

Reviewer #1

We would like to thank the Reviewers for their constructive feedback. The reviewer comments are reproduced below in black, and our responses are provided below each comment in blue. We will also be uploading a track-changed version of the manuscript along with all responses as required by ACP.

Major comments:

With regards to calculating aging times: The authors integrated over the spectral flux for the two types of lights and normalized this to the spectral flux of the sun. However, shining light onto a particle collected onto a filter is different than shining a light on an aerosol particle. The filter will absorb and reflect light back through the collected particle, which will alter the amount of radiation the particles experiences compared to aerosol particles up to double the amount of radiation. Do the authors know how the filter will alter calculated photochemical lifetimes?

This is an excellent point, which we neglected to explain in this paper. Presser et al. (2014) measures the absorption enhancement due to scattering by different kinds of filters coated with nigrosine dye. They found that the absorption enhancement was highest for the Teflon filters, and was highly dependent upon the mass loading and temperature, and perhaps even pore size. This is an additional source of error in our lifetimes since we are not able to quantify the absorption enhancement specifically for our filters. We now clarify in the paper that these lifetimes of BrC absorption and chromophores are lower limits. It is now mentioned three times in the paper, once in the Experimental section and twice in the Results and Discussion section (Pages 9, 12, 13).

Page 12, line 366: The authors comment how the same chromophore exhibited different lifetimes between fuels. Judging from figure 5, the range of lifetimes is within a factor of 2-3 (0.4-1.2 days). The authors provide several reasonable explanations on why the wide range of lifetimes for the same chromophore (or compounds that elute at the same time). However, the authors in the previous paragraph note that brown carbon chromophores from chamise burns have shorter lifetimes than lodgepole pine burns. Can the authors comment on the uncertainty range for these lifetimes as it seems like the variation for just one chromophore is enough to explain and differences in specific chromophore lifetimes observed between fuels.

This comment must have been triggered by our lack of error bars in the initial submission. We have added error bars for the lifetimes provided in the paper (Figure 5 and Table 4). Error bars were calculated from the standard error of the linear trendline's slope, which is the first order rate constant. This error only accounts for the uncertainty in describing the measurements with the model. There are uncertainties in the measurement method that cannot necessarily be quantified, such as differences in extraction efficiency between photolyzed and unphotolyzed parts of the same filter and the final concentration volume of HPLC/PDA/HRMS samples.

Minor comments:

Page 2, line 47: "Wildfires continue to. . ." This sentence semi-repeats previously stated information.

We agree that the sentence is somewhat repetitive and disrupts the flow of the paragraph. It was deleted.

Page 2, line 59: "large effect on radiative forcing" In which direction?

It is now clarified in the paper with “positive.”

Page 2, line 65: “broader range” broader range than what?

We mean broad range in terms of the diversity of molecules and combustion sources which can produce different molecules. We hope it is clearer now.

Page 4, line 123: “irradiated BBOA water extracts. . .” The phrasing of these sentences a bit confusing as it seems like the solution just randomly lost WSOC.

Thank you, we clarified that this is in response to irradiation of the extract.

Page 4, line 126: “produced from Alaskan peat” produced from burning Alaskan peat

Clarified.

Page 5, line 138: the semi colon is not used properly

We replaced the semicolon with a comma in the revised sentence.

Page 6, line 173: How long were the filters stored for before analysis? If it was a long time (months later), do the authors know/guess how these chromophores degraded with time?

In the revised manuscript, we added that the BrC chromophore analysis was done no more than 2 months later. Since the samples were always frozen, we do not expect BrC chromophores to decay on this timescale (although no one has ever verified the chemistry occurring on frozen filters!). The partitioning of semi-volatile components may be different from the fresh emissions, but we are not as concerned with comprehensive particle composition in this paper.

Page 9, line 252: For the structures of compounds given in Table 1, did the authors run standards to try to better confirm the identities/structures of the reported compounds? By reference spectrum, do the authors mean spectra from running standard compounds?

“Reference” was corrected to “standard.” Standards were run for select compounds based on availability. The caption in Table 1 was clarified to show that the standard spectrum is in blue.

Page 14 line 418: Please provide another sentence or phrase explaining why photodegradation occurs more rapidly in solution.

The sentence has been added to and now reads:

“However, in Lin et al. (2016) BBOA was extracted and irradiated in solution where photodegradation could occur more rapidly due to molecular diffusion (Lignell et al., 2014).”

Page 14 line 419: no comma after campaign

Done.

Page 14, line 420: What does AAE stand for?

Thanks. This was corrected.

Figure 1 and 2: Since there are not too many lines, please make the lines distinguishable for black and white printers.

Thanks for the suggestion. With four traces, the authors prefer colors rather than using dash/grayscale color variations.

Figure 2: Maybe label on the graph the two compounds.

Thanks, we took your suggestion.

Figure 3 and 4: There appears to be a bracket-shaped line border around these figures. Can this be removed? Also, caption says photolysis but which type of photolysis?

These lines seem to appear in PDF conversion. We will work with the publisher to edit them out from the final version. Thanks, we have clarified that this is 300 nm photolysis.

Figure 5: Along with the comment from before, it would be useful to have uncertainty bars on this figure so the reader knows what constitutes a pattern or not.

Please see the above comment. In short, we did add uncertainty bars.

Table 1: Why do the peak # stop after 43?

Thanks, this was corrected.

Table 3: What does "Figured used" column mean? Is this important information?

The title of the column is now "Sample used in figure #" and it was moved to the SI (now Table S2).

Table 4: The caption says irradiation was done for condensed phase, filter, and all samples. This is confusing as the columns only reference condensed phase. Overall, the column headings are confusing. Should average not be capitalized? And averaged?

The column headings were simplified/changed to "BrC absorption lifetime averaged LA (equivalent days)."

Supporting Information:

Figure S1: Please make this graph more readable. Which equation goes to which line? Which lines describes which points? There appears to be only two data points on the condensed phase line (not counting 0,0). Why were more points not taken? Seems like 0,0 is dominating the trend line which makes the measured points seem very off. Also please add in the text that this method was used for both types of aging experiments (specific chromophores and overall BrC) unless this is not the case.

The trend lines are very similar, and we agree it is difficult to tell which is which, although the R^2 is a good indicator that it's the solution phase measurement (since there's only two points). We agree that more points should have been taken to be more confident in the trend. However, it is important that the trend line go through 0,0 and it is important to keep in mind that the photolysis will likely not follow a first order decay process perfectly, and some variation is expected.

The following is said in the text (SI p3). We have also clarified the title of the section in the SI to "Calculation of the estimated BrC absorption lifetime and individual BrC chromophore lifetime"

"This procedure is used for individual chromophores as well as overall BrC absorbance."

Relating to the previous comment, there seems to be pretty high uncertainty in estimating lifetimes as this Figure S1 shows 1-2 data points and a linear regression. Please add a significant discussion on uncertainty bounds.

Please see the above comment about added error bars.

Is condensed phase filter-based? In the main text (page8 line 239), you refer to both filter-based and condensed phase. Could you please clarify which term refers to what?

We now explicitly state “filter-based” when contrasted with “solution phase” absorption spectroscopy measurements. Condensed phase is still used in the paper, but only used to describe the particulate matter photolysis.

Reviewer #2

We would like to thank the Reviewers for their constructive feedback. The reviewer comments are reproduced below in black, and our responses are provided below each comment in blue. We will also be uploading a track-changed version of the manuscript along with all responses as required by ACP.

1) The extraction procedure in the first paragraph of section 2.2 requires further elaboration. What is the rationale behind using the 3 organic solvents in these proportions? Is that based on an already established protocol? Have you verified that none of the BrC precipitates out of the water+DMSO mixture after evaporating the organic solvents? Why are there different extraction protocols for the fresh (water+DMSO) and photolyzed (only DMSO) particles?

An earlier publication (below) established that this organic solvent mixture resulted in the highest light absorption over the near UV and visible range, presumably due to a higher extraction efficiency. This is represented in Figure 1 of the paper. This paper is now cited.

Lin, P., Bluvshstein, N., Rudich, Y., Nizkorodov, S., Laskin, J., & Laskin, A. (2017). Molecular Chemistry of Atmospheric Brown Carbon Inferred from a Nationwide Biomass-Burning Event. *Environmental Science & Technology*, 51(20), 11561–11570. <https://doi.org/10.1021/acs.est.7b02276>

By visual inspection, there is not any precipitate from the water/DMSO mixture. However, there could be small, insoluble particles in the solution which we have not been able to see scattering from since the volume is very small (150 microliters). This is now clarified in the paper on page 6.

For the extracts of photolyzed extracts, the volume is much smaller at 30 microliters, and because many of the chromophores seem to dissolve better in DMSO than water, we simplified it by just adding DMSO. This does not affect the chromatography or the quality or the photodiode array spectra.

2) Line 235: Along the same lines, why is the extraction procedure for UV-vis different from HPLC/PDA/HRMS?

The extraction solvent mixture was altered depending on their advantages and disadvantages for the application: HPLC/PDA/HRMS or UV-Vis spectroscopy. Dichloromethane was avoided in the overall BrC photolysis experiments (UV-Vis experiments) and methanol was used instead. Dichloromethane absorbs strongly at <240 nm, and could interfere in the measurement of BrC absorption at near-UV wavelengths. In addition, from a safety standpoint, DCM is not a convenient solvent for absorption spectroscopy since it needs to be used in the hood due to its high volatility. Regardless of the solvent mixture used, it is impossible to extract all the material from filter with any solvent combination, and this is why the transmission spectroscopy measurements of the entire filter were done. The decay of absorption of visible wavelengths was consistent across both measurements (solution versus filter).

We now have explained the origins of the extraction protocol on page 6. An additional sentence on page 8 discusses why methanol was used in place of DCM.

3) The binning of the chromophores into Major, Intermediate, and Weak is informative, but can be confusing. I think it is helpful to stress that these categories involve the combined effects of abundance and absorption efficiency. For instance, an abundant chromophore with moderate

absorption efficiency can exist in the same bin as a less abundant chromophore with high absorption efficiency.

This is a good point. Our approach in this paper is to emphasize the observed contribution to the overall absorption by individual chromophores (rather than their relative concentration). Species such as nodakenetin ($C_{14}H_{14}O_4$) are a major contributor to the observed absorption for many of the fires. However we have not run standards to ascertain the emission factor for each compound and cannot determine the relative abundances of any of these compounds. This was the focus of Jen et al., 2018, which quantified the emission of particle phase compounds from the same fires, publishing the % contribution from each of the compound classes. To emphasize this point, we added the following sentence on page 9.

“Abundance and absorption cross section of BrC chromophores both factor into their assigned absorbance bin, as absorbance was not mass normalized with standards. It is possible that the chromophores labelled as “M” are present in small concentrations but have large absorption coefficient.”

4) In addition to integrating the DPA signal over 300nm – 700 nm, can the authors also report wavelength-dependent information? Are there significant differences in AAE across the different chromophores? If yes, integrating absorption over say 4 sections (UV, short visible, mid visible, long visible) can provide interesting information. For example, a chromophore under category W but with say a relatively large AAE might be an I or an M in the UV range.

In general, BrC chromophores in this study are most absorbing in the UV and near UV, with some extending their absorption into the visible. While many have features in the near UV and visible with different λ_{max} values, their relative integrated absorbance does not change all that much depending on the wavelength range (200-700 nm versus 300-700 nm), although many chromophores are excluded if only including visible wavelengths (400-700 nm). We have included absorption spectra in Tables 1 and 2 so that readers can check which chromophores are important in certain wavelength ranges (such as the long visible).

Reviewer #3

We would like to thank the Reviewers for their constructive feedback. The reviewer comments are reproduced below in black, and our responses are provided below each comment in blue. We will also be uploading a track-changed version of the manuscript along with all responses as required by ACP.

General comments

The Authors noted a decrease in absorption following photolysis that leveled off. This observation of a longer-lived fraction of BrC is consistent with several measurements in the lab (e.g. Wong et al. (2017)) and real environment (e.g. Forrister et al. (2015) and Di Lorenzo et al. (2017)). The previous work is not effectively reflected in the text of the paper. For example, lines 60-62 suggest that field measurements demonstrate a short lifetime for BrC. While observations of a short-lived fraction have been made, long-lived fractions have also been observed. In addition, the results described leading up to line 406 should be discussed in the context of this literature.

We have added to the introduction that these studies have observed a recalcitrant fraction of BrC, just as we did. This is in two places, on pages 3 and 4.

“However, there is a recalcitrant fraction of BrC that persists even after long aging times. Di Lorenzo et al. 2017 found that the fraction of higher molecular weight chromophores (>500 Da) relative to lower molecular weight chromophores (<500 Da) increased with plume transport time, on the order of hours to days.”

“Size exclusion chromatography showed that low molecular weight BrC chromophores (<400 Da) were quickly formed and photodegraded giving yield to a photoenhancement due to the formation of high molecular weight species (>400 Da). They concluded that this high molecular weight fraction was responsible for long-lived light absorption.”

We have also added a few sentences in the “Results and Discussion” section stating that other papers have observed the change in molecular composition of BrC chromophores, and this is consistent with our results.

“The results of both photolysis experiments is consistent with work by Di Lorenzo et al. (2017) and Wong et al. (2017) which show that during aging, high molecular weight BrC chromophores are formed after lower molecular weight chromophores are photodegraded. The high molecular weight fraction of BrC chromophores persist even at long aging times and are referred to as the recalcitrant fraction. This theory is one explanation for the short lifetimes of low molecular weight BrC compounds, while observing longer overall BrC absorption lifetimes.”

More information should be provided about the solvents chosen for filter extraction. On line 139, the Authors say, “filters were extracted by solvents with a range of polarities”. Only two solvent mixtures were used, and these were used to extract different samples.

This is still the introduction section and the purpose of this paragraph is to show the scope of the study and the main goals/results. We explain the choice of extraction solvents in the experimental section where we think it is more appropriate. See the below comment or details.

A mixture of dichloromethane/acetonitrile/hexanes was used to extract samples prior to HPLC/PDA/HRMS analysis, while a mixture of methanol/acetonitrile/hexane was used to extract

PTFE filters following transmission measurements. A justification should be provided for the choice of each solvent mixture. The impact of the solvent choice on the results described in lines 393-395 should also be discussed.

The extraction solvent mixture was altered depending on their advantages and disadvantages for the application: HPLC/PDA/HRMS or UV-Vis spectroscopy. Dichloromethane was avoided in the overall BrC photolysis experiments (UV-Vis experiments) and methanol was used instead. Dichloromethane absorbs strongly at <240 nm, and could interfere in the measurement of BrC absorption at near-UV wavelengths. In addition, from a safety standpoint, DCM is not a convenient solvent for absorption spectroscopy since it needs to be used in the hood due to its high volatility. Regardless of the solvent mixture used, it is impossible to extract all the material from filter with any solvent combination, and this is why the transmission spectroscopy measurements of the entire filter were done. The decay of absorption of visible wavelengths was consistent across both measurements (solution versus filter).

We now have explained the origins of the extraction protocol on page 6. An additional sentence on page 8 discusses why methanol was used in place of DCM.

Specific comments

Line 70: Typo in polycyclic aromatic hydrocarbons.

Thanks, we corrected this.

Line 122-123: Wong et al. showed not just a decrease in WSOC, but also a decrease in BrC absorption.

Indeed. We have clarified the text, which now reads:

“Wong et al. (2017) found that irradiated BBOA water extracts lost water soluble organic carbon (WSOC) when irradiated with 300-400 nm light. Simultaneously, the absorption coefficients at 365 nm and 400 nm first increased, in the latter case to about $0.035 \text{ m}^2 \text{ g}^{-1}$ after 20 minutes of illumination time, and then decreased to nearly zero in 60 minutes.”

Line 266: Should be “one fewer methoxy ring substituent”.

Done.

Line 318: Saying that PAHs are “stable during atmospheric transport” is an oversimplification. Although they may end up in pristine regions, the conditions that allow them to undergo long range transport are complex. The review from Keyte et al. (2013) and recent work from Zhou et al. (2019), along with other relevant work, should be consulted and discussed in this section.

Thank you. The text has been modified to clarify this point.

“Polycyclic aromatic hydrocarbons (PAHs) are known to be products of incomplete combustion, and they have the potential to be long-lived BrC chromophores despite their reactivity (Keyte et al., 2013). PAHs have been observed in pristine environments, and it has been suggested that this is due to phase separation of particles and slow diffusivity of PAHs to surfaces where they react with atmospheric oxidants (Fernández et al., 2002; Keyte et al., 2013; Macdonald et al., 2000; Sofowote et al., 2011; Zhou et al., 2012, 2019).”

Figure 1: Suggest this figure could be relocated to the SI.

We elected to keep this figure in the main paper for ease of reading since we reference it twice in the Results and Discussion.

