of the O:C (**Figure**
618 **S18**), discussed further in Section 3.2.4.

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619 SOA type-specific **405 nm** MAC_{BrC} values determined from the model were $MAC_{fast} = 0.81 (\pm$
620 $0.2) \text{ m}^2 \text{ g}^{-1}$, $MAC_{slow} = MAC_{Vs} = 0.05 (^{+0.05}_{-0.025}) \text{ m}^2 \text{ g}^{-1}$, $MAC_{2G} = 0.17 (\pm 0.05) \text{ m}^2 \text{ g}^{-1}$, and $MAC_{het} =$
621 $0.05 (\pm 0.025) \text{ m}^2 \text{ g}^{-1}$. The SOA_{fast} is substantially more absorbing than the other SOA types. It is
622 difficult to estimate a comprehensive uncertainty on these values; the above uncertainties were
623 qualitatively estimated based on the model sensitivity to changing the parameter values (see
624 Supplementary Material). The strong absorptivity of the fast-forming SOA and the substantial
625 difference between MAC_{fast} and MAC_{slow} and MAC_{2G} are unexpected and somewhat surprising.
626 The identities of the likely precursor NMOG characterized (Koss et al., 2018) can be interrogated
627 to understand this difference along with the evolving chemical conditions in the chamber.

628 The measurements indicate precursor NMOG most likely to contribute to fast SOA formation
629 include: monoterpenes, guaiacol, benzenediol, methyl furfural, methyl guaiacol, vanillin, vinyl
630 guaiacol, creosol, isoeugenol, syringol, and styrene (**Figure S13**). The precursor NMOG most
631 likely to contribute to slow SOA formation include: toluene, 2-furanmethanol, phenol, o-cresol,
632 highly oxygenated levoglucosan dehydration products, naphthalene, tolualdehyde, 5-
633 hydroxymethyl tetrahydro 2-furanone, and C9 aromatic species. Benzene is the most likely very
634 slow SOA contributor, although contributes little here. These species are identified based on their
635 (i) measured emission factors and (ii) reaction rates with OH radicals (Koss et al., 2018), and (iii)
636 their estimated SOA yields (Bruns et al., 2016).

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637 SOA absorptivity varies between precursors (Lambe et al., 2013; Romonosky et al., 2016; Xie
638 et al., 2017), suggesting different precursors contribute differentially to the SOA absorption here.
639 Monoterpenes form SOA that is non-to-weakly absorbing. In contrast, SOA from aromatic

642 precursors can be quite absorbing, more so in the presence of NO_x . Formation of nitro-aromatics
643 is often linked to the enhanced absorptivity when NO_x is present, and condensed phase reactions
644 producing highly conjugated, potentially N-containing compounds also contribute to light
645 absorption (Laskin et al., 2015). Garmash et al. (2020) recently reported ROOR' dimer formation
646 in the gas phase from OH oxidation of aromatics, which we speculate could also contribute to light
647 absorption.

648 Given the potential importance of nitro-aromatic formation to SOA light absorption, the
649 organonitrogen (ON) aerosol contribution here is characterized from the HR-AMS using the
650 method of Kiendler-Scharr et al. (2016) (see Supplemental Material in [McClure et al. \(2020\)](#)). (We
651 use the term “organonitrogen” quite generally here, as the measurements do not directly provide
652 the particular chemical nature of the N-containing organic species, which could be nitro-aromatics
653 or organic nitrates. Further work is required to quantitatively differentiate ON functionalities in
654 the AMS.) The $[\text{ON}]/[\text{OA}]$ ratio for primary particles varies by SSA class and inversely with
655 $[\text{OA}]/[\text{rBC}]$, from 5.7% (class 1) to 0.25% (class 6) ([McClure et al., 2020](#)). Upon oxidation, the
656 $[\text{ON}]/[\text{OA}]$ ratio exhibits an initial rapid increase for all SSA classes (**Figure 5** and **Figure S19**),
657 demonstrating rapid formation of ON linked to oxidation of the fast-reacting NMOG. However,
658 over time the $[\text{ON}]/[\text{OA}]$ ratio decreases for all SSA classes, with the exception of class 6 which
659 remains approximately constant. The slow and very slow NMOG and the MG species are,
660 apparently, comparably less likely to form ON in our experiments, leading to a decline in their
661 relative contribution to OA.

662 That the observed $[\text{ON}]/[\text{OA}]$ ratio first increases then decreases with aging while the average
663 $MAC_{\text{Br,C}}$ derived for the SOA decreases with aging (owing to the $MAC_{\text{fast}} > MAC_{2\text{G}} > MAC_{\text{slow}} =$
664 MAC_{VS}) suggests a relationship between the processes driving these behaviors as well as a shift
665 with aging. While the $[\text{ON}]/[\text{OA}]$ ratio would depend on the formation of any organonitrogen
666 species, the SOA absorption likely depends, at least in part, on nitro-aromatic formation. Organic
667 nitrates form from reaction of NO with peroxy radicals (RO_2), which competes with $\text{RO}_2 + \text{HO}_2$,
668 $\text{RO}_2 + \text{RO}_2$, and RO_2 autoxidation and is thus sensitive to variations in the availability of NO
669 (Orlando and Tyndall, 2012; Bianchi et al., 2019). However, nitro-aromatics typically form in the
670 gas phase from reaction of NO_2 with phenoxy radicals or with OH/aromatic adducts (Grosjean,
671 1984; Berndt and Böge, 2003; Vereecken, 2019). Phenoxy radicals generally derive from OH
672 reaction with phenolic molecules and both NO and O_3 compete with NO_2 for reaction with

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676 phenoxy radicals; products from reaction with NO and O₃ are not well established (Vereecken,
677 2019). The importance of the OH-aromatic adduct + NO₂ pathway to nitro-aromatic formation is
678 suggested as small for species such as toluene and phenol owing to efficient reaction with O₂
679 (Atkinson et al., 1992;Vereecken, 2019), although has been proposed as the major pathway for
680 nitro-aromatic formation from guaiacol and similar species (Lauraguais et al., 2014;Sun et al.,
681 2019).

682 The [NO]/[NO₂] ratio in the primary smoke varied from 4.88 to 0.84 (Selimovic et al., 2018).
683 Modeling by Coggon et al. (2019) for a few of the experiments indicates a rapid decrease in the
684 [NO]/[NO₂] ratio towards zero with time owing to inefficient photolysis of NO₂ in the mini
685 chamber. Consequently, organic nitrate formation should be fastest early on, becoming very small
686 as time progresses. This can help explain the observed dependence of [ON]/[OA] on aging.
687 However, as nitro-aromatic formation involves NO₂, rather than NO, the evolving [NO]/[NO₂]
688 would not explain the evolution of the *MAC*_{BrC}. The fast reacting aromatics (e.g., guaiacol,
689 syringol, eugenol, styrene, vanillin, vinyl guaiacol, creosol, catechol) tend to be more substituted
690 than the slow reacting (e.g., phenol, o-cresol, toluene, benzaldehyde, tolualdehyde, naphthalene).
691 SOA formed from guaiacol with NO_x present is substantially more absorbing than SOA from
692 either toluene or m-xylene (Romonosky et al., 2016). Additionally, the nitro-aromatic yield from
693 reaction of guaiacol exceeds that of phenol, reflecting, in part, faster H-abstraction from the phenol
694 group in more substituted aromatics (Harrison et al., 2005;Lauraguais et al., 2014), and production
695 of nitro-aromatic species from reaction of non-phenolic molecules, such as toluene, requires
696 multiple reactions with OH. Thus, it may be that the fast reacting aromatic species generally
697 produce more absorbing nitro-aromatic species and with higher SOA yields compared to the slow
698 reacting aromatic species, contributing to the decrease in both the [ON]/[OA] and the *MAC*_{BrC} with
699 aging in the mini chamber.

700 Analogous to the treatment of the *MAC*_{BrC} for SOA, we have attempted to model the ON
701 formation by assigning a NMOG type-specific, yet particle class-independent ON yield. Unlike
702 the *MAC*_{BrC}, no model parameters allow for good model-measurement agreement using this
703 approach. This primarily results from the different particle classes having very different
704 [ON]/[OA]. For example, for the [ON]/[OA] ratio for class 1 particles to increase from the initial
705 value (5.7%) to the peak value (18%) requires a much larger model ON species SOA yield than

706 for the class 6 particles, for which the [ON]/[OA] increases from 0.3% to only 0.6%. The reason
707 for these substantial differences likely relates to the factors discussed above.

708 The reasonableness of the derived MAC_{BrC} values for SOA is assessed by estimating
709 approximate upper (high- NO_x) and lower (low- NO_x) MAC_{BrC} values for the SOA types based on
710 literature MAC values for SOA from individual precursors (Romonosky et al., 2016), the NMOG
711 emission factors (Koss et al., 2018), and estimated SOA yields (Bruns et al., 2016):

$$712 \quad MAC_{BrC,x} = \frac{\sum_i EF_i \alpha_i MAC_{BrC,i}}{\sum_i EF_i \alpha_i} \quad (7.)$$

713 where x is the SOA type and i is for an individual NMOG. We note the highly uncertain nature of
714 these estimates and therefore only consider them qualitatively. The estimated $MAC_{BrC,fast}$ fall in
715 the range $0.3 \text{ m}^2 \text{ g}^{-1}$ (low- NO_x) to $2.4 \text{ m}^2 \text{ g}^{-1}$ (high- NO_x). This encompasses contributions from
716 highly absorbing and abundant guaiacol SOA, moderately absorbing benzene diol (and related
717 species), and effectively non-absorbing monoterpene SOA. For slow SOA, the estimated
718 $MAC_{BrC,slow}$ ranges from $0.1 \text{ m}^2 \text{ g}^{-1}$ to $0.6 \text{ m}^2 \text{ g}^{-1}$, encompassing major contributions from
719 moderately absorbing phenol and cresol SOA. The estimated $MAC_{BrC,VS}$ depends almost entirely
720 on the benzene SOA, ranging from $0.21 \text{ m}^2 \text{ g}^{-1}$ (low- NO_x) to $0.88 \text{ m}^2 \text{ g}^{-1}$ (high- NO_x). Our derived
721 $MAC_{BrC,fast}$ falls between the upper and lower estimates, while the $MAC_{BrC,slow}$, $MAC_{BrC,VS}$, and
722 $MAC_{BrC,MG}$ are more similar to the lower estimates.

723 3.2.3 Extending the mini chamber results to the atmosphere

724 In the experiments, particles and gases experience different decay rates, with particle loss rates
725 exceeding NMOG precursor loss rates and the loss rates of BC-rich particles enhanced. The model
726 allows for simulation of the evolution of the overall system in the absence of such experimental
727 differences by setting the dilution of all components to the same value and wall losses to zero. This
728 provides insights into the likely influence of photochemical oxidation on the evolution of smoke
729 in the atmosphere, although likely does not fully account for the influence of NO_x and the evolving
730 NO/NO_2 ratio. For simplicity, we use a dilution rate of zero for these “atmospheric” simulations,
731 but any value could be used so long as the focus is on variability in intensive properties.

732 Simulated OA composition profiles are compared for particle classes 1 and 6, as examples, for
733 chamber (“chm”) and atmospheric (“atm”) simulations in **Figure 4**. In the atmospheric
734 simulations, the POA influence persists to much longer times than in the chamber simulations. For

735 example, for class 1 the POA fraction after 2 days of equivalent aging is 0.05 for the chamber
736 simulation but 0.35 for the atmospheric simulations; for class 6 the increase in the POA fraction,
737 from 0.2 (chamber) to 0.3 (atmospheric), is smaller, but still notable. Some of the increase in the
738 POA contribution for the atmospheric versus chamber simulations results from the POA and
739 NMOG having the same loss rates in the atmospheric simulations. This leads to a decreased
740 relative contribution of SOA. The larger difference between the atmospheric and chamber
741 simulations for particle class 1 also reflects the comparably greater influence of enhanced decay
742 of BC-rich particles.

743 The fractional contribution of the 2nd generation SOA decreases in the atmospheric
744 simulations, for all classes. This too results from the particle decay rate equaling the gas decay rate
745 in the atmospheric simulations. In the chamber simulations, the OA is lost at a faster rate than the
746 gases, and thus the 2nd generation SOA, which forms later than the fast and slow SOA, is
747 effectively enhanced; this enhancement does not influence the atmospheric simulations. There is
748 little difference in the fractional contribution of heterogeneous oxidation products between
749 simulations, a consequence of the ensemble treatment of heterogeneous oxidation products here.

750 Differences between the chamber and atmospheric simulations are shown in **Figure 6** for the
751 $MAC_{BrC,405}$, $[OA]/[rBC]$, O:C, AMS f_{60} , and the $[SOA]/[POA]$ ratio. Averages across all particle
752 classes are shown to facilitate comparison; atmospheric simulation results for individual particle
753 classes are compared with the observations in **Figure S20**. Given the relatively large (albeit
754 particle class-dependent) absorptivity of the POA, the $MAC_{BrC,atm}$ decays more slowly than the
755 $MAC_{BrC,chl}$. This is accentuated by the fraction of fast SOA being somewhat greater at longer aging
756 times for the atmospheric simulations, since the $MAC_{fast} > MAC_{sec} > MAC_{slow}$. The evolution of the
757 MAC_{BrC} for the atmospheric simulations is empirically well described by a bi-exponential decay.
758 A fit to the model prediction for the average behavior across all classes (**Figure 6**) yields time
759 constants of 0.4 day and 2.8 days. (The overall fit equation is: $MAC_{BrC} = 0.29 + 0.59 \exp(-t_{OH}/2.8)$
760 $+ 0.13 \exp(-t/2.78)$, where t_{OH} is in days and the MAC_{BrC} in $m^2 g^{-1}$.)

