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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.

$$D(\lambda) = \alpha \times OO(\lambda) \tag{S1}$$

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 ((λ)), 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).

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

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

Calculation of the estimated BrC absorption lifetime

The natural log of the integrated absorbance (300-700 nm) divided by the initial integrated absorbance (300-700 nm) is plotted as a function of the irradiation time, as shown below in Figure S1. This is done for both the condensed-phase 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.
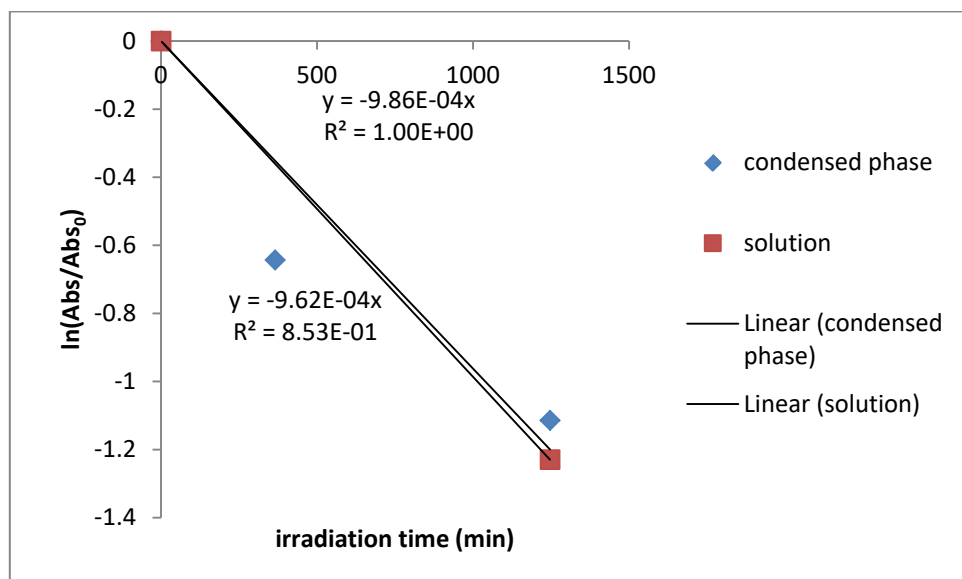
Figure S1. The natural logarithm of the integrated absorbance (300-700 nm), Abs/Abs$_0$, plotted as a function of irradiation time. The magnitude of the slope of the trend line corresponds to the first-order decay constant (s^{-1}) according to the integrated first order rate law. The inverse of the first-order decay constant is the lifetime of the overall absorption (300-700 nm) of the BBOA material.
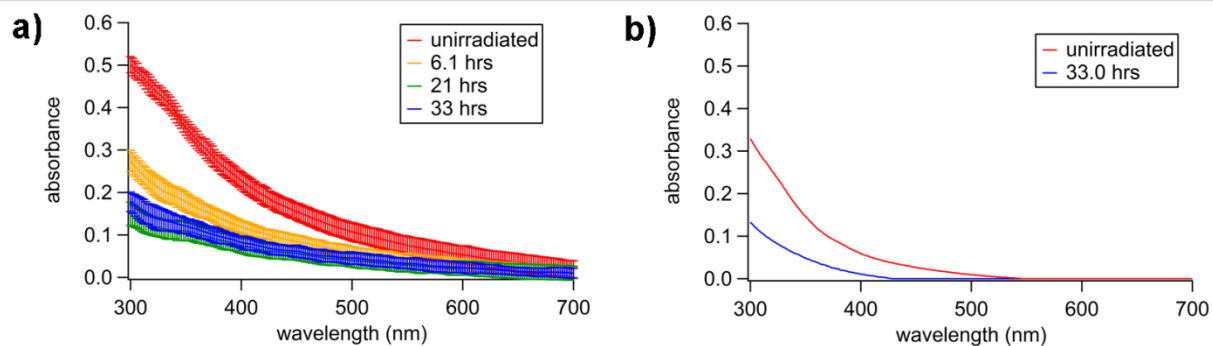
Figure S2. Absorption spectra of the same subalpine fir BBOA sample, recorded in a) the condensed phase (by measuring transmission through particle-loaded filter material) and b) the solution phase (by measuring transmission through a cuvette with a solvent extracted sample). The average of four absorption spectra is shown for each irradiation time point in a), and the standard deviation of these measurements are indicated with error bars.

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

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

*Different configuration– Stack burn

References

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

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