Molecular composition and photochemical lifetimes of brown carbon chromophores in biomass burning organic aerosol

Lauren T. Fleming,¹ Peng Lin,^{2,*} James M. Roberts,³ Vanessa Selimovic,⁴ Robert Yokelson,⁴ Julia Laskin,² Alexander Laskin,² Sergey A. Nizkorodov¹

¹Department of Chemistry, University of California, Irvine, Irvine, CA 92697, USA

²Department of Chemistry, Purdue University, West Lafayette, IN 47907, USA

³Chemical Sciences Division, Earth System Research Laboratory, National Oceanic and Atmospheric Administration, Boulder, CO 80305, USA

⁴Department of Chemistry, University of Montana, Missoula, 59812, USA

*Now at California Air Resources Board, El Monte, CA, 91731

Correspondence to: Sergey A. Nizkorodov (nizkorod@uci.edu)

Abstract. To better understand the effects of wildfires on air quality and climate, it is important to assess the occurrence of chromophoric compounds in smoke and characterize their optical properties. This study explores the molecular composition of light-absorbing organic aerosol, or brown carbon (BrC), sampled at the Missoula Fire Sciences laboratory as a part of the FIREX Fall 2016 lab intensive. Twelve biomass fuels from different plant types were tested, including gymnosperm (coniferous) and angiosperm (flowering) plants, and different ecosystem components such as duff, litter, and canopy. Emitted particles were collected onto Teflon filters and analyzed offline using high performance liquid chromatography/photodiode array/ high resolution mass spectrometry (HPLC/PDA/HRMS). Separated BrC chromophores were classified by their retention times, absorption spectra, integrated PDA absorbance in the near-UV and visible spectral range (300-700 nm), and chemical formulas from the accurate m/z measurements. BrC chromophores were grouped into the following classes and subclasses: lignin-derived, which includes lignin pyrolysis products; distillation products, which include coumarins and flavonoids; nitroaromatics; and polycyclic aromatic hydrocarbons (PAHs). The observed classes/subclasses were common across most fuel types, although specific BrC chromophores varied based on plant type (gymnosperm or angiosperm) and ecosystem component(s) burned. To study the stability of the observed BrC compounds with respect to photodegradation, biomass burning organic aerosol (BBOA) particle samples were irradiated directly on filters with near UV (300-400 nm) radiation, followed by extraction and the HPLC/PDA/HRMS analysis. Lifetimes of individual BrC chromophores depended on the fuel type and the corresponding combustion conditions, but lignin-derived and flavonoid classes of BrC generally had the longest lifetimes with respect to UV photodegradation. Moreover, lifetimes for the same type of BrC chromophores varied depending on biomass fuel and combustion conditions. While individual BrC chromophores disappeared on a timescale of several days, the overall light absorption by the sample persisted longer, presumably because the photolysis processes converted one set of chromophores into another without complete photobleaching, or from undetected BrC

35 chromophores that photobleached more slowly. To model the effect of BrC on climate, it is important to understand the
change in the absorption coefficient with time. We measured the equivalent atmospheric lifetimes of the overall BrC
absorption coefficient which ranged from 10 to 41 days, with subalpine fir having the shortest lifetime, and conifer canopies
| [i.e. juniper](#) having the longest. BrC emitted from biomass fuel loads encompassing multiple ecosystem components (litter,
shrub, canopy) had absorption lifetimes on the lower end of the range. These results indicate that photobleaching by
40 atmospheric photolysis is relatively slow. Other chemical aging mechanisms, such as heterogeneous oxidation by OH, may
be more important for BrC degradation than photolysis for predicting the decay of BBOA BrC absorption in models.

1 Introduction

Forests have naturally occurring wildfire cycles that maintain the forest ecosystem, but global climate change is altering the
45 cycles with unpredictable consequences (Shvidenko and Schepaschenko, 2013; Weber and Stocks, 1998). In addition to the
impacts of wildfires on ecosystems, biomass burning plumes have pronounced effects on atmospheric chemistry and climate.
| ~~Wildfires continue to increase in frequency and intensity worldwide with climate change~~ (Boulanger et al., 2014; Moriondo
et al., 2006; Shvidenko and Schepaschenko, 2013; Wotton et al., 2010; Wotton and Flannigan, 1993). Wildfire plumes
contain a complex mixture of greenhouse gases (carbon dioxide and methane), multiple non-methane organic compounds
50 (NMOCs), and carbonaceous and ash particles. The effects arising from biomass burning organic aerosol (BBOA) particles
are not well understood because BBOA composition and optical properties may depend on many factors, such as the type of
fuel burned and combustion conditions (Chen and Bond, 2010; Jen et al., 2019; Kirchstetter et al., 2004), wind speed,
heading or backing fires (Surawski et al., 2015), and fuel moisture content (Tihay-Felicelli et al., 2017). Global climate
models are starting to include contributions from light-absorbing organic carbon, termed brown carbon (BrC), because
55 treating BBOA particles as purely scattering leads to incorrect predictions of climate forcing (Bond et al., 2011; Laskin et al.,
2015; Ma et al., 2012). One of the first studies incorporating BrC into models was by Feng et al. (2013), which found that in
areas where primary BrC emissions are high, the absorbing component of BBOA particles can dominate over the scattering
component, switching net radiative forcing by organic aerosols from negative (cooling) to positive (warming) at the top of
the atmosphere. Other modeling studies have demonstrated that BrC can have large [positive](#) effects on the radiative forcing
60 (Bahadur et al., 2012; Chung et al., 2012; Laskin et al., 2015; Ramanathan et al., 2007). However, field measurements to
date indicate that BrC has a short lifetime of ~10 hours, which would considerably reduce its impact if included in models
(Forrister et al., 2015; Selimovic et al., 2019). Light-absorption by BrC can also result in a significant decrease in the
photolysis rates of photochemically active gases, such as HONO and nitrogen dioxide, which affect the mixing ratios of
ozone and hydroxyl radicals (Jiang et al., 2012; Li et al., 2011). To better quantify their effect on climate, [the chemical
65 composition and lifetimes of BrC as well as; their](#) light absorption properties [should be studied.](#) ~~and chemical composition~~

~~of a broader range~~ Further, for a comprehensive understanding, we should consider the diversity of ~~of~~ BrC, spanning nonpolar to polar molecules, and BBOA particles from a range of sources~~should be studied~~.

70 Previous studies have identified important classes of BBOA chemical components that are responsible for light absorption. A major class includes lignin-pyrolysis products, which are typically substituted aromatics with a high degree of unsaturation, such as coniferaldehyde (Budisulistiorini et al., 2017; Fleming et al., 2018; Simoneit et al., 1993). Another class is nitroaromatics, such as nitrocatechols, which are readily produced in the presence of NO_x and absorb strongly with a λ_{max} around 340 nm (Iinuma et al., 2010; Lin et al., 2017). ~~Polyaromatic~~ Polycyclic aromatic compounds (PAHs) have long been known to be emitted from incomplete combustion processes, and large PAHs can be significantly light-absorbing at the near-UV and visible wavelengths (Simoneit, 2002). Budisulistiorini et al. (2017) observed sulfur-containing species from fern and peat pyrolysis, and suggested that they are formed via acid-catalyzed heterogeneous reactions. Tar balls are largely externally-mixed spheres or spherical aggregates produced from smoldering combustion or through multi-phase secondary chemistry (Sedlacek III et al., 2018; Tóth et al., 2014). In terms of their chemical composition, tar balls are thought to be comprised primarily of oxygenated organic compounds, similar to that of BBOA particles (Chakrabarty et al., 2010; Giroto et al., 2018; Li et al., 2019; Pósfai et al., 2004; Sedlacek III et al., 2018).

80 BrC components undergo photochemical transformations during atmospheric transport, including photobleaching or photoenhancement of their absorption coefficients. For example, the field studies of Forrister et al. (2015) and Selimovic et al. (2019) observed a substantial decay in aerosol UV light absorption in biomass burning plumes corresponding to a half-life of 9 to 15 hours. Similarly, Lin et al. (2017) reported rapid evolution of both the BBOA composition and optical properties during a nationwide biomass burning event in Israel. However, there is a recalcitrant fraction of BrC that persists even after long aging times. (Di Lorenzo et al., 2017) found that the fraction of higher molecular weight chromophores (>500 Da) relative to lower molecular weight chromophores (<500 Da) increased with plume transport time, on the order of hours to days. These changes in BBOA properties are supported by laboratory studies of photochemical aging of BBOA particles or relevant surrogates via heterogeneous photooxidation (exposure of particles to gaseous OH), aqueous photooxidation (exposure of BBOA compounds to OH within cloud/fog water droplets), direct photolysis (exposure of particles or their aqueous extracts to actinic UV radiation), and indirect photolysis (photosensitized reactions between BBOA molecules and electronically-excited triplet states of photosensitizers). Several studies have characterized changes in the UV-Vis spectra of nitrophenols, common in BBOA particles, as they are exposed to UV radiation. For example, Hinks et al. (2016) irradiated 2,4-dinitrophenol incorporated in limonene secondary organic aerosol material and observed the absorbance decrease in the range of 250-320 nm, while the absorbance from 400-450 nm increased. Similarly, Zhao et al. (2015) observed a photoenhancement at 420 nm for a 4-nitrocatechol aqueous solution in response to direct photolysis. During photooxidation with OH (produced by an intentional addition of hydrogen peroxide to the photolyzed solution), photoenhancement at 420 nm was observed initially, but the solution photobleached within an hour. In Hems and Abbatt (2018), aqueous solutions of nitrophenols and hydrogen peroxide were irradiated, atomized, and then analyzed by an aerosol-CIMS. This study attributed

the photoenhancement at 420 nm to the functionalization of nitrophenols, followed by their photodegradation at 420 nm as was evidenced by fragmentation of functionalized nitrophenols. Lignin pyrolysis products and other lignin-derived molecules have been shown to be oxidized into light-absorbing compounds under certain conditions. For example, Gelencsér et al. (2003) observed an increase in absorption at visible wavelengths during the photooxidation of single component aromatic hydroxyl acids in aqueous solutions. Chang and Thompson (2010) and Tang and Thompson (2012) observed production of light absorbing compounds during aqueous reactions of OH with multiple phenolic compounds. Smith et al. (2016) found that triplet-excited molecules can react with phenolic compounds in cloud water mimics producing BrC chromophoric products. In Kaur et al. (2019), five model BBOA model compounds were irradiated and hydroxyl radicals, singlet molecular oxygen, and triplet excited state molecules were detected with probe molecules. They found that all model compounds decayed on the order of hours from indirect photooxidation. There are many studies that have investigated the photodegradation of PAHs on ice surfaces, ocean water mimics, and soil (Smol and Włodarczyk-Makula, 2017). The degradation of the three-ring PAH phenanthrene had a half-life of 13 to 23 hours depending on the solvent it was dissolved in (Shankar et al., 2019). Using infrared spectroscopy they observed the emergence of carboxylic acid, aldehyde, and ketone functionalities during photolysis. Miller and Olejnik, 2001 irradiated aqueous solutions of PAH mixtures with UVC lamps. They found that the photodegradation of benzo[a]pyrene and chrysene proceeds more rapidly at acidic pH values and proposed a mechanism based on their findings (Miller and Olejnik, 2001).

The photochemical aging of actual mixtures of BBOA compounds, not just surrogates, was also reported in the literature. For example, Tomaz et al. (2018) found that aqueous BBOA mixtures from the 2016 FIREX lab intensive decayed rapidly, with most having lifetimes due to aqueous OH oxidation mimicking clouds of a half a day or less. The decay of compounds such as catechol, benzoic acid, and methylfurfural lead to the formation of oxalate, which made up 13-16% of total dissolved organic carbon after 150 hours. Saleh et al. (2013) burned pocosin pine and oak, and diluted smoke was irradiated with UV lights in a smog chamber. Aerosol optical properties were monitored with an aethalometer at seven wavelengths. They found that aged emissions were more absorbing than fresh emissions at 370 and 470 nm after one hour. Zhong and Jang, (2014) tracked the absorption coefficients of BBOA during solar exposure in a smog chamber, and observed an increase of 11-54% in the integrated mass absorption cross section (280-600 nm) in the first half of the day followed by decrease in the afternoon. In Lin et al. (2016), BBOA particles collected from ponderosa pine and Indonesian peat burns were dissolved in a 50% by volume water/acetonitrile solvent and irradiated with actinic wavelengths. They found that regardless of the fuel type the half-life of the absorbance at 300 nm was roughly 16 hours under sunlight for soluble BBOA particles. Wong et al. (2017) found that irradiated BBOA water extracts lost water soluble organic carbon (WSOC) [when irradiated with 300-400 nm light](#). Simultaneously, the absorption coefficients at 365 nm and 400 nm first increased, in the latter case to about 0.035 m² g⁻¹ after 20 minutes of illumination time, and then decreased to nearly zero in 60 minutes. [Size exclusion chromatography showed that low molecular weight BrC chromophores \(<400 Da\) were quickly formed and photodegraded giving yield to a photoenhancement due to the formation of high molecular weight species \(>400 Da\). They concluded that this high](#)

[molecular weight fraction was responsible for long-lived light absorption](#). In Sumlin et al. (2017), BBOA particles produced from [burning](#) Alaskan peat were aged by reactions with OH in an oxidation flow reactor (OFR), and light absorption coefficients of aged and unaged BBOA particles were measured by an integrated photoacoustic nephelometer. They found that the mass absorption coefficient at 375 nm decreased roughly 45% after an equivalent of 4.5 days of photochemical aging.

To summarize the brief literature survey above, much work has been done in terms of characterizing optical properties of photochemically aged BBOA particles and surrogates, but a consensus on what drives the photobleaching and photoenhancement of chromophores in BBOA and the relative importance of these processes on atmospherically relevant time scales has not been reached. This study aims to better understand the molecular composition of BrC for different fuel types and combustion conditions as it may be essential to understanding the optical properties of BBOA and predicting their evolution during photochemical aging.

This study explored the diversity in the molecular composition of BrC chromophores found in BBOA samples generated by burning forest fire fuels, and examined how the chemical composition and optical properties change during UV irradiation of BrC materials in the absence of gas-phase oxidants. BBOA samples from twelve biomass fuels collected from around the United States, encompassing both gymnosperm and angiosperm plant types and different parts of the ecosystem, including duff, litter, and canopy were examined. Samples collected on filters were extracted by solvents with a range of polarities and analyzed by high performance liquid chromatography coupled to a photodiode array and high resolution mass spectrometer (HPLC/PDA/HRMS) to target BrC chromophores. To investigate whether the BrC chromophores are photolabile or photostable, BBOA particles samples were directly irradiated on filter substrates before analysis by HPLC/PDA/HRMS or UV-Vis spectrometry. We estimated their photolysis lifetimes in BBOA particles by measuring the time resolved absorbance of individual chromophores. We found that the equivalent atmospheric lifetime due to photolysis of individual chromophores ranged from 0.4-1.6 days, which is a relevant timescale for long-range atmospheric transport. BrC chromophores could survive the exposure to UV radiation on different timescales, depending on their molecular structure or their interactions with neighboring molecules dictated by BBOA type. However, the overall absorption by BrC (integrated over 300-700 nm) persisted longer due to direct photolysis, with lifetimes ranging from 10-41 days, because some photolysis products of the original BrC are also light-absorbing. The equivalent atmospheric photolysis lifetimes of BrC absorption are long compared to typical lifetimes for heterogeneous oxidation of BBOA particles by OH. For climate modeling applications these results suggest that chemical aging mechanisms other than photolysis may play a more significant role in the evolution of BrC properties.

2 Experimental methods

2.1 Sample collection and information

BBOA particle samples were collected at the FIREX Fall 2016 lab intensive at the Missoula Fire Lab (<https://www.esrl.noaa.gov/csd/projects/firex/firelab/>). One of the BBOA samples used in this study was from a “stack” burn and the other samples were from “room” burns. Selimovic et al. (2018) explains room and stack burns and fuels in detail. Briefly, the combustion of forest fire fuels lasted 5-20 minutes and during stack burns emissions were collected from a constant, diluted flow of entrained emissions by way of the stack. In room burns, the smoke from the fire was allowed to mix in the room during sample collection, and BBOA was collected during both the burn and mixing periods. Smoke was purged from the room by clean air in between burns. Fuels were collected from different US regions and brought to the Missoula Fire Lab for test burns. This manuscript focuses on twelve fires covering gymnosperm or conifers, including ponderosa pine (*Pinus ponderosa*), lodgepole pine (*Pinus contorta*), Engelmann spruce (*Picea engelmannii*), Douglas fir (*Pseudotsuga menziesii*), juniper (*Juniperus*), longleaf pine (*Pinus palustris*), rotten log, and subalpine fir (*Abies lasiocarpa*). Angiosperm forest fire fuels included Montana sagebrush and two types of chaparral, manzanita (*Arctostaphylos*) and chamise (*Adenostoma fasciculatum*). In some test burns, a representative “ecosystem” mix of biomass was used, including canopy, duff, litter, herbaceous, and shrub components. In other test burns, single biomass components of the ecosystem were used. Information for each fire is provided in Table S1.

Copper tubing with a PM_{2.5} cyclone inlet was placed in the combustion room while the pump and filter were located in an adjacent room. The pump was operating at a flow of 16.7 L/min with the aid of a critical orifice, and BBOA particle samples were collected on PTFE filter substrates (FGLP04700, Millipore, 47 mm diameter, 0.2 μm pore size) during both of the combustion and smoke mixing stages of the room burns. Loaded filters were stored at -18°C until they were analyzed [for BrC chromophores no more than 2 months after sampling](#). The room burn protocols allowed for long collection times and therefore higher aerosol mass loading, which is desirable for the analysis described below.

2.2 HPLC/PDA/HRMS

The molecular identity and relative abundance of BrC chromophores were determined using the High Performance Liquid Chromatography/Photodiode Array/High Resolution Mass Spectrometry (HPLC/PDA/HRMS) platform (Fleming et al., 2018; Lin et al., 2018). Segments of the filter were extracted into a mixture of organic solvents composed of 2.0 mL dichloromethane, 2.0 mL acetonitrile, and 1.0 mL of hexanes, [which was shown to optimize the extraction efficiency](#) (Lin et al., 2017). The extraction occurred overnight on a platform shaker. Extracts were filtered with PVDF syringe filters (Millipore, Duropore, 13 mm, 0.22 μm) to remove undissolved suspended particles. Water (50 μL) and DMSO (100 μL) were added to the extracts, which were then concentrated under a flow of N₂ until the volume was reduced to roughly 150 μL, which signified that the extracting solvent evaporated and (mostly) water and DMSO remained in the solution. For photolyzed BBOA particles, DMSO (30 μL) was exclusively added to the extract, and evaporated to a volume of 30 μL. [The extracted material did not precipitate out of solution.](#)

The HPLC utilized a reverse-phase column (Luna C18, 2 × 150 mm, 5 μm particles, 100 Å pores, Phenomenex, Inc.). The injection volume was 5.0 μL for unphotolyzed or 10 μL for extractions of post-photolysis samples, with the latter providing more analyte mass since only a quarter of the filter was used in photolysis experiments. The mobile phase consisted of 0.05 % formic acid in LC–MS grade water (A) and LC–MS grade acetonitrile (B). Gradient elution was performed with the A–B mixture at a flow rate of 200 μL min⁻¹: 0–3 min hold at 90 % A, 3–62 min linear gradient to 10 % A, 63–75 min hold at 10 % A, 76–89 min linear gradient to 0 % A, 90–100 min hold at 0 % A, then 101–120 min hold at 90 % A. The electrospray ionization (ESI) settings of the Orbitrap HRMS were as follows: 4.0 kV spray potential, 35 units of sheath gas flow, 10 units of auxiliary gas flow, and 8 units of sweep gas flow. The solutions were analyzed in both positive and negative ion ESI-HRMS modes.

