

## RC1:

The manuscript “Constraining the particle-scale diversity of black carbon light absorption using a unified framework” by Payton Beeler et al. reveals the effect of morphology of BC core on light absorption enhancement of BC due to the “lensing effect”. The study used the Amsterdam Discrete Dipole Approximation (ADDA) method to calculate the particle absorption with varying BC core morphology and different coating compositions. Based on the results of the studies the authors found a factor (phase shift parameter) to describe the increase and decrease of absorption enhancements of BC caused by its morphology, and formulate universal scaling laws centered on the phase shift parameter. This study also provides physics-based insights regarding core-shell approximation overestimating BC light absorption. The presentation is concise and clear, and the topic fits well into the scope of the journal. The manuscript could be considered for publication with the following concerns being addressed.

The novelty of the manuscript is not well presented. There have been a number of numerical studies on optical properties of BC with complex morphology using DDA and T-matrix method. Either the fractal aggregate model or coating scheme has been considered before. It is recommended to explain the advance specifically for this work at least in the introduction section.

While T-matrix and DDA methods have been used extensively to investigate light absorption by BC, this study is the first to provide physics-based scaling laws for quick calculation of BC optical properties. It is also one of the first studies to provide insight into causes of discrepancies in modeled and measured light absorption enhancement due to internal mixing of BC. Without the use of the scaling laws developed by this work, one would need to rely on computationally expensive methods (T-matrix or DDA) or incomplete models (such as core-shell Mie theory or scaling laws given by Chakrabarty and Heinson, 2018). Additionally, this study is the first to show (per our knowledge) that measurements of BC light absorption using contemporary instruments can be used to infer the morphology of fractal BC aggregates. We have emphasized these points in the introduction of the revised manuscript.

In this study,  $\rho_{BC}$  (the phase shift parameter of BC core) shows the influence of BC core morphology on its light enhancement, but  $\rho_{BC}$  was determined not only by the morphology, but the size of BC can also influence  $\rho_{BC}$  according to formula (1). In 2.1 section, the authors state to calculate with BC core masses between 1 fg and 70 fg, but the BC size calculation was missing in the results. In addition, previous fractal aggregate studies used the fractal dimension ( $D_f$ ) to represent the morphology, what is the  $D_f$  for the freshly emitted, partially collapsed, and collapsed aggregate in this study?

The gyration radius of BC aggregates in this study ranged from 50 – 300 nm. The  $D_f$  of freshly emitted, partially collapsed, and fully collapsed BC was  $1.832 \pm 0.089$ ,  $2.105 \pm 0.223$ , and 3.0, respectively. This has been added to section 2.1 of the revised manuscript.

The absorption enhancement of BC core through the “lensing effect” was also investigated for light-absorbing coating materials like BrC, and the author notices that the total particle absorption is very sensitive to the image refractive index of the coating material. The increase of particles absorption with coating increase was a competition between the increase of BrC absorption and

the decrease of the BC enhancement due to less light on the BC core. However, MAEBC in this study shows the total absorption of the particle (e.g. in Fig. 4). It is recommended to subtract the absorption by the BrC shell in order to investigate the “lensing effect” of BC.

The choice was made to focus on total particle absorption as opposed to separating BC absorption due to lensing and BrC absorption because common methods for measuring light absorption by BC will measure total particle absorption, and will likely not be able to parse whether absorption enhancement is the result of absorbing coatings or increased lensing. Therefore, we chose to develop scaling laws based on total particle absorption in order to make the results applicable for experimentalists. The contribution of BrC absorption to absorption enhancement, as well as the change in BC absorption due to the so-called “sunglass effect” is left for future work (Luo et al., 2021).

4 Section 2.1: The discussion about the influence of spherical monomer of BC aggregates on its optical properties is missing. Berry and Percival (1986) discussed that optical properties of fractal-like aggregates were determined by the primary spheres. In this study the primary sphere was chosen to be 20nm, Shetty et al., (2021) used 40nm. (<https://doi.org/10.1080/02786826.2021.1873909>).

The radius of BC monomers will affect the radius of gyration, and eventually the phase shift parameter. Therefore, the developed framework is able to account for changing BC monomer size. Shetty et al., (2021) utilized BC spheres with diameter of 40 nm, we have chosen the same monomer size, with radius of 20 nm.

Section 2.2: The settings about the ADDA are not well described. The accuracy of ADDA depended on the size of the sub-volume compared to the wavelength of the incident light. What’s the resolution of dipoles per wave-length in this study?

