Response to 2nd review by Reviewer #3

Fleming et al. have carefully addressed the concerns of reviewers. I commend the authors on their thorough responses. They have addressed my concerns and, apart from a few minor comments/suggestions listed below, I believe this manuscript is suitable for publication in ACP. There is some inconsistency with using English names or molecular formulas for chemical species (e.g. line 62 "HONO and nitrogen dioxide").

We went through the manuscript trying to make names more consistent and refine writing in general. We did a number of other minor editing changes to improve the manuscript readability. The track-changed document is attached below for your reference.

My previous comment regarding the phrase (line 145) was not well expressed. My concern with this sentence is that it currently reads as if the same sample was extracted with solvents of multiple polarities (i.e. an extraction study), which this is not. I suggest re-phrasing slightly to clarify that different methods are applied to different samples.

Good point. We now say "Samples collected on filters were extracted by a mixture of dichloromethane, acetonitrile, and hexanes…"

The phrase on line 410 "…exhibited a reduction in absorbance almost exactly to that observed in the filter…" is awkward. Suggest re-phrasing."

The new sentence is: "The reduction in absorbance in the solution-phase spectra was comparable to that observed in the filter transmission spectra (Figure S2)."

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

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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 biomass burning organic aerosol (BBOA) 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 condensed-phase photochemical processes

converted one set of chromophores into another without complete photobleaching, or from undetected BrC chromophores that photobleached more slowly. To model the effect of BrC on climate, it is important to understand the change in the overall 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 lifetime. 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 of BBOA particles by atmospheric photolysiscondensed-phase photochemistry is relatively slow. Other Competing chemical aging mechanisms, such as heterogeneous oxidation by OH, may be more important for controlling the rate of BrC degradationphotobleaching in BBOA 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 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. (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 (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 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 who 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 (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 dioxideNO$_2$, which affect the mixing ratios of ozone and hydroxyl radicalsatmospheric oxidants (Jiang et al., 2012; Li et al., 2011). To better quantify the ir effect of BrC on climate, the chemical composition and lifetimes of individual BrC chromophores, as well as

~~their light absorption properties~~the effect of photochemical aging on the optical properties of BrC particles should be studied. Further, for a comprehensive understanding, we should consider the diversity of BrC, spanning nonpolar to polar molecules, and BBOA particles from a range of sources.

70 Previous studies have identified important classes of BBOA chemical components that ~~are responsible for~~ contribute to 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). Polycyclic aromatic compounds (PAHs) have long been known to

75 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 be comprised

80 primarily of oxygenated organic compounds, similar to that of BBOA particles (Chakrabarty et al., 2010; Girotto et al., 2018; Li et al., 2019; Pósfai et al., 2004; Sedlacek III et al., 2018).

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

85 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

90 relevant surrogates via heterogeneous photooxidation (exposure of particles to gaseous OH and other oxidants), 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.

95 (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-Makuła, 2017). Shankar et al. (2019) found that Tthe 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 $m^2 g^{-1}$ 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 deceased 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 a mixture of dichloromethane, acetonitrile, and hexanes~~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 under UV irradiated conditions by measuring the time resolved absorbance of individual chromophores. We found that the equivalent atmospheric lifetime ~~due to photolysis~~for photochemical transformations 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~~under UV irradiation, with lifetimes ranging from 10-41 days, presumably because ~~some photolysis~~ products of the condensed-phase photochemical reactions of the original BrC chromophores are also light-absorbing. The equivalent atmospheric ~~photolysis~~ lifetimes of BrC absorption under UV irradiation 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~~ condensed-phase photochemistry may play a more significant role in the evolution of the BrC optical properties.

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2 Experimental methods

2.1 *Sample collection and information*

BBOA particle samples were collected ~~at~~ during 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 engelmanii*), 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 N_2 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. Visual inspection confirmed that tThe 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 irradiated samples, with the latter providing more analyte mass since only a quarter of the filter was used in photolysis irradiation 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 photochemistry experimentslysis*

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 S2. 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.

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

The spectral flux density for the LED and the sun as a function of wavelength is shown in Figure 1. The solar flux density
230 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
235 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.

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
240 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/cm^2. 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
245 without any material extraction using a Jasco V-670 absorption spectrometer, with a blank PTFE filter used as a reference. 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~~ irradiation 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
250 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 down to 5 mL 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,
255 with the Y-axis converted to effective base-10 absorbance, A = -log(T), where T is the wavelength-dependent transmittance

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through the filter or the cuvette. For filter-based transmission spectra, the baseline was manually corrected by assuming the absorbance at 850 nm was ~~zero~~0 for BrC.

In all ~~photolysis~~ UV irradiation experiments, the integrated absorbance from 300 to 700 nm was calculated and normalized to the ~~un-irradiated~~ starting integrated absorbance before the UV exposure. 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 standards 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 table~~s~~.

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 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).

290   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.

295   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

300 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

305 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

310 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.

315   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). 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 still 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

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in the tables. Due to this constraint, chromophores in Table 2 may also be present in other fires, but at very low PDA 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.

3.2 Aging by condensed-phase photochemistry~~lysis~~

Gymnosperm (lodgepole pine) and angiosperm (ceanothus) BBOA particle samples were selected for the initial condensed-phase photochemistry~~lysis~~ experiments. BBOA filter samples from a lodgepole pine burn were ~~photolyzed~~ irradiated for 6 hours by an LED centered around 300 nm (which corresponds to approximately 33 hours of ~~photochemical aging~~irradiation from 24-hour average ~~spectral~~ solar flux density, see equation 1). BBOA particles from the ceanothus burn were ~~photolyzed~~ irradiated 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 photoresistant in both samples.

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 remained 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 we~~a~~re observed exclusively in this fire. These comparatively resilient species are aromatic, which helps them be more resistant to photodegradation.

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~~ chromatographically-separated BrC chromophores in the starting samples and for up to three ~~photolysis~~irradiation time points (listed in Table S2)~~ 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 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).

