

Evolution of Brown Carbon in Wildfire Plumes

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45 **Key Points:**

- 46 • Biomass burning brown carbon has unknown lifecycle and atmospheric
- 47 stability
- 48 • Brown carbon and aerosol properties from two fires are measured for 50 hours
- 49 • Wildfire brown carbon lifetime was 9-15 hours, but a small fraction is stable

50

51 **Abstract**

52 Particulate brown carbon (BrC) in the atmosphere absorbs light at sub-visible
53 wavelengths and has poorly constrained but potentially large climate forcing impacts.
54 BrC from biomass burning has virtually unknown lifecycle and atmospheric stability.
55 Here, BrC emitted from intense wildfires was measured in plumes transported over
56 two days from two main fires, during the 2013 NASA SEAC4RS mission. Concurrent
57 measurements of organic aerosol (OA) and black carbon (BC) mass concentration,
58 BC coating thickness, absorption Ångström exponent, and OA oxidation state, reveal
59 the initial BrC emitted from the fires was largely unstable. Using back trajectories to
60 estimate the transport time indicates that BrC aerosol light absorption decayed in the
61 plumes with a half-life of 9 to 15 hrs, measured over day and night. Although most
62 BrC was lost within a day, possibly through chemical loss and/or evaporation, the
63 remaining persistent fraction likely determines the background BrC levels most
64 relevant for climate forcing.

65

66 **Index Terms:** Aerosols and particles, Chemical kinetic and photochemical properties,
67 Evolution of the atmosphere, Troposphere: constituent transport and chemistry.

68

69 **Keywords:** Brown carbon, biomass burning, lifetime, plume evolution,

70 photo-oxidation, bleaching

71

72 **1. Introduction**

73 Brown carbon (BrC) is the component of organic aerosol (OA) that absorbs light in

74 the UV and visible spectral regions. Light absorption by BrC may globally offset the

75 total climate cooling at the top of the atmosphere from direct radiative forcing of OA

76 [*Feng et al.*, 2013]. Vertical profiles of BrC measured *in-situ* confirm its importance,

77 as it can account for 20% of the aerosol direct radiative forcing at the top of the

78 atmosphere [*Liu et al.*, 2014a]. Atmospheric BrC has two major sources: incomplete

79 combustion of either fossil fuels [*Bond*, 2001; *Yang et al.*, 2009; *Zhang et al.*, 2011]

80 or biomass [*Hoffer et al.*, 2006; *Chakrabarty et al.*, 2010; *Hecobian et al.*, 2010;

81 *Kirchstetter and Thatcher*, 2012; *Desyaterik et al.*, 2013; *Lack et al.*, 2013; *Mohr et*

82 *al.*, 2013]; and secondary formation often involving carbonyl or aromatic compounds

83 [*Shapiro et al.*, 2009; *Sareen et al.*, 2010; *Kampf et al.*, 2012; *Nguyen et al.*, 2012;

84 *Zarzana et al.*, 2012; *Laskin et al.*, 2013; *Nakayama et al.*, 2013; *Yu et al.*, 2014].

85 Coupled charge transfer complexes formed in organic molecules may combine with

86 individual chromophores and contribute to BrC absorption [*Phillips and Smith*, 2014].

87 When sensitive direct measurement techniques—such as light absorption of aerosol

88 extracts—are used, BrC is found to be ubiquitous, present even in the remote

89 continental troposphere at 10 km altitude [*Kieber et al.*, 2006; *Hecobian et al.*, 2010;

90 *Liu et al.*, 2014; *Liu et al.*, 2015]. Recent studies suggest that aerosol components

91 from biomass burning are more prevalent than previously thought [*Hennigan et al.*,
92 2010; *Hennigan et al.*, 2011; *Bougiatioti et al.*, 2014], and may strongly contribute to
93 this observed background BrC [*Washenfelder et al.*, 2015].

