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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Molecular composition and photochemical lifetimes of brown carbon chromophores in biomass burning organic aerosol" *by* Lauren T. Fleming et al.

Anonymous Referee #1

Received and published: 18 July 2019

Fleming et al. present brown carbon observations from biomass burning emissions collected during FIREX. Smoke samples were analyzed using HPLC/PDA/HRMS to determine which compounds absorb in the 300-700 nm wavelength and their corresponding molecular formula. 46 brown carbon chromophores were separated and roughly identified. These compounds were further divided into classes such as lignin pyrolysis products and nitroaromatics. In addition, filters were photochemically aged. Two techniques were used to age the filters (1) LED light exposure and liquid extraction for HPLC/PDA/HRTMS analysis (2) irradiation of filters with xenon arc lamp and analysis by an absorption spectrometer. Their results indicate that smoke produced from specific fuels or fuel mixtures photochemically age at different rates, between 10-

41 days. Canopy fuels showed longer photochemical lifetimes than subalpine fir fuel mixtures. The authors point out that chemical aging mechanisms likely play a larger role in aging on these time scales than photochemical processes.

Overall, this study provides very interesting information on specific brown carbon compounds found in fresh and aged emissions. The topic of the paper is appropriate for ACP and is clearly written. The authors should address the below comments.

Major comments:

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

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

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

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

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

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

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

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

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

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

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

Page 14 line 419: no comma after campaign

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

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

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

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

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

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

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

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

Supporting Information:

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

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

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

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