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~~ UV irradiation were obtained across fuel types for veratraldehyde (#4 in Table 1, $C_9H_8O_3$), 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~~ condensed-phase photochemical transformations 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 due to direct photolysis 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 3 summarizes the resulting lifetimes for BrC from four fuel types, longleaf pine, juniper, lodgepole pine, and subalpine fir. ~~It~~ Once again, 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 reduction in absorbance in the solution-phase spectra was comparable ~~exhibited a reduction in the absorbance almost exactly~~ to that observed in the filter transmission spectra (Figure S2). 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 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 3) are much longer than those of individual chromophores (Figure 5). There are two likely reasons for that. First, the ~~photodegradation~~ photochemical transformation of individual chromophores creates product(s) that may also absorb in the same wavelength range. The integrated BrC absorption (300-700 nm) may significantly decrease only after the compounds go through several successive stages of photodegradation, finally resulting in products that no longer absorb above 300 nm. The results of both ~~photolysis~~ UV irradiation 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 individual chromophores, has a higher density of higher energy photons compared to the Xe lamp (Figure 1), which could accelerate the observed photodegradation rate.

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-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 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 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.

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 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 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. Interestingly, individual BrC chromophore lifetimes varied based on the fuel burned and perhaps the underlying combustion

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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~~ photochemical mechanisms, such as photosensitized reactions, ~~the release of absorbed energy by a~~energy loss to neighboring

480   molecule~~s~~ ~~as heat depending on intermolecular forces~~, and shielding of light by other absorbing molecules could change depending on the specific BBOA 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.

Despite the rapid change in the absorbance of individual chromophores, the overall integrated BrC absorbance from 300 nm

485   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~~ UV irradiation 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

490   more smoldering combustion and had the shortest equivalent lifetime of 10 days, while BBOA from the juniper and lodgepole 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~~ that optical properties of BrC particles change slowly under UV-irradiated conditions, and other chemical aging mechanisms such as OH oxidation may be more important under atmospheric conditions. Based on these results, climate modelers should

495   first focus on chemical aging mechanisms other than ~~photolysis~~condensed-phase photochemistry, such as heterogeneous oxidation by OH.

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

500   wrote the paper. All co-authors provided edits and critical feedback for the paper.