The HPLC/PDA/HRMS data were acquired and first analyzed using Xcalibur 2.4 software (Thermo Scientific). Possible exact masses were identified based on the corresponding LC retention time using the open source software toolbox MZmine version 2.23 (<http://mzmine.github.io/>) (Pluskal et al., 2010). Chemical formulas were assigned from exact *m/z* values using the Formula Calculator v1.1. More details about experimental procedures and data processing can be found elsewhere (Lin et al., 2015b, 2016, 2018).

2.3 Condensed-phase photolysis

A quarter of the filter was directly irradiated by either an ultraviolet light-emitting diode (LED, Thorlabs M300L4) or a filtered Xenon arc lamp. The LED was used in experiments aimed at estimating lifetimes of individual chromophores. The LED emission spectrum was centered at 300 nm with a FWHM of 20 nm. This wavelength was chosen because it corresponds to the most energetic UV photons available in the lower troposphere. It is a common practice in photochemical experiments to use narrow band UV sources, as opposed to a broadband simulator, as it limits sample heating and evaporation (Calvert and Pitts, 1966). The LED was fixed half a centimeter away from the filter resulting in an incident power density of 11 mW cm⁻². Irradiation times for these experiments are given in Table S23. After the irradiation step, the photolyzed BBOA particles were extracted and analyzed using HPLC/PDA/HRMS as described in the previous section.

The irradiation time by the LED was converted into an equivalent time under sunlight by calculating the ratio of the 290–350 nm integrated spectral flux of the sun and the 300 nm LED, given in equation 1. This conversion assumes that photochemistry is limited to the < 350 nm range, consistent with the photochemistry of many organic molecules, which exhibit a sharp drop in the photochemical quantum yields at longer wavelengths (Turro et al., 2009). Because the radiation source does not replicate the solar spectrum, the lifetimes calculated from the formula below should be regarded as estimates.

$$\tau_{atm} = \tau_{LED} \times \frac{\int_{290nm}^{350nm} F_{LED}(\lambda) d\lambda}{\int_{290nm}^{350nm} \langle F_{solar}(\lambda) \rangle_{24hr} d\lambda} \quad (1)$$

225 The spectral flux density for the LED and the sun as a function of wavelength is shown in Figure 1. The solar flux density was estimated every hour and averaged over a 24-hour period for Los Angeles, CA (34°N 118°W) on June 20, 2017 from the quick TUV calculator (Madronich et al., 2002), using the following parameters: 300 du overhead ozone column, 0.1 surface albedo (0-1), and ground elevation of 0 km with default outputs for aerosols and clouds. The procedure for calculating the spectral flux density of the LED is described in the supporting information. The maximum possible spectral flux density from the sun was also calculated at a solar zenith angle (SZA) of 0° using the TUV calculator. The equation for calculating the equivalent atmospheric lifetime at an SZA of 0° is the same as equation (1) except that the 24-hour averaged flux density is replaced by the peak flux density at SZA = 0. The SZA=0° comparison represents the lower limit of BrC absorption lifetimes.

235 In a separate series of experiments, filter samples were irradiated by the filtered radiation from a xenon arc lamp to determine the characteristic lifetime for the photobleaching of the overall absorption by BrC molecules. A quarter of a PTFE filter sample was exposed to filtered light emitted from a xenon-arc lamp (Newport 66902). Broadband light was reflected at a 90° angle using a dichroic mirror, then filtered through a 295 nm long-pass filter (Schott WG295), and finally passed through a UV bandpass filter (Schott BG1) ultimately transmitting light in the range of 290-400 nm. The incident overall power density was 196 mW/cm². Particles were irradiated for ~12 hours to 1.8 days; the exact time varied from sample to sample depending on the offline transmission spectra. Transmission spectra were acquired directly from the PTFE filter without any material extraction using a Jasco V-670 absorption spectrometer, with a blank PTFE filter used as a reference. 240 Four to six transmission spectra were collected at each time point as the filter was rotated, to minimize the effect of the filter orientation. The filter was then returned to the photolysis set up for further irradiation. When there was no longer any change in the transmission spectrum due to irradiation, the filter was extracted into an organic solvent mixture of 10 mL methanol, 5.0 mL acetonitrile, and 2.0 mL of hexane in a scintillation vial using a vortex mixer. While dichloromethane would be a better solvent for BBOA material, methanol was used for these experiments, since dichloromethane absorbs at longer wavelengths in the UV (up to 240 nm) and could interfere with the measurement. The solution was then evaporated in order to increase the analyte concentration. For comparison, an un-irradiated quarter of the filter was prepared identically in a separate vial, and solution-phase transmission spectra of both solutions were recorded using a dual beam UV-Vis spectrometer (Shimadzu UV-2450). Sample filter-based and solution phase spectra are shown in Figure S2, with the Y-axis converted to effective base-10 absorbance, A = -log(T), where T is the wavelength-dependent transmittance through the filter or the cuvette. For filter-based transmission spectra, the baseline was manually corrected by assuming the absorbance at 850 nm was 0 for BrC. 245 250

In all photolysis experiments, the integrated absorbance from 300 to 700 nm was calculated and normalized to the un-irradiated absorbance. The decay constants and corresponding lifetimes were calculated as described in Figure S1. The linear regression trend line was constrained to have a y-intercept of zero, since this represents the log of the un-irradiated absorbance normalized to itself. [Error bars were calculated from the standard error of the slope of the linear trend line, the first-order rate constant. It should be noted that lifetimes of BrC absorption and chromophores given in this paper are lower limit estimates since there are uncertainties due to scattering by the Teflon substrate](#) (Presser et al., 2014).

3 Results and Discussion

3.1 BrC Chromophores

Table 1 summarizes BrC chromophores observed in two or more fires or fuel types. The table numbers BrC chromophores by their ascending retention time on the HPLC column, i.e., with smaller, more polar compounds appearing first. Each entry includes the absorption spectrum recorded by the PDA detector, the chemical formula/s corresponding to the detected characteristic masses at that retention time, and a potential structure based on a [spectra acquired from reference standards spectrum](#) or observations in previous studies. All PDA chromatograms were integrated over 300-700 nm and normalized to the maximum integrated absorbance. Chromophores in Table 1 are binned with respect to their normalized PDA absorbance as M-Major (75%-100%), I-Intermediate (25%-75%), or W-Weak (5%-25%). [Abundance and absorption cross section of BrC chromophores both factor into their assigned absorbance bin, as absorbance was not mass normalized with standards. It is possible that the chromophores labelled as “M” are present in small concentrations but have large absorption coefficient.](#) Compounds making up less than 5% of the normalized absorbance are not included in the tables.

Lignin pyrolysis products make up one group of BrC chromophores observed. Lignin is a large, heterogeneous biopolymer that is a significant component of wood, along with cellulose and hemicellulose. Lignin monomer units vary depending on the class of the plant, but generally possess phenolic moieties that are largely preserved during pyrolysis (Simoneit et al., 1993). Sinapaldehyde (8) and coniferaldehyde (9) are known lignin pyrolysis products derived from the corresponding lignin monomer units, sinapyl and coniferyl alcohol, respectively. However, they are detected in varying abundance depending on the lignin monomer units of the plant class. Sinapaldehyde and coniferaldehyde are separated by the column, but elute only 0.3 minutes apart as shown in Figure 2. Sinapaldehyde is a major BrC chromophore for nearly all angiosperm or flowering fuel types, including ceanothus, chamise, and sagebrush, while coniferaldehyde is a major BrC chromophore largely among conifers or soft wood species such as subalpine fir duff, longleaf pine, juniper, and ponderosa pine litter. Coniferaldehyde has one [fewer less](#)-methoxy ring substituent compared to sinapaldehyde, and its PDA intensity is generally anti-correlated to that of sinapaldehyde. In other words, for fuel types with low sinapaldehyde absorbance, we observe coniferaldehyde as a major BrC chromophore and vice versa. This is consistent with the composition of lignin monomers for angiosperms and gymnosperms (Sarkanen and Ludwig, 1971; Simoneit et al., 1993).

Other BrC chromophores cannot be classified as lignin pyrolysis products but are clearly lignin-derived. Vanillic acid (1) elutes at 10.07-10.29 minutes as the first, shared chromophore across multiple fuel types that is notable in terms of absorption. It is observed in three fires as a weak chromophore, including subalpine fir duff, ponderosa pine rotten log, and Engelmann spruce duff. All three fires are dominated by smoldering combustion and have the lowest modified combustion efficiencies (MCEs) of all fires (Table S1). This evidence suggests that vanillic acid is a product of smoldering combustion. Further, it also has the coniferyl moiety observed for softwoods. Salicylic acid (3) is an intermediate absorbing BrC chromophore produced during lodgepole pine burning, and weakly absorbing among other softwoods and duffs. Veratraldehyde (4) is another lignin-derived BrC chromophore, which appears in nearly all BBOA samples of this study, regardless of whether they are gymnosperm or angiosperm fuels.

There are other BrC chromophores with $C_xH_yO_z$ composition that can be explained as distillation products, or the volatilization of molecules originating in plants as secondary metabolites (Agati et al., 2012; Iranshahi et al., 2009). Found in plants, coumarins such as umbelliferone (5) and nodakenetin (13) have been researched because of their positive pharmacological properties (Venugopala et al., 2013). The absorption spectrum for nodakenetin has not been reported, however, the molecule has previously been detected in plant tissues (Lee et al., 2003; Wang et al., 2014), and is a major/intermediate BrC chromophore in smoke from all fuel types except chamise and ceanothus. Another type of distillation product is flavonoids, which give leaves, flowers, and fruits their color protecting the plant from solar UV radiation, and are antioxidants-- guarding the plant from reactive oxygen species (Agati et al., 2012). Flavones and flavonols have the backbone structure of 2-phenyl-1-benzopyran-4-one, and flavonols additionally require a hydroxy substituent on the only available carbon of the pyranone ring. BrC chromophores 11, 14, and 16 could have flavonoid structures based on their chemical formulas. Interestingly, tentatively assigned kaempferol (11) and diosmetin (14) are observed in only conifer species, such as lodgepole pine and longleaf pine. On the other hand, 7-hydroxy-3',4'-dimethoxyflavone (16) is only observed in angiosperm BBOA particles: ceanothus, chamise, and sagebrush. The former two plants appear to be related as they have the order *rosales* in common, which could explain the same flavone detected in both. Coumarins and flavonoids were distillation products observed across fuel types, although the observation of specific BrC chromophores depends on the plant class, angiosperm or gymnosperm.

Nitroaromatics are a strongly-absorbing class of BrC chromophores that are formed from the reaction of aromatics with NO_x in plumes (Harrison et al., 2005). This class of compounds is represented in Table 1 with nitropyrogallol (2), nitrocatechol (6), hydroxynitroguaiacol (7), and methyl nitrocatechol (10). Xie et al. (2019) suggests that chromophore (12) with the chemical formula $C_{11}H_{13}NO_5$ is not a nitroaromatic compound, but rather, a compound containing a different nitrogen-containing functional group, such as a nitrile group. We did not observe this group of chromophores for fires with low NO_x levels, such as duff, as qualitatively indicated by the peak NO level (Table S1). Nitrocatechol and methyl-nitrocatechol are tracers for BBOA emissions formed from the photooxidation of phenol or *m*-cresol, toluene and other aromatic compounds in the presence of NO_x (Iinuma et al., 2010, 2016; Lin et al., 2015a). These chromophores are most prominent in BBOA

particles from chamise and sagebrush burns. Those two fires exhibited the highest NO mixing ratios in the entire study— 3.79 ppmv (82% of total N emissions) and 1.62 ppmv (57% of total N emissions) peak NO values, respectively. Nitropyrogallol (2) has an additional hydroxy group and is likely formed in the same way as nitrocatechol and methyl nitrocatechol, but is more oxidized. A compound with the same formula as nitropyrogallol (2) was observed during the photooxidation of nitrocatechol in the lab (Hems and Abbatt, 2018). This is an intermediate or major BrC chromophore detected in BBOA samples from longleaf pine, manzanita, and ponderosa pine litter fires. Hydroxynitroguaiacol (7) was observed in 10 of the 12 fires, and is most prominent in ponderosa pine log BBOA particles despite this fire having the lowest NO levels. However, it may still form through photooxidation of guaiacol in the presence of NO_x (Hems and Abbatt, 2018). Nitrocatechol and methyl nitrocatechol are often used as biomass burning tracers in aged plumes (Al-Naiema and Stone, 2017; Iinuma et al., 2010; Li et al., 2016). However in addition to these, we observed more oxidized versions of these nitroaromatic species with varying abundance depending on the BrC chromophore and test fire. This suggests that the BBOA markers nitrocatechol and methyl nitrocatechol become more functionalized on relatively short time scales (less than two hours) due to photooxidative aging.

Polycyclic aromatic hydrocarbons (PAHs) are known to be products of incomplete combustion, and they have the potential to be long-lived BrC chromophores despite their reactivity (Keyte et al., 2013). PAHs have been observed in pristine environments, and it has been suggested that this is due to phase separation of particles and slow diffusivity of PAHs to surfaces where they react with atmospheric oxidants (Fernández et al., 2002; Keyte et al., 2013; Macdonald et al., 2000; Sofowote et al., 2011; Zhou et al., 2012, 2019).~~Polycyclic aromatic hydrocarbons (PAHs) are known to be products of incomplete combustion, and they have the potential to be long-lived BrC chromophores. PAHs have been observed in pristine environments, suggesting this class of BrC chromophores is stable during atmospheric transport (Fernández et al., 2002; Keyte et al., 2013; Macdonald et al., 2000; Sofowote et al., 2011; Zhou et al., 2012, 2019).~~ In addition to its climatic effects, PAHs are mutagenic and carcinogenic as their metabolites, diol epoxides, bind to guanidine nucleobases in DNA effectively leading to mutations (Finlayson-Pitts and Pitts, 2000; Moorthy et al., 2015; Wood et al., 1984; Xue and Warshawsky, 2005; Zhou et al., 2017). Various PAHs (17-25, Table 1) were observed in only ceanothus, chamise, and sagebrush BBOA particles. PAHs in Table 1 are detected from positive ion mode ESI, and although positive mode ESI is not optimal for observing PAHs, larger PAHs are detectable by this method (Cha et al., 2018). The same PAHs were previously observed by Lin et al., 2018 for sagebrush using atmospheric pressure photoionization (APPI) coupled with HPLC/PDA/HRMS, which is more sensitive for the detection of non-polar aromatic compounds. In general, individual PAH chromophores are binned as “weak” in Table 1 based on their contribution to optical absorption, but for BBOA sampled from flaming sagebrush and chamise burns, they make up a significant fraction of the overall light-absorption by BrC.

Table 2 presents abundant BrC chromophores observed only in a single type of biomass fuel emissions. It should be noted that compounds making up less than 5% of the normalized PDA absorbance (integrated from 300-700 nm) are not included in the tables. Due to this constraint, chromophores in Table 2 may also be present in other fires, but at very low PDA

350 absorbance values. Despite BrC chromophores in Table 2 being observed significantly for only one fuel type, they belong to the same compound classes as the BrC chromophores in Table 1. For example, a coumarin known as scopoletin (26) was observed from sagebrush BBOA. Previously we discussed these coumarins are possible distillation products, along with flavonoids, which we also observe as a product (40) from the ceanothus fire. These distillation products (26 and 40) are among the most strongly absorbing of the BrC chromophores, characterized as intermediate or “I” in Table 2.

355

3.2 Aging by condensed-phase photolysis

Gymnosperm (lodgepole pine) and angiosperm (ceanothus) BBOA particle samples were selected for the initial condensed-phase photolysis experiments. BBOA filter samples from a lodgepole pine burn were photolyzed for 6 hours by an LED centered around 300 nm (which corresponds to approximately 33 hours of photochemical aging from 24-hour average spectral flux density, see equation 1). BBOA particles from the ceanothus burn were photolyzed by the same LED for 16 hours (equivalent to 88 hours of 24 hour averaged atmospheric sunlight). The burning of gymnosperm (lodgepole pine) and angiosperm (ceanothus) resulted in different distributions of BrC chromophore classes. However the same compound classes, lignin-derived and flavonoid compounds, were photo-resistant in both samples.

360 Most chromophores from the lodgepole pine burn sample experienced complete photobleaching during this exposure, but six of them remained observable, including coniferaldehyde ($C_{10}H_{10}O_3$, 80% decrease), salicylic acid ($C_7H_6O_3$, 70% decrease), veratraldehyde ($C_9H_8O_3$, 90% decrease), flavonoids ($C_{15}H_{10}O_6$ & $C_{16}H_{12}O_6$, both 70% decrease), and nodakenetin ($C_{14}H_{14}O_4$, 90% decrease), as shown in Figure 3. Figure 4 shows five chromophores from the ceanothus burn sample that remain observable under these conditions including sinapaldehyde ($C_{11}H_{12}O_4$, 90% decrease), a lignin-derived chromophore ($C_{18}H_{16}O_6$, 80% decrease), and flavonoids ($C_{16}H_{12}O_5$, $C_{17}H_{14}O_6$, and $C_{17}H_{14}O_5$, all 80% decrease), some of which are observed exclusively in this fire. These comparatively resilient species are aromatic, which helps them be more resistant to photodegradation.

