RESPONSE LETTER (EGUSPHERE-2024-1000)

Title: Retrieval of refractive index and water content for the coating materials of aged black carbon aerosol based on optical properties: a theoretical analysis

Dear Referee:

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.

Comments:

This study focuses on complex refractive index of black carbon with coatings under different RHs. They retrieved the refractive index and water content for the non-absorbing coating of BC particles, and then calculated the optical properties using MSTM. This study is very basic study to retrieved the optical properties of the aged BC with different RHs. Based on my opinion, the study had one certain innovation working on the water contents of coatings, because there is limitation on water contents on coatings of BC particles and their refractive index. Basically, I like this work which provide more information for future studies.

Response:

Thanks a lot for reviewing our manuscript and for your suggestion! We have responded to the comments point by point and modified related descriptions in the revised manuscript.

Of course, we should notice there is some limitation of this study. All the study did not consider the realistic particles in ambient air. Even the authors did not cite some from other studies which has been well described the coating thickness and mixing structures. I would strongly recommend the authors should considered this issue. Moreover, the authors used lots of long sentences and subordinate clause. It is difficult for people to understand this paper well. I would ask the revisions. Certainly, I would ask the authors revised the manuscript.

Response:

Thanks a lot for reviewing our manuscript and all these constructive comments. In practical situations, the mixed state and relative humidity are quite complex. This complexity makes it challenging to find a specific scenario that connects simulations with realistic particles in ambient air. Therefore, we have taken into account a wide range of humidity and volume fractions to explore whether there are any systematic conclusions among them. This aims to provide some references for practical observational studies. Li et al. (2023) from Peking University studied the effect of black carbon content on the mass size distribution and mixing state of black carbon, finding that an increase in black carbon content leads to a greater tendency for the particles to be in an internally mixed state. Wang et al. (2017), Zhejiang University conducted a detailed characterization of the physicochemical properties of soot particles using a soot particle-aerosol mass spectrometer (SP-AMS). They stressed that soot particles with different mixing structures exhibit varying fractal dimensions, ranging from 1.80 to 2.16. Liu et al. (2020), Zhejiang University studied the microscopic morphology of particles containing refractory black carbon (rBC) using the CPMA-SP2 system. The results showed that as the coating thickness increased, the morphology of rBC-containing particles transitioned from a loose structure to a compact core-shell structure. On the whole, the mixed structures and coating thickness vary in different ambient air Thus, by analyzing microscopic images, we summarized three typical models: coated-aggregated model, closed-cell model, and partially-coated model for further study. We have cited the necessary literature for the subsequent questions, as well as in the main text.

We carefully read and reviewed the entire text, rewriting some difficult sentences and subordinate clauses. Please conduct a second review of our revised article.

Abstract

Line 18-20: the number is difficult to be understood their meanings.

Response:

Thank you for the comment! The results of refractive index and water content retrieve under different models are discussed in this study. The effects of different models and relative humidity on the results of water content retrieve and refractive index retrieve are quite similar. For coated-aggregated model, the retrieved error for water content ranges from 2% to 63%. To clarify, we have made the following modifications to the relevant descriptions in the main text:

"The regularity of retrieved water content is similar to that of refractive index retrieve, and the water content retrieved errors range from 2% to 63% for heavily-coated BC."

Introduction:

I would like to recommend the authors revised this part carefully.

L27-28 Fresh bare BC will be coated by inorganic salts or organics during aging process such as condensation and collision in the atmosphere, and hydrophobic BC aerosol becomes hydrophilic.

This sentence should cite some references here. The BC aging process has been provided by the Li . J. Geophys. Res. 2016, 121(22): 13,784-13,798.