ADDA recommends 10 dipoles per wavelength for accurate estimation of absorption and scattering properties. Our study utilizes > 100 dipoles per wavelength. This has been added to Section 2.2, for clarity.

Fig. 2: Y axis label is missing.

This has been corrected.

## RC2:

This manuscript presented a method to predict the optical properties of internally mixed black carbon. Based on this manuscript, we can use a single factor called the phase shift parameter to estimate the change of light absorption of internally mixed BC due to different morphology, mixing-state, mass, and coating composition. The method also can be used to predict the absorption properties of coating material and morphology of BC core. This study is significant for BC optical research since it can help improve uncertainties in the current climate model related to BC absorption. The manuscript is well written, and the presentation is clear. The topic also fits very well into the scope of the journal. However, I have some comments and questions about the paper. After considering, responding, and revising the manuscript based on them, this paper should be considered for publication.

### Major Comments:

- 1) This manuscript discusses the influence of the mixing state of BC and coating on the absorption of the entire particle. Have you conducted any simulation for BC mixed with inorganics (e.g., dust, sea salt) then coated by other materials? How would that affect your model results?

We have not considered BC mixed with inorganics. This would alter the effective refractive index of the core, and subsequently alter the phase shift parameter and the absorption cross-section. The model developed in this work will not be accurate for aggregates whose properties vary significantly from those outlined in section 2.2. However, the properties given in section 2.2 are commonly used in large scale models.

- 2) For the ADDA model, could you provide a short description of it? I suggest adding a table of import parameters you used.

The most important input parameter for ADDA calculations is the number of dipoles per wavelength of incident light. We have added a description of this input to section 2.2 of the revised manuscript.

- 3) The first Section 3.1 is not clear to me.
  - a) Does  $\Delta MAC_{BC}$  represent the MAC of the entire particle - MAC of BC core? Same question for  $\Delta k_{coat}$  and  $\Delta n_{coat}$ . Please clarify them.

$\Delta MAC_{BC} / \Delta k_{coat}$  and  $\Delta MAC_{BC} / \Delta n_{coat}$  represent partial derivatives of  $MAC_{BC}$  with respect to the refractive index. We have changed the notation to  $\partial MAC_{BC} / \partial k_{coat}$  and  $\partial MAC_{BC} / \partial n_{coat}$ , and clarified in the text.

- b) You used 30 BC aggregates. Does that mean for each aggregate, you used a different combination of  $n_{coat}$  and  $k_{coat}$ ? Why do you only have 7 points in figure 3? Shouldn't you have 3 points for  $k$  and 3 points for  $n$  at each  $R_{BC}$ ?

For each aggregate, we calculated the optical properties using 9 combinations of  $n_{\text{coat}}$  and  $\kappa_{\text{coat}}$  at 7 different values of  $R_{\text{BC}}$ . The 7 points in figure 3 are representative of the 7 values of  $R_{\text{BC}}$ , and the points and error bars are the average and standard deviation of the partial derivative of total particle absorption normalized by BC mass with respect to  $n_{\text{coat}}$  and  $\kappa_{\text{coat}}$ .

- c) I also noticed that in Fig. 3, at  $R_{\text{BC}} = 10$ , the ratio decreases. Do you have any explanation for that?

We do not have any insights to the reason for this. However, since these aggregates are randomly selected this may be washed away if more aggregates are used in the averaging.

- d) I am not surprised to see  $\Delta\text{MAC}_{\text{BC}}/\Delta\kappa_{\text{coat}}$  is always greater than  $\Delta\text{MAC}_{\text{BC}}/\Delta n_{\text{coat}}$  since  $k$  changes over an order of magnitude, while  $n$  only changes within 0.2.

We wanted to show that changes in  $\kappa_{\text{coat}}$  which have been observed in ambient particles cause large changes in  $\text{MAC}_{\text{BC}}$ . However, the real part of the refractive index does not show as much variability. Therefore, we opted to constrain the sensitivity analysis to observations.

- e) You used  $k_{\text{coat}}$  between 0.00 and 0.05. What is the step size? Moreover, I think the upper limit of  $k$  might be too low to represent a highly absorbing coating. I am wondering why you choose 0.05 instead of 0.1? Also, a range of  $n$  instead of 1.55 can better represent ambient particles. I recommend adding sensitivity analysis with a broader range of  $k$  and  $n$ .