370 Next, we estimate the lifetime of individual BrC chromophores in BBOA particles. For chamise, manzanita, and lodgepole pine fires we measured the integrated PDA intensity over 300-700 nm for resolved BrC chromophores for up to three photolysis time points (listed in Table S23) and before photolysis. The limited number of samples and destructive nature of the chemical analysis only made it possible to do measurements for very few time points. Integrated PDA intensities as a function of irradiation time were fit assuming that the decay was exponential in time. LED lifetimes were then converted to equivalent lifetimes in the atmosphere, calculated from the average spectral flux density over June 20, 2017 in Los Angeles. It should be noted that due to scattering of light by the Teflon filter substrate, which effectively increases the absorption efficiency of particles trapped on the filter, lifetimes in Figure 5 are lower limits (Presser et al., 2014). Regardless of the chromophore identities, BrC chromophores from chamise burns have shorter predicted lifetimes (0.4-0.5 days) than those

380

from manzanita burns (0.5-0.9 days), which in turn have shorter predicted equivalent atmospheric lifetimes due to sunlight exposure than BrC from lodgepole pine burns (1.0-1.6 days), as shown in Figure 5. These lifetimes of BrC chromophores are consistent with atmospheric observations of a rapid evolution in a California wildfire, which showed that the BrC absorbance lifetime at 370 nm was 9-15 hours (Forrister et al., 2015).

385 The same chromophores were found to decay at different rates depending on the fuel/fire type (Figure 5). For example, very different equivalent atmospheric lifetimes due to photolysis were obtained across fuel types for veratraldehyde (#4 in Table 1, C₉H₈O₃), a BrC chromophore common to all three fires. One explanation is that there are multiple chromophores co-eluting at this retention time, and therefore the calculation is an average lifetime for multiple compounds. A more interesting explanation is that the surrounding matrix could affect the rate of photolysis for individual chromophores by several possible mechanisms. First, different matrices could quench the electronic excitation in the chromophores to a different extent. Another possibility is that photodegradation of BrC chromophores could be not direct but rather occurring through condensed-phase photosensitized reactions (Malecha and Nizkorodov, 2017; Monge et al., 2012), in which case the rate of decomposition would depend on concentration of photosensitizers in the samples as well as viscosity of the material (Hinks et al., 2016; Kaur et al., 2019). Lastly, other absorbing species, such as black carbon could be shielding BrC chromophores from irradiation, altering the amount of radiation absorbed by BrC chromophores. Given the different mechanisms, the potential contributions from each are difficult to distinguish in this study. The particle matrix is different for all three BBOA particle samples and could contribute to the very different equivalent atmospheric lifetimes of individual BrC chromophores observed in Figure 5.

We also estimated the decay lifetime for the overall BrC absorption, integrated over 300-700 nm, from different fuel types. In these experiments, BBOA filters were irradiated with a filtered xenon arc lamp, which gave a spectral flux density more similar to the sun, although more intense (Figure 1). The advantage of taking transmission spectra directly through the filters is that it makes it possible to monitor photodegradation of BrC absorption at several irradiation times, which is not possible with the solution-phase spectrophotometry, which irreversibly destroys the filter sample by extraction. The filter transmission spectra indicated that the decay of absorbance was not actually exponential. After a certain irradiation time, the BrC absorbance no longer decreased, as observed for the samples from subalpine fir and longleaf pine burns. For example, in Figure S2, after 21 hours the [recalcitrant or](#) “baseline BrC” level has already been reached, as revealed by the next measurement at 33 hours. The absorbance decreased 70% before it reached the baseline BrC level for subalpine fir, and 60% for longleaf pine. For estimates of the BrC absorbance lifetimes, we used only the time before reaching the final light-absorbance state. Table 34 summarizes the resulting lifetimes for BrC from four fuel types, longleaf pine, juniper, lodgepole pine, and subalpine fir. [It should be noted that BrC absorption lifetimes are lower limits, due to the enhanced efficiency of absorption by particles caused by scattering of UV radiation scattering by the Teflon filter substrate \(Presser et al., 2014\).](#)

Once there was no further significant change in the transmission spectrum, the filter was extracted for the solution phase UV-Vis measurement, in order to compare the spectra obtained from the filter and in solution. The solution-phase spectra exhibited a reduction in the absorbance almost exactly to that observed in the filter transmission spectra (Figure S2).
415 However, there were differences in the shape of the spectra – there was no measurable absorbance above 550 nm in the extracted samples, but filter samples absorbed even at these long wavelengths (Figure S2). It is likely that the extraction from the filter was not complete, and some of the absorbers remained on the filter after the extraction. The latter is another advantage of doing these experiments with filter samples as opposed to their solvent extracts.

BBOA from subalpine fir (litter + other components) had the shortest equivalent absorption lifetime at 10 days, and ponderosa pine (litter + canopy) having the next shortest equivalent absorption lifetime at 17 days. Different ecosystem biomass components were burned in the long leaf pine fire, such as duff, litter, and canopy, and had the next longest absorption lifetime of 25 days. The longest living BrC absorbance, at 41 days, was observed for the sample from juniper (canopy only) burn. Fuel components appear to affect BrC absorption lifetimes, as it does seem that non-canopy fuel components, such as litter and duff lower the BrC absorption lifetimes. However, it is difficult to correlate the BrC
420 absorption lifetimes with quantitative measures such as NO levels or MCE (Table S1). Table S1 shows that the peak NO level was lower for long leaf pine (0.67 ppmv) compared to juniper (1.72 ppmv) and ponderosa pine (1.61 ppmv), suggesting less flaming combustion may have occurred for the long leaf pine fire (although this is not reflected in the MCE trends). Regardless, the data suggests that BrC absorption can be long-lived from direct photodegradation.

In general, the lifetimes for the loss of the absorbance integrated over 300-700 nm (Table 34) are much longer than those of
430 individual chromophores (Figure 5). There are two likely reasons for that. First, the photodegradation of individual chromophores creates product(s) that may also absorb in the same wavelength range. The integrated BrC absorption (300-700 nm) may ~~go to zero~~ significantly decrease only after the compounds go through several stages of photodegradation, finally resulting in products that no longer absorb above 300 nm. The results of both photolysis experiments is consistent with work by Di Lorenzo et al. (2017) and Wong et al. (2017) which show that during aging, high molecular weight BrC chromophores are formed after lower molecular weight chromophores are photodegraded. The high molecular weight fraction of BrC chromophores persist even at long aging times and are referred to as the recalcitrant fraction. This theory is one explanation for the short lifetimes of low molecular weight BrC compounds, while observing longer overall BrC absorption lifetimes. Second, equation 1 that we use to estimate lifetimes does not take into account photochemical quantum yields, which tend to increase greatly at shorter wavelengths. The LED, which was used in measurements of lifetimes of
440 individual chromophores, has a higher density of higher energy photons compared to the Xe lamp (Figure 1), which could accelerate photodegradation.

The lifetimes for BrC photobleaching due to UV irradiation (10 to 41 days) are longer than what other studies have observed or approximated for other aging mechanisms. Lin et al. (2016) found that peat and ponderosa pine BBOA had similar half-

445 lives of around 16 hours based on absorption coefficients at 300 nm. However, in Lin et al. (2016) BBOA was extracted and irradiated in solution where photodegradation could occur more rapidly [due to molecular diffusion](#) (Lignell et al., 2014). Forrister et al. (2015) collected filter samples in the plumes of wildfires with different transport times during the SEAC4RS campaign; and found that the BrC absorbance lifetime at 370 nm was 9-15 hours. Similarly, Selimovic et al. (2019) found a significant decrease in [the Absorption Angstrom Exponent-AAE](#) after 10 hours of daytime aging during a wildfire event in the Northwestern US. Sumlin et al. (2017) aged smoldering peat BBOA in an OFR, and reported a decrease of ~40-50% in 450 the aerosol mass absorption coefficients at 375 nm and 405 nm after 4.5 equivalent aging days. They attributed this decrease to fragmentation of BrC chromophores due to photooxidation (oxidation by gaseous OH). Based on the comparison of these observations, photooxidation could be a more important aging mechanism affecting BrC absorption lifetimes than the UV-induced photochemical processes inside the particles.

455 **4 Conclusions and Implications**

BBOA particles from laboratory burns of twelve forest fire fuels collected around the United States were analyzed for BrC chromophores. Biomass fuels spanned plant types (gymnosperm versus angiosperm) and ecosystem components (duff, litter, canopy, etc.). BrC chromophores were grouped among classes, including: lignin pyrolysis products, lignin-derived, distillation (coumarins and flavonoids), nitroaromatics, and PAHs. While most BrC chromophore classes were observed in 460 all burns, regardless of fuel type, there were specific BrC chromophores that were divided across angiosperm (flowering) and gymnosperm (conifer) lines. For example, sinapaldehyde was mainly observed in BBOA particles when angiosperm fuels were burned and coniferaldehyde when gymnosperm fuels were burned. Additionally, there were flavonoids specific to conifers, tentatively kaempferol and diosmetin (Table 1, chromophores 11 & 14), and unique to angiosperms such as chromophore 16. PAHs are largely angiosperm BrC chromophores, showing up mainly for sagebrush, chamise, and 465 ceanothus fuels. There are some BrC chromophores that are only appreciably observed in a single fuel type/burn; many of these are likely distillation or lignin-derived products. The most absorbing of these BrC chromophores are components of the angiosperm BBOA particles (Table 2).

UV irradiation of BBOA particles from different fuels directly on filters removes some BrC chromophores but some appear to be photo-stable, specifically, lignin-derived compounds (including lignin-pyrolysis products) and flavonoids. 470 Interestingly, individual BrC chromophore lifetimes varied based on the fuel burned and perhaps the underlying combustion conditions, rather than just the structure of the chromophore. Part of the reason is that co-elution of chromophores with different stabilities complicates measurements of individual chromophore lifetimes. In addition, indirect photolysis mechanisms, such as photosensitized reactions, the release of absorbed energy by a neighboring molecule as heat depending on intermolecular forces, and shielding of light by other absorbing molecules could change depending on the specific BBOA

475 material. The BrC chromophores of chaparral fuels had shorter equivalent photochemical lifetimes compared to BBOA
generated from the canopies of conifer fuel types. On the whole, these results suggest that some of the primary BrC
chromophores may be destroyed by UV irradiation after several hours.

480 Despite the rapid change in the absorbance of individual chromophores, the overall integrated BrC absorbance from 300 nm
to 700 nm decayed with a much longer lifetime of 10 days to 41 days. These observations contrast with individual
chromophores in particles that decayed on the time scale of 0.4 to 1.6 days. Taken together the two types of photolysis
experiments suggest that the absorption by the complete pool of BrC compounds persists during irradiation longer than the
individual BrC chromophores detected. Our findings also show that ecosystem components, and the combustion conditions
they create, could influence the apparent BrC absorption lifetimes. BrC from the subalpine fir mix burned with more
smoldering combustion and had the shortest equivalent lifetime of 10 days, while BBOA from the juniper and ~~L~~odgepole
485 canopy fuels had longer BrC absorption lifetimes of 25-41 days. The canopy fuels contributed to more flaming combustion.
These fairly long BrC absorption lifetimes suggest that the BrC was likely photostable upon direct photolysis, and other
chemical aging mechanisms such as OH oxidation may be more important under atmospheric conditions. Based on these
results, modelers should first focus on chemical aging mechanisms other than photolysis, such as heterogeneous oxidation by
OH.

490 **Author contributions**

LF, PL and AL collected and analyzed particulate matter samples, and JR, VS and RY analyzed gaseous composition of
BBOA. JL, AL and SN assisted with interpretation of mass spectrometry data. LF did the photochemistry experiments and
wrote the paper. All co-authors provided edits and critical feedback for the paper.

Acknowledgements

495 The chemical analysis portion of this work by ~~LTF and SAN~~ were supported by NOAA-CPO grant NA16OAR4310102
(LTF and SAN), ~~PL, JL, and AL~~ were supported by and NOAA-CPO grant NA16OAR4310101 (PL, JL, and AL). VS and
RY were supported by NOAA-CPO grant NA16OAR4310100. The photochemistry portion of this work was supported by
NSF grant AGS-1853639. We thank the USFS Missoula Fire Sciences Laboratory for their help in conducting these
experiments. This work was also supported by NOAA's Climate Research and Health of the Atmosphere Initiative. The
500 HRMS measurements were performed at the W.R. Wiley Environmental Molecular Sciences Laboratory (EMSL) – a
national scientific user facility located at PNNL, and sponsored by the Office of Biological and Environmental Research of
the U.S. DOE. PNNL is operated for U.S. DOE by Battelle Memorial Institute under Contract No. DE-AC06-76RL0 1830.

References

- 505 Agati, G., Azzarello, E., Pollastri, S. and Tattini, M.: Flavonoids as antioxidants in plants: location and functional significance, *Plant Sci.*, 196, 67–76 [online] Available from: https://ac.els-cdn.com/S0168945212001586/1-s2.0-S0168945212001586-main.pdf?_tid=e9cabe99-c212-43bf-b2f5-c6ca9baa8b0a&acdnat=1537563547_3ccdb2c4854a6df2354c96f84942d9f4 (Accessed 21 September 2018), 2012.
- 510 Al-Naiema, I. M. and Stone, E. A.: Evaluation of anthropogenic secondary organic aerosol tracers from aromatic hydrocarbons, *Atmos. Chem. Phys.*, 17(3), 2053–2065, doi:10.5194/acp-17-2053-2017, 2017.
- Bahadur, R., Praveen, P. S., Xu, Y. and Ramanathan, V.: Solar absorption by elemental and brown carbon determined from spectral observations, *Proc. Natl. Acad. Sci.*, 109(43), 17366–17371, doi:10.1073/pnas.1205910109, 2012.
- 515 Bond, T. C., Zarzycki, C., Flanner, M. G. and Koch, D. M.: Quantifying immediate radiative forcing by black carbon and organic matter with the Specific Forcing Pulse, *Atmos. Chem. Phys.*, 11(4), 1505–1525, doi:10.5194/acp-11-1505-2011, 2011.
- Boulanger, Y., Gauthier, S. and Burton, P. J.: A refinement of models projecting future Canadian fire regimes using homogeneous fire regime zones, *Can. J. For. Res.*, 44(4), 365–376, doi:10.1139/cjfr-2013-0372, 2014.
- 520 Budisulistiorini, S. H., Riva, M., Williams, M., Chen, J., Itoh, M., Surratt, J. D. and Kuwata, M.: Light-Absorbing Brown Carbon Aerosol Constituents from Combustion of Indonesian Peat and Biomass, *Environ. Sci. Technol.*, 51(8), 4415–4423, doi:10.1021/acs.est.7b00397, 2017.
- Calvert, J. G. and Pitts, J. N.: *Photochemistry*, John Wiley & Sons, Ltd, New York City, New York., 1966.
- Cha, E., Jeong, E. S., Han, S. B., Cha, S., Son, J., Kim, S., Oh, H. Bin and Lee, J.: Ionization of Gas-Phase Polycyclic Aromatic Hydrocarbons in Electrospray Ionization Coupled with Gas Chromatography, , doi:10.1021/acs.analchem.8b00401, 2018.
- 525 Chakrabarty, R. K., Moosmüller, H., Chen, L.-W. A., Lewis, K., Arnott, W. P., Mazzoleni, C., Dubey, M. K., Wold, C. E., Hao, W. M. and Kreidenweis, S. M.: Brown carbon in tar balls from smoldering biomass combustion, *Atmos. Chem. Phys.*, 10(13), 6363–6370, doi:10.5194/acp-10-6363-2010, 2010.
- 530 Chang, J. L. and Thompson, J. E.: Characterization of colored products formed during irradiation of aqueous solutions containing H₂O₂ and phenolic compounds, *Atmos. Environ.*, 44(4), 541–551, doi:10.1016/J.ATMOSENV.2009.10.042, 2010.
- Chen, Y. and Bond, T. C.: Light absorption by organic carbon from wood combustion, *Atmos. Chem. Phys.*, 10(4), 1773–1787, doi:10.5194/acp-10-1773-2010, 2010.
- Chung, C. E., Ramanathan, V. and Decremer, D.: Observationally constrained estimates of carbonaceous aerosol radiative forcing, *Proc. Natl. Acad. Sci.*, 109(29), 11624–11629, doi:10.1073/pnas.1203707109, 2012.
- 535 Feng, Y., Ramanathan, V. and Kotamarthi, V. R.: Brown carbon: a significant atmospheric absorber of solar radiation?, *Atmos. Chem. Phys.*, 13(17), 8607–8621, doi:10.5194/acp-13-8607-2013, 2013.
- Fernández, P., Grimalt, J. O. and Vilanova, R. M.: Atmospheric Gas-Particle Partitioning of Polycyclic Aromatic Hydrocarbons in High Mountain Regions of Europe, *Environ. Sci. Technol.*, 36(6), 1162–1168, doi:10.1021/es010190t, 2002.
- 540 Finlayson-Pitts, B. J. and Pitts, J. N.: *Chemistry of the Upper and Lower Atmosphere: Theory, Experiments, and Applications*, Academic Press, San Diego, CA., 2000.

