Atmospheric Measurement Techniques Discussions

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Comment on amt-2021-214

Anonymous Referee #2

Referee comment on "Comparing black-carbon- and aerosol-absorption-measuring instruments – a new system using lab-generated soot coated with controlled amounts of secondary organic matter" by Daniel M. Kalbermatter et al., Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2021-214-RC2, 2021

Manuscript: Response of black carbon and aerosol absorption measuring instruments to laboratory-generated soot coated with controlled amounts of secondary organic matter (Kalbermatter et al