RESPONSE LETTER OF REVISION (EGUSPHERE-2024-3781)

Title: Numerical quantitation on the effect of coating materials on the mixing state retrieval accuracy of fractal black carbon based on single particle soot photometer

Dear Editor and Referee:

We have revised our manuscript based on the comments. The corrections and modifications have been included in the revised manuscript and the details are listed as follows. The responses are highlighted in blue font. The changes made in the revised manuscript are marked in red font.

General comments

In this study, the authors used closed-cell model (CCM) and coated-aggregate model (CAM) to retrieve three types of coatings, i.e., sulfate, non-absorbing OC and BrC on black carbon (BC) and investigate their potential impact on the optical properties of BC. It is good that the retrieval uncertainties are also quantified and discussed. The study underscored the importance to consider the coating material when measuring the mixing state of BC and estimating the absorption enhancement (E_{ab}) and radiative forcing (RF). The potential contribution of this study is within the scope of AMT. However, the current version lacks some descriptions of important details and further discussions. It is behind publication quality. Therefore, I recommend that substantial revision needs to be done before considering publication.

Response:

Thanks a lot for reviewing our manuscript and for all these constructive comments. All these comments are very helpful in further refining the manuscript, and we have responded to the comments point by point. Necessary details and discussions of results have been supplemented in the revised manuscript. Thank you again for reviewing our manuscript.

Major comments:

Definitions of some terms, i.e., Dc, Dp, and mixing state, are not clear in the introduction which causes confusing at the very beginning. However, some of them are very well described in the method section. Please consider reorganizing.

Response:

Thank you very much for the valuable comments and suggestions. We have reorganized the relevant descriptions of the important terms in the revised manuscript. The D_c denotes the equivalent volume diameter of the black carbon core, and D_p denotes the optical equivalent diameter of the coated black carbon. The particle diameter ratio of the whole particles to the BC core (D_p/D_c) is used to characterize the mixing state. The related description has been modified in the revised manuscript as follows:

"The differential scattering property can be derived subsequently, and the optical equivalent diameter of the whole coated BC particle (D_p) can be retrieved based on the Mie scattering theory in combination with the spherical core-shell model."

"After the coating is completely evaporated, the bare BC emits incandescent signals, since the peak of the incandescent signal is proportional to BC mass, the volume equivalent diameter of BC core (D_c) can be obtained by using BC density of 1.8 g/cm^3 (Schwarz et al., 2006; Bond and Bergstrom, 2006)."

"Finally, the mixing state of coated BC at the single particle level can be characterized by the SP2 as the particle diameter ratio of the whole particles to the BC core (D_p/D_c) (Schwarz et al., 2008a; Schwarz et al., 2008b)."

The effect of complex morphology is not very well discussed. Although it is mentioned in the abstract, introduction and methodology, it is not emphasized in the results and discussions. Please consider reshape the manuscript accordingly.

Response:

Thanks for this constructive comment. We have added in-depth discussions about the effects of complex morphology (coating structures, fractal parameters, and volume fractions of BC core) on the retrieval results of the mixing states and the evaluation of both absorption enhancement and radiative forcing in the revised manuscript.

The results section is like experiment report. This should be revised by adding logical linkage between different paragraphs, rather than only listing descriptions of the figures one by one. The authors should reshape this part.

Response:

Thank you for your valuable comments. We have rewritten most of the section of "result and discussion" in the revised manuscript.

A big concern is that some results are apparently affected by the leakage points; however, the author didn't give enough explanation for such missing data, which needs to be discussed, and an improvement should be considered and/or done. Would it be possible that some of the similar results between sulfate and OC coatings, and their difference from the BrC coating, mainly due to the amount of data points? If yes, this is technical issue which must be well addressed before discussing the scientific questions and drawing conclusions.

Response:

Thanks for the valuable suggestion. The reason for the existence of a certain number of missed points of the retrieved D_p/D_c is the inherent differences between the fractal BC model and the spherical core-shell model, in other words, there is no core-shell model whose differential optical scattering properties could match the coated BC particle with morphological parameters corresponding to the missed points. As for the single particle level, the missed points would not affect the analysis of variation trends of the results. While the missed points do affect the retrieved mixing states and the evaluated radiative effects for particle groups. However, the phenomenon of missed points of the SP2 due to the unreasonable assumptions of both the particle shape and the refractive index of the coating is what we want to stress. And the coating materials have obvious effects on the amount of missed points, the BrC coating leads to more missed points. To truly reflect the missed points of the SP2 and evaluate the effects of the missed points on the further application of the observation results of the SP2, the missed points are all considered in the evaluation of absorption enhancement and radiative forcing in our study.