In figure 3, the step size for  $\kappa_{\text{coat}}$  is 0.05. This sensitivity analysis is not intended to give robust estimations of  $\Delta\text{MAC}_{\text{BC}}/\Delta\kappa_{\text{coat}}$ , but to demonstrate that  $\text{MAC}$  is more sensitive to  $\kappa_{\text{coat}}$  than to  $n_{\text{coat}}$ . We chose to limit our study to weakly absorbing coatings because highly absorbing coatings will cause accumulation of phase shift as light passes through the coating. It is not clear whether the scaling laws provide in this work will be accurate for highly absorbing coatings, but due to computation limits we have left this for future work.

- 4) For equations 3 a and b, how did you come out with this function? Is there any physical meaning? Moreover, does equation 3 only work with  $k = 0, 0.01, \text{ and } 0.05$ ?

Equations 3a and 3b come from damped power law distributions of  $\text{MAC}_{\text{BC}}$  as a function of  $R_{\text{BC}}$  and  $\rho_{\text{BC}}$ . Other than  $\rho_{\text{BC}} = 1$  representing the crossover from Rayleigh to geometric optics, equation 3 is an empirical fit based on previous work by Chakrabarty and Heinson 2018. Equation 3 is accurate for  $\kappa_{\text{coat}}$  between 0.00 and 0.05, but has not been tested for  $\kappa_{\text{coat}}$  outside of this range.

## Specific comments

1. L83-85, “The mass of the BC ... (Bond and Bergstrom, 2006).” For the density you chose, I suggest using a range instead of single values so that you can represent the wide range of ambient particle density and uncertainties in the literature. Thus, I am also curious to see the dependence or uncertainties related to the density.

Uncertainty related to the density can be calculated by multiplying the calculated  $MAC_{BC}$  by the ratio of  $1.8 \text{ g/cm}^3$  to the density in question. We have done this calculation and added a supplementary figure showing  $MAC_{BC}$  with densities between  $1.6$  and  $2.0 \text{ g/cm}^3$ . We have left the main figure text showing BC with density of  $1.8 \text{ g/cm}^3$ , as this is a commonly used value.

2. Figure 2 is very blurry. Please make sure the final version has a higher resolution.

This will be corrected upon revision.

3. Figure 3, What are these error bars represent?

They represent one standard deviation. This has been added to the caption.

4. In the manuscript, you used  $\rho$  to represent the phase shift parameter. However,  $\rho$  is usually used for density. I suggest using a different Greek letter.

We chose to stay with notation which has been used in previous publications (Sorenson 2011, <https://doi.org/10.1080/02786820117868>). While we understand that  $\rho$  is also used for density, we are hopeful that section 2.3 clarifies the notation.

5. L132-133, “The BC refractive ... ,2006).” Could you clarify whether you use this RI value for all wavelengths or just 550 nm?

This has been clarified in the revised text.

6. Section number for sub-sections in Sect. 3 need to be corrected.

This has been corrected.

7. In figure 4, I can see the authors want to keep the same scale for all sub-figures, but there are too many white spaces in b, d, and f, making it very difficult to see the trend in the  $\rho < 1$  regime. Please consider changing the y-axis limit. Moreover, in b and f, why the number of RBC dots is different from other RBC?

There were some issues in the orientation averaging of the optical properties of these particles, so they were excluded from figure 4. We have filled in data points where possible.

8. L232-234, “It has been ... fixed at 0.00.” Could it be that the coating is absorbing, but  $\rho$  is greater than 1?

This is possible, but unlikely given that these studies all use wavelengths  $> 532$  nm, where there would be very weak absorption by organic coatings.

9. Figure 7 b should be a table, not a figure.

We have moved figure 7b to a table.

10. L250, should not Figure 3(b) be Figure 7(b)?

Yes, this has been corrected.

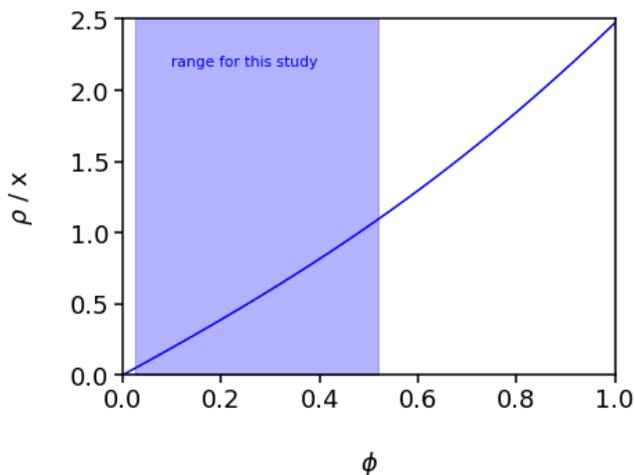
## CC1:

- 1) Could the authors add a more quantitative discussion of  $\phi$ ? As stated, the entire discussion of the BC-core  $\rho$  comes down to  $\phi$ , which can be constrained as about 0.1 to 0.4 (Zangmeister et al., 2018, <http://www.pnas.org/cgi/doi/10.1073/pnas.1403768111>; also Schnitzler et al. 2017 is relevant <http://dx.doi.org/10.1016/j.jaerosci.2017.01.005>). If there was some reason the authors did not discuss  $\phi$  directly, could they please comment? If not,
  - a) can the authors calculate  $\phi$  for their model aggregates, and discuss whether the upper-limit packing density identified by Zangmeister et al. 2018 allows the literature trends to be fully explained by  $\phi$ ?

