# *Referee comment on "Absorption enhancement of BC particles in a Mediterranean city and countryside: effect of PM chemistry, aging and trend analysis" by Jesús Yus-Díez et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2022-145-RC1, 2022*

## Answer from the authors to Referee #1

On behalf of all the authors of the manuscript, below we reply to the main comments presented by Referee #1. We would like to thank the Referee#1 for providing interesting and useful insights that we think contributed to improve the quality of this manuscript.

Hereafter we provide all the information and analysis required by the Referee#1.

All comments and/or changes we present below will be reported in the revised version of this manuscript.

### Comments.

**1. The use of a constant correction factor (*C*) to account for the multiple scattering effect of AE33. According to the reference provided (AMT 2021, 14: 6335-6355), the *C* values actually had considerable variations for the urban site (2.44 ± 0.57). Thus, instead of applying a constant *C* to the AE33 results, the wavelength-resolved *b*abs should be determined using the MAAP-based *b*abs@637 nm and the AE33-based AAE, given that the *C* values showed little wavelength dependence (AMT 2021, 14: 6335-6355).**

With this comment, the Referee#1 suggests to simulate the absorptions at the seven AE33 wavelengths using MAAP absorption data (at 637 nm) and the experimental AAE from AE33 absorption measurements.

As far as we know, the procedure suggested by the Referee#1 has never been reported in literature, thus we found this suggestion new and interesting. The basis for this suggestion is that the MAAP is generally considered as a "reference" instrument for absorption measurements because the filter-tape artefacts are dynamically calculated by the MAAP instrument. Conversely, AE33 data must be corrected off-line in order to consider the filter tape artefacts. Indeed, given that the C depends on the physical properties of the collected particles, the assumption of a constant C to correct the AE33 data leads to an overall higher uncertainty of the AE33 measurements compared to the MAAP measurements.

In fact, it has been reported (e.g. Zanatta et al., 2016; Rigler et al., 2020) that the absorption derived from AE33 data has a higher uncertainty (20-25%) compared to the MAAP (12%; Petzold and Schönlinner, 2004) and that this higher uncertainty is mostly due to the uncertainty associated to filter tape influence on the AE33 measurements. The standard deviation of the C reported in Yus-Diez et al. (2021) is around 23%. Yet the measurements reported in this manuscript have been calculated using error propagation laws and the effect of the measurement error in comparison with the standard deviation of the measurements is below 10%.

However, the data we presented in the manuscript prevent the application of the procedure suggested by the Referee#1 because MAAP data were collected with a cut-off inlet of PM10 whereas the AE33 measurements were performed in PM2.5. Thus, given that the semi continuous EC measurements used in this manuscript were also performed with a PM2.5 cut-off, the application of the procedure suggested by the Referee#1 could introduce an additional uncertainty

in the calculation of $E_{abs}$ due to the possible presence of coarse BC. In fact, as reported in Figure 1b below, on average offline EC concentrations in PM10 were 26% higher compared with online EC concentrations in PM2.5, whereas offline and online EC measurements in PM2.5 correlated well (slope = 1.02). A small bias (4%) between offline and online EC measurements in PM2.5 was also reported by Karanasiou et al. (2020).