The authors used two models and showed the differences between them. As a technical paper, this is good but not enough. It would be necessary to discuss the similarities and differences between their results, and model limitations, respectively.

Response:

Thank you for the meaningful comment.

The closed-cell model and the coated aggregate model are constructed to represent thinly coated and thickly coated BC, respectively. Due to the inherent optical difference between the fractal model and the core-shell model, the retrieval results of the mixing states for both kinds of fractal models contain obvious retrieval errors. The effects of the fractal dimension and volume fractions of BC on the retrieved mixing state are similar, while the effects of coating materials are slightly different. The mixing states for most coated BC, represented by two fractal models, would be underestimated by the SP2. Even though there are widespread phenomena of missed points, the amount of missed points is quite distinct for different models with various morphological parameters. When the retrieved mixing states are used to evaluate the absorption enhancement of coated BC, the evaluated E_{ab} is overestimated at first and then underestimated for most cases. In short, when compared with the core-shell model, the closed-cell model and coated aggregate model show some similarity, however, there are also obvious differences between these two models coated by three components.

In addition, even though the closed-cell and coated-aggregate models could represent realistic coated BC to some extent, with the development of the morphology model, there are more advanced models for coated BC, such as fractal BC with more irregular coatings, partially coated BC, and BC with non-spherical monomers (Luo et al., 2018). Therefore, to more precisely evaluate the optical retrieval errors in the mixing states using the SP2, more realistic morphological models and more coating types still need to be employed. Necessary descriptions have been added to the revised manuscript.

"For the future, the more advanced morphological models for coated BC, such as fractal BC with irregular coatings, partially coated BC, and BC with non-spherical monomers, and more diverse coating components should be considered to further quantify the retrieval errors in the mixing states using the SP2."

The conclusion part needs a rewrite after evaluating and/or resolving the issue of leakage points. In addition, the conclusion is not only repeating the results and summarizing the main findings but also discussing the main limitations and the importance of this study in the field of atmospheric science and /or broader field, and proposing future work if possible, etc.

Response:

Thank you for your valuable comments on our research. We have revised the conclusion section to summarize our main findings in a better way. The obvious retrieval errors in the mixing states measured by the SP2 due to the unsuitable assumption on both the core-shell structure and the single complex refractive index 1.50+0*i* of coatings are stressed. We emphasize the fractal morphologies and the coating components should be considered in the retrieval principle of the SP2 to improve the retrieval accuracy and facilitate the application of the observed mixing states of BC. We also put forward that more advanced morphological models should be considered to obtain more valuable information about the effect of complex shape and diversity of coatings on the measurement accuracy of the mixing state of BC using the SP2. Specific revisions are detailed in the revised manuscript.

Minor Comments:

Line 50: The definition of D_c is unclear here. Please revise. How does the D_p/D_c represent mixing state? Please explain it here. Please define the mixing state in this study. Otherwise, refer the readers to the method section.

Response:

Thank you very much for the valuable comments. We have reorganized the relevant descriptions of the important terms in the revised manuscript. The D_c denotes the volume equivalent diameter of the black carbon core, and D_p denotes the optical equivalent diameter of the coated particle. The diameter ratio of the whole coated particle to the BC core (D_p/D_c) is used by the SP2 to characterize the mixing state of coated BC. The related descriptions have been modified in the revised manuscript as follows:

"The differential scattering property can be derived subsequently, and the optical equivalent diameter of the whole coated BC particle (D_p) can be retrieved based on the Mie scattering theory in combination with the spherical core-shell model."

"After the coating is completely evaporated, the bare BC emits incandescent signals, since the peak of the incandescent signal is proportional to BC mass, the volume equivalent diameter of BC core (D_c) can be obtained by using BC density of 1.8 g/cm^3 (Schwarz et al., 2006; Bond and Bergstrom, 2006)."

