

Review of: Production of particulate brown carbon during atmospheric aging of wood-burning emissions
by Kumar et al.

Overall, I find that the authors have presented novel and interesting results on the influence of photochemical aging on absorption by residential wood combustion emissions. They have done a better job than I often see in assessing the performance of the aethelometer for their specific situation, but should include additional details regarding measurement uncertainties, and how these measurement uncertainties propagate to their final atmospheric implications. I have numerous comments, mostly just asking for clarification. I believe this paper should be publishable, with revisions.

Title: It would be good to state “residential wood-burning emissions.”

L14: It might be good to indicate this was under (likely) high NOx conditions.

L15: It would be good to clarify what wavelength, or if this is integrated in some way.

L17: Reporting the GSD is informative, but an actual uncertainty estimate would be better.

L54: It would be good to also cite the work from the Georgia Tech group (*Forrister et al., 2015*).

L229: It is not clear to me why the MAC for POA would be unaffected. The authors write for Eqn. 13 what amounts to:

$$\begin{aligned}\alpha(\lambda, 880) &= \frac{-1}{\ln\left(\frac{\lambda}{880}\right)} \ln\left(\frac{[EC]MAC_{BC\lambda}}{[EC]MAC_{BC_{880}}} + \frac{[OA]MAC_{OA\lambda}}{[EC]MAC_{BC_{880}}}\right) \\ &= \frac{-1}{\ln\left(\frac{\lambda}{880}\right)} \ln\left(\frac{[EC]MAC_{BC\lambda}}{[EC]MAC_{BC_{880}}} + \frac{[OA]MAC_{OA\lambda}}{b_{abs,880}}\right)\end{aligned}$$

and where they have only included the second line, not the first. The $b_{abs,880}$ value, while seemingly independent of the EC measurements as the authors have written them, actually do depend on the EC measurements because everything has been referenced to the EC measurement. Perhaps I am simply missing something, but I think that the authors statement must be further justified. Yes, the MAC of OA is fundamentally independent of the MAC of BC. But I am not certain that these are practically separated to the extent indicated by the authors. This is the same challenge that all AAE extrapolation methods face in quantitatively determining OA absorption in the presence of BC. See e.g. the cited Moosmuller paper or (*Lack and Langridge, 2013*). Also, the statement on L231 is self-evident. Of course the AAE at a given wavelength depends on the relative contributions of BC and OA.

L264: What about chemically induced changes of POA mass, as opposed to just absorption?

L287: It is unclear what is meant by “a higher than measured lensing effect.”

L290: The authors mention uncertainties here for the UV-Vis measurements. But what about for all of the in situ or other measurements? This includes [EC], [OA], absorption. Further discussion of uncertainties is necessary.

L305: It is not clear how this uncertainty estimate was arrived at. Also, this differs from the figure. Finally, it is not clear whether this fit has been forced to zero or not.

L307: Bond et al. did not “report” a value at 880 nm. They reported at a shorter wavelength. This value is inferred assuming an AAE = 1. It should be noted as such.

L308: While the authors obtain a value of the MAC in good agreement with extrapolated values from Bond et al., it is not clear to me how this definitely indicates no lensing effect is present. An uncertainty analysis is necessary. What if, hypothetically, the EC was biased high and the absorption biased low? The obtained MAC might appear in agreement with literature, but only within the bounds of the measurement uncertainty. This statement should be quantified.

L315: It is clear that the distribution is reasonably log-normal with a single mode when considered in number space. But what about in surface area or in volume space, which is important for the calculation of the MAC_OA_bulk (Eqn. 20)? Also, to what extent does the volume-weighted distribution exceed the SMPS bounds?

L325 and Fig. S2: I do not understand why in Fig. S2 it says the “reported value” is 2.6 while here 3.0 is given. This should be clarified.

L332: Not only wood combustion, but really any aerosol if it is assumed that the true MAC for BC at 880 nm is $\sim 4.7 \text{ m}^2/\text{g}$.

L336: This seems circular to me, if the authors are using $C = 3$ in coming to this conclusion. This is demanded through the various inequalities.

Fig. S5 must indicate which studies are being used to define the literature bounds, and also note that this is not the entire range of reported values over the many papers on this topic. This is a subset of values. Consider e.g. (*Lewis et al.*, 2008) or (*Liu et al.*, 2013). The authors have selected a very narrow subset of literature results to present here, and to reference in the text.

