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.

Summary:

In this paper, the authors perform several modeling experiments to evaluate the ways in which different coating materials are likely missed by the DMT SP2 and their effects on retrieved coating diameters, absorption enhancement, and radiative forcing. They find that organic carbon and sulfate coating lead to larger relative errors of the mixing state than black carbon coated with brown carbon and this effect leads to moderate-to-large impacts on the radiative forcing. This work is interesting and provides insightful context on the limitations and potential errors of using SP2 measurements to assess black carbon effects on climate and is well motivated, but the paper is not written well to make these point compelling based on the results. Many details are missing, and the discussion is vague without specific directed attention to the very detailed figures and tables. A large driver of this lack of clarity is the poor writing. The authors should make a concerted effort to carefully review and revise the syntax and diction of this paper so that thoughts are clearly and fully described. I do not recommend this paper for publication in its current form but encourage the authors to make use of the comments and suggestions provided below to improve the paper. Because the issues were somewhat numerous, I was not able to comment on every single one but have highlighted a number of them that I believe can be applied in general.

Response:

Thanks a lot for reviewing our manuscript and the constructive comments. All

Major Comments:

• The introduction of this paper is not written well. Many grammatical errors and sentence structure issues persist throughout. On my first pass of the introduction, I started to provide some comments and suggestions (in the Technical Corrections below), but they became far too numerous and minute. The current state of the introduction makes it hard for the reader to follow the motivation of this work. I would suggest taking the specific suggestions provided below and apply them generally throughout this section.

Response:

Thank you for the valuable comments. We have reorganized the Introduction section to improve the overall logical coherence and make the motivation clearer. The grammatical errors and sentence structure issues have also been corrected to our best. The detailed modifications are shown in the revised manuscript.

I am not convinced on the fidelity of this work based on the writing of the Methodology section. Many citations are missing, and the writing is unclear. Several components of this section are not defined and there are far too many variables and parameters to keep track of. I have provided a few suggestions (many issues exist here than I have time and space to note) below that could help with the clarity of this section, but the authors should take more time and care in revising this section so that it can be clear to readers what was done and how.

Thank you very much for the suggestions. Most descriptions in the Methodology section have been modified. All the variables and parameters have been clearly defined, and necessary references about the parameters and their values have been added and cited. The whole section has also been reorganized to provide much clearer descriptions about model construction for coated BC, optical property simulation, retrieval process of the mixing state, and the evaluation of both absorption enhancement and radiative effect. The detailed modifications are given in the revised manuscript.

The results sections of this work is difficult to follow and lacks specificity. I believe there is a lot (of useful) information provided in each figure and table, but they are not fully described and detailed in the text when they key findings are discussed. I would recommend to the authors to, in addition to providing better figure detail, place their results in context by citing previous literature.

Response:

Thanks for your valuable comments. The "Results and discussion" section has been reorganized and rewritten in the revised manuscript. More information in the Figures and Tables is described and analyzed in detail. The influences of coating structures, morphological parameters, and coating materials on the retrieved mixing states of coated BC are discussed. The effects of the retrieval errors in retrieved mixing states on the evaluation accuracies of absorption enhancement and simple forcing efficiency are also analyzed. In addition, important references have been added and cited as needed. The detailed modifications can be found in the revised manuscript.

I believe the conclusion section of this work is inadequate. A vague listing of very general results is not appropriate. More detail, specifically quantified errors in summary, should be provided to what is already included in the text of this section. This section would also benefit from describing the implications of the results that are found in this

work. Given the rather large error in radiative forcing, what does this imply for BC effects on climate that motivate how SP2 measurements are used and how they can be improved in the future?

Response:

Thanks for your valuable suggestion. We have modified the conclusion section in the revised manuscript, with more descriptions about quantified errors in the retrieved mixing states as well as the evaluated absorption enhancements and radiative effects. Based on the results of the study, we found that the assumption of the core-shell model for coated BC and the assumption of $1.50+0i$ for the refractive index of the coating in the retrieval scheme of the SP2 are inappropriate. The mixing states of coated BC measured by the SP2 would contain remarkable errors. When the measurement results are further employed to evaluate the radiative forcing of BC aerosol, the evaluated results would also be inaccurate. Therefore, the fractal morphologies for coated BC and the diversity of coatings should be considered in the retrieval principle of the SP2, then the accuracy of the retrieved mixing state and the evaluated radiative effect of BC could be improved. In addition, more advanced morphological models and more kinds of coating materials should be considered for further quantification of retrieval errors caused by inappropriate assumptions. Detailed modifications are given in the revised manuscript.