Acknowledgements

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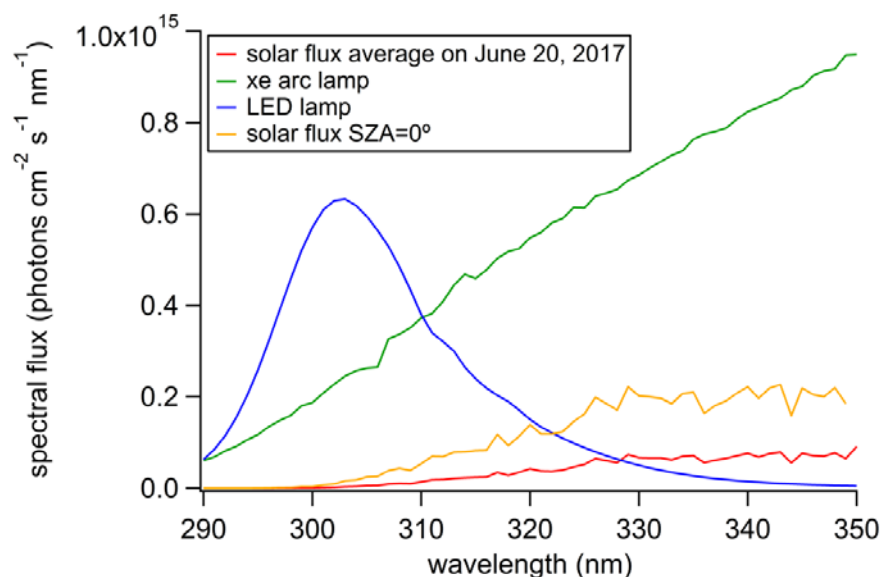
Figure 1. Spectral flux density (photons cm^{-2} s^{-1} nm^{-1}) approximated for a solar zenith angle of 0° (orange) as well as the 24-hour average for the latitude and longitude of Los Angeles (34° latitude, 118° longitude) on June 20, 2017 (red). The spectral flux density for the 300 nm LED (blue) and the filtered Xe arc lamp (green) are also shown.
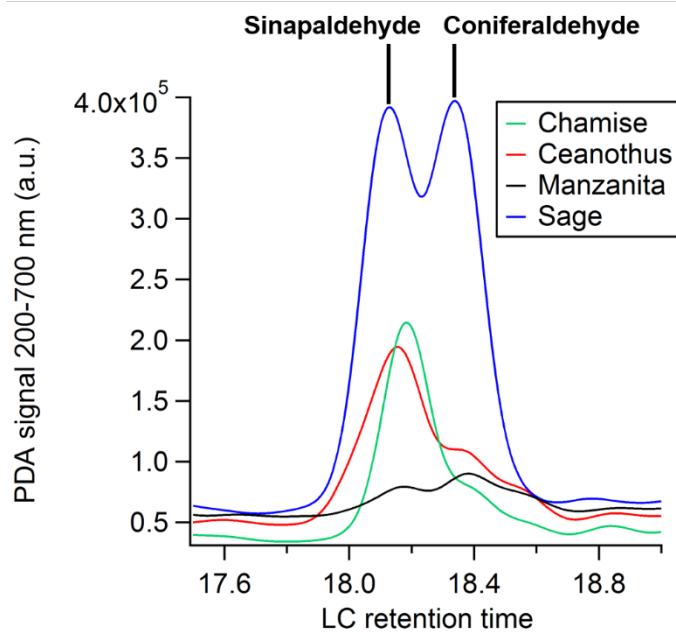
Figure 2. Lignin pyrolysis products sinapaldehyde ($C_{11}H_{12}O_4$) and coniferaldehyde ($C_{10}H_{10}O_3$) elute at slightly different retention times, at roughly 18.1 and 18.4 min, respectively.
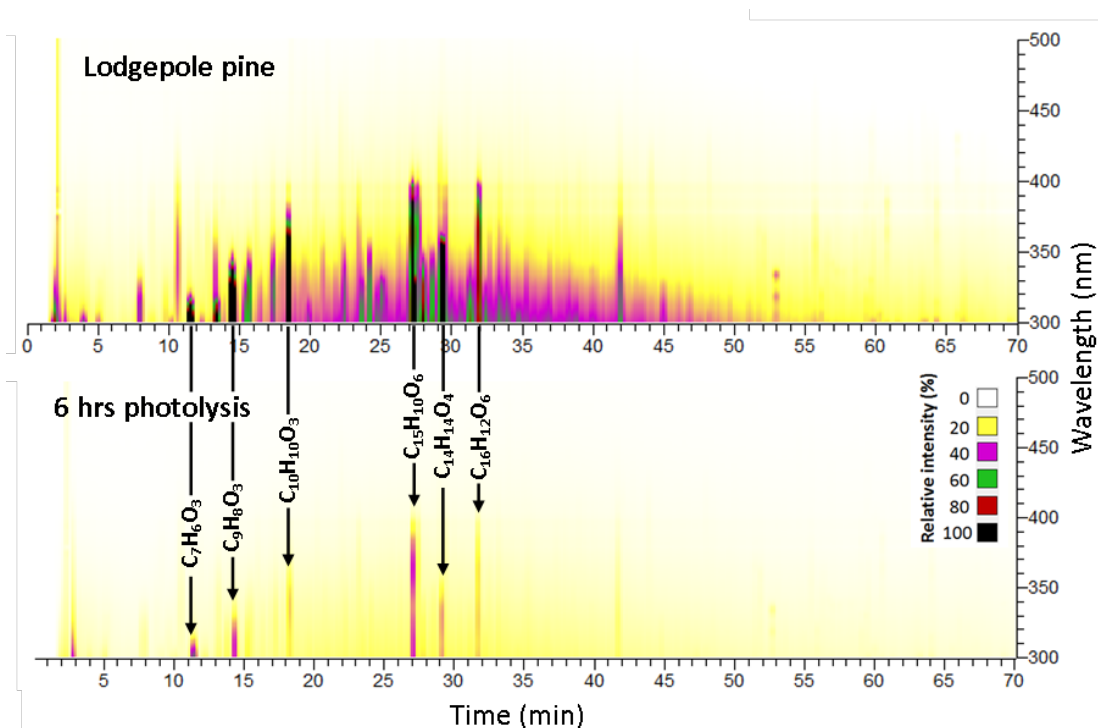
750 | **Figure 3. BrC chromophores present in the BBOA sample before (top panel) and after (bottom panel) 300 nm ~~photolysis~~ irradiation for a conifer fuel, lodgepole pine.**
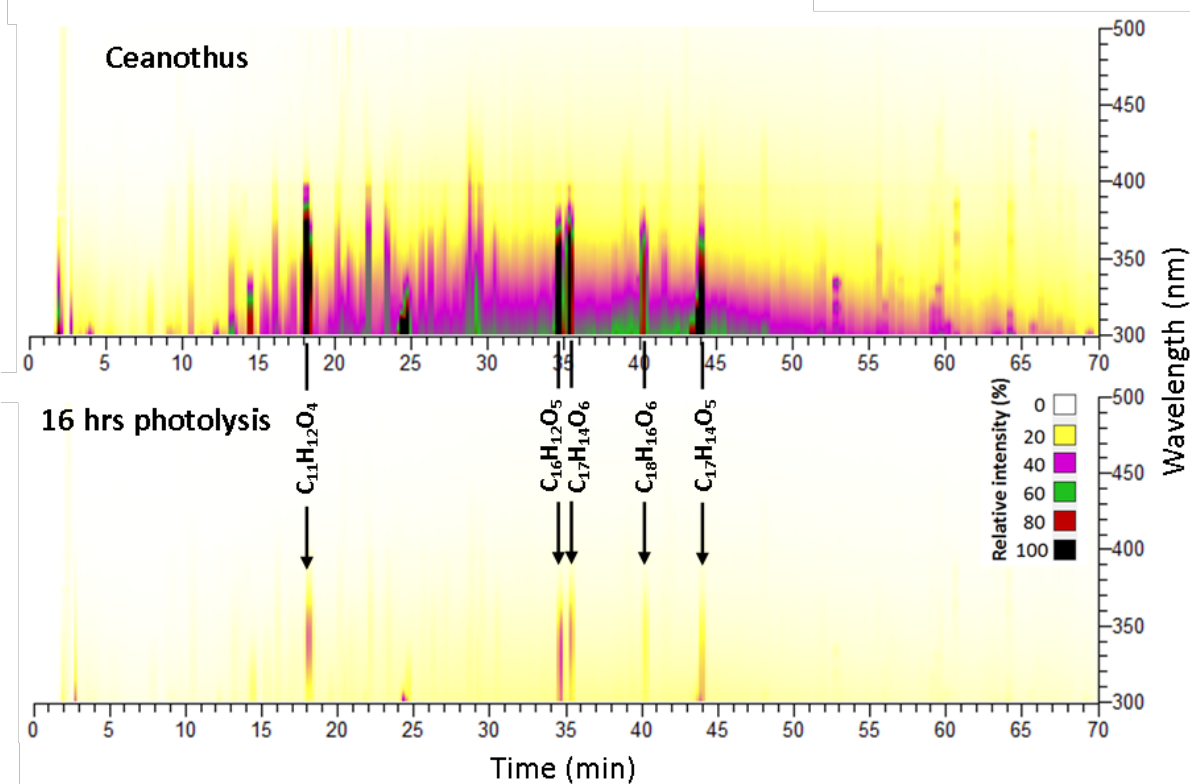
Figure 4. BrC chromophores present in the BBOA sample before (top panel) and after (bottom panel) 300 nm ~~photolysis~~ irradiation for angiosperm fuel, ceanothus.

