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 Joshua Schwarz:

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.

I was happy to see this submission out focusing on improving interpretation of data types such as obtained with a single particle soot photometer (SP2). As a specialist with this instrument, I can clearly understand (and appreciate) the value of this to the community of SP2 users. The SP2 measures a few quantities on a per-particle basis relevant to determining mixing state. First, it provides the refractory black carbon (rBC) mass content of a particle (within some range of mass). This is based on an optical measurement of thermal emission, and is quite robust. Secondly, with appropriate analysis and setup, the instrument *measures* the total particle optical size – it detects a scattered light signal, and quantifies it. This is also valid only over some range of particle optical size, and is specific to the geometry of detection of the SP2. Third, some groups use the optical size of *only* the rBC portion of the particle (which can often be measured after the detection technique evaporates non-rBC material). Finally, inspection of the evolution of scattered light as a particle interacts with the SP2 laser provides another indication of internal mixing of materials with rBC. These measurements have been dealt with at length in the literature. After a measurement one can say: this particle had XX femtograms of rBC content, scattered as much light as a YY nm-diameter polystyrene latex sphere (PSL) into the SP2 scattering detector, and showed (or did not) evidence of shrinking during heating. These measurements have statistical and systematic errors associated with them, but are independent of Mie or any other theory of light scattering from particles. Now, the point at which this submitted manuscript becomes relevant is in the interpretation of those measured quantities. With knowledge about the amount of rBC mass and the total particle scattering signal, how can we interpret these quantities to infer conclusions about the amount of non-rBC material and its impacts on light absorption?

Presently, the paper is presented as though dealing with "SP2 measurement errors". This is not the case. Rather, it deals with assessing Mie-theory inadequacies for complex aerosols (which are highly relevant to SP2 analyses). This is a more general topic of interest to a wider slice of the community than SP2 users/interpreters, but has been addressed often in the literature in the broad sense. Hence, I recommend maintaining the focus on the SP2 community.

Response:

Thanks a lot for reviewing our manuscript and for your appreciation! The highly condensed introduction of SP2 you gave is very meaningful for us to deepen our understanding of how SP2 works and improve our research. We have responded to all these constructive comments point by point and modified related descriptions in the revised manuscript.

Broad comments:

The focus on "measurement errors" should be adjusted to more correctly address "interpretation effects". This is important because there is nothing wrong with the measurements that are published, and which remain valid independent of the interpretation method. Note that this manuscript does not actually determine "errors" (which would require measurements for comparison) - rather it determines differences between different optical calculations applied to interpretations. I think this was reasonably summed up in our 2015 paper on measurements and interpretation with a humidified SP2, which I quote here in part to suggest some additional references that should be added to the paper and considered. The final sentence of this quoted section speaks directly to the value of the manuscript under consideration:

"The SP2 user community often relies on Mie theory to interpret SP2-measured particle scattering cross-section and rBC mass content for the amount of non-rBC material internally mixed with the particles [Schwarz et al., 2008]. Although there is mild experimental support for the SP2 determination of coating thickness via Mie-theory assuming a shell-and-core morphology [Laborde et al, 2012], recent results hint at the uncertainties associated with this approach. Scarnato et al. [2013] used discrete dipole approximations as well as Mie theory to explore morphology effects on scattering and absorption of bare and internally mixed BC. They show (their Figure 3) that there can be considerable differences (~2X) between the exact numerical methods and the Mie-theory approximation for light-scattering at 1000 nm wavelength (near the SP2 wavelength of 1064 nm). Moteki et al. [2014] included comparison of SP2 light-scattering observations from near core-shell morphologies of BC coated with oleic acid via vapor deposition. They observed a bias up to 40% compared to Mie shell-and-core theory estimates constrained by total particle mass, rBC mass, and the (known) index of refraction of the oleic acid. Exploration of the validity of Mie theory approximations is beyond the scope of this manuscript, but is clearly relevant."