Technical Corrections:

Abstract: This whole section needs to be revised for clarity and flow. There are several run-on sentences here, missing or redundant commas, and missing articles ("the" before nouns such as, "the SP2"). I will not provide guidance line-for-line, but an example place of improvement includes lines 22-24 which have 3 separate thoughts: (1) the absorption enhancement retrieval deviations due to coatings, (2) the radiative forcing error from coating of BrC, and (3) RF error from sulfate and OC. It is possible that these three thoughts can be combined in one sentence, but the current verbiage is not coherent and far too long of a sentence.

Response:

    Thank you for the constructive suggestions. We have reviewed and rewritten most of the Abstract in the revised manuscript. The sentence in lines 22-24 has been split for clarity. The modifications in the revised manuscript are as follows:

    "Fractal closed-cell model and coated-aggregate model are constructed to represent BC with thin and thick coatings, multiple sphere T-matrix (MSTM) simulation results are regarded as optical properties of realistic coated BC, and the mixing states are optically retrieved based on Mie theory according to the retrieval principle of the SP2."

    "Furthermore, when the SP2 measured mixing states are employed to estimate the absorption enhancement (E_{ab}) and radiative forcing of BC aerosols, the estimation error of E_{ab} for BC with BrC coating is significantly larger than that with sulfate and OC coatings, and the estimation E_{ab} could be 6.19 times of the inherent value of fractal BC. Compared with fractal BC, the radiative forcing estimation error at 1064 nm for BrC-coated BC can reach -88.7%, while the estimation errors of BC coated by the other two materials range from -64.3% to -38.4%. This study highlights that the coating materials and fractal morphology should be considered when the SP2 is used to measure the mixing state of BC."

Line 36: I suggest adding "and" in the sentence: "melting of snow and ice, [and] alters the atmosphere…"

Response:

    Thanks for your comments. The related descriptions have been modified in the revised manuscript as follows:

    "BC also prevents the vertical diffusion of pollutants by altering the atmospheric temperature structure and accelerates the melting of snow and ice when it deposits on their surfaces (Ding et al., 2016)."

Lines 37-41: The two sentences in these lines contain disjointed thoughts and do not connect ideas. These should be improved for clarity.

Response:

Thank you for the comments. We have modified these two sentences in Lines 37-41 in the revised manuscript as follows:

"Optical absorption-dominated fresh BC particles usually present as loose chain-like aggregates consisting of numerous near-spherical monomers (Ceolato et al., 2020). During the aging in the atmosphere, fresh BC particles are coated by various chemical components such as sulfate, non-absorbing organic carbon (OC), and brown carbon (BrC) through the condensation and coagulation processes, forming aged BC aerosols with complex mixing structures (China et al., 2013). The heterogeneous mixing has a complicated and profound influence on the radiative effect of BC aerosols."

Lines 42-43, Lines 45-47: These sentences joined by commas should be broken up into two sentences. Appropriate citations for claims should also be added where appropriate.

Response:

Thanks a lot for your comments. The descriptions in Lines 42-43 have been modified, and necessary references have been added. The descriptions in Lines 45-47 were removed to improve the logical coherence of the whole paragraph. The modifications in the revised manuscript are as follows:

"The "mixing state" is a key microphysical property for aged BC to describe the mixing structure of BC and coating, and it can be characterized through different principles and instruments (Liu et al., 2023b; Liu et al., 2025)."

Line 49: If the authors are referring to, as I assume, the DMT SP2, they should identify the manufacturer (Droplet Measurement Technologies) and provide a citation for this instrument.

Response:

Thank you very much for the suggestions! We have modified related descriptions and added references in the revised manuscript as follows:

"The single particle soot photometer (SP2, Droplet Measurement Technology, Inc.) is one of the effective online instruments that can effectively measure the mixing state of coated BC, based on the combination of laser-induced incandescence and light scattering measurement, and has been widely employed in laboratory and field observations (Liu et al., 2020a; Liu et al., 2022; Schwarz, 2019)."

Line 53: an example of where an article is missing: "The optical cavity of [the] SP2…"
Response:

Thanks for your valuable comments! We have reviewed the whole manuscript. The articles have been added as needed in the revised manuscript.

