

Biomass-burning-derived particles from a wide variety of fuels: Part 2: Effects of photochemical aging on particle optical and chemical properties

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KEY POINTS

- Despite wide diversity in properties of primary particles produced from biomass combustion, photochemical aging engenders generally consistent changes
- Photochemical aging alters the absorptivity of brown carbon (aka absorbing organic aerosol) resulting from secondary organic aerosol production and heterogeneous oxidation

30

31 **ABSTRACT**

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

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54 **PLAIN LANGUAGE SUMMARY**

55 Particles and gases from combustion of a wide range of biomass fuels (e.g. leaves, twigs, logs,
56 peat, dung) were continuously photochemically aged in a small chamber up to eight days of
57 equivalent atmospheric aging. The properties of the emitted particles and smoke depended on the
58 fuel used and the combustion conditions. Upon aging, the particle chemical composition and
59 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.

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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).

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

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

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

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

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

122 **2 Methods**

123 **2.1 Campaign overview and sampling strategy**

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

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

146 2.2 The mini chamber

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

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

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

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

189 **2.3 Instrumentation**

190 The suite of instruments sampling from the mini chamber are listed in **Table S2** and further
191 details of instrument operation and uncertainties are provided in McClure et al. (2020), Lim et al.
192 (2019), and Coggon et al. (2019). In brief, particle-phase instruments sampled alternatingly
193 through a two-stage thermodenuder that operated at 150°C and 250 °C with a residence time of ~5
194 seconds. The cycle rate between ambient and thermodenuder sampling was 2 minutes. The ambient
195 (“bypass”) line on the thermodenuder was lined with charcoal cloth to remove excess NMOG, O_3 ,
196 and NO_2 that might otherwise interfere with the measurements. Light absorption and extinction
197 coefficients (b_{abs} and b_{ext} , respectively) were measured at 405 nm and 532 nm using the UC Davis
198 cavity ringdown-photoacoustic spectrometer (CRD-PAS) and at 781 nm using a DMT
199 photoacoustic soot spectrometer (PASS-3). Estimated uncertainties for the absorption
200 measurements were 8%, 5%, and 10% at 405 nm, 532 nm, and 781 nm, respectively. Particle size
201 distributions were measured using a scanning electrical mobility spectrometer (SEMS; Model
202 2002, Brechtel Mfg., Inc.). The overall concentration and composition of sub-micron non-
203 refractory particulate matter (NR- PM_{10}) were measured using a high-resolution time-of-flight
204 aerosol mass spectrometer (HR-AMS; Aerodyne Research, Inc.). The concentration and
205 composition of refractory BC-containing particles was characterized using a soot particle aerosol
206 mass spectrometer (SP-AMS; Aerodyne Research, Inc.); the SP-AMS was operated with only

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

218 **2.4 Brown carbon, coatings, and particle classification**

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

$$220 \quad MAC_{BC} = \frac{b_{abs}}{[BC]}, \quad (1.)$$

221 where b_{abs} is the absorption coefficient (Mm^{-1}) and $[BC]$ is the concentration of refractory black
 222 carbon ($\mu g m^{-3}$). The observed MAC_{BC} may include contributions to absorption from both the BrC
 223 (the BrC enhancement, $E_{abs,BrC}$) and from the so-called lensing effect that can occur when non-
 224 absorbing coatings mix with BC (the coating-induced enhancement, $E_{abs,coat}$) (Cappa et al.,
 225 2012;Lack et al., 2012). The observable absorption enhancement is characterized as:

$$226 \quad E_{abs} = \frac{MAC_{BC,obs}}{MAC_{BC,pure}}, \quad (2.)$$

227 where $MAC_{BC,obs}$ is the observed value and $MAC_{BC,pure}$ is a reference value for pure, uncoated BC.
 228 The reference $MAC_{BC,pure}$ can be established from the literature or from the observations; we take
 229 the latter approach here, using wavelength-specific $MAC_{BC,pure}$ values determined by McClure et
 230 al. (2020) for this data set by extrapolation of the observed $MAC_{BC,obs}$ versus $[OA]/[BC]$
 231 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
 232 nm), and $5.5 \pm 0.6 m^2 g^{-1}$ (781 nm). We assume these reference values are applicable to all burns,
 233 consistent with the negligible dependence of the primary particle $MAC_{BC,781nm}$ on the coating-to-
 234 BC mass ratio ($R_{coat-rBC}$) (McClure et al., 2020) and the lack of size dependence of the $MAC_{BC,pure}$

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

238 We observe limited change in the $E_{abs,781nm}$ with photochemical aging here, with $E_{abs,781nm}$ for
 239 aged particles averaging 1.19 for $R_{coat-rBC} < 9$ (**Figure S2**). The $E_{abs,781nm}$ (and $MAC_{BC,781nm}$) only
 240 increases notably (by more than 10%) when $R_{coat-rBC} > 9$, while theory predicts the $MAC_{BC,781nm}$
 241 should increase by this amount for individual particles when $R_{coat-rBC} > 1$ (Fuller et al., 1999).
 242 Other laboratory experiments, often performed using mono-disperse BC seed particles, have
 243 observed substantial coating-induced enhancements and a dependence on the $R_{coat-rBC}$ (e.g. Cross
 244 et al., 2010; Shiraiwa et al., 2010; Cappa et al., 2012; Metcalf et al., 2013; Peng et al., 2016a; You et
 245 al., 2016). We suggest that the small $E_{abs,coat}$ for photochemically aged biomass combustion
 246 particles results from three phenomena: (i) condensation occurring onto a polydisperse rBC
 247 distribution, leading to some particles having very thick coatings and some quite thin, yielding a
 248 large average $R_{coat-rBC}$ yet small enhancement (Fierce et al., 2016; Fierce et al., 2020); (ii) the coated
 249 biomass burning-derived rBC particles not having a core-shell morphology and reduced $E_{abs,coat}$
 250 (Helgestad, 2016; Liu et al., 2017); and, (iii) weak absorption by BrC at 781 nm by both internally
 251 and externally mixed BrC that becomes notable only when the total [OA] greatly exceeds [BC]
 252 (McClure et al., 2020). This is supported by the comparably much stronger relationship for
 253 photochemically aged particles between $MAC_{BC,781nm}$ and the [OA]/[rBC] ratio than with the
 254 $R_{coat-rBC}$ (**Figure S2**). This suggests that the majority of the variability in the $MAC_{BC,781nm}$ derives
 255 from varying contributions of BrC, rather than in $E_{abs,coat}$, and that $E_{abs,coat}$ is near unity.

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

$$257 \quad b_{abs,BrC} = b_{abs,obs} - MAC_{BC,pure} \cdot [rBC] \cdot E_{abs,coat} \quad (3.)$$

258 Given the above discussion and the complementary discussion in McClure et al. (2020), we assume
 259 $E_{abs,coat}$ is unity, with the derived $b_{abs,BrC}$ an upper limit. A lower limit for $b_{abs,BrC}$ can be obtained
 260 using an empirical $E_{abs,coat}$ versus $R_{BC-coat}$ relationship. For the aged particles, the average upper-
 261 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
 262 532 nm. The brown carbon-specific mass absorption coefficient (MAC_{BrC}) is:

$$263 \quad MAC_{BrC} = \frac{b_{abs,BrC}}{[OA]} \quad (4.)$$

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

270 The Ångström absorption exponent (AAE) characterizes the wavelength dependence of
271 absorption:

$$272 \quad AAE_{\lambda_1-\lambda_2} = -\log\left(\frac{b_{abs,\lambda_1}}{b_{abs,\lambda_2}}\right) / \log\left(\frac{\lambda_1}{\lambda_2}\right); \quad (5.)$$

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

$$276 \quad SSA_{\lambda} = \frac{b_{ext}-b_{abs}}{b_{ext}} = \frac{b_{sca}}{b_{ext}} \quad (6.)$$

277 McClure et al. (2020) classified individual experiments into six classes dependent on the primary
278 particles SSA_{405nm} ; the SSA_{405nm} exhibited strong relationships with a variety of other intensive
279 optical properties and with the [OA]/[rBC] mass ratio. We use these same classifications, ranging
280 from class 1—primary particles having low SSA_{405nm} values (0.22 - 0.38) and small [OA]/[rBC]
281 (0.3 - 2.6)—to class 6—primary particles having high SSA_{405nm} values (0.94 to 0.96) and very large
282 [OA]/[rBC] (400 to 1×10^5)—to interpret the influence of photochemical aging. **Table S3** provides
283 the general relationship between fuel type, SSA, and $\log([OA]/[BC])$. As noted by McClure et al.
284 (2020), the classifications relate somewhat to the burn-average modified combustion efficiency
285 (MCE), which characterizes the burn efficiency, with class 1 generally deriving from more
286 efficient, flaming burns having higher MCE and class 6 from more less efficient, smoldering burns
287 having lower MCE. The average dependence of the various aerosol properties on photochemical
288 age is determined for each SSA class. Grouping experiments by SSA classification is justified
289 given the substantial variability in the primary particle properties between individual burns. The
290 focus on average behavior increases robustness of the resulting interpretation as sensitivity to
291 experiment-by-experiment differences (e.g., length of experiment, initial concentration, amount of
292 fuel consumed) is reduced.

293 3 Results and Discussion

294 3.1 Observations of the influence of photochemical aging on optical properties

295 3.1.1 Total particles (black + brown carbon)

296 The suite of intensive optical (e.g. SSA , MAC , AAE) and chemical and physical properties (e.g.
297 $[OA]/[rBC]$, $R_{\text{coat-rBC}}$) vary with photochemical aging; the average behavior for each particle class
298 is shown in **Figure 1** and the experiment-specific behavior within each class in **Figure S3** through
299 **Figure S8**. The majority of the mass formed is OA, with minor contributions from inorganic
300 species. A detailed assessment of SOA formation is provided by Lim et al. (2019).

