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.

General comments:

This study aims to evaluate the uncertainty of the amount of coating material derived from the measured scattering-cross section by SP2 depending on the particle shape assumption. In particular, the authors focused on evaluations of the systematic error due to the assumption of the shell-core particle shape model, which has been widely used but unrealistic for real-world BC-containing particles. The research focus is of significance to every SP2 user. However, I found some issues which must be addressed (corrected) before considering 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 “closed-cell model” adopted for thinly-coated BC looks very different from the real-world BC-containing particles. I can’t agree with using such a fictitious model as a “reference” for quantifying the error of the conventional shell-core model. In my opinion, the authors should use another more realistic shape model (e.g., according to TEM images) for thinly-coated BC. The distance between neighboring BC monomers, which artificially depends on the BC volume fraction in the closed-cell model, can be a critical factor in determining the optical properties of BC aggregates because the multipole interaction between monomers strongly depends on the distance, as implied by, for example, Mackowski 1995 https://doi.org/10.1364/AO.34.003535. If the authors are using “the closed-cell model”, the authors should show evidence of its accuracy.

Response:

Thanks a lot for your valuable comments!

We employed the closed-cell model to simulate the thinly coated BC particle at the early stage of atmospheric aging, because a number of previous studies have chosen this model to represent coated BC particles, and simulation results of optical properties were in good agreement with the corresponding results measured from laboratory experiments and field observations. He et al. (2016) used closed-cell model to represent black carbon coated by sulfuric acid, results showed that optical properties such as scattering cross-section, absorption cross-section, and asymmetry factor of closed-cell models can closely match the laboratory measurements. Romshoo et al. (2022) conducted comparisons of optical properties between laboratory measurements and model simulations of closed-cell models, they also found the modeled light absorption coefficient, the single-scattering albedo, and the mass absorption cross-section are in good consistencies with the measurements.

Furthermore, the closed-cell model consists of numerous core-shell structures of soot and coating, the coating structure is fixed, and the effects of fractal parameters of coated particles will be more evident. However, the calculated optical properties will be affected by the distance between neighboring BC cores caused by the change in the volume fraction of BC, as the reviewer pointed out. We agree that realistic shape models based on TEM images, like models developed by Luo et al. (2023), will be more meaningful, and this is our further direction for effort. With the assistance of such models, the effects of the complex coating structure of soot on the measurements of SP2 are expected to be revealed.

2. The authors seem to (implicitly) assume the scattering cross-section measured by the SP2 as if it is the total scattering cross-section. In fact, the scattering cross-section measured by the SP2 is only a small fraction of the “4pi str integral” of the differential scattering cross-section. The authors should explain this fact and evaluate the maximum error caused by the assumption.

Response:

Thank you very much for pointing this out! We re-conducted the retrieval of mixing states of coated soot aerosols based on differential scattering cross-section corresponding to the specific detection geometry of SP2 rather than total scattering cross-section during our revision, which is more in line with the measurement principle of SP2. The Figures and Tables in the manuscript vary more or less, and the discoveries and conclusions are re-drawn. All these modifications are included in the revised manuscript.

Specific comments:

L11: "measured mixing state"

The meaning of the "mixing state" could depend on the context and it is not obvious if it is a well-defined physical quantity (such as "volume"). I recommend using "volume of coating" or "volume fraction of coating" for clarity throughout the manuscript.

Response:

Thanks a lot for this valuable suggestion! We have modified the related descriptions to "diameter ratio of coated particle to BC core" or directly "D_p/D_c" in the revised manuscript. The L11 in the original manuscript has been modified as follows:

"The mixing state of black carbon (BC) aerosols, that is the diameter ratio of coated particle to BC core (D_p/D_c), can be retrieved by the single-particle soot photometer (SP2). However, the retrieved D_p/D_c contains errors, because the core-shell model and Mie scattering calculation are normally employed in the retrieval principle of SP2 and the spherical core-shell structure seriously deviated from the real morphology of coated BC."

L13: "thinly and heavily"

"thinly and thickly" or "lightly and heavily" sounds more accurate.

Response:

Thank you very much for this suggestion! We have modified "heavily" to "thickly" in the revised manuscript. The L13 in the original manuscript has been modified as follows:

"In this study, fractal models are constructed to represent thinly and thickly coated BC particles for optical simulations, …"

L15: "the diameter of BC core (D_c)"

Is it volume-equivalent diameter? Please clarify.

Response:

Thanks for pointing this out! The diameter of the BC core (D_c) is the volume equivalent diameter, which can be derived from the mass equivalent diameter measured by SP2 with the assistance of soot density 1.8g/cm^3. The L15 in the original manuscript has been modified as follows for clarity:

"…, and the volume equivalent diameter of BC core (D_c) is the same for fractal and spherical models."

L25: "is considered to be the second most important factor affecting global warming after carbon dioxide (Zhang et al., 2021)"

I'm not sure how this statement is still supported by recent climate research. In the IPCC AR6 report, methane was considered to have a larger positive effective radiative forcing than BC.