94 As controls continue to reduce fossil fuel emissions and a changing climate
95 potentially leads to more fires, both the relative and total impact of biomass burning
96 on air quality and climate forcing is expected to increase [*Fuzzi et al.*, 2015].
97 Although studies have focused on the emissions of relatively briefly aged biomass
98 burning BrC for use in large scale modeling by predicting BrC behavior and radiative
99 forcing effects from a ratio of black carbon (BC) to OA [*Saleh et al.*, 2014], there is a
100 growing body of evidence that atmospheric BrC evolves differently from both BC and
101 bulk OA, owing to production of BrC from secondary organic aerosol and loss of BrC
102 from photo-bleaching [*Lee et al.*, 2014; *Zhong and Jang*, 2014; *Zhao et al.*, 2015],
103 volatilization, or aerosol-phase reactions. In order to understand the difference
104 between BrC and bulk OA evolution and ultimately determine the effects of BrC on
105 climate, a focused effort to measure its atmospheric distribution and evolution are
106 needed.

107 In this study, we determine the evolution of BrC related to large wildfire plumes
108 sampled from near-emission to over two days of atmospheric transport. To our
109 knowledge, this study constitutes the first reported evolution of brown carbon from
110 biomass burning smoke in the natural atmosphere.

111

112 **2. Method**

113 *In situ* measurements were conducted onboard the NASA DC-8 airborne platform as
114 part of the SEAC4RS (Studies of Emissions, Atmospheric Composition, Clouds and
115 Climate Coupling by Regional Surveys) mission. Sampling occurred from 6 August to
116 23 September 2013 over the western, central, and southeastern regions of the
117 continental US. SEAC4RS followed the DC3 (Deep Convective Clouds and
118 Chemistry) campaign, where the DC8 flew with the same instrument payload. The
119 instrumentation used to measure BrC and identify biomass burning plumes is
120 described in detail by *Liu et al.* [2014a] and is briefly summarized here.

121 BrC was determined by direct measurement of the light absorption spectra over a
122 wide wavelength range from liquid extracts of aerosol collected on Teflon (EMD
123 Millipore) filters. Individual filters each collected aerosol mass (for particles less than
124 4.1 μm aerodynamic diameter) for 5 to 10 minutes and were stored at nominally
125 -10°C . A 2.5 m path-length Liquid Waveguide Capillary Cell (LWCC), a UV-Vis
126 light source (200 to 800 nm range), and a spectrophotometer, provided a measure of
127 BrC with higher sensitivity than established aerosol optical methods. Filters were
128 extracted first in water, then methanol, to extract most biomass burning BrC
129 components [*Chen and Bond, 2010*]. Light absorption spectra relative to that of the
130 pure solvent were determined for each sample. Here, we focus on BrC light
131 absorption of the dissolved aerosol in the solvent averaged between 360 and 370 nm
132 (in Mm^{-1}) and refer to it simply as BrC (see *Hecobian et al.*, [2010] for method).
133 Complete spectra are also provided.

134 Aerosol light absorption coefficients ($b_{ap}(\lambda)$) at three wavelengths (470, 532,
135 660nm) were measured with a Particle Soot Absorption Photometer (PSAP) for
136 aerosols below 4.1 μm aerodynamic diameter and were corrected for artifacts
137 associated with filter-based optical absorption measurements as described by *Virkkula*
138 *et al.* [2010]. Absorption Ångström exponents were determined from the 470 and 532
139 nm wavelength pair by:

$$140 \quad AAE_{PSAP} = - \frac{\ln(b_{ap,PSAP}(532)) - \ln(b_{ap,PSAP}(470))}{\ln(532) - \ln(470)} \quad (1)$$