301 The changes observed for the lower number (more BC-rich) particle classes are typically more
302 pronounced than for the higher number (more OA-rich) particle classes. For example, the class 1
303 $SSA_{405\text{nm}}$ increases from 0.3 to 0.7 and the $AAE_{405-532}$ from 1.4 to 3.5 with aging, while the class
304 6 $SSA_{405\text{nm}}$ remains near constant at 0.94 and the $AAE_{405-532}$ decreases slightly from ca. 7 to 5.
305 Notably, the $AAE_{405-532}$ converge towards a common value, around 4, with aging. While there
306 remain some class specific differences, this indicates that the SOA that is forming has similar
307 optical properties independent of the initial burn conditions.

308 Also, the $[OA]/[BC]$ for class 1 increases by a factor of nearly 70 while the increase for class
309 6 is ten times smaller, and the particle class 1 $R_{\text{coat-rBC}}$ increases by a factor of 11 while there is
310 negligible change for particle class 6. Generally, the most rapid changes occur when the equivalent
311 aging time is less than a day, with slower changes after this. Some of the observed changes, in
312 particular for class 1 and class 2 particles, results from enhanced loss of BC-rich particles when
313 the lights are turned on, although this alone cannot explain the differing extents of change and
314 would not directly impact the $R_{\text{coat-rBC}}$ (Section 3.2.1). These observations indicate substantial
315 formation of secondary OA and a net increase in the overall (dilution-corrected) OA, consistent
316 with Lim et al. (2019). If secondary OA formation were offset by evaporation of primary OA then
317 the SSA would not have increased, nor would the $[OA]/[rBC]$ or $R_{\text{coat-rBC}}$ ratios have increased.

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

321 are generally similar between SSA classes, despite some variability in the primary particle
322 properties (McClure et al., 2020). The changes in both O:C and f_{60} occur more rapidly than can be
323 explained by heterogeneous oxidation, implying rapid photochemical production of secondary OA
324 (Lim et al., 2019). The O:C increases rapidly at $t_{OH} < 1$ day with continual increases with further
325 aging. The f_{60} values decline rapidly at $t_{OH} < 1$ day to around $f_{60} = 0.008$, changing negligibly with
326 continued aging. It is noteworthy that the f_{60} plateaus around 0.008 upon aging, rather than at
327 0.003, the value denoted by Cubison et al. (2011) as the nominal background outside of biomass
328 burning influenced areas. This suggests that observation of f_{60} values much smaller than 0.008 in
329 ambient measurements indicate an influence of OA from non-biomass combustion sources (both
330 POA + SOA).

331 3.1.2 Brown Carbon

332 **Observations:** The class-average $MAC_{BrC,405}$ and the $AAE_{BrC,405-532}$ evolve with photochemical
333 aging (**Figure 2**). Results for individual experiments are shown in **Figure S10** and **Figure S11**.
334 Overall, the $MAC_{BrC,405}$ values decrease from the primary values with aging. However, for the
335 initially less absorbing BrC, corresponding to the higher SSA classes (i.e., class 5 and 6), the
336 $MAC_{BrC,405}$ first increase at $t_{OH} < 1$ day before decreasing. This behavior suggests rapid formation
337 of SOA more absorbing than the primary OA for these classes, with production of less absorbing
338 SOA or conversion of POA or SOA via heterogeneous oxidation into less absorbing forms at later
339 times (discussed further in Section 3.2.2). The $MAC_{BrC,532}$ behave similarly (**Figure S12**). The
340 class-average $MAC_{BrC,405}$ values all converge around $0.2 \text{ m}^2 \text{ g}^{-1}$ after many days (~ 5) of equivalent
341 aging. The class-average $AAE_{BrC,405-532}$ converge towards $AAE_{BrC,405-532} \sim 5$ after many days of
342 equivalent aging, with the exact behavior dependent on the initial $AAE_{BrC,405-532}$.

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

351 ~ 6 h). Saleh et al. (2013) also report smaller SOA absorptivity compared to POA at 550 nm,
352 qualitatively consistent with our observations. Zhong and Jang (2014a) observed the 550 nm
353 absorptivity of class 5 particles initially increased over ~2 h, but then gradually declined upon
354 photochemical aging of smoke from smoldering combustion. This general behavior is consistent
355 with the behavior of the class 5 and 6 particles here, for which the MAC_{BrC} increased slightly in
356 the first few hours of equivalent aging followed by a continuous decline.

357 Similar to our observations, Kumar et al. (2018) observed $AAE_{370-660}$ values for class 1
358 particles increased from around 1.4 to 2 for photochemically aged beechwood smoke over $t_{OH} \sim 1$
359 day. They report that the primary OA is more absorbing than the SOA formed. We interpolate their
360 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
361 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
362 g^{-1} . However, their primary $MAC_{BrC,405}$ substantially exceeds our class 1 average ($2.25 \text{ m}^2 \text{ g}^{-1} \pm$
363 1.0) as does their primary BrC AAE (4.6 versus 2.2 ± 1.1 , respectively), while their AAE for SOA
364 is similar to that observed here at longer aging times (5.5 versus ~5, respectively). Over their ~1
365 day of equivalent aging they find little variability in the MAC_{BrC} for SOA. Cappa et al. (2019b)
366 reported $MAC_{BrC,405}$ and $AAE_{405-532}$ for relatively fresh biomass burning derived organic aerosol in
367 the ambient atmosphere, reporting values ($0.84 \text{ m}^2 \text{ g}^{-1}$ and 3.02, respectively) similar to those for
368 class 2 particles here.

369 Sumlin et al. (2017) heterogeneously aged class 6 particles with OH and observed negligible
370 changes in the absorptivity and SSA_{405} at 1 and 3.5 days of equivalent aging, but then a sudden
371 change at 4.5 days of equivalent aging. This differs substantially from our observations, where
372 changes occurred continuously; the reasons for this difference are unclear, although a
373 discontinuous change with increasing exposure is unexpected. Browne et al. (2019) also
374 heterogeneously aged class 6 particles with OH, but observed a continuous decrease in the
375 absorptivity with OH oxidation, consistent with the long-time behavior observed here. Wong et al.
376 (2017) photolytically aged (at 300-400 nm) water-soluble and water-insoluble solution extracts of
377 particles from smoldering combustion and observed that the particle absorptivity initially increased
378 over the course of about a day, peaked, and then declined over longer times to below the initial
379 value. While this general behavior is consistent with the evolution of our class 5 and 6 particles,
380 the photon flux here was likely too low for direct photolytic aging to contribute substantially (Peng
381 et al., 2016b), especially given the short absolute aging timescale in the mini chamber (tens of

382 minutes). Lee et al. (2014) photolytically aged water-soluble extracts of secondary BrC produced
383 from photooxidation of naphthalene and observed a continuous decrease in the absorptivity, but
384 again with a time constant that was likely too long to have influenced our experiments. Fleming et
385 al. (2020) photolytically aged particles from 12 of the FIREX burns that were collected on Teflon
386 filters. They observed a wide diversity of equivalent lifetimes (referenced to the time-averaged
387 photon flux in Los Angeles, CA) for different BrC chromophores, some of which were quite short
388 (<1 day). However, the equivalent lifetime of the total absorption was >10 days for all samples,
389 and with a recalcitrant component making up ca. 30% of the total absorption.

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

395 **3.2 Understanding and modeling the photochemical evolution of smoke**

396 **3.2.1 Chamber photochemical model description**

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

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

412 **Reactive gases:** Biomass burning releases a wide variety of NMOG (Koss et al.,
413 2018; Sekimoto et al., 2018; and references therein). Upon oxidation, these NMOG can form SOA.
414 In general, higher molecular weight NMOG have a higher propensity to form SOA (Cappa and
415 Wilson, 2012). We consider the suite of gas-phase compounds measured by PTR-ToF-MS (Koss
416 et al., 2018) having molecular weights greater than 50 amu as potential SOA precursor compounds.
417 (Consideration of all species measured, including those with MW < 50 amu does not change the
418 results, consistent with Lim et al. (2019).) These 107 identified gas-phase compounds have been
419 binned according to their OH reaction rate coefficients reported by Koss et al. (2018) (**Figure S13**
420 and **Figure S14**). The OH rate coefficients range from $3 \times 10^{-10} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ (for
421 sesquiterpenes) to 1.4×10^{-13} (for nitrobenzene); most compounds have k_{OH} values greater than 4
422 $\times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$. Based on these observations, we make a simplifying assumption that
423 there are three general classes of SOA precursor molecules: those that react fast ($3 \times 10^{-10} \geq k_{\text{OH}} >$
424 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}
425 $< 2 \times 10^{-12}$). The corresponding SOA type-specific k_{OH} values we use in the model are: $k_{\text{OH,fast}} = 4$
426 $\times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ ($\tau_{\text{OH,fast}} = 0.19$ days), $k_{\text{OH,slow}} = 9 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ ($\tau_{\text{OH,slow}} =$
427 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**).
428 (The time constants given correspond to $[\text{OH}] = 1.5 \times 10^6 \text{ molecules cm}^{-3}$.) The dividing lines
429 between the NMOG classes are somewhat arbitrary, but capture the general overall behavior and
430 are consistent with variable observed formation timescales of secondary NMOG (Coggon et al.,
431 2019). Loss of primary species due to photolysis is not considered; Coggon et al. (2019) show that
432 rapid photolysis dominates loss for a small number of primary species, notably furfural. These
433 species tend to be fast reacting, and thus are incorporated in the fast NMOG group, although their
434 actual loss rate is likely underestimated.