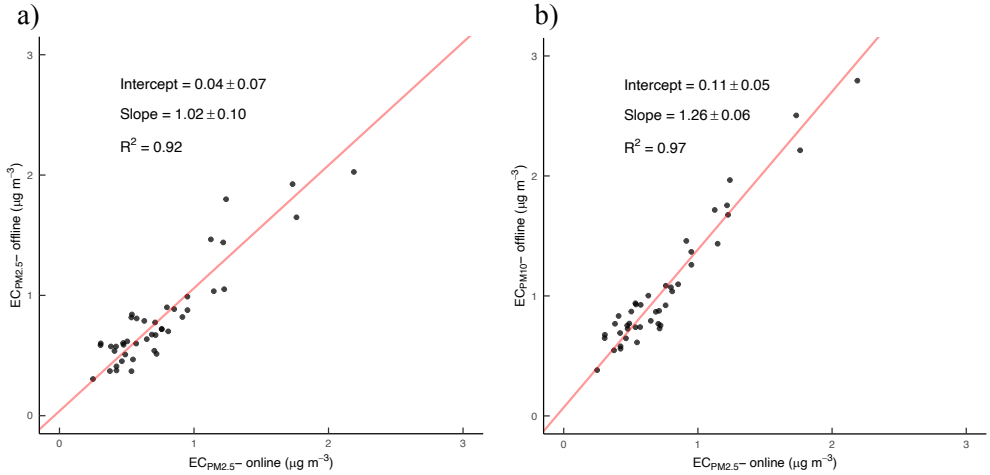


**Figure 1:** Scatterplot between the offline 24-hour filter measurements of EC with an inlet cut-off of a) PM2.5 and b) PM10, and the online retrieved measurements of EC with an inlet cut-off of PM2.5.

Moreover, the figure below (Fig. 2) shows the relationship between the absorption at 660 nm measured with the AE33 and the absorption at the same wavelength extrapolated from MAAP measurements. As shown in the figure, there is a high correlation between the two absorptions with a slope of 1.1 (10% difference) and a positive intercept. Slope higher than 1 and positive intercept (even if small) were likely due to the different inlets used for AE33 and MAAP measurements.

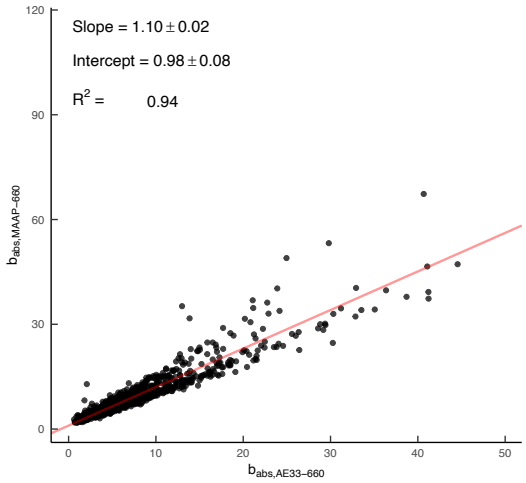


**Figure 2:** Scatter plot between the MAAP absorption coefficients ($b_{abs,MAAP-660}$) extrapolated to 660 nm and the absorption coefficient at 660 nm from AE33 measurements, ($b_{abs,AE33-660}$).

Thus, with the data we have at disposal, we could only apply the procedure suggested by the Referee#1 using off-line EC measurements in PM10 from filter analysis to estimate $E_{abs}$ from MAAP-simulated absorptions. However, the filters were collected during 24h and only 2/3 filters per week were analyzed during the measurement period used for this manuscript. Thus, the application of the suggested procedure to filter data will dramatically reduce the temporal resolution and the amount of data available for this study.

Finally, we would also consider the fact that the AE33 instrument is the most widely used instrument worldwide for on-line attenuation measurements in monitoring stations. The MAAP instrument was discontinued a few years ago and only few stations nowadays deploy both AE33 and MAAP. At many monitoring stations only the AE33 is deployed and many papers have been published using the 7 absorptions obtained from AE33 measurements without MAAP data. Given the high correlation between the simulated and derived absorption reported in the Figure 2 above, we consider that the use of the seven absorptions provided experimentally by the AE33 is of higher interest for the scientific community and that the differences in $E_{abs}$ obtained from experimental and MAAP-simulated AE33 absorptions will be small compared to the total uncertainty.

The reasons causing the observed differences between online and offline measurements will be better commented in the revised version of the manuscript.