Response:

Thank you very much for the valuable comments and suggestions! We fully agree that there is nothing wrong in the original data measured by SP2, the errors concerned and investigated in our study occur when the optical equivalent diameter (D_p) of coated black carbon is retrieved based on original data using different interpretation methods and models, that is the core-shell model and the fractal model.

For the sake of accuracy, all the "measurement error" have been modified to "retrieval error", the title of the manuscript also has been modified, and the descriptions of recommended references have been added to the introduction in the revised manuscript:

"Numerical investigation on retrieval errors of mixing states of fractal black carbon aerosols using single-particle soot photometer based on Mie scattering and the effects on radiative forcing estimation"

"Mie scattering theory, which assumes that coated BC particle has a concentric core-shell structure consisting of coating sphere and BC sphere, is usually employed to retrieve the optical equivalent diameter of the coated BC based on differential scattering cross-section measured by SP2 (Schwarz et al., 2008; Kompalli et al., 2021). Finally, the particle size ratio of the whole particle to the BC core (D_p/D_c) can be obtained. Experimental results obtained by Laborde et al. (2012) showed that Mie scattering theory can be employed to retrieve the coating thickness of aged BC particles based on SP2 measurements. However, comparisons conducted by Scarnato et al. (2013) revealed that the scattering and absorption of the internally mixed BC calculated by the discrete dipole approximation (DDA) and the Mie scattering theory may be considerably different at 1000 nm (close to the 1064 nm used by SP2). Moteki et al. (2014) emphasized that the optical properties simulated by Mie theory deviate from the SP2 observations as much as 40% affected by the total particle mass, the rBC mass, and the refractive index of oleic acid coating. Schwarz et al. (2015) also proposed that when the SP2 was used to quantify the water-uptake of BC particles coated by ammonium sulfate, the uncertainty of SP2 measured results was mainly caused by the significant deviations in predicting SP2 scattering properties of BC particles using Mie scattering. In summary, it can be deduced that there are unavoidable retrieval errors in D_p/D_c because the core-shell model used in the retrieval of optical equivalent particle size D_p does not conform to the non-spherical complex morphology of the coated BC particles."

Response:

Thanks for this constructive comment! We re-conducted the retrieval of mixing states D_p/D_c of coated soot aerosols based on partial 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.

A lot of value would be added to the paper for the SP2 community if, in addition to addressing this error, it was made easier for SP2 users to use the results of the numerical simulations. I'm suggesting that the authors consider including lookup tables that could be used by SP2 users (rather than the mie-theory look ups that are currently more commonly used). The format of these tables would be up to the authors, but I'd suggest something similar to what we use: a dimension for the rBC mass content (or volume-equivalent diameter for an assumed density) and a dimension for the amount of internally mixed material (a mass or volume ratio, again with an assumed density for the internally mixed material). In our lookups we also vary the real index of refraction of the internally mixed material as a third dimension, but this would likely be overkill here. Each entry of the table would then provide the partial scattering cross-section, as would be measured with the the LEO approach with the SP2. Different tables for the different fractal dimensions of the rBC could be used, or that could be added as an additional dimension of the table. Additional tables with absorption information would then complete the set that would be commonly used by the community. I don't think this is necessary for publication, but would represent a great contribution and example for how future numerical studies could be more impactful, if the authors are willing to publish it. Note, too, that this would strengthen the relevance of the paper for AMT.

Response:

Thanks for this constructive suggestion! We cannot agree more a lookup table or database as you mentioned is very necessary and meaningful for the SP2 users and the community. In our opinion, such a lookup table must include a large amount of calculated differential scattering cross-section corresponding to SP2 measurements for coated soot particles, morphological models for coated soot particles at different aging stage such as thinly coated model, partially coated model, and thickly coated models should be considered, different micro-physical parameters with wide value range and small step size such as fractal dimension, monomer size, monomer number, soot volume fraction, complex refractive index also should be taken in to consideration. In this manuscript, we only tentatively explore the errors in retrieved D_p/D_c of coated soot aerosols caused by core-shell morphological assumption using closed-cell model and coated aggregate model with several micro-physical parameters. Therefore, a public lookup table based on this manuscript will not be helpful to SP2 users and even can be misleading to some degree. After sufficient exploration as mentioned above, then a comprehensive lookup table will be more meaningful for the community.

