RESPONSE LETTER (amt-2023-53)

Title: Numerical investigation on measurement errors of mixing states of fractal black carbon aerosols using single-particle soot photometer and the effects on radiative forcing estimation

Dear reviewer：

We have revised our manuscript based on your 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.

Authors have brought to the attention of the scientific community the potential "flaw" in the current retrieval process for the Single Soot Photometers (SP2). They compared the current method, which is based on the spherical Mie core-shell assumption, with the closed-cell and coated aggregate models. It has been nicely illustrated by the authors what the differences would be in the D_p/D_c, C_{sca}, MAC, MSC, and RF if a closed-cell and coated aggregate model is used. In light of the increasing use of SP2 in atmospheric sciences, this paper is important, well-written and relevant for publication in this journal. It is a well-constructed study, the methodology is clearly explained, and reasonable conclusions are drawn. After addressing some comments mainly regarding the results and discussion, my recommendation is for publication.

Response:

Thanks a lot for reviewing our manuscript and all these constructive comments. We have responded to the comments point by point and modified related descriptions in the revised manuscript.

1. The authors mostly provide the message that: “The measurement errors of mixing state have larger effect on the estimation accuracy of radiative forcing for heavily coated BC particles than that for thinly coated BC particles at both 1064 and 532 nm wavelengths.”

Generally, the authors report that discrepancies are primarily concentrated in heavily coated particles (for all parameters D_p/D_c, C_{sca}, MAC, MSC, and RF). In my opinion, it is relevant to both thinly coated particles and heavily coated particles. When a fractal morphology is used to model BC in thinly coated particles (uniform coating around a BC fractal - closed cell model), it underestimates D_p/D_c and Csca when compared to current Mie theory-based retrievals. In contrast, for heavily coated particles (where the BC fractal is completely enclosed in a spherical coating), the D_p/D_c and Csca are overestimated compared to the current Mie theory-based estimates. In other words, it may be necessary to change the retrieval process depending on the type of mixture or age of the aerosols the SP2 measures. A major message from this research is that the community should adapt the current Mie core-shell retrieval according to the ageing stage of BC being measured.

Response:

Thanks a lot for your valuable comments!

We re-conducted the retrieval of mixing states of coated soot aerosols based on differential scattering cross-section corresponding to the detectors of SP2 rather than total scattering cross-section during our revision, which is more in line with the measurement principle of SP2. Results showed that the measurement errors of the mixing state have larger effects on the estimation accuracy of radiative forcing for thinly coated BC particles than that for heavily coated BC particles at both 1064 and 532 nm wavelengths. Since the retrieved values of D_p/D_c generally decrease with the preset volume equivalent diameter of the soot core, the measured mixing states based on Mie theory can be underestimated or overestimated for coated particles with different morphologies, as shown in Figures 3 and 4 in the revised manuscript.

We agree with you that the retrieval progress for thinly and heavily coated soot particles are necessary to be improved respectively. Furthermore, it should be noted that the micro parameters and coating structures of soot aerosols are various at different regions and times because of photochemical aging and hygroscopic growth, these aging processes should be systematically considered from numerical aspects and the corresponding measurement errors of BC mixing states should also be noticed by the community. We have modified related descriptions in the revised manuscript as follows:

"The retrieval errors of mixing state have larger effects on the estimation accuracy of radiative forcing for thinly coated BC particles than that for thickly coated BC particles at both 1064 and 532 nm wavelengths."

2. What I found lacking was a discussion of comparisons between experimental and field applications. In light of the findings of this study, the next step would be to validate the D_p/D_c derived from the actual SP2 measurements using the spherical Mie core-shell assumption and the closed-cell and coated aggregate models. There should also be a comparison between this measurement and maybe other chemical measurements that report the BC mass/volume fraction, such as filter measurements. In order for the findings of this study to be fully validated, the findings of a field or laboratory study are necessary (outlook).

Response:

Thanks for this constructive suggestion!

