

1 **Characterization of water-soluble brown carbon chromophores**
2 **from wildfire plumes in the western US using size exclusion**
3 **chromatography**

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17 **Abstract**

18 Wildfires are an important source of carbonaceous aerosol in the atmosphere. Organic
19 aerosol that absorbs light in the ultraviolet to visible spectral range is referred to as “brown carbon”
20 (BrC), and its impact on Earth’s radiative budget has not been well characterized. We collected
21 water-soluble brown carbon using a particle into liquid sampler (PILS) onboard a Twin Otter
22 aircraft during the Fire Influence on Regional to Global Environments and Air Quality (FIREX-
23 AQ) campaign. Samples were collected downwind of wildfires in the western United States from
24 August to September 2019. We applied size exclusion chromatography (SEC) with ultraviolet-
25 visible spectroscopy to characterize the molecular size distribution of BrC chromophores. The
26 wildfire plumes had transport ages of 0 to 5 h and the absorption was dominated by chromophores
27 with molecular weights <500 Da. With BrC normalized to a conserved biomass burning tracer,
28 carbon monoxide, a consistent decrease in BrC absorption with plume age was not observed during
29 FIREX-AQ. These findings are consistent with the variable trends in BrC absorption with plume
30 age reported in recent studies. While BrC absorption trends were broadly consistent between the
31 offline SEC analysis and the online PILS measurements, the absolute values of absorption and
32 their spectral dependence differed. We investigate plausible explanations for the discrepancies
33 observed between the online and offline analyses. This included solvent effects, pH, and sample
34 storage. We suspect that sample storage impacted the absorption intensity of the offline
35 measurements without impacting the molecular weight distribution of BrC chromophores.

36 1. Introduction

37 The wildfire season across the western United States has greatly intensified over the past
38 century. The U.S. Forest Service reports that the amount of western U.S. land burned by “high
39 severity” wildfires (i.e., fires that destroy more than 95% of vegetation) has increased eightfold
40 since 1985 (Parks and Abatzoglou, 2020). A variety of factors influence the number and intensity
41 of wildfires, including fuel availability, temperature, drought conditions, location of lightning
42 strikes, and direct human influence. During the 20th century, fire suppression tactics were applied
43 throughout the western U.S. and these efforts caused fuel to accumulate (Marlon et al., 2012). The
44 combination of dry conditions, warmer temperatures, and fuel availability contributes to the
45 intensity of present-day wildfires in the western U.S. Consequently, the impact that these climatic
46 conditions have on wildfire activity has been established. However, feedback effects that wildfires
47 have on climate is an ongoing area of research.

48 Wildfires emit carbonaceous particulate matter into the atmosphere (Bond et al., 2004; van
49 der Werf et al., 2010). Based on volatility and optical properties, carbonaceous aerosol particles
50 emitted from biomass burning are categorized as elemental carbon (EC) and organic carbon (OC)
51 (Turpin et al., 1990). Elemental carbon, referred to as black carbon (BC), is refractory and is
52 characterized by broad absorbance across the ultraviolet (UV) to infrared wavelengths (Seinfeld
53 and Pankow, 2003; Andreae and Gelencsér, 2006; Laskin et al., 2015). The light-absorbing
54 components of organic aerosols are referred to as brown carbon (BrC) (Laskin et al., 2015). The
55 direct absorption and scattering of solar radiation by these aerosol particles impacts the global
56 radiative budget (Boucher, O.; Randall, D.; Artaxo, P.; Bretherton, C.; Feingold et al., 2013;
57 Forster, P.; Ramaswamy, V.; Artaxo, P.; Berntsen, T.; Betts et al., 2007), but there is uncertainty
58 about the magnitude of this effect. Currently, more information is known about BC and its impact
59 on climate than BrC, as BrC is more chemically complex and more reactive (Buis, 2021; Di
60 Lorenzo et al., 2017). The direct radiative forcing of BC has been estimated to be the second largest
61 anthropogenic climate forcing species (Ramanathan and Carmichael, 2008) and studies have
62 suggested that BrC can contribute between 20 to 40 % to positive radiative forcing from total
63 carbonaceous absorbing aerosol (Feng et al., 2013; Zhang et al., 2017; Zeng et al., 2020a).

64 Wildfire emissions are a dominant primary source of BrC (Washenfelder et al., 2015). The
65 brown colour results from a combination of species with varying abilities to absorb light in the
66 UV-visible region (from highly to weakly absorbing) (Hems et al., 2021). The pyrolysis of lignin

67 and cellulose contributes to the major chemical constituents in wildfire plumes, such as phenolic
68 compounds and organic acids (Simoneit, 2002; Xie et al., 2019; Smith et al., 2014). Lignin
69 pyrolysis products with aromatic functionalities absorb visible light and may contribute to the
70 absorption properties of BrC (Hems et al., 2021). Secondary processes also contribute to BrC
71 formation. The generation of secondary organic aerosol (SOA) stemming from gas phase reaction
72 products includes nitration of aromatic compounds in the presence of NO_x or NO_3 (Harrison et al.,
73 2005; Finewax et al., 2018; Xie et al., 2017). For example, catechol can react with either the NO_3
74 or OH radical to form 4-nitrocatechol (Finewax et al., 2018) and oxidation of toluene under
75 elevated NO_x conditions has been observed to form over 15 absorbing compounds with
76 nitroaromatics contributing up to 60% of absorption in the visible region (Liu et al., 2016).
77 Although there are hypotheses about the identity of BrC chromophores, up to 40% of BrC
78 constituents remain unidentified (Lin et al., 2017; Bluvshstein et al., 2017).