"Finally, the mixing state of coated BC at the single particle level can be characterized by the SP2 as the particle diameter ratio of the whole particles to the BC core (D_p/D_c) (Schwarz et al., 2008a; Schwarz et al., 2008b)."

Line 57 and 62: Please remove the full names of D_c and D_p but just keep the abbreviations. Please do it throughout the manuscript.

Response:

Thank you for the comments. The full names of D_c and D_p involved have been modified to abbreviations in the revised manuscript, except for the first time they appear.

"The morphology simplification of aged BC would result in inherent errors in the D_p and the mixing state."

"Our previous studies have preliminarily revealed that fractal morphology and coating structure can result in mixing state retrieval errors up to approximately 80%, and it is worth noting that the characterization of D_p/D_c based on Mie theory would miss some amount of mixing state results for coated BC with certain microphysical parameters (Liu et al., 2023b)."

"Nevertheless, the refractive index of the coating shell is roughly assumed to be constant 1.50+0i in the current optical retrieval scheme of the SP2, so the single refractive index would also lead to retrieval errors in both D_p and D_p/D_c."

Line 63-65: The current descriptions for light and heavy coatings are unclear. Please add more.

Response:

Thanks for your constructive comments. Based on the lag time between the appearance of the scattered signal and the incandescent signal recorded by the SP2, the coated BC can be classified into thinly and thickly coated BC. BC with light coatings means that the BC aggregate is covered by a thin coating film, which can be represented by the closed-cell model. On the contrary, BC with heavy coatings means that the BC aggregate is fully encapsulated in a mass of coating material, which can be represented by the coated aggregate model. The related descriptions in the revised manuscript have been modified as follows:

"More specifically, the BC core and outer coating are assumed to be concentric double spheres, while the realistic BC can be an aggregate covered by a film (thinly-coated) or encapsulated in a package (heavily-coated) (Qin et al., 2022)."

"The CCM is also a fractal aggregate whose monomer is a concentric double-layer sphere, the inner sphere represents BC, and the outer sphere represents the coating. For the construction of the CCM, the original fractal aggregate generated by DLA is enlarged according to the BC volume fraction, and then a soot sphere is added into each enlarged monomer. As for the coated aggregate model (CAM), the whole fractal aggregate generated by DLA is encapsulated using a spherical coating (Liu et al., 2023a)."

Line 189: Define real and imaginary components of refractive index, and give references.

Response:

Thank you very much for the meaningful comments. The real and imaginary parts of the complex refractive index have been defined in the revised manuscript, and the necessary reference has been added as follows:

"The distinction in complex refractive indices of coatings is one of the fundamental reasons for the optical differences. As for coating materials, the real part of the complex refractive index refers to the ratio of the propagation speed of light in a vacuum to that in the coatings, reflecting the scattering ability of the coating material. While the imaginary part refers to the attenuation of light during the propagation, reflecting the absorption ability of the coating material (Mishchenko et al., 2002)."

Line 202: Please give the reasons for that SP2 will lose data in the retrieval of the mixing state of BC with BrC coating.

Response:

Thank you very much for the valuable comments. The SP2 misses data in the retrieved mixing states of BC because of the inherent optical distinction between the realistic fractal BC coated by different materials and the core-shell model with single refractive index of the shell. Furthermore, not only would the BrC-coated BC lose some of the mixing states, but similar phenomena also occur for BC coated by sulfate and OC, for the same reason. More detailed explanation have been added in the revised manuscript:

"It should be noted that there are a certain number of missed data points of retrieved D_p/D_c, because of the inherent differences between the fractal coated BC model and the spherical core-shell model. More specifically, there is no core-shell model whose differential optical properties could match the coated BC particle with certain parameters corresponding to the missed points. There are missed values of retrieved D_p/D_c for sulfate coated both CCM and CAM with BC core diameter ranges from about 200 to 400 nm, just like the situation revealed by Liu et al. (2023b)."

Line 204-206: Remove the figure caption, which should only be shown with the corresponding figure. Please do it for all the figure and table captions embedded in the main text.

Response:

Thank you for the suggestions. All the captions of both figures and tables embedded in the main text have been removed in the revised manuscript.