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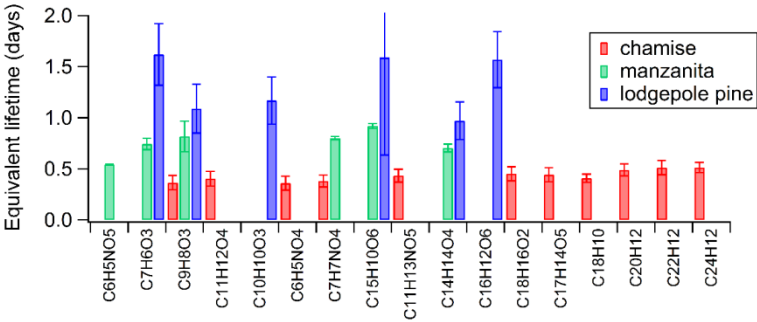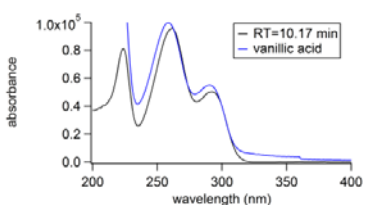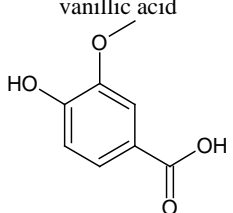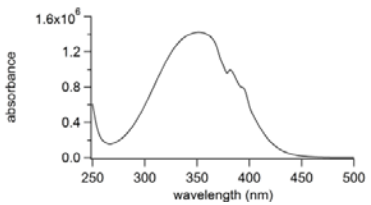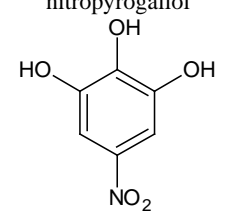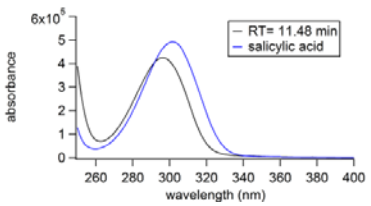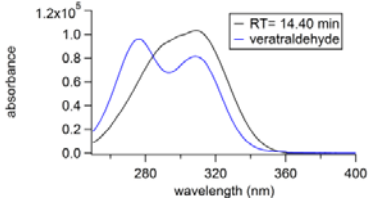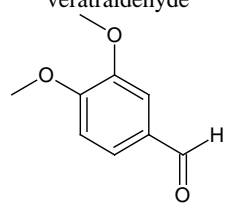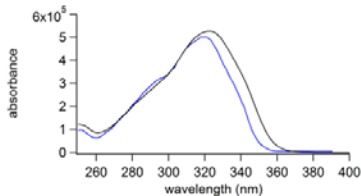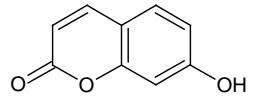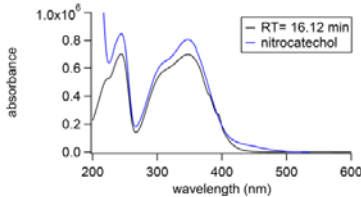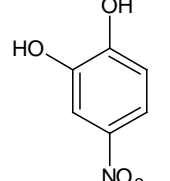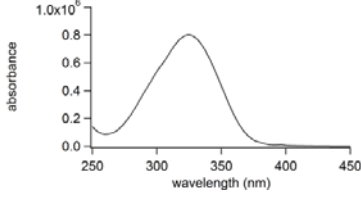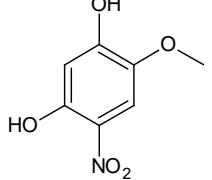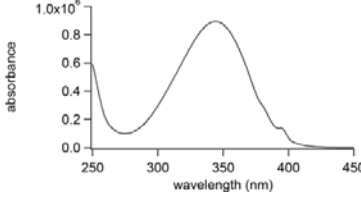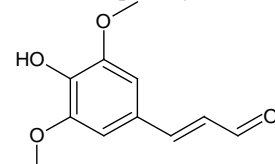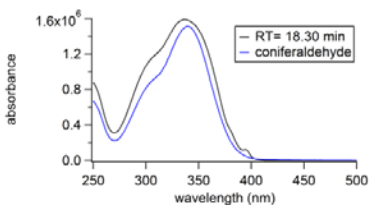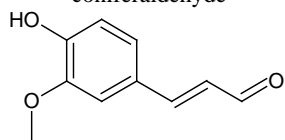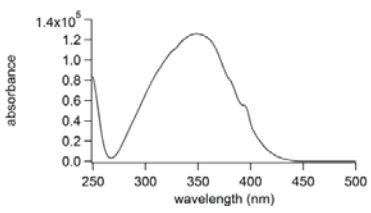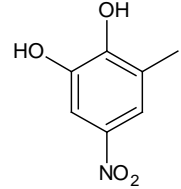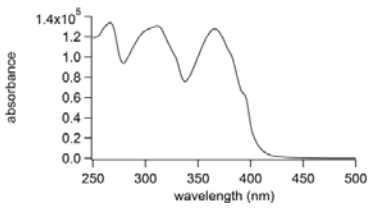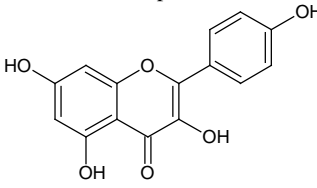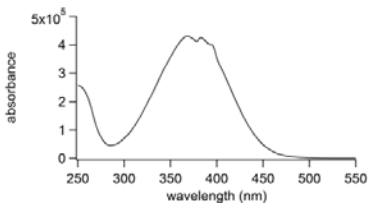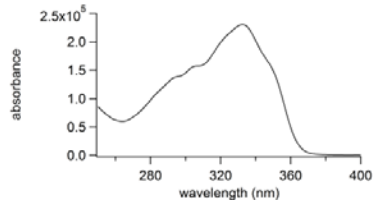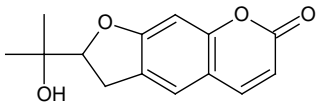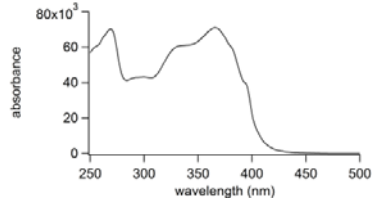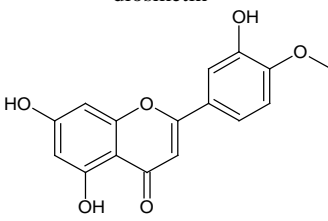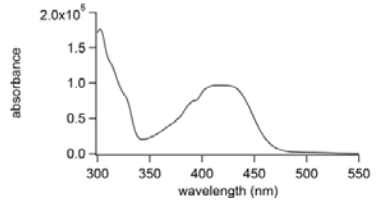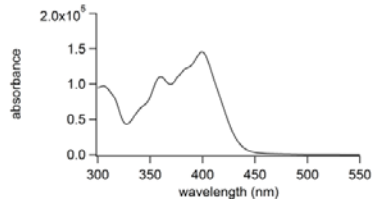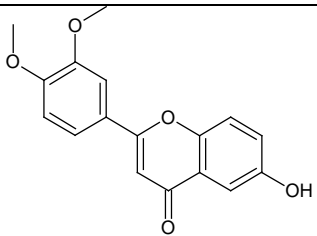
Figure 5. Approximate atmospheric lifetimes for select individual BrC chromophores due to ~~direct photolysis~~UV irradiation ~~that exist~~ in BBOA particles from chamise, manzanita, and lodgepole pine fires (the ~~photolysis~~ irradiation times are listed in Table S2). These lifetimes are shorter than those calculated for overall BrC absorption.
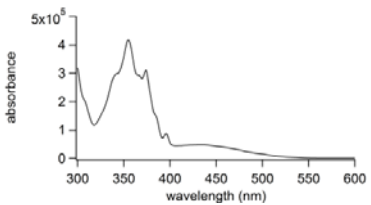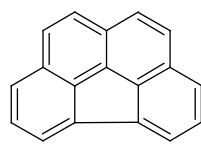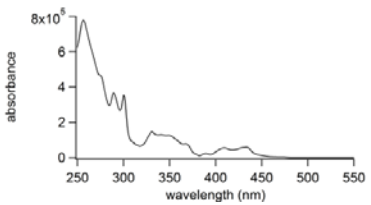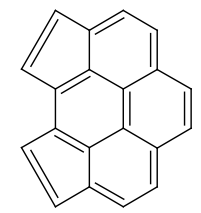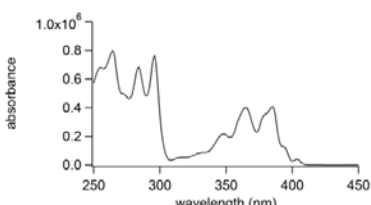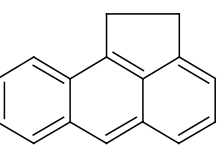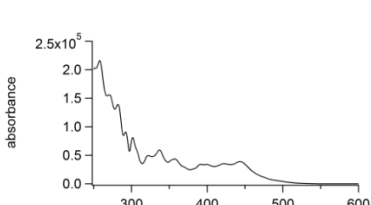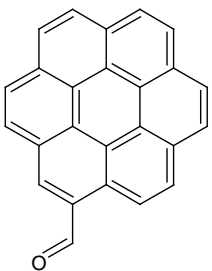