- 545 Fleming, L. T., Lin, P., Laskin, A., Laskin, J., Weltman, R., Edwards, R. D., Arora, N. K., Yadav, A., Meinardi, S., Blake, D. R., Pillarisetti, A., Smith, K. R. and Nizkorodov, S. A.: Molecular composition of particulate matter emissions from dung and brushwood burning household cookstoves in Haryana, India, *Atmos. Chem. Phys.*, 18(4), 2461–2480, doi:10.5194/acp-18-2461-2018, 2018.
- Forrister, H., Liu, J., Scheuer, E., Dibb, J., Ziemba, L., Thornhill, K. L., Anderson, B., Diskin, G., Perring, A. E., Schwarz, J. P., Campuzano-Jost, P., Day, D. A., Palm, B. B., Jimenez, J. L., Nenes, A. and Weber, R. J.: Evolution of brown carbon in wildfire plumes, *Geophys. Res. Lett.*, 42(11), 4623–4630, doi:10.1002/2015GL063897, 2015.
- 550 Gelencsér, A., Hoffer, A., Kiss, G., Tombác, E., Kurdi, R. and Bencze, L.: In-situ Formation of Light-Absorbing Organic Matter in Cloud Water, *J. Atmos. Chem.*, 45(1), 25–33, doi:10.1023/A:1024060428172, 2003.
- Giroto, G., China, S., Bhandari, J., Gorkowski, K., Scarnato, B. V., Capek, T., Marinoni, A., Veghte, D. P., Kulkarni, G., Aiken, A. C., Dubey, M. and Mazzoleni, C.: Fractal-like Tar Ball Aggregates from Wildfire Smoke, *Environ. Sci. Technol. Lett.*, 5(6), 360–365, doi:10.1021/acs.estlett.8b00229, 2018.
- 555 Harrison, M. A. J., Barra, S., Borghesi, D., Vione, D., Arsene, C. and Iulian Olariu, R.: Nitrated phenols in the atmosphere: a review, *Atmos. Environ.*, 39(2), 231–248, doi:10.1016/J.ATMOSENV.2004.09.044, 2005.
- Hems, R. F. and Abbatt, J. P. D.: Aqueous Phase Photo-oxidation of Brown Carbon Nitrophenols: Reaction Kinetics, Mechanism, and Evolution of Light Absorption, *ACS Earth Sp. Chem.*, 2(3), 225–234, doi:10.1021/acsearthspacechem.7b00123, 2018.
- 560 Hinks, M. L., Brady, M. V., Lignell, H., Song, M., Grayson, J. W., Bertram, A. K., Lin, P., Laskin, A., Laskin, J. and Nizkorodov, S. A.: Effect of viscosity on photodegradation rates in complex secondary organic aerosol materials, *Phys. Chem. Chem. Phys.*, 18(13), 8785–8793, doi:10.1039/C5CP05226B, 2016.
- Iinuma, Y., Böge, O., Gräfe, R. and Herrmann, H.: Methyl-Nitrocatechols: Atmospheric Tracer Compounds for Biomass Burning Secondary Organic Aerosols, *Environ. Sci. Technol.*, 44(22), 8453–8459, doi:10.1021/es102938a, 2010.
- 565 Iinuma, Y., Keywood, M. and Herrmann, H.: Characterization of primary and secondary organic aerosols in Melbourne airshed: The influence of biogenic emissions, wood smoke and bushfires, *Atmos. Environ.*, 130, 54–63, doi:10.1016/J.ATMOSENV.2015.12.014, 2016.
- Iranshahi M, Askari M, Sahebkar A and Hadjipavlou-Litina D: Evaluation of antioxidant, anti-inflammatory and lipoxygenase inhibitory activities of the prenylated coumarin umbelliprenin. [online] Available from: <https://ikee.lib.auth.gr/record/226183/files/Litina.pdf> (Accessed 21 September 2018), 2009.
- 570 Jen, C. N., Hatch, L. E., Selimovic, V., Yokelson, R. J., Weber, R., Fernandez, A. E., Kreisberg, N. M., Barsanti, K. C. and Goldstein, A. H.: Speciated and total emission factors of particulate organics from burning western US wildland fuels and their dependence on combustion efficiency, *Atmos. Chem. Phys.*, 19(2), 1013–1026, doi:10.5194/acp-19-1013-2019, 2019.
- Jiang, X., Wiedinmyer, C. and Carlton, A. G.: Aerosols from Fires: An Examination of the Effects on Ozone Photochemistry in the Western United States, *Environ. Sci. Technol.*, 46(21), 11878–11886, doi:10.1021/es301541k, 2012.
- 575 Kaur, R., Labins, J. R., Helbock, S. S., Jiang, W., Bein, K. J., Zhang, Q. and Anastasio, C.: Photooxidants from brown carbon and other chromophores in illuminated particle extracts, *Atmos. Chem. Phys.*, 19, 6579–6594, doi:https://doi.org/10.5194/acp-19-6579-2019, 2019.
- Keyte, I. J., Harrison, R. M. and Lammel, G.: Chemical reactivity and long-range transport potential of polycyclic aromatic hydrocarbons-a review, *Chem. Soc. Rev.*, 42(24), 9333–9391, doi:10.1039/c3cs60147a, 2013.

- 580 Kirchstetter, T. W., Novakov, T. and Hobbs, P. V.: Evidence that the spectral dependence of light absorption by aerosols is affected by organic carbon, *J. Geophys. Res. Atmos.*, 109(D21), doi:10.1029/2004JD004999, 2004.
- Laskin, A., Laskin, J. and Nizkorodov, S. A.: Chemistry of Atmospheric Brown Carbon, *Chem. Rev.*, 115(10), 4335–4382, doi:10.1021/cr5006167, 2015.
- 585 Lee, S., Shin, D.-S., Kim, J. S., Oh, K.-B. and Kang, S. S.: Antibacterial coumarins from *Angelica gigas* roots, *Arch. Pharm. Res.*, 26(6), 449–452, doi:10.1007/BF02976860, 2003.
- Li, C., He, Q., Schade, J., Passig, J., Zimmermann, R., Meidan, D., Laskin, A. and Rudich, Y.: Dynamic changes in optical and chemical properties of tar ball aerosols by atmospheric photochemical aging, *Atmos. Chem. Phys.*, 19(1), 139–163, doi:10.5194/acp-19-139-2019, 2019.
- 590 Li, G., Bei, N., Tie, X. and Molina, L. T.: Aerosol effects on the photochemistry in Mexico City during MCMA-2006/MILAGRO campaign, *Atmos. Chem. Phys.*, 11(11), 5169–5182, doi:10.5194/acp-11-5169-2011, 2011.
- Li, X., Jiang, L., Hoa, L. P., Lyu, Y., Xu, T., Yang, X., Iinuma, Y., Chen, J. and Herrmann, H.: Size distribution of particle-phase sugar and nitrophenol tracers during severe urban haze episodes in Shanghai, *Atmos. Environ.*, 145, 115–127, doi:10.1016/j.atmosenv.2016.09.030, 2016.
- 595 Lignell, H., Hinks, M. L. and Nizkorodov, S. A.: Exploring matrix effects on photochemistry of organic aerosols., *Proc. Natl. Acad. Sci. U. S. A.*, 111(38), 13780–5, doi:10.1073/pnas.1322106111, 2014.
- Lin, P., Liu, J., Shilling, J. E., Kathmann, S. M., Laskin, J. and Laskin, A.: Molecular characterization of brown carbon (BrC) chromophores in secondary organic aerosol generated from photo-oxidation of toluene, *Phys. Chem. Chem. Phys.*, 17(36), 23283–23676, doi:10.1039/c5cp02563j, 2015a.
- 600 Lin, P., Laskin, J., Nizkorodov, S. A. and Laskin, A.: Revealing Brown Carbon Chromophores Produced in Reactions of Methylglyoxal with Ammonium Sulfate, *Environ. Sci. Technol.*, 49(24), 14257–14266, doi:10.1021/acs.est.5b03608, 2015b.
- Lin, P., Aiona, P. K., Li, Y., Shiraiwa, M., Laskin, J., Nizkorodov, S. A. and Laskin, A.: Molecular Characterization of Brown Carbon in Biomass Burning Aerosol Particles, *Environ. Sci. Technol.*, 50(21), 11815–11824, doi:10.1021/acs.est.6b03024, 2016.
- 605 Lin, P., Bluvshstein, N., Rudich, Y., Nizkorodov, S., Laskin, J. and Laskin, A.: Molecular Chemistry of Atmospheric Brown Carbon Inferred from a Nationwide Biomass-Burning Event, *Environ. Sci. Technol.*, 51(20), 11561–11570, doi:10.1021/acs.est.7b02276, 2017.
- Lin, P., Fleming, L. T., Nizkorodov, S. A., Laskin, J. and Laskin, A.: Comprehensive Molecular Characterization of Atmospheric Brown Carbon by High Resolution Mass Spectrometry with Electrospray and Atmospheric Pressure Photoionization, *Anal. Chem.*, 90(21), 12493–12502, doi:10.1021/acs.analchem.8b02177, 2018.
- 610 Di Lorenzo, R. A., Washenfelder, R. A., Attwood, A. R., Guo, H., Xu, L., Ng, N. L., Weber, R. J., Baumann, K., Edgerton, E. and Young, C. J.: Molecular-Size-Separated Brown Carbon Absorption for Biomass-Burning Aerosol at Multiple Field Sites, *Environ. Sci. Technol.*, 51(6), 3128–3137, doi:10.1021/acs.est.6b06160, 2017.
- Ma, X., Yu, F. and Luo, G.: Aerosol direct radiative forcing based on GEOS-Chem-APM and uncertainties, *Atmos. Chem. Phys.*, 12(12), 5563–5581, doi:10.5194/acp-12-5563-2012, 2012.
- 615 Macdonald, R. W., Barrie, L. A., Bidleman, T. F., Diamond, M. L., Gregor, D. J., Semkin, R. G., Strachan, W. M. J., Li, Y. F., Wania, F., Alaei, M., Alexeeva, L. B., Backus, S. M., Bailey, R., Bowers, J. M., Gobeil, C., Halsall, C. J., Harner, T., Hoff, J. T., Jantunen, L. M. M., Lockhart, W. L., Mackay, D., Muir, D. C. G., Pudykiewicz, J., Reimer, K. J., Smith, J. N.,

- 620 Stern, G. ., Schroeder, W. H., Wagemann, R. and Yunker, M. B.: Contaminants in the Canadian Arctic: 5 years of progress in understanding sources, occurrence and pathways, *Sci. Total Environ.*, 254(2–3), 93–234, doi:10.1016/S0048-9697(00)00434-4, 2000.
- Madronich, S., Flocke, S., Zeng, J., Petropavlovskikh, I. and Lee-Taylor, J.: Tropospheric Ultraviolet and Visible (TUV) Radiation Model, [online] Available from: http://cprm.acom.ucar.edu/Models/TUV/Interactive_TUV/, 2002.
- Malecha, K. T. and Nizkorodov, S. A.: Feasibility of Photosensitized Reactions with Secondary Organic Aerosol Particles in the Presence of Volatile Organic Compounds, *J. Phys. Chem. A*, 121(26), 4961–4967, doi:10.1021/acs.jpca.7b04066, 2017.
- 625 Miller, J. S. and Olejnik, D.: Photolysis of polycyclic aromatic hydrocarbons in water, *Water Res.*, 35(1), 233–243, doi:10.1016/S0043-1354(00)00230-X, 2001.
- Monge, M. E., Rosenørn, T., Favez, O., Müller, M., Adler, G., Abo Riziq, A., Rudich, Y., Herrmann, H., George, C. and D’Anna, B.: Alternative pathway for atmospheric particles growth., *Proc. Natl. Acad. Sci. U. S. A.*, 109(18), 6840–4, doi:10.1073/pnas.1120593109, 2012.
- 630 Moorthy, B., Chu, C. and Carlin, D. J.: Polycyclic Aromatic Hydrocarbons: From Metabolism to Lung Cancer, *Toxicol. Sci.*, 145(1), 5–15, doi:10.1093/toxsci/kfv040, 2015.
- Moriondo, M., Good, P., Durao, R., Bindi, M., Giannakopoulos, C. and Corte-Real, J.: Potential impact of climate change on fire risk in the Mediterranean area, *Clim. Res.*, 31(1), 85–95, doi:10.3354/cr031085, 2006.
- 635 Pósfai, M., Gelencsér, A., Simonics, R., Arató, K., Li, J., Hobbs, P. V. and Buseck, P. R.: Atmospheric tar balls: Particles from biomass and biofuel burning, *J. Geophys. Res. Atmos.*, 109(D6), n/a-n/a, doi:10.1029/2003JD004169, 2004.
- Presser, C., Conny, J. M. and Nazarian, A.: Filter material effects on particle absorption optical properties, *Aerosol Sci. Technol.*, 48(5), 515–529, doi:10.1080/02786826.2014.890999, 2014.
- 640 Ramanathan, V., Li, F., Ramana, M. V., Praveen, P. S., Kim, D., Corrigan, C. E., Nguyen, H., Stone, E. A., Schauer, J. J., Carmichael, G. R., Adhikary, B. and Yoon, S. C.: Atmospheric brown clouds: Hemispherical and regional variations in long-range transport, absorption, and radiative forcing, *J. Geophys. Res.*, 112(D22), D22S21, doi:10.1029/2006JD008124, 2007.
- Saleh, R., Hennigan, C. J., McMeeking, G. R., Chuang, W. K., Robinson, E. S., Coe, H., Donahue, N. M. and Robinson, A. L.: Absorptivity of brown carbon in fresh and photo-chemically aged biomass-burning emissions, *Atmos. Chem. Phys.*, 13(15), 7683–7693, doi:10.5194/acp-13-7683-2013, 2013.
- Sarkanen, K. V. and Ludwig, C. H.: *Lignins*, J. Wiley & Sons, New York City., 1971.
- 645 Sedlacek III, A. J., Buseck, P. R., Adachi, K., Onasch, T. B., Springston, S. R. and Kleinman, L.: Formation and evolution of tar balls from northwestern US wildfires, *Atmos. Chem. Phys.*, 18(15), 11289–11301, doi:10.5194/acp-18-11289-2018, 2018.
- 650 Selimovic, V., Yokelson, R. J., Warneke, C., Roberts, J. M., de Gouw, J., Reardon, J. and Griffith, D. W. T.: Aerosol optical properties and trace gas emissions by PAX and OP-FTIR for laboratory-simulated western US wildfires during FIREX, *Atmos. Chem. Phys.*, 18(4), 2929–2948, doi:10.5194/acp-18-2929-2018, 2018.
- Selimovic, V., Yokelson, R. J., McMeeking, G. R. and Coefield, S.: In situ measurements of trace gases, PM, and aerosol optical properties during the 2017 NW US wildfire smoke event, *Atmos. Chem. Phys.*, 19(6), 3905–3926, doi:10.5194/acp-19-3905-2019, 2019.
- Shankar, R., An, J. G., Loh, A. and Yim, U. H.: A systematic study of the effects of solvents on phenanthrene

- 655 photooxidation, *Chemosphere*, 220, 900–909, doi:10.1016/J.CHEMOSPHERE.2018.12.206, 2019.
- Shvidenko, A. Z. and Schepaschenko, D. G.: Climate change and wildfires in Russia, *Contemp. Probl. Ecol.*, 6(7), 683–692, doi:10.1134/S199542551307010X, 2013.
- Simoneit, B. R. T.: Biomass burning — a review of organic tracers for smoke from incomplete combustion, *Appl. Geochemistry*, 17(3), 129–162, doi:10.1016/S0883-2927(01)00061-0, 2002.
- 660 Simoneit, B. R. T., Rogge, W. F., Mazurek, M. A., Standley, L. J., Hildemann, L. M. and Cass, G. R.: Lignin pyrolysis products, lignans, and resin acids as specific tracers of plant classes in emissions from biomass combustion, *Environ. Sci. Technol.*, 27(12), 2533–2541, doi:10.1021/es00048a034, 1993.
- Smith, J. D., Kinney, H. and Anastasio, C.: Phenolic carbonyls undergo rapid aqueous photodegradation to form low-volatility, light-absorbing products, *Atmos. Environ.*, 126, 36–44, doi:10.1016/J.ATMOSENV.2015.11.035, 2016.
- 665 Smol, M. and Włodarczyk-Makuła, M.: The Effectiveness in the Removal of PAHs from Aqueous Solutions in Physical and Chemical Processes: A Review, *Polycycl. Aromat. Compd.*, 37(4), 292–313, doi:10.1080/10406638.2015.1105828, 2017.
- Sofowote, U. M., Hung, H., Rastogi, A. K., Westgate, J. N., Deluca, P. F., Su, Y. and McCarry, B. E.: Assessing the long-range transport of PAH to a sub-Arctic site using positive matrix factorization and potential source contribution function, *Atmos. Environ.*, 45(4), 967–976, doi:10.1016/J.ATMOSENV.2010.11.005, 2011.
- 670 Sumlin, B. J., Pandey, A., Walker, M. J., Pattison, R. S., Williams, B. J. and Chakrabarty, R. K.: Atmospheric Photooxidation Diminishes Light Absorption by Primary Brown Carbon Aerosol from Biomass Burning, *Environ. Sci. Technol. Lett.*, 4(12), 540–545, doi:10.1021/acs.estlett.7b00393, 2017.
- Surawski, N. C., Sullivan, A. L., Meyer, C. P., Roxburgh, S. H. and Polglase, P. J.: Greenhouse gas emissions from laboratory-scale fires in wildland fuels depend on fire spread mode and phase of combustion, *Atmos. Chem. Phys.*, 15(9), 5259–5273, doi:10.5194/acp-15-5259-2015, 2015.
- 675 Tang, H. and Thompson, J. E.: Light-Absorbing Products Form during the Aqueous Phase Reaction of Phenolic Compounds in the Presence of Nitrate and Nitrite with UV Illumination, *Open J. Air Pollut.*, 01(02), 13–21, doi:10.4236/ojap.2012.12002, 2012.
- Tihay-Felicelli, V., Santoni, P. A., Gerandi, G. and Barboni, T.: Smoke emissions due to burning of green waste in the Mediterranean area: Influence of fuel moisture content and fuel mass, *Atmos. Environ.*, 159, 92–106, doi:10.1016/J.ATMOSENV.2017.04.002, 2017.
- 680 Tomaz, S., Cui, T., Chen, Y., Sexton, K. G., Roberts, J. M., Warneke, C., Yokelson, R. J., Surratt, J. D. and Turpin, B. J.: Photochemical Cloud Processing of Primary Wildfire Emissions as a Potential Source of Secondary Organic Aerosol, *Environ. Sci. Technol.*, 52(19), 11027–11037, doi:10.1021/acs.est.8b03293, 2018.
- 685 Tóth, A., Hoffer, A., Nyirő-Kósa, I., Pósfai, M. and Gelencsér, A.: Atmospheric tar balls: aged primary droplets from biomass burning?, *Atmos. Chem. Phys.*, 14(13), 6669–6675, doi:10.5194/acp-14-6669-2014, 2014.
- Turro, N. J., Ramamurthy, V. and Scaiano, J. C.: *Modern molecular photochemistry of organic molecules*, University Science Books, Sausalito, CA., 2009.
- Venugopala, K. N., Rashmi, V. and Odhav, B.: Review on natural coumarin lead compounds for their pharmacological activity., *Biomed Res. Int.*, 2013, 963248, doi:10.1155/2013/963248, 2013.
- 690 Wang, Y., Liang, H., Zhang, Q., Cheng, W. and Yi, S.: Phytochemical and chemotaxonomic study on *Ficus tsiangii* Merr. ex

Corner, *Biochem. Syst. Ecol.*, 57, 210–215, doi:10.1016/j.bse.2014.08.003, 2014.