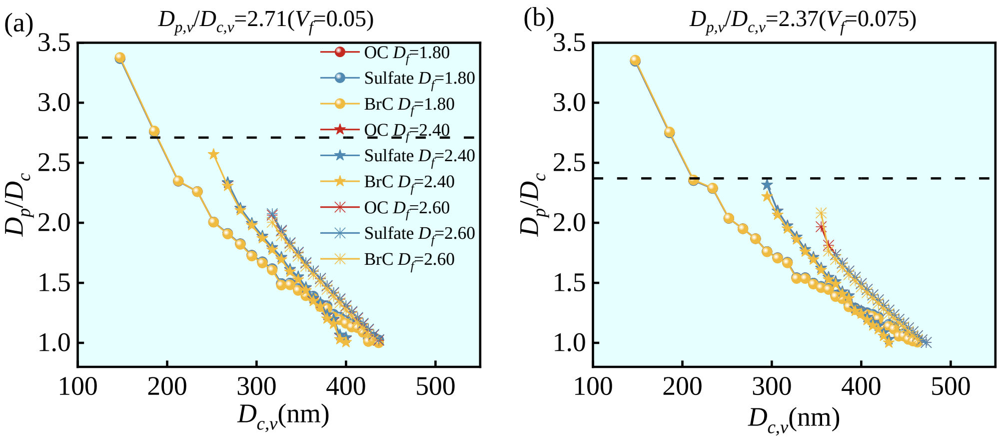
Line 212: This statement is not accurate: not all the retravel results of BrC coating are obviously different from the other two coatings. Only 1/3 of the results, i.e., Fig 2 e) and f) show the obvious difference, which is huge and interesting. Please revise and give the explanation.

Response:

Thanks a lot for the valuable comments. After careful examination, we discovered that there were mistakes in the data usage and plotting for the retrieved mixing state of the closed-cell model coated by BrC with D_f=2.60. We are very sorry for these mistakes. Figure 2 has been modified and redrawn in the revised manuscript as shown below. The retrieval results of the mixing state (D_p/D_c) for the closed-cell model coated by different materials are very similar due to the coupling effect of coating structure, volume fraction of BC core, and the relatively small difference in refractive indices for different coating components. The related descriptions and explanations have been modified in the revised manuscript.

"Essentially, the BC aerosols with different coating materials have almost identical optical properties, including differential scattering properties observed by the SP2, due to the joint influence of refractive index and coating structure. On the one hand, compared with the BC, the distinctions in both the real and imaginary parts of the refractive indices of all these coatings at 1064 nm are not very significant. On the other hand, the soot cores are distributed in each of the coating monomers in the closed-cell model, the interaction of each soot would be weakened due to the isolation of coatings.

Furthermore, the lensing effect of the coating would also be reduced with the volume fraction of BC decreasing to a certain degree, like 0.075 and 0.05 in this study (Lack and Cappa, 2010). The enlargement of optical properties caused by the coating would also be inconspicuous anymore. This is also the reason why the retrieved results of D_p/D_c for coated BC are comparable with the V_f increases from 0.05 to 0.075."



"Figure 2. Retrieved mixing state (D_p/D_c) of BC particles coated by different materials represented using the closed-cell model."