760 **Table 1. Chromophores common among multiple fuel types are listed by their HPLC retention times, absorption spectra, assigned elemental formulas, and examples of possible structures. The absorbance by each chromophore is binned by <u>integrated</u> photodiode array absorbance normalized to the 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.**
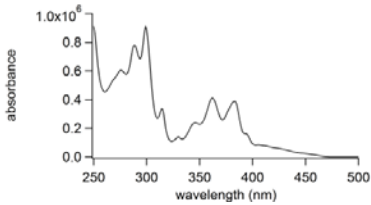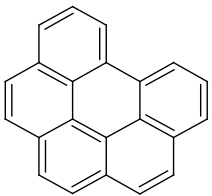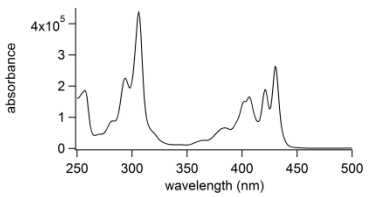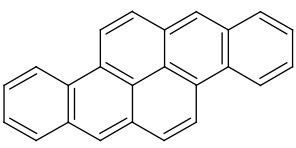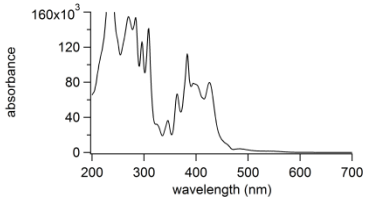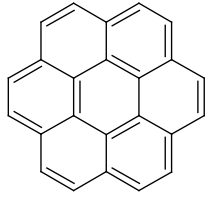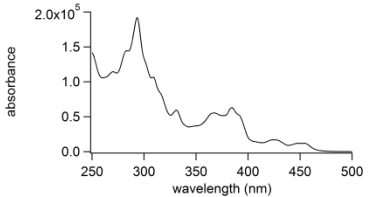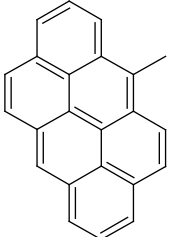
Peak #	LC RT (min)	Absorption spectrum	Elemental formula of neutral species	Examples of possible structures	subalpine fir duff	ceanothus	chamise	longleaf pine	juniper	ponderosa pine log	manzanita	lodgepole pine	engelmann spruce duff	ponderosa pine litter	douglas fir	sagebrush
1	10.07-10.29		$C_8H_8O_4$	vanillic acid	W						W			W		
2	10.52-10.71*		$C_6H_5NO_5$	nitropyrogallol		W			I	W	M	W		I	W	
3	11.37-11.61		$C_7H_6O_3$	salicylic acid					W			W	I		W	W	
4	14.37-14.56		$C_9H_8O_3$	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		$C_{10}H_{10}O_3$	coniferaldehyde	M	I	W	M	M	M	W	M		M	M	M
10	23.32-23.49		$C_7H_7NO_4$	methyl nitrocatechol		W	W	W		W	W	W		W		I
11	27.15-27.29		$C_{15}H_{10}O_6$	kaempferol				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		$C_{14}H_{14}O_4$	nodakenetin	M			M	M	I	W	M	I	M	M	I
14	31.85-31.90		$C_{16}H_{12}O_6$	diosmetin				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
16	43.95-44.05		$C_{17}H_{14}O_5$ $C_{19}H_{10}O$			I	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
17	55.51-55.63		$C_{18}H_{10}$			W	I		W							I
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