We agree that experimental validation is meaningful for both making our work more complete and for researchers using SP2. However, a comprehensive field or laboratory study includes aerosol particle sampling, electron microscope observation, chemical analysis, particle diameter characterization, SP2 measurement, and optical modeling, and it is difficult for us to organize such observations at the present stage. Furthermore, there are still several technological challenges unresolved, for example, the conversion between the measured electrical mobility diameter or aerodynamic diameter and the volume equivalent diameter for coated BC particles. Our previous study (Liu et al., 2020) found that the relationship between electrical mobility diameter and volume equivalent diameter is very complicated for BC, the unsuitable conversion parameters will also bring huge uncertainties to the measurements. On the other hand, even though these two kinds of fractal models we employed are typical to some degree, they cannot be representative of all types of atmospheric BC particles, and more morphological models should be considered in our research framework. Therefore, we focus on the retrieval errors from numerical aspects only in this study. And we have added the necessary descriptions as future works in the revised manuscript as follows:

“This study is a pilot work for the characterization of possible retrieval errors in mixing states of coated soot aerosols using SP2 and Mie theory. For future work, more morphological models that are suitable for modeling the microstructure of coated soot aerosols should be considered, and unified parameterization schemes of retrieval errors are much needed. Furthermore, comprehensive field or laboratory studies for the validation of the possible errors in mixing states are also future directions worth the effort.”

3. As a follow-up to comment 2, the authors should mention previous experimental studies that have demonstrated how important it is to consider BC as a fractal aggregate. Until now, no one has presented any information regarding SP2.

He, C., Liou, K.-N., Takano, Y., Zhang, R., Levy Zamora, M., Yang, P., Li, Q., and Leung, L. R.: Variation of the radiative properties during black carbon aging: theoretical and experimental intercomparison, Atmos. Chem. Phys., 15, 11967–11980, h.ps://doi.org/10.5194/acp-15-11967-2015, 2015.

Romshoo, B., Pöhlker, M., Wiedensohler, A., Pfeifer, S., Saturno, J., Nowak, A., Ciupek, K., Quincey, P., Vasilatou, K., Ess, M. N., Gini, M., ElePheriadis, K., Robins, C., GaieLevrel, F., and Müller, T.: Importance of size representation and morphology in modelling optical properties of black carbon: comparison between laboratory measurements and model simulations, Atmos. Meas. Tech., 15, 6965–6989, h.ps://doi.org/10.5194/amt-15-6965-2022, 2022.

Forestieri, S. D., Helgestad, T. M., Lambe, A. T., Renbaum-Wolff, L., Lack, D. A., Massoli, P., Cross, E. S., Dubey, M. K., Mazzoleni, C., Olfert, J. S., Sedlacek III, A. J., Freedman, A., Davidovits, P., Onasch, T. B., and Cappa, C. D.: Measurement and modeling of the multiwavelength optical properties of uncoated flame-generated soot, Atmos. Chem. Phys., 18, 12141–12159, h.ps://doi.org/10.5194/acp-18-12141-2018, 2018.

Response:

Thank you for the valuable comments and recommendations!

We have added related descriptions in the introduction, and the above three references have been cited in the revised manuscript.

“In short, abundant models and numerical simulation algorithms of BC provide convenience for accurate calculation of BC optical properties and also create an effective way to quantify the possible errors of the mixing states D_p/D_c of BC retrieved by SP2. In addition, there have been a number of experimental studies demonstrating the importance of considering BC as fractional aggregates. He et al. (2015) developed three different fractal aggregate models to simulate three typical evolution stages of BC particles and demonstrated that the dynamic aging process and the fractal shape should be considered for accurate estimations of the radiation effects. Romshoo et al. (2022) calculated the optical properties of three fractal particle models, results showed that the aggregate representation performs well in modeling the light absorption coefficient, the single-scattering albedo, and the mass absorption cross-section for laboratory-generated BC particles with mobility diameters larger than 100 nm. The fractal aggregate model was selected by Forestieri et al. (2018) to model uncoated soot particles, optical calculation results were used to compare with experimentally measured optical properties at multiwavelength, they emphasized that the sphere model and Mie theory widely used in climate models may lead to obvious underprediction in absorption of BC. All these studies have demonstrated the excellent performances of fractal aggregates in the optical modeling of black carbon. However, the fractal particle models have not been employed in the SP2 retrieval research, and the retrieval errors of the soot mixing state caused by morphological model selection also have not been evaluated."

