

Interactive Comment on “Impact of Brown and Clear Carbon on Light Absorption Enhancement, Single Scatter Albedo and Absorption Wavelength Dependence of Black Carbon” (ACP-2009-770) by D. A. Lack and C. D. Cappa

We thank all of the reviewers for their detailed comments that have improved the manuscript. Our response to each reviewer follows below. Original reviewer comments are given in bold and our response in normal text.

Response to Reviewer 1 From Open Discussions:

Main Comments:

1. The authors appear apologetic for using Mie calculations for large, spherical core-shell particles. It is certainly possible (and has been shown) that in some or many cases, the aggregated spherules collapse and approach an approximately spherical shape (as a limiting case) upon atmospheric processing and aging, and measurements that suggest that a significant amount of mass of black carbon in the atmosphere is above 70nm (and is not just a modeling assumption). The manuscript would be strengthened by referencing this literature. Also, the results of Liu, Mishchenko, Arnott (2008) should be discussed to communicate potential differences in radiative properties among collapsed and uncollapsed black carbon particles, albeit in the uncoated case, to provide context for the calculations in this manuscript.

Agreed. We have added the following the end of section 2:

“We also note hear that the use of Mie theory assumes spherical particles. There is sufficient evidence that BC, usually fractal when emitted from efficient combustion, can become more compact and spherical when coated in other

inorganic and organic material (Alexander et al., 2008; Lewis et al., 2009; Zhang et al., 2008). Our modeling mostly deals with coated BC cores. In the limit of thinly coated cores, where fractal BC is more likely, the work of Liu et al. (2008) provides guidance on the differences in absorption for fractal vs spherical BC. For smaller (15nm) and larger (25nm) BC spherule sizes, absorption will likely be overestimated by up to 10% and underestimated by up to 20% if represented as spherical.”

2. The authors suggest that concurrent measurements of size distribution of BC and coatings thicknesses are necessary to interpret the Angström exponent (to determine the presence of an absorbtive coating).

This is a valid point, but given the uncertainties in definition, measurement, and actual morphology of BC and BC-containing particles (e.g., particles with non-spherical morphologies may require additional parameters), there should be some acknowledgement and discussion of the difficulty in executing this directive.

We agree that the unknown morphologies of BC cores will complicate this task, and have added the following to section 4.5.3:

“Therefore, when attempting to investigate the impact of CBrown on AAE it is important to consider to some degree the underlying core shape, spherule density, shell diameter, mixing state and SSA before any reliable quantification can be undertaken. The difficulty in simultaneously quantifying these parameters in ambient measurements, particularly core shapes, spherule densities and coating thickness will be a challenging task.”

3. The Angström exponent analysis appears to be over-interpreted, and is presented in a way that may be over-interpreted by readers. While the authors have made a case that AAE of 1.6 is a threshold for unambiguous determination of brown carbon in their modeled system, the actual

threshold may be different when interpreting measurements from field campaigns as these mixed particles may appear in different morphologies. The phrasing in section 4.5.3 (and abstract) should be re-evaluated in the context of this uncertainty.

We agree that the AAE analysis is complicated, and we believe this provides the needed message that simply using a single AAE without any other considerations is likely not going to provide quantitative data on C_{Brown} .

We added the following to section 4.5.3:

“Although an AAE of 1.6 is not an absolute reference point, especially given results from 4.5.2, at the wavelengths considered here it does serve as a general first approximation and lower limit to AAE for absolute attribution of C_{Brown} . With this in mind it is interesting”

and

“Although differences in particle morphology may contribute to the observed variability in these ambient AAE observations,...”

The abstract clarifies the generality of AAE of 1.6 and does not go into any details of the potential more quantitative analysis that could be done with knowledge of particle size and morphology.

Minor Comments:

Comments 1 – 3 have all been accepted and changes made to the manuscript.

4. The $X=Y$ line is in fact undefined however the line we have placed over that covers this fact. We have added a line to the figure caption to explain this.