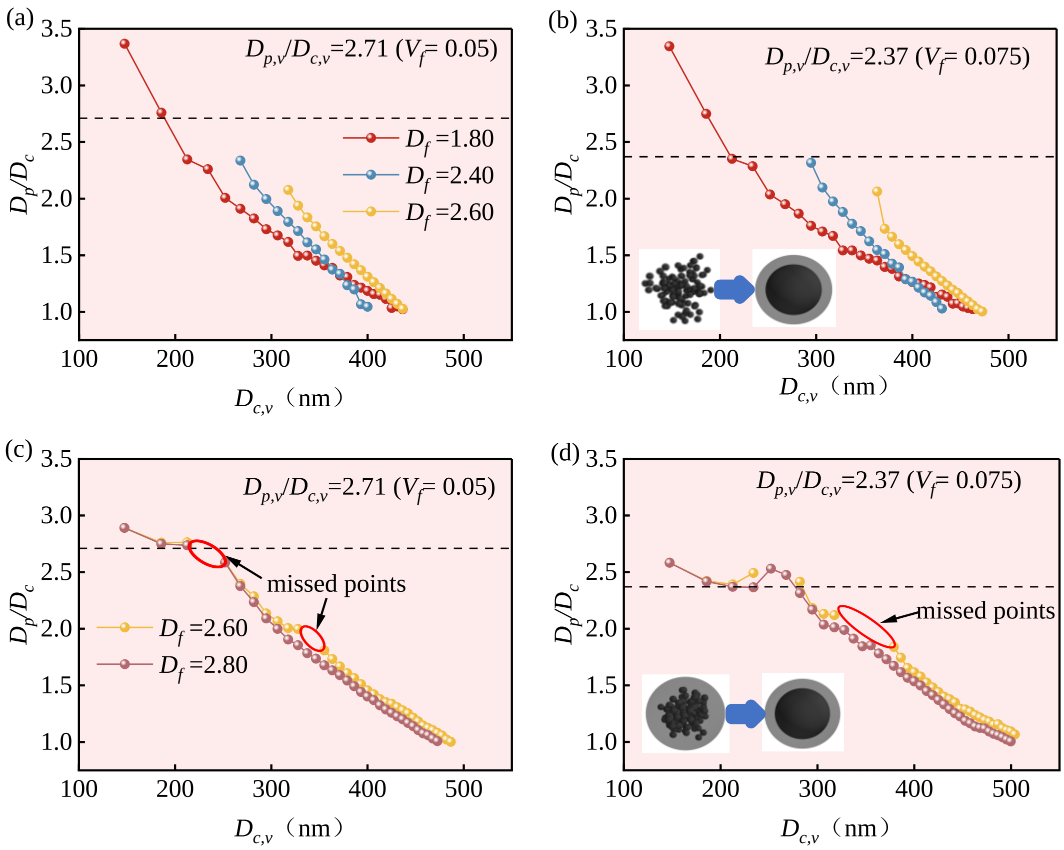
Fig 1: c) and d) why there are some data gaps, especially for Df=2.6? What are the differences between light and heavy coatings? d) Change Y scale to keep consistency with the other three.

Response:

Thank you for the constructive comments. The reason for the missed data points of the retrieved D_p/D_c is that there are inherent optical differences for the fractal BC and the core-shell model, so when the differential optical properties of the core-shell model are used to match those of the fractal BC, such a core-shell model whose differential optical properties are similar to the fractal BC cannot be found. The fractal dimension controls the compactness of fractal BC models. When the fractal dimension for coated-aggregate models is 2.80, the shape of the BC core becomes a sphere. The coated BC is close to a core-shell model in morphology, and the optical properties are close to the core-shell model. Thus, the mixing state for coated BC with D_f=2.80 can be retrieved to some degree and shows fewer missed points. On the contrary, the optical distinctions between BC with a smaller fractal dimension (D_f=2.60) and the core-shell model are larger, which leads to more missed points.

The thinly coated BC is represented by the closed-cell model (CCM), which is a fractal aggregate formed by core-shell monomers. While the thickly coated BC is represented by the coated-aggregate model (CAM), which consists of a bare BC aggregate and a spherical coating. Even though the retrieved D_p/D_c for both CCM and CAM decrease with the diameter increase of the BC core, the retrieved D_p/D_c for these two models show different sensitivity to the coating structure and the morphological parameters such as fractal dimension and volume fraction of BC core. The variation of morphological parameters also leads to different amounts of missed points and retrieval errors in the retrieved D_p/D_c.

Figure 1 has been modified in the revised manuscript, and related descriptions have also been modified.



"**Figure 1.** Retrieved mixing state (D_p/D_c) of sulfate-coated BC particles with different fractal dimensions. (a, b) thinly coated BC particles with the preset $D_{p,v}/D_{c,v}$=2.37 and 2.71. (c, d) thickly coated BC particles with the preset $D_{p,v}/D_{c,v}$=2.37 and 2.71."

