

Interactive comment on “Light absorption by polar and non-polar aerosol compounds from laboratory biomass combustion” by Deep Sengupta et al.

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Interactive comment on “Light absorption by polar and non-polar aerosol compounds from laboratory biomass combustion” by Deep Sengupta et al. Anonymous Referee #2
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This manuscript describes the study of the absorption spectra of water- and hexane soluble components of biomass burning aerosols. Aerosols were generated from selected fuels under both flaming and smoldering conditions and these were studied nascently and after chemical aging in an oxidation flow reactor. The authors found that the solar-weighted hexane-soluble fraction was 2-3 times more absorbing (per mass of fuel consumed) than the water-soluble fraction. They also found that absorbance

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of the hexane-soluble fraction of all samples decreased after aging while the aged water-soluble fractions of two of the samples increased. Furthermore, the shape of the spectrum, as indicated by the absorption Ångström exponent, was found to change upon aging. Higher NO_x levels were observed from the flaming combustion, and the high-resolution mass spectra show evidence for organic-nitrogen species that may be formed during aging in the presence of NO_x. Overall, this manuscript provides an interesting comparison between polar and nonpolar light-absorbing components of model biomass burning aerosols. The data and results are presented clearly, though some of the interpretations are confusing or not consistent with the figures. For example, it is stated that the hexane-soluble extracts were more absorbing than the water-soluble extracts for all samples except for the Siberian peat; yet, Figure 3 clearly shows that this is true for all four samples, including the Siberian peat. Such an inconsistency makes it confusing for the reader and undermines his/her confidence in the interpretation of the data, especially since this is one of the primary conclusions from the study. Given that relatively few studies have explored the differences in optical properties of polar and non-polar aerosol extracts, this work serves to advance the understanding of brown carbon in biomass burning aerosols. However, despite the plethora of data presented, including high-resolution mass spectra and pH dependence of the absorption measurements, there are very few insights or general conclusions drawn from this work. Additionally, the absorbance data are presented as solar-weighted, i.e. weighted by the actinic solar spectrum, which makes interpretation difficult. For example, Figure 3 shows that the (solar-weighted) hexane-soluble fraction has a larger absorbance than the (solar-weighted) water-soluble fraction for all four fuels studied, but is this true for all wavelengths, or is the difference larger at some (e.g. UV) wavelengths than at others? While Figure 2 does compare the spectra from the two fractions, it is not clear how the spectral dependencies differ. Perhaps a plot of the ratio of the two spectra would be helpful. In summary, the work presented here might be worthy of publication in ACP but only if the conclusions drawn were more clearly stated. As it stands now, it is a jumble of results riddled with typos and mistakes making it difficult for the

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reader to appreciate what has been learned from these experiments. The conclusions need to be generalized to provide some more fundamental insight into the nature of the differences in absorption between the polar and non-polar fractions.

AC: We thank the reviewer for a constructive review of the manuscript. We agree that some conclusions are not clear. We revised our manuscript accordingly. Regarding the use of solar-weighted values, we chose this representation to simplify the comparison between different experiments. Spectral dependence of measured absorbances and how it differs from experiment to experiment can be observed in Fig.11, Fig. S5, and Fig. S6 that show imaginary refractive index values.

Specific comments:

1. Page 1, lines 23-24: It should be clearly stated that the non-polar fraction is “2-3 times more absorbing” when weighted by the solar spectrum and normalized to mass of fuel consumed.

AC: This is an important reviewer’s observation. The sentence was re-written “Results of spectrophotometric measurements (absorption weighted by the solar spectrum and normalized to mass of fuel consumed) over the 190 to 900 nm wavelength range showed that the non-polar (hexane-soluble) fraction is 2-3 times more absorbing than the polar (water-soluble) fraction.”

2. Page 1, line 26: It is stated that “an increased absorbance was observed for water extracts of oxidized/aged emissions,” but that appears to be true only for two of the four samples, FASMEE and Hawken Fire; the other two, Florida Peat and Siberian Peak, show a decrease upon aging (Figure 3).

AC: Yes, the increased absorbance was only for FASMEE and Hawken Fire fuel which comes under flaming combustion type fuel. This condition is added as text in the revised manuscript.

3. Page 1, line 28, P2. Lines 1-3: The statement “Comparing the absorption Ångström

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Exponent (AAE) values, we observed changes in the light absorption properties of BB aerosols with aging that was dependent on the fuel types.” is vague. What is meant by “light absorption properties”? The only observed difference was in the AAE values themselves.

AC: We agree, “light absorption properties” did not clearly refer to the AAE values. We changed the statement in the revised manuscript.

4. Page 3, line 11: “Just a decade ago . . .” is followed by a citation to a paper from 2001, 17 years ago. That’s not a decade.

AC: We agree that “Just a decade ago” is not equivalent to 17 years of time as mentioned by the reviewer. We changed the beginning of the sentence to “Until recently”.

5. Page 4, line 22: “muck” is not a very scientifically specific word and should be replaced.

AC: The term ‘muck’ is replaced with “mucky peat” in the revised version of the manuscript. According to the report of natural resources and conservation service (https://www.nrcs.usda.gov/Internet/FSE_DOCUMENTS/nrcs142p2_053171.pdf), Mucky peat is hemic organic material, which is characterized by decomposition that is intermediate between that of fibric material and that of sapric material

6. Page 10, line 9: “700 to 900 nm and” should read “700 to 900 nm”.

AC: The sentence was re-written in the revised manuscript.