761 Additionally, the increase in the $[OA]/[rBC]$ is much smaller in the atmospheric simulations
762 and the O:C values somewhat smaller. The AMS f_{60} at longer aging times remain similar to the
763 observations but are somewhat larger at shorter times for the atmospheric simulations. The
764 $([SOA]+[POA_{ox}])/[POA]$ is substantially smaller for the atmospheric simulations, with the

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766 difference growing over time. After $t_{OH} = 1$ day the geometric average atmospheric
767 $([SOA]+[POA_{het}])/[POA]$ equals 1.7 while the chamber $([SOA]+[POA_{het}])/[POA]$ equals 3.7.
768 After $t_{OH} = 6$ days the atmospheric $([SOA]+[POA_{het}])/[POA]$ equals 5.8 while the chamber
769 $([SOA]+[POA_{het}])/[POA]$ equals 20.8.

770 3.2.4 Secondary OA versus heterogeneous oxidation

771 The particle properties evolve from both SOA formation and heterogeneous oxidation. To
772 separate these processes, two additional sets of model simulations are run: (i) with the gas-phase
773 rate coefficients set to zero such that only heterogeneous oxidation occurs, and (ii) with the OH
774 uptake coefficient set to zero, and thus only SOA formation occurs (**Figure 6**). It is evident that
775 the evolution of all intensive properties occurs much more slowly with only heterogeneous
776 oxidation. With heterogeneous oxidation only, the class-average $MAC_{BrC,405}$ decays to a much
777 lesser extent, even for the atmospheric simulations. Similarly, the increase in O:C is much too
778 small and the AMS f_{60} decays to a much lesser extent. The OA-to-BC ratio for the heterogeneous-
779 only simulations differ notably from the full simulations. For the heterogeneous-only chamber
780 simulations, this ratio increases initially until about 1.5 days of aging, at which point it decreases.
781 The decrease results from loss of mass over time from fragmentation, while the increase results
782 from faster loss of BC-rich particles in the chamber. For the atmospheric simulations, the OA-to-
783 BC ratio decreases continuously when only heterogeneous oxidation is included. In contrast, for
784 most properties the SOA-only simulations differ by only small amounts from the full simulations.
785 The exception is the MAC_{BrC} , for which the decrease in the class-average value with time is notably
786 smaller in the SOA-only simulation compared to the full simulation for both chamber and
787 atmospheric simulations. Our simulations assumed an OH reactive uptake coefficient of unity. We
788 note that if a substantially larger value is assumed ($\gamma_{OH} \sim 10$), the predicted changes due to
789 heterogeneous oxidation are much larger and reasonably in line with the observations. Values
790 substantially greater than unity have been found for some chemical systems (Richards-Henderson
791 et al., 2016; Schnitzler and Abbatt, 2018), but for compounds such as levoglucosan—a notable
792 component of BB particles—values less than unity are common (Kroll et al., 2015).

793 Under the assumption that $\gamma_{OH} \leq 1$ for BB particles, these observations point to an important
794 conclusion that is in line with various ambient observations. Large changes in key intensive
795 properties of BB particles, such as O:C, and AMS f_{60} , result primarily from secondary OA

796 formation, with heterogeneous oxidation having a smaller influence. While the BrC absorptivity
797 is comparably more sensitive to heterogeneous oxidation, SOA formation remains the major driver
798 of the observed changes. Thus, in ambient observations of biomass burning plumes (Vakkari et
799 al., 2014;Forrister et al., 2015;Garofalo et al., 2019), a notable increase in the O:C (or related
800 measures) and a decrease in the f_{60} can be taken as a clear indication of SOA formation.

801 3.2.5 Absolute absorption

802 The observations indicate that the observable (i.e. bulk average) MAC_{BrC} decreases with
803 photochemical aging. However, this results primarily from mixing of absorbing POA with various
804 types of absorbing SOA, with some contribution from heterogeneous oxidation. As such, the
805 absolute absorption in the atmospheric simulations typically increases over time, at least initially,
806 due to the production of new, absorbing particle mass. The exact behavior is particle class-specific
807 (**Figure 7**). The initial increase slows over time as the pool of NMOG precursors depletes. At even
808 longer times the absolute absorption for some classes decreases as heterogeneous oxidation
809 converts more absorbing BrC (specifically, POA and SOA_{fast}) into less absorbing BrC and
810 engenders some mass loss over time due to fragmentation. However, this is only true for some of
811 the particle classes. The simulations indicate that, on average, after one day of equivalent aging
812 the absolute absorption increases by a factor of 1.6 owing to production of new, absorbing OA
813 mass.

814

815 3.2.6 POA volatility and the impact of dilution

816 Upon dilution, semi-volatile particle components may evaporate, which should lead to a
817 decrease in the OA-to-BC ratio and, potentially, changes in other particle properties; the MAC_{BrC}
818 could change if the absorptivity of the evaporating versus low-volatility (or non-volatile)
819 components differ. Given the semi-batch operation (Section 2.2) substantial, continual dilution
820 occurs throughout an experiment. Rapid dilution also occurs upon sampling of smoke into the
821 clean mini chamber air. Dilution-driven evaporation has been suggested as an important factor in
822 the chemical evolution of BB in ambient biomass burning plumes (Hodshire et al., 2019).

823 We assessed the impact of continual dilution on our observations by conducting one
824 experiment during which the chamber was left dark, although ozone was present at about 50 ppb

825 **(Figure 8)**. The primary particles corresponded to class 3 particles ($SSA_{405nm} = 0.73$). After
826 sampling, the OA and rBC concentrations decreased by about a factor of 33 over 45 minutes owing
827 to dilution and other losses. For comparison, the [ACN] dilution tracer decreased by a factor of 21.

828 During this experiment the [OA]/[rBC] ratio was nearly constant (19.6 ± 0.7 , 1σ), even slightly
829 increasing over time. Also, the O:C remained constant (0.39 ± 0.03 , 1σ), as did the H:C ($1.74 \pm$
830 0.01 , 1σ). These observations together indicate that there was little, if any, evaporative loss of OA.
831 However, the AMS f_{60} declined continually, by about 30%. The signal at $m/z = 60$ is only a small
832 fraction of the total OA, and thus changes in f_{60} can occur even if only small changes in total mass
833 occur. The AMS f_{60} could also evolve over time from in-particle reactions that occur even in the
834 absence of oxidants. The mass fraction of OA remaining (MFR_{OA}) after heating in the
835 thermodenuder increased slightly over time, from 0.05 to 0.07. This could indicate evaporation of
836 more volatile components, although could result from “ripening” of the particles over time
837 (Tritscher et al., 2011).

838 SOA from reaction of some NMOG with O_3 may have offset some evaporative OA mass loss,
839 keeping the total OA mass constant while the f_{60} and MFR_{org} changed. Monoterpenes are the most
840 important SOA precursor class here that reacts readily with O_3 . The measured initial monoterpene
841 concentration ($8.6 \text{ ppb} = 50 \mu\text{g m}^{-3}$) constrains the potential SOA formed. Accounting for
842 differential losses of particles and gases in the mini chamber, with 50 ppb O_3 and an assumed SOA
843 yield of 0.3, we estimate that SOA formation might have increased the [OA]/[rBC] ratio by about
844 4%. Given the constancy of the [OA]/[rBC], we estimate no more than 8% of the OA evaporated
845 despite the substantial dilution over the 45-minute experiment. Much greater POA evaporation is
846 expected based on the volatility distribution of May et al. (2013) for biomass burning OA,
847 assuming evaporation is facile. Using their distribution, we estimate a factor of 33 decrease in the
848 OA should have resulted in a decrease in the [OA]/[rBC] from 19.6 to 11.2 from evaporation; a
849 factor of 21 dilution (the observed value for ACN) should have caused a decrease to [OA]/[rBC]
850 = 12.1. Thus, we conclude that evaporation due to dilution had minimal influence on our
851 observations and, more broadly, suggests minimal influence of dilution in general.

852 The reason for the insensitivity to dilution of our experiments may result from the
853 concentration range considered. May et al. (2013) established the volatility distribution for
854 biomass burning OA from thermodenuder measurements. They compared predictions from their

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856 derived volatility distribution to observations of OA emission factors for different fuel types at
857 varying levels of dilution and initial concentrations. At the lowest initial [OA] ($\sim 100 \mu\text{g m}^{-3}$),
858 active dilution had little influence and in some cases the OA emission factor actually increased
859 after dilution in their experiments. In contrast, when the initial [OA] was much larger, on order of
860 $1000 \mu\text{g m}^{-3}$, there was a clearer relationship between the OA emission factor and the OA
861 concentration and better agreement with their predictions. For comparison, in our experiments, the
862 initial [OA] in the mini chamber had a geometric average of $76 \mu\text{g m}^{-3}$, ranging from $8 \mu\text{g m}^{-3}$ to
863 $384 \mu\text{g m}^{-3}$; notably, the dark experiment was at the highest initial [OA]. Dilution into the mini
864 chamber was a factor of seven. Most likely, evaporation resulting from dilution occurred upon
865 initial injection of the particles into the mini chamber with little additional evaporation as
866 experiments progressed, to the extent that the particles evaporated much at all.

867 3.3 Comparison with ambient observations

868 There are very few ambient assessments of how photochemical oxidation influences brown
869 carbon absorptivity. Forrister et al. (2015) measured dilution-corrected water-soluble + methanol-
870 soluble BrC absorption in above-ground ambient wildfire plumes at various distances downwind
871 from the fires. The measured O:C and AMS f_{60} changed with time as the BrC absorption decreased,
872 indicating that chemical changes occurred as the plume aged. They observed that the absolute BrC
873 absorption decreased over time, with a timescale of only 10 h; this was associated with a decay in
874 the AAE determined from *in situ* measurements. Surface measurements of aged smoke plumes by
875 Selimovic et al. (2019) are also suggestive of a decay in the AAE with aging. The BrC decay time
876 from Forrister et al. (2015) is substantially faster than we observe for any of the particle classes.
877 Interestingly, we predict that over 10 h the absorption by BrC in a wildfire plume should have
878 increased, and only at much later times should have decreased (**Figure 7**). In the case where only
879 heterogeneous oxidation is included (with $\gamma_{\text{OH}} = 1$), the predicted decay in BrC absorption based
880 on our observations has a timescale of ca. 4 days, substantially slower than observed by Forrister
881 et al. (2015).

882 It is possible that the smoke sampled by Forrister et al. (2015) differed significantly from any
883 of the burns sampled here. However, this seems unlikely given the wide-range of fuels and burn
884 conditions considered here, and since the plumes sampled by Forrister et al. (2015) likely derived

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886 from combustion of similar fuels as used here. Also unlikely is that greater dilution in the
887 atmosphere played an important role, as it is thought that more absorbing primary OA has lower
888 volatility than less absorbing primary OA (Saleh et al., 2014). Thus, it is possible that the difference
889 between Forrister et al. (2015) and our results indicates that direct photobleaching rapidly degrades
890 BrC absorptivity, as direct photolysis in our experiments was likely of minimal importance owing
891 to the relatively low light intensity, single initiation wavelength (254 nm), and short absolute
892 timescale (<1 h) compared to the atmosphere.

893 However, an additional difference is that we measured absorption by suspended particles at
894 low-to-moderate relative humidity whereas Forrister et al. (2015) characterized BrC absorption
895 after extracting material collected onto filters into water and then methanol. It is possible that
896 solvent extraction alters the BrC absorptivity in some OA-composition-dependent manner, leading
897 to an apparent time-dependent decay in the BrC absorption. Consistent with this suggestion,
898 Fleming et al. (2020) reported that (i) the total absorptivity lifetime of BB particles photolytically
899 aged on a filter greatly exceeded those of individual chromophores (>10 days versus <2 days), and
900 (ii) the apparent changes in total absorption depended on whether the absorption was measured for
901 particles on the filter versus for solution extracts. There is also evidence that the larger molecules
902 comprising OA from biomass burning, which are often more absorbing yet less soluble than small
903 molecules (Di Lorenzo et al., 2017; Saleh et al., 2018), are less susceptible to photobleaching
904 (Wong et al., 2017; Wong et al., 2019). This could lead to absorption measurements from solvent
905 extracts overestimating the effects of photobleaching. Nonetheless, the suggestion that the
906 measurement method contributes to the lab-field difference remains speculative as direct,
907 quantitative comparisons between BrC absorption measured for suspended particles versus from
908 solution extracts are limited; we suggest that targeted comparisons between absorption
909 measurement methods would be informative.

910 Wang et al. (2016) also characterized changes in BrC absorptivity of BB particles in the
911 Amazon. They found that the BrC absorptivity decreased initially over an estimated ca. 20 h of
912 photochemical aging, after which the absorptivity remained constant. As above, this timescale
913 seems too short for heterogeneous oxidation to have a major impact, thus implicating direct
914 photolysis as the reason for the photobleaching. However, there are two important considerations.
915 First, Wang et al. (2016) note that they cannot rule out production of less absorbing SOA as the
916 reason for the absorptivity decrease. While the OA concentration was constant over time and

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918 therefore suggestive of little SOA formation, it may be that dilution of the plume offset SOA
919 formation and consequently that SOA formation precipitated the decrease in absorptivity. Second,
920 their estimated lifetimes are determined from NO_x losses, and thus sensitive to assumptions about
921 the average OH; as such, longer lifetimes cannot be ruled out.