141 Particle chemical composition was determined with a High Resolution Time of Flight
142 Aerosol Mass Spectrometer (HR-ToF-AMS) [*DeCarlo et al.*, 2006] that measured
143 bulk aerosol particles nominally below 1 μm aerodynamic diameter. Here, we use
144 the overall OA concentrations and the O/C (oxygenation) [*Aiken et al.*, 2008]. O/C
145 was determined using the organic mass fraction of the HR-ToF-AMS data using the
146 updated calibrations of Canagaratna *et al.* [2015]. The mass ratio of biomass
147 burning tracer signal (arising from levoglucosan and related molecules) to OA, f_{60} ,
148 was calculated from the HR-ToF-AMS data by taking the ratio of the signal at m/z 60
149 to the total organic mass signal [*Cubison et al.*, 2011]. Refractory black carbon (rBC)
150 mass concentrations were determined with a SP2 (Single Particle Soot Photometer)
151 and were corrected for particle sizes outside the measurement range [*Schwarz et al.*,
152 2008]. SP2 data were also used to estimate rBC coating thickness for dried aerosol
153 sampled in the individual plumes using the methodology of *Schwarz et al.* [2008] for
154 particles with 3 to 5 fg rBC mass content. The dry modal coating thickness was
155 reported every 5 to 10 min. Carbon monoxide (CO) was measured as a mixing ratio

156 using Diode laser spectrometry to make a Differential Absorption CO Measurement
157 (DACOM) at 1 s intervals [*Sachse et al.*, 1987].

158 In the analysis, BrC was first plotted against the CO concentration to identify
159 which filter sampling periods corresponded to the most intense regions of the plume
160 and to exclude filters with a significant sample integration period not associated with
161 the plume. For each aircraft transit through a plume, BrC data from the filters were
162 selected based on filter sample integration times corresponding to the most significant
163 CO enhancements within the plume (CO “peaks”). If more than one filter sample
164 existed within a given “peak”, the data were averaged over those filter sampling times.
165 Once the in-plume filters were identified, all parameters of interest were merged to
166 the filter sampling times if the data covered was greater than 75% of the filter
167 integration time; this merged data was retrieved from the NASA SEAC4RS archive
168 (the 19 May 2014 merge), except for the HR-ToF-AMS data that were updated 24 Oct.
169 2014. Aerosol data are reported at STP (1 atm, 273.15 K).

170 To account for dilution with plume transport, Normalized Excess Mixing Ratios
171 (NEMRs) [*Hobbs et al.*, 2003] were calculated using CO as the conservative tracer
172 (e.g., $\Delta X/\Delta \text{CO}$). Background concentrations for the various NEMRs and CO were
173 determined from data averaged before and after each plume intercept. NEMRs were
174 generated for BrC, rBC, and OA. Intensive parameters, including the AAE, rBC
175 coating thickness, O/C, and f60, are not presented as NEMRs.

176 Air mass transport times, in hours since emission, are used as the metric for
177 degree of plume evolution based on HYSPLIT back trajectories from the point of

178 aircraft measurement to the fire source location. The fire source latitude and longitude
179 were retrieved from INCIWEB reports (<http://inciweb.nwccg.gov/>) for the Rim and Elk
180 Complex Fires, described below. For each plume measurement, the amount of time
181 the air mass was exposed to sunlight during transport from the fire to the point of
182 measurement was also estimated in order to investigate possible photochemical
183 effects on BrC evolution. HYSPLIT back trajectories verified that the various plume
184 intercepts analyzed were from a common fire, or region of fires given the limited
185 degree of spatial resolution available by this method.

186

187 **3. Results**

188 ***3.1 The Rim Fires***

189 Although many plumes from both agricultural and wildfires were intercepted during
190 SEAC4RS, here we focus on the Rim fires (named due to their proximity to the scenic
191 point “Rim of the World”) since these were the largest plumes detected, and hence
192 most amenable to aerosol analyses via filters. The Rim fires produced smoke plumes
193 studied over two consecutive days. On the first day, 26 Aug. 2013, the aircraft
194 investigated the smoke downwind from an extensive fire near Yosemite National Park,
195 CA, referred to as the Rim 1 fire. Throughout this flight, the smoke was tracked as it
196 moved northeast through Nevada, Oregon and Idaho, where other regional fires were
197 by and large avoided by the aircraft (Figure 1). On the following day, 27 Aug. 2013,
198 the goal was to pick up this plume and continue to track it. However, the Rim 1
199 plume passed over another active burning region in Idaho, the Elk Creek Complex fire,