79 To characterize the absorbing constituents that contribute to BrC absorption, reverse phase
80 high performance liquid chromatography (HPLC) coupled to high resolution mass spectrometry
81 has been applied (Fleming et al., 2020). However, fresh and aged BrC consist of extremely low
82 volatile organic compounds (ELVOCs) that may be irreversibly retained on a traditional C_{18}
83 reverse phase HPLC column (Di Lorenzo and Young, 2016). Size exclusion chromatography
84 coupled to ultraviolet-visible absorption spectroscopy (SEC-UV) has been demonstrated as an
85 alternative that successfully measures the absorption properties of high and low molecular weight
86 (MW) ELVOCs in fresh and aged biomass burning-derived samples (Di Lorenzo and Young,
87 2016; Di Lorenzo et al., 2017; Wong et al., 2019). Analysis by SEC-UV has been previously
88 applied to samples collected during ground-based field measurement campaigns, where the
89 method has established the quantification of BrC absorbance as a function of MW and provided
90 insight into the composition of BrC. High MW (>400 Da) compounds with unknown structural
91 identities have been determined to contribute to BrC absorption and the relative contribution to
92 BrC absorption by high MW species increases with smoke age (Di Lorenzo et al., 2017; Wong et
93 al., 2017, 2019). These findings suggested that lower MW species are less persistent in biomass
94 burning smoke relative to higher MW species, likely due to volatilization, oxidation,
95 polymerization, or other processes (Di Lorenzo et al., 2017; Hems et al., 2021).

96 The Fire Influence on Regional to Global Environments and Air Quality (FIREX-AQ) field
97 campaign examined the impact of wildfires on atmospheric chemistry and air quality in the western

98 United States. In this work, we present the SEC-UV analysis of water-soluble BrC that was
99 collected on board the National Oceanic and Atmospheric Administration (NOAA) Twin Otter
100 aircraft during plume transects downwind from western U.S forest fires. These represent the first
101 aircraft samples analyzed by SEC-UV to characterize BrC. We compare the total absorption
102 measured in online and offline samples and assign the BrC absorption to different MW classes.
103 Finally, we examine how the composition of the mobile phase used in the SEC-UV analysis
104 impacts elution time and spectral features. This provides cautionary information about interpreting
105 absorption results in studies that apply chromatographic separation in an aqueous-organic matrix.
106

107 **2. Experimental Approach**

108 **2.1 Overview of the FIREX-AQ field campaign**

109 FIREX-AQ was a multi-platform field campaign that investigated wildfire emissions in the
110 western United States from Jul to Sep 2019. Instrumented aircraft and mobile laboratories were
111 used to intercept and sample smoke plumes throughout multiple western U.S. states. These
112 included a DC-8, ER-2, and two Twin Otter aircraft. This study focuses on smoke sampled by the
113 “Chemistry” Twin Otter aircraft, which was based in Boise, Idaho, from 29 Jul to 5 Sep 2019, and
114 briefly in Cedar City, Utah, from 19 Aug to 23 Aug 2019. The Twin Otter payload included gas
115 and aerosol instruments to measure smoke composition, transport, and transformation. This
116 included CO measurements by near infrared cavity ring-down spectroscopy (G2401-m; Picarro
117 Inc., Santa Clara, CA, USA) (Crosson, 2008; Karion et al., 2013). A complete description of the
118 payload installed on the Twin Otter can be found in Warneke et al. (2023). The payload weight
119 limited the duration of in-flight sampling to 2.5 – 3 h, with a typical schedule of two or three flights
120 per day during the afternoon, evening, or night. A total of 40 flights were completed in Arizona,
121 Idaho, Nevada, Oregon, and Utah. Airmass back trajectory analyses were used to estimate the
122 plume age of each transect, as described in Liao et al. (2021) and Washenfelder et al. (2022).
123 Briefly, the smoke age was calculated by summing the horizontal advection and vertical plume
124 rise ages between the time of emission and the aircraft interception of the smoke plume. For the
125 Twin Otter flights, many plume intercepts by the aircraft were approximately Lagrangian
126 (Washenfelder et al., 2022).

127 **2.2 Online measurement of water-soluble absorption and offline sample collection**

128 The Brown Carbon-Particle into Liquid Sampler (BrC-PILS) collected online absorption
129 data and offline aqueous samples for the SEC-UV analysis. A complete description of the BrC-
130 PILS instrument and sampling can be found in Zeng et al. (2021) and Washenfelder et al. (2022).
131 Briefly, the BrC-PILS sampled smoke through a shared aerosol inlet on the Twin Otter. A parallel-
132 plate carbon filter denuder removed volatile organic compounds prior to the aerosol entering the
133 PILS. The PILS consisted of a steam generator and droplet impactor to collect aerosols into
134 aqueous solution. The liquid flow then entered a liquid waveguide capillary cell (LWCC) to
135 measure absorption. The instrument precision (3σ) for absorption at 365 nm was $\pm 0.02 \text{ Mm}^{-1}$ for
136 10 s in-flight data, with an uncertainty of $\pm 11 \%$ (Zeng et al., 2021). The flow exiting the LWCC
137 was split between a total organic carbon (TOC) analyzer and an automated 14-port valve. The
138 valve directed aqueous sample flow to one of 12 polypropylene sample tubes for offline SEC-UV
139 analysis (Figure S1). Prior to deployment, each polypropylene tube was rinsed with 18.2 $\text{M}\Omega\cdot\text{cm}$
140 deionized water (DIW) (Thermo Scientific Barnstead Smart2Pure) eight to ten times. The sample
141 flow rate was monitored by a liquid mass flow meter prior to the flow diverting between the
142 automated valve and the TOC analyzer. The sample flow was 1.53 mL min^{-1} during inflight
143 sampling, and the excess 0.43 mL min^{-1} was collected into an individual polypropylene tube for
144 12 s to 10 min. During in-flight sampling, the flight scientist actively controlled the sample
145 collection into each polypropylene tube to target transects of the smoke plume (example shown in
146 Figure S2). Six to twelve aqueous samples were collected for each flight, with 201 total samples
147 from 39 science flights. Field blanks of the DIW used to operate the BrC-PILS were stored
148 similarly in clean polypropylene sample tubes at the beginning, halfway point, and end of
149 campaign. Once collected in the field, the samples and blanks were stored on ice for several hours
150 prior to refrigeration until analysis.