5. We have confirmed that the non-monotonic increase in the Angstrom exponent with increasing core diameter is correct. In fact, this is not only observed in the 3rd panel but in the other two as well, albeit for different size pairs. We have moved the figure caption as suggested to make the figure easier to read. We have also added a sentence that mentions this non-monotonic variability: “However, it should be noted that the AAE varies in a non-monotonic manner with core diameter.”

Response to Reviewer 2 From Open Discussions:

1. P4L12: aged atmospheric BC may also be coated/mixed with secondary material, not only POM.

In this instance POM refers to Particulate Organic Matter, not Primary Organic Matter, so POM includes primary and secondary material. This has been clarified in the text.

2. P4L18: Adler et al (PNAS early edition)(Adler et al., 2009) measured recently the complex refractive indices of organic matter intrinsic to diesel soot. Dinar et al (Dinar et al., 2008) measured the complex refractive index of primary and secondary water soluble HULIS. These measurements provide additional input that can be directly used in the calculations and should be added.

These have been added. Thanks for pointing out these important references.

3. P5L16: Adler et al estimated that the MAC of aggregate soot at 355 nm would be 13.3 m²g⁻¹ in line of the estimation here.

This reference has been added.

4. The effects of coatings on the extinction of light has been recently studied experimentally by Lang et al as well as by (Abo Riziq et al., 2008), and results with this study can be compared.(Lang-Yona et al., 2010).

We now mention the light extinction results of Lang-Yona (2010) and Abo Riziq (2008), in addition to light absorption measurements of Shiraiwa et al. (2009) and Lack et al. (2009), using these measurements to illustrate that the computational results presented in this manuscript will ultimately require detailed experimental validation. Specifically, the following has been added:

“Recent laboratory studies of spherical particles using absorbing cores with non-absorbing coatings showed generally good agreement with predictions from Mie theory for spherical particles for absorption (Shiraiwa et al., 2009;Lack et al., 2009) and extinction (Abo-Riziq et al., 2008; Lang-Yona et al., 2010) . However, when non-absorbing cores with slightly absorbing coatings were considered the model/measurement agreement for extinction measurements was found to be worse (Lang-Yona et al., 2010). This suggests that the computational results presented here should be considered as a guide to understanding the general influence of C_{Brown} on aerosol absorption, but that experimental verification will ultimately be needed.”

5. P7L1: add after CBrown “and layer thickness”.

This has been done.

6. P7L22: In light of the increased absorption by brown carbon at short wavelength I suggest that the calculations will be conducted down to 300nm.

We initially attempted to do this, however the lack of measurements of k_{Brown} or MAC of C_{Brown} down to these wavelengths convinced us not to model down to that wavelength. We attempted to maintain a link to measurements in this study. The accepted visible wavelength spectrum window seemed to be the next logical limit to model.

7. P8L3: the values of k_{Brown} given in Dinar et al (Dinar et al., 2008) at 390 nm are higher for primary HULIS (about 0.1) and lower for secondary HULIS (0.02). These numbers can be used in the calculation for more realistic scenarios and also for demonstrating the effects of increasing absorption on the enhancement.

We have included the Dinar et al. results in our discussion of the effect of RI. Our lower and upper bounds on RI were very similar to the results reported by that study.

8. P9L9: the discussion is mostly for thick coatings. However, thinner coatings are probably more prevalent in the atmosphere. What happens with thin coatings? What is the threshold for an effect? How does it relate to the wavelength (thin and thick would relate to the wavelength).

The results in Figure 4 suggest that the effect is minimal for very thin coatings, which suggest that thin coatings of C_{Brown} effectively act as C_{Clear} . The following has been added to section 4.1:

“For very thin shells (regime 4) the E_{Abs} loss can be up to 10% and as shell thickness decreases, the C_{Brown} coating behaves more like C_{Clear} .”

9a. P9L22 and throughout the paper: most of the discussion is limited to calculations for a fixed wavelength (400 nm). While the general conclusions are valid, I think that in all the discussion a caveat about this fact should be

added. As stated above, the behavior will be different for different wavelength because of the varying absorption and also because the ratio of the layer thickness to the incident wavelength will change.