200 and then moved from Idaho, through Montana, and into Manitoba, Canada (Figure 1).
201 The plume from this second day is referred to as Rim 2, since delineating the smoke
202 from the Yosemite and Elk Creek Complex fires is not clear-cut. In the following,
203 we analyze the BrC evolution in two ways: 1) assuming all smoke is from the
204 Yosemite fire; and 2) assuming that the primary smoke sampled during the Rim 2
205 flight was from the Elk Creek Complex fire. This provides a discrete range in the
206 evolution times of BrC. Other parameters of interest are plotted assuming the Rim 2
207 smoke is solely from the Elk Creek Complex fire, for simplicity. The Rim 1 data
208 tracks from about 1 to 7 hours of plume age, while the Rim 2 data tracks from 9 to 50
209 hours if assuming the source is the Elk Creek Complex fire (or 17 to 40 hours,
210 assuming the Yosemite fire). The combined Rim 1 and 2 data provide an
211 opportunity to study the evolution of BrC and other aerosol properties for over two
212 days of transport, corresponding to a transport distance of 1500 km.

213

214 ***3.2 Measurements in Smoke Plume***

215 For the two Rim flights, the plumes are easily identified close to the fires by high
216 correlations between BrC and CO concentrations (for both flights combined, BrC and
217 CO were correlated with $r^2 = 0.98$), indicating BrC enhancements are associated with
218 smoke plumes (see Supplemental Figure 1 for BrC and CO time series).

219 To test our analysis method, given uncertainty imposed by the filter sampling
220 times and plume widths, we first plot the NEMR for rBC for all smoke plumes
221 sampled (Figure 2), assuming Rim 2 data resulted from the Elk Creek Complex fire.

222 CO and rBC are both emitted from biomass burning and should both be
223 approximately conserved in transport in the free troposphere in the absence of
224 precipitation over these timescales. Thus little change is expected with plume age, as
225 is seen. At the beginning of both the Rim 1 and Rim 2 fires, there was scatter in the
226 $\Delta rBC/\Delta CO$ (Supplemental Figure 2), which appear to result from smoke plumes from
227 separate local fires having different rBC relative to CO emissions. These data are
228 excluded from the overall plume evolution for the following analysis.

229 Figure 3 shows the evolution of BrC concentration (via proxy solution extract
230 light absorption at 365 nm), where the transport time was calculated assuming Rim 2
231 originated from both the Elk Creek Complex and the Yosemite fires. In contrast to
232 $\Delta rBC/\Delta CO$, which was relatively constant over time, BrC in these plumes decreased
233 over transport with an approximate half-life of 9 hours, assuming the Elk Creek
234 Complex fire, or 15 hours, assuming the Yosemite fire as the source of Rim 2 smoke.
235 If any mixing of the smoke from the two fires occurred, the half-life should fall
236 between these two extremes. The color scale on Figure 3 represents the approximate
237 amount of sunlight that the sampled smoke aerosol was exposed to, with specified
238 values in hours provided in Supplemental Figure 3. With increased sun exposure,
239 the BrC continued to decrease. However, after about 12 hours, continued sun
240 exposure showed no effect; it is likely all the chromophores that could be affected by
241 photochemistry or photobleaching were eliminated by this time. This result is
242 consistent with laboratory experiments showing BrC photo-bleaching [*Zhong and*
243 *Jang, 2014; Lee et al., 2014; Zhao et al., 2015*], although the photo-bleaching

244 experiments found much shorter half-lives of a few minutes to a few hours and/or do
245 no correlate with the solar cycle. Reduced light absorption with time suggests a BrC
246 loss mechanism such as chemical bleaching (chemical reactions resulting in the
247 destruction of the chromophores). Evaporation (or volatilization) may also be
248 occurring. BrC absorption at all wavelengths measured follows a similar decrease
249 (Supplemental Figure 4), indicating net light absorption should also decrease over
250 time.