Weber, M. G. and Stocks, B. J.: Forest Fires and Sustainability in the Boreal Forests of Canada, *Ambio*, 27(7), 545–550 [online] Available from:

695 http://ucelinks.cdlib.org:8888/sfx_local?sid=google&aunit=MG&aunit=Weber&atitle=Forest+fires+and+sustainability+in+the+boreal+forests+of+Canada&title=AMBIO:+A+Journal+of+the+Human+Environment&volume=27&issue=7&date=1998&spage=545&issn=0044-7447 (Accessed 8 October 2018), 1998.

Wong, J. P. S., Nenes, A. and Weber, R. J.: Changes in Light Absorptivity of Molecular Weight Separated Brown Carbon Due to Photolytic Aging, *Environ. Sci. Technol.*, 51(15), 8414–8421, doi:10.1021/acs.est.7b01739, 2017.

700 Wood, A. W., Chang, R. L., Levin, W., Thakker, D. R., Yagi, H., Sayer, J. M., Jerina, D. M. and Conney, A. H.: Mutagenicity of the Enantiomers of the Diastereomeric Bay-Region Benzo(c)phenanthrene 3,4-Diol-1,2-epoxides in Bacterial and Mammalian Cells. [online] Available from: <http://cancerres.aacrjournals.org/content/44/6/2320.full-text.pdf> (Accessed 28 September 2018), 1984.

705 Wotton, B. M. and Flannigan, M. D.: Length of the fire season in a changing climate, *For. Chron.*, 69(2), 187–192, doi:10.5558/tfc69187-2, 1993.

Wotton, B. M., Nock, C. A. and Flannigan, M. D.: Forest fire occurrence and climate change in Canada, *Int. J. Wildl. Fire*, 19(3), 253, doi:10.1071/WF09002, 2010.

710 Xie, M., Chen, X., Hays, M. D. and Holder, A. L.: Composition and light absorption of N-containing aromatic compounds in organic aerosols from laboratory biomass burning, *Atmos. Chem. Phys.*, 19(5), 2899–2915, doi:10.5194/acp-19-2899-2019, 2019.

Xue, W. and Warshawsky, D.: Metabolic activation of polycyclic and heterocyclic aromatic hydrocarbons and DNA damage: A review, *Toxicol. Appl. Pharmacol.*, 206(1), 73–93, doi:10.1016/J.TAAP.2004.11.006, 2005.

Zhao, R., Lee, A. K. Y., Huang, L., Li, X., Yang, F. and Abbatt, J. P. D.: Photochemical processing of aqueous atmospheric brown carbon, *Atmos. Chem. Phys.*, 15(11), 6087–6100, doi:10.5194/acp-15-6087-2015, 2015.

715 Zhong, M. and Jang, M.: Dynamic light absorption of biomass-burning organic carbon photochemically aged under natural sunlight, *Atmos. Chem. Phys.*, 14(3), 1517–1525, doi:10.5194/acp-14-1517-2014, 2014.

Zhou, S., Lee, A. K. Y., McWhinney, R. D. and Abbatt, J. P. D.: Burial Effects of Organic Coatings on the Heterogeneous Reactivity of Particle-Borne Benzo[a]pyrene (BaP) toward Ozone, *J. Phys. Chem. A*, 116(26), 7050–7056, doi:10.1021/jp3030705, 2012.

720 Zhou, S., Yeung, L. W. Y., Forbes, M. W., Mabury, S. and Abbatt, J. P. D.: Epoxide formation from heterogeneous oxidation of benzo[a]pyrene with gas-phase ozone and indoor air †, *Environ. Sci. Process. Impacts*, 19(10), 1292–1299, doi:10.1039/c7em00181a, 2017.

725 Zhou, S., Hwang, B. C. H., Lakey, P. S. J., Zuend, A., Abbatt, J. P. D. and Shiraiwa, M.: Multiphase reactivity of polycyclic aromatic hydrocarbons is driven by phase separation and diffusion limitations, *Proc. Natl. Acad. Sci.*, 201902517, doi:10.1073/pnas.1902517116, 2019.

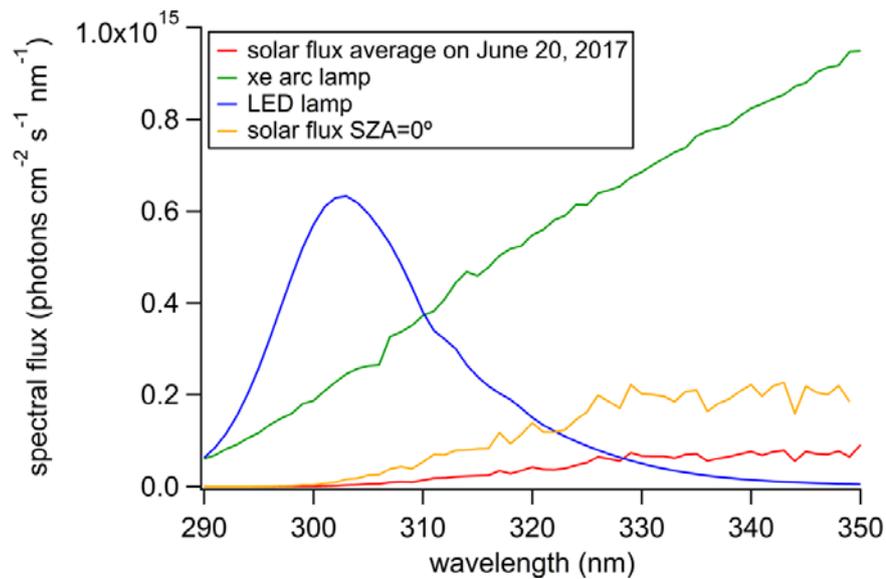


Figure 1. Spectral flux density (photons $\text{cm}^{-2} \text{s}^{-1} \text{nm}^{-1}$) approximated for a solar zenith angle of 0° (orange) as well as the 24-hour average for the latitude and longitude of Los Angeles (34° latitude, 118° longitude) on June 20, 2017 (red). The spectral flux density for the 300 nm LED (blue) and the filtered Xe arc lamp (green) are also shown.

730

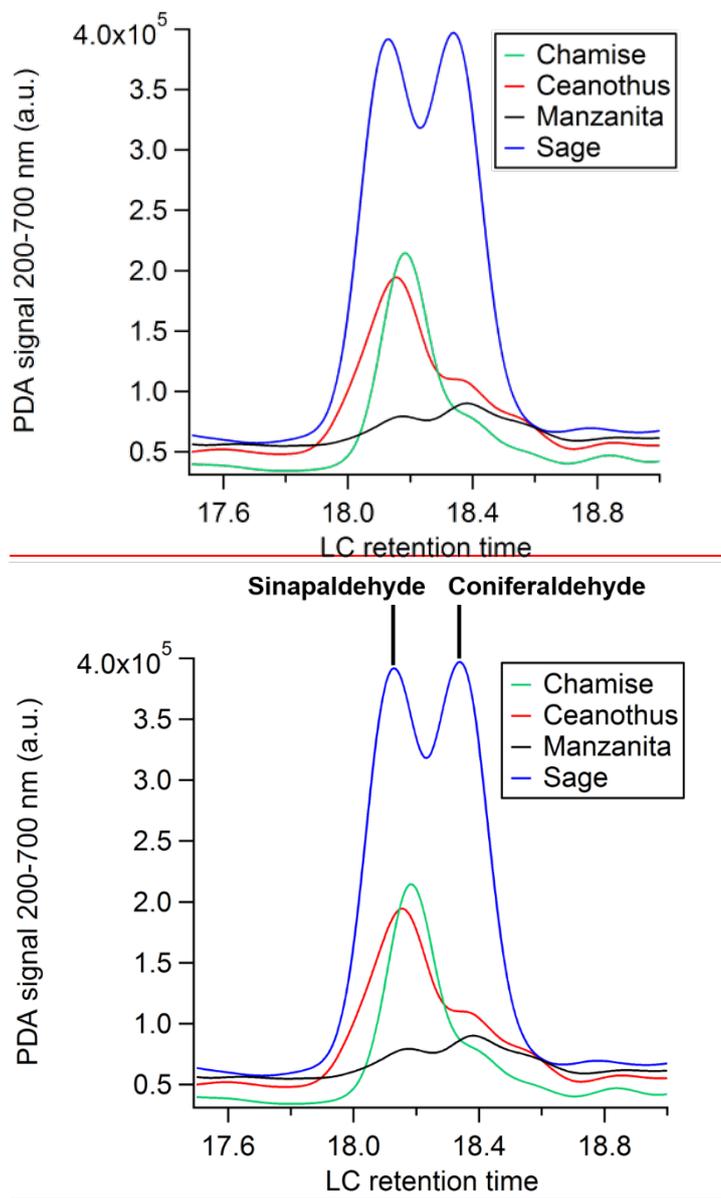
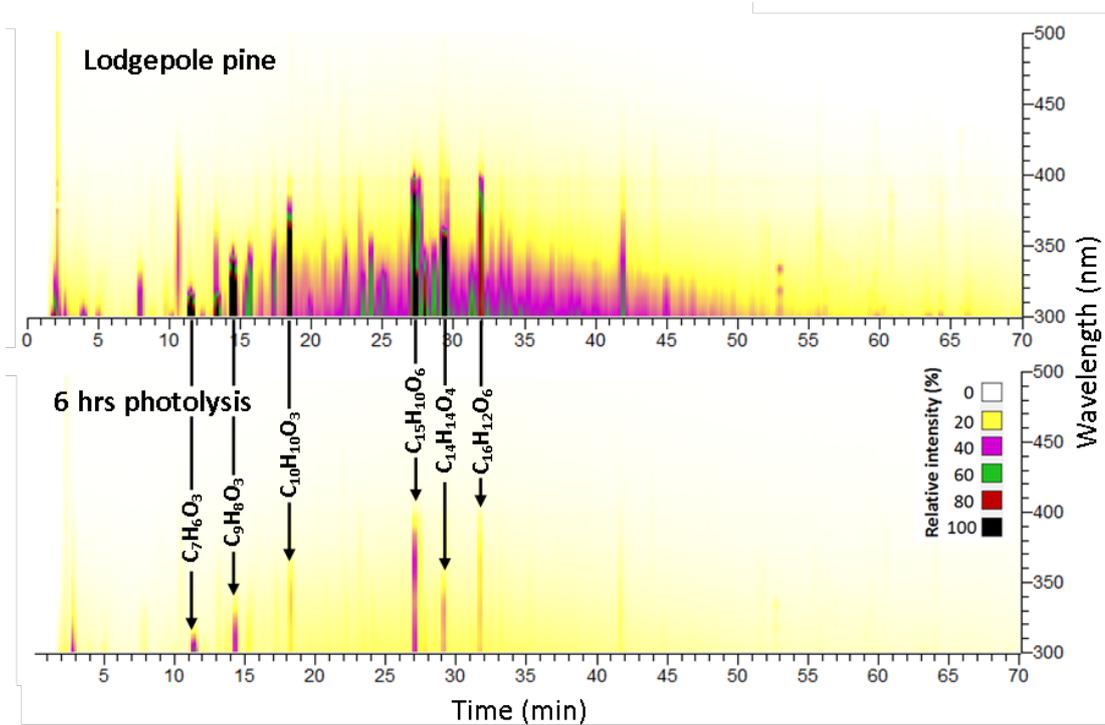


Figure 2. Lignin pyrolysis products sinapaldehyde ($C_{11}H_{12}O_4$) and coniferaldehyde ($C_{10}H_{10}O_3$) elute at slightly different retention times, at roughly 18.1 and 18.4 min, respectively.



735

Figure 3. BrC chromophores present in the BBOA sample before (top panel) and after (bottom panel) [300 nm](#) photolysis for a conifer fuel, lodgepole pine.

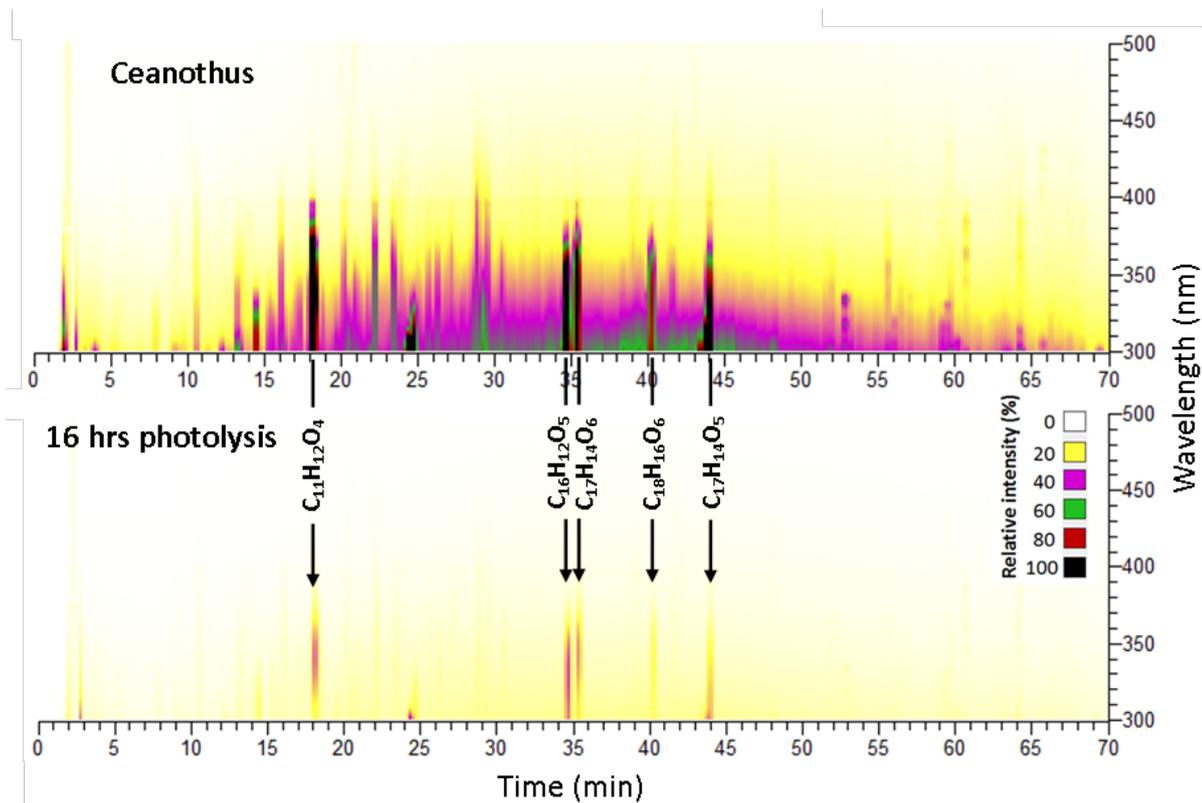
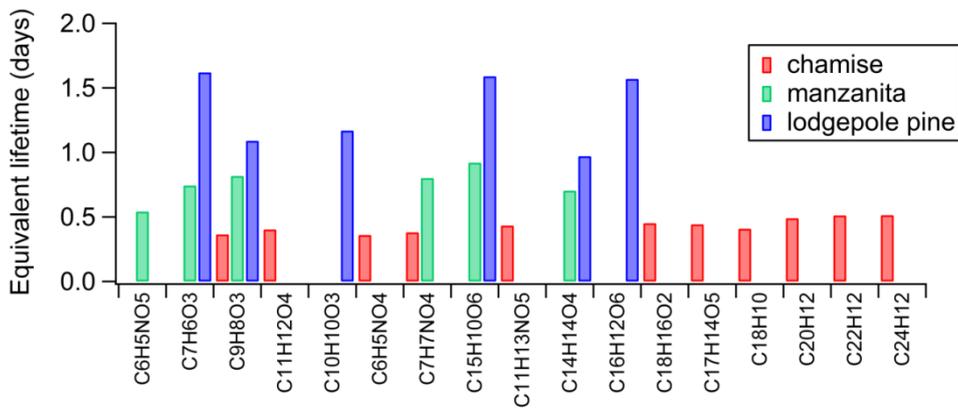


Figure 4. BrC chromophores present in the BBOA sample before (top panel) and after (bottom panel) [300 nm](#) photolysis for angiosperm fuel, ceanothus.

