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-RC21, 2022

Answer from the authors to Referee #2

On behalf of all the authors of the manuscript, we would like to thank Referee #2 for the comments and suggestions to improve the manuscript. Below we provide all the information and analysis requested by the Referee#2.

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

Comments.

In general, AE33 and MAAP are filter-based measurements. Several studies imply the corrections are needed for filter-based light absorption measurements, including multiple light scattering within the filter, filter loading, and particle scattering corrections (Lack et al., 2014; Moosmueller et al., 2009). Could you add the related description how the correction is down in this study? Moreover, OC/EC is a widely used instrument. But previous study shows there are several limitations associated with OC/EC measurement that complicate the interpretation of the results and introduce uncertainties that cannot be completely minimized (Lack et al., 2014). How do you think it affects your results?

Indeed, filter-based measurements are characterized by numerous artifacts affecting the measurements. In relationship with the two instruments used in this study, AE33 and MAAP, the corrections performed were:

- AE33: Filter leakage was taken into account following the values provided by the manufacturer. The filter loading effect was corrected online by the instrument using the factor *k*, which corrects for the filter loading effect. In fact, the AE33 instrument uses the dual spot technology (Drinovech et al., 2015) that allows for an online correction for this artifact. Then, the multiple scattering parameter, C, was corrected using the value reported in Yus-Díez et al. (2021) for Barcelona station used in this study. The C was found to have an average value of 2.44, and did not present a marked dependence with the single scattering albedo (SSA) of the particles collected on the filter-tape. Yus-Díez et al. (2021) showed that the C values can considerably increase when SSA is high (> 0.95). However, these high SSA are rarely measured in the city of Barcelona (cf. Fig. 1). Moreover, Yus-Díez et al. (2021) reported that the C is wavelength independent in Barcelona (cf. Fig. 1). Therefore, we used the average value of 2.44 for the deriving the absorption measurements.

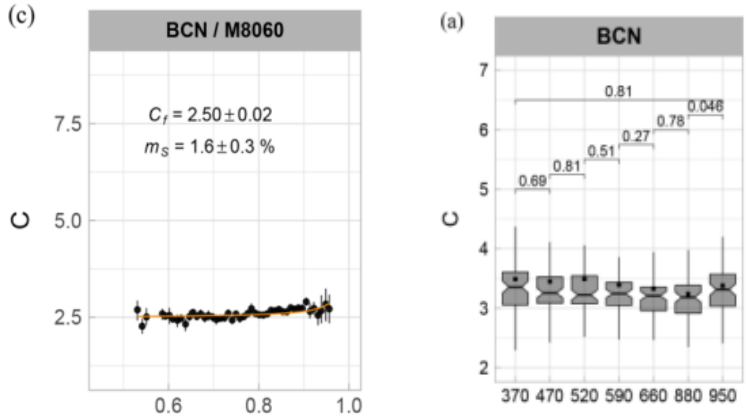

Fig. 1: The left panel represents the subplot c) of the Figure 1, and the right panel the subplot a) of Figure 4, respectively of Yus-Díez et al. (2021).

- MAAP: We followed Muller et al., (2011) recommendations for correcting the MAAP data, and we reported the absorption at 637 nm. The MAAP corrects online for filter tape artifacts by simultaneously measuring light transmitted through and scattered back from the particle laden filter. The only correction was considering the correction factor (1.05; Muller et al., 2011) due to the difference between the nominal (670 nm) and actual (637 nm) wavelength used by the instrument.

With regards to the limitations associated to the OC/EC measurements performed with the Sunset OC/EC analyzer, interferences in thermal-optical analysis of OC/EC in PM filter samples are well discussed in previous works. Different thermal protocols, light absorbing carbon, carbonates and other chemical components might influence the split point between EC and OC leading to overestimation or underestimation of EC concentrations (Kuhlbusch 2009; Karanasiou et al., 2015). For obtaining both the online and offline OC/EC measurements we used the reference methodology elaborated by WG35 of the European Committee for Standarization (CEN) that adopted the EUSAAR2 protocol with transmittance correction for OC/EC determination in PM2.5 (EN16909:2017). We calculated the combined relative standard uncertainty of EC concentrations using the method described in EN16909. This was equal to 18% for both online and offline OC/EC analyzers (Karanasiou et al., 2020).

It is very interesting to attribute E_{abs} to different species. However, I wonder if the effects could be well estimated by using multiple linear regression due to the limitations of the method. Could you add discussion on the applicability of this method on this attribution?

Previous studies (e.g. Zhang et al., 2018) have used this technique to derive the contribution to E_{abs} from different species. Figure 3 in the manuscript shows that the absorption enhancement depends on the concentration of particles available for mixing (non-refractory PM; $R_{NR\text{-}PM}$). Hence, by studying E_{abs} variations with time and its relationship with the variations of each of the different sources contributing to $R_{NR\text{-}PM}$, we can infer the relative contribution of each source to the E_{abs} variations. MLR analysis has been used in other papers with the objective of studying the relative importance of different sources/species to a given variable (e.g. Ealo et al., 2018; Zhang et al., 2020; among many others).