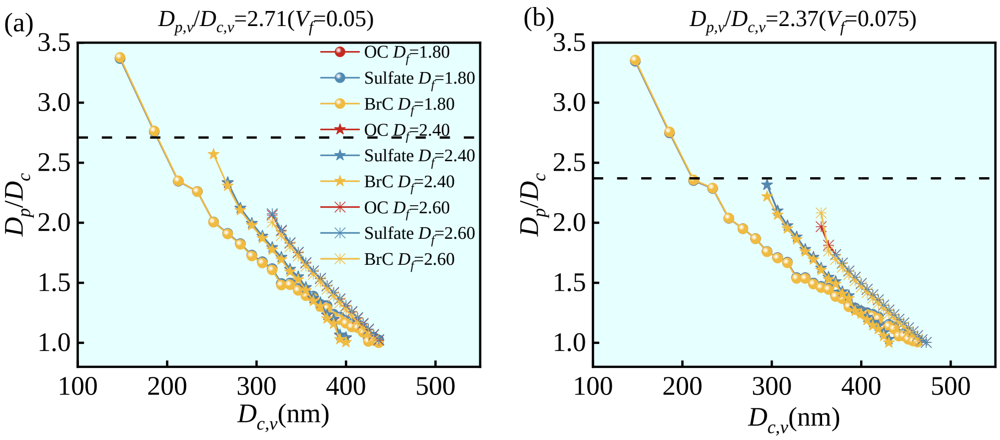
“With the fractal dimension increasing from 2.60 to 2.80, the BC core becomes a sphere and the coated-BC is closer to the core-shell model, optical distinctions between fractal BC and the core-shell model are smaller, which reduces the missed points of retrieved D_p/D_c.”

“As can be seen from Fig.1 (a) and (b) that the retrieved D_p/D_c for thinly coated BC decreases with the diameter of the BC core, and the retrieved mixing states for BC core diameters larger than 200 nm are smaller than the preset values, which signifies that the SP2 will underestimate the mixing states for coated BC whose core size larger than 200 nm. On the contrary, when the BC core is smaller than 200 nm, the SP2 will overestimate the mixing states for thinly coated BC. With the increase of the fractal dimension, the fractal closed-cell structure becomes more compact the retrieval errors in D_p/D_c decrease. The increase of BC volume fraction, that is a small amount of coatings, also leads to reduced values of *RE*. Fig. 1 (c) and (d) indicate that the values of *RE* for thinly sulfate-coated BC particles with D_f=2.60 represented by the closed-cell model are larger than those of thickly coated BC particles represented by the coated-aggregate model, especially for larger BC volume fraction, which reveals that the SP2 has better performance in characterizing the mixing state of thickly coated BC. Unlike the thinly coated BC, as the increase of D_f, the retrieved D_p/D_c for the thickly coated BC deviates more from the preset value, the *RE* becomes more obvious.”

Fig 2: Keep consistency of Y and X scales; change color codes to better distinguish sulfate and BrC.

Response:

Thank you very much for the valuable comments. We have redrawn Figure 2 in the revised manuscript for better comparison and understanding. Since the retrieved mixing states for BC particles coated by different materials under various fractal dimensions and volume fractions of BC core are very similar, even different colors and symbols in the figure cannot exhibit these distinctions in the retrieved D_p/D_c.