251 As expected if BrC is being bleached or removed, the net aerosol AAE should
252 decrease with age, as can be seen in Figure 4a, where AAEs of 3.5 to 4.0 near the fire
253 drop toward 1 at long ages, the approximate AAE for pure BC. The AAEs reach about
254 1.5 after 50 hours of transport, roughly the value recorded in this study of background
255 conditions. This decrease in AAE highly correlates with the decrease in BrC, with r^2
256 = 0.83 (Figure 5a). The rBC is highly coated in the plumes, with a coating thickness
257 typically near 100 nm, significantly thicker than outside the plumes where it averages
258 25 nm. However, the coating thickness does not vary with plume age (Figure 4b),
259 indicating the OA coating the rBC particles must be non-volatile. Application of
260 shell-and-core Mie theory has suggested that rBC light absorption is enhanced with
261 decreasing wavelength in a manner similar to BrC [*Bond et al., 2006; Lack and*
262 *Cappa, 2010*], so coatings might alter the light absorption spectral properties of rBC.
263 However, since both rBC and the coatings atop rBC were observed to be constant, the
264 decrease in AAE with age must be due to the loss of some other light-absorbing

265 compound—specifically, BrC—and cannot be explained by a shrinking shell over a
266 rBC core.

267 Since the chromophore-containing molecules that comprise BrC are expected to
268 constitute a small mass fraction of bulk OA, differing trends in $\Delta\text{OA}/\Delta\text{CO}$ and
269 $\Delta\text{BrC}/\Delta\text{CO}$ are not surprising (Figure 4c). OA initially decreases rapidly with a
270 half-life of less than 2 hours, followed by little change after about 3 hours. In these
271 plumes, evaporation losses apparently dominated over any SOA formation processes.
272 Having a steady thickness of rBC coating while bulk OA decreases is not inconsistent
273 since the coating mass concentration is small relative to OA (estimated to be <10%,
274 assuming OA and BC densities of 0.9 and 0.75 g cm⁻³, respectively). In addition,
275 OA is produced mainly by smoldering combustion, while rBC is mainly by flaming
276 combustion, thus the small fraction of OA associated with rBC particles may have
277 different composition from the bulk of OA coming from different processes in the fire.
278 As the plume ages, the O/C (oxygenation) of the OA increases and f_{60} (biomass
279 burning OA relative to OA) decreases (Figure 4d), which has been previously
280 observed [Cubison *et al.*, 2011]. The decay in f_{60} is likely due to a combination of
281 evaporation and oxidation, as studied before [Molina *et al.*, 2004; Robinson *et al.*,
282 2007; Lambe *et al.*, 2012; Donahue *et al.*, 2014], and indicates that, although the bulk
283 OA concentration stabilizes, its molecular composition changes with time. This is
284 consistent with the evolving BrC. Indeed, the rate of change of both O/C and f_{60}
285 better follow the decrease in BrC rather than the decrease of OA. The chemical
286 transformations of the observed biomass burning OA, including changes in BrC, seem

287 to occur approximately simultaneously, as indicated by correlations between the
288 various variables (see Figure 5). Overall, this correlation between increasing O/C
289 and decreasing BrC and f_{60} suggests a possible linked process, like photo-oxidation
290 [Zhao *et al.*, 2015]. A photo-oxidation process leading to BrC loss is also consistent
291 with the greater sunlight exposures correlating with decreases in BrC (Fig. 3). Other
292 processes could also be occurring, such as loss of volatile BrC. Further experiments
293 and analyses of more ambient smoke plumes are needed to provide a better
294 understanding of the life cycle of BrC from biomass burning.

295

296 ***4 Conclusions***

297 The scale of the Rim 1 and 2 fires allowed for an unprecedented investigation
298 into the evolution of wildfire smoke in the ambient atmosphere. These data show
299 that absorption at 365 nm (Figure 3), and over the complete wavelength range
300 associated with BrC (Supplemental Figure 4), decreased with a half-life of roughly 9
301 to 15 hours. While the processes causing loss of BrC in the Rim smoke plumes
302 combine to remove most emitted BrC within a day, this decay rate is typically far
303 slower than losses observed solely due to photo-bleaching in current environmental
304 chamber experiments with realistic conditions. However, both ambient and chamber
305 data [Lee *et al.*, 2014; Zhao *et al.*, 2015; Zhong and Jang, 2014] imply that
306 predictions of the prevalence or optical impacts of BrC cannot simply be inferred
307 from emission or near-emission measurements without considering complex
308 processing with age. Our data is unique in that plume evolution was observed over a