4. Figures 3, 4, show the value of $D_{p,v}/D_{c,v}$, which is the standard constant in each subfigure. It would be helpful to include the value of volume fraction in brackets in order to make it more relevant to those who do not use SP2, as well.

Response:

Thanks for this valuable suggestion! The corresponding values of volume fractions have been added in parentheses after the values of $D_{p,v}/D_{c,v}$ in Figures 3 and 4 in the revised manuscript. In addition, Figures 3 and 4 have been redrawn due to the modification of the retrieval process. We have modified the figures in the revised manuscript as follows:

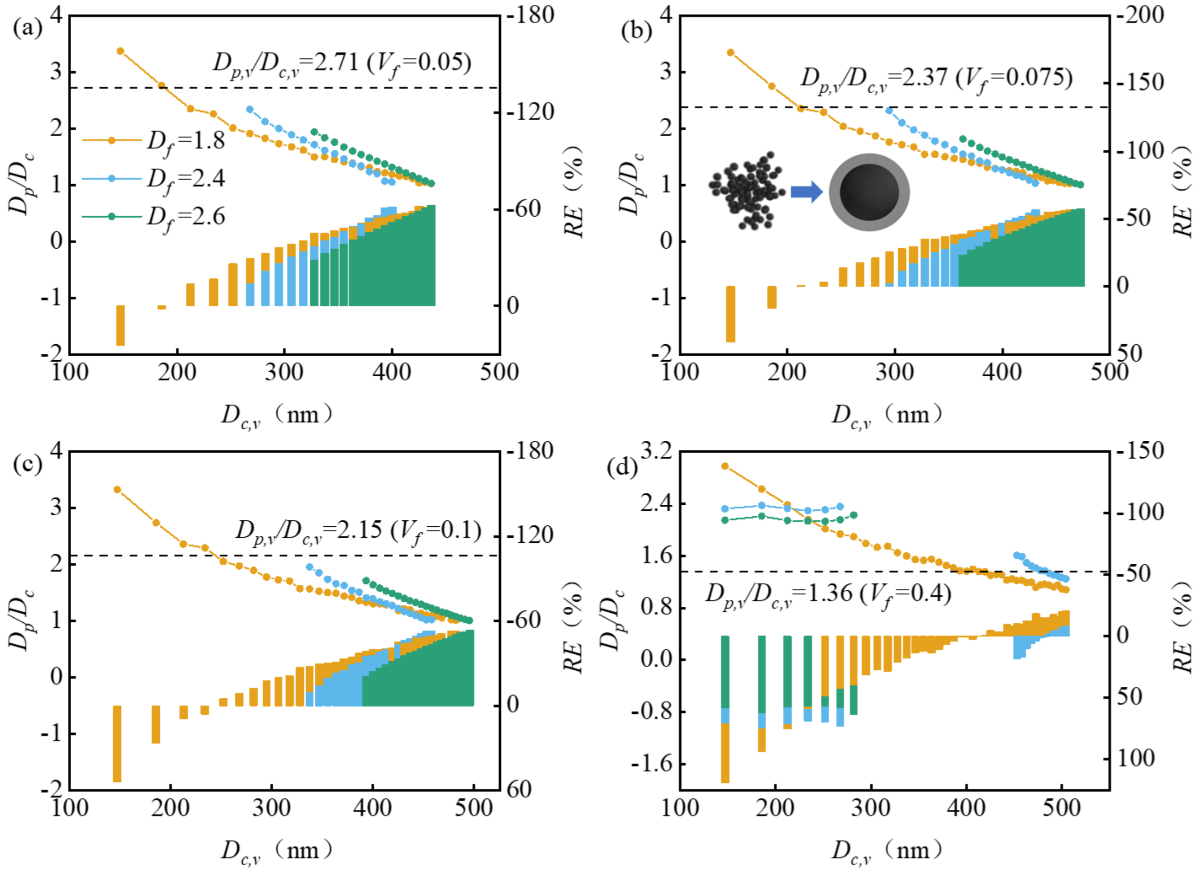

Figure 3. Retrieved mixing state (D_p/D_c) and relative error (RE) as functions of volume equivalent diameter ($D_{c,v}$) for thinly coated BC particles with different D_f and $D_{p,v}/D_{c,v}$. The colored lines stand for retrieved D_p/D_c and the colored bars stand for RE.