151

152 **2.3 Offline Analysis by SEC-UV**

153 Measurement by SEC-UV provides information about size-dependent light absorption
154 properties of BrC chromophores. The offline aerosol samples were separated using an aqueous
155 gel-filtration column with a MW range of 250 Da to 75 kDa (Polysep GFC P-3000, Phenomenex,
156 Torrance, CA). Size-resolved components were detected using a diode array detector from 190 to
157 800 nm (UltiMate 3000, Thermo Scientific, Sunnyvale, CA) coupled to an ion chromatograph

158 (ICS 6000; Thermo Scientific) pump with an AS autosampler (Thermo Scientific). The isocratic
159 method was run using a mobile phase that contained a 1:1 mixture of acetonitrile and 25 mM
160 ammonium acetate in solution at a flow rate of 1 mL min⁻¹ and a sample injection volume of 100
161 μL. A solution of Suwannee River Humic Acid (SRHA II, International Humic Substances
162 Society, Saint Paul, MN, USA) was run prior to the FIREX-AQ samples to ensure proper operation
163 of the SEC-UV set-up.

164 The aqueous samples collected by the BrC-PILS did not require post-sampling processing
165 and were injected onto the SEC column under mobile phase flow to the diode array detector. The
166 uncertainty for the offline total absorption measurements considers the uncertainty of the liquid
167 flow and PILS collection efficiency, for a total uncertainty of ±10.5 %. Discussion of the SEC-UV
168 method development and details of the conversion of SEC-UV signal to ambient absorption in
169 units of Mm⁻¹ can be found in the SI. We calculated BrC absorption as a function of MW by
170 applying the calibration method described by Di Lorenzo and Young (2016) (Figure S3). Sample
171 measurements were blank subtracted. The detection limit of the total integrated absorption
172 (equivalent to 3σ of n=6 field blanks) was 2.5±0.2 mAU×min and 0.70±0.02 mAU×min at 250 nm
173 and 300 nm, respectively. This corresponds to a 3σ detection limit of approximately 525 Mm⁻¹ at
174 250 nm and 150 Mm⁻¹ at 300 nm.

175 **2.4 Absorption in different mobile phases**

176 To assess the impact of pH and mobile-phase composition on wavelength-dependent
177 absorption, the ammonium acetate solution was adjusted to pH 5 and pH 9 with acetic acid and
178 ammonium hydroxide, respectively, prior to combining with acetonitrile. A 15 μg/mL in DIW
179 solution of Suwannee River Fulvic Acid (SRFA II; International Humic Substances Society, Saint
180 Paul, MN, USA) and a FIREX-AQ aqueous sample were injected onto the diode array detector
181 without the SEC column in line with the following mobile phases: DIW only; 25 mM ammonium
182 acetate solution; the default mobile phase (described in Sect. 2.3); 25 mM ammonium acetate
183 solution adjusted to pH 5; and 25 mM ammonium acetate solution adjusted to pH 9. Solutions of
184 4-nitrocatechol, 4-hydroxy-3-methoxy cinnamaldehyde, vanillin, and 7-hydroxycoumarin in DIW
185 with concentrations of 3.9×10⁻⁸, 3.4×10⁻⁸, 3.9×10⁻⁸, 3.7×10⁻⁸ mol/mL, respectively, were prepared
186 and injected onto the diode array detector to observe differences in their absorption profiles. To
187 confirm the diode array detector results, measurements of the SRFA solution were also made with
188 UV-visible spectroscopy (8453; Agilent Technologies, Santa Clara, CA, USA) where the solution

189 was mixed (1:1 ratio) with the various mobile phases prior to transferring to a cuvette for
190 absorption measurements (Figure S7).

191 **3. Results and discussion**

192 **3.1. Trends in absorption with plume age**

193 We present molecular size-resolved absorption for flights that met the following criteria:
194 (1) maximum CO concentrations greater than 0.2 ppmv; (2) three or more downwind plume
195 transects; (3) three or more aqueous samples collected; and (4) consistent wind direction. Of the
196 201 aqueous samples collected, 47 samples from six flights met the criteria and are summarized
197 in Table S1. Each aqueous sample had a measurable absorption signal in the deep UV region (250
198 to 300 nm), while the absorption signal above 300 nm was nearly indistinguishable from the
199 blanks, because the samples were relatively dilute. The average (\pm standard deviation) integrated
200 absorption of the 47 samples that met the criteria was 10.4 ± 4.9 mAU \times min (8134 ± 3857 Mm $^{-1}$) and
201 0.36 ± 0.28 mAU \times min (316 ± 214 Mm $^{-1}$) for 250 and 300 nm, respectively.

202 To account for plume dilution, we follow the convention of normalizing BrC absorption to
203 a conserved tracer, to calculate $\Delta\text{Abs}_{\lambda, \text{BrC}}/\Delta\text{CO}$ (Forrister et al., 2015; Di Lorenzo et al., 2017;
204 Washenfelder et al., 2022; Zeng et al., 2021; Sullivan et al., 2022), where ΔCO is the average CO
205 mixing ratio measured during each aqueous sample collection subtracted by the average CO
206 background outside the plume. Background BrC absorption at 365 nm (a common wavelength to
207 report BrC absorption) was less than 0.2 Mm $^{-1}$ and no background correction was made to
208 determine $\Delta\text{Abs}_{\lambda, \text{BrC}}$ (Washenfelder et al., 2022). The average CO and variation of CO measured
209 for each flight are shown in Figure S9. Figure 1 shows $\Delta\text{Abs}_{300\text{nm}, \text{BrC}}/\Delta\text{CO}$ as a function of plume
210 age for the six selected flights, with a linear fit to each flight. The fitted slopes for $\Delta\text{Abs}_{300\text{nm},$
211 $\text{BrC}/\Delta\text{CO}$ vs plume age vary from -0.21 to 0.88 Mm $^{-1}$ ppbv $^{-1}$ h $^{-1}$, and show different trends between
212 flights. This indicates that BrC absorption increased downwind in some plumes and decreased
213 downwind in others.