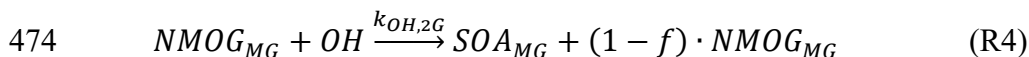
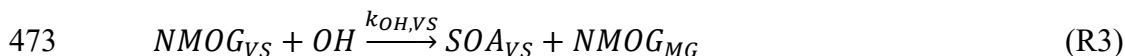
435 The initial total NMOG concentration is specified relative to the initial [OA], consistent with
436 Lim et al. (2019). The observed average ratio between the total carbon mass concentration
437 measured by the PTR-ToF-MS and the initial [OA] carbon mass is 7 ± 3 . SSA class-specific initial
438 [NMOG]/[OA]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

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

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

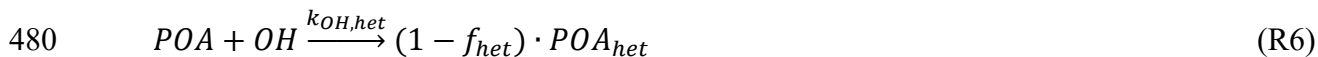
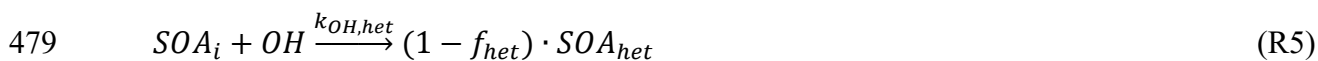
458 **SOA formation and processing:** SOA forms upon reaction of the primary NMOG types and
459 MG species, referred to here as SOA_{fast} , SOA_{slow} , SOA_{vs} , and SOA_{MG} . SOA formation occurs here
460 with fixed yields (α) assuming both instantaneous and irreversible (i.e., non-volatile)
461 condensation, simplifications over more detailed approaches. The influence of vapor wall losses
462 (Zhang et al., 2014) is not explicitly considered, and thus reflected in the derived α values. SOA
463 and POA also react heterogeneously with OH, producing oxidized OA that can also react with OH.
464 We assume an OH reactive uptake coefficient (γ_{OH}) of unity for all OA types. Upon oxidation,
465 15% of the POA and SOA mass is assumed lost owing to fragmentation and volatilization of the
466 products (i.e., $f_{het, x} = 0.15$). Heterogeneous oxidation of oxidized OA leads only to fragmentation
467 reflecting the greater propensity for more oxidized species to fragment upon reaction (Kroll et al.,
468 2015). The $k_{OH, het}$ values are calculated using the $[OH]$ with the observed surface-weighted particle
469 diameters and appropriate mass-transfer corrections (Smith et al., 2009).

470 The overall reaction scheme is summarized below:



475 Reactions 1-4 represent oxidation of gas-phase species and SOA formation, where $SOA_i = \alpha_i \cdot$
476 $NMOG_i$ and for a given reaction $NMOG_{MG} = (1 - \alpha_i) \cdot NMOG_i$; the subscript i indicates which
477 NMOG type reacted. Also,

478



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

486 **Dilution and particle wall losses:** Given the semi-batch operation method for the mini
487 chamber, the concentration of particles and gases all decreased over time owing to dilution and
488 losses to the chamber walls. The non-OH loss rate of gases was assumed constant in the model,
489 consistent with observations during an experiment where the lights were left off. However, we
490 observed that the overall decay of BC particles containing little coating material (e.g. class 1 and
491 class 2) was enhanced when the lights were turned on, while it was not for particles having thicker
492 initial coating amounts (**Figure S15** and **Figure S16**). This enhanced loss was unique to BB
493 particles, as no such behavior was observed for either atomized fullerene soot (highly absorbing)
494 or ammonium sulfate (non-absorbing). That enhanced decay occurs for the BC-rich particles
495 suggests that this phenomenon is related to the amount of coating material, since the class 1 and 2

496 particles have substantially smaller initial $R_{\text{coat,rBC}}$ values compared to the other classes (**Figure 1**
497 and McClure et al. (2020)). We speculate that the enhanced loss of BC-rich particles results from
498 their having a greater propensity towards photoelectric charging with the 254 nm light, as
499 photoelectric charging is highly sensitive to the state of the particle surface (Burtcher, 1992). We
500 determined an empirical relationship between the observed time-varying rBC decay rate and the
501 coating amount for use in the model (**Figure S17**). The decay rate slows as particles become more
502 coated (i.e., have larger $R_{\text{coat,rBC}}$), eventually reaching a plateau. We also account for the mixing
503 state of the particles when determining particle loss rates, as McClure et al. (2020) showed that the
504 fraction of total OA that is internally mixed with BC decreases as $[\text{OA}]/[\text{rBC}]$ increases. We
505 assume that the population of particles containing BC exhibit faster loss than the population that
506 does not. Independent of the enhanced decay for BC-rich particles, particle decay is faster than for
507 dilution-driven decay of gases because the particles are more subject to wall losses. The reference
508 decay rates for particles and gases were determined from experiments conducted using atomized
509 ammonium sulfate, atomized fullerene soot, and a “dark” smoke experiment. It is assumed that
510 POA does not evaporate upon dilution in the chamber, and thus does not contribute further to the
511 available NMOG, discussed further in Section 3.2.6.

512 **SOA properties and model fitting:** The different types of SOA in the model, which form
513 from different NMOG, can have different properties. The properties that are allowed to differ
514 between SOA types and heterogeneous oxidation products, besides k_{OH} , are the MAC_{BrC} , SOA
515 yields, O:C, and the f_{60} (**Table 1** and **Table 2**). While allowed to vary between SOA type, these
516 parameters are assumed to be independent of the SSA class. In this manner, we aim to find an
517 overall solution that allows for one set of SOA-type specific parameters that gives good model-
518 measurement agreement for all of the SSA classes. The choice of SOA yields influences all model
519 outputs, while the choice of the other parameters influence only that parameter output. The type-
520 specific MAC_{BrC} and SOA yields (α) are determined by fitting the model to the observations,
521 specifically to the evolution of $[\text{OA}]/[\text{rBC}]$ and MAC_{BrC} with the OH exposure (**Table 1**). The
522 Global Fit package in Igor v.8.03 (Wavemetrics) allowed for simultaneous fitting of the observed
523 $[\text{OA}]/[\text{rBC}]$ and MAC_{BrC} for all particle classes. Thus, the retrieved MAC_{BrC} and α values are those
524 that minimize the model-observation difference across all of the particle classes. After determining
525 the best-fit, type-specific MAC_{BrC} and SOA yields, separate global fits were performed to the

526 observed O:C and f_{60} to determine the type-specific O:C and f_{60} (**Table 1**). The model time step
527 was 2 mins, as this matched the averaging time for the observations.

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

535 Tuned values for the O:C for the SOA types are consistent with expected physical behavior,
536 guided by single-component studies (Chhabra et al., 2011). The fit O:C atomic ratios of the first-
537 generation SOA formed are 0.73 (fast), 0.59 (slow), and 0.59 (very slow, assumed the same as
538 slow). The O:C of multi-generation SOA and heterogeneously oxidized POA and SOA vary with
539 time, with the model fit indicating 1.22 oxygen atoms added per oxidation reaction, generally
540 consistent with expectations (Kroll et al., 2015). The observed AMS f_{60} rapidly falls to 0.008. To
541 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
542 f_{60} for products of heterogeneous oxidation dependent on whether SOA ($f_{60,het} = 0.01$), externally
543 mixed POA ($f_{60,het} = 0.003$), or internally mixed POA ($f_{60,het} = 0.008$) reacts. We note that similar
544 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
545 $m/z = 60$ that most corresponds to levoglucosan.)

546 3.2.2 Model-measurement comparison

547 The optimized model does a good job (reduced chi-square = 0.4) of describing the evolution
548 of MAC_{BrC} , $[OA]/[rBC]$, O:C atomic ratio, and AMS f_{60} (**Figure 3**). The reasonable agreement for
549 $[OA]/[rBC]$ indicates the appropriateness of the empirical correction for enhanced decay of rBC-
550 containing particles, the specified SOA yields and initial $[NMOG]/[OA]$ ratio, and the
551 apportionment between the different NMOG types. The model-measurement agreement improves
552 if the unknown model parameters are allowed to vary somewhat between particle classes; again,
553 some variability is expected given the burn-to-burn variability in the mix of NMOG species
554 (Sekimoto et al., 2018). However, that use of class-independent parameters provides for a

555 generally good description across classes demonstrates an overall general nature of the
556 photochemical evolution.

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

566 SOA type-specific 405 nm MAC_{BrC} values determined from the model were $MAC_{fast} = 0.81 (\pm$
567 $0.2) \text{ m}^2 \text{ g}^{-1}$, $MAC_{slow} = MAC_{VS} = 0.05 \text{ }^{(+0.05)}_{(-0.025)} \text{ m}^2 \text{ g}^{-1}$, $MAC_{2G} = 0.17 (\pm 0.05) \text{ m}^2 \text{ g}^{-1}$, and $MAC_{het} =$
568 $0.05 (\pm 0.025) \text{ m}^2 \text{ g}^{-1}$. The SOA_{fast} is substantially more absorbing than the other SOA types. It is
569 difficult to estimate a comprehensive uncertainty on these values; the above uncertainties were
570 qualitatively estimated based on the model sensitivity to changing the parameter values (see
571 Supplementary Material). The strong absorptivity of the fast-forming SOA and the substantial
572 difference between MAC_{fast} and MAC_{slow} and MAC_{2G} are unexpected and somewhat surprising.
573 The identities of the likely precursor NMOG characterized (Koss et al., 2018) can be interrogated
574 to understand this difference along with the evolving chemical conditions in the chamber.