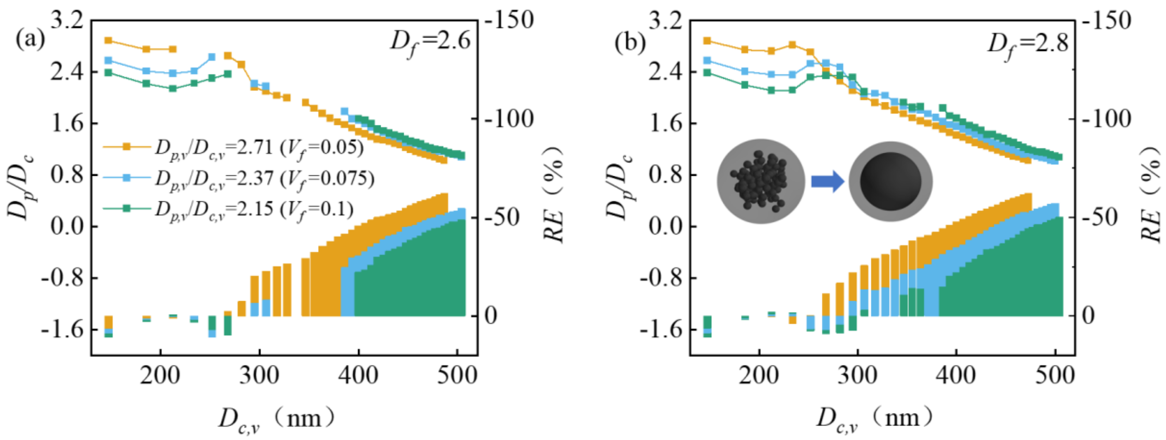

Figure 4. Retrieved mixing state (D_p/D_c) and relative error (RE) as functions of volume equivalent diameter ($D_{c,v}$) for heavily coated BC particles with different D_f and $D_{p,v}/D_{c,v}$. (a) Coated-aggregates with D_f = 2.60; (b) Coated-aggregates with D_f = 2.80. The colored lines stand for retrieved D_p/D_c and the colored bars stand for RE.

5. In Figure 5, it would be helpful to be able to see the slope in each sub-plot. By doing so, one would be able to determine how high or low the models are in relation to one another in terms of numbers.

Response:

Thanks for this suggestion! In the course of our research, the volume fractions were preset, and the values of $D_{p,v}/D_{c,v}$ were derived subsequently. Therefore, the horizontal axis $D_{p,v}/D_{c,v}$ in Figure 5 is not equally spaced and we draw this figure using independent scatters, then the slope in each sub-plot may make little sense. However, it can still be clearly observed that the averaged D_p/D_c slightly decreases with the decrease of $D_{p,v}/D_{c,v}$, except for thinly coated soot particles with $D_{p,v}/D_{c,v}$ = 1.36, 1.13, because of the loss of some retrieved values of D_p/D_c.

6. There is a higher error in the calculation of the radiative forcing for thickly coated particles when $D_{p,v}/D_{c,v}$ is higher. It would be interesting to see how the forcing values change for cases with $D_{p,v}/D_{c,v}$ close to 1, i.e., thinly coated particles (as I discussed in the first comment).

Response:

Thank you for the valuable comment! We set the values of volume fractions of soot core in coated particles in this study, and the volume fractions can be related to $D_{p,v}/D_{c,v}$ one by one. The $D_{p,v}/D_{c,v}$ roughly covers the retrieved results D_p/D_c using SP2 in previous literature, and the $D_{p,v}/D_{c,v}$ is close to 1(1.13) when the volume fraction is 0.70. However, the inherent differences between the optical properties of fractal models calculated using MSTM and optical properties of fractal models calculated using Mie theory result in the loss of retrieved values of mixing state, especially for particles with $D_{p,v}/D_{c,v}$ close to 1. Therefore, these cases were not considered for the evaluation of radiative forcing. We are developing complex morphological models more realistic than closed-cell models for thinly coated particles, and we expect to be able to investigate the radiative forcing of thinly coated particles in detail based on the new morphological model.