214 Previous studies of normalized BrC absorption with plume age have reported conflicting
215 results. In the earliest aircraft study, Forrister et al. (2015) collected filter samples from two fires
216 in the western U.S. and measured the BrC absorption from water and methanol extracts. They
217 observed that BrC absorption at 365 nm decayed exponentially over a plume age range spanning
218 0 to 50 h (Figure S10) (Forrister et al., 2015). Di Lorenzo et al. (2017) reported total absorption of
219 size-resolved BrC chromophores using SEC-UV from three locations that were influenced to

220 varying degrees by biomass burning smoke, and observed minimal $\Delta\text{Abs}_{\lambda,\text{BrC}}/\Delta\text{CO}$ change as a
221 function of transport times from 10 to >72 h (Figure S10). In contrast to these measurements of
222 relatively aged biomass burning aerosol, two studies from other FIREX-AQ instruments showed
223 different trends for relatively fresh plumes. Using BrC-PILS measurements from the Twin Otter,
224 Washenfelder et al. (2022) showed variable trends in $\Delta\text{Abs}_{365\text{nm},\text{BrC}}/\Delta\text{CO}$ slope values ranging
225 from -0.02 to 0.02 $\text{Mm}^{-1} \text{ppbv}^{-1} \text{h}^{-1}$ over 0 to 5 h. Using filter samples from the DC-8 aircraft, (Zeng
226 et al., 2022) showed that BrC increased, decreased, or was unchanged as a function of plume age
227 over 0 to 8 h. In another study of fresh plumes, aircraft based measurements during the Western
228 Wildfire Experiment for Cloud Chemistry, Aerosol Absorption and Nitrogen (WE-CAN; Sullivan
229 et al., 2022) investigated the evolution of water-soluble BrC at 405 nm normalized to CO and
230 observed BrC depletion with a smoke age of <2 h, and PILS water-soluble BrC absorption that
231 broadly remained stable for a smoke age up to 9 h (Sullivan et al., 2022).

232 Our results are broadly consistent with measurements from FIREX-AQ and WE-CAN that
233 sampled fresh plumes, and differ from the studies that sampled more aged smoke. The relatively
234 limited plume age range of the FIREX-AQ sampling makes it challenging to deduce long-term
235 trends associated with changes in total absorption as a function of transport time. In addition, the
236 disparity in $\Delta\text{Abs}_{\lambda,\text{BrC}}/\Delta\text{CO}$ time dependence between FIREX-AQ observations and those reported
237 by Forrister et al. (2015) may be attributed to i) FIREX-AQ having sampled a greater number of
238 western U.S forest fires; and ii) the younger age of the FIREX-AQ plumes. More in-flight sampling
239 would be required to observe BrC absorption of plume ages 5 h to 50 h to determine if the results
240 observed by Forrister et al. (2015) would also show variability with a greater number of fires, or
241 if the BrC lifetime would converge to a similar value.

242 **3.2 Chemical evolution of brown carbon with plume age**

243 Chromophores <500 Da were responsible for most of the absorption at 250-300 nm
244 measured in the aqueous samples (Figure 2, Figure S11). For the 47 samples, molecular species
245 >500 Da contributed an average of 3.0 ± 1.9 % to total measured absorption at 250 nm, while
246 molecular species <500 Da contributed an average of 72 ± 4.5 %. Absorption past the exclusion
247 volume represents an unidentified MW, as elution past this retention time (Figure S3) indicates
248 non-SEC analyte-column interactions were occurring. The average contribution to total measured
249 absorption by undefined MW species was 25.1 ± 5.7 %. Previous SEC-UV analyses have observed
250 elution beyond the exclusion volume and non-size exclusion effects (Wong et al., 2017; Lyu et al.,

251 2021). Elution at later retention times has also been observed for fresh BrC separated in a mobile
252 phase containing 50% acetonitrile (Lyu et al., 2021). This result was attributed to non-size
253 exclusion effects, such as hydrophobic interactions of BrC with the SEC stationary phase, which
254 may also have contributed to elution past the exclusion volume in our samples. The absorption
255 density plots of the aqueous samples from the flights listed in Table S1 had similar size-resolved
256 features with varying magnitude in absorption (Figure S5).

257 These results are the first reported SEC-UV measurements of very fresh (0-5 h) field
258 samples of biomass burning smoke, and they confirm some of the observations from field studies
259 that measured more aged smoke, as well as laboratory studies that generated fresh or aged smoke.
260 Previous studies that examined biomass burning BrC using SEC-UV have similarly concluded that
261 fresh, less aged smoke contains a large fraction of lower MW absorbing species (Di Lorenzo et
262 al., 2017; Wong et al., 2017; Lyu et al., 2021). In the examination of field samples, Di Lorenzo et
263 al. (2017) collected ambient biomass burning aerosols that had been aged 10 to >72 h. They
264 observed that low MW (<500 Da) chromophores contributed more to total absorption than higher
265 MW (>500 Da) compounds in the least aged (10 to 15 h) biomass burning-derived filter extracts
266 (Di Lorenzo et al., 2017). These findings resemble the absorption features of our FIREX-AQ
267 samples, which span a plume age range from 0 to 5 hours. Wong et al. (2019) used SEC-UV to
268 analyze filter extracts collected during fire seasons in Greece with atmospheric ages of 1 to ~70 h
269 and observed that high MW species dominated total BrC absorption of the fresh and aged smoke.
270 Differences between the FIREX-AQ aqueous samples and the results presented by Wong et al.
271 (2019) can be driven by varying types of fuel emissions, photochemical conditions, meteorology,
272 and differences in back trajectory analyses.

273 Two studies have applied SEC-UV analysis to lab-generated or lab-aged smoke samples.
274 Wong et al. (2017) pyrolyzed dry hardwood and aged the samples from 0 to 10 h with UV light.
275 They found that low MW chromophores dominated total absorption compared to high MW
276 species, which is generally consistent with our observations. Lyu et al. (2021) generated biomass
277 burning aerosol from laboratory combustion of boreal peat and also analyzed the aerosol by SEC-
278 UV. Under the same SEC-UV separation conditions, the FIREX-AQ water aqueous samples
279 parallel the findings of Lyu et al. (2021), with low MW BrC chromophores dominating total
280 absorption for unaged fresh smoke and smoke aged between 0 to 5 h in the atmosphere.