Fig. 3: It is not clear why the data in Fig. A do not overlap with the data in Fig. B. Presumably the data in figure B evolved from the data in Fig. A. Also, in Fig. A is not clear if each point is for one experiment or whether the variability in f_{OA} is due to variability within an experiment.

L344: I do not dispute that the AAE values increase with f_{OA} . However, it is evident that as wavelength decreases the difference from AAE = 0.9-1.1 and the observations increases. This is not clear from the discussion here.

L346: The range reported is inconsistent with what is shown in the graph.

L350: this could be strengthened simply by showing a graph of the observations as a function of wavelength, and showing that a single AAE value does not provide for a good fit.

Fig. 2: For consistency, it would be helpful if the color scale were labeled as f_{OA} , similar to fig. 3 and the text.

L356: Looking at Fig. 3B, it is not clear that this is generally the case. The highest f_{OA} in Fig. 3B does not have the highest AAE. Perhaps the authors mean this just for the high OH exposures. If so, they might consider plotting AAE vs. f_{OA} for subsets of data binned according to OH exposure. But, as presented, it is not evident that this is a fully general conclusion.

L362: While I don't necessarily disagree with this point, I will reiterate that the relationship between Fig. 3A and 3B is not clear. The authors give a dashed curve, but it is not clear how, for example, the data in Fig. 3B that start at such low AAE values at high f_{OA} values come from Fig. 3A. A stronger connection needs to be made to make this clearer

L364: For the data in Fig. 3B, extrapolation to $f_{OA} \rightarrow 0$ for wavelengths < 600 nm suggests an AAE ~ 1.2 - 1.3 , larger than the 0.9-1.1 range the authors have taken for BC. This is consistent with the derived $MAC(370) = 13.7 \text{ m}^2/\text{g}$ for BC, given the value at 880 nm. There is, however, a bit of an inconsistency with how the authors compare with Bond. They state that 13.7 is within the 95% confidence interval of the 11.1 m^2/g value reported by Bond. But, they have also stated that the AAE = 0.9-1.1. If this is the case, then isn't the range actually narrower? Really, my question here is about the consistency of the statistical interpretation/uncertainty representation.

Fig. 7: I find the legend to be incomplete in that it leaves the reader thinking that the Lu and Saleh measurements are from methanol extraction, which they are not. Also, for Saleh (2014), the authors do not at all make clear that the Saleh measurements are at 550 nm, not 370. This is not a fair comparison. Neither is which fuel type of Saleh's has been considered. The authors should provide a fuller picture. Also, the Saleh reference is missing from the bibliography.

Fig. S7: It is not clear why the propagated uncertainty in the AAE increases with wavelength or f_{OA} . The AAE is a measured quantity that depends only on the measured absorption at two wavelengths. Why would uncertainty in absorption depend on f_{OA} ? And are the authors saying that the uncertainty in absorption increases with wavelength? Uncertainty in the AAE should directly propagate from Eqn. 10, which is independent of f_{OA} . Perhaps I am misunderstanding?

L384: A larger GSD does not necessarily mean a larger uncertainty. This could be variability that is independent of uncertainty. I do not regard this as a true assessment of "uncertainty." It is only an assessment of variability. The authors should, however, consider uncertainties explicitly.

L386: Given that the authors show distributions and fits for the AAE, it would seem appropriate to also show similar for the MAC_{POA} and MAC_{SOA} so that the reviewer can judge. Given the width of the

SOA distribution, is a normal fit even appropriate? (Probably not, in a fundamental sense, since MAC values cannot be < 0 . But perhaps a normal distribution is appropriate in a practical sense.)

L398: The authors should provide the resulting uncertainties, or at least ranges, based on the multivariate analysis, for the AAE values.

L402: I suggest removing the “this is the first study” statement. Saleh (2014) reported very closely related “w” values, from which AAE values can be calculated, for SOA from biomass burning.

Fig. S10: I find that the use of the log scale for the y-axis makes it difficult for the reader to see what sort of changes did/did not occur. Variability in the AAE over so many orders of magnitude is not expected, but a factor of 2 would be reasonable. Thus, a linear scale should be used.