Line 95: "According to the observations using electron microscopes, …" What observations? Are these the authors' observations or from literature? Please clarify and provide citations where appropriate. The sentence also contains disjointed thoughts; please revise.
Response:

Thank you for the helpful comments. According to the electron microscope observation results of China et al. (2013), Liu et al. (2020), and Wang et al. (2021), two fractal models of were constructed in this study. For simplification, the related descriptions have been modified, and references have been added in the revised manuscript as follows:

"The freshly emitted bare BC particles are fractal clusters that consist of a large number of near-spherical monomers, following the scaling rule (China et al., 2013; Liu et al., 2020b; Wang et al., 2021b):"

Section 2.1-2.2: Can the authors please provide a table detailing the parameter settings for the models/numerical simulations and provide citations where appropriate. The listing of these parameters in the text alone are very difficult to follow and keep track of. A table or list of the variables defined in this work (likely as an appendix) should also be provided as there are many variables provided in this section.

Response:

Thank you for the valuable comments. We have added a table to summarize the morphological parameters of BC models in the revised manuscript. In section 2.2, there are parameters and variables related to optical simulation, microphysical parameters, and radiative evaluation. This section has been rewritten to improve clarity and logicality. According to the order of optical property simulation, mixing state retrieval, and absorption enhancement and radiative effect calculation, some important equations are given in sequence. The variables in the equations and supplementary formulas are defined, and the corresponding value settings are given with necessary references. Furthermore, a list of the variables in the study is provided as an appendix. More detailed modifications have been made in the revised manuscript as follows:

"Table 1. Morphological parameters of coated BC aerosol models."

Model	Parameters	Values
All	Monomer radius (a_0)	20 (nm)
All	Monomer numbers (N_s)	50-2000, step length 50
All	Fractal prefactor (k_f)	1.20
Closed-cell	Fractal dimension (D_f)	1.80, 2.40, 2.60
	Volume fraction (V_f)	0.70, 0.40, 0.10, 0.075, 0.05
	Volume equivalent diameter ratio of shell/core ($D_{p,v}/D_{c,v}$)	1.13, 1.36, 2.15, 2.37, 2.71
Coated-aggregate	Fractal dimension (D_f)	2.60, 2.80
	Volume fraction (V_f)	0.10, 0.075, 0.05
	Volume equivalent diameter ratio of shell/core ($D_{p,v}/D_{c,v}$)	2.15, 2.37, 2.71

Line 134: MSTM is not defined in the main text before it is used here. Please specify this acronym. In addition, the MSTM algorithm that you used is not detailed anywhere in the methodology section. Did you use a previously written algorithm or did you develop your own. This should be clarified.

Response:

Thanks a lot for your comments. The MSTM employed in this study is the acronym of the multiple sphere *T*-matrix algorithm developed by Mackowski and Mishchenko (2011). The related descriptions have been modified in the revised manuscript as follows:

"In this study, optical properties such as optical cross-section and scattering matrix at 1064 nm, which is consistent with the observation wavelength of the SP2, are simulated using the multiple sphere T-matrix (MSTM) method developed by Mackowski and Mishchenko (2011)."

Line 165-167: is there a citation for ASTM G173-03 so that readers can reference where these parameter numbers come from?

Response:

Thank you very much for the comments! We have added and cited necessary references for the parameter settings in the equation of simple forcing efficiency in the revised manuscript as follows:

"The $dS(\lambda)/d\lambda$ is the spectral solar irradiance according to ASTM G173-03 (ASTM G173-03 Reference Spectra https://www.nrel.gov/grid/solar-resource/spectra.html), the atmospheric transmittance τ=0.79 (Bhandari et al., 2019), the cloud fraction F_c=0.6 (Bond and Bergstrom, 2006), the typical urban surface albedo a_s=0.19 (Liu et al., 2023b), and the backscattering fraction β=0.15 (Peng et al., 2022)."

Line 198: clarify "leakage points"

Response:

Thanks a lot for your helpful comments! To improve clarity, we replaced the "leakage points" with the "missed point". When the differential scattering cross-sections of the fractal BC cannot be matched using the core-shell models based on the retrieval principle of the SP2, there would be missed points in the retrieved mixing states. And the essential reason for the missed points is that the inherent difference in the morphological model results in distinct optical properties. The related descriptions have been modified as follows:

"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."

Discussion of Figure 1 in the main text: The authors should direct the reader to which panel they are discussing when they refer to results shown in the plots.