To check for the goodness of the fit, we performed a series of analysis, such as the VIF (Variance Inflation Factor), and the statistical significance. Overall, the tests showed good enough results that allow applying the MLR analysis.

This analysis can be find in a set of tables that were included in the Supplementary material of the revised version of the manuscript (Tables S2-S6 reported below):

Table S2: VIF (Variance Inflation Factor) between the independent variables of the multi-linear regression analysis, i.e. the chemical species and sources obtained with the Q-ACSM, and a test of the statistical significance using the p-value of each coefficient (*: p<0.05,**<0.01,***<0.001).

	Cold period		Warm period	
	VIF	**p-value**	**VIF**	**p-value**
Intercept	-	***	-	***
HOA-to-EC	1.405	*	1.132	*
BBOA-to-EC	2.247	**	-	-
MO.OOA-to-EC	6.045	*	3.015	
LO.OOA-to-EC	1.385	*	1.827	
SO4-to-EC	2.215		1.913	*
NO3-to-EC	3.315		1.207	***
COA-to-EC	1.179	**	1.515	*

As reported in Table S2, VIF values were in the acceptable range of values indicating that the independent variables were not correlated (VIF close to 1) or moderately correlated (VIF<5). The exception was for the MO-OOA/EC independent variable that showed a VIF of around 6 during the cold period. This means that the standard error for the regression coefficient of the MO-OOA/EC in winter was around 2.3 ($\sqrt{6.04}$) times larger than if that predictor variable had 0 correlation with the other predictor variables. However, in some studies (e.g. Vittinghoff et al., 2006; Hair, 2009) VIF < 10 has been considered as acceptable. Moreover, for the cold period the MLR analysis provided slightly negative values for SO4-to-EC and NO3-to-EC (Table 3 in the manuscript) indicating negligible contribution to E_{abs} from these two variables during the cold period. In fact, the p-values in Table S2 for these two variables were not statistically significant (s.s.). However, the MO-OOA-to-EC ratio shows s.s. p-values indicating that the MLR analysis results are acceptable

Line 483: This study mentioned increase of E_{abs} at the near-ultraviolet wavelengths during the cold period and we related the observed increase to the presence of brown carbon particles externally mixed with BC particles. Several studies estimate the impact of brown carbon internally mixed (brown carbon coating) with BC (Lack and Cappa, 2010; Feng et al., 2021). Is it different if brown carbon is internally mixed with BC particles?

We thank the Referee #2 for this comment. Indeed, with the method presented in the manuscript, by the assumption that the absorption enhancement due to internal mixing was constant, we could not account for the possible internal mixing of absorbing material (brown coating) with the BC cores. Lack and Cappa. (2010) have shown that in the case that there is an absorbing brown coating, actually, the absorption enhancement decreases towards the shorter wavelength as there is less light radiation reaching the BC cores (Figs. 1 and 5 in Lack and Cappa, 2010). Thus, BrC externally or internally mixed with BC can present different effects on the absorption enhancement.

To test this, as also suggested by the Refree #1, and to try to better incorporate the BrC internally mixed with the BC cores, we have recalculated the absorption enhancement for each wavelength, $E_{abs}(\lambda)$, 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.

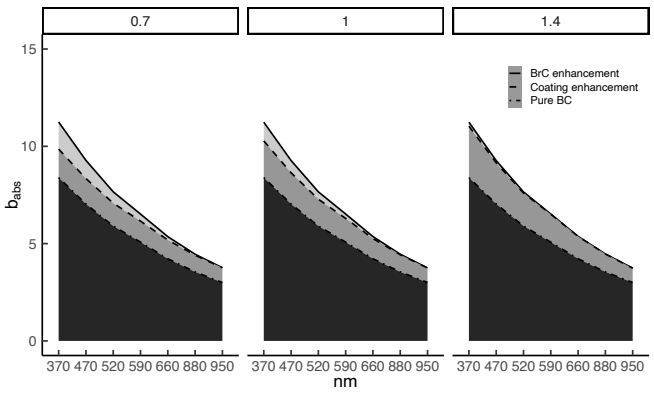

Figure 3: Contribution to the absorption coefficients of pure BC, coated BC, and BrC particles.

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.