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
21	64.11-64.28		$C_{22}H_{12}$			W	I									I
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
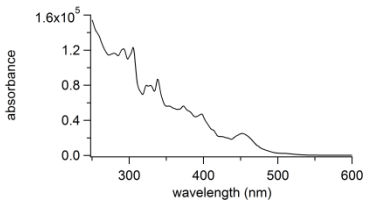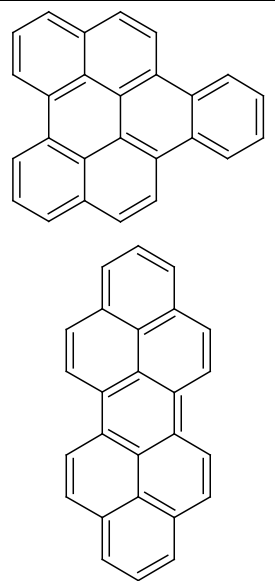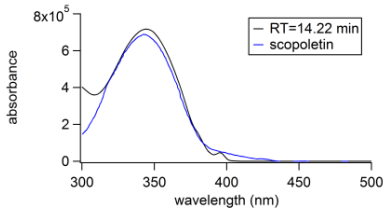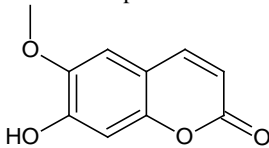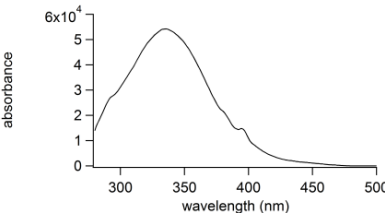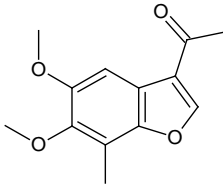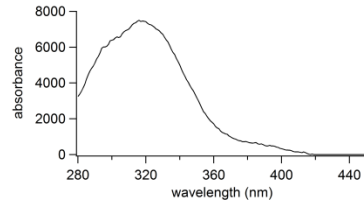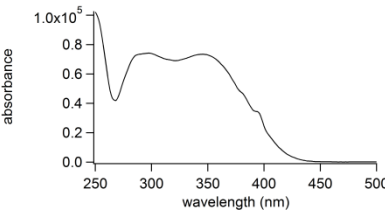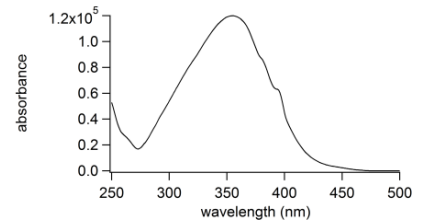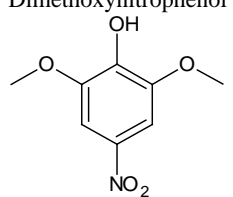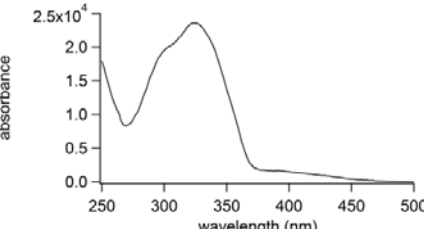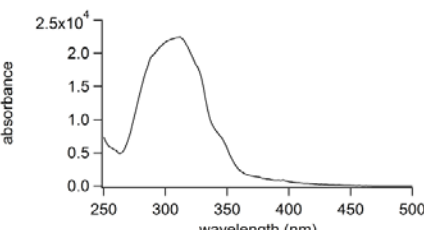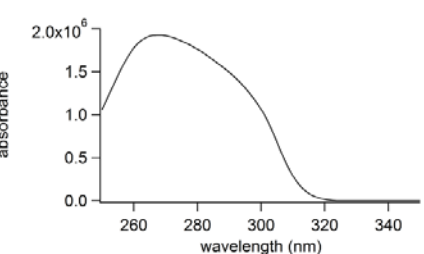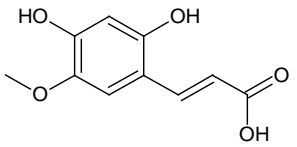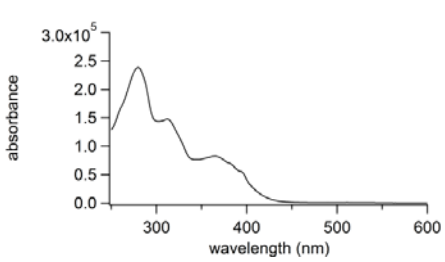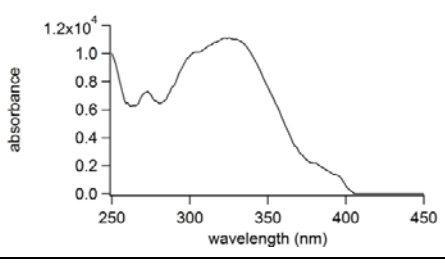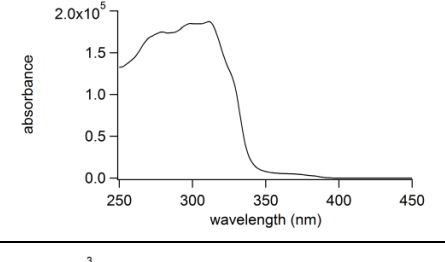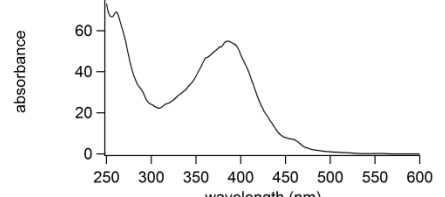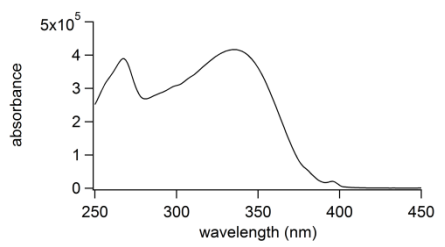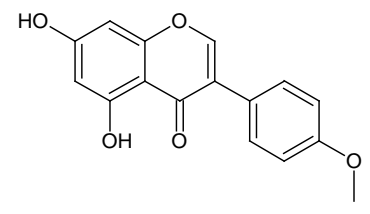
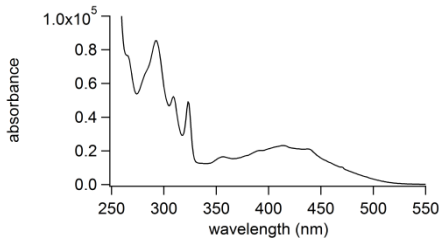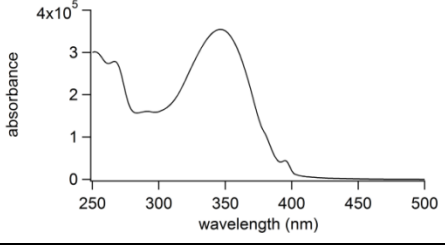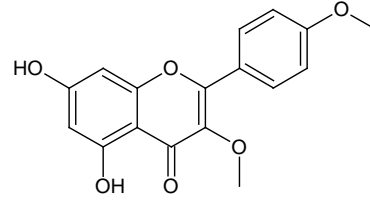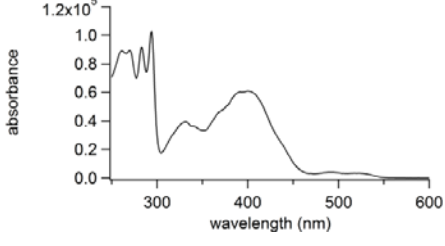| Peak #	LC RT (min)	Absorption spectrum	Elemental formula of neutral species	Examples of possible structures	subalpine fir duff	ceanothus	chamise	longleaf pine	juniper	ponderosa pine log	manzanita	lodgepole pine	engelmann spruce duff	ponderosa pine litter	douglas fir	sagebrush
25	71.77-71.89*		$C_{26}H_{14}$ $C_{26}H_{12}$				W									W