Response:

Thank you for the valuable comment! We have carefully read the IPCC AR6 report, for the sake of rigor, the L25 in the original manuscript has been modified as follows:

"Black carbon (BC) produced from the incomplete combustion of biomass and fossil fuels is considered to be an important contributor to global warming (Zhang et al., 2021)."

L34: "affects the vertical diffusion" suppress the vertical diffusion?

Response:

Thanks a lot for your comments! Black carbon aerosols can significantly weaken the diffusion and dilution of pollutants by heating the atmosphere, which in turn worsens air quality. In order to be more precise, the "affects" have been modified by "suppresses".

"…, which further suppresses the vertical diffusion of air pollutants, enhances haze events, harms human health, and reduces atmospheric visibility (Huang et al., 2018)."

L57: "single-particle soot photometer" You should use "SP2" which has already been defined.

Response:

Thanks for this suggestion! The L57 in the original manuscript has been modified as follows:

"The SP2 measures the mass and differential scattering cross-section of each single BC particle based on the combination of laser-induced incandescent light technology and light scattering measurement technology."

L59: "The scattering cross-section of the BC particle can be rapidly retrieved based on the measurement results of the scattering signal detectors (Schwarz et al., 2006)." The methods for retrieval of the scattering cross-section (integrated over the solid angle of light collection) using SP2 were introduced by Gao et al. 2007 AST (with position-sensitive detector) and Moteki and Kondo 2008 JAS (without position-sensitive detector). Please refer to at least one of these papers here.

Response:

Thank you for the constructive suggestion. We have added related descriptions and the above two references in the revised manuscript:

"The SP2 measures the mass and differential scattering cross-section of each single BC particle based on the combination of laser-induced incandescent light technology and light scattering measurement technology. In the optical cavity, when a coated BC particle vertically passes through the high-energy laser beam at a wavelength of 1064 nm, there are two scattering signal detectors collect the scattering signal over certain solid angles at forward and backward directions, respectively (Schwarz et al., 2006). Gao et al. (2007) developed the leading-edge-only (LEO) fit method to deal with the collected scattering signal for SP2 with position-sensitive detector, the undisturbed leading edge of the scattering signal was employed to construct a Gaussian scattering function, then the Gaussian function can be used to determine the differential scattering cross-section of the BC-containing particle. On the other hand, for SP2 without position-sensitive detector, Moteki and Kondo (2008) proposed to measure the time-dependent differential scattering cross-section ($\Delta C_{sca}(t)$) as each particle flowing across the Gaussian laser beam, and the differential scattering cross-section for coated BC particles can be further obtained. In general, the coated particles rapidly absorb the laser energy, the coating is heated to vaporization at first, and then the refractory BC (rBC) is heated and emits incandescent light (Zhao et al., 2021)."

L62: "The intensity of the incandescent light signal is proportional to the mass of rBC" This statement sounds like oversimplifying the truth. The linear proportionality between the LII signal and BC mass is only valid under a limited condition of BC size and LII detection wavelengths.

Pease see Moteki and Kondo 2010 AS&T https://doi.org/10.1080/02786826.2010.484450.

Response:

Thank you very much for this valuable comments! In order to be more precise, we have modified the description in the revised manuscript as follows:

"At 1064 nm wavelength, when the rBC with particle masses range between the lower and upper detection limits of SP2, the intensity of the incandescent light signal is proportional to the mass of rBC, and the volume equivalent particle diameter of rBC can be obtained based on the preset density (1.80g/cm^3) (Moteki and Kondo, 2010)."

L217: "The distribution of retrieved results of mixing states for single-particle with different fractal dimensions over the entire particle size range is shown in Figure 5, and the filling width represents the probability distribution of retrieved D_p/D_c." I'm not sure if this can be regarded as a "probability" distribution. I guess from the context that each violin plot in Figure 5 shows a histogram of the retrieved D_p/D_c values for uniformly-sampled $D_{c,v}$ ordinate. Is my guess correct? If so, Figure 5 is just a different plot of the data shown in Figures 3 and 4?

Response:

Thank you for the meaningful comment!

Indeed, Figures 3, 4, and 5 are drawn based on the same database of calculated optical properties of closed-cell model, coated aggregate model, and core-shell model. However, these figures are drawn for the analyses of retrieved D_p/D_c from different aspects. Figure 3 and 4 are plotted to reveal the variation of retrieved D_p/D_c and retrieval error with volume equivalent diameter of soot core, while Figure 5 shows the variation of retrieved D_p/D_c with the preset $D_{p,v}/D_{c,v}$, and all the coated BC particles with different core diameter are considered at each $D_{p,v}/D_{c,v}$. Essentially, Figure 5 is a diagram of probability distribution or frequency distribution, but it should be noted that the value of $D_{p,v}/D_{c,v}$ is not sampled uniformly, because the volume fraction of soot core was preset and $D_{p,v}/D_{c,v}$ is derived correspondingly. The violin plot is statistically significant, and the filling width represents the frequency of retrieved $D_\mathrm{p}/D_\mathrm{c}$. A wider violin plot indicates that the corresponding retrieved result of $D_\mathrm{p}/D_\mathrm{c}$ accounts for a larger proportion of all the retrieved results.

References

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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