740



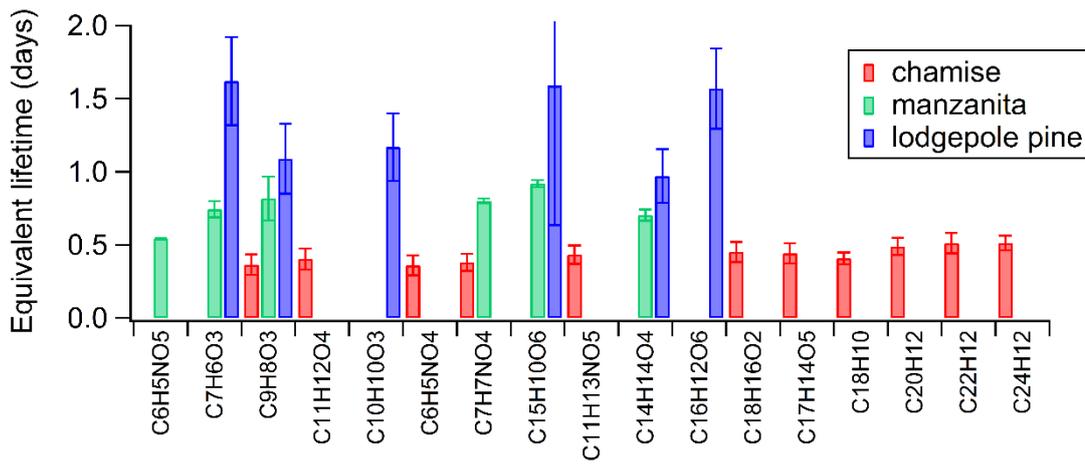
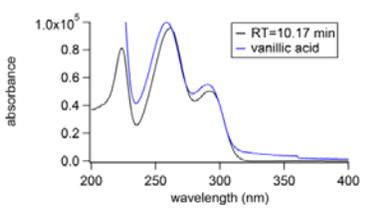
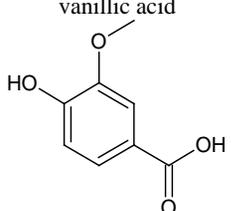
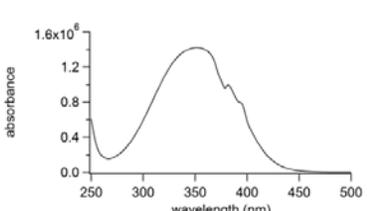
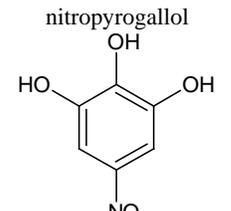
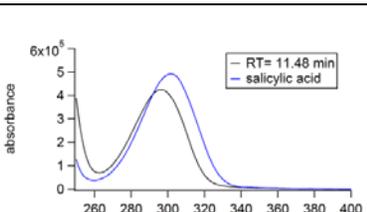
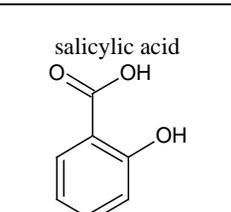
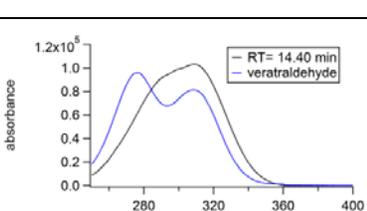
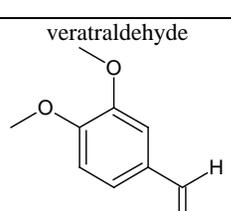
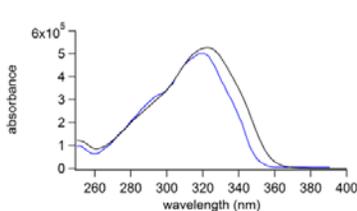
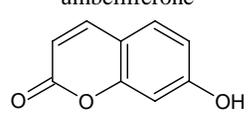
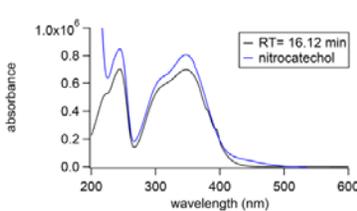
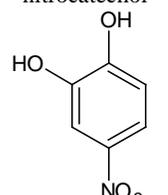
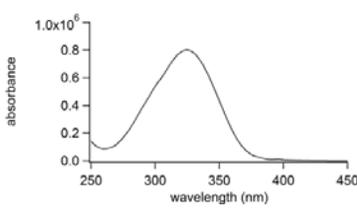
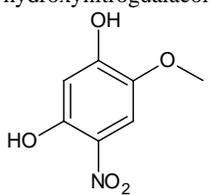
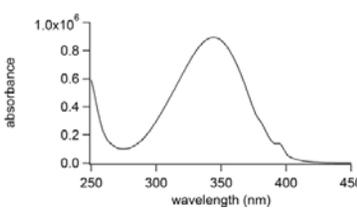
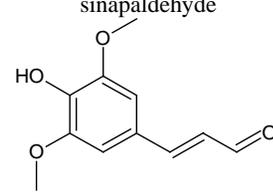


Figure 5. Approximate atmospheric lifetimes for select individual BrC chromophores due to direct photolysis that exist in BBOA particles from chamise, manzanita, and lodgepole pine fires (the photolysis times are listed in [Table S23](#)). These lifetimes are shorter than those calculated for overall BrC absorption.

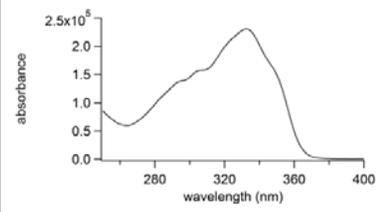
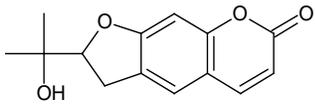
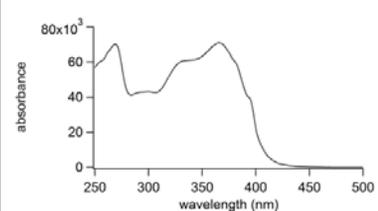
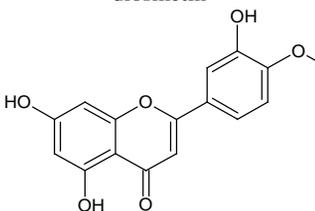
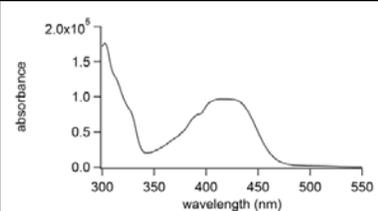
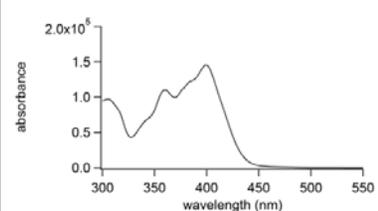
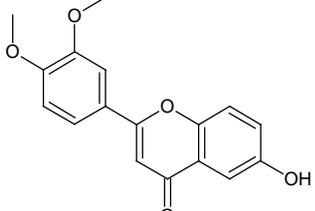
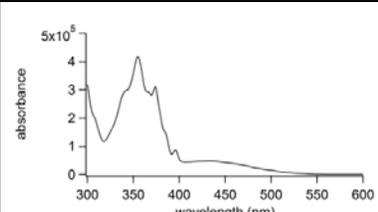
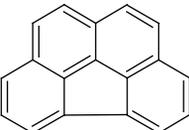
745

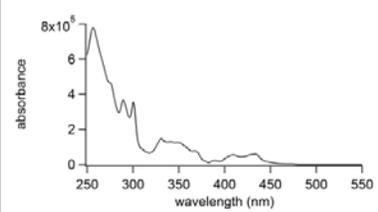
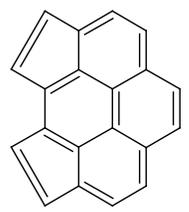
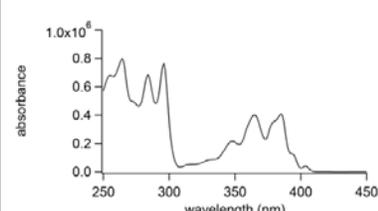
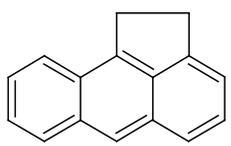
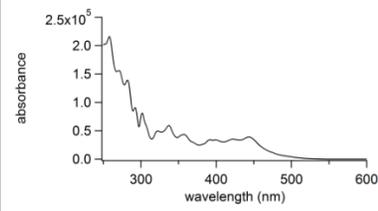
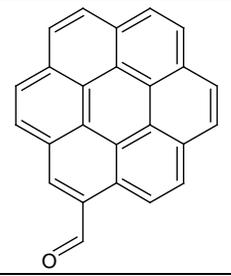
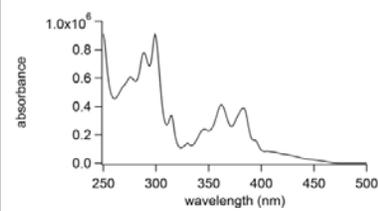
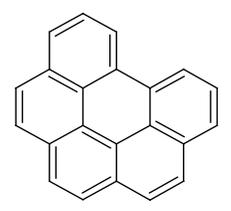
Table 1. Chromophores common among multiple fuel types are listed by their HPLC retention times, absorption spectra, assigned elemental formulas, and examples of possible structures. The absorbance by each chromophore is binned by photodiode array absorbance normalized to the highest absorbance in each chromatogram: M-Major (75%-100%), I-Intermediate (25%-75%), or W-Weak (5%-25%). The absorption spectra of the standard (blue) may not fully match the absorption spectra of the eluents because the separation is not complete, and more than one compound may elute at any given time. The shown absorption spectra are baseline corrected by subtracting the spectrum at a nearby retention time where the PDA absorbance is low.

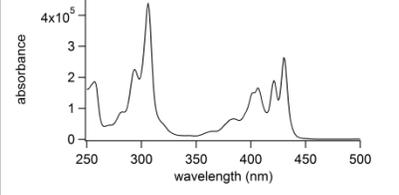
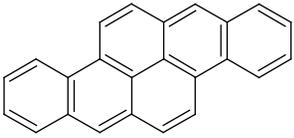
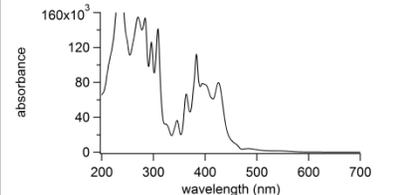
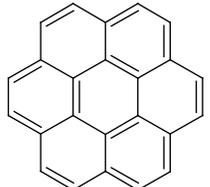
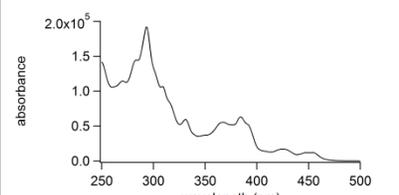
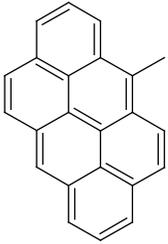
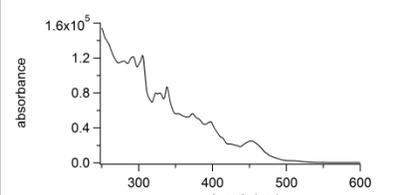
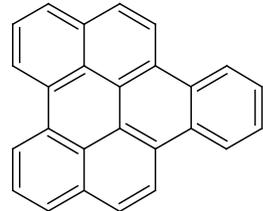
Peak #	LC RT (min)	Absorption spectrum	Elemental formula of neutral species	Examples of possible structures	subalpine fir duff	ceanothus	chamise	longleaf pine	juniper	ponderosa pine log	manzanita	lodgepole pine	engelmann spruce duff	ponderosa pine litter	douglas fir	sagebrush	
1	10.07-10.29		C ₈ H ₈ O ₄	vanillic acid 	W					W			W				
2	10.52-10.71*		C ₆ H ₅ NO ₅	nitropyrogallol 		W		I	W		M	W		I	W		
3	11.37-11.61		C ₇ H ₆ O ₃	salicylic acid 				W			W	I		W	W		
4	14.37-14.56		C ₉ H ₈ O ₃	veratraldehyde 	W	W	W	I	W		I	M	W	W	I	W	

Peak #	LC RT (min)	Absorption spectrum	Elemental formula of neutral species	Examples of possible structures	subalpine fir	duff	ceanothus	chamise	longleaf pine	juniper	ponderosa pine log	manzanita	lodgepole pine	engelmann spruce duff	ponderosa pine litter	douglas fir	sagebrush
5	15.17-15.46		$C_9H_6O_3$	umbelliferone 	W		W		W	I	W	W	W	W		W	W
6	16.12-16.24		$C_6H_5NO_4$	nitrocatechol 			W	I	W						W		I
7	17.20-17.42		$C_7H_7NO_5$	hydroxynitroguaiacol 	W				W	W	I	W	W	W	W	W	W
8	18.13-18.18		$C_{11}H_{12}O_4$	sinapaldehyde 			M	M	W		M	W		M			M

Peak #	LC RT (min)	Absorption spectrum	Elemental formula of neutral species	Examples of possible structures	subalpine fir duff	ceanothus	chamise	longleaf pine	juniper	ponderosa pine log	manzanita	lodgepole pine	engelmann spruce duff	ponderosa pine litter	douglas fir	sagebrush
9	18.33-18.47		$C_{10}H_{10}O_3$	<p>coniferaldehyde</p>	M	I	W	M	M	M	W	M		M	M	M
10	23.32-23.49		$C_7H_7NO_4$	<p>methyl nitrocatechol</p>		W	W	W		W	W	W		W		I
11	27.15-27.29		$C_{15}H_{10}O_6$	<p>kaempferol</p>				I	W		W	M		W	I	
12	28.80-28.85		$C_{11}H_{13}NO$ 5			W	M									M

Peak #	LC RT (min)	Absorption spectrum	Elemental formula of neutral species	Examples of possible structures	subalpine fir	duff	ceanothus	chamise	longleaf pine	juniper	ponderosa pine log	manzanita	lodgepole pine	engelmann spruce duff	ponderosa pine litter	douglas fir	sagebrush
13	29.08-29.34		$C_{14}H_{14}O_4$	<p>nodakenetin</p> 	M				M	M	I	W	M	I	M	M	I
14	31.85-31.90		$C_{16}H_{12}O_6$	<p>diosmetin</p> 					W				I		W		
15	41.63-41.98		$C_{18}H_{16}O_2$ $C_{17}H_{10}O$ $C_{16}H_{10}O$				W	W	W		W		W	W	W	W	W
16	43.95-44.05		$C_{17}H_{14}O_5$ $C_{19}H_{10}O$				I	I									W
17	55.51-55.63		$C_{18}H_{10}$				W	I		W							I

Peak #	LC RT (min)	Absorption spectrum	Elemental formula of neutral species	Examples of possible structures	subalpine fir duff	ceanothus	chamise	longleaf pine	juniper	ponderosa pine log	manzanita	lodgepole pine	engelmann spruce duff	ponderosa pine litter	douglas fir	sagebrush	
18	59.54-59.63		$C_{20}H_{12}$ $C_{20}H_{14}$ $C_{20}H_{10}$			W	W										W
19	60.61-60.78		$C_{16}H_{12}$			W	W										W
20	63.15-63.23		$C_{25}H_{12}O$ $C_{23}H_{10}O_2$				W										W
21	64.11-64.28		$C_{22}H_{12}$			W	I										I

Peak #	LC RT (min)	Absorption spectrum	Elemental formula of neutral species	Examples of possible structures	subalpine fir duff	ceanothus	chamise	longleaf pine	juniper	ponderosa pine log	manzanita	lodgepole pine	engelmann spruce duff	ponderosa pine litter	douglas fir	sagebrush	
22	65.61-65.74*		$C_{24}H_{14}$ $C_{23}H_{14}$ $C_{27}H_{12}O$				W										W
23	67.37-67.46*		$C_{24}H_{12}$ $C_{24}H_{14}$ $C_{23}H_{12}$				W										W
24	68.15-68.27		$C_{23}H_{14}$				W										W
25	71.77-71.89*		$C_{26}H_{14}$ $C_{26}H_{12}$				W										W

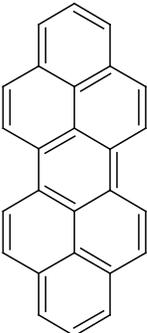
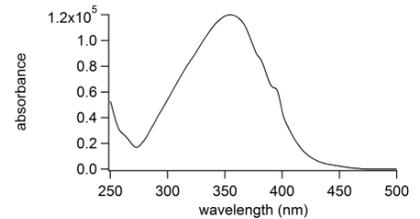
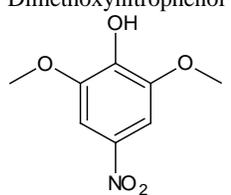
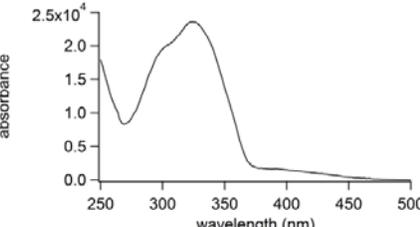
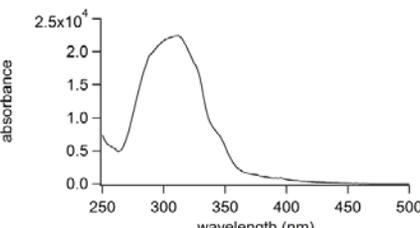
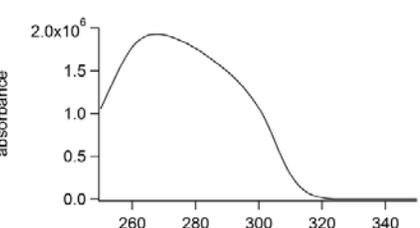
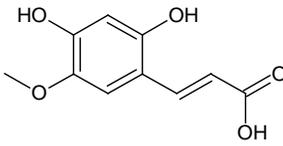
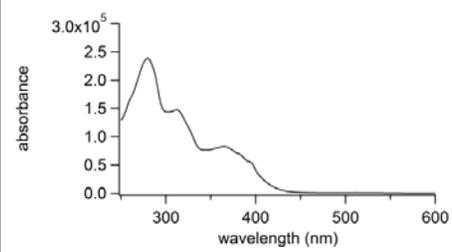
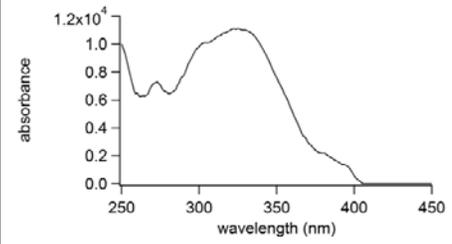
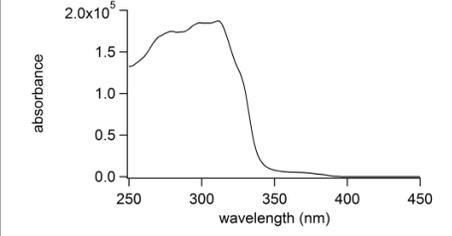
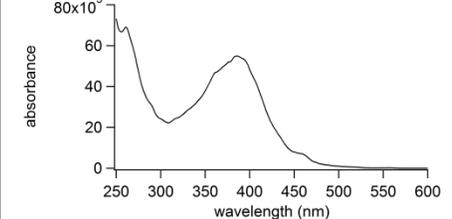
Peak #	LC RT (min)	Absorption spectrum	Elemental formula of neutral species	Examples of possible structures	subalpine fir duff	ceanothus	chamise	longleaf pine	juniper	ponderosa pine log	manzanita	lodgepole pine	engelmann spruce duff	ponderosa pine litter	douglas fir	sagebrush
																

Table 2. Chromophores found appreciably in only one fuel type listed by their HPLC retention time, absorption spectra, assigned elemental formulas, and examples of possible structures. The absorbance by each chromophore is binned by photodiode array absorbance normalized to the highest absorbance in each chromatogram: M-Major (75%-100%), I-Intermediate (25%-75%), or W-Weak (5%-25%).