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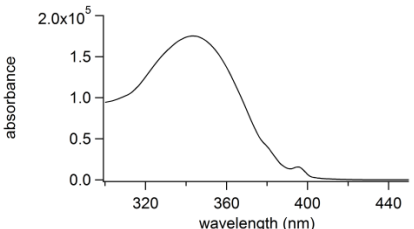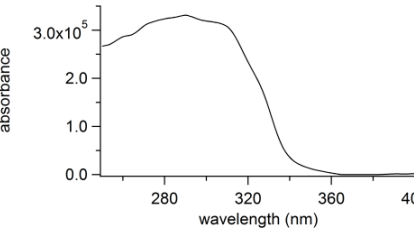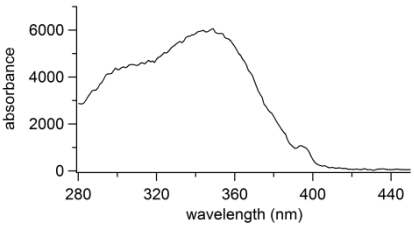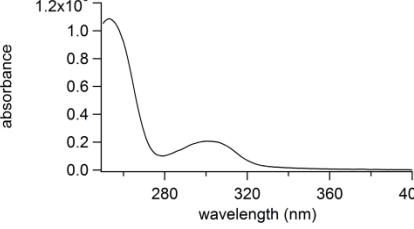
Table 2. Chromophores found appreciably in only one fuel type listed by their HPLC retention time, absorption spectra, assigned elemental formulas, and examples of possible structures. The absorbance by each chromophore is binned by <u>integrated</u> photodiode array absorbance normalized to the highest absorbance in each chromatogram: M-Major (75%-100%), I-Intermediate (25%-75%), or W-Weak (5%-25%).
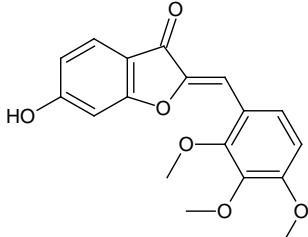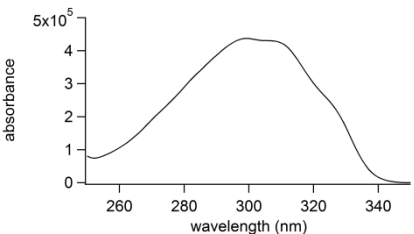
Peak #	LC RT (min)	Absorption spectrum	Elemental formula	Intensity bin	Examples of possible structures	Fuel type
26	14.22		$C_{10}H_8O_4$	I	scopoletin	sagebrush
27	17.08		$C_{13}H_{14}O_4$	W		chamise
28	18.87		$C_{10}H_{10}O_2$	W		subalpine fir duff
29	21.82		$C_7H_7NO_5$ (isomer of methyl nitrocatechol)	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		$C_{20}H_{22}O_6$	W		ponderosa pine log
35	26.95		$C_{11}H_6O_3$ $C_{17}H_{14}O_8$	W		lodgepole pine
36	30.35		$C_{12}H_{13}NO_4$ $C_{16}H_{16}O_6$	W		ponderosa pine log
37	32.55		$C_{10}H_7NO_3$	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