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

584 SOA absorptivity varies between precursors (Lambe et al., 2013; Romonosky et al., 2016; Xie
585 et al., 2017), suggesting different precursors contribute differentially to the SOA absorption here.
586 Monoterpenes form SOA that is non-to-weakly absorbing. In contrast, SOA from aromatic
587 precursors can be quite absorbing, more so in the presence of NO_x. Formation of nitro-aromatics
588 is often linked to the enhanced absorptivity when NO_x is present, and condensed phase reactions
589 producing highly conjugated, potentially N-containing compounds also contribute to light
590 absorption (Laskin et al., 2015). Garmash et al. (2020) recently reported ROOR' dimer formation
591 in the gas phase from OH oxidation of aromatics, which we speculate could also contribute to light
592 absorption.

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

607 That the observed [ON]/[OA] ratio first increases then decreases with aging while the average
608 MAC_{BrC} derived for the SOA decreases with aging (owing to the $MAC_{fast} > MAC_{2G} > MAC_{slow} =$
609 MAC_{vs}) suggests a relationship between the processes driving these behaviors as well as a shift
610 with aging. While the [ON]/[OA] ratio would depend on the formation of any organonitrogen
611 species, the SOA absorption likely depends, at least in part, on nitro-aromatic formation. Organic
612 nitrates form from reaction of NO with peroxy radicals (RO₂), which competes with RO₂ + HO₂,
613 RO₂ + RO₂, and RO₂ autoxidation and is thus sensitive to variations in the availability of NO
614 (Orlando and Tyndall, 2012; Bianchi et al., 2019). However, nitro-aromatics typically form in the

615 gas phase from reaction of NO₂ with phenoxy radicals or with OH/aromatic adducts (Grosjean,
616 1984;Berndt and Böge, 2003;Vereecken, 2019). Phenoxy radicals generally derive from OH
617 reaction with phenolic molecules and both NO and O₃ compete with NO₂ for reaction with
618 phenoxy radicals; products from reaction with NO and O₃ are not well established (Vereecken,
619 2019). The importance of the OH-aromatic adduct + NO₂ pathway to nitro-aromatic formation is
620 suggested as small for species such as toluene and phenol owing to efficient reaction with O₂
621 (Atkinson et al., 1992;Vereecken, 2019), although has been proposed as the major pathway for
622 nitro-aromatic formation from guaiacol and similar species (Lauraguais et al., 2014;Sun et al.,
623 2019).

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

642 Analogous to the treatment of the *MAC*_{B_rC} for SOA, we have attempted to model the ON
643 formation by assigning a NMOG type-specific, yet particle class-independent ON yield. Unlike
644 the *MAC*_{B_rC}, no model parameters allow for good model-measurement agreement using this
645 approach. This primarily results from the different particle classes having very different

646 [ON]/[OA]. For example, for the [ON]/[OA] ratio for class 1 particles to increase from the initial
647 value (5.7%) to the peak value (18%) requires a much larger model ON species SOA yield than
648 for the class 6 particles, for which the [ON]/[OA] increases from 0.3% to only 0.6%. The reason
649 for these substantial differences likely relates to the factors discussed above.

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

$$654 \quad MAC_{BrC,x} = \frac{\sum_i EF_i \cdot \alpha_i \cdot MAC_{BrC,i}}{\sum_i EF_i \cdot \alpha_i} \quad (7.)$$

655 where x is the SOA type and i is for an individual NMOG. We note the highly uncertain nature of
656 these estimates and therefore only consider them qualitatively. The estimated $MAC_{BrC,fast}$ fall in
657 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
658 highly absorbing and abundant guaiacol SOA, moderately absorbing benzene diol (and related
659 species), and effectively non-absorbing monoterpene SOA. For slow SOA, the estimated
660 $MAC_{BrC,slow}$ ranges from $0.1 \text{ m}^2 \text{ g}^{-1}$ to $0.6 \text{ m}^2 \text{ g}^{-1}$, encompassing major contributions from
661 moderately absorbing phenol and cresol SOA. The estimated $MAC_{BrC,vs}$ depends almost entirely
662 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
663 $MAC_{BrC,fast}$ falls between the upper and lower estimates, while the $MAC_{BrC,slow}$, $MAC_{BrC,vs}$, and
664 $MAC_{BrC,MG}$ are more similar to the lower estimates.

665 3.2.3 Extending the mini chamber results to the atmosphere

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

674 Simulated OA composition profiles are compared for particle classes 1 and 6, as examples, for
675 chamber (“chm”) and atmospheric (“atm”) simulations in **Figure 4**. In the atmospheric
676 simulations, the POA influence persists to much longer times than in the chamber simulations. For
677 example, for class 1 the POA fraction after 2 days of equivalent aging is 0.05 for the chamber
678 simulation but 0.35 for the atmospheric simulations; for class 6 the increase in the POA fraction,
679 from 0.2 (chamber) to 0.3 (atmospheric), is smaller, but still notable. Some of the increase in the
680 POA contribution for the atmospheric versus chamber simulations results from the POA and
681 NMOG having the same loss rates in the atmospheric simulations. This leads to a decreased
682 relative contribution of SOA. The larger difference between the atmospheric and chamber
683 simulations for particle class 1 also reflects the comparably greater influence of enhanced decay
684 of BC-rich particles.

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

692 Differences between the chamber and atmospheric simulations are shown in **Figure 6** for the
693 $MAC_{BrC,405}$, $[OA]/[rBC]$, O:C, AMS f_{60} , and the $[SOA]/[POA]$ ratio. Averages across all particle
694 classes are shown to facilitate comparison; atmospheric simulation results for individual particle
695 classes are compared with the observations in **Figure S20**. Given the relatively large (albeit
696 particle class-dependent) absorptivity of the POA, the $MAC_{BrC,atm}$ decays more slowly than the
697 $MAC_{BrC,chm}$. This is accentuated by the fraction of fast SOA being somewhat greater at longer aging
698 times for the atmospheric simulations, since the $MAC_{fast} > MAC_{sec} > MAC_{slow}$. The evolution of the
699 MAC_{BrC} for the atmospheric simulations is empirically well described by a bi-exponential decay.
700 A fit to the model prediction for the average behavior across all classes (**Figure 6**) yields time
701 constants of 0.4 day and 2.8 days. (The overall fit equation is: $MAC_{BrC} = 0.29 + 0.59 \cdot \exp(-t_{OH}/2.8)$
702 $+ 0.13 \cdot \exp(-t/2.78)$, where t_{OH} is in days and the MAC_{BrC} in $m^2 g^{-1}$.)

703 Additionally, the increase in the $[OA]/[rBC]$ is much smaller in the atmospheric simulations
704 and the O:C values somewhat smaller. The AMS f_{60} at longer aging times remain similar to the
705 observations but are somewhat larger at shorter times for the atmospheric simulations. The
706 $([SOA]+[POA_{ox}])/[POA]$ is substantially smaller for the atmospheric simulations, with the
707 difference growing over time. After $t_{OH} = 1$ day the geometric average atmospheric
708 $([SOA]+[POA_{het}])/[POA]$ equals 1.7 while the chamber $([SOA]+[POA_{het}])/[POA]$ equals 3.7.
709 After $t_{OH} = 6$ days the atmospheric $([SOA]+[POA_{het}])/[POA]$ equals 5.8 while the chamber
710 $([SOA]+[POA_{het}])/[POA]$ equals 20.8.

711 3.2.4 Secondary OA versus heterogeneous oxidation

712 The particle properties evolve from both SOA formation and heterogeneous oxidation. To
713 separate these processes, two additional sets of model simulations are run: (i) with the gas-phase
714 rate coefficients set to zero such that only heterogeneous oxidation occurs, and (ii) with the OH
715 uptake coefficient set to zero, and thus only SOA formation occurs (**Figure 6**). It is evident that
716 the evolution of all intensive properties occurs much more slowly with only heterogeneous
717 oxidation. With heterogeneous oxidation only, the class-average $MAC_{BrC,405}$ decays to a much
718 lesser extent, even for the atmospheric simulations. Similarly, the increase in O:C is much too
719 small and the AMS f_{60} decays to a much lesser extent. The OA-to-BC ratio for the heterogeneous-
720 only simulations differ notably from the full simulations. For the heterogeneous-only chamber
721 simulations, this ratio increases initially until about 1.5 days of aging, at which point it decreases.
722 The decrease results from loss of mass over time from fragmentation, while the increase results
723 from faster loss of BC-rich particles in the chamber. For the atmospheric simulations, the OA-to-
724 BC ratio decreases continuously when only heterogeneous oxidation is included. In contrast, for
725 most properties the SOA-only simulations differ by only small amounts from the full simulations.
726 The exception is the MAC_{BrC} , for which the decrease in the class-average value with time is notably
727 smaller in the SOA-only simulation compared to the full simulation for both chamber and
728 atmospheric simulations. Our simulations assumed an OH reactive uptake coefficient of unity. We
729 note that if a substantially larger value is assumed ($\gamma_{OH} \sim 10$), the predicted changes due to
730 heterogeneous oxidation are much larger and reasonably in line with the observations. Values
731 substantially greater than unity have been found for some chemical systems (Richards-Henderson

732 et al., 2016;Schnitzler and Abbatt, 2018), but for compounds such as levoglucosan—a notable
733 component of BB particles—values less than unity are common (Kroll et al., 2015).