281 3.3 Comparison of SEC-UV and BrC-PILS absorption

282 Online and offline absorption sampling are complimentary. The online sampling by the
283 BrC-PILS provides continuous data with much higher time resolution (reported at 10 s), but it is
284 limited to two measurements: water-soluble absorption as a function of wavelength and water-
285 soluble organic carbon concentration. In contrast, offline samples can be examined using SEC-
286 UV, C₁₈ chromatography, and other analytical techniques that are not feasible onboard an aircraft.
287 During FIREX-AQ, the BrC-PILS measured online water-soluble absorption in the same aqueous
288 flow that was collected for offline sampling. These are the only BrC samples whose absorption
289 was measured online and then subsequently offline during FIREX-AQ. We observe differences
290 between the online and offline samples. First, absorption by the offline SEC-UV at wavelengths
291 greater than 300 nm did not exceed its detection limit. To facilitate comparison of absorption
292 magnitudes, a power law fit was applied to the BrC-PILS absorption between 315–395 nm to
293 extrapolate absorption to 300 nm (Figure 3). The total absorption by the SEC-UV measurements
294 is approximately an order of magnitude greater than the BrC-PILS measurements at 300 nm
295 (Figure 3). To determine if the differences could be attributed to differences in the diode array
296 detector from the SEC-UV analysis and the BrC-PILS spectrometer, a standard solution of 4-
297 nitrocatechol was run on both systems in pure water (without the SEC column in line and bypassing
298 the PILS). At 350 nm, the agreement between the online, offline, and literature measurements of
299 4-nitrocatechol absorption was $\pm 2.1\%$ (Figure S13) (Hinrichs et al., 2016).

300 The comparison between the online and offline work presented here can be compared to
301 previous non-co-located online-offline intercomparison studies. Di Lorenzo et al. (2017) compared
302 offline absorption measurements of filter extracts by SEC-UV to PILS-LWCC online
303 measurements during the Southern Oxidant and Aerosol Study (SOAS). Although the SEC-UV
304 offline samples and online measurements during SOAS were not co-located, a median ratio (SEC-
305 UV offline at 300 nm to PILS-LWCC online at 365 nm) of 0.9 and r^2 of 0.53 (Figure S12). Zeng
306 et al. (2021) also present an online-offline absorption comparison of water-soluble BrC collected
307 on board the NASA DC-8 aircraft during FIREX-AQ. Online absorption measurements by a
308 LWCC and aqueous filter extracts injected onto a LWCC offline showed good agreement at 365
309 nm ($r^2 = 0.84$). The correlation suggested that the filter measurement of BrC is not significantly
310 influenced by possible sampling artifacts associated with absorption of gases or evaporative loss
311 of BrC components associated with filter collection (Zeng et al., 2021).

312 Differences observed in the FIREX-AQ aqueous samples indicate the necessity to
313 investigate a potential explanation for these inconsistencies. Since the online BrC-PILS and offline
314 SEC-UV samples represent the same samples, solubilization differences between aerosol
315 collection methods cannot explain the variability observed between our measurements. Although
316 reasonable agreement between online measurements and offline filter analyses has been
317 demonstrated (Di Lorenzo et al., 2017; Zeng et al., 2021), Resch et al. (2023) indicated that filter
318 extracts that are not refrigerated immediately or extracts that remain refrigerated for an extended
319 storage time are susceptible to compositional changes. For logistical reasons, our aqueous samples
320 were collected into polypropylene tubes in the field and were not immediately subjected to
321 controlled refrigeration or to the SEC-UV analysis. The greater absorption observed by the SEC-
322 UV analysis (Figure 3) could reflect the possible hydrolysis of oligomeric compounds stored in
323 aqueous solution resulting in an increase the intensity of precursor monomers as decomposition
324 products (Resch et al., 2023). We consider this, as well as other potential causes for the differences
325 in the next section.

326 **3.4 Investigating the impact of solvent effects, pH, and storage effects on absorption spectra**

327 The analysis of fresh biomass burning samples by SEC-UV may be affected by mobile
328 phase solvation effects, pH, and sample storage conditions. We analyze and discuss these variables
329 below and make recommendations for SEC-UV analysis. Plausible chemical structures of
330 chromophores responsible for BrC absorption have been identified and consist of conjugated
331 systems functionalized with hydroxyls, amines, nitro, carbonyls, and carboxylic acid groups
332 (Laskin et al., 2015; Hems et al., 2021; Lin et al., 2017; Fleming et al., 2020; Zeng et al., 2020b;
333 Hettiyadura et al., 2021; Marrero-Ortiz et al., 2019; De Haan et al., 2018; Ji et al., 2022). The
334 molecular complexities of BrC species may be susceptible to changes in the absorption spectra
335 depending on the analysis conditions.

336 First, we assess solvation effects due to changes in the mobile phase composition. The PILS
337 solubilizes BrC in pure water for the online measurements to facilitate absorption measurements
338 (Weber et al., 2001). In contrast, the mobile phase used for the offline SEC-UV analysis was a
339 mixture of acetonitrile and DIW with 25 mM ammonium acetate. Chromatographic packing
340 materials are often incompatible with pure water and require a mixture with an organic solvent to
341 elute compounds from the stationary phase or, in SEC separations, to prevent sorption to the
342 stationary phase. For this reason, chromatographic partitioning-based separations occur in

343 aqueous-organic mixtures, where the composition can be deliberately modified to optimize
344 interactions of the target molecules between the stationary phase and mobile phase. In SEC, non-
345 size exclusion interactions between the analyte and stationary phase are dominated by electrostatic
346 and hydrophobic interactions (Hong et al., 2012). If the analyte and stationary phase are identically
347 charged, ion exclusion effects can occur, resulting in an earlier elution time as the analyte is
348 prevented from entering the pores. If the analyte and stationary phase are oppositely charged,
349 adsorption can result, leading to a later elution time. Hydrophobic effects can occur if the analyte
350 interacts with hydrophobic sites of the column matrix (Hong et al., 2012). The purpose of adding
351 ammonium acetate to the mobile phase is to increase the ionic strength of the mobile phase and
352 facilitate ion-pairing, which suppresses electrostatic interactions between the stationary phase and
353 the polar and charged functional groups. The organic solvent used in our mobile phase was
354 acetonitrile, which has been shown to be unreactive towards typical BrC components and has been
355 recommended as an inert solvent for BrC extraction and analysis (Walser et al., 2008; Bateman et
356 al., 2008; Chen et al., 2022). Therefore, we do not expect the mobile phase to chemically alter BrC
357 compounds while effective at mitigating column stationary phase-analyte interactions.

