

Reply to Reviewer Comments on “Contribution of Organic Carbon to Wood Smoke Particulate Matter Absorption of Solar Radiation” by Kirchstetter and Thatcher, acpd-12-5803-2012

We are very appreciative of the time both reviewers committed to reading and commenting on our manuscript. Recognizing that such comments improve the quality of published manuscripts, we considered each comment carefully. In almost all cases, we made the suggested revisions. We provide a detailed response to each and every comment below.

Reviewer 1 general comment: The manuscript is well written and provides interesting and valuable information. The results and significance sections are well presented and the graphical information is easily readable. Also, a good discussion of the significance of the results is presented. Publish after minor refinement.

Reviewer 1 requested refinements with author responses (in blue colored text):

1) The introduction needs a more in-depth discussion of biomass PM optical properties. It would be helpful to provide a discussion of more recent literature and how the filter based absorption spectra presented qualitatively relate to in situ spectra (if such data are available).

Author response. Agreed on both points. Regarding including more recent literature, we added to the introduction two recent references that report AAE for ambient biomass burning smoke: Sandradewi et al., 2008 and Rizzo et al., 2011. Regarding the second point, we agree that it would be great to add a discussion of how filter-based absorption spectra compare to in-situ spectra, but, to our knowledge, these data have not been published. (We infer from the reviewer’s comment that the reviewer is also unaware of such data.) Short of comparing filter-based and in-situ measurements, we do dedicate a considerable portion of the methods section to a fair and open discussion of caveats (artifacts) associated with filter-based absorption measurements.

2) The methods section is missing the amount of detail needed to reproduce the results. It should provide more information on the measurements and data analysis methods; i.e. it is unclear if the AAE values were determined by regression of $\ln(ATN)$ and $\ln(\lambda)$ and how exactly the ATN of BC was subtracted. Even though this information might seem obvious for the authors and is mostly covered in Kirchstetter et al. (2004), it would strengthen the manuscript and make it easier to read and understand.

Author response. Agreed. We added lots of explicit detail so that readers can follow our method step by step. This includes explicitly calling out six equations in the intro and methods and adding a new paragraph to the methods section to provide the requested extra details.

In the introduction, we now explicitly define AAE:

“The spectral absorption of BC is reasonably well approximated by a power law relationship from the near ultraviolet to the near infrared:

$$\text{absorption}(\lambda) \propto \lambda^{-\text{AAE}} \quad (1)$$

where the symbol \propto means “is proportional to,” λ is wavelength, and the exponent is referred to as the absorption Ångström exponent (AAE).”

In the methods section, we now explicitly detail how we compute attenuation and AAE:

“Light transmission through (dry) particulate matter on quartz filters is predominantly due to particle light absorption rather than particle light scattering when the particulate matter is even weakly absorbing (Arnott et al., 2005):

$$\text{absorption}(\lambda) = k' \text{ATN}(\lambda) \quad (2)$$

where k' is nominally constant and $\text{ATN}(\lambda)$ is the optical attenuation computed from measured transmission, $T(\lambda)$:

$$\text{ATN}(\lambda) = 100 \ln[1/T(\lambda)] \quad (3)$$

... we compute the AAE for each particulate matter sample by performing a linear regression of $\ln(\text{ATN})$ against $\ln(\lambda)$ over the range $360 < \lambda < 700$ nm.”

Likewise, in the methods section, we now explicitly detail how we apportion absorption to OC and BC by defining new variables and including new equations:

“We estimate the contribution of BC to each sample’s spectral attenuation, $\text{ATN}_{\text{BC}}(\lambda)$, by (a) attributing all attenuation at 880 nm to BC, an assumption consistent with prior work (Kirchstetter et al., 2004; Sun et al., 2007), and (b) extrapolating to other wavelengths assuming that the AAE of BC is 0.86. ... The contribution of OC to each sample’s spectral attenuation, $\text{ATN}_{\text{OC}}(\lambda)$, is determined by subtracting the BC attenuation from the total attenuation:

$$ATN_{OC}(\lambda) = ATN(\lambda) - ATN_{BC}(\lambda) \quad (4)$$

Based on the apportionment of spectral attenuation to BC and OC, we compute for every wood smoke sample the fraction of radiation at each wavelength in the solar spectrum that would be absorbed by OC:

$$f_{OC}(\lambda) = ATN_{OC}(\lambda) / ATN(\lambda) \quad (5)$$

Last, we compute the fraction of solar radiation that OC in the wood smoke would absorb in the atmosphere:

$$F_{OC} = \frac{\int_{300 \text{ nm}}^{2500 \text{ nm}} f_{OC}(\lambda) i(\lambda) d\lambda}{\int_{300 \text{ nm}}^{2500 \text{ nm}} i(\lambda) d\lambda} \quad (6)$$

where $i(\lambda)$ is the clear sky air mass one global horizontal solar spectrum at the earth's surface (Levinson et al., 2010)."