770   *Lin et al. (2018)

Table 3. 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 absorption lifetime averaged LA (equivalent days)	BrC absorption lifetime 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	10 ± 2	3.4 ± 1

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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.

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

The proportionality constant, α, with units of photons cm^{-2} s^{-1} 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 $\langle\varphi_{act}\rangle$, the fraction of the cuvette irradiated ($f_{irradiated}$), the base-e absorption cross section ($\sigma(\lambda)$), the number concentration in molecules cm^{-3} (n), and $\frac{-dn_{act}}{dt}$ (molecules cm^{-3} s^{-1}) is the rate at which the actinometer is consumed as it is irradiated (see below for details).

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

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 at 458 nm. Ultimately, after multiple unit conversions, we calculate $\frac{-dn_{act}}{dt}$ from this experiment. The calculated spectral flux as a function of wavelength is shown in Figure 1 of the main text.

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 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.
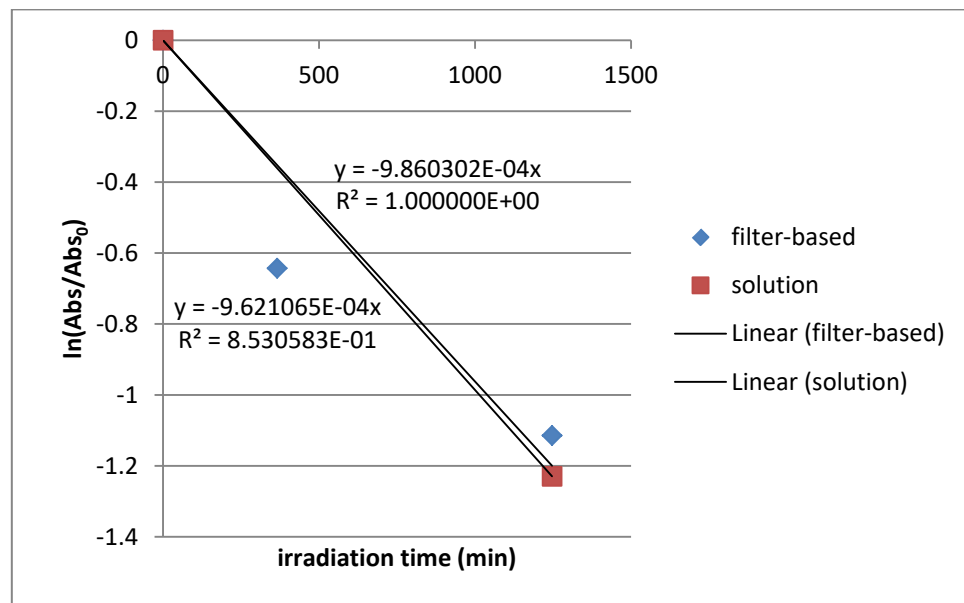

Figure S1. The natural logarithm of the integrated absorbance (300-700 nm), Abs/Abs$_0$, plotted as a function of irradiation time. The magnitude of the slope of the trend line corresponds to the first-order decay constant (s^{-1}) according to the integrated first order rate law. The inverse of the first-order decay constant is the lifetime of the overall absorption (300-700 nm) of the BBOA material. The fit was constrained to pass through the origin at time zero.
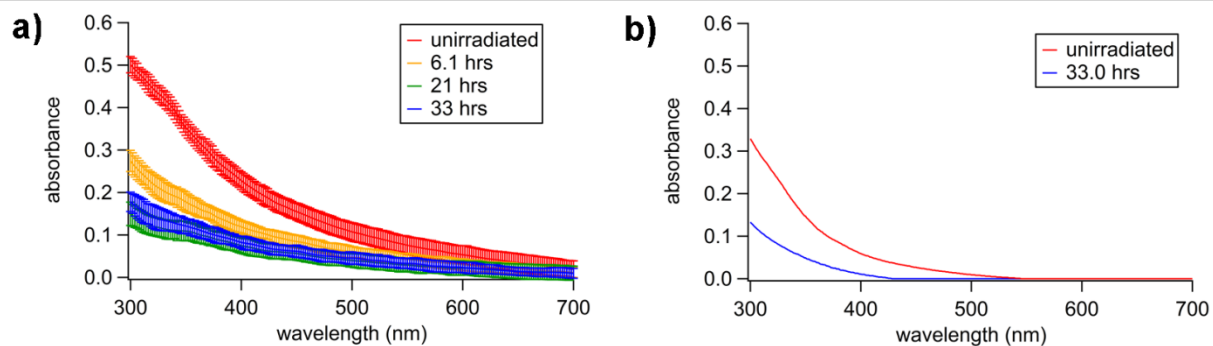
Figure S2. Absorption spectra of the same subalpine fir BBOA sample, recorded a) through a filter (by measuring transmission through particle-loaded filter material) and b) in the solution phase (by measuring transmission through a cuvette with a solvent extracted sample). The average of four absorption 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~~photochemistry (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~~photochemistry (X~~xe~~-arc, overall BrC abs)
Juniper	88	0.95	1.72	Canopy	BrC chromophores Condensed phase ~~photolysis~~photochemistry (X~~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~~photochemistry (LED, individual)
Lodgepole pine	87	0.93	0.99	Canopy	BrC chromophores Condensed-phase ~~photolysis~~photochemistry (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~~photochemistry (X~~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~~photochemistry (LED, individual)
Subalpine fir	81	0.93	0.35	Litter, debris, shrub, herbaceous, canopy	Condensed phase ~~photolysis~~photochemistry (X~~xe~~-arc, overall BrC abs)

*Different configuration– Stack burn

Table S2. 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)	Sample used in figure #
Lodgepole pine	6	16.8		3,5
Ceanothus	16			4
Chamise	1	3	12	5
Manzanita	6	16.8		5

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 tTheoretical sStudy of aAqueous *cis*--pPinonic aAcid pPhotolysis, J. Phys. Chem. A, 117(48), 12930–12945, doi:10.1021/jp4093018, 2013.