358 While chemical changes caused by our mobile phase are unlikely, it is possible that other
359 solvent effects on absorption could be occurring. Effects of solvent on molecular absorption are
360 well established in the photochemistry literature (Lignell et al., 2014; Mo et al., 2017; Zheng et
361 al., 2018; Lyu et al., 2021; Chen et al., 2022; Dalton et al., 2023). The polarity of the solvent affects
362 the absorption wavelength by changing stabilization of the ground and/or excited states. With a
363 decrease in solvent polarity, (acetonitrile-water is less polar relative to pure water), this can lead
364 to a decrease in stabilization of the ground state of BrC compounds (such as 4-nitrocathol), but
365 this effect is molecule-dependent. The impact of solvation on red and blue spectral shifting will
366 likely be several nanometers, which could contribute to the observed differences in the offline and
367 online absorption measurements. Previous work has shown that acetonitrile could disrupt π - π
368 interactions between BrC molecules, which could cause the liberation of adsorbed low MW BrC
369 chromophores from larger chromophores or disrupt BrC aggregates (Lyu et al., 2021). Smaller,
370 less conjugated systems typically absorb in the ultraviolet-blue wavelength region, and their $\pi \rightarrow$
371 π^* transition red shifts when more conjugated systems are fused together (Gorkowski et al., 2022).
372 Thus, we would expect absorption measurements in the presence of acetonitrile to be blue-shifted
373 relative to those in pure water. This represents a possible explanation for greater absorption

374 intensity at lower wavelengths measured in the offline SEC-UV analysis compared to the online
375 analysis.

376 Second, we assess the pH of the sample matrix, which is known to affect the absorption profile
377 of BrC compounds. Multiple studies have investigated the impact of pH on wavelength-dependent
378 absorption. For example, Phillips et al. (2017) directly adjusted the pH of SRFA and biomass-
379 burning derived aqueous extracts (with sodium hydroxide or hydrochloric acid) and observed no
380 measurable shift in the spectra to shorter or longer wavelengths; however they did observe that as
381 the pH increased, there was an increase in the magnitude of absorption, which was more
382 pronounced at higher wavelengths. The pH of the default mobile phase solution was 7.2, while the
383 pH of the deionized water solutions in the PILS was approximately 5 (due to carbon dioxide
384 dissolution). To investigate the impact pH has on BrC absorption, we measured several compounds
385 that have been shown to contribute to BrC absorption (4-nitrocatechol, vanillin, 7-
386 hydroxycoumarin, 4-hydroxy-3-methoxy cinnamaldehyde, and mixture of the four compounds)
387 under different solvent and pH conditions: DIW, DIW with 25 mM ammonium acetate, as well as
388 the mobile phase at pH 5, 7.2, and 9. When the matrix conditions have a pH greater than the pK_a
389 of the compound in question, the species will deprotonate, resulting in a shift to longer wavelengths
390 (Hinrichs et al., 2016). For compounds with a pK_a between 5 and 9 (i.e., 4-nitrocatechol, 7-
391 hydroxycoumarin, vanillin), we observed this phenomenon (Figure S6). To assess the impact of
392 pH and mobile phase on a complex mixture, we also measured the absorption of a SRFA aqueous
393 solution and a FIREX-AQ aqueous sample with the abovementioned mobile phases (Figure 4 and
394 Figure S8). In contrast to the individual BrC compounds, no major changes in the spectral shape
395 were observed under different mobile phase conditions. To confirm these results, we measured the
396 absorption of SRFA in each solvent using a separate spectrophotometer (Figure S7). This suggests
397 that the pK_a of the majority of functional groups in the absorbing compounds present were less
398 than 5 or above 9. Nitroaromatic compounds typically have pK_a values between 5 and 8;
399 suggesting low levels of this class of compounds present in the aqueous samples. This observation
400 is comparable to the online BrC-PILS analysis; for aqueous absorption, Washenfelder et al. (2022)
401 observed the average absorption contribution at 365 nm of 4-nitrocatechol was less than 1.1 % and
402 the summed contribution to absorption by 2-nitrophenol, 4-nitrophenol, 4-nitrocatechol, 4-
403 nitroguaiacol, and 2,4-dinitrophenolate was less than 3.6 %. Since the absorption profile of SRFA
404 and the FIREX-AQ sample appear similar in all mobile phase conditions, we have no evidence

405 that pH of the mobile phase in the SEC separation conditions impacts the wavelength dependent
406 absorption of the FIREX-AQ aqueous samples.