922 Finally, Zhang et al. (2017) characterized water + methanol extracted BrC in the outflow of
923 storm clouds and, in one case, were able to measure BrC absorption for freshly expelled versus
924 particles sampled one day later. The BrC absorption for the fresh and aged particles were nearly
925 identical, with no indication of bleaching despite the high altitude, 11 km, and thus high UV photon
926 flux. Thus, this study indicates that photobleaching of BrC may have little influence on at least
927 some types of BrC. Further, Zhang et al. (2017) report absolute absorption values that, it seems,
928 are not dilution corrected. Thus, the constancy of the absolute absorption between the fresh and
929 aged particles implies potential BrC production, as dilution is expected. Ultimately, further
930 experiments investigating direct photolysis of biomass-derived BrC and additional field
931 observations of the evolution of BrC absorptivity will be necessary to reconcile our findings and
932 the limited number of field observations.

933

934 **4 Conclusions**

935 We characterized the photochemical evolution of smoke (particles + gases) produced from
936 combustion of a wide variety of biomass fuels. Particle properties were characterized as a function
937 of equivalent photochemical aging, with a focus on the particle optical properties. Photochemical
938 aging led to dramatic changes in the particle chemical composition, as evidenced by a large and
939 rapid increase in the O:C atomic ratio of the organic aerosol and a decrease in the marker ion f_{60}
940 in the OA mass spectrum. These chemical changes occurred concurrent with large changes in the
941 [OA]/[rBC] ratio, indicating substantial production of secondary organic aerosol mass. The
942 particle optical properties also changed substantially upon aging. Experiments were classified into
943 six classes according to the SSA of the primary particles. The average evolution of the optical
944 properties of particles in each class was characterized; the observed behavior was generally class-
945 specific. The total particle absorptivity normalized to black carbon (the MAC_{BC}) generally
946 increased with aging due to production of new, somewhat absorbing OA. The single scatter albedo
947 also generally increased with aging, although to a much less extent for experiments in which the

948 initial particles already had a large SSA. The absorptivity of the organic aerosol components, i.e.
949 of the brown carbon mass absorption coefficient (MAC_{BrC}), exhibited class-specific behavior. For
950 particles having an initially large SSA, the MAC_{BrC} exhibited an initial increase at short times (<0.5
951 days of equivalent aging) but then decreased monotonically with continued aging. For particles
952 having an initially small SSA, there was a rapid decline in the MAC_{BrC} at short times and then a
953 continued slower decline at longer times. At long times the MAC_{BrC} for the high SSA and low SSA
954 initial particles behaved similarly.

955 The evolution of the BrC absorptivity was shown via application of a mechanistic model to be
956 consistent with a combination of production of strongly absorbing and much more weakly
957 absorbing secondary OA, along with heterogeneous conversion of absorbing POA and SOA into
958 a less absorbing oxidized OA. This was the case for all particle classes. The SOA formed could be
959 distinguished into four general types: (i) a fast-forming, relatively highly absorbing type; (ii) a
960 more slowly-forming, weakly absorbing type; (iii) a very slowly forming, weakly absorbing type;
961 and (iv) a weakly absorbing, second-generation type. The relative abundances of these different
962 types were similar between the different particle classes. The combination of SOA formation and
963 heterogeneous oxidation causes the MAC_{BrC} to evolve in time on three timescales: (i) an initial
964 rapid increase occurring at aging times < 0.25 days, (ii) a moderately fast decrease, occurring with
965 a timescale of ~ 1day, and (iii) a longer decay, occurring with a time scale of about ~ 1 week. Our
966 results demonstrate that, while primary particle properties derived from biomass combustion can
967 vary dramatically in terms of their properties, the overall evolution upon photochemical aging is
968 reasonably independent of the initial conditions.

969 **5 Data Availability**

970 All data used to create this manuscript are available at: <http://www.esrl.noaa.gov/csd/FIREX/>.

971 **6 Author Contributions**

972 CDC and JHK designed the experiments. CDC, CYL, DHH, MC, AK, TBO and KS carried
973 out the measurements and data processing, with additional assistance from CW and JdG. CDC and
974 CL analyzed data. CDC wrote the manuscript, with contributions from all co-authors.

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1490 **10 Tables**

1491 **Table 1.** Model parameters for NMOG

Property	Fast	Slow	Very Slow	Multi Generation	Heterogeneous
$MAC_{BrC,405nm}^{**}$	0.81	0.05	0.05	0.17	0.05
α^{**}	0.43	0.13	0.05	0.45	--
k_{OH} (cm ³ molecules ⁻¹ s ⁻¹)	4 x 10 ⁻¹¹	9 x 10 ⁻¹²	7 x 10 ⁻¹³	5 x 10 ⁻¹²	--
γ_{OH}	--	--	--	--	1
O:C ^{^***}	0.73	0.59	0.59 ^{&}	+1.22 [#]	+1.22 [#]
AMS f_{60}^{***}	0.008	0.003	0.003 ^{&}	0.006	0.008,0.003,0.01 [*]

-- = not applicable

[^] It is assumed that the carbon backbone has 8 carbon atoms. The assumed O:C values therefore correspond to 5.8, 4.7, and 4.7 oxygen atoms per molecule for the fast, slow and very slow SOA.

[&] Assumed to equal the slow SOA

[#] It is assumed that every reaction leads to addition n oxygen atoms, where n is the indicated value. Consequently, the average O:C for multi-generation products increases over time as the multi-generation species accumulate oxygen.

^{*} Values for oxidation products from internally mixed POA, externally mixed POA, and SOA.

^{**} Determined from global fit to the $MAC_{BrC,405nm}$ and [OA]/[rBC] observations.

^{***} Determined from a global fit to the O:C or f_{60} observations after determining the α values.

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1494 **Table 2.** Model parameters by particle class

Property	class 1	class 2	class 3	class 4	class 5	class 6
$[\text{NMOG}]:[\text{POA}]^{*,\wedge}$	2.8	4.4	3.8	6.3	5.6	6.2
$[\text{POA}]/[\text{BC}]^{*,*}$	1.3	3.5	12	24	85	12,000
$\text{MAC}_{\text{BrC},405\text{nm},\text{POA}}^{\#}$	2.5	1.2	0.73	0.66	0.57	0.39
$\text{O}:\text{C}_{\text{POA}}^{\#}$	0.45	0.35	0.40	0.42	0.37	0.2
Fraction internally mixed [#]	0.90	0.32	0.14	0.12	0.09	0.01
$\text{AMS } f_{60,\text{POA}}^{\#}$	0.015	0.019	0.021	0.025	0.021	0.0124
$F_{\text{NMOG,fast}}^{\wedge}$	0.20	0.36	0.27	0.47	0.53	0.42
$F_{\text{NMOG,slow}}^{\wedge}$	0.70	0.54	0.63	0.43	0.37	0.48
$F_{\text{NMOG,VS}}^{+}$	0.1	0.1	0.1	0.1	0.1	0.1

[#] Directly constrained from observations

* Mass ratio (unitless); + units = $\text{m}^2 \text{g}^{-1}$

[^] Determined from a global fit to the $\text{MAC}_{\text{BrC},405\text{nm}}$ and $[\text{OA}]/[\text{rBC}]$

⁺ Specified as a constant

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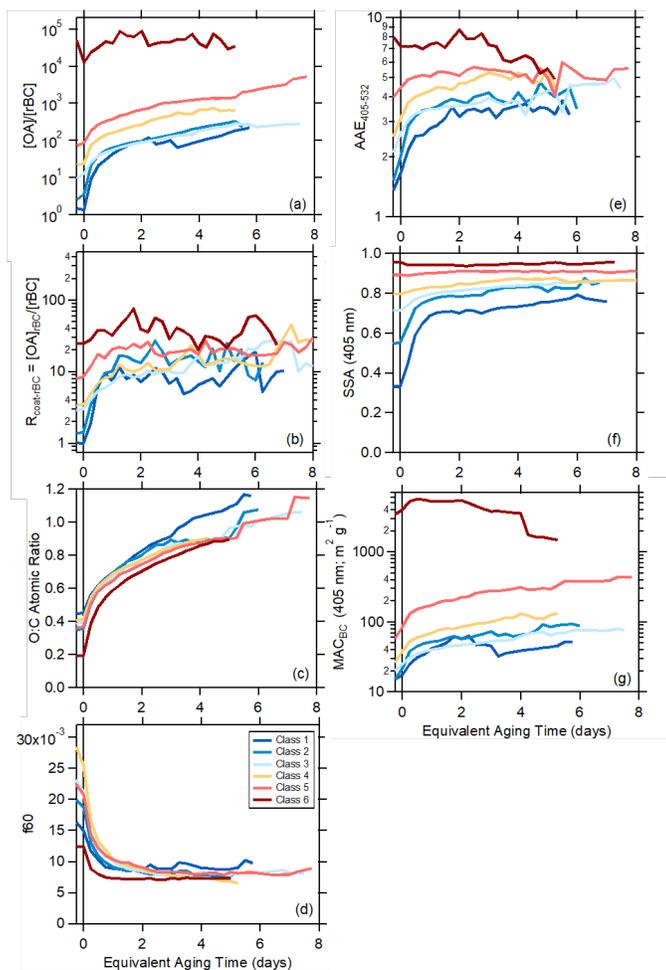
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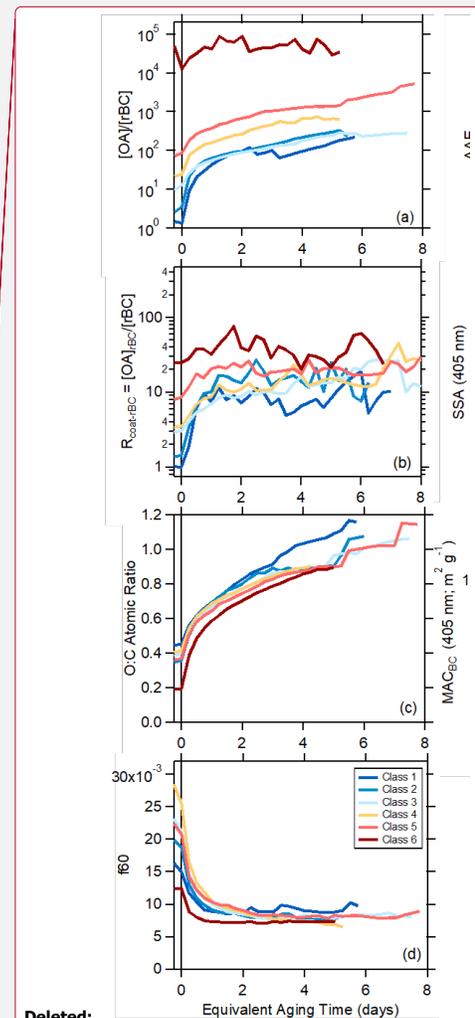
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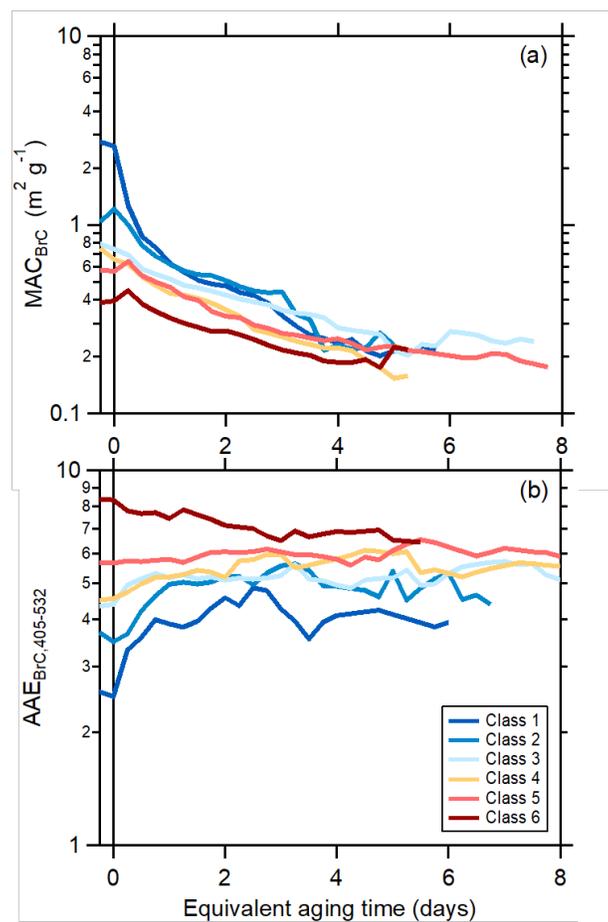


1502
 1503 **Figure 1.** Relationship between (a) the $[OA]/[rBC]$ ratio, (b) $R_{\text{coat-rBC}}$, (c) $AAE_{405-532}$, (d) the SSA
 1504 at 405 nm, (e) the O:C atomic ratio, (f) the AMS f_{60} , and (g) the MAC_{BC} at 405 nm as a function
 1505 of equivalent photochemical aging time (assuming $[OH] = 1.5 \times 10^6$ molecules cm^{-3}). The different
 1506 lines are colored according to the SSA classification, and are averages for all burns within a class
 1507 (see Panel D). Figures showing results for each burn are available in the Supplementary Material.
 1508 Some of the apparent discontinuities for individual classes with certain properties results from a
 1509 change in the number of individual experiments contributing to the average above a given aging
 1510 time.