309 sufficient time that a stable fraction of BrC was observed to persist. Approximately
310 6% of the BrC emitted remained above background levels even after 50 hours
311 following emission and was no longer affected by sunlight. This BrC should be
312 further investigated as it likely accounts for the ubiquitous BrC previously observed
313 throughout the troposphere in our previous study with this aircraft payload, which was
314 shown to have important radiative impacts [Liu *et al.*, 2014a]. Since the total and
315 relative impact of biomass burning on air quality is expected to increase [Fuzzi *et al.*,
316 2015], future studies should focus on the mechanisms responsible for the reduction of
317 light absorption following biomass burning we observed and the difference in
318 timescales with current laboratory experiments. Knowledge of the mechanisms
319 governing biomass burning BrC behavior in the atmosphere would allow us to
320 determine the overall climate forcing due to biomass burning BrC, and the degree to
321 which it will affect air quality in general in the future.

322

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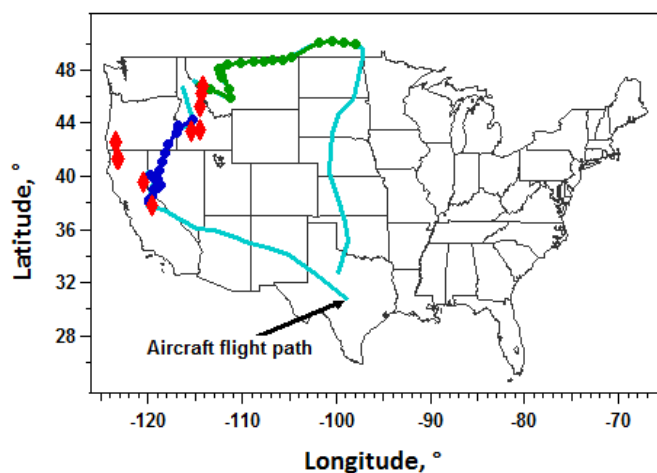
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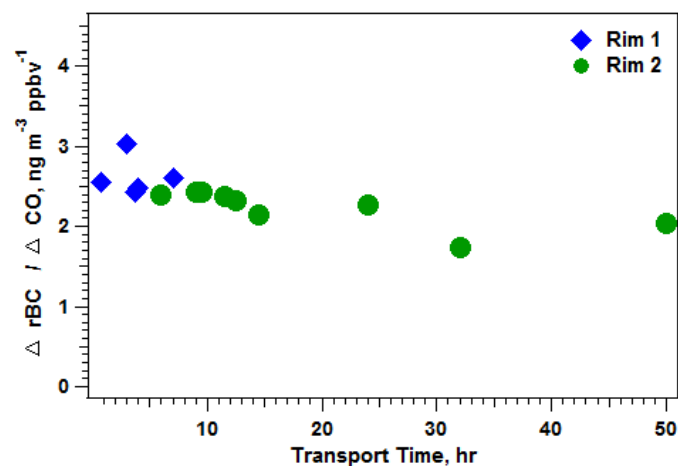
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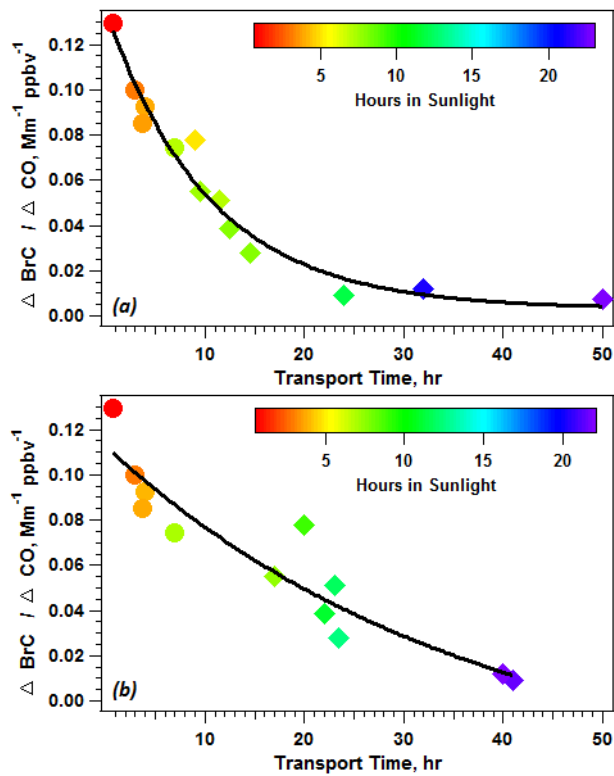
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Figure 1: Map of the SEAC4RS flight trajectory, with: (blue) Rim Fire 1 biomass burning data points, (green) Rim Fire 2 biomass burning data points, and (red) regional wildfires identified.