Response:

Thank you very much for the comments. Specific subfigure numbers have been mentioned in the main text when the corresponding subfigures are discussed and analyzed for all the figures in the manuscript. The descriptions related to Figure 1 have been modified in the revised manuscript as follows:

"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."

"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 CCM are larger than those of thickly coated BC particles represented by the CAM, especially for larger BC volume fraction, which reveals that the SP2 has better performance in characterizing the mixing state of thickly coated BC."

Figures 1-3: The authors should quantify the differences in the lines of these plots. Throughout the results section, the differences are discussed as "identical", "similar", "smaller", but these differences are not convincing based on these vague qualities.

Response:

Thank you for the valuable suggestions. The descriptions of Figures 1-3 have been rewritten. The results are discussed from both qualitative and quantitative perspectives. Specific values of retrieval errors in the mixing states of coated BC have also been illustrated. Detailed modifications are shown in the revised manuscript.

Line 216: If the authors are going to discuss retrieval errors, the table listing these errors should be referenced.

Response:

Thanks a lot for your comments. There were mistakes in the data usage for the retrieved mixing states of the closed-cell model coated by BrC. Figure 2 has been modified and redrawn in the revised manuscript. The related descriptions in Line 216 have been removed. Quantitative discussions about the retrieval errors in mixing states are added according to necessity in the revised manuscript.

Tables 1 and 2: please provide in the table caption or footer, a description of the acronyms in the table (RR, RE, etc…)

Response:

Thank you very much for pointing this out. We have added footnotes to explain the meanings of the acronyms in the related Tables in the revised manuscript as follows:

"**Table 2.** Retrieval results and relative errors of the mixing state for black carbon particle groups with different coating materials."

Model		Closed-cell model						Coated-aggregate model			
D_f		1.80		2.40		2.60		2.60		2.80	
$D_{p,v}/D_{c,v}$	Coating material	RRs[a]	REs[b]	RRs	REs	RRs	REs	RRs	REs	RRs	REs
	BrC	1.45	-46.8%	1.27	-53.2%	1.26	-53.7%	1.26	-53.5%	1.64	-39.6%
2.71	Sulfate	1.49	-45.2%	1.31	-51.8%	1.26	-53.6%	1.65	-39.2%	1.62	-40.3%
	OC	1.49	-45.2%	1.30	-52.0%	1.25	-53.9%	1.63	-40.0%	1.63	-40.1%
	BrC	1.47	-37.9%	1.25	-47.2%	1.23	-48.2%	1.31	-44.6%	2.09	-12.0%
2.37	Sulfate	1.51	-36.5%	1.28	-45.9%	1.20	-49.5%	1.91	-19.5%	1.75	-26.2%
	OC	1.51	-36.5%	1.28	-45.9%	1.20	-49.2%	1.96	-17.5%	1.78	-25.0%
	BrC	1.53	-29.0%	1.25	-42.1%	1.20	-44.1%	2.29	6.4%	2.27	5.2%
2.15	Sulfate	1.53	-28.9%	1.21	-43.8%	1.19	-44.9%	1.97	-8.7%	1.93	-10.2%
	OC	1.53	-29.1%	1.21	-43.9%	1.18	-45.2%	2.02	-6.2%	1.99	-7.4%

a: The retrieval results of the mixing states for BC particle groups. b: Relative errors in the retrieved mixing states.

"**Table 3.** The simple forcing efficiency of BC particle groups coated by different components based on the preset and retrieved mixing states."

D_f		1.80			2.40			2.60		
$D_{p,v}/D_{c,v}$	Coating material	CCM[a]	CSM[b]	Errors	CCM	CSM	Errors	CCM	CSM	Errors
	BrC	0.71	0.08	-88.7%	0.71	0.09	-87.3%	0.71	0.08	-88.5%
2.71	Sulfate	0.15	0.08	-45.0%	0.16	0.10	-38.4%	0.16	0.08	-48.4%
	OC	0.15	0.08	-45.0%	0.22	0.09	-57.4%	0.23	0.08	-64.3%
	BrC	0.51	0.07	-85.6%	0.51	0.08	-84.2%	0.51	0.08	-85.2%
2.37	Sulfate	0.15	0.08	-49.1%	0.15	0.08	-44.4%	0.15	0.07	-54.0%
	OC	0.15	0.08	-49.2%	0.15	0.08	-44.3%	0.15	0.07	-53.3%
	BrC	0.40	0.07	-83.1%	0.40	0.08	-80.5%	0.41	0.07	-82.9%
2.15	Sulfate	0.15	0.07	-51.9%	0.15	0.08	-48.5%	0.15	0.07	-55.6%
	OC	0.18	0.07	-60.3%	0.18	0.08	-57.2%	0.15	0.07	-55.4%

a: The closed-cell model. b: The core-shell model.