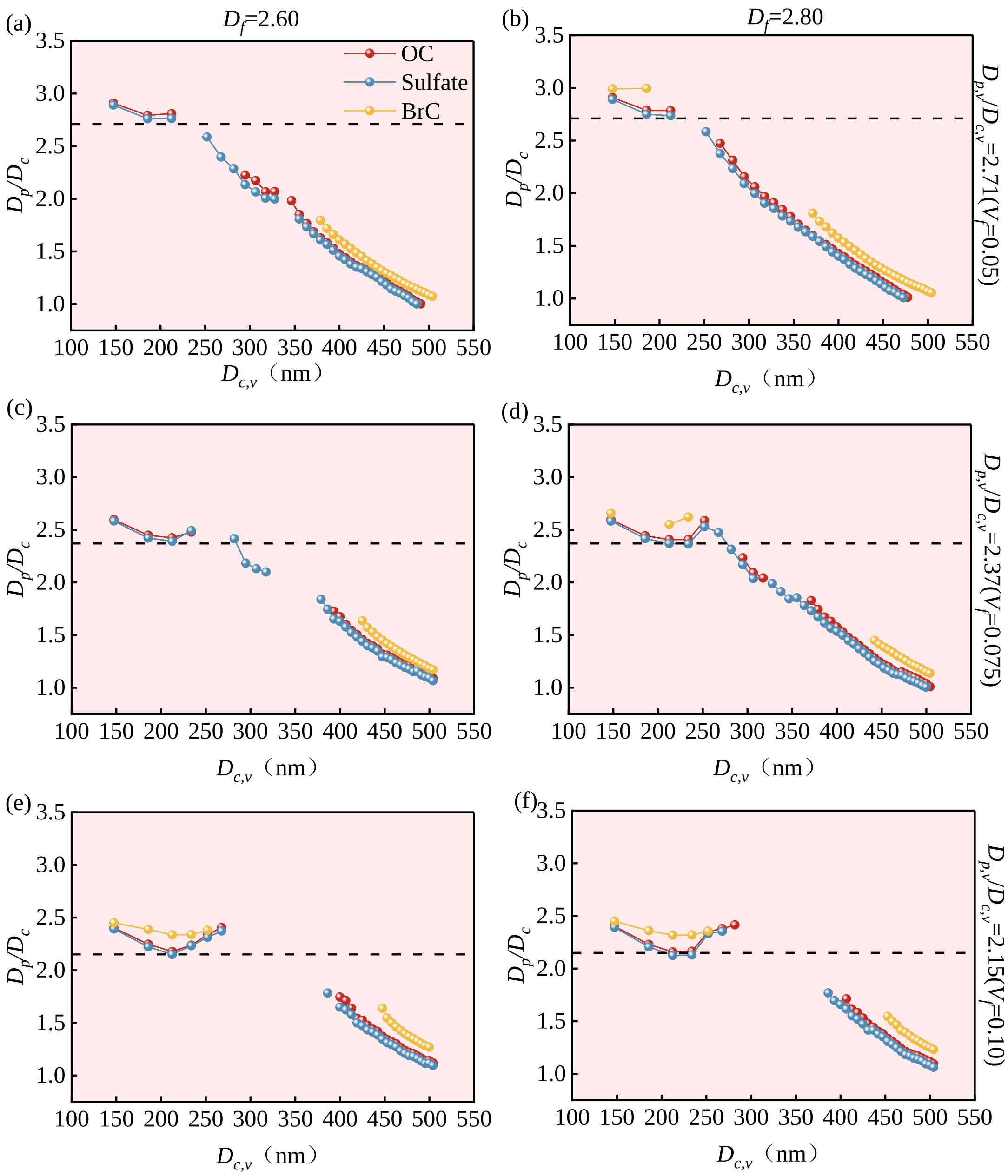


"Figure 2. Retrieved mixing state (D_p/D_c) of BC particles coated by different materials represented using the closed-cell model."

Fig 3: Keep consistency of Y and X scales; It is hard to compare Fig 2 and 3 due to the criteria chosen for showing the results. Please try to keep consistency and if it cannot be maintained, please explain the reasons and/or limitations.

Response:

Thank you very much for the suggestions. We have redrawn both Figure 2 and Figure 3 in the revised manuscript to keep the consistency of both Y and X scales.



"**Figure 3**. Retrieved mixing state (D_p/D_c) of BC particles coated by different materials represented using the coated-aggregate model."

Fig 6: The legend is the same as Fig 5 rather than Fig 4. Please revise.

Response:

Thanks a lot for pointing this out. The related descriptions have been modified in the revised manuscript as follows:

"**Figure 6**. The absorption enhancement of BC thickly coated by different materials and the corresponding core-shell model. (a) The preset $D_{p,v}/D_{c,v}$ is 2.71 and $D_f = 2.60$; (b) The preset $D_{p,v}/D_{c,v}$ is 2.71 and $D_f = 2.80$; (c) The preset $D_{p,v}/D_{c,v}$ is 2.37 and $D_f = 2.60$; (d) The preset $D_{p,v}/D_{c,v}$ is 2.37 and and $D_f = 2.80$; (e) The preset $D_{p,v}/D_{c,v}$ is 2.15 and $D_f = 2.60$; (f) The preset $D_{p,v}/D_{c,v}$ is 2.15 and and $D_f = 2.80$."

Reference

Luo, J., Zhang, Y. M., Wang, F., and Zhang, Q. X.: Effects of brown coatings on the absorption enhancement of black carbon: a numerical investigation, Atmos. Chem. Phys., 18, 16897-16914, 10.5194/acp-18-16897-2018, 2018.