Peak #	LC RT (min)	Absorption spectrum	Elemental formula	Intensity bin	Examples of possible structures	Fuel type
26	14.22		$C_{10}H_8O_4$	I	<p>scopoletin</p>	sagebrush
27	17.08		$C_{13}H_{14}O_4$	W		chamise
28	18.87		$C_{10}H_{10}O_2$	W		subalpine fir duff
29	21.82		$C_7H_7NO_5$ (isomer of methyl nitrocatechol)	W		sagebrush

Peak #	LC RT (min)	Absorption spectrum	Elemental formula	Intensity bin	Examples of possible structures	Fuel type
30	22.21		$C_8H_9NO_5$	W	Dimethoxynitrophenol 	chamise
31	22.43		$C_{12}H_{12}O_4$	W		lodgepole pine
32	23.65		$C_{18}H_{18}O_5$	W		lodgepole pine
33	24.42		$C_{10}H_{10}O_5$	W		ceanothus

Peak #	LC RT (min)	Absorption spectrum	Elemental formula	Intensity bin	Examples of possible structures	Fuel type
34	26.17	 <p>The graph shows absorbance on the y-axis (0.0 to 3.0x10⁻⁵) and wavelength in nm on the x-axis (250 to 600). The curve has a primary peak at ~280 nm (absorbance ~2.3x10⁻⁵) and a secondary peak at ~350 nm (absorbance ~0.8x10⁻⁵).</p>	C ₂₀ H ₂₂ O ₆	W		ponderosa pine log
35	26.95	 <p>The graph shows absorbance on the y-axis (0.0 to 1.2x10⁻⁴) and wavelength in nm on the x-axis (250 to 450). The curve has a peak at ~330 nm (absorbance ~1.1x10⁻⁴) and a secondary peak at ~270 nm (absorbance ~0.6x10⁻⁴).</p>	C ₁₁ H ₆ O ₃ C ₁₇ H ₁₄ O ₈	W		lodgepole pine
36	30.35	 <p>The graph shows absorbance on the y-axis (0.0 to 2.0x10⁻⁵) and wavelength in nm on the x-axis (250 to 450). The curve has a broad peak centered at ~320 nm (absorbance ~1.8x10⁻⁵).</p>	C ₁₂ H ₁₃ NO ₄ C ₁₆ H ₁₆ O ₆	W		ponderosa pine log
37	32.55	 <p>The graph shows absorbance on the y-axis (0 to 80x10⁻³) and wavelength in nm on the x-axis (250 to 600). The curve has a peak at ~380 nm (absorbance ~55x10⁻³) and a secondary peak at ~270 nm (absorbance ~70x10⁻³).</p>	C ₁₀ H ₇ NO ₃	W		sagebrush

Peak #	LC RT (min)	Absorption spectrum	Elemental formula	Intensity bin	Examples of possible structures	Fuel type
38	34.69		$C_{16}H_{12}O_5$	W		ceanothus
39	35.25		$C_{11}H_9NO_3$	W		chamise
40	35.37		$C_{17}H_{14}O_6$	I		ceanothus
41	39.38		$C_{16}H_{10}O_3$	W		chamise

Peak #	LC RT (min)	Absorption spectrum	Elemental formula	Intensity bin	Examples of possible structures	Fuel type
42	40.22		$C_{18}H_{16}O_6$	I		ceanothus
43	40.53		$C_{17}H_{20}O_4$	W		ponderosa pine log
44	44.26		$C_{32}H_{28}O_4$	W		subalpine fir duff
45	45.7		$C_{22}H_{26}N_4O$	W		subalpine fir duff

Peak #	LC RT (min)	Absorption spectrum	Elemental formula	Intensity bin	Examples of possible structures	Fuel type
46	49.05		$C_{20}H_{24}O_4$	W		ponderosa pine log

*Lin et al. (2018)

Table 3. Filter irradiation times for different samples used to estimate lifetimes of individual chromophores.

Fuel type	Irradiation time #1 (hrs)	Irradiation time #2 (hrs)	Irradiation time #3 (hrs)	Figure used
Lodgepole-pine	6	16.8		3,5
Ceanothus	16			4
Chamise	4	3	12	5
Manzanita	6	16.8		5

760 | **Table 3.4. Lifetimes for the loss of the measured integrated absorbance from 300 to 700 nm. The results are expressed in equivalent days of solar exposure to either time-averaged solar flux in Los Angeles (middle column) or peak solar flux at SZA=0° (right column). The lifetimes were calculated from the transmission spectra measured for particles on PTFE filters. The irradiation was done in the condensed phase, on the filter, for all samples.**

Fuel type	BrC <u>absorption</u> lifetime based on condensed phase measurements averaged LA (equivalent days)	BrC <u>absorption</u> lifetime based on condensed phase measurements SZA=0° (equivalent days)
Longleaf pine	25 ± 0	8.5 ± 0
Juniper	41 ± 4	14 ± 1
Ponderosa pine litter	17 ± 1	6.0 ± 0
Subalpine fir duff	10 ± 2	3.4 ± 1

Table of Contents

Spectral flux/irradiance measurements for LED and Xe Arc lamps (2)

Calculation of the estimated BrC absorption lifetime and individual BrC chromophore lifetime ~~Calculation of the estimated BrC absorption lifetime~~ (3)

Example transmission spectrum of condensed phase BBOA sample on a Teflon substrate (4)

Summary of fires (5)

Filter irradiation times for different samples used to estimate lifetimes of individual chromophores (6)

References (76)

Formatted: Font: Not Italic

Formatted: Font: 10 pt, Not Bold

Formatted: Font: Not Bold

Spectral flux/irradiance measurements for LED and Xe Arc lamps

The spectral flux density of the LED is calculated from actinometry measurements. The procedure is described in detail in Lignell et al. (2013) and described briefly here. We assume that the relative spectral density ($OO(\lambda)$) or the radiation from the LED lamp as detected by an Ocean Optics spectrometer (USB4000), is proportional to the spectral flux density ($D(\lambda)$) of the LED lamp as shown in equation 2.

$$D(\lambda) = \alpha \times OO(\lambda) \quad (S1)$$

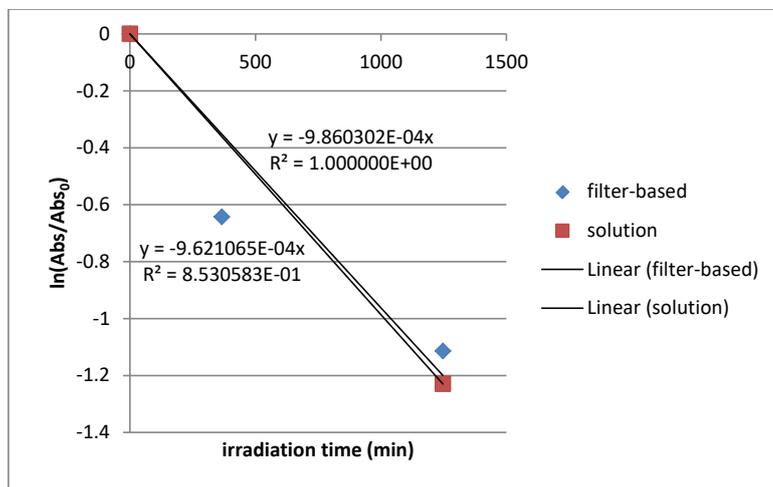
The proportionality constant, α , with units of photons $\text{cm}^{-2} \text{s}^{-1} \text{nm}^{-1}$ was calculated using equation S2. The parameter in this equation include: pathlength through the cuvette (b), the average quantum yield of the actinometer ($\langle \varphi_{\text{act}} \rangle$), the fraction of the cuvette irradiated ($f_{\text{irradiated}}$), the base-e absorption cross section ($\sigma(\lambda)$), the number concentration in molecules cm^{-3} (n), and $\frac{-dn_{\text{act}}}{dt}$ (molecules $\text{cm}^{-3} \text{s}^{-1}$) is the rate at which the actinometer is consumed as it is irradiated (see below for details).

$$\alpha = \frac{\frac{-dn_{\text{act}}}{dt} \times \frac{b}{\langle \varphi_{\text{act}} \rangle \times f_{\text{irradiated}}}}{\int_{290}^{320} OO(\lambda) [1 - e^{-\sigma(\lambda) \times n \times b}] d\lambda} \quad (S2)$$

Azoxybenzene was selected as the actinometer because it has a known photoisomerization quantum yield of roughly 0.020 that is independent of temperature and concentration over the wavelength range of interest, 250-350 nm (Bunce et al., 1984). A solution of 0.2 mM azoxybenzene and 6.0 mM KOH in ethanol was prepared. A cuvette containing the solution was irradiated by the LED in a similar configuration (0.5 cm from cuvette) for 10 s intervals. UV-Vis spectra were collected at each interval using a UV-2450 Shimadzu UV-Vis spectrometer. The appearance of the photoisomerization product was probed from the absorbance at 458 nm. This absorbance is converted to concentration using the known molar absorptivity of the actinometer. Ultimately, after multiple unit conversions, we calculate $\frac{-dn_{\text{act}}}{dt}$ from this experiment. The calculated spectral flux as a function of wavelength is shown in Figure 1.

Calculation of the estimated BrC absorption lifetime and individual BrC chromophore lifetime

The natural log of the integrated absorbance (300-700 nm) divided by the initial integrated absorbance (300-700 nm) is plotted as a function of the irradiation time, as shown below in Figure S1. This is done for both the ~~condensed phase~~ filter-based and solution phase absorption measurements (for solution only two points could be obtained at the start and end of the experiment because of the limited number of filter samples). Example absorption spectra are shown in Figure S2. The data points are fitted to a linear trend line with the y-intercept forced through 0, from which the magnitude of the slope is the rate constant, k (min^{-1}). The reciprocal of k gives the lifetime of the integrated absorption (300-700 nm) under the lamp. The lifetime is converted to an atmospheric lifetime with equation 1 in the main paper. This procedure is used for individual chromophores as well as overall BrC absorbance.



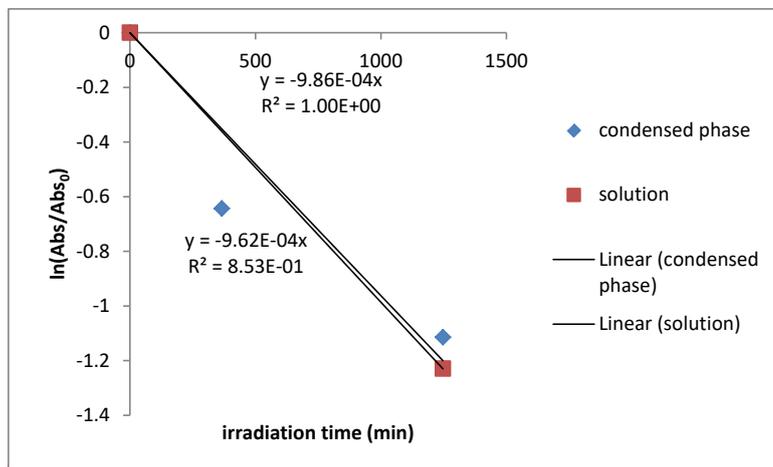


Figure S1. The natural logarithm of the integrated absorbance (300-700 nm), Abs/Abs_0 , plotted as a function of irradiation time. The magnitude of the slope of the trend line corresponds to the first-order decay constant (s^{-1}) according to the integrated first order rate law. The inverse of the first-order decay constant is the lifetime of the overall absorption (300-700 nm) of the BBOA material.

Comment [LF1]: Change condensed phase in graph to filter

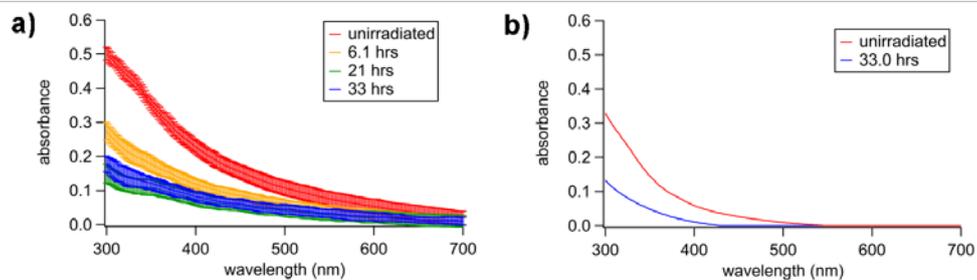


Figure S2. Absorption spectra of the same subalpine fir BBOA sample, recorded **in a) the condensed phase through a filter** (by measuring transmission through particle-loaded filter material) and **b) in the solution phase** (by measuring transmission through a cuvette with a solvent extracted sample). The average of four absorption spectra is shown for each irradiation time point in a), and the standard deviation of these measurements are indicated with error bars.

Table S1. Summary of the test fires from which BBOA samples were collected. The last column gives the section(s) of the paper for which the sample was used.

Fuel name	Fire ID#	Modified Combustion Efficiency	Max NO (ppmv)	Ecosystem components	Section(s) used
Subalpine fir duff	90	0.92	0.27	Duff	BrC chromophores
Ceanothus	89	0.95	2.48	Shrub	BrC chromophores Condensed phase photolysis (LED, individual)
Chamise	84	0.95	3.79	Canopy	BrC chromophores
Longleaf pine	97	0.93	0.67	Duff, litter, shrub, herbaceous, canopy	BrC chromophores Condensed phase photolysis (xe-arc, overall BrC abs)
Juniper	88	0.95	1.72	Canopy	BrC chromophores Condensed phase photolysis (xe-arc, overall BrC abs)
Ponderosa pine log	105	0.92	0.13	Log	BrC chromophores
Manzanita	91	0.95	2.33	Canopy	BrC chromophores Condensed phase photolysis (LED, individual)
Lodgepole pine	87	0.93	0.99	Canopy	BrC chromophores Condensed-phase photolysis (LED, individual)
Engelmann spruce	83	0.82	0.08	Duff	BrC chromophores
Ponderosa pine	106	0.95	1.61	Litter, canopy needle and branch	BrC chromophores Condensed phase photolysis (xe-arc, overall BrC abs)
Douglas fir	80	0.93	0.43	Duff, litter, shrub, herbaceous, canopy	BrC chromophores
Sagebrush	85	0.94	1.62	shrub	BrC chromophores
Chamise	46*	0.96	12.18	Canopy	Condensed-phase photolysis (LED, individual)
Subalpine fir	81	0.93	0.35	Litter, debris, shrub, herbaceous, canopy	Condensed phase photolysis (xe-arc, overall BrC abs)

*Different configuration– Stack burn

Table S2. Filter irradiation times for different samples used to estimate lifetimes of individual chromophores.

<u>Fuel type</u>	<u>Irradiation time #1 (hrs)</u>	<u>Irradiation time #2 (hrs)</u>	<u>Irradiation time #3 (hrs)</u>	<u>Sample used in figure #</u>
<u>Lodgepole pine</u>	<u>6</u>	<u>16.8</u>		<u>3,5</u>
<u>Ceanothus</u>	<u>16</u>			<u>4</u>
<u>Chamise</u>	<u>1</u>	<u>3</u>	<u>12</u>	<u>5</u>
<u>Manzanita</u>	<u>6</u>	<u>16.8</u>		<u>5</u>

References

Bunce, N. J., Lamarre, J. and Vaish, S. P.: Photorearrangement of azoxybenzene to 2-hydroxyazobenzene: a convenient chemical actinometer, *Photochem. Photobiol.*, 39(4), 531–533, doi:10.1111/j.1751-1097.1984.tb03888.x, 1984.

Lignell, H., Epstein, S. A., Marvin, M. R., Shemesh, D., Gerber, B. and Nizkorodov, S.: Experimental and Theoretical Study of Aqueous *cis* -Pinonic Acid Photolysis, *J. Phys. Chem. A*, 117(48), 12930–12945, doi:10.1021/jp4093018, 2013.