We have added the following to section 2:

“We have also performed some calculations at a specific wavelength of 400 nm to illustrate a single wavelength impact. Wavelengths around 400 nm are commonly used in in-situ aerosol optical property measurements. In general, the solar spectrum averaged results are more relevant for the overall climate impacts, whereas the single wavelength results will assist in assessing in-situ measurements.”

9b. Finally, estimation for the entire solar spectrum should be done in all cases (was done in several cases) followed by discussion of the effects of coatings on the entire solar spectrum.

We have recalculated the results from Figure 6 for an additional wavelength. For some of the modeling work it is difficult to introduce the 4th dimension without complicating the presentation.

The following has been added to section 4.3:

An updated Figure 6:

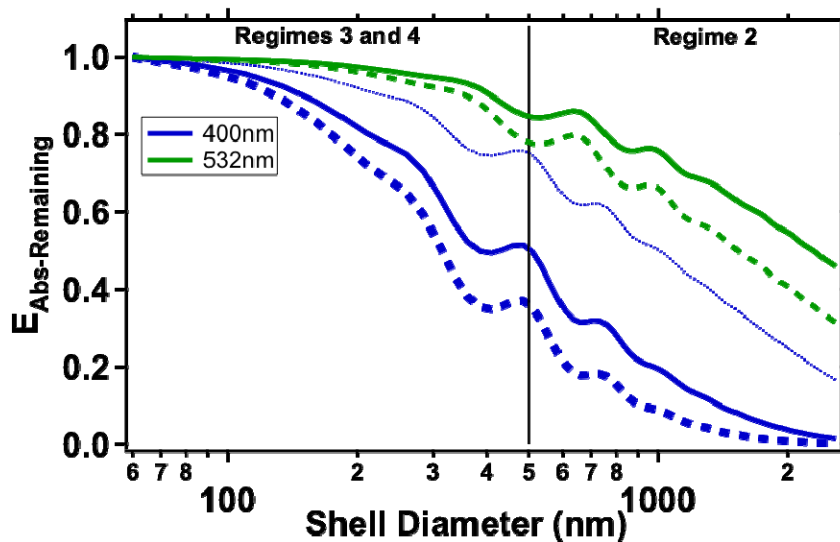


Figure 6, Calculated $E_{Abs-Remaining}$ for a 60nm diameter BC core and varying C_{Brown} shell diameters at 400 nm and 532 nm wavelength for high (thick dashed line), mid (solid black line) and low (thin dashed line) k_{Brown} values corresponding to Fig. 2.

and “At 532 nm, increases in k_{Brown} lead to an increase E_{Abs} loss by only a few percent for reasonable coating thicknesses (<500 nm) but lead to larger increases when very thick coatings are present.

9c. Flores et al (Flores et al., 2009) for instance found that integrating over the entire solar spectrum, brown carbon can be treated as purely reflective material (in terms of Q extinction). Is this also correct for coatings by brown carbon? Probably not according to this paper. This is an interesting point to discuss.

The conclusion from Flores et al. with respect to being able to treat the coating as purely reflective appears to be specific to the spectral behavior of Swanee River Fulvic Acid (SRFA), which absorbs most strongly at wavelengths below 380 nm. In comparison, Flores et al. find that for Nigrosin dye the imaginary refractive index, averaged over the entire spectrum, is actually ~0.2. This

suggests that the overall impacts of C_{Brown} will depend importantly on the actual spectral dependence of the imaginary refractive index for C_{Brown} in the atmosphere. This is now mentioned in the conclusions section where we have added:

“Estimates of the absorption strength of C_{Brown} from the literature are highly variable, likely depending on the C_{Brown} source and composition; certainly further research is required to fully understand this variability as the overall climate impacts of C_{Brown} will depend importantly on the exact wavelength dependence of the absorption (e.g. Flores et al., 2009).”

10. P9L22: This phenomenon is a function of wavelength. Hence one has to discuss and study this “hyperspectrally” and the discussion should emphasize the wavelength dependence.

Section 3 has been updated to discuss more explicitly the wavelength dependence.

11. P11L3: state the wavelength of the calculation in the text.

400nm radiation was used for these calculations and is stated in the text.