7. Page 10, line 11: The use of the term “AbS λ ” is confusing; why not use “Abs λ ”? Why use a capital S?

AC: All capital ‘S’ was replaced by ‘s’ in Abs λ expressions everywhere in the text and Figures.

8. Page 11, line 4: remove “was calculated”.

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AC: “was calculated” was removed as per suggestion

9. Page 16, line 14: The results don't “suggest”, they show/indicate/demonstrate. There is no inference in this statement.

AC: ‘suggest’ was replaced by ‘demonstrate’

10. Page 16, line 14: Figure 3 clearly shows that there is more absorbance in the hexane-soluble fraction than the water-soluble fraction for all four samples, including the Siberian peat

AC: Thank you for pointing this out. The “except for Siberian peat” was mentioned by mistake and has been corrected.

11. Page 16, lines 16: It should be made clear here that the “total absorbance” referred to is the solar-weighted total absorbance.

AC: “total absorbance” was changed on “TotalAbs” in order to maintain proper reference/ consistency to the equations in section 2.6 (Page 10, line 22).

12. Page 20, line 18: First, the authors refer to Fig. 1, but the absorption spectra appear in Fig. 2.

AC: Thank you! In the revised version of the manuscript, we refer to Fig. 2 at this point. Second, “FAASME” should be “FASMEE.”

AC: “FASMEE” was corrected.

Third, the FASMEE and Florida Peat absorption spectra are shown in Fig. 2, not FASMEE and Hawken Fire samples as stated.

AC: The ‘typo’ was corrected.

Fourth, the increase in absorption observed occurred over a wider range of wavelengths than just 380-500 nm.

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AC: Yes, we agree that the increase in absorbance was observed in wider wavelength range than 380-500 nm and hence the range was changed to 380-580 nm in the current manuscript

Fifth, are the authors referring to an increase in absorbance for the water-soluble fraction or the hexane-soluble fraction?

AC: We thank the reviewer for pointing out this mistake. The increase is only observed for water extracts and we corrected that in the manuscript.

Sixth, an increase in absorbance over a wide range of wavelengths such as observed here most certainly does not suggest that the “primary precursors for secondary emissions . . . are mostly aromatic in nature”; this statement is highly speculative and should be removed.

AC: We agree with the reviewer that this statement is highly speculative and it was removed from the text (P.20, Lines 19-20)

13. Page 25, line 8: how does the decrease in absorbance with decreasing pH compare to the results of (Phillips et al., 2017) mentioned? Is it similar or not, and if not why not?

AC: Phillips et al. measured change in absorbance for a wide range of pH in ambient aerosol samples and they showed that with the decrease of pH, the absorbance also decreased. In the present study, our samples were acidified to pH=2 and we observed a similar trend – absorption decreased. The sentence is added into the text (Page 26, lines 2-4).

14. Page 26, lines 1-2: how does the protonation of functional groups explain the decrease in absorption with lower pH? This statement needs to be clarified.

AC: The organic fraction of BB aerosols is comprised of several chromophores and identification of specific chromophores responsible for light absorbance from different fuels is challenging (Liu et al., 2014). We suspect light absorption by BB aerosols

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can be due to the presence nitro-phenols (Mohr et al., 2013), an adduct of amine and carbonyl compounds (Powelson et al., 2014), and charge transfer complexes (Phillips and Smith, 2014). These compound are pH sensitive and lose their ionic structures (responsible for color) on protonation in lower pH (e.g. pH=2).

Literature Cited:

Liu, J., Scheuer, E., Dibb, J. E., Ziemba Nasa, L. D., Thornhill, K. L., Ziemba, L. D., Anderson, B., Wisthaler, A., Mikoviny, T., Devi, J. J., Bergin, M., Weber, R. J., Dibb, J., Thornhill, K. L., Anderson, B. E., Devi, J. J. and Bergin, M.: Brown carbon in the continental troposphere Brown carbon in the continental troposphere Brown carbon in the continental troposphere, *Geophys. Res. Lett.*, 41(10), 2191–2195, doi:10.1002/2013GL058976. Received, 2014. Mohr, C., Lopez-Hilfiker, F. D., Zotter, P., Prévôt, A. S. H., Xu, L., Ng, N. L., Herndon, S. C., Williams, L. R., Franklin, J. P., Zahniser, M. S., Worsnop, D. R., Knighton, W. B., Aiken, A. C., Gorkowski, K. J., Dubey, M. K., Allan, J. D. and Thornton, J. A.: Contribution of nitrated phenols to wood burning brown carbon light absorption in detling, united kingdom during winter time, *Environ. Sci. Technol.*, 47(12), 6316–6324, doi:10.1021/es400683v, 2013. Phillips, S. M. and Smith, G. D.: Light Absorption by Charge Transfer Complexes in Brown Carbon Aerosols, *Environ. Sci. Technol. Lett.*, 1(10), 382–386, doi:10.1021/ez500263j, 2014. Powelson, M. H., Espelien, B. M., Hawkins, L. N., Galloway, M. M. and De Haan, D. O.: Brown carbon formation by aqueous-phase carbonyl compound reactions with amines and ammonium sulfate, *Environ. Sci. Technol.*, 48(2), 985–993, doi:10.1021/es4038325, 2014.

Please also note the supplement to this comment:

<https://www.atmos-chem-phys-discuss.net/acp-2018-161/acp-2018-161-AC2-supplement.pdf>

Interactive comment on *Atmos. Chem. Phys. Discuss.*, <https://doi.org/10.5194/acp-2018-161>,

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