734 Under the assumption that $\gamma_{OH} \leq 1$ for BB particles, these observations point to an important
735 conclusion that is in line with various ambient observations. Large changes in key intensive
736 properties of BB particles, such as O:C, and AMS f_{60} , result primarily from secondary OA
737 formation, with heterogeneous oxidation having a smaller influence. While the BrC absorptivity
738 is comparably more sensitive to heterogeneous oxidation, SOA formation remains the major driver
739 of the observed changes. Thus, in ambient observations of biomass burning plumes (Vakkari et
740 al., 2014;Forrister et al., 2015;Garofalo et al., 2019), a notable increase in the O:C (or related
741 measures) and a decrease in the f_{60} can be taken as a clear indication of SOA formation.

742 3.2.5 Absolute absorption

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

755

756 3.2.6 POA volatility and the impact of dilution

757 Upon dilution, semi-volatile particle components may evaporate, which should lead to a
758 decrease in the OA-to-BC ratio and, potentially, changes in other particle properties; the MAC_{BrC}
759 could change if the absorptivity of the evaporating versus low-volatility (or non-volatile)
760 components differ. Given the semi-batch operation (Section 2.2) substantial, continual dilution

761 occurs throughout an experiment. Rapid dilution also occurs upon sampling of smoke into the
762 clean mini chamber air. Dilution-driven evaporation has been suggested as an important factor in
763 the chemical evolution of BB in ambient biomass burning plumes (Hodshire et al., 2019).

764 We assessed the impact of continual dilution on our observations by conducting one
765 experiment during which the chamber was left dark, although ozone was present at about 50 ppb
766 (**Figure 8**). The primary particles corresponded to class 3 particles ($SSA_{405nm} = 0.73$). After
767 sampling, the OA and rBC concentrations decreased by about a factor of 33 over 45 minutes owing
768 to dilution and other losses. For comparison, the [ACN] dilution tracer decreased by a factor of 21.

769 During this experiment the [OA]/[rBC] ratio was nearly constant (19.6 ± 0.7 , 1σ), even slightly
770 increasing over time. Also, the O:C remained constant (0.39 ± 0.03 , 1σ), as did the H:C ($1.74 \pm$
771 0.01 , 1σ). These observations together indicate that there was little, if any, evaporative loss of OA.
772 However, the AMS f_{60} declined continually, by about 30%. The signal at $m/z = 60$ is only a small
773 fraction of the total OA, and thus changes in f_{60} can occur even if only small changes in total mass
774 occur. The AMS f_{60} could also evolve over time from in-particle reactions that occur even in the
775 absence of oxidants. The mass fraction of OA remaining (MFR_{OA}) after heating in the
776 thermodenuder increased slightly over time, from 0.05 to 0.07. This could indicate evaporation of
777 more volatile components, although could result from “ripening” of the particles over time
778 (Tritscher et al., 2011).

779 SOA from reaction of some NMOG with O_3 may have offset some evaporative OA mass loss,
780 keeping the total OA mass constant while the f_{60} and MFR_{org} changed. Monoterpenes are the most
781 important SOA precursor class here that reacts readily with O_3 . The measured initial monoterpene
782 concentration ($8.6 \text{ ppb} = 50 \mu\text{g m}^{-3}$) constrains the potential SOA formed. Accounting for
783 differential losses of particles and gases in the mini chamber, with 50 ppb O_3 and an assumed SOA
784 yield of 0.3, we estimate that SOA formation might have increased the [OA]/[rBC] ratio by about
785 4%. Given the constancy of the [OA]/[rBC], we estimate no more than 8% of the OA evaporated
786 despite the substantial dilution over the 45-minute experiment. Much greater POA evaporation is
787 expected based on the volatility distribution of May et al. (2013) for biomass burning OA,
788 assuming evaporation is facile. Using their distribution, we estimate a factor of 33 decrease in the
789 OA should have resulted in a decrease in the [OA]/[rBC] from 19.6 to 11.2 from evaporation; a
790 factor of 21 dilution (the observed value for ACN) should have caused a decrease to [OA]/[rBC]

791 = 12.1. Thus, we conclude that evaporation due to dilution had minimal influence on our
792 observations and, more broadly, suggests minimal influence of dilution in general.

793 The reason for the insensitivity to dilution of our experiments may result from the
794 concentration range considered. May et al. (2013) established the volatility distribution for
795 biomass burning OA from thermodenuder measurements. They compared predictions from their
796 derived volatility distribution to observations of OA emission factors for different fuel types at
797 varying levels of dilution and initial concentrations. At the lowest initial [OA] ($\sim 100 \mu\text{g m}^{-3}$),
798 active dilution had little influence and in some cases the OA emission factor actually increased
799 after dilution in their experiments. In contrast, when the initial [OA] was much larger, on order of
800 $1000 \mu\text{g m}^{-3}$, there was a clearer relationship between the OA emission factor and the OA
801 concentration and better agreement with their predictions. For comparison, in our experiments, the
802 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
803 $384 \mu\text{g m}^{-3}$; notably, the dark experiment was at the highest initial [OA]. Dilution into the mini
804 chamber was a factor of seven. Most likely, evaporation resulting from dilution occurred upon
805 initial injection of the particles into the mini chamber with little additional evaporation as
806 experiments progressed, to the extent that the particles evaporated much at all.

807 **3.3 Comparison with ambient observations**

808 There are very few ambient assessments of how photochemical oxidation influences brown
809 carbon absorptivity. Forrister et al. (2015) measured dilution-corrected water-soluble + methanol-
810 soluble BrC absorption in above-ground ambient wildfire plumes at various distances downwind
811 from the fires. The measured O:C and AMS f_{60} changed with time as the BrC absorption decreased,
812 indicating that chemical changes occurred as the plume aged. They observed that the absolute BrC
813 absorption decreased over time, with a timescale of only 10 h; this was associated with a decay in
814 the *AAE* determined from *in situ* measurements. Surface measurements of aged smoke plumes by
815 Selimovic et al. (2019) are also suggestive of a decay in the *AAE* with aging. The BrC decay time
816 from Forrister et al. (2015) is substantially faster than we observe for any of the particle classes.
817 Interestingly, we predict that over 10 h the absorption by BrC in a wildfire plume should have
818 increased, and only at much later times should have decreased (**Figure 7**). In the case where only
819 heterogeneous oxidation is included (with $\gamma_{\text{OH}} = 1$), the predicted decay in BrC absorption based

820 on our observations has a timescale of ca. 4 days, substantially slower than observed by Forrister
821 et al. (2015).

822 It is possible that the smoke sampled by Forrister et al. (2015) differed significantly from any
823 of the burns sampled here. However, this seems unlikely given the wide-range of fuels and burn
824 conditions considered here, and since the plumes sampled by Forrister et al. (2015) likely derived
825 from combustion of similar fuels as used here. Also unlikely is that greater dilution in the
826 atmosphere played an important role, as it is thought that more absorbing primary OA has lower
827 volatility than less absorbing primary OA (Saleh et al., 2014). Thus, it is possible that the difference
828 between Forrister et al. (2015) and our results indicates that direct photobleaching rapidly degrades
829 BrC absorptivity, as direct photolysis in our experiments was likely of minimal importance owing
830 to the relatively low light intensity, single initiation wavelength (254 nm), and short absolute
831 timescale (<1 h) compared to the atmosphere.

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

849 Wang et al. (2016) also characterized changes in BrC absorptivity of BB particles in the
850 Amazon. They found that the BrC absorptivity decreased initially over an estimated ca. 20 h of
851 photochemical aging, after which the absorptivity remained constant. As above, this timescale
852 seems too short for heterogeneous oxidation to have a major impact, thus implicating direct
853 photolysis as the reason for the photobleaching. However, there are two important considerations.
854 First, Wang et al. (2016) note that they cannot rule out production of less absorbing SOA as the
855 reason for the absorptivity decrease. While the OA concentration was constant over time and
856 therefore suggestive of little SOA formation, it may be that dilution of the plume offset SOA
857 formation and consequently that SOA formation precipitated the decrease in absorptivity. Second,
858 their estimated lifetimes are determined from NO_x losses, and thus sensitive to assumptions about
859 the average OH; as such, longer lifetimes cannot be ruled out.

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

871

872 **4 Conclusions**

873 We characterized the photochemical evolution of smoke (particles + gases) produced from
874 combustion of a wide variety of biomass fuels. Particle properties were characterized as a function
875 of equivalent photochemical aging, with a focus on the particle optical properties. Photochemical
876 aging led to dramatic changes in the particle chemical composition, as evidenced by a large and
877 rapid increase in the O:C atomic ratio of the organic aerosol and a decrease in the marker ion f_{60}
878 in the OA mass spectrum. These chemical changes occurred concurrent with large changes in the

879 [OA]/[rBC] ratio, indicating substantial production of secondary organic aerosol mass. The
880 particle optical properties also changed substantially upon aging. Experiments were classified into
881 six classes according to the SSA of the primary particles. The average evolution of the optical
882 properties of particles in each class was characterized; the observed behavior was generally class-
883 specific. The total particle absorptivity normalized to black carbon (the MAC_{BC}) generally
884 increased with aging due to production of new, somewhat absorbing OA. The single scatter albedo
885 also generally increased with aging, although to a much less extent for experiments in which the
886 initial particles already had a large SSA. The absorptivity of the organic aerosol components, i.e.
887 of the brown carbon mass absorption coefficient (MAC_{BrC}), exhibited class-specific behavior. For
888 particles having an initially large SSA, the MAC_{BrC} exhibited an initial increase at short times (<0.5
889 days of equivalent aging) but then decreased monotonically with continued aging. For particles
890 having an initially small SSA, there was a rapid decline in the MAC_{BrC} at short times and then a
891 continued slower decline at longer times. At long times the MAC_{BrC} for the high SSA and low SSA
892 initial particles behaved similarly.