The  $\phi$  of our model aggregates ranged from 0.026 to 0.52. Full explanation of some literature trends requires packing densities that are larger than the upper limit observed by Zangmeister et al. in their 2017 paper. While it is not impossible for monomers to arrange in a way that achieves these higher packing fractions (face-centered cubic arrangement with  $\phi = 0.74$ , for example). However, based on recent findings we think it is unlikely that BC monomer would compact to this degree. Therefore, we think that it is extremely likely that other mechanisms are also playing a role in the decreased MAC observed by some studies, most notably heterogeneity in Rbc. The intention of this work and subsequent discussion is to demonstrate that BC morphology affects light absorption properties, and to provide a tool which eliminates reliance on models which make assumption about BC morphology. We will add further discussion on the packing fraction of our modeled aggregates and the limits of ambient BC packing fraction upon editing.

- b) Also, can the authors provide more information about the  $\phi$  of their modelled particles, for example by plotting  $\phi$  versus  $\rho$  or MAC?

Since the phase shift parameter is dependent on the size parameter and  $\phi$ , we will include the following supplemental figure, which shows the size parameter normalized phase shift parameter as a function of  $\phi$ . This plot also shows the range of  $\phi$  which was included in this study.



2) The authors state that “Our results indicate that studies which find little to no increase in MACBC with increased RBC are measuring BC aggregates which have undergone significant coating-induced restructuring, while studies that find significant increases in MACBC are measuring aggregates which have undergone little to no restructuring.” How confident are the authors that alternatives have been excluded, and that this statement is the most likely given all available evidence? For example:

a) Based on a recent review of soot-restructuring studies ([Corbin, Modini, and Gysel-Beer, arXiv.2206.03646](#)) I believe this statement should be reconsidered or discussed in terms of the fundamental physics it implies. To briefly summarize that review, we identified multiple studies that demonstrated unequivocally that liquid condensation typically induces restructuring. These studies used various materials including organics of varying polarity and sulfuric acid. Our review of these studies and complementary laboratory demonstration, showed that condensation-compaction coatings can only be avoided when solid coatings or liquids with very high contact angles (which may result in heterogeneous nanodroplet activation and therefore avoid compacting surface tension forces) were used. Examples of such solids include SOA formed at low RH or anthracene (relevant only to the laboratory). Compaction can also be avoided by coagulation. So, if internally mixed BC has not undergone extensive restructuring, it must have mixed with solids (including highly viscous glasses) or by coagulation.

My impression from the recent studies by Fierce et al. (cited by the authors) is that while night-time coagulation can be significant, it is unlikely that most soot particles mix by coagulation. But, perhaps the authors’ work implies that my impression was inaccurate. My impression is also that solid organic coatings form only rarely, since they require very low RH or low temperatures, while organic vapours are emitted most often at higher temperatures. It seems to me less likely that solid coatings explain the field data on absorption enhancement.

So, the authors’ conclusions can be reconciled with the known mechanisms of soot restructuring by arguing that some studies primarily observe liquid-condensation coatings while other primarily observe solid-like coatings or coagulation coatings.

We agree with all points given above, and that our previous statement needs to be altered. The original intention of our statement was not to imply that some studies are measuring soot which has not restructured, but that some studies are measuring soot which has achieved  $\rho_{BC} > 1$  and others are measuring soot with  $\rho_{BC} < 1$ . We agree with the conclusions of the above comment that it is unlikely for solid coatings to form in ambient conditions, and therefore unlikely that BC morphology would remain unaltered during coating uptake. We believe that studies which find significant absorption enhancement could be measuring particles which have undergone restructuring, but  $\rho_{BC}$  has not increased past unity. This could happen when the product of size parameter and packing fraction is small. For example, small soot particles which undergo significant restructuring (large  $\phi$ ) may still have  $\rho_{BC} < 1$ , and based on our results would show significant absorption enhancement with increasing coating amounts. We will rephrase our previous statement as follows:

“Our results indicate that studies which find little to no increase in  $MAC_{BC}$  with increased  $R_{BC}$  may be measuring BC aggregates which have undergone significant coating-induced restructuring, leading to  $\rho_{BC} > 1$ . On the other hand, studies that find significant increases in  $MAC_{BC}$  may be measuring aggregates which have  $\rho_{BC} < 1$ , and may also be measuring particles which have significant heterogeneity in  $R_{BC}$ . This does not imply that these studies are measuring BC which has not restructured, only that the product of the size parameter and core packing fraction of BC is not large enough such that  $\rho_{BC} < 1$ .”

