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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Absorptivity of brown carbon in fresh and photo-chemically aged biomass-burning emissions" *by* R. Saleh et al.

Anonymous Referee #2

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Review of Saleh, et al., ACPD, 2013

Summary and General Comments:

Care was taken in mentioning that Aethelometer measurements are biased during periods when the filter is heavily loaded, however, the authors did not attempt to remove the data just prior to the filter change which would potentially diminish this issue. The authors use the aethelometer data in a relativistic sense due to the uncertainties in the measurement; however, it seems that could be avoided by removing the data just prior to the filter change. It was also not clear how scaling the absorption data removed the bias in the aethelometer data, which appears to affect the absorption measurement to a greater extent for shorter wavelengths, effectively changing AAE in addition

to the magnitude of absorption. In SI F2 the authors show that the data before the filter change biases the AAE, therefore, scaling the absorption data would not take into account the change in slope of the absorption signal versus wavelength. For this reason, I think some of the analysis and interpretation in this manuscript needs to be redone in order to minimize the decreased AAE that results from using the aethelometer data when the filters are heavily loaded. One way to do this would be to eliminate the data just prior to the filter change, while another would be to at least to quantify the uncertainties, which would affect AAE and refractive index calculations. The real magnitude of the absorption measurement is discarded, and the focus is redirected to AAE's, yet this limits the level of interpretation that can be done with the data. I would suggest trying to remove or understand the uncertainties with the data taken while the filters were heavily loaded and using the real magnitude of the abosrpton data to help bound the different assumptions being used in the manuscript. This could be added to the discussion section, along with some other situations/issues that should be addressed that are discussed below.

Data from 3 aging BB experiments are discussed; however, aged gallberry data is not shown since the concentrations were determined to be too low for reliable absorption data. However, in Fig. S1(a) the AMS data is shown. It appears that the experiment did not produce appreciable SOA, however, this was not discussed in the draft. Either in the experimental or discussion session, whichever is relevant, it should be mentioned whether no conclusions can be drawn from this or whether it appears that gallberry does not produce SOA under similar conditions that do produce SOA for the pine and oak.

The authors attempt to bound the kOA values with two different scenarios based on the mixing state of the aerosol. Case 1 assumes an external mixture of BC and OA, while case 2 assumes non-absorbing coatings on the BC. The magnitude of the absorption measurements are scaled based on these two scenarios, Case 1 being the lower bound and Case 2 being the upper bound for the imaginary part of the refractive

index of the OA. However, it is mentioned in the discussion section that "if the magnitude of the absorption coefficient measurements were assumed to be true rather than scaled by BC concentration, limiting case 1 would yield larger kOA than limiting case 2. Rather than scale the aethelometer absorption measurements due to uncertainties when the filters have high loading, why not remove the data before the filter changes and use the SP2 data to determine whether coatings are present on the BC in order to constrain the data.

Despite using the 2 cases to bound the real scenario, the authors do not discuss which case they believe to be most likely based on comparison with other data sets, etc. A section on this would be a nice addition to the discussion section.

It would be interesting to see a case 3 where the BC coatings of POA are assumed to be absorbing. What happens with this case/why was it not mentioned/addressed, what would it's assumptions require of the data presented here?

The authors deduce that BB SOA is absorbing, however, they do not consider that the increased absorption over the primary emissions could also be due to aging of the original POA/BC mixture. This issue should be addressed in the text and discussion.

Why is there no discussion section of the relative amount of SOA formed versus the initial POA/BC present in the samples?

Specific Comments:

P11512 L2: A little more detail is needed about the reference to this work. What is meant by "no BC"? The sentence seems to imply that there was no BC from the smoldering data.

L9: Cappa et al. shows that the enhanced absorption of ambient BC is less than what was predicted from MIE calculations and laboratory data, however, to say that it shows core-shell morphology as "unlikely for aged urban aerosol" is a bit speculative.

P11516: L25: Rather than ignoring the issues from OA loading, is it not possible to

remove the data just prior to the filter change? If this is too difficult to do or, since the bias is only expected to be 10% of the AAE, perhaps this could be used and reported in terms of the uncertainty in the extracted kOA values. It seems like this would have been simple to just remove the data though, and eliminate the issue.

P11517: L27: I suggest changing the reference to "details can be found in Sect. 3.2" since referring ahead is generally not recommended.

P11519: How was the SP2 calibrated and with what? What density was assumed for the experimental data? Please provide details of how this was done so that future comparisons can be referenced to the results discussed here. If aquadag calibrations were done, they should be converted to fullerene soot values as is referenced in Baumgardner et al., 2012 as this is coming to be the new standard.

P11520: L16: There is no discussion about how the oak has higher SOA/OA values than the pine. Was this expected? Is this relevant or perhaps is not discussed since is thought to be due to differences between the experimental setups?

P11521: L15: Does "investigated fuels" mean the two samples? The number should be stated in the text.

P11522: L4-6: How does the fact that limiting case 1, which is used as the lower limit for kOA, could be larger than case 2 if the absorption measurements were not scaled with BC mass not undermine using case 1 and 2 to bound the derived kOA values? Please describe this in detail since it seems to unsubstantiated the whole analytical method used in this manuscript. What range of kOA values would this increase the uncertainty to/or why is this not a good assumption?

L22: Why not remove the points with heavily loaded filters and then use the magnitude of the absorption coefficients? Are there other uncertainties associated with this that would make this not possible?

P11524: L1: How do you know that the increased absorption over the original POA

emitted and BC is due to SOA? Could the increased absorption be from aging of the POA?

L6-9: The statement does not appear to be supported by the data shown in Figure 2. What is meant by "SOA absorbs light less efficiently than POA in the long visible wavelengths"? It is also mentioned that the SOA has a higher AAE, but in Fig. 2 this appears to be true for the pine sample, but only marginally true for the oak. Why should the reader focus on this difference, which is significant for picosin pine, with an aged AAE of 1.73 vs 1.48 for fresh, but is not very large for oak, 1.42 vs 1.38, respectively. Is a difference of $\sim$3% AAE for aged versus fresh oak larger than the uncertainty in determining the AAE? How is this small relative difference AAE constrained when it was mentioned earlier that the AAE's have at least a 10% error associated with them due to using the data when the aethelometer filters were heavily loaded?

Tables and Figures:

Table 1: The kOA's and w's should have uncertainties or error measurements associated with them in order for the reader to understand the level of uncertainty in the methods used for the two cases.

Figure 5: Line 5: Change (a) to (d).

References:

Baumdardner, D. et a l., Soot reference materials for instrument calibrations and comparisons. Atmospheric Measurement Techniques, 5, 2315-2362, 2012.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 11509, 2013.