407 Third, we assess the potential effect of storage on the aqueous samples measured by SEC-UV.
408 A recent study by Resch et al. (2023) observed that biomass burning-derived filter extracts stored
409 at temperatures above freezing may undergo compositional changes that can increase in signal for
410 various compounds. Hydrolysis reactions include converting alkenes to alcohols and esters to
411 carboxylic acids, and the breakdown of oligomers. The hydrolysis of oligomers such as dimer
412 esters stored in an aqueous solution can result in an increase in precursor monomers as
413 decomposition products leading to an increase in signal (Zhao et al., 2018; Resch et al., 2023).
414 Further, ammonium and alkylamines have been observed in high levels in biomass burning
415 aerosols (Di Lorenzo et al., 2018); aqueous reactions between dicarbonyls (e.g., glyoxal,
416 methylglyoxal) with ammonium and amines may also contribute to an increase in absorption
417 intensity at pH 4 to 7 (Powelson et al., 2014; Yang et al., 2023). The FIREX-AQ aqueous samples
418 had a pH of 5 and were stored at 4 °C for two years prior to analysis. Assuming they contained
419 dicarbonyl compounds and reduced nitrogenous species, it is possible reactions leading to products
420 that can contribute to greater absorption during storage occurred. To further investigate the impacts
421 of storage on a complex aqueous mixture, we measured the absorption spectra of two SRFA
422 solutions: one freshly made and one stored for one year at 4 °C. We observed an increase in
423 absorption in the aged SRFA solution, in which integrated absorption was 39 % higher than the
424 freshly-made solution. This same effect was also observed with SRHA solutions (Figure S14).
425 Thus, it is possible that processes during storage could have led to increased absorption measured
426 in the offline SEC samples.

427 Among the three processes discussed here, we conclude that the storage of aqueous extracts is
428 the most plausible explanation for the higher absorption observed in the offline samples from
429 FIREX-AQ. If hydrolysis reactions are occurring, we might expect this to impact the MW profile
430 (i.e., SEC elution times). We examined the MW profile of freshly-made and one year-aged SRFA
431 solutions (Figure 4C). The increase in absorption with storage does not measurably affect the
432 molecular size-resolved absorption of the mixtures. The same effect was observed for SRHA
433 (Figure S14). This demonstrates that any storage-induced changes in these complex mixtures of
434 organic molecules have a minimal impact on the molecular weight relative to the wide MW range
435 of the SEC column. The MW of the BrC species would have to change by ~ 100 Da to be noticeable

436 on the MW scale of our separation (250 Da to 75 kDa). Such a drastic change in MW is unlikely
437 the case in most hydrolysis reactions. Thus, our results above in which we broadly categorize MW
438 species to be less than or greater than 500 Da are likely robust. The SEC separation of the aqueous
439 samples signify that low MW (<500 Da) chromophores contribute more to total absorption than
440 higher MW (>500 Da), this finding is supported by previous SEC-UV analyses of BrC aged less
441 than 10 hrs (Di Lorenzo et al., 2017; Lyu et al., 2021). The consistent MW profiles between the
442 freshly-made and stored solutions of SRFA and SRHA reasonably suggest that storage did not
443 have a major impact on the MW of BrC.

444 **4. Conclusions and implications**

445 During FIREX-AQ, instruments onboard the NOAA Twin Otter aircraft sampled smoke
446 plumes from wildfires in the western United States with plume ages of 0 to 5 h. The BrC-PILS
447 measured water-soluble BrC absorption online and collected aerosol in aqueous solution for offline
448 SEC-UV analysis. The aqueous samples were collected during downwind plume transects and the
449 online data was collected continuously during inflight sampling. SEC-UV analysis shows that BrC
450 absorption was dominated by chromophores <500 Da. This finding is consistent with reports of
451 laboratory-generated fresh smoke samples. Integrated absorption at 300 nm from the SEC-UV
452 analysis was used to calculate trends in normalized BrC absorption as a function of plume age.
453 These trends were variable and did not show an exponential decay, which is consistent with
454 recently published results from the FIREX-AQ field campaign that examined normalized BrC
455 absorption trends for plumes over 0 to 10 h. Comparison of the online and offline analyses of the
456 same aqueous extracts reveals discrepancies, specifically higher absorption intensity and
457 absorption at lower wavelengths. These discrepancies between online and offline samples
458 demonstrate the importance of considering the conditions in which the absorption measurements
459 are made. The inconsistencies between the offline SEC-UV analysis and the online measurements
460 are not explained by pH or solvent effects, but may be due to reactions occurring during storage.
461 Although increases in absorption may occur during storage of aqueous solutions, it is less likely
462 to impact the MW of the FIREX-AQ BrC species. This highlights that BrC species are more stable
463 collected on filters rather than in aqueous solution and the importance of inter-comparison
464 absorption measurements by multiple methods.

465

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473 **Data Availability Statement**

474 The data used in the study are publicly available at [https://www-air.larc.nasa.gov/missions/firex-](https://www-air.larc.nasa.gov/missions/firex-aq/)
475 [aq/](https://www-air.larc.nasa.gov/missions/firex-aq/)

476 **Competing Interests**

477 At least one of the (co-)authors is a member of the editorial board of Atmospheric Chemistry and
478 Physics.

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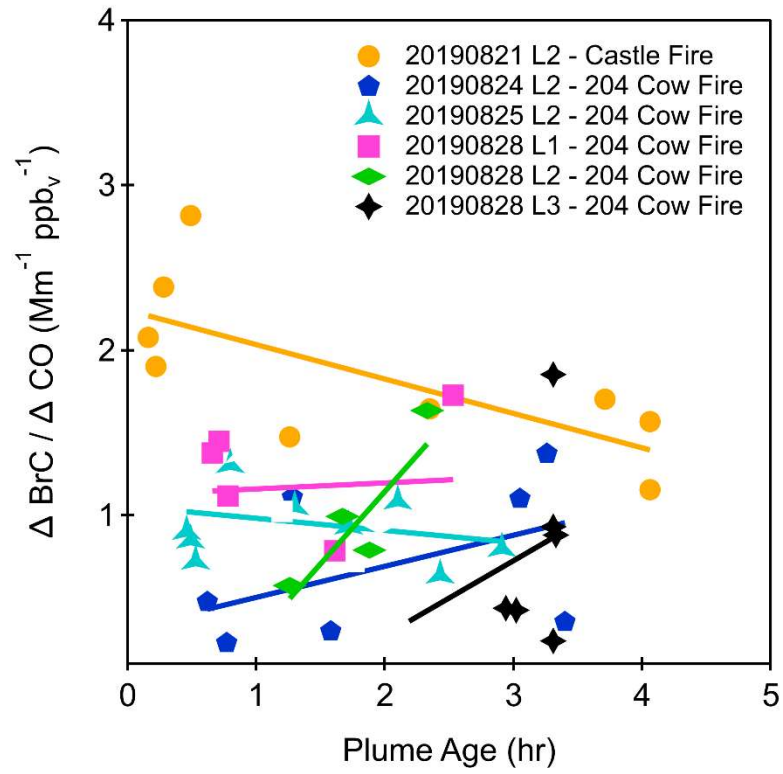
726 **Figure 1.** Ratio of absorption measured by SEC-UV at 300 nm to CO enhancement as a function
727 of plume age for aqueous samples collected for six flights during FIREX-AQ 2019.