**2. Consistency of online and offline EC for the urban site. It is essential to present their relationship, e.g., using a scatter plot, and quantitatively determine the inter-method discrepancy. Unless this discrepancy could be properly accounted for, it does not make sense to compare the online and offline *E*abs (or MAC) results. In addition, the MAC of uncoated BC, i.e., MACref, were calculated for the urban site using both the online and offline EC. But it appears that the results differed substantially (Figures S1 and S2, after accounting for the wavelength dependence). This does not make sense, again raising concerns on whether the online and offline *E*abs (or MAC) results were comparable.**

Indeed, the inter-method discrepancies should have been better tackled in the submitted manuscript. Below, following the Referee#1 suggestion, we provide the necessary analysis to reply to this comment.

The differences between the online and offline MAC, $MAC_{ref}$ and $E_{abs}$ reported in the manuscript were most likely due to the different size cut-off used for online and offline measurements. As aforementioned, offline EC and absorption (from MAAP) measurements were performed in PM10 whereas the online EC and absorption (from AE33) measurements were performed in PM2.5.

As shown in Figure 1a above, PM2.5 offline and online EC measurements presented a very good correlation, in agreement with Karanasiou et al. (2020), and offline EC concentrations in PM10 were on average 26% higher compared to online EC concentrations in PM2.5 (Fig. 1b), and as shown in Fig. 2 above, the absorption at 660 nm in PM10 was on average 10% higher compared to the absorption measured in PM2.5. Besides the different inlets used, this difference was in part driven by the fact that different instruments (MAAP and AE33) were used to measure absorption.

However, the differences reported in Figs. 1 and 2 explained the differences reported in the manuscript for the MAC and $E_{abs}$.

Thus, we would like to highlight again that in our manuscript we used different techniques (and different cut-off) to estimate MAC and $E_{abs}$ and that this was the main reason for the differences between offline and online measurements reported in the manuscript. Despite this, we think that presenting results from different techniques in the manuscript is valuable because measurements with different cut-off and with different instruments (e.g. MAAP and AE33) are commonly performed worldwide. Moreover, we used the measurements we performed with different objectives rather than just for comparison between the techniques we used. In fact, online EC and AE33 measurements were used with the main objectives of studying the effect of chemistry and aging on the BC coating as a function of wavelength, and the offline EC and online MAAP measurements to study the trend of the MAC.

We would like to point out that the analysis presented here will be better clarified in the revised version of the manuscript, and that the corresponding figures will be included in the supplementary material.

**3. The assumption that "the lensing-driven absorption enhancement for BC particles was wavelength independent" was not supported by the references provided, even for the clear coating scenario (e.g., as indicated by Figure 5 in Lack and Cappa, ACP 2010).**
**4. The effects of brown coating were ignored, indicating the discussions on mixing state were highly uncertain, especially for the cold season when the influence of biomass burning was stronger.**

We would like to thank the Referee#1 for these comments. In fact, following the Referee#1 suggestions we changed the method to estimate the lensing driven BC absorption enhancement from experimental measurements. This new method presented below seems to confirm the wavelength dependence of the internally mixed BC absorption enhancement highlighted by the Refreee#1 and reported in other studies (mostly theoretical).

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Below we reply to the comments 3 and 4 from Referee#1.

Indeed, we assumed that the absorption enhancement due to the internal mixing was wavelength independent, as stated in the manuscript lines 206-208: "Moreover, we assumed that the lensing-driven absorption enhancement for BC particles was wavelength independent (Lack and Cappa, 2010; Liu et al., 2015; Zhang et al., 2018)."

As correctly pointed out by Referee#1, we misinterpreted Lack and Cappa (2010). The main reason for our assumption was mostly based on the fact that the approximation of a wavelength independent $E_{abs}$ was used in some recent papers as for example in Liu et al. (2015) and Zhang et al. (2018). For example, Lack and Langridge (2013) commented (*author's note: $BC_{Int}$ corresponds to the attribution to the absorption of the internal mixing, i.e. coating, whilst $BC_{Ext}$ refers to the contribution from the pure BC particles*), that:

"As described previously, the theoretical AAE for $BC_{Int}$ can range from the uncoated baseline to ~ 1.7 (Gyawali et al., 2009; Lack and Cappa, 2010). In contrast, Bahadur et al. (2012) assumed that internal mixtures did not affect the AAE and used an AAE for $BC_{Int}$ = 0.55. Analysis of a range of atmospheric measurements of the AAE for aerosol sourced from fresh fossil fuel burning and urban pollution (where the dominant absorber was BC) shows an average value for the AAE of 1.1 ± 0.3 (1σ ) derived using the wavelength pair 467 nm and 660 nm (Lack et al., 2008; Clarke et al., 2007; Virkkula et al., 2005; Rosen et al., 1978; Bergstrom et al., 2002, 2007; Kirchstetter et al., 2004). This suggests that the AAE extremes presented (0.55 and 1.7) are likely not common in the atmosphere for $BC_{Ext}$ and $BC_{Int}$, and serve here as extreme boundaries only. Although there is variability in the AAE, these studies have been used previously to support the use of an AAE = 1 for $BC_{Ext}$ (Bond et al., 2013), **and it is common to assume that the AAE for $BC_{Int}$ is equal to that of $BC_{Ext}$**. These studies provide evidence that although an AAE of 1 may be an accepted average for $BC_{Ext}$ and $BC_{Int}$, an uncertainty range should be considered and propagated through any absorption attribution procedure performed"

However, as correctly commented by the Referee#1, assuming a wavelength independent $E_{abs}$ is not supported by other studies (mostly theoretical studies) and by the Lack and Cappa (2010) reference provided in this manuscript. Indeed, Figs. 1 and 5 in Lack and Cappa (2010) show that under different core-shell and clear-brown coating scenarios, the absorption enhancement produced by the coating can vary with the wavelength.

In order to take into account this comment of the Referee#1 we recalculated the $E_{abs}(\lambda)$ following the procedure described below.

- First, differently from what was presented in the manuscript, we have used seven $MAC_{ref}$ values (calculated as the intercept of the relationship between the observed ambient MAC and the ratio OC:EC when the ratio is zero for each AE33 wavelength) to calculate $E_{abs}(\lambda)$ of coated BC, instead of using for all wavelengths the $E_{abs}$ value (1.20) for coated BC calculated at 880 as the ratio $MAC/MAC_{ref}$.
- Second, we performed a sensitivity study changing the AAE of coated BC, using the same AAE range as used in Fig. 1 from Lack & Langridge (2013) from 0.8 to 1.4.

Thus, in the revised version of the manuscript we calculated the contribution of the BC coating absorption to $E_{abs}(\lambda)$ as follows:

$$b_{abs}(\lambda) = b_{abs,BC\ core} + b_{abs,int} + b_{abs,BrC};$$

hence if we remove the contribution to the absorption by the BrC, then $E_{abs,BC\ coated}(\lambda)$ is:

$$E_{abs,BC\ coated}(\lambda) = \frac{b_{abs,BC\ core} + b_{abs,int}}{EC} \cdot \frac{1}{MAC_{ref}(\lambda)} =$$

$$= \frac{MAC_{BC\ coated}^{880\ nm} \cdot \left(\frac{880}{\lambda}\right)^{AAE} + MAC_{ref}(\lambda)}{MAC_{ref}(\lambda)} = 1 + \frac{MAC_{BC\ coated}^{880\ nm} \cdot \left(\frac{880}{\lambda}\right)^{AAE}}{MAC_{ref}(\lambda)}$$

Where, for the sensitivity study, different AAE were considered: 0.8, 1 and 1.4.

Thus, following Lack and Langridge (2013), we studied the variation of the absorption coefficients attributed to BC, the BC coating and BrC by varying the absorption Ångström exponent (AAE) of coated BC. An AAE below 1 has been observed for scenarios with large BC cores, whereas an AAE above 1 is often associated to the presence of brown coatings.