7. Last but not least, a "beta" version of the retrieval code based on the closed-shell or coated aggregate model would be helpful to the community. It is possible for the authors to share the codes that they used in this study. However, this will only be a test version that would be developed in the future.

Response:

Thanks for this constructive suggestion! A complete and user-friendly code package of the whole calculation and retrieval progress is meaningful for the researchers of SP2 observation and optical simulation. However, our current study conducted optical calculation and retrieval based on several independent scripts written based on Matlab, and such a code package has not been developed yet. On the other hand, as further research of this manuscript, we are investigating the effects of hygroscopic growth and photochemical aging on the SP2 measurements on the basis of these scripts, so we would to publish our scripts and package when we finish the ongoing study in the future.

References

Forestieri, S. D., Helgestad, T. M., Lambe, A. T., Renbaum-Wolff, L., Lack, D. A., Massoli, P., Cross, E. S., Dubey, M. K., Mazzoleni, C., Olfert, J. S., Sedlacek, A. J., Freedman, A., Davidovits, P., Onasch, T. B., and Cappa, C. D.: Measurement and modeling of the multiwavelength optical properties of uncoated flame-generated soot, Atmospheric Chemistry and Physics, 18, 12141-12159, 10.5194/acp-18-12141-2018, 2018.

He, C., Liou, K. N., Takano, Y., Zhang, R., Zamora, M. L., Yang, P., Li, Q., and Leung, L. R.: Variation of the radiative properties during black carbon aging: theoretical and experimental intercomparison, Atmospheric Chemistry and Physics, 15, 11967-11980, 10.5194/acp-15-11967-2015, 2015.

Liu, J., Zhang, Q. X., Wang, J. J., and Zhang, Y. M.: Light scattering matrix for soot aerosol: Comparisons between experimental measurements and numerical simulations, Journal of Quantitative Spectroscopy & Radiative Transfer, 246, 14, 10.1016/j.jqsrt.2020.106946, 2020.

Romshoo, B., Pohlker, M., Wiedensohler, A., Pfeifer, S., Saturno, J., Nowak, A., Ciupek, K., Quincey, P., Vasilatou, K., Ess, M., Gini, M., Eleftheriadis, K., Robins, C., Gaie-Levrel, F., and Muller, T.: Importance of size representation and morphology in modeling opticalproperties of black carbon: comparison between laboratory measurements and model simulations, Atmospheric Measurement Techniques, 15, 6965-6989, 10.5194/amt-15-6965-2022, 2022.

Furthermore, other detailed revisions are listed below.

LOCATION	**REVISED MANUSCRIPT**	**ORIGINAL MANUSCRIPT**
Abstract, paragraph 1	deviated from the real morphology	deviated the real morphology
	references	reference
	the diameter of BC core (D_c) is	the diameter of BC core (D_c) are
	the mixing state (D_p/D_c)	mixing state (D_p/D_c)
	aspects	aspect
	at most particle sizes	for most particle sizes
Introduction, paragraph 1	acts	act
Introduction, paragraph 3	mixing state of each single BC particle	mixing state of a single BC particle
	at first	first
Introduction, paragraph 5	observation	observed
	provide insight into the possible errors	provide insight of the possible errors
Section 2.1, paragraph 2	organic	organics
Section 2.1, paragraph 3	ranges	range
	relationships	relationship

Section 2.3, paragraph 1	the scattering signal of each coated BC particle	the scattering signal of coated BC particles
	the coated BC	coated BC
Section 2.3, paragraph 2	with the value of D_c	and the value of D_c
Section 3.3, paragraph 3	effects	effect
	of the coated-aggregate model	on the coated-aggregate model
Section 3.4, paragraph 1	have significant impacts	have a significant impact
	The SP2 retrieves	SP2 measurement
Section 3.4, paragraph 2	effects	effect