12. P11L19: again, depends on the incident wavelength.

The text contains a clarification that this effect is dominant at shorter wavelengths.

13. P15L4: As shown by Adler et al(Adler et al., 2009) the calculation by equivalent volume spheroid, or aggregates gives different results depending on the size of the spherule and the overall size of the agglomerate. Adler et al suggest that the coatings should be treated in the

calculation, in line with the conclusions of this paper.

The following section has been added at the end of section 2:

“We also note here that the use of Mie theory assumes spherical particles. There is sufficient evidence that BC, usually fractal when emitted from efficient combustion, can become more compact and spherical when coated in other inorganic and organic material (Alexander et al., 2008; Lewis et al., 2009; Zhang et al., 2008). Our modeling mostly deals with coated BC cores. In the limit of thinly coated cores, where fractal BC is more likely, the work of Liu et al. (2008) provides guidance on the differences in absorption for fractal vs. spherical BC. For smaller (15nm) and larger (25nm) BC spherule sizes, absorption will likely be overestimated by up to 10% and underestimated by up to 20% if represented as spherical.”

14. P21L18: add “and the shell thickness” before the end of the sentence.

This has been added.

15. P22L5: again, the statement is probably not completely true as it will be different for short and long wavelengths.

The wavelength dependence to this has been added to make this a more accurate statement.

Response to Reviewer 3 From Open Discussions:

1. The authors devote much of their efforts into separating the lensing effects and the absorption of the shell. This introduces substantial uncertainty and even bias to their calculations. An important question

arises in connection with the basic assumption supporting this separation (Page 791, line 27-28): is it really so that the absorption by brown carbon shell is exactly the same on a purely scattering core as on black carbon? Basic optics implies that the two should be different: absorption must be higher in shells surrounding a scattering core, since scattered radiation can again be captured by the shell, which is not the case for a shell above highly absorbing black core. If the basic assumption is not true, it will essentially invalidate the entire concept of ‘remaining absorption’ (e.g. page 792, line 9) to which a substantial part is devoted in the manuscript.

In light of this comment we have re-run the code to see if there was a better way to represent the absorption of the C_{Brown} core. We now calculate the absorption of a C_{Brown} particle having the diameter of a) the core and b) the shell. The absorption of the shell-sized particle is subtracted from the absorption of the core-sized particle to provide absorption of what would be the C_{Brown} shell on top off any core.

This slightly different calculation does not affect the results substantially; however we agree that the old method may have introduced some bias. Section 3 has been modified accordingly:

“First, the σ_{Abs} of a homogenous particle (with diameter d_{Shell}) of C_{Brown} (e.g. using k_{Brown} RI from Fig. 2) system is calculated across all visible wavelengths. This is repeated for a C_{Brown} particle with diameter d_{Core} . The difference between these two σ_{Abs} provides a measure of the absorption by the C_{Brown} coating after accounting for the size dependence of absorption and scattering.”

2. The manuscript focuses on what may happen with absorption when a transparent shell is replaced with a slightly absorbing one. From [a] modelers’ perspective, it is the overall absorption that matters, i.e. there is little interest in how much absorption is lost relative to a hypothetical case.

A more interesting issue would be to see what happens in the model case (slightly absorbing shell on BC core) relative to the case in which brown carbon and BC is treated separately (as an external mixture). Nevertheless, this manuscript is one of the first attempts to introduce the concept of brown carbon to the modeling community.

In this manuscript we assumed that the absorption of C_{Brown} itself is a quantity that can be easily modeled if the refractive index is well-known (which it is not at this point). However, many studies in the past have raised the alarm that lensing of BC by clear shells will increase the absorption by up to 100%. Our motivation here was to see if a C_{Brown} shell would affect this. We agree that a study on internal and external mixtures would be valuable, however we believe it is beyond the scope of this study.

Minor comments: Figure 1 I would have also indicated ‘scattered light’ on the right half-panel of the figure (brown carbon case).

This has been added.

Page 798 line 5 typing error

After looking in the manuscript we were unable to locate this typing errors. Please feel free to contact us if it the error is still there with specifics of the correction needed.

Page 801 line 7 typing error

This has been fixed.

References:

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