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

907 **5 Data Availability**

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

909 **6 Author Contributions**

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

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10Tables1274 **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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1277 **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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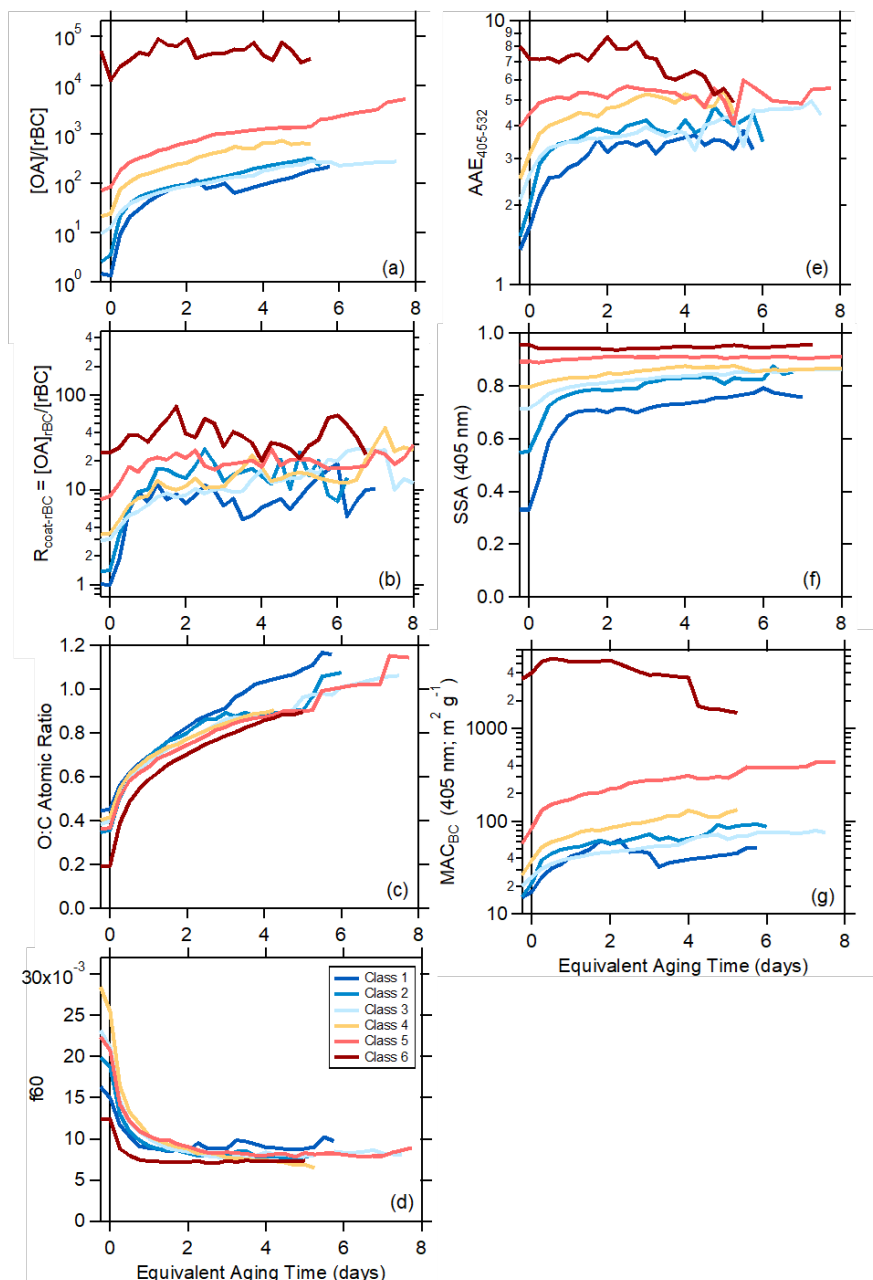
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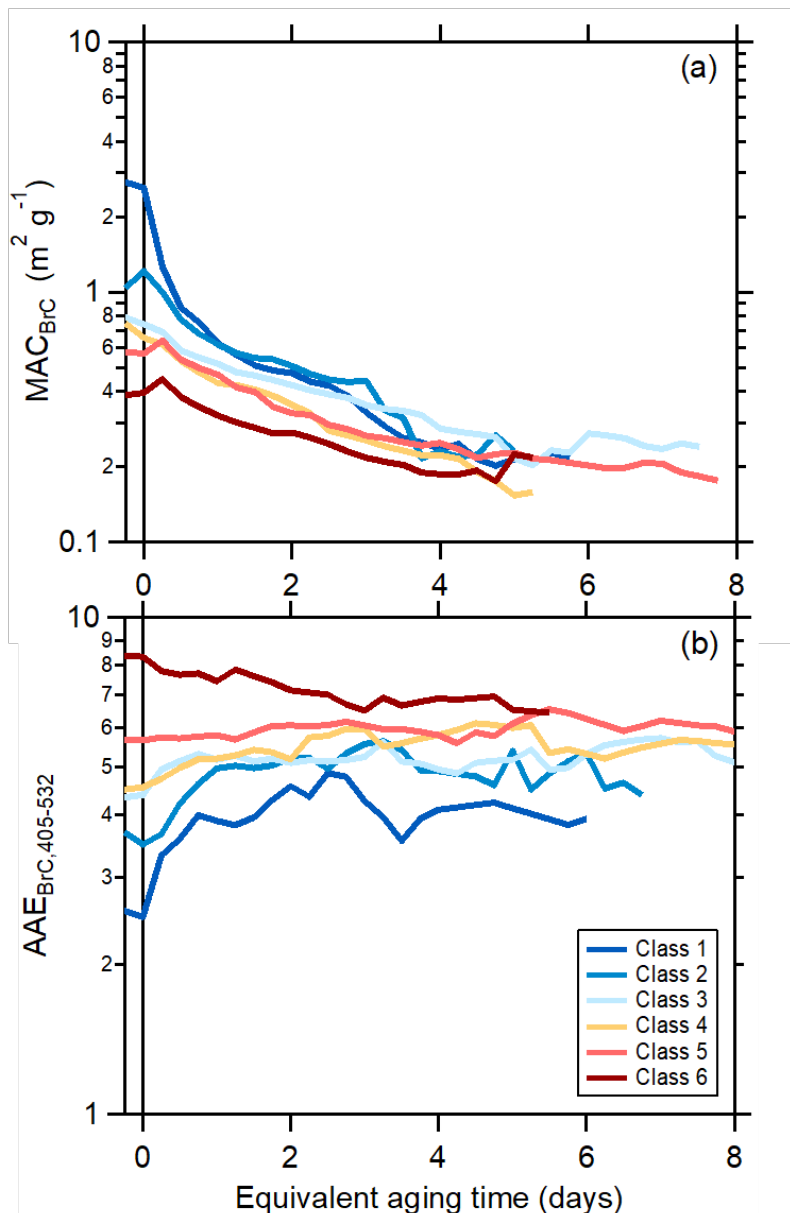
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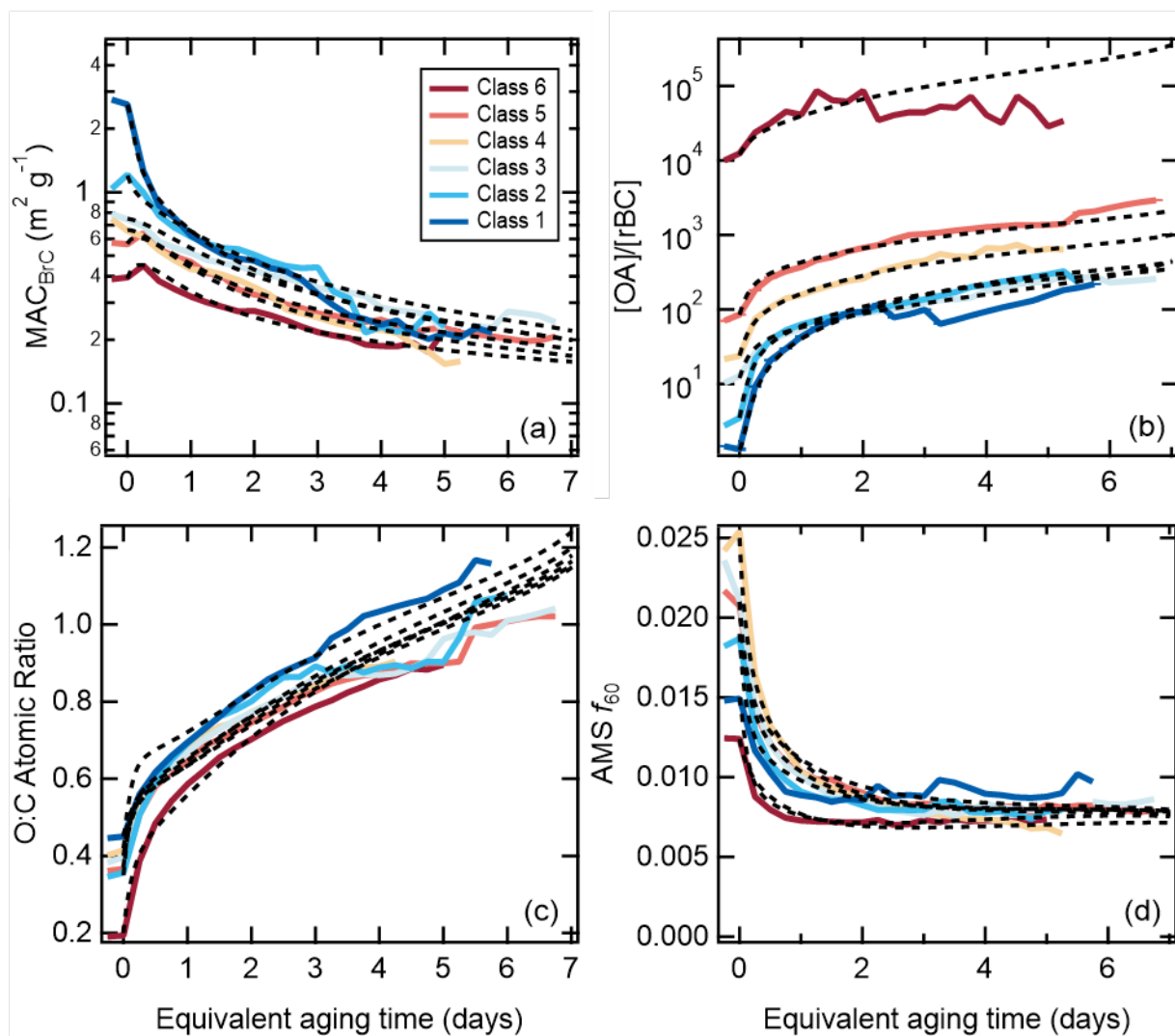