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Figure 2: Evolution of refractory black carbon (rBC) in the Rim smoke plumes. Transport time for Rim 2 is calculated assuming smoke was from the Elk Creek Complex fire.



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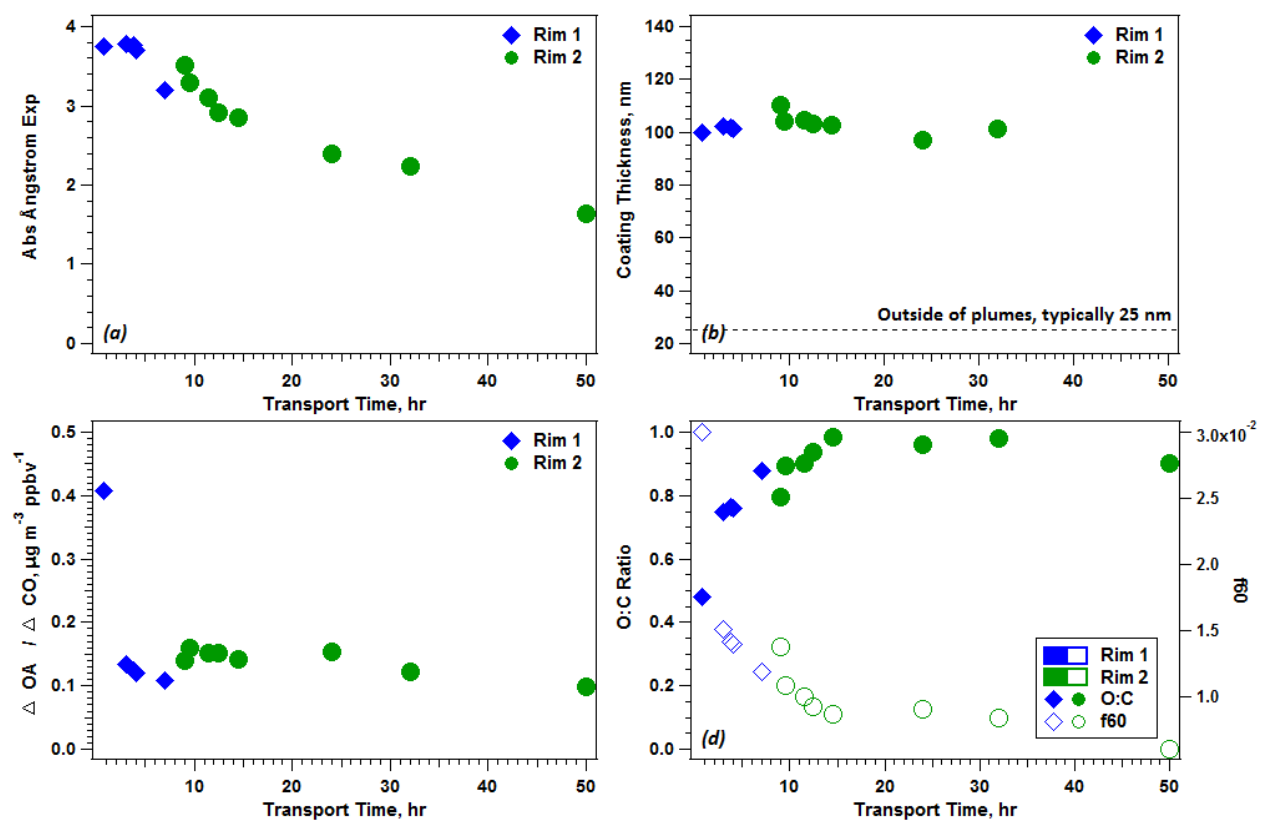
537 **Figure 3:** Evolution of BrC in the Rim smoke plumes. Circle symbol indicates Rim 1;
 538 diamond symbol indicates Rim 2. Color designates amount of time the smoke was exposed to
 539 sunlight during transport. The line is an exponential fit indicating the loss of BrC. Transport
 540 times are calculated for Rim 2 using (a) the Elk Creek Complex fire as the source, and (b) the
 541 Yosemite fire as the source.