728 **Figure 2.** Absorption contribution at 300 nm of high (>500 Da), low (<500 Da), and unidentified
729 molecular weight species for aqueous samples collected during the second flight leg on 21 Aug
730 2019.

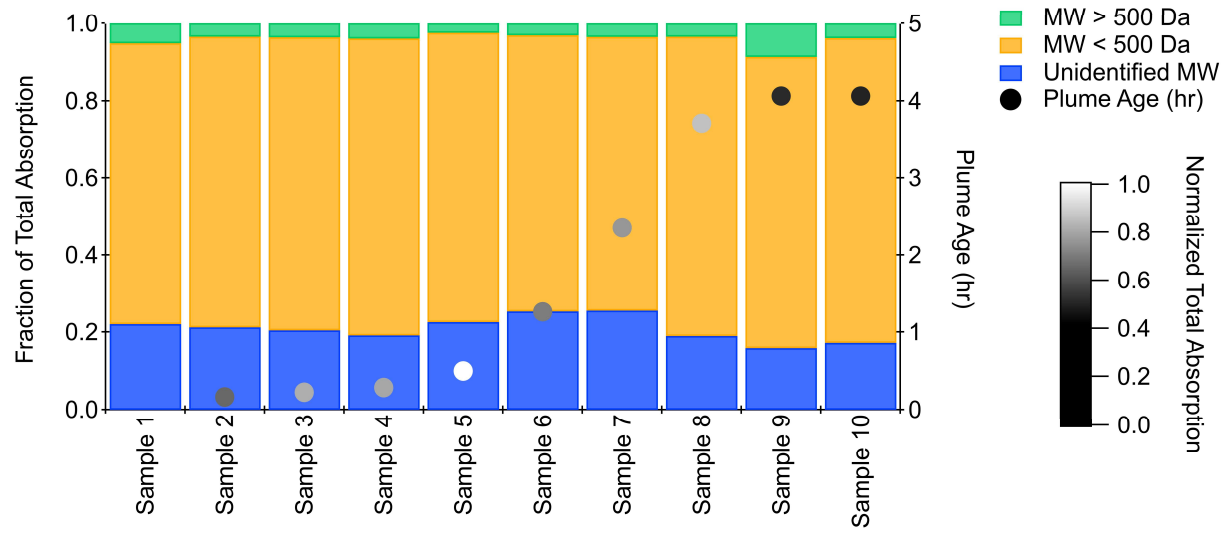
731 **Figure 3.** Total absorption measured offline by the SEC-UV (at 300 nm) compared to the total
732 absorption measured online by the BrC-PILS (extrapolated to 300 nm using a power-law fit). Each
733 colour represents a different flight leg and each marker represents the integrated absorption at 300
734 nm for each aqueous sample measured by SEC-UV. The online BrC-PILS absorption measurement
735 was averaged over the collection time of each aqueous sample. The error bars represent the total
736 uncertainty in the online and offline measurements.

737 **Figure 4.** Absorption as a function of wavelength of (a) SRFA and (b) a FIREX-AQ aqueous
738 sample collected on 28 Aug 2019 L3 with varying mobile phases. (c) Molecular weight profile of
739 a freshly-made 15 $\mu\text{g}/\text{mL}$ SRFA solution and the same solution one year later. The shaded region
740 represents the coefficient of variation for absorption at each wavelength using $n = 3$ DIW.

Figure 1.

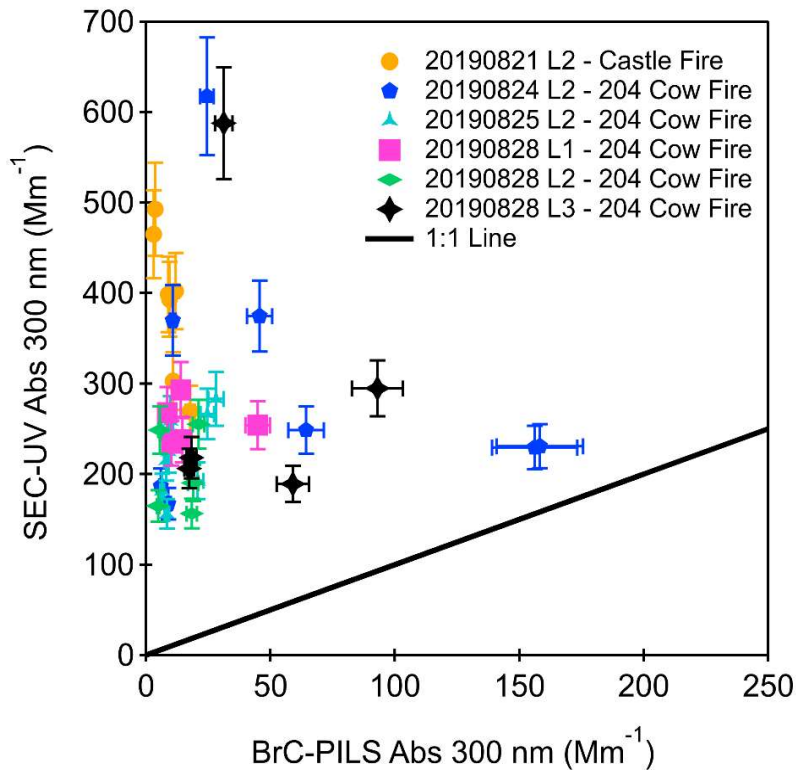


741 **Figure 2.**



742

743 **Figure 3.**



744

Figure 4.