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 1286 **Figure 1.** Relationship between (a) the $[OA]/[rBC]$ ratio, (b) $R_{\text{coat-rBC}}$, (c) $AAE_{405-532}$, (d) the SSA
 1287 at 405 nm, (e) the O:C atomic ratio, (f) the AMS f_{60} , and (g) the MAC_{BC} at 405 nm as a function
 1288 of equivalent photochemical aging time (assuming $[OH] = 1.5 \times 10^6 \text{ molecules cm}^{-3}$). The different
 1289 lines are colored according to the SSA classification, and are averages for all burns within a class
 1290 (see Panel D). Figures showing results for each burn are available in the Supplementary Material.
 1291 Some of the apparent discontinuities for individual classes with certain properties results from a
 1292 change in the number of individual experiments contributing to the average above a given aging
 1293 time.

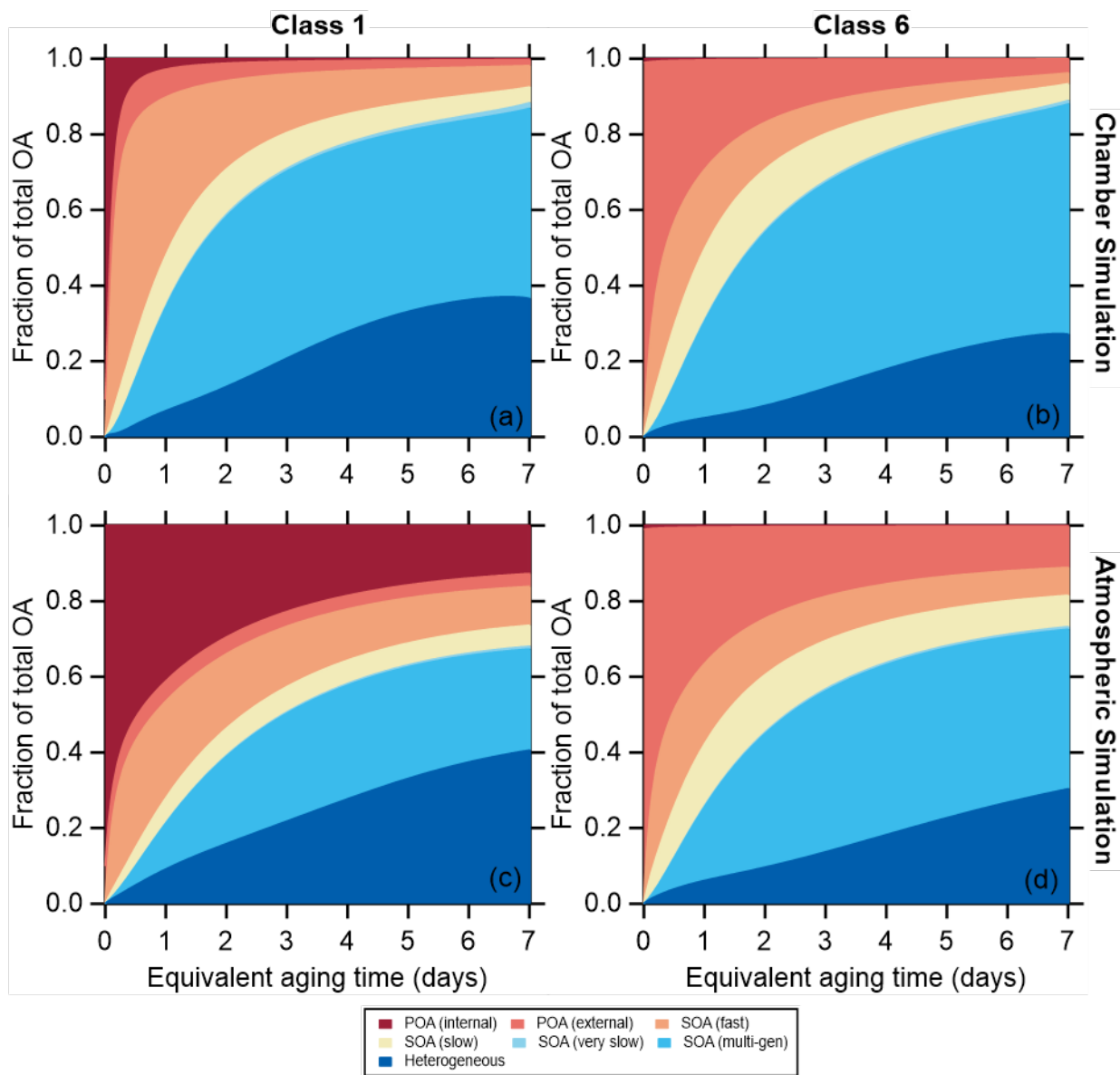


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 1296 **Figure 2.** Relationship between the brown carbon (a) MAC_{BrC} and (b) the AAE_{BrC} as a function of
 1297 equivalent photochemical aging time (assuming $[OH] = 1.5 \times 10^6$ molecules cm^{-3}). The different
 1298 lines are colored according to the SSA classification, and are averages for all burns within a class.
 1299 class 1 corresponds to particles having low SSA_{405} and class 6 to particles having high SSA_{405nm} .
 1300 Figures showing results for each burn are available in the Supplementary Material.

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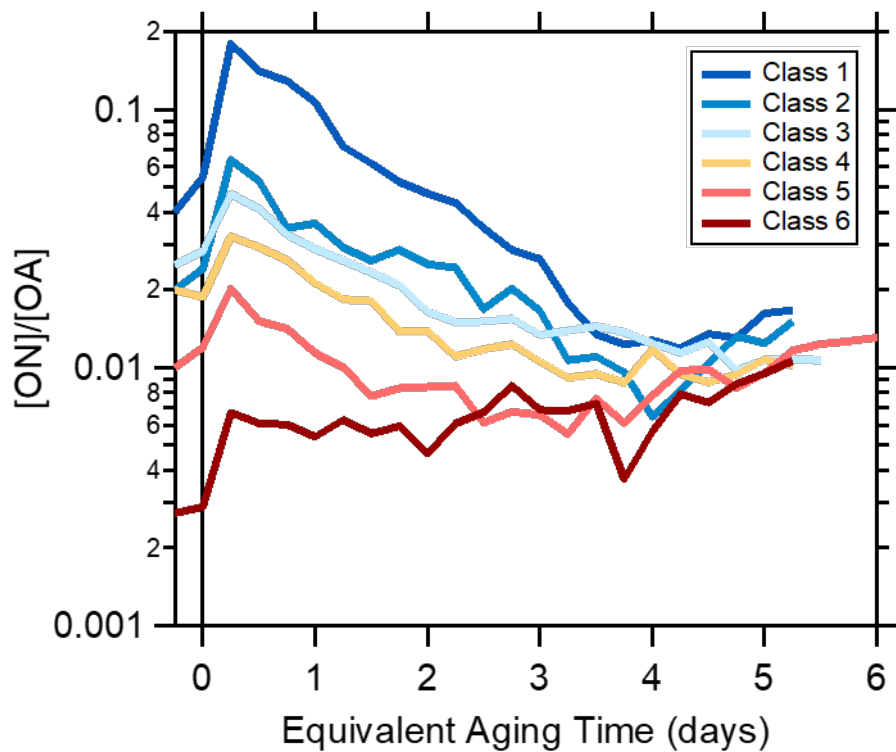