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547 **Figure 4:** Evolution of other pertinent aerosol properties in the Rim smoke plumes, including:

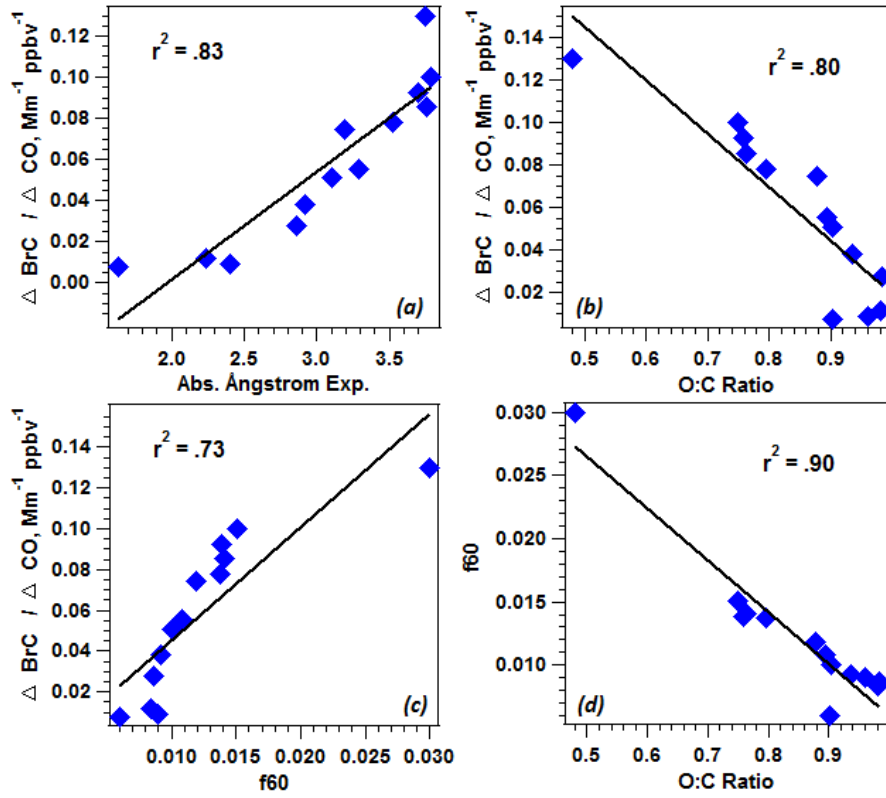
548 (a) the absorption Ångström exponent, (b) rBC coating thickness, (c) $\Delta \text{OA} / \Delta \text{CO}_2$, and (d) OA

549 oxygen-to-carbon ratio and f_{60} (tracer of biomass burning primary OA). Transport time for

550 Rim 2 is calculated using the Elk Creek Complex fire as the smoke source.

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554 **Figure 5:** Correlations between: (a) $\Delta \text{BrC} / \Delta \text{CO}$ and the absorption Ångström exponent, (b)
 555 $\Delta \text{BrC} / \Delta \text{CO}$ and O/C, (c) $\Delta \text{BrC} / \Delta \text{CO}$ and f_{60} , and (d) f_{60} and O/C.

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