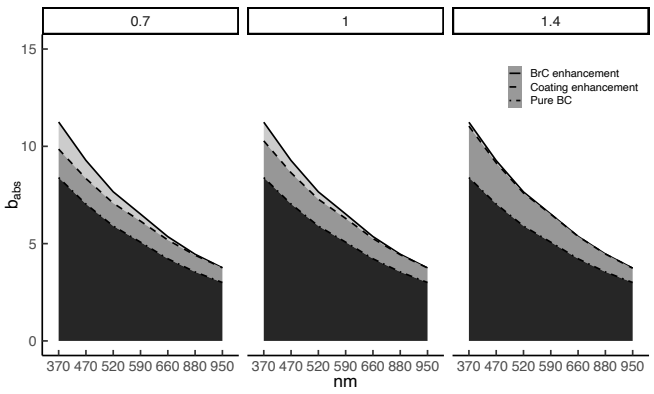


**Figure 3:** Contribution to the absorption coefficients of pure BC, coated BC, and BrC particles.

As it can be seen in Fig. 3, as the AAE increases/decreases above/below 1, the contribution to the absorption of the coating material increases/decreases with the wavelength. In fact, in the case of an AAE for coated BC of 1.4, the proportion of the absorption due to the BrC material becomes much smaller. An increase of the AAE of the internally mixed BC particles is linked with an increase in the relative contribution of brown material to the internal mixing (Zhang et al., 2020).

Indeed, Fig. 4 below shows that for AAE=1.4, the $E_{abs}$ for the internal mixing increases towards the shorter wavelengths, as observed in the simulations performed in Fig. 3 of Lack and Cappa (2010), where the dashed grey line represents the absorption enhancement produce by brown coating. In the case of AAE=1, the contribution of the coating material remains fairly constant (Fig. 4 below), although it presents a slight decrease with decreasing wavelengths, which is due

to the fact the MAC Ångström Exponent for the experimental reference MAC for pure BC particles is slightly above 1. Conversely, a clear decrease of the contribution to $E_{abs}$ from coated BC with decreasing wavelengths was observed for an AAE of 0.8, which is expected given that the contribution to the absorption from the coating decreases, as indicated by the AAE<1. Overall, this sensitivity analysis of the behavior of the impact of AAE of the coated BC particles shows that the assumption of a constant $E_{abs}$ for the internal mixing, although useful in a first approximation, is not always accurate. Thus, a variation in the AAE proves useful to determine the possible range of values of the $E_{abs}$ for the different mixing scenarios.

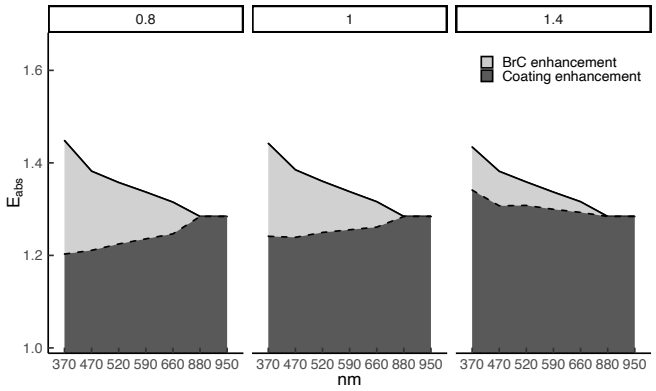


**Figure 4:** Absorption enhancement produced by the coating material and the BrC for different AAE values of the coating material.

However, since a modelization using Mie theory falls out of the scope of this work and given that modelling studies have been published that can be used as reference, we cannot determine how much the brown coating or the different possible core-shell particle diameters contribute to the observed behaviour of the absorption enhancement due to BC coating. We can only present, along with the sensitivity study, how much will vary the contribution of coated BC under different AAE scenarios for this coated BC, and by extension the BrC, to the absorption enhancement. Based on previous modelling studies, we could assume that, as reported in Fig. 5b of Lack and Cappa (2010), the observed contributions of coated BC to $E_{abs}$ could be related to a Bond et al. (2006) regime #2 with a BC particle central core diameter of 100 nm and a shell of 1500 nm.

The new analysis presented above will be included in the revised version of the manuscript.

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