Section 3.2: The authors need to write out the numbers that are referenced in Table 1 when they describe the differences. Lots of vague language about what is shown in this section. "The relative error of black carbon particle swarm retrieval results…" what does that mean? If the authors are going to use verbiage such as "significantly different" then a statistical test of difference needs to be done and described.

Response:

Thanks a lot for your constructive comments. To improve the logical coherence of the discussion, we combined Sections 3.1 and 3.2 in the original manuscript into one subsection. The particle groups have been clarified in the revised manuscript, and the vague language has also been modified. Quantitative comparisons have been analyzed based on the values of retrieval results and retrieval errors for the mixing states of BC coated by different materials. Detailed modifications are shown in the revised manuscript.

Section 3.3: It is unclear to me if a lognormal BC particle distribution was employed for comparison (lines 263-279). If so, how was the lognormal distribution characterized (number concentration, diameter, width) and did you test the sensitivity of these selections?

Response:

Thank you very much for the helpful comments. The typical lognormal distribution for the volume equivalent diameter of the BC core is employed to discuss the retrieved mixing states and the radiative effect for BC aerosol groups with different coating materials. As parameters describing the distribution pattern, the geometric mean diameter is assumed to be 0.15 μm, and the standard deviation is set to 1.59 in this study, which are the parameter values frequently used by optical numerical simulation research (Liu et al., 2023; Yu and Luo, 2009; Zhang et al., 2012). The related descriptions have been modified in the revised manuscript as follows:

"Atmospheric BC aerosols mostly exist as particle groups that follow certain size distributions. The retrieval results (RR) of the mixing states for BC particle groups

coated by different components and the corresponding retrieval errors (RE) are analyzed, under the assumption that the volume equivalent diameter of BC follows the typical lognormal distribution:

$$n(d) = \frac{1}{\sqrt{2\pi} d \ln(\sigma_g)} \exp\left[-\left(\frac{\ln(d) - \ln(d_g)}{\sqrt{2} \ln(\sigma_g)} \right)^2 \right] \qquad (14)$$

where d is the diameter of BC, d_g and σ_g are the geometric mean diameter and standard deviation, which are set to 0.15 μm and 1.59 in this study, respectively (Yu and Luo, 2009; Zhang et al., 2012)."

Section 3.4: The authors should speak to the atmospheric/climatic implications of the retrieval errors between the SP2 and their model results based on the coating and fractal shape.

Response:

Thanks a lot for the constructive suggestions. We have added descriptions about the atmospheric implications in the Conclusion section for logical coherence in the revised manuscript as follows:

"Based on the analyses of the errors in the retrieved mixing states and the errors in both the evaluated absorption enhancements and the simple forcing efficiencies, it should be emphasized that the oversimplification of the morphology of coated BC to the core-shell model and the complex refractive index of coatings to 1.50+0i is inappropriate. The mixing states of coated BC measured by the SP2 would contain remarkable errors. When the measurement results are further employed to evaluate the radiative forcing of coated BC, the evaluated results would also be inaccurate. Therefore, the fractal morphologies for both thinly and thickly coated BC and the diversity of coating components should be considered in the retrieval principle of the SP2 to improve the retrieval accuracy and facilitate the wider application of the observation of the mixing states of BC aerosols."

Conclusion: Except for point (4), points (1)-(3) should have quantified differences included. Language such as "similar", "swarm", "small", "different" is not appropriate to describe the differences. The authors need to include numbers to detail what was observed. It also preferred that implications are described based on your results. These should be placed in context with previous literature and what these new results bring to the field.

Response:

Thank you very much for the helpful comments and suggestions. We have rewritten the Conclusion in the revised manuscript. The points (1)-(3) have been reorganized with quantitative analyses, and the vague language has also been modified. The atmospheric implications of this study and future works have been emphasized. Research focusing on the effects of BC structure and coating on measurement errors of the SP2 is still relatively scarce. Our previous study investigated the effect of different morphological parameters on the optical retrieval errors in the mixing state, and the results are in line with the BC coated by sulfate and OC in this current study (Liu et al., 2023). According to the necessities of the discussion, the discoveries in our previous study have been added and cited in Section 3.1 in the revised manuscript.

Reference

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