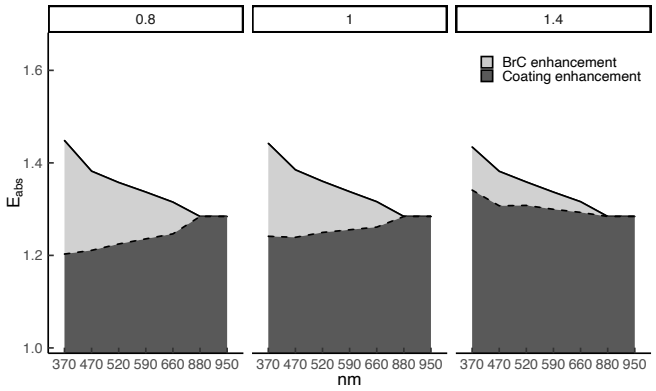

Figure 4: Absorption enhancement produced by the coating material and the BrC for different AAE values of the coating material.

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 has been included in the revised version of the manuscript in the methodology section 2.4 and the results section 3.1.1.

Text included in Sect. 2.4 (in bold), in lines 214-225:

"Furthermore, we have assumed here that BrC particles do not absorb at 880 nm (Kirchstetter et al., 2004) and that the measured absorption at this wavelength was only driven by the BC internally mixed particles (i.e. the lensing effect). **Moreover, although some studies assumed a wavelength independent lensing-driven absorption enhancement for BC particles (Liu et al., 2015; Zhang et al., 2018), other studies showed that the presence of brown coatings can produce variations in the spectral behaviour of** E_{abs} **with the wavelength (Lack and Cappa, 2010). Consequently, in order to take into account the possible influences of the brown coatings on** E_{abs}**, following Lack and Langridge (2013) we performed a sensitivity study by studying the variation of the absorption enhancement attributed to BC, the BC coating and BrC by varying the absorption Ångström exponent (AAE) of internally mixed BC (cf. Fig. S5). For this, the absorption enhancement,** E_{abs} **attributed to the different values of AAE for the internally mixed BC can be described as follows (Eq. 3):**

$$E_{abs,BC\ coated}(\lambda) = 1 + \frac{MAC_{BC\ coated}^{880\ nm} \cdot \left(\frac{880}{\lambda}\right)^{AAE}}{MAC_{ref}(\lambda)}, \quad (3)$$

where for the sensitivity study presented here, different AAE (0.8, 1 and 1.4) were considered following Lack and Langridge (2013)."

Text included in Sect. 3.1 (in bold), in lines 301-324:

"As already stated, ambient BC particles can be either externally or internally mixed with other aerosols (Bond and Bergstrom, 2006). In order to separate the relative contributions to E_{abs} of these two mixing states, i.e. external ($E_{abs,ext}$) and internal ($E_{abs,int}$) we used the multi-wavelength AE33 and the semi-continuous OC:EC measurements obtained in BCN (see Sect. 2.4). We assumed that the E_{abs} at the near-infrared (880 nm) was only produced by the internal mixing of BC particles, whereas at the short-UV (370 nm) the Eabs is due to both the internal and external mixing of BC particles. Given the spectral characteristic of BrC absorption, the contribution to E_{abs} due to external mixing was the highest at 370 nm compared to the other AE33 wavelengths. **In addition, here we analyzed the possible contribution of different internal mixing states of BC using different AAE for internally mixed BC, since the presence of brown coatings over the BC cores can actually produce a reduction of the enhancement of the absorption towards the shorter wavelengths (cf. Lack and Cappa, 2010).**

Figure 2 shows the evolution of the contribution of the internal and the external mixing to the total E_{abs} for the three AAE values considered for internally mixed BC. Indeed, Fig. 2 shows that an AAE of 0.8 could be related with a larger proportion of brown coatings reducing the absorption enhancement due to the internally mixed BC (cf. Fig. 5 Lack and Cappa, 2010). In the case of AAE=1, the contribution of the coating material remains fairly constant (Fig. 2), 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 (Fig. S6). Moreover, Fig. 2 shows that for an AAE of 1.4 the internal mixing increases towards the shorter wavelengths, as observed in the simulations performed in Fig. 3 of Lack and Cappa (2010) for the case of BC core with a brown shell that does not absorb.

The overall contribution due to the internal mixing ($E_{abs,int}$) ranged between a 100% at 880 nm, and 83, 86, and 93.5% of the total E_{abs} at 370 for an AAE of 0.8, 1 and 1.4, respectively. Thus, the BrC externally mixed particles represented a non-negligible fraction of the total E_{abs} at near-ultraviolet wavelengths (Table S1), especially for the AAE=0.8 case, for which it increased from 0.069 ± 0.066 (5.2%) at 660 nm up to 0.17 ± 0.18 at 370 nm (16.9%). Conversely, if an AAE=1.4 is used, then the increase and relative contribution of E_{abs} due to the BrC externally mixed particles remains lower, from 0.023 ± 0.049 (1.7%) at 660 nm up to 0.093 ± 0.200 at 370 nm (6.5%)."

Line 237: Table 2 occurs earlier than Table 1.

We thank the referee for taking notice. Line 237, now 252 has been changed to: "in Table 1 and Table 2, respectively."

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