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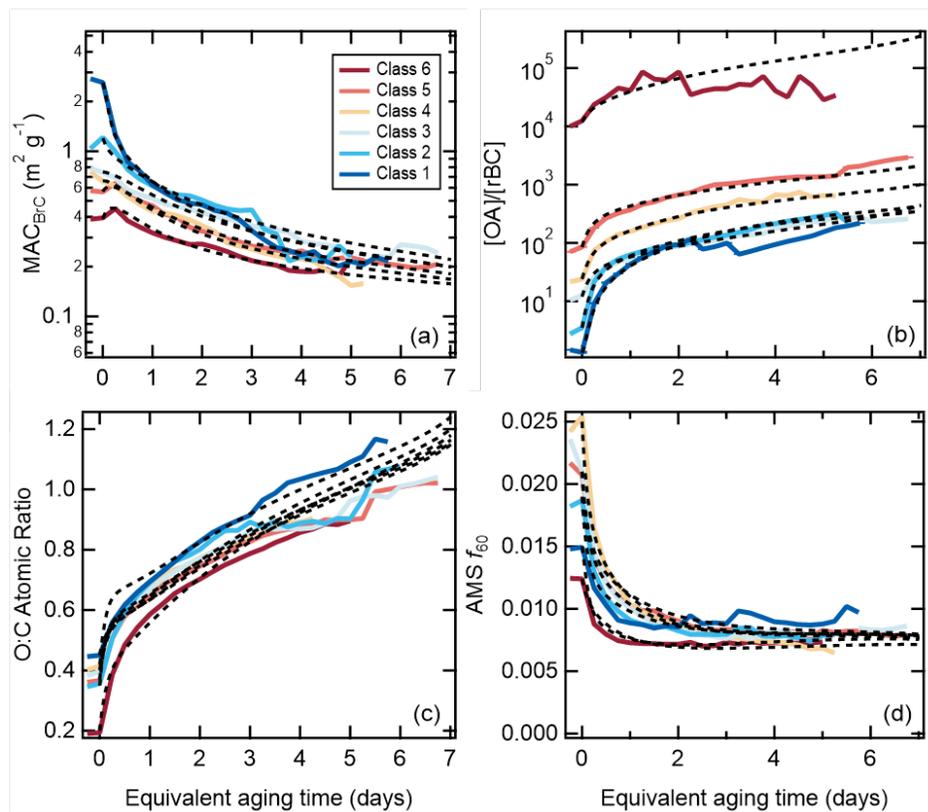
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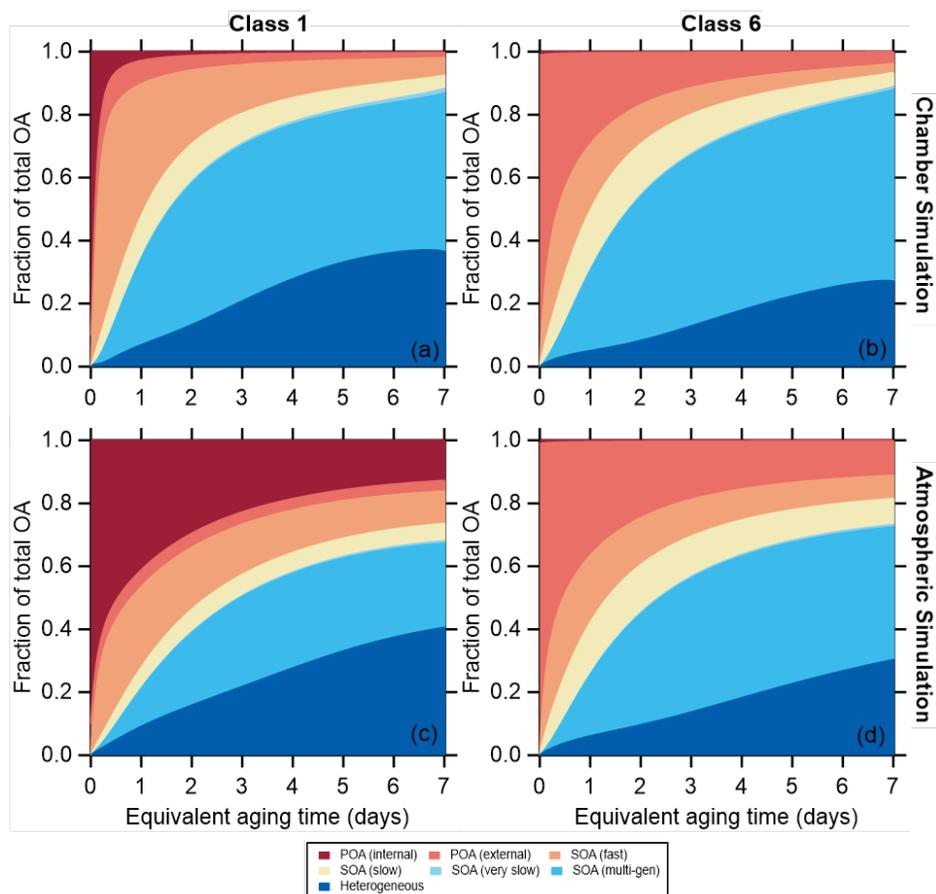
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1515 **Figure 2.** Relationship between the brown carbon (a) MAC_{BrC} and (b) the $AAE_{BrC,405-532}$ as a function of
1516 equivalent photochemical aging time (assuming $[OH] = 1.5 \times 10^6$ molecules cm^{-3}). The different
1517 lines are colored according to the SSA classification, and are averages for all burns within a class.
1518 class 1 corresponds to particles having low SSA_{405} and class 6 to particles having high SSA_{405nm} .
1519 Figures showing results for each burn are available in the Supplementary Material.

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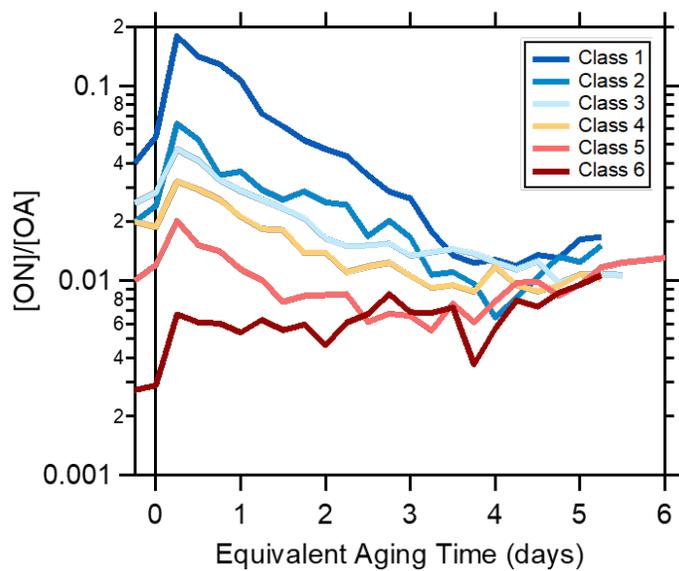


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 1523 **Figure 3.** Comparison between observed (solid lines) and modeled (dashed lines) values of the
 1524 (a) MAC_{BrC} , (b) the $[OA]/[rBC]$ ratio, (c) the O:C atomic ratio, and (d) the $AMS f_{60}$ and the
 1525 equivalent photochemical aging time (assuming $[OH] = 1.5 \times 10^6$ molecules cm^{-3}), with results
 1526 shown for each SSA class.
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 1530 **Figure 4.** Variation in the simulated OA fractional composition with equivalent aging time for (a)
 1531 and c) SSA class 1 (BC rich) and (b and d) SSA class 6 (OA rich) for the mini chamber
 1532 experiments. For the “chamber” simulations in (a and b) the differences in decay rates between
 1533 particle types and gases are accounted for. For the “atmospheric” simulations in (c and d) it is
 1534 assumed that gases and particles all decay with the same rate.
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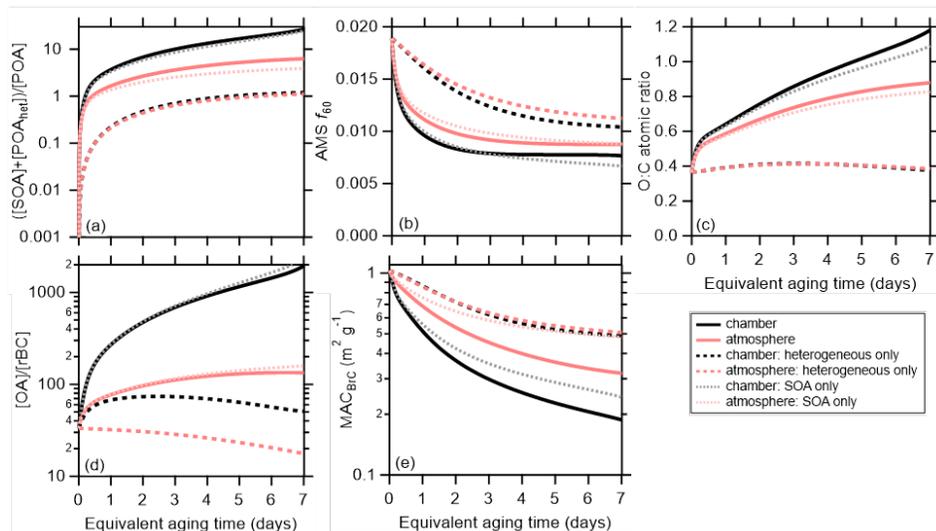
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Figure 5. Dependence of the observed organic nitrate-to-total OA ratio for each SSA class on the equivalent aging time (assuming $[OH] = 1.5 \times 10^6$ molecules cm^{-3}).

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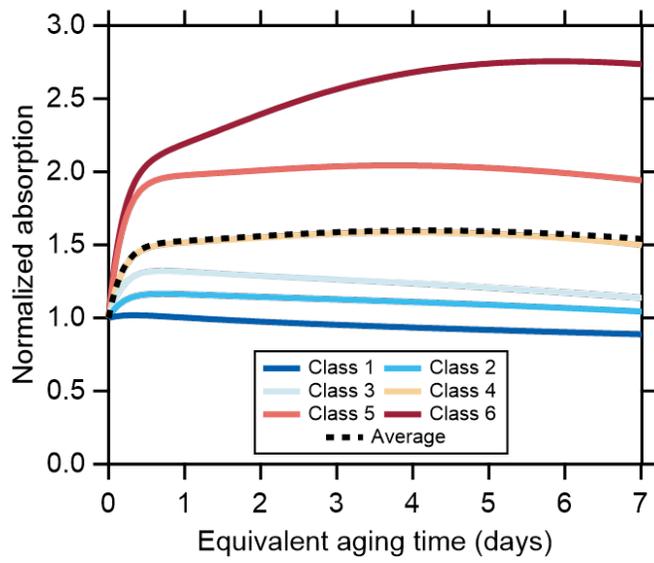


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1545 **Figure 6.** Comparison between the model results when dilution and wall-losses are included (the
1546 chamber simulation, black lines) or turned off (the atmospheric simulation, red lines). The model
1547 has been run with both SOA formation and heterogeneous oxidation (solid lines), with
1548 heterogeneous oxidation only (dashed lines), or with SOA formation only (dotted lines).
1549 Averages (either arithmetic or geometric) across all particle classes are shown for (a) the SOA
1550 plus oxidized POA to unoxidized POA ratio, (b) the AMS f_{60} , (c) the organic O:C, (d) the OA-to-
1551 rBC ratio, and (e) the $MAC_{BrC,405}$.

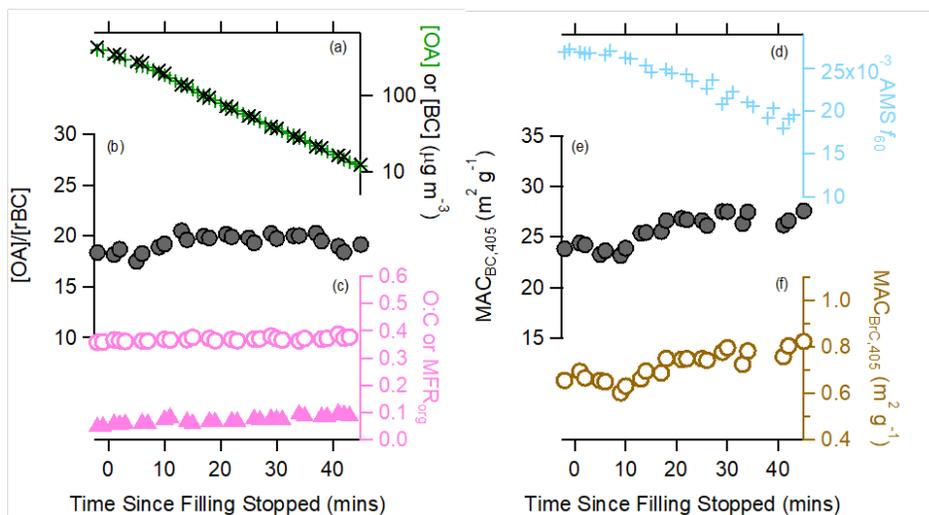
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Figure 7. Modeled change in the absolute absorption with aging, assuming no dilution, normalized to the value at $t = 0$. Results are shown for each particle class (colors) and the average (black).