- b) On Line 71, the authors state, “Recent studies have found that the non-sphericity of BC containing particles (partial encapsulation of BC) can decrease absorption enhancement (Hu et al., 2022, 2021). While these findings are notable, previous studies have not observed a prevalence of partially-encapsulated BC, yet decreased light absorption is still observed”. Is it possible that the authors have too readily rejected the hypothesis of H1) partially encapsulated, or off-center mixing states, in favour of H2) condensation-without-compaction? Given the abovementioned review, I believe H1 is plausible while H2 is extremely unlikely. I would consider the entire manuscript to remain valid and valuable if H1 is rejected over H2. The only change is that  $\phi$  becomes  $\phi_{eff}$ . (Would the same trends in MAC be observed?)

We do not consider here the effects of off-center mixing states, as it is outside the scope of this work. We agree that we should not reject H1 altogether, but the effects of off-center coatings will be more prevalent at small  $R_{BC}$ , and we do not believe that H1 can fully explain observations of low  $E_{abs}$  at large  $R_{BC}$ . Since our definition of  $\phi$  only includes the BC monomers, the  $\phi$  of modeled aggregates will be unaffected by coating location for modeled aggregates.

3. This is more of an editorial comment. The highest  $\rho_{BC}$  in Figure 7b were measured at the shortest wavelengths and the two highest studies were both first-authored by Cappa. Some readers may wonder whether there was a systematic effect here (for wavelength, it is expected by definition; and for the Cappa group, the question is whether they use a unique experimental approach that caused a bias relative to other data sets). I do not personally believe that these are real issues, but they deserve may a brief comment for the reader’s benefit.

We believe that it is possible that the estimated  $\rho_{BC}$  for the Cappa studies may be slightly higher than the true  $\rho_{BC}$  of the measured particles. This is because the Cappa studies both made use of thermodenuders. Thermodenuders may not completely remove low-volatility organics from BC, causing overestimation of absorption by BC, and subsequently lower  $E_{abs}$  (Shetty et al., 2021 <https://doi.org/10.1080/02786826.2021.1873909>). It is unclear whether low-volatility organics in fact did bias the absorption measurements in these studies, but is a possible explanation for the elevated  $\rho_{BC}$ .

While reading, I also made various minor notes. I will list them below as suggestions for the authors.

- a) I'd add a row showing partially encapsulated/collapsed examples in Figure 2.  
[We will move the partially collapsed BC example shown in figure S1 to the main text.](#)
- b) Line 105-109 may need clarifying. Why would someone use the RDG MAC when estimating Eabs? To me, a "literature value" would be a measured MAC of mature, open-structured BC (Liu et al., linked below). Text may not convey your intention here.  
[This section will be altered to reflect the intention that consideration of fractal morphology can affect the MAC of pure BC.](#)
- c) What is the role of  $\phi$  in Figure 3? No effect?  
[The change in MAC for changing coating refractive index was calculated with constant  \$\phi\$ , so there is no effect. This will be clarified in the text.](#)
- d) Line 161, there may be a better citation for the imaginary refractive index (Sun and Bond?).  
[This study will be cited upon revision.](#)
- e) Line 163, add SOA after pinene.  
[This will be incorporated upon revision.](#)
- f) Line 164, consider citing Lu et al <http://dx.doi.org/10.1021/acs.est.5b00211>  
[This will be incorporated upon revision.](#)
- g) Line 180, are the four digits of precision meaningful in 6.819 m<sup>2</sup>/g? What is the corresponding standard deviation? Also, it may be worth discussing this value in comparison to the measured mean value of 8.0 ± 0.7 m<sup>2</sup>/g (Liu et al. <https://doi.org/10.1080/02786826.2019.1676878>)  
[The number of significant digits in the calculated MAC<sub>0</sub> is limited by the density of BC, therefore it will be changed to 6.8 m<sup>2</sup>/g upon revision. We will also discuss this finding in comparison with Liu et al.](#)