Response:

Thank you very much for the suggestion! In many scenarios, such as combustion in motor vehicles, a large amount of fresh, bare particles are emitted and subsequently coated with organic compounds or inorganic salts through various physical or chemical processes in the air. This phenomenon has been repeatedly confirmed by researchers in microscopic morphology analysis studies in the past few years. we have revised related description in the revised manuscript:

"Fresh bare BC will be coated by inorganic salts or organics during aging process such as condensation and collision in the atmosphere, and hydrophobic BC aerosol becomes hydrophilic(Li et al., 2016; Wang et al., 2017)."

L30-31, the sentence should cite more references here. Certainly Luo et al. is one of this study. The general conclusions should cite more references. Such as Fierce et al., Nat. Commun. 2016, 7: 12361; npj Climate and Atmospheric Science 2024, 7(1): 65. Wang et al., J. Geophys. Res. 2021, 126(10): e2021JD034620. And others.

Response:

Thank you for the meaningful comment! We have modified relevant descriptions and add the necessary references in the manuscript:

"Coating materials with different complex refractive indices produce different "lensing effect" or "sunglass effect" (Liu et al., 2021; Feng et al., 2021). In addition, the optical properties of coated BC are significantly different from those of bare BC due to the morphological changes of fractal structure, thus increasing the uncertainty of radiative effect (Luo et al., 2018; Fierce et al., 2016; Li et al., 2024; Wang et al., 2021a; Wu et al., 2017; Pang et al., 2023; Mishchenko et al., 1995)."

L60-75, the paragraph did not cover the recent studies using different methods. For example, Wang et al., Geophy. Res. Lett. 2021, 48(24): e2021GL096437. developed one EMBS method to calculate BC and their absorption; Fierce et al., Nat. Commun. 2016 developed the inhomogeneous thickness of coatings on BC particles and improved the absorption. Please make more to cover the knowledge there.

Response:

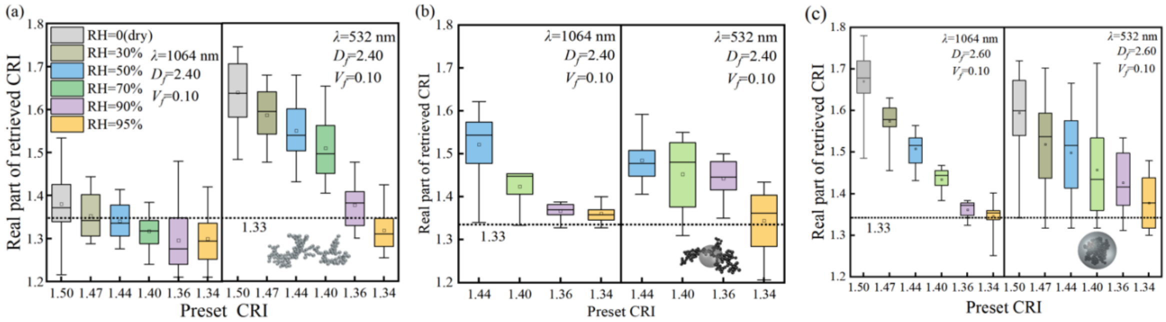
Thank you for your meaningful suggestion! The two articles you recommended are of great significance for expanding our knowledge and have made notable contributions to the development of optics, optical modeling, and the simulation of the optical properties of black carbon. Wang et al. (2021b) developed one EMBS method to calculate the optical properties of black carbon particles and explored how the differences in embedded fraction of BC particle groups in different geographic locations affect the absorption enhancement effect. Fierce et al. (2016) emphasizes the importance of considering diversity in particle composition and water uptake in determining absorption enhancement for a more accurate representation of light absorption by BC-containing particles. We have revised the relevant descriptions and added the necessary references in the manuscript:

"which can be explored through numerical simulation and theoretical analysis. It can be explored through numerical simulation and theoretical analysis. Wang et al. (2021b) apply a new electron-microscope-to-BC-simulation (EMBS) tool to produce shape models for BC optical calculation through DDA. The results show that the mixed structure and morphology of BC particles have a significant effect on its radiation absorption capacity. Fierce et al. (2016) used the particle-resolved model PartMC-MOSAIC to simulate diversity in per-particle composition for populations of BC-containing particles. The results show that the composition diversity of black carbon particles significantly affects the absorption properties predicted by the model. Pang et al. (2022) developed a novel image recognition technology to automatically identify fractal dimension individuals from microscope images. Research indicated that these methods could effectively describe the fractal morphology of soot particles. This provides an important scientific basis and methodological support for simulating individual soot models and observing the aging process of soot particles in the atmosphere. Wang et al. (2023) build a unified theoretical framework to describe the complex mixture state of black carbon and other components in the atmosphere. Research showed that the direct radiative forcing of black carbon (DRFBC) calculated using the new scheme showed significant reductions in all four selected regions: Europe, North America, South America, and Asia. Zhang et al. (2022) used HAADF-STEM and cryo-TEM to study the behavior of black carbon aerosols during the liquid-liquid phase separation (LLPS) process and its impact on radiative absorption. They revealed that, under relative humidity below 88%, most secondary particles containing black carbon undergo phase separation, with black carbon particles tending to migrate from the inorganic salt core to the organic coating. This contributes to understanding the aging process of black carbon aerosols in the atmosphere and their environmental impacts."

L205 please display the simply model on top of the figure. Then people can know the what are these models.

Response:

Thank you for the comment! Since there was no place at the top, we searched for a suitable location at the bottom of Figure 3 in the revised manuscript to display the simple model:



L260 deleted the well.

Response:

Thank you for the meaningful comment! The L260 in the original manuscript has been modified as follows:

"The effective medium theory can deal with the dielectric constant and refractive index of homogeneous mixtures of different species."

L265-268, this sentence is too long. The similar sentence should be simplified.

Response:

Thank you very much for this suggestion! Changes have been made in our resubmitted manuscript.

"Figure 8(a-c) illustrates results for heavily aged coated-aggregate models with the same fractal dimension. When RHs are larger than 50% and BC volume fractions decrease from 0.10

to 0.05, the retrieved water contents are closer to preset values. This rule can also be seen in the 1:1 dividing lines of each subplot.”

Similar sentences in other place of the original manuscript are simplified as follows:

“With the assistance of a self-developed cavity-enhanced albedometer, (Zhao et al., 2014; Xu et al., 2016) measured the extinction coefficient, scattering coefficient, absorption coefficient and single scattering albedo (SSA) for atmospheric aerosols at Jing-Jin-Ji Area. The effective CRI of aerosols is retrieved based on the Mie theory of homogeneous sphere by using the optical properties and volume mixing. The real part of CRIs is about 1.38 ~ 1.44, and the imaginary part is about 0.008 ~ 0.04.

they stressed the adopted size distribution of spheres have significant effects on the CRIs. Furthermore, Kong et al. (2024) employed the inhomogeneous super-spheroid model, which consists of several separate mineral components, to simulate dust aerosol. The calculated scattering and absorption coefficients were used to retrieve effective complex refractive indices (CRIs) based on homogeneous super-spheroid and sphere models. The results showed that the imaginary part of the CRIs can be retrieved more credibly from absorption than from the retrieval of both the real and imaginary parts.

Zhang et al. (2019a) developed coated aggregates to represent aged BC aerosol. They simulated scattering and absorption properties using the multiple-sphere T-matrix method (MSTM) and obtained optically effective complex refractive indices (CRIs) through Mie theory. The results showed that the shell/core ratio, geometry, and size distribution have complicated effects on the retrieved CRIs; while the VWA and EMT methods performed well in predicting optical effective CRIs for aerosols in accumulation mode, they produced imaginary parts that were two times higher than the optical effective ones for coarse coated BC.