L424: In Fig. S13, and Fig. 6, it is unclear why the authors fit only the “aged” data. Why exclude the primary, especially in Fig. S13? Because the relationship is visibly much worse? This goes to the statement about sensitivity to Mie calculations.

L427: Fig. 6 normalizes out any uncertainty/variability in the measured [OA], because both absorption values are normalized by this. Fig. 4, in contrast, does not. How can the authors rule out the possibility that there is not some variability in the measurement of OA between burns, perhaps dependent on particle shape or variability in bounce in the AMS (which can differ between POA and SOA)?

L432: This 46% must state that it is for aged OA only. It remains unclear to me why the primary is excluded.

L440: Is this a fair comparison, given that the authors have focused on the aged OA?

L431: Are these fits forced through zero?

L441: The authors seem to be implying that SOA formed from oxidation of aromatic precursors is not especially water soluble, or at least less soluble than in methanol. The authors might consider citing e.g. (Zhang *et al.*, 2011), to strengthen this argument.

Fig. 7: As already noted above, I find the comparison here insufficient. Saleh *et al.* (2014) and Lu *et al.* (2015) report values not at 370 nm. This is unclear. Also, the line shown for Lu *et al.* (2015) appears to be incorrect. See their Fig. 1D. Further, and importantly, the Lu *et al.* (2015) data are largely, although not entirely, derived from the Saleh measurements. Thus, they are not really an independent assessment.

Fig. 7: The logic of a linear fit to the observations is not clear to me. The authors have argued that the SOA is absorbing, and differently absorbing than the POA. If I use the equation given and extrapolate towards $M_{BC}/M_{OA} \rightarrow 0$, the $k_{OA} \rightarrow 0$. If the SOA is absorbing, and if SOA formation drives the decrease in the M_{BC}/M_{OA} , then the limiting value of k_{OA} should be equal to the value for k_{SOA} . As

such, the provided fit does not seem appropriate and requires justification. Some of this may be experiment-to-experiment variability. But the limiting case issue remains.

Fig. 7: The authors should be able to, from their observations and within their assumptions, calculate M_{POA}/M_{SOA} . They might consider plotting k_{OA} vs. this ratio instead of versus M_{BC} . These will be related, of course, since the authors assume POA is proportional to BC during aging for a given experiment.

L471: The origin of these “uncertainties” is unclear. They are explained later for f_{OA} , but for the MAC values it is not abundantly clear.

L486: This statement regarding mass yields of SOA requires much further detail.

L512: A note about terminology. I am not certain that “error analysis” is appropriate here. Variance in the POA fraction is not “error.” It is variability. A substantial aspect of this “error analysis” is really just a “sensitivity analysis.” I suggest that the authors limit the term “error analysis” to when they are truly considering errors, and use some other term when they are considering variability. This is true here and elsewhere.

L499: The authors should clarify the origin of the solar irradiance data that they have used.

Forrister, H., et al. (2015), Evolution of brown carbon in wildfire plumes, *Geophysical Research Letters*, 42(11), 4623-4630, doi:10.1002/2015GL063897.

Lack, D. A., and J. M. Langridge (2013), On the attribution of black and brown carbon light absorption using the Angstrom exponent, *Atmospheric Chemistry and Physics*, 13(20), 10535-10543, doi:10.5194/acp-13-10535-2013.

Lewis, K., W. P. Arnott, H. Moosmüller, and C. E. Wold (2008), Strong spectral variation of biomass smoke light absorption and single scattering albedo observed with a novel dual-wavelength photoacoustic instrument, *Journal of Geophysical Research: Atmospheres*, 113(D16), D16203, doi:10.1029/2007JD009699.

Liu, S., et al. (2013), Aerosol single scattering albedo dependence on biomass combustion efficiency: Laboratory and field studies, *Geophysical Research Letters*, 2013GL058392, doi:10.1002/2013GL058392.

Zhang, X. L., Y. H. Lin, J. D. Surratt, P. Zotter, A. S. H. Prevot, and R. J. Weber (2011), Light-absorbing soluble organic aerosol in Los Angeles and Atlanta: A contrast in secondary organic aerosol, *Geophysical Research Letters*, 38, doi:10.1029/2011gl049385.