3) Introduction pg.5804, ln.24; missing word "of" before atmospheric particulate matter

Author response. Thanks, we added the missing word "of" to this sentence.

4) Introduction pg.5805, ln.9; careful wording is required, wavelength selectivity alone does not explain brown appearance but wavelength selectivity in UV/blue does

Author response. Agreed. We re-wrote the sentence in question (Biomass smoke particles often look brown rather than black because they absorb solar radiation with a stronger wavelength selectivity than BC, which...); so that it now reads:

"Biomass smoke particles often look brown rather than black because, compared to BC, they absorb solar radiation with stronger wavelength selectivity in the blue and ultraviolet spectral regions, which..."

5) Introduction pg.5805, ln.20; support abundance statement with a reference

Author response. Agreed. To support the statement that wood smoke typically contains much more OC than BC, we added a reference to Piazzlunga et al., 2011 (Estimates of wood burning contribution to PM by the macro-tracer method using tailored emission factors, ES&T, 2011), which contains a nice table that summarizes published wood burning emissions data and shows that the OC/EC ratio averages 14%.

6) Methods pg.5805, ln.26; correct “radiate” to “radiata” and use italics for *Pinus radiata*

Author response. We corrected this typo and used italics as suggested.

7) Methods pg.5806, ln.25; it would be beneficial to expand this section with a couple of brief sentences about the sampling, i.e. location in relation to sources/ equipment/ typical filter loadings, handling if available to support these significant results.

Author response. Agreed. We added details that we thought would be helpful to the reader. The added details are underlined in the following paragraph excerpted from our revised manuscript.

“In this paper, we consider the spectral absorption selectivity of 115 particulate matter samples that were collected outside of 12 houses in the residential community of Cambria, which is located in a rural portion of San Luis Obispo County, California. In Cambria, wood burning is prevalent and the only significant source of nighttime particulate matter generation (Thatcher et al., 2011). It is likely that many residents burn *Pinus radiata*, also known as Monterey Pine, as it is the native species in region. Particulate matter samples were collected during evening and nighttime hours (from 1800h to 0600h) in the winter (of 2010) to maximize the collection of wood smoke particles and minimize the collection of particles from other anthropogenic or natural sources, such as restaurants along the single main street in downtown Cambria. Elevated chimney temperatures, measured using an infrared camera, verified that residents were operating their fireplaces. Little vehicle activity was observed in the area during the evening and nighttime. Particulate matter samples were collected on quartz filters using a sampling device equipped with a single stage impactor to select particles smaller than 2.5 μm in aerodynamic diameter (SKC Inc. PEM model 200).”

Regarding filter loadings, we added a relevant note to the methods section:

“... filter loading expressed in terms of ATN at 880 nm, which ranged between 3 and 23 for 98% of samples, and...”

8) Methods, pg.5806, ln.6 to 13; This section is key for the understanding of the results and needs to be further elaborated as stated in the general comments above. It would also

beneficial to separate formulae from the text for better clarity. The determination of FOC could also be added here in a new paragraph (see comment below) for better structure and readability of the manuscript.

Author response. Agreed. We modified the manuscript as suggested, as we noted above in response to comment (2).

9) Methods, pg.5806, ln.19; rephrase/check the sentence of the collapsing coating.

Author response. Agreed, this sentence was difficult to parse. We re-wrote the sentence in question (Gyawali et al. (2009) noted that coating of BC by light scattering (i.e., non-absorbing) OC, which may amplify the light absorbed by BC, also may increase spectral absorption selectivity if the coating collapses the fractal BC aggregate) so that it now reads:

“Gyawali et al. (2009) noted that coatings of non-absorbing species may collapse the fractal aggregate structure of BC particles and, consequently, increase spectral absorption selectivity.”

10) Results, pg.5807, ln.6; explain briefly why this sample is representative (e.g. all samples show same trend)

Author response. We re-wrote the sentence in question (Figure 1 shows the spectral attenuation of a representative particulate matter sample collected for this study) so that it now reads:

“Figure 1 shows the spectral attenuation of a particulate matter sample, which is similar to the spectral attenuation of many other samples in this study.”

11) Results, pg.5807, ln.18; explain the determination of OC attenuation in the methods section and just refer to it here.

Author response. Agreed. We modified the manuscript as suggested, as we noted above in response to comment (2).

12) Results, pg.5807, ln.20; replace “current” with a better word.

Author response. Agreed. We re-wrote the sentence to fix the issue.

“The AAE of OC is 4.89 for this sample.”

13) Results, pg.5807, ln.28; Do you mean the publication Chen and Bond (2010) instead of Sun (2007) for AAE values of filter extracts at various combustion conditions?

Author response. No, the AAE values we cited are those of Sun et al. (2007). The confusion is entirely our fault as we admittedly did a poor job in explaining the work of Sun et al. in our original manuscript. Therefore, we re-wrote this passage with a better description of the work of Sun et al.:

“These values are consistent with those recommended by Sun et al. (2007), who used band-gap and Urbach relationships to describe the absorption spectra of water-soluble humic-like OC (AAE = 6) and more polymerized OC (AAE = 4).”

We are familiar with the study of Chen and Bond (2010), but in this case refrained from comparing our results to theirs b/c they measured liquid extracts of OC particles and we measured OC particles. It is not clear to us if such a comparison would be one of apples to apples or apples to oranges, so to speak.

14) Results, pg.5808, ln. 2 - 22; It would be useful to describe the method for determining FOC in the methods section and just show/ discuss the results here. It is not entirely clear to me why a 5th order polynomial fit had to be used; is it because of different wavelength increments in the solar data in comparison to the measurements?

Author response. Agreed. We modified the manuscript as suggested, as we noted above in response to comment (2).

Yes, we used a polynomial fit to F_{OC} because our spectrometer wavelength increments were different than those of the solar spectrum data. To make this clear, we added the following sentence to this relevant discussion in the results section:

“We use a model fit for $f_{OC}(\lambda)$ simply because the wavelength increments of our spectrometer and the solar spectrum data sets differed.”

15) Please also cite the source of the solar spectrum data and to what condition it refers (standard atmosphere?)

Author response. The condition and reference were (and still are) contained in the caption to Figure 3. We added these same details to the manuscript text (just below Eq. (6), which was Eq. (1) in the submitted manuscript) to ensure that they will not be missed by the reader:

“where $i(\lambda)$ is the clear sky air mass one global horizontal solar spectrum at the earth’s surface (Levinson et al., 2010).”

16) Significance, pg.5809, ln.15 ~ 24; You discuss similarities to other OC field data. Would you expect that atmospheric processing does not have a significant or limited effect on biomass OC absorption spectra?

Author response. Atmospheric aging processes can change the physical, chemical, and optical properties of particulate matter. For example, several pathways convert organic gases into the particle phase and there is some evidence that SOA is also light absorbing. However, we can only speculate how atmospheric processing might alter biomass OC absorption spectra. Short of adding anything speculative, we did add to this discussion that aging is an important variable. In the same section, we added other details to better illustrate how our results may be related to results of other studies. The underlined text in the following passage excerpted from our revised manuscript highlights the newly added text.

“The fraction of solar radiation that would be absorbed by OC rather than BC in wood smoke particulate matter (14%) indicates that BC is the dominant light absorbing species in atmospheres burdened with residential wood smoke and OC absorption is secondary but not insignificant. Since the relative amounts of OC and BC emitted from fires have been shown to depend on combustion conditions and wood type (e.g., Mazzoleni et al., 2007; McMeeking et al., 2009) and have been reported to vary widely (Piazzalunga et al., 2011), the results of this study apply strictly to the residential wood smoke samples collected in Cambria. The contribution of OC to solar radiation absorption may be more or less in other situations than we find in this study.”

A broad comparison can be made with other studies that have characterized particulate matter in regions with open burning (e.g., wildfires in Africa and South America) and residential biofuel combustion (e.g., wood and crop residues used for cooking and heating in Asia). On a global scale, these others sources are dominant emitters of carbonaceous particulate matter (Bond et al., 2004). ...

The similarities across studies, despite different analytical methods and differences in fuels, combustion processes, and atmospheric processing, indicates that light-absorbing OC is ubiquitous in atmospheres influenced by biomass and biofuel burning. Since ...”

17) Significance, pg.5810, ln.4; “appreciably” is perhaps not the right word in this context.

Author response. We deleted the word “appreciably”

18) Table 1; please check caption (missing and unclear wording)

Author response. Agreed, the title was awkwardly phrased. We re-wrote the title for increased clarity (and, as it turns out, using fewer words).

19) Fig 3; please check caption (remove “to” in ln.3)

Author response. We removed the unnecessary “to” in the caption of Figure 3.

Reviewer 2 general comment: This is a well-written, interesting, and relevant manuscript that should be published in ACP after the following comments have been addressed.

Reviewer 2 comments with author responses (in blue colored text):

1) The manuscript discusses the UV light absorption of OC from residential wood burning and then generalizes in section 4 “Significance” to biomass burning aerosols in the global atmosphere. While the authors present some evidence that their results on the UV absorption in residential wood burning are similar to results obtained for ambient measurements of biomass burning emissions in southern Africa and in the Amazon, this matter needs further discussion. There are significant differences in emissions from residential and open (e.g., wildland fires and agricultural burning) burning; see for example Zielinska and Samburova (2011), Conny and Slater (2002), and Mazzoleni et al., (2007). In particular PM emissions from open biomass burning generally have a much larger OC/BC PM mass ratio which could indicate more UV absorption if the brown carbon fraction of OC is comparable. Other differences that need to be pointed out include the lack of atmospheric processing in this study compared to biomass burning aerosols in the global atmosphere and the fact that wood is only a minor fuel type in global biomass burning emission inventories.

Author response. Agreed. Our comparison to open biomass burning should acknowledge these issues. In response to this comment, we added the underlined text in the following passage excerpted from our revised manuscript.

“The fraction of solar radiation that would be absorbed by OC rather than BC in wood smoke particulate matter (14%) indicates that BC is the dominant light absorbing species in atmospheres burdened with residential wood smoke and OC absorption is secondary but not insignificant. Since the relative amounts of OC and BC emitted from fires have been shown to depend on combustion conditions and wood type (e.g., Mazzoleni et al., 2007; McMeeking et al., 2009) and have been reported to vary widely (Piazzalunga et al., 2011), the results of this study apply strictly to the residential wood smoke samples collected in Cambria. The contribution of OC to solar radiation absorption may be more or less in other situations than we find in this study.”

A broad comparison can be made with other studies that have characterized particulate matter in regions with open burning (e.g., wildfires in Africa and South America) and residential biofuel combustion (e.g., wood and crop residues used for cooking and heating in Asia). On a global scale, these others sources are dominant emitters of carbonaceous particulate matter (Bond et al., 2004). ...

The similarities across studies, despite different analytical methods and differences in fuels, combustion processes, and atmospheric processing, indicates that light-absorbing OC is ubiquitous in atmospheres influenced by biomass and biofuel burning. Since ...”

2) The discussion of literature values of AAE for biomass burning smoke needs to be expanded beyond Kirchstetter et al., (2004) and Bergstrom et al., (2007).

Author response. Agreed and thanks for the suggested references. We read and added to the introduction two additional references that report AAE for ambient biomass burning smoke: Sandradewi et al., 2008 and Rizzo et al., 2011.

3) The discussion of artifacts of filter-based light absorption measurements needs to include the effect of particle morphology changes for liquid OC particles (Subramanian et al., 2007). In addition, the authors refer to “The so-called filter-loading or shadowing artifact” (p. 5806, line 23). The term “shadowing should be deleted because it refers to a geometric optics concept and has no application for submicron combustion particles and near-visible wavelengths.

Author response. As requested, we deleted the term “shadowing artifact,” so that the manuscript refers to this artifact only as the “filter-loading” artifact. We didn’t add a reference to the liquid-like OC particles observed by Subramanian et al. because that study did not reach a decisive conclusion about the impact of the liquid (rather than solid) particles on filter-based absorption measurements. Referring to the potential overestimation or underestimation of a filter-based absorption measurement, the authors conclude, “We do not have sufficient data to comment on the direction of the change.” Moreover, the authors don’t make any statements, definitive or otherwise, about spectral absorption selectivity, which is the subject of our paper. Additionally, their study observed undiluted source emissions (whereas in our study we measure ambient particles) and liquid-like OC particles have not been widely recognized as a problem (whereas the other artifacts we discuss in our paper are the subject of many other papers).