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Figure 8. Variation in various particle properties with time during the dark experiment. The change in (a) either the [OA] (green) or [rBC] (black), with [rBC] multiplied by 20; (b) the [OA]/[rBC] ratio; (c) the O:C ratio (circles) or OA mass fraction remaining (triangles); (d) the AMS f_{60} biomass burning marker; (e) the $MAC_{BC,405nm}$; and (f) the $MAC_{BrC,405nm}$.

1571 **12 Supplementary**

1572 **12.1 Model parameter cross-sensitivities and uncertainties**

1573 The SOA yields are most sensitive to the initial [NMOG]/[OA] ratio. When the [NMOG]/[OA]
1574 ratio is assumed larger, the necessary SOA yields are smaller. There is an approximately inverse
1575 relationship between the assumed initial [NMOG] and the SOA yield for each NMOG type (fast,
1576 slow, very slow). However, the influence of multi-generational impacts the relationship to some
1577 extent.

1578 The O:C ratios for the different SOA types are weakly dependent on the relative abundances
1579 specified for the different types. There is also a weak cross-sensitivity between the O:C values
1580 specified for the different SOA types, especially between the fast and slow-forming SOA. In
1581 general, if the $O:C_{fast}$ is increased, the $O:C_{slow}$ must be decreased. However, only relatively minor
1582 variations in the O:C of each type is allowable to obtain reasonable model-measurement
1583 agreement, especially at short photochemical ages. The f_{60} values for the different SOA types
1584 exhibit similar cross-sensitivities as the O:C values. However, they are generally less sensitive, in
1585 comparison, because the f_{60} values are so similar for all SOA types.

1586 The model k_{OH} values also exhibit some dependence on the assumed initial [NMOG]/[OA] and
1587 yields. In general, if $k_{OH,fast}$ is decreased the $k_{OH,slow}$ must be increased. However, the $k_{OH,fast}$ is
1588 reasonably well-constrained by the rapid rise in the [OA]/[rBC] and O:C for all particle classes,
1589 and by the increase in the $MAC_{BrC,405nm}$ that is observed at very short photochemical ages for some
1590 of the particle classes. The assumed k_{OH} for multi-generational aging is most sensitive to the choice
1591 of the $k_{OH,slow}$, with the two generally exhibiting an inverse relationship.

1592 It is difficult to estimate a comprehensive uncertainty on these values; we qualitatively estimate
1593 uncertainties based on the model sensitivity to changing these parameter values. If the MAC_{fast}
1594 were as small as the values for the other SOA types the modeled MAC_{BrC} would decline much too
1595 rapidly compared to the observations. Also, it is necessary that the MAC_{fast} be greater than the
1596 MAC_{BrC} of the primary OA for SSA class 5 and class 6 to reproduce the initial increase at short
1597 aging times. However, if the MAC_{fast} were much larger than our estimate the model predicts an
1598 initial increase in the MAC_{BrC} for the intermediate SSA classes 3 and 4, in contrast to the
1599 observations. We therefore estimate a uncertainty of $\pm 0.2 \text{ m}^2 \text{ g}^{-1}$ based on the model sensitivity to

1600 variations in this parameter. The MAC_{slow} values are largely determined by the behavior at
1601 intermediate equivalent ages, as this is where they have the largest fractional contributions; we
1602 estimate the uncertainty as $\pm 0.05 \text{ m}^2 \text{ g}^{-1}$. The MAC_{VS} is not especially well-constrained as it only
1603 makes up a very small fraction of the OA mass. A value of $MAC_{\text{VS}} = 0.05 \text{ m}^2 \text{ s}^{-1}$ is used for
1604 consistency with the MAC_{slow} , but a value of $MAC_{\text{VS}} = 0 \text{ m}^2 \text{ g}^{-1}$, i.e. non-absorbing, is not entirely
1605 unreasonable. The $MAC_{2\text{G}}$ and MAC_{het} values are primarily determined by the behavior at long
1606 equivalent ages. The estimated uncertainty in $MAC_{2\text{G}}$ is $\pm 0.05 \text{ m}^2 \text{ g}^{-1}$ while the estimated
1607 uncertainty in MAC_{het} is $\pm 0.025 \text{ m}^2 \text{ g}^{-1}$. That the MAC_{het} is smaller than the MAC_{BrC} values for the
1608 various SOA types indicates that over longer time the overall MAC_{BrC} will continue to decline until
1609 it reaches $0.05 \text{ m}^2 \text{ g}^{-1}$.

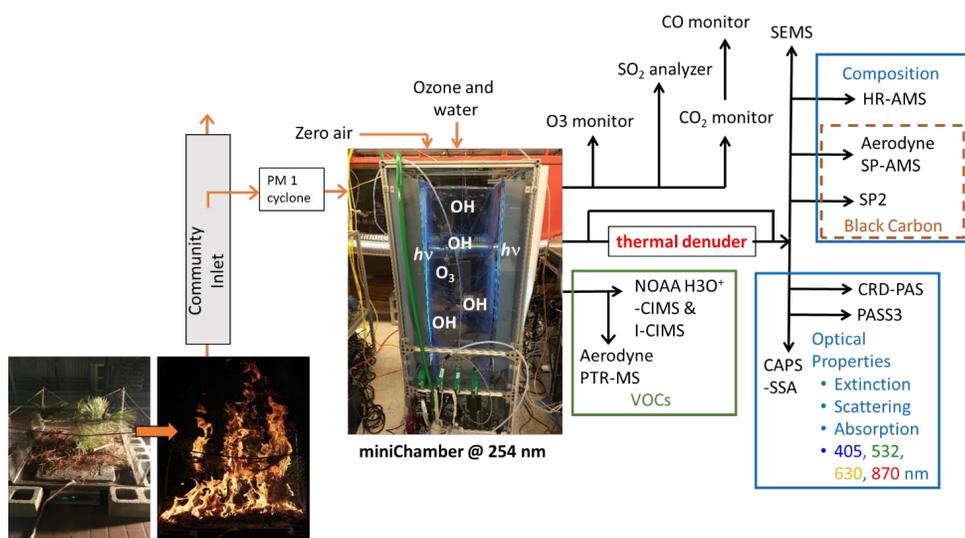
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1613 **12.2 Supplemental Figures**

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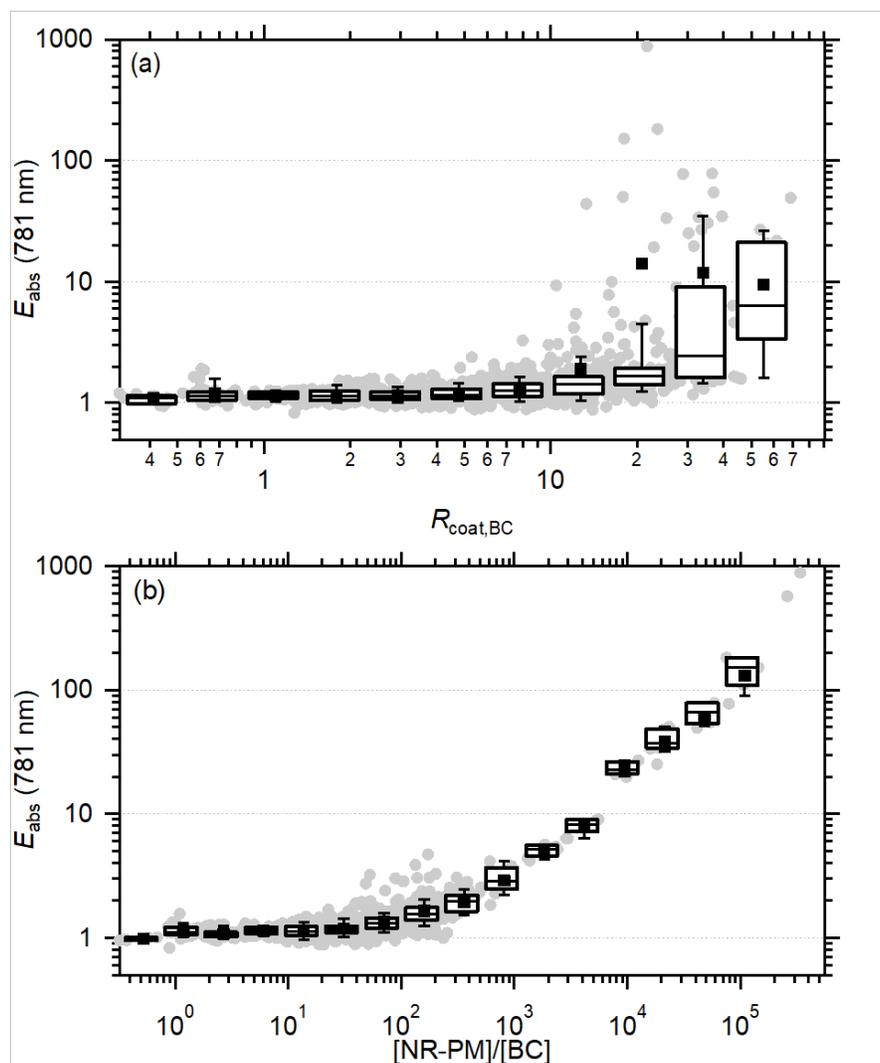


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1616 **Figure S1.** Cartoon schematic of sampling into and from the mini chamber during FIREX.