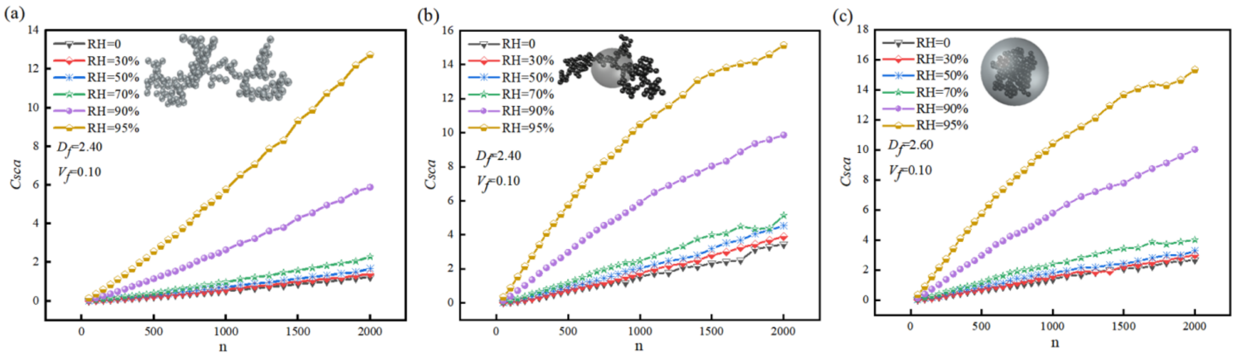
Most of the studies focusing on the optically effective CRIs, from both experimental and numerical perspectives, were conducted under the assumption that aerosols, especially black carbon (BC), are homogeneous or that their coatings are at least homogeneous. This assumption does not align with the realistic aging processes, which involve condensation, photochemical reactions, and hygroscopic growth.

On the other hand, if the variation of optically effective CRIs of BC coating materials at different RHs can be accurately retrieved based on their scattering and absorption properties, the water content in the coatings can then be calculated using mixing rules. This process is significant for understanding the water uptake speed of coating materials. Additionally, it can provide insights into the mechanisms of heterogeneous chemical reactions.”

Finally, I would ask what kinds of condition should be considered the water contents. In realistic, could you provide how much difference between water and non-water in coatings influence optical properties of aged particles? If the author could make such comparison, this could be important for the potential readers.

Response:

Thanks a lot for your valuable comments! During the actual measurement process, there is indeed a significant amount of humidity. Li et al. (2021) conducted experiments to study the behavior of particles collected in different environments (forest and city) under varying relative humidity (RH) conditions. They stressed that particles began to grow at an RH of 50% and transitioned to a liquid state when the RH increased to 84% or 83%. Zhang et al. (2023) studied the collapse of particle soot structure and changes in coating composition during long-distance transport. The results showed that when the relative humidity (RH) is between 60% and 90%, it is conducive to forming secondary aerosol coatings on soot particles and facilitates the transition of soot from a partially coated state to an embedded state. Zhao et al. (2018) calculated the aerosol asymmetry factor (g) using the humidifying turbidity meter system. The g value of dry aerosols varies between 0.54 and 0.67, while at an environmental relative humidity of 90%, the g value increases significantly by 1.2 times. The varying water content of combustible materials, such as wood and straw, can result in different humidity in the environment. We agree that the difference between water and non-water in coatings effects the optical properties of aged particles. The following figures show the comparison of different models under different hygroscopic conditions. It can be seen from the figure that the relative humidity has a significant positive influence on the optical characteristics. When the relative humidity reaches 95%, the scattering cross section increases by 10.84, 6.35 and 7.14 times, respectively, compared with different models when the relative humidity is 0.



Furthermore, other detailed revisions are listed below.

LOCATION	**REVISED MANUSCRIPT**	**ORIGINAL MANUSCRIPT**
Abstract	performs best	has the best performance
Introduction paragraph 2	increased slowly	increase slowly
Introduction paragraph 3	cross-sections	cross sections
Section 3.1, paragraph 1	Figure 2	Fig. 2.
Section 3.1, paragraph 2	decrease	decreases
Section 3.3, paragraph 1	Figure 8	Fig. 8.
	Figure 9	Fig. 9.

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