Specific comments:

The authors make the point that aging leads to more compact particles. I think it would be good to also cite China et al, "Morphology and Mixing State of Aged Soot Particles at a Remote Marine Free-tropospheric Site: Implications to Optical Properties", 2015 for context here (with their conclusion that Mie theory is within 12% of DDA for the older rBC-containing aerosol).

Response:

Thank you very much for the suggestion! The descriptions of recommended reference have been added to the introduction in the revised manuscript:

"During the aging process in the atmospheric environment, BC will be coated by other species, and their aggregate morphology tends to be more compact (China et al., 2013). Combined observation and simulation carried out by China et al. (2015) showed that Mie calculations provide reasonable approximations for compact soot above remote marine clouds, and the distinction of radiative forcing estimated using Mie theory and using discrete dipole approximation is within 12% for a high surface albedo."

Line 44 – there has also been a fair number of publications using the SP2 fraction of rBC-containing particles that show evidence of being internally mixed (often referred to as "thinly vs thickly coated rBC".

Response:

Thanks a lot for this comment! For the sake of accuracy, the related description have been modified in the revised manuscript as follows:

"Currently, the mixing states of rBC-containing particles are mainly characterized using the following methods: the particle diameter ratio of the whole particles to the BC core (D_p/D_c), the coating thickness (CT), the SP2 measured numerical fractions of thinly and thickly coated rBC, and the mass ratio of the coating material to the BC core (M_R)."

Line 67: this connects to my first broad comment. SP2 does not measure D_p/D_c, and does not have unavoidable errors in the LEO scattering measurement. The Mie theory interpretations do not destroy the information in the quantities measured by the SP2, they only transform them into different spaces (coating thickness or D_p/D_c), which can still be used to infer the original observed quantities, and allow reinterpretation with another optical model. Similarly, the table headings titled "SP2 retrieved core-shell models" – these are Mie-theory core-shell models. (Note that we have also used RDG to interpret SP2 data… Mie theory is not tied to the SP2 or vice versa.)

Response:

Thanks a lot for the constructive comments! As in the response to the first broad comment, we have modified the description "measurement error" to "retrieval error" in the revised manuscript. In addition, Line 67 and the headings of Tables 3 and 4 in the original manuscript have been modified as follows:

"In summary, it can be deduced that there are unavoidable errors in the retrieved D_p/D_c based on Mie theory because the core-shell model used in the retrieval of optical equivalent particle size D_p does not conform to the nonspherical complex morphology of the coated BC particles. At present, the retrieval error in D_p/D_c of coated BC based on SP2 measurement results is difficult to be quantified directly through experimental investigations. Nevertheless, the rapid developments of both morphology modeling and optical simulation of coated BC particles provide an investigative strategy for evaluating the retrieval accuracy of D_p/D_c."

"**Table 3.** The SFE values of both the core-shell models used to interpret the SP2 measurements and the fractal soot models at 1064 nm."

"**Table 4.** The SFE values of both the core-shell models used to interpret the SP2 measurements and the fractal soot models at 532 nm."

To summarize – this is a very promising entry that could provide a lot of value to the SP2 community. Making sure that the calculations are as relevant as possible to the geometry of the SP2 is one requirement. Another is correcting the association of interpretation differences to instrumental error. The authors also have the opportunity to provide a data set that I suspect would be broadly used in SP2-science.

Response:

Thank you for your valuable suggestions. We have responded to the comments point by point and revised the manuscript. We sincerely invite you to review our manuscript again.

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