1617 Instrument names are given in

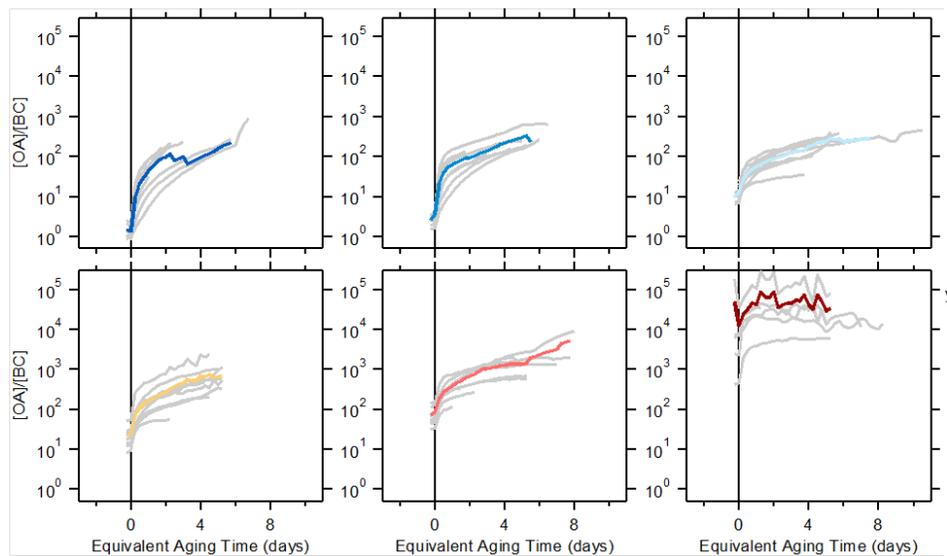
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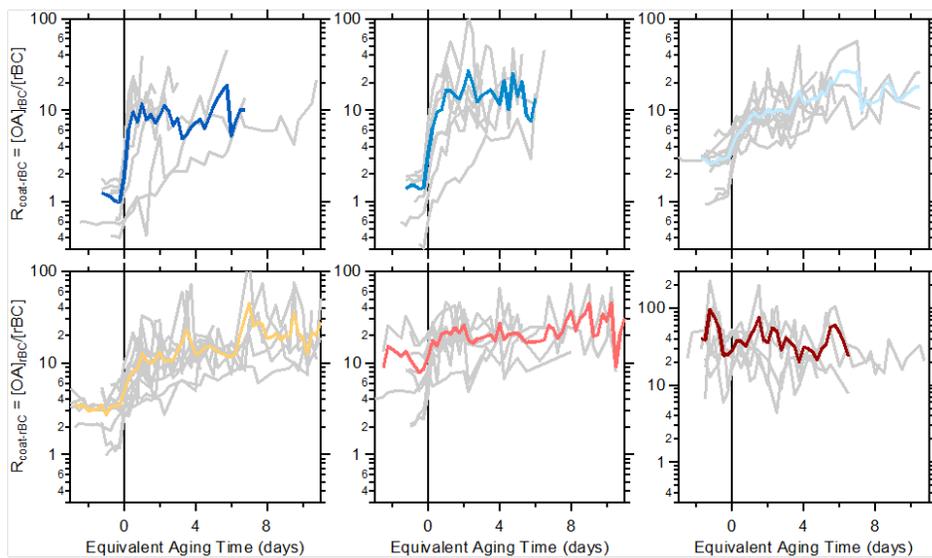
1620 **Figure S2.** (a) Dependence of the observed E_{abs} 781 nm on the coating-to-rBC core mass ratio,
 1621 $R_{\text{coat-rBC}}$. (b) Dependence of the E_{abs} at 781 nm on the $[\text{NR-PM}]/[\text{rBC}]$ ratio. The observations
 1622 have been binned according to either the $R_{\text{coat-rBC}}$ or $[\text{NR-PM}]/[\text{rBC}]$ ratio, shown as box-and-
 1623 whisker plots.
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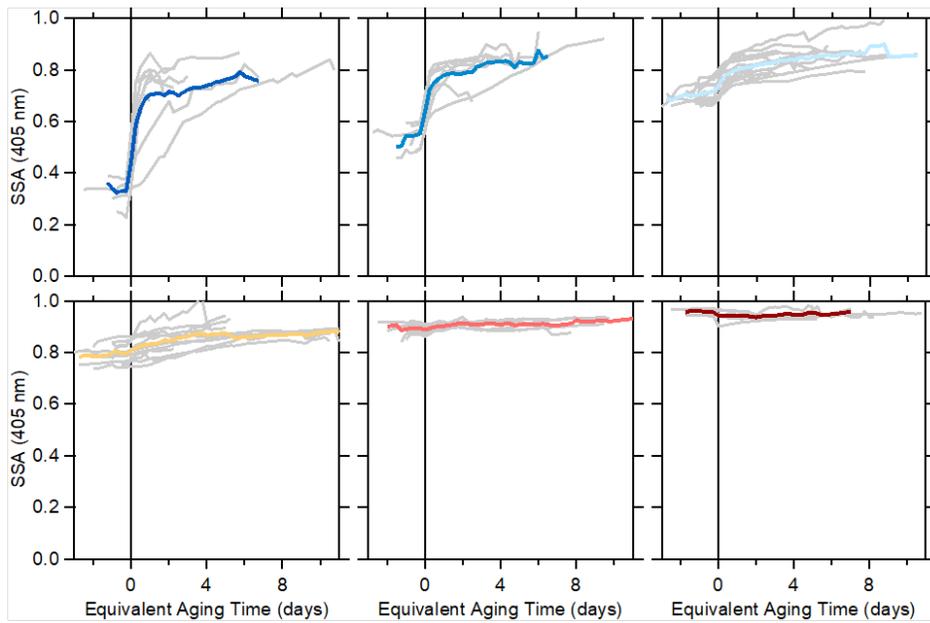
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1628 **Figure S3.** Relationship between $[OA]/[BC]$ and the equivalent atmospheric aging time for each
1629 SSA classification. Individual burns are shown as gray lines, and the average for each SSA class
1630 as the colored line.
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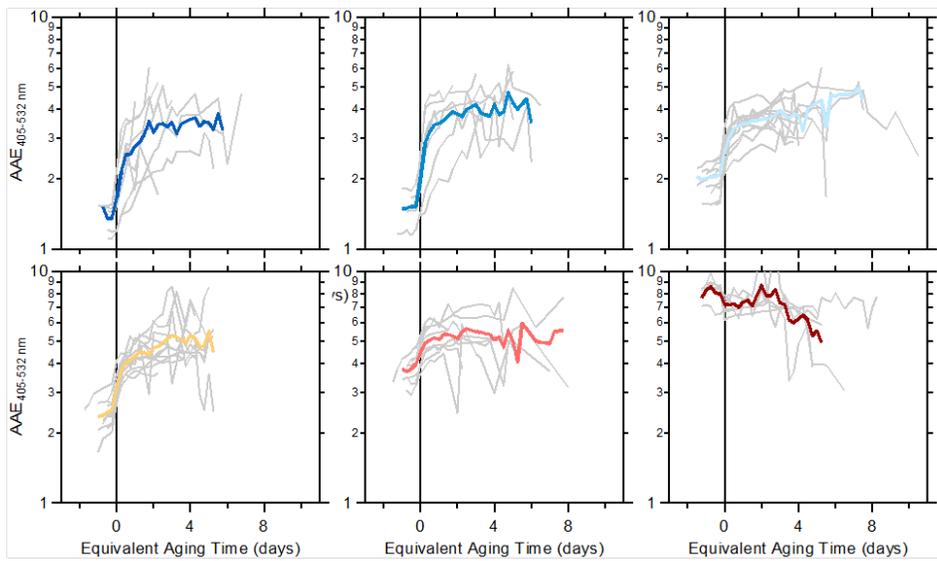
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1634 **Figure S4.** Relationship between $R_{\text{coat-rBC}}$ and the equivalent atmospheric aging time for each
1635 SSA classification. Individual burns are shown as gray lines, and the average for each SSA class
1636 as the colored line.
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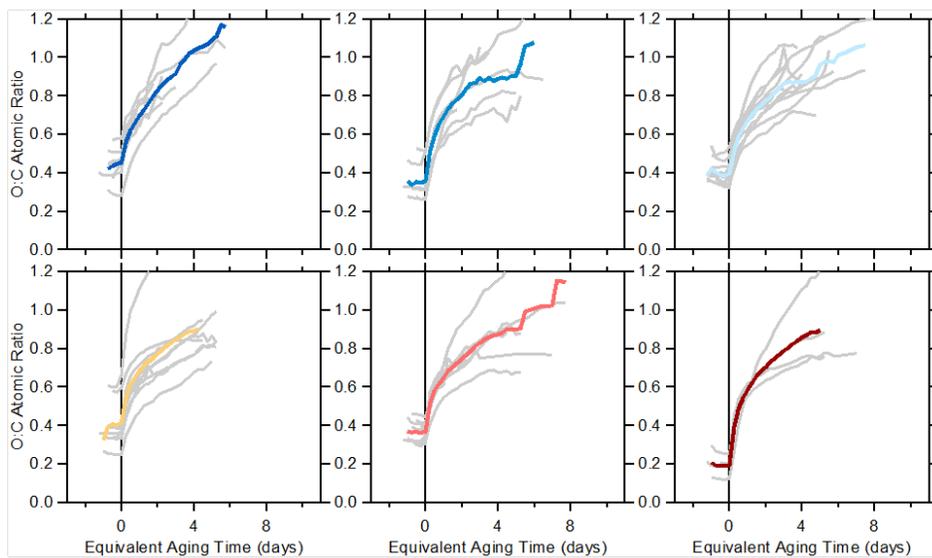
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Figure S5. Relationship between SSA at 405 nm and the equivalent atmospheric aging time for each SSA classification. Individual burns are shown as gray lines, and the average for each SSA class as the colored line.



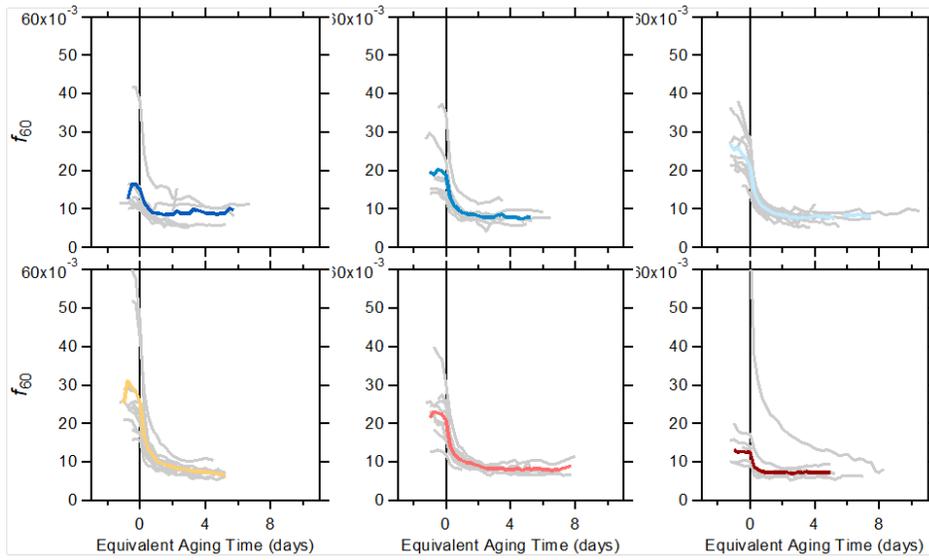
1644
 1645 **Figure S6.** Relationship between the $AAE_{405-532}$ and the equivalent atmospheric aging time for
 1646 each SSA classification. Individual burns are shown as gray lines, and the average for each SSA
 1647 class as the colored line.
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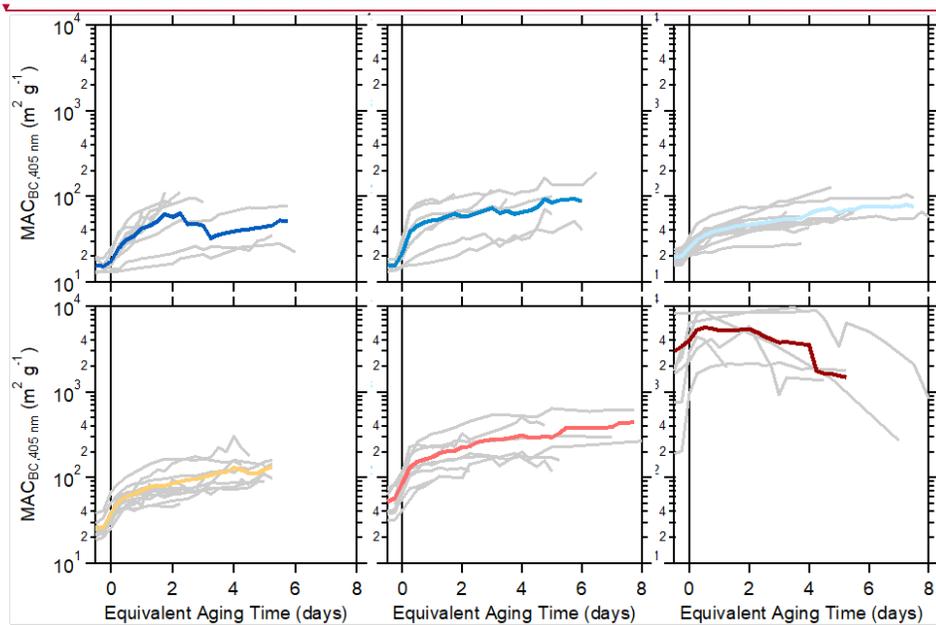
1651 **Figure S7.** Relationship between the O:C atomic ratio at 405 nm and the equivalent atmospheric
1652 aging time for each SSA classification. Individual burns are shown as gray lines, and the average
1653 for each SSA class as the colored line.
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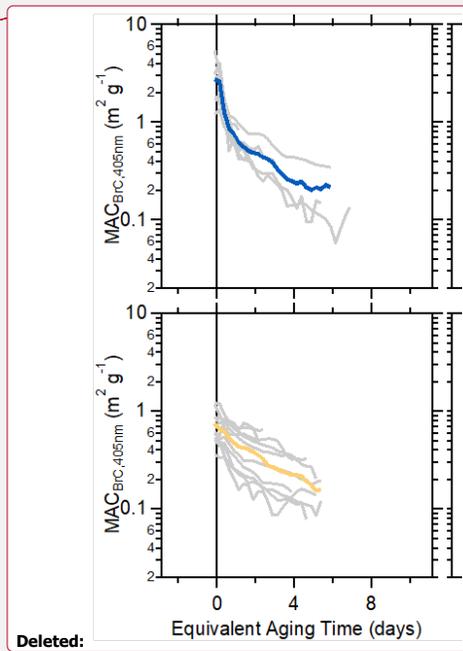
1658 **Figure S8.** Relationship between the AMS f_{60} and the equivalent atmospheric aging time for
1659 each SSA classification. Individual burns are shown as gray lines, and the average for each SSA
1660 class as the colored line.
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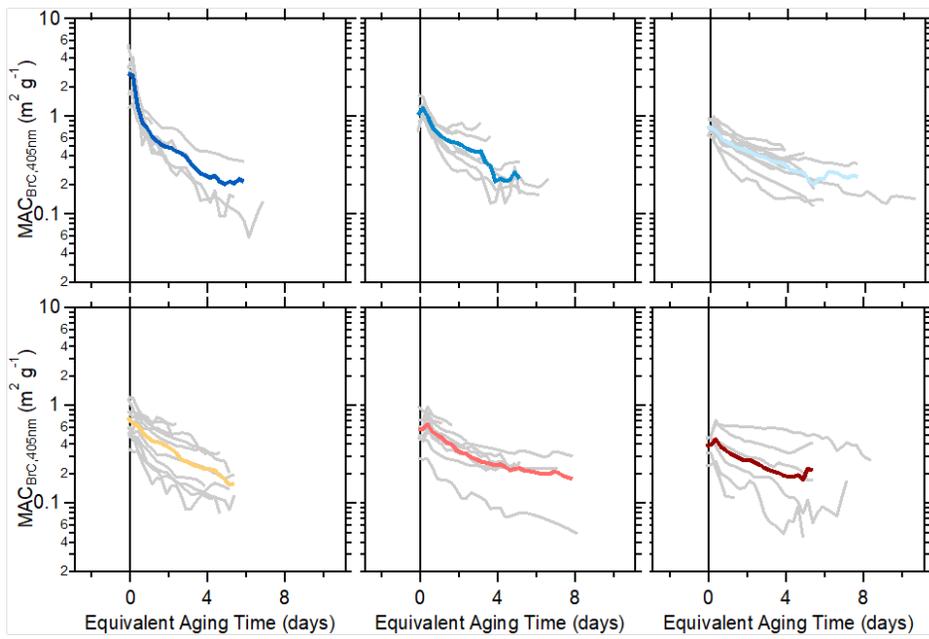


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Figure S9. Relationship between the $MAC_{BC,405\text{ nm}}$ and the equivalent atmospheric aging time for each SSA classification. Individual burns are shown as gray lines, and the average for each SSA class as the colored line.

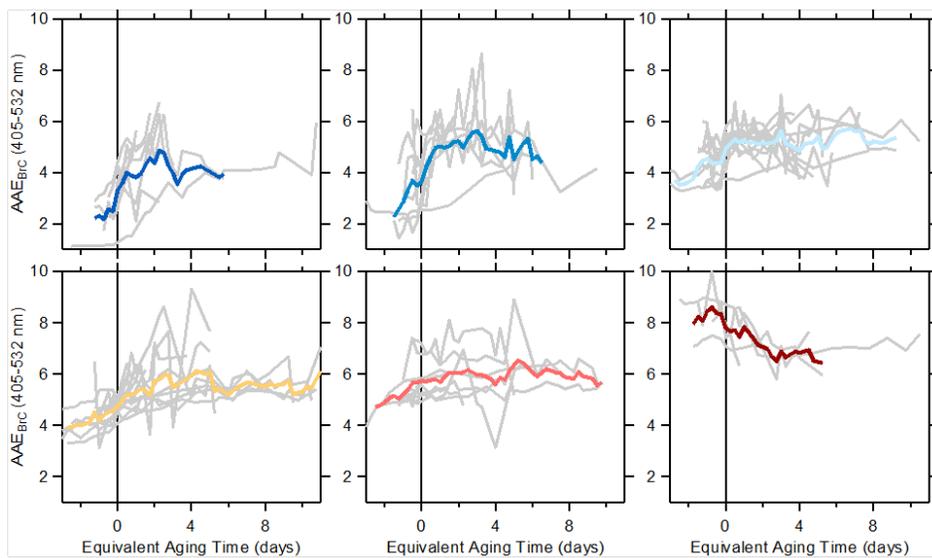


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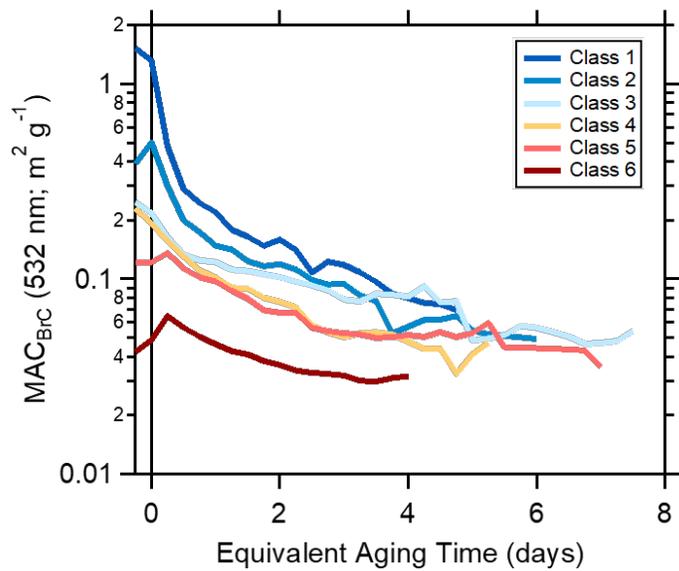
1671
 1672 **Figure S10.** Relationship between the MAC_{BrC} at 405 nm and the equivalent atmospheric aging
 1673 time for each SSA classification. Individual burns are shown as gray lines, and the average for
 1674 each SSA class as the colored line.
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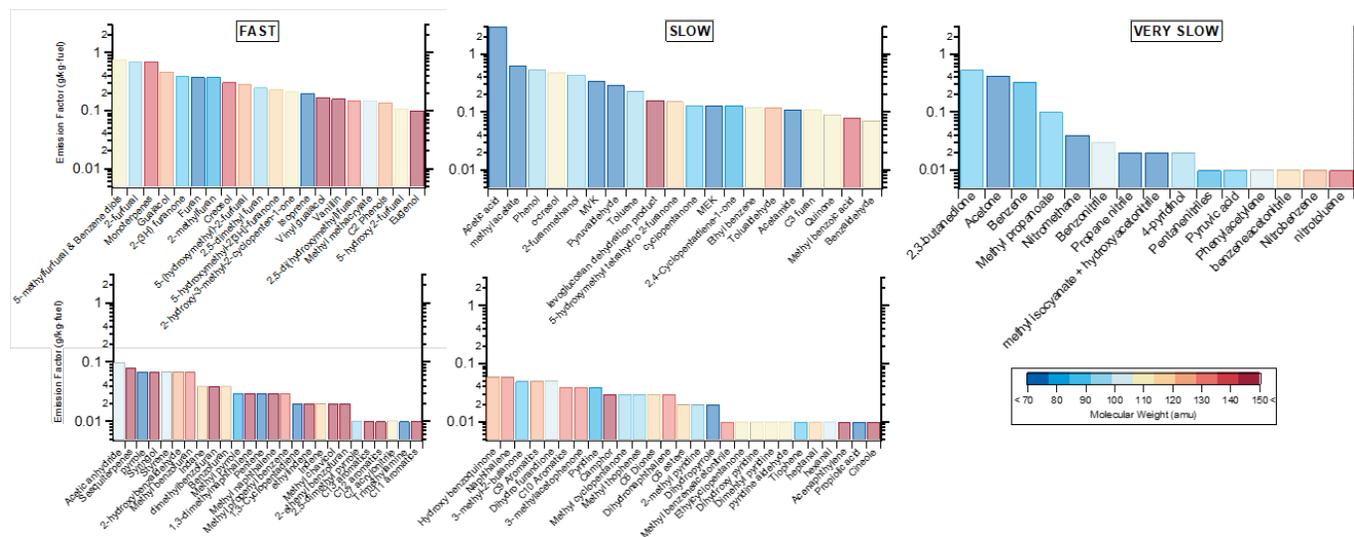
1677
1678 **Figure S11.** Relationship between the AAE_{BRC} for the 405-532 nm pair and the equivalent
1679 atmospheric aging time for each SSA classification. Individual burns are shown as gray lines,
1680 and the average for each SSA class as the colored line. Top row, left-to-right: class 1-3. Bottom
1681 row, left-to-right: class 4-6.
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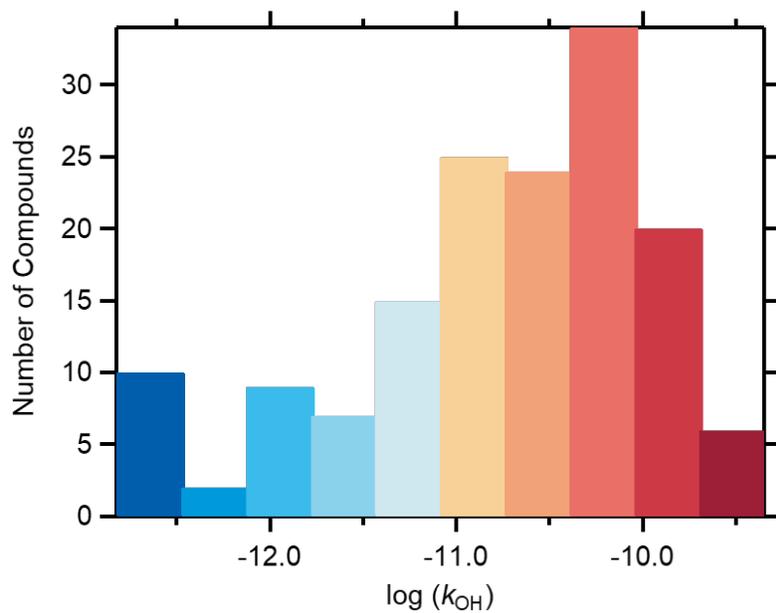


1684 **Figure S12.** Influence of photochemical aging on MAC_{BrC} at 532 nm. The equivalent aging time
1685 assumes $[OH] = 1.5 \times 10^6$ molecules/cm³. The averages for each SSA classification are shown.
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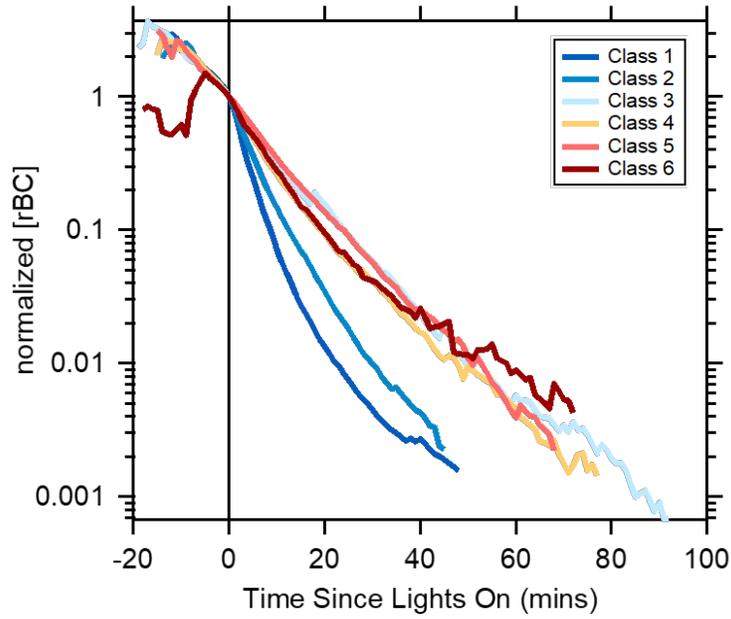
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Figure S14. Histogram of rate coefficients for the NMOG having MW > 50 amu, as measured by Koss et al. (2018).

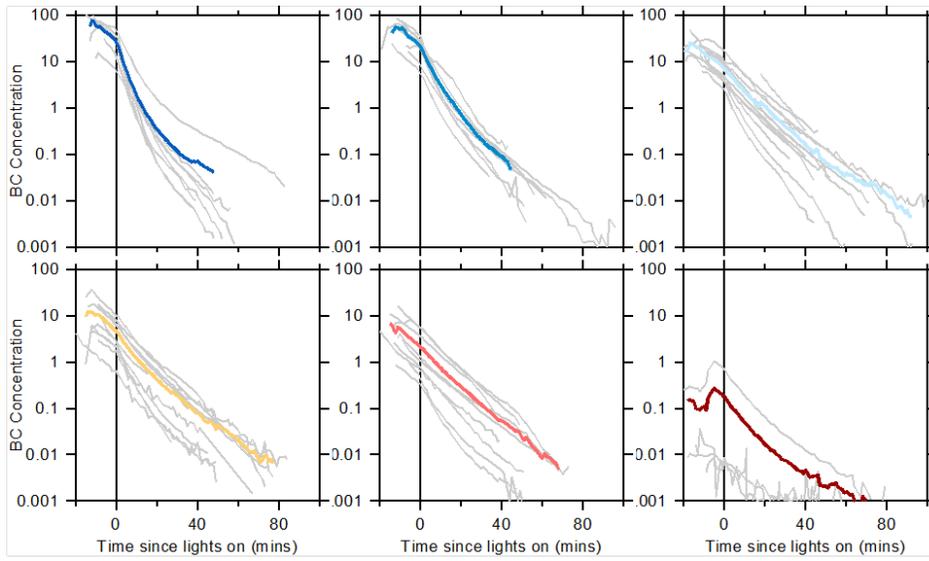
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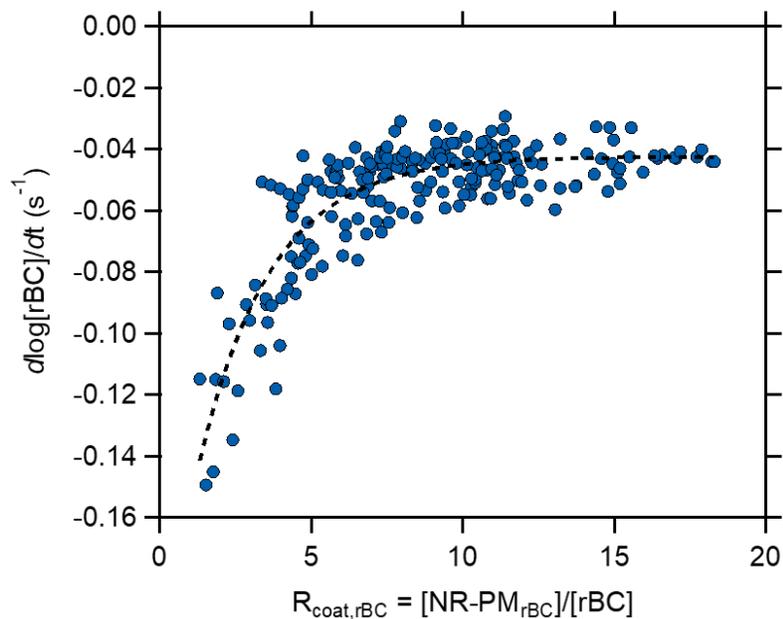
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Figure S15. Normalized rBC concentration as a function of experiment time, averaged for each SSA classification. Results for each experiment are shown in **Figure S16**.

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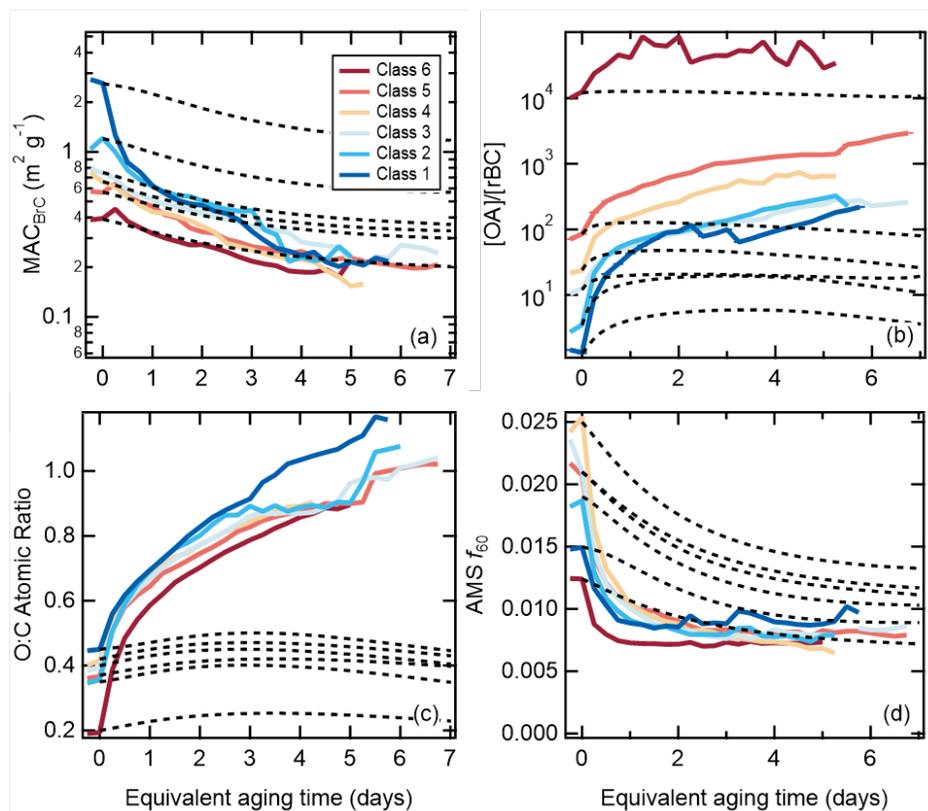


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 1708 **Figure S16.** Normalized rBC concentration as a function of experiment time, with individual
 1709 experiments shown as gray lines and the averages for each SSA classification as colored lines.
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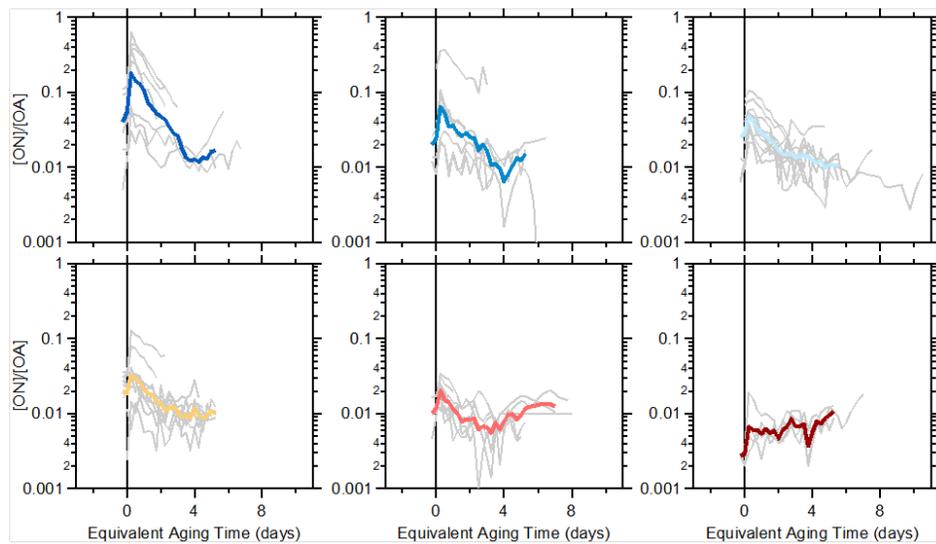
1711
 1712
 1713 **Figure S17.** Observed loss rate of refractory BC as a function of the coating-to-core mass ratio.
 1714 The data are fit using an exponential function, with $-\text{dlog}[r\text{BC}]/\text{dt} = -0.0424 -$
 1715 $0.172 \exp(-0.419 R_{\text{coat},r\text{BC}})$.
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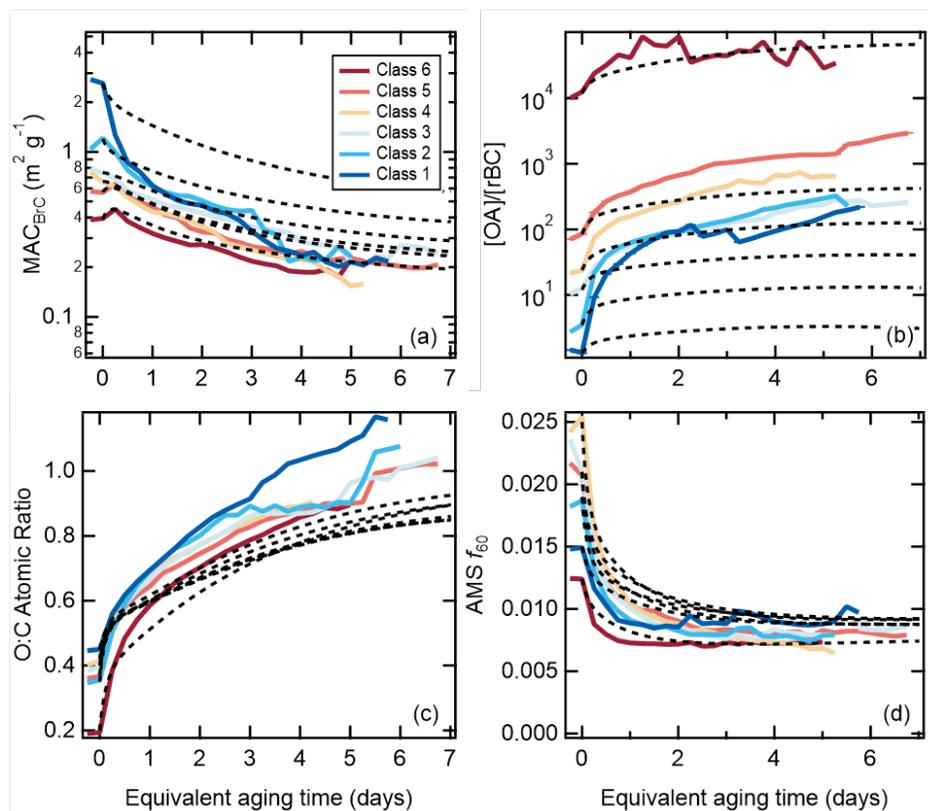
1720
1721 **Figure S18.** Comparison between observations (solid lines) and model results when only
1722 heterogeneous oxidation is included, i.e. no SOA (dashed lines). Results shown for values of the
1723 (a) MAC_{BrC}, (b) the [OA]/[rBC] ratio, (c) the O:C atomic ratio, and (d) the AMS *f*₆₀ versus
1724 equivalent photochemical aging time (assuming [OH] = 1.5 × 10⁶ molecules cm⁻³), with results
1725 shown for each SSA class. The increase in the modeled [OA]/[rBC], despite there being no SOA
1726 formation in this model formulation, results from faster loss of OA that is internally mixed with
1727 rBC compared with the OA that is externally mixed.
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1734 **Figure S19.** Dependence of the organic nitrate-to-total OA ratio on equivalent aging time for the
1735 different SSA classes. Individual burns are shown as gray lines, and the average for each SSA
1736 class as the colored line. Top row, left-to-right: class 1-3. Bottom row, left-to-right: class 4-6.

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1740 **Figure S20.** Same as **Figure 3**, but where dilution is turned off entirely for both gases and particles.
1741 This corresponds to an “atmospheric” simulation.
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1744 **12.3 Supplemental Tables**

1745 **Table S1.** Fuel types used.

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Fuel Types*	
bear grass	lodgepole pine, mixed
ceanothus	lodgepole pine, canopy
chaparral (chamise), canopy	lodgepole pine, litter
chaparral (manzanita), canopy	Peat, Kalimantan
Douglas fir, mixed	ponderosa pine, mixed
Douglas fir, canopy	ponderosa pine, canopy
Douglas fir, litter	ponderosa pine, litter
Douglas fir, rotten log	ponderosa pine, rotten log
Engelmann spruce, mixed	rice straw
Engelmann spruce, canopy	sagebrush
Engelmann spruce, duff	subalpine fir, mixed
Engelmann spruce, Fish Lake, canopy	subalpine fir, canopy
Excelsior	subalpine fir, duff
Excelsior (poplar)	subalpine fir, litter
jeffrey pine, duff	subalpine fir
juniper, canopy	untreated lumber
loblolly pine, litter	yak dung

*Further details on each fuel type, including the particular mix for mixed-type burns, elemental composition, and moisture content are available on the NOAA FIREX project website at

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1750 **Table S2.** Instruments sampling from the mini chamber.

Instrument	Property Measured
<i>Particles</i>	
UCD CRD-PAS	Light absorption and dry/humidified light extinction at 405 nm and 532 nm
PASS-3	Light absorption and scattering at 781 nm
CAPS-SSA	Light extinction and scattering at 630 nm
HR-ToF-AMS	Bulk particle non-refractory composition and concentration for PM ₁
SP-AMS	rBC-containing particle composition and concentration for PM ₁
SP2	rBC concentrations and size distributions
SEMS	Mobility size distributions (10-1200 nm)
<i>Gases</i>	
Ozone monitor	O ₃ concentrations
PTR-ToF-MS	Select non-methane organic gases
I-CIMS	Select non-methane organic gases (not used here)
CO ₂	CO ₂ concentrations
RH probe	Relative humidity

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1754 **Table S3.** Fuels by particle Class.

Class	Fuel	SSA range	Log([OA]/[BC]) range
Class 1	Chaparral, canopy, litter (pine), building materials, excelsior	0.23-0.43	-0.52 – 0.38
Class 2	Manzanita, Sage, litter (fir)	0.43-0.60	0.18 – 0.61
Class 3	Pine, fir, litter, canopy, juniper	0.60-0.74	0.82 – 1.3
Class 4	Pine, fir, canopy, rotten log, ceonothos	0.74-0.87	0.92 – 1.74
Class 5	Canopy (pine), rice, bear grass, duff	0.87-0.93	1.49 – 2.16
Class 6	Rotten log, duff, peat, dung	0.93-1.00	2.63 – 2.02

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1757 **Table S4.** Summary of conditions for literature brown carbon aging experiments.

Reference	Aging method/notes	Fuel type/burning notes
Martinsson et al. (2015)	Aging of smoke in oxidation flow reactor (potential aerosol mass reactor); <u>370 nm</u> ; $t_{OH} = 8.3$ days; <u>Observed notable decrease in absorptivity after aging</u>	Birch; Combustion in a natural-draft conventional wood stove; likely class 1 to class 3 particles
Saleh et al. (2013)	Photochemical aging of smoke in 7 m ³ chamber for $t_{OH} \sim$ a few hours; aging of pine likely > oak; <u>Report SOA absorptivity < POA absorptivity</u>	Pocosin pine and oak; combustion at Missoula fire lab; likely class 1 particles
Zhong and Jang (2014b)	Photochemical aging of smoke in a 104 m ³ outdoor chamber using natural sunlight; $t_{OH} =$ a few hours; continual characterization; <u>Observed initial increase in absorptivity to 2 h followed by gradual decline</u>	Hickory hardwood; Smoldering combustion; likely class 5
Kumar et al. (2018)	Photochemical aging of smoke in an 8 m ³ chamber; t_{OH} up to a day; Interpolate their observations to 405 nm; <u>Observed increase in AAE with aging</u>	Beechwood; combustion in a residential wood stove; likely class 1
Sumlin et al. (2017)	<u>Rapid</u> heterogeneous OH aging in an oxidation flow reactor (potential aerosol mass reactor); $t_{OH} = 1, 3.5, 4.5$ days; <u>Observed non-monotonic change in absorptivity</u>	Alaskan peak; smoldering; likely class 6
Wong et al. (2017)	Photolytic aging (300-400 nm) of water-soluble and water-insoluble (methanol) extracts in a photoreactor; up to 130 h; photolysis of solutions; <u>Observed continuous decrease in absorptivity</u>	Cherry hardwood; Controlled pyrolysis; likely class 6, although measurements of suspended particles not available
Lee et al. (2014)	Photolytic aging (275-390 nm) of aqueous extracts; photolysis of solutions	SOA produced from naphthalene + OH
Fleming et al. (2020)	Photolytic aging (300-400 nm) of particles on filters; absorption by individual chromophores or total particles measured; <u>wide range of equivalent lifetimes with respect to photolysis observed for different chromophores</u>	Variety of fuels from FIREX, comprising different species and ecosystem components; range of particle classes likely
<u>Browne et al. (2019)</u>	<u>Rapid heterogeneous OH aging in a flowtube; equivalent t_{OH} up to 1.2 h; Observed continuous decline in BrC absorptivity</u>	<u>Smoldering combustion of ponderosa pine needles; negligible BC, likely class 6</u>
<u>Cappa et al. (2019b)</u>	<u>Ambient observations in Fresno, CA, where the properties of wood smoke OA were estimated from multi-linear regression of the observed absorption and the time-varying concentrations of individual factors from PMF analysis of the organic aerosol</u>	<u>Smoke likely derived from wood combustion for home heating in fireplaces and stoves; based on MAC_{BrC} and AAE, likely similar to class 2</u>

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