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 1304 **Figure 3.** Comparison between observed (solid lines) and modeled (dashed lines) values of the
 1305 (a) MAC_{BrC} , (b) the $[OA]/[rBC]$ ratio, (c) the O:C atomic ratio, and (d) the AMS f_{60} and the
 1306 equivalent photochemical aging time (assuming $[OH] = 1.5 \times 10^6$ molecules cm^{-3}), with results
 1307 shown for each SSA class.
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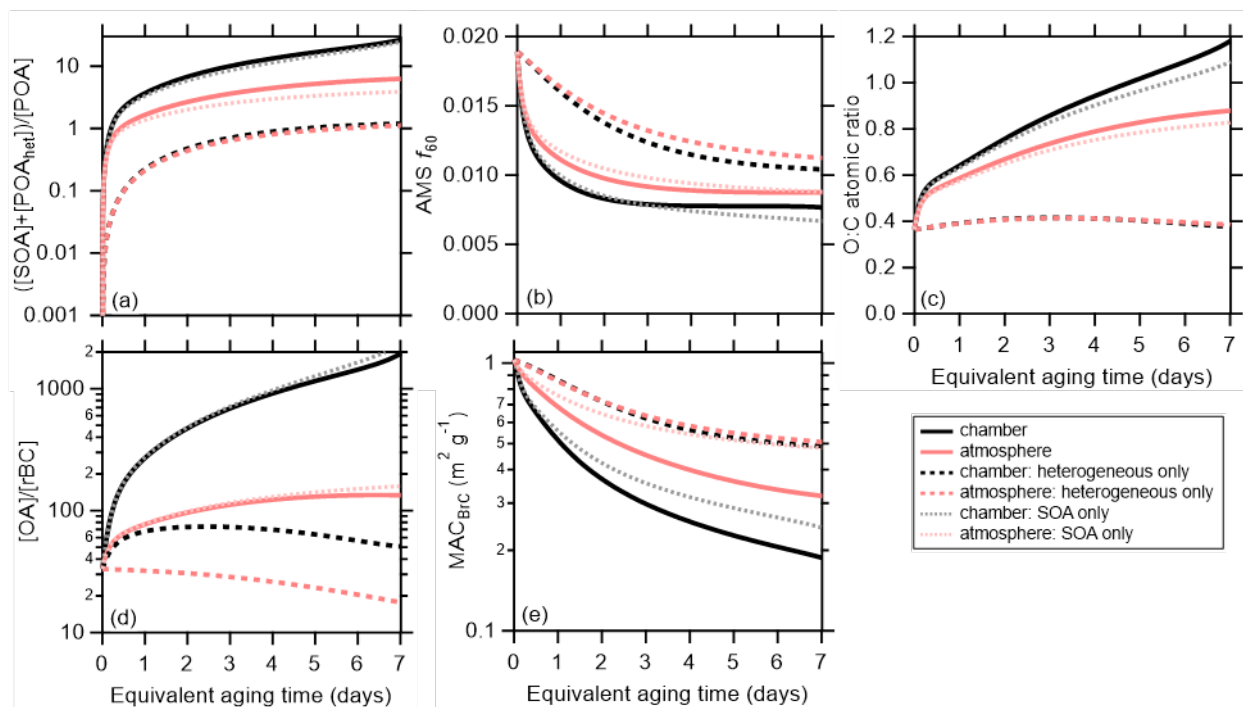
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 1311 **Figure 4.** Variation in the simulated OA fractional composition with equivalent aging time for (a
 1312 and c) SSA class 1 (BC rich) and (b and d) SSA class 6 (OA rich) for the mini chamber
 1313 experiments. For the “chamber” simulations in (a and b) the differences in decay rates between
 1314 particle types and gases are accounted for. For the “atmospheric” simulations in (c and d) it is
 1315 assumed that gases and particles all decay with the same rate.
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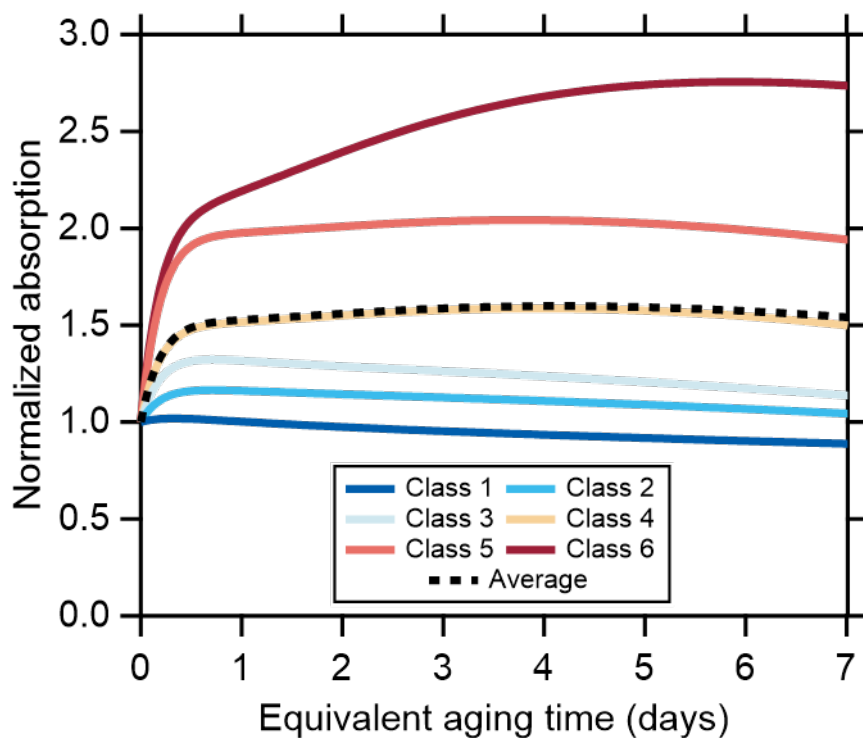
Figure 5. Dependence of the observed organic nitrate-to-total OA ratio for each SSA class on the equivalent aging time (assuming $[\text{OH}] = 1.5 \times 10^6$ molecules cm^{-3}).

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1326 **Figure 6.** Comparison between the model results when dilution and wall-losses are included (the
 1327 chamber simulation, black lines) or turned off (the atmospheric simulation, red lines). The model
 1328 has been run with both SOA formation and heterogeneous oxidation (solid lines), with
 1329 heterogeneous oxidation only (dashed lines), or with SOA formation only (dotted lines).
 1330 Averages (either arithmetic or geometric) across all particle classes are shown for (a) the SOA
 1331 plus oxidized POA to unoxidized POA ratio, (b) the $\text{AMS } f_{60}$, (c) the organic O:C, (d) the OA-to-
 1332 rBC ratio, and (e) the $\text{MAC}_{\text{BrC},405}$.

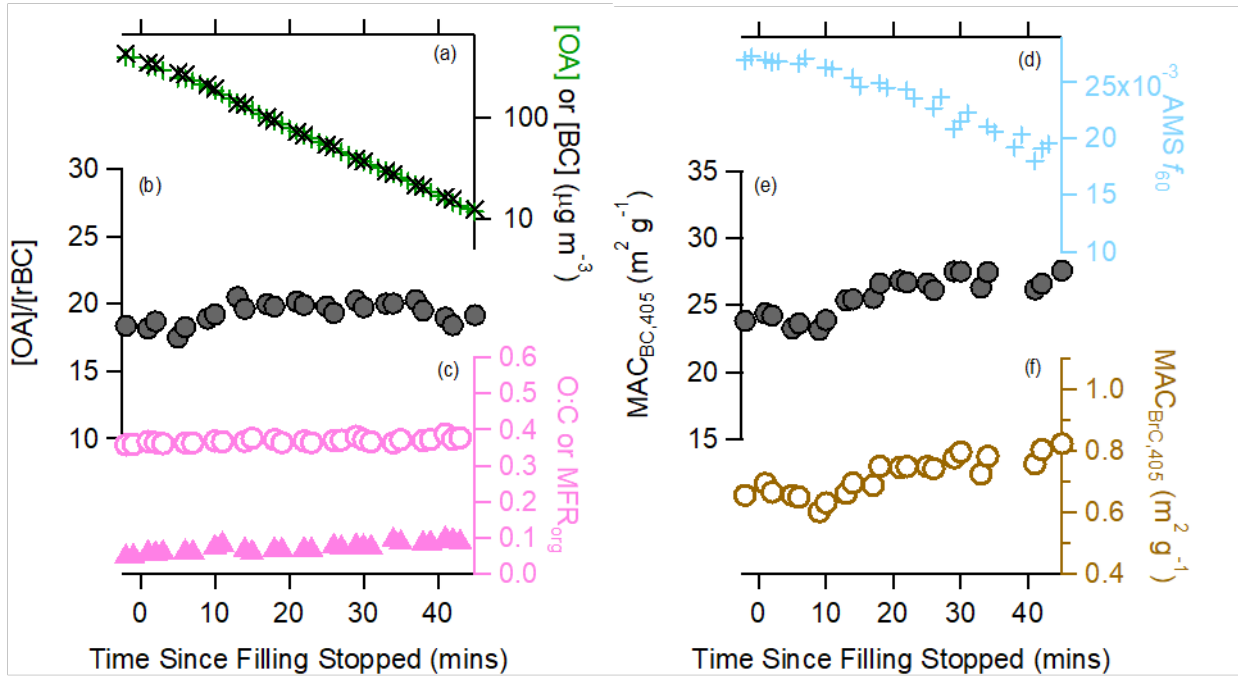
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Figure 7. Modeled change in the absolute absorption with aging, assuming no dilution, normalized to the value at $t = 0$. Results are shown for each particle class (colors) and the average (black).



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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 $\text{MAC}_{\text{BC},405\text{nm}}$; and (f) the $\text{MAC}_{\text{BrC},405\text{nm}}$.