Response to PhD Ye Kuang: *Characterization of Brown Carbon absorption in different European environments through source contribution analysis*

November 18, 2024

As claimed by authors in the manuscript that

> "However, theoretical simulations have shown that the AAE_{BC} can reasonably vary between 0.9 and 1.1 depending on the size and internal mixing of BC particles."

Lack and Langridge (2013) reviewed a range of field measurements of "encapsulated" BC and suggested an AAE_{BC} of 1.1 ± 0.3 (0.8–1.4). Luo et al. (2022) simulated variations of AAE_{BC} and discussed key factors influencing variations in AAE_{BC} and found that the largest factor that influences the variations in AAE_{BC} is the black carbon mass size distribution, and the AAE_{BC} could even be out of the range of 0.8–1.4 (Figure 1a), which is larger than the range stated by the authors:

> "However, theoretical simulations have shown that the AAE_{BC} can reasonably vary between 0.9 and 1.1 depending on the size and internal mixing of BC particles" (Bond et al. (2013); Lu et al. (2015), e.g.).

This could be verified by results from field measurements. For example, the probability distribution of $AAE_{880\text{-}950}$ and $AAE_{660\text{-}880}$ is shown in Figure 2a of Luo et al. (2022).

Let's assume three cases and ignore the spectral dependence of AAE_{BC} in this part. The first case is that AAE_{BC} is equal to 0.9; however, the significant contribution of BrC made the fitted AAE 0.95. The second case is that AAE_{BC} is equal to 1.05; however, the contribution of BrC is negligible, which made the fitted AAE still 1.05. The third case is that AAE_{BC} is equal to 1.1; however, the contribution of BrC resulted in the fitted AAE of 1.15. Based on the method used by the authors, the AAE of 0.95 would be chosen to represent AAE_{BC}, but it would bias from the true average AAE_{BC} of 1.02.

This example tells us the 1st percentile of fitted AAE depends on the covariations of AAE_{BC} and BrC contributions; it does not help acquire the average AAE_{BC}. The most important factor influencing variations in AAE_{BC}—black carbon mass size distribution—and BrC absorptions are controlled by complex processes that are quite difficult to disentangle. The derived AAE_{BC} lying between 0.9 and 1.1 does not make this method valid.

Authors argued that

> "Zhang et al. (2020) have reported an uncertainty of approximately 11% in the estimation of the BrC contribution to total absorption at 370 nm when using different AAE_{BC} values ranging from 0.9 and 1.1."

That being the case, using AAE_{BC} of 1 is just fine; there is no need to derive AAE_{BC} using a method that seems reasonable. I agree with the authors that sometimes signals at 950 nm can be very low; however, those at 660 nm should be fine. I suggest that the authors present the probability distribution of $AAE_{660\text{-}880}$ to show possible variation ranges of AAE_{BC} and directly

use the average $AAE_{660\text{-}880}$ to represent average AAE_{BC} at each site, which might be more reasonable because BrC absorption at 660 nm is also very small.

With respect to the spectral dependence of AAE_{BC}, Wang et al. (2018) found that the spectral dependence of AAE_{BC} should be considered. However, the proposed method assumes that BrC absorption is negligible, which is not the real case, as stated by the authors. Therefore, Luo et al. (2022) proposed an improved AAE ratio method considering both variations and the spectral dependence of black carbon AAE to differentiate brown carbon (BrC) absorptions from total aerosol absorptions. They use $AAE_{880\text{-}950}$ to account for the variations embedded in AAE_{BC}, and the ratio $R_{AAE}(\lambda) = \frac{AAE_{BC,\lambda-880}}{AAE_{BC,950-880}}$ to take the spectral dependence of AAE_{BC} into account, not using $AAE_{880\text{-}950}$ to account for AAE_{BC} as stated in the responses of the authors.

Therefore, the formula for deriving $\sigma_{BrC}(\lambda)$ is:

$$\sigma_{BrC}(\lambda) = \sigma_a(\lambda) - \sigma_{BC}(880\,\text{nm}) \times \left(\frac{880}{\lambda}\right)^{AAE_{BC,950-880} \times R_{AAE}(\lambda)}$$

Let's move back to the BrC(370) calculation formula presented by the authors:

$$\sigma_{BrC}(\lambda) = \sigma_a(\lambda) - \sigma_{BC}(880\,\text{nm}) \times \left(\frac{880}{\lambda}\right)^{AAE_{BC}}$$

Authors used $\sigma_{BC}(880\,\text{nm})$ to derive $\sigma_{BrC}(\lambda)$. Based on the definitions of AAE, the $AAE_{BC,\lambda-880}$ should be the focus. If using a constant AAE_{BC} derived through fitting BC absorptions at multiple wavelengths, it would result in different uncertainties at different λ values. Therefore, if we want to accurately retrieve, for example, $\sigma_{BrC}(370)$, then we should focus on representing $AAE_{BC,370-880}$ accurately. However, as simulated by Luo et al. (2022), $AAE_{BC,370-880}$ would be much smaller than $AAE_{BC,660-880}$ or $AAE_B, 880-950$, and the ratio of $R_{AAE}(370)$ depends mostly on black carbon mass size distributions (Figure 1b). The used $R_{AAE}(370)$ in Luo et al. (2022) for deriving $\sigma_{BrC}(370)$ is 0.79; if this ratio holds for the sites of this manuscript, then $AAE_{BC,370-880}$ should be less than 0.8, which I believe would result in non-negligible underestimations of $\sigma_{BrC}(370)$ if authors use AAE_{BC} of 1 or other values to derive $\sigma_{BrC}(370)$.

In summary, I agree with the authors that

> "This is a reasonable uncertainty considering the overall uncertainty of the AAE method. Moreover, the modeling part presented in this work is prone to uncertainties, and any change of AAE_{BC} can add uncertainties that, however, lie well within the overall uncertainty of the approach presented in this manuscript."

Now that the authors have mentioned variations in AAE_{BC} and tried to derive a reasonable one, we should comprehensively discuss the best way of deriving $\sigma_{BrC}(\lambda)$ on the basis of limited multi-wavelength aerosol absorption measurements and deliver this clearly to readers.

In summary, I suggest that the authors use the average $AAE_{660\text{-}880}$ to represent AAE_{BC} variations at different sites and account for the spectral dependence by simulating a ratio $R_{AAE}(370) = \frac{AAE_{BC,370-880}}{AAE_{BC,660-880}}$ using typical black carbon mass size distributions in Europe on the basis of Mie theory. If not, at least discuss the potential uncertainties associated with the spectral dependence of AAE_{BC} to deliver a comprehensive understanding of $\sigma_{BrC}(\lambda)$ derivations that include the latest advancements. Moreover, I want to highlight that considering

Response: Here we considered a reasonable AAE_{BC} range between 0.9 and 1.1 based on values obtained, for example, by constraining the AAE_{BC} determination with ^{14}C analysis (AAE_{BC} = 0.9 in Zotter et al. (2017), further confirmed by Blanco-Alegre et al. (2022) using aethalometer measurements in a road tunnel). It has also been stated in the literature that the AAE of externally mixed BC is approximately 1 for particles < 50 nm in diameter, and can range from 0.8 to 1.1 for diameters of 50–200 nm (Gyawali et al., 2009). Extreme AAE values for internally

mixed BC up to 1.7 have also been reported (Gyawali et al., 2009). Other studies have reported an average AAE_{BC} of 1.1 (Lack and Langridge (2013) and references herein).

As stated in Lack and Langridge (2013), the extreme values ($0.55 < AAE_{BC} < 1.7$) that have been reported in the literature for very specific BC particles "are likely not common in the atmosphere for BC_{Ext} and BC_{Int}, and serve here as extreme boundaries only."

Thus, the extreme AAE_{BC} reported in the literature were associated with very specific BC particles that do not necessarily represent the heterogeneity of BC particles under ambient conditions. Some of these extreme AAE_{BC} values were, for example, obtained from laboratory experiments or from theory.

As an example, we applied the range of AAE_{BC} mentioned by Dr. Kuang ($0.8 < AAE_{BC} < 1.4$) to the Barcelona dataset. The Barcelona measurement station is highly affected by BC emissions from vehicles passing the busiest road of the city located 200 m from the measurement site. Previous studies conducted in Barcelona have shown a low contribution from biomass burning in the city (e.g., Via et al. (2021)). Via et al. (2021) reported an average contribution of biomass burning to OA mass concentration in Barcelona of 4% during 2017–2018. If an AAE_{BC} of 0.8 is used, the BrC contribution to absorption at 370 nm reached 50% of total absorption (annual average), which is clearly too high for Barcelona. If an AAE_{BC} of 1.4 is used, then a negative (-20%) BrC contribution to absorption is obtained. The first percentile of R^2-filtered AAE provided a value of 1 for Barcelona, which resulted in a very reasonable estimation of BrC contribution to absorption in Barcelona based on previous studies performed in the city (14%). In Ispra (located in the Po Valley in Northern Italy), an AAE_{BC} of 0.8 would provide a BrC contribution to absorption close to 90% (too high), and an AAE_{BC} of 1.4 would provide a BrC contribution to absorption of 10% (too low). Similarly, for Krakow (where the 1st percentile provided an AAE_{BC} of 1.07), using 0.8 and 1.4 provided BrC contributions to absorption of 85% and 9%, respectively, which were, respectively, too high and too low. This small sensitivity study confirms that the extreme AAE_{BC} values cannot be used to represent BC under ambient conditions and that AAE_{BC} values closer to one provide the best estimation.

We would like to comment that the use of the R^2-filtered AAE frequency distribution (FD) for the determination of AAE_{BC} has been published by Tobler et al. (2021) and Glojek et al. (2024). These authors estimated the AAE_{BC} by visually inspecting the AAE frequency distributions and set the AAE_{BC} somewhere in the very left tail of the FD. Here, we suggested a possible mathematical approach using the 1st percentile to avoid a too subjective determination of AAE_{BC} from AAE data.

We also highlight that the first percentile represents conditions when the absorption is dominated by BC and not by both BC and OA. Consequently, the possible presence of very specific BC particles (causing too low or too high AAE_{BC} in other studies) should be reflected in the experimental AAE values, and consequently in the 1st percentile. But this is not the case for the 12 sites used in the manuscript, where the 1st percentile provided AAE_{BC} values mostly from 0.9 to 1.1.

We are aware that Luo et al. (2022) proposed an improved AAE ratio method using the AAE calculated from 880 and 950 nm to account for the spectral variation of AAE_{BC}. However, Dr. Kuang agrees with us that the absorption at 950 nm can be very noisy and that its systematic use at many sites (especially at regional/remote sites) cannot be guaranteed. Thus, a true harmonization of the attribution method at the 12 sites cannot be applied in this manuscript if the absorption at 950 nm is used. For this reason, Dr. Kuang suggests using the AAE calculated from 660 to 880 nm instead of from 880 to 950 nm. Thus, Dr. Kuang suggests applying the method proposed in Luo et al. (2022), but using a new wavelength pair (i.e., 660–880 nm). Consequently, there are two issues: one is that we would need to apply a methodology that has never been applied before in the literature using this new specific wavelength pair from aethalometer data. This is out of the scope of this manuscript. Second, the assumption that BrC particles do not absorb at 660 nm is not reasonable in many cases. Thus, exploring the

possible spectral dependence of AAE_{BC}, as done in Luo et al. (2022), or its modified version as suggested by Dr. Kuang, is not systematically possible at all the sites included in the manuscript. Moreover, the approach from Luo et al. (2022) implies the use of BC size distribution data that are not available at the measurement sites included in the manuscript. Dr. Kuang suggests using some typical BC size distribution for Europe, but this introduces an additional uncertainty that cannot be estimated considering that BC size distribution is highly variable. It should be noted that the aerosol particle size distribution was measured in Luo et al. (2022) and not assumed from other studies.

For the aforementioned reasons and in order to discuss the potential uncertainties associated with the attribution method, we modified the sentences from Line 152 as follows:

> "... where AAE_{BC} is the Absorption Ångström Exponent (AAE) of BC, which allows for the calculation of $b_{abs,BC(\lambda)}$ (in units of Mm^{-1}) from the measurements of $b_{abs,BC(\lambda)}$ at 880 nm assuming that BrC does not absorb at 880 nm (e.g., Qin et al. (2018)). The main source of uncertainty in equations 1 and 2 is the AAE assumed for BC. In many studies, a value of 1 was used (Liakakou et al. (2020); Tian et al. (2023); Cuesta-Mosquera et al. (2023), e.g.). However, theoretical simulations have shown that the AAE_{BC} can reasonably vary between 0.9 and 1.1 depending on the size and internal mixing of BC particles (e.g., Bond et al. (2013); Lu et al. (2015)). Here we estimated the site-dependent AAE_{BC} as the first percentile of the AAE frequency distribution. The AAE can be calculated from multi-wavelength (370, 470, 520, 590, 660, 880, and 950 nm) total absorption measurements as the linear fit in a log-log plot of the total absorption versus the measuring wavelengths. The effect of BrC absorption is to increase the AAE, and consequently, the first percentile of AAE represents conditions where the absorption is dominated by BC. In order to reduce the noise, the 1st percentile at each site was calculated from AAE values obtained from fits with $R^2 > 0.99$ (Tobler et al., 2021; Glojek et al., 2024). Other approaches used a combination of Mie theory and experimental data to explore the wavelength dependence of AAE_{BC} and proposed an estimation of $b_{abs,BrC(\lambda)}$ based on the ratio between the AAE calculated from 370 to 520 nm and from 520 to 880 nm (Wang et al., 2018; Li et al., 2019). However, this methodology assumed that BrC particles do not absorb at 520 nm whereas it has been shown that the contribution of BrC to absorption at this wavelength can be high (e.g. Cuesta-Mosquera et al. (2023)). As a consequence, other studies (e.g. Zhang et al. (2019); Luo et al. (2022)) used the AAE calculated from 880 to 950 nm to calculate the AAE_{BC} assuming that BrC particles do not absorb in the near IR. Nevertheless, the latter methodology may suffer from additional uncertainties related to the possible low aethalometer signal at 950 nm, frequently observed especially at remote sites. Thus, it should be considered that the methodologies proposed to estimate AAE_{BC}, including the use of the 1st percentile applied here, are prone to uncertainties. On the other hand, Zhang et al. (2020) have reported an uncertainty of approximately 11% in the estimation of the $b_{Abs,BrC(370)}$ contribution to $b_{Abs,370}$ when using different AAE values ranging from 0.9 and 1.1. For the sites included here, the 1st percentile method provides AAE_{BC} values ranging from 0.928 to 1.088 confirming that this experimental method can provide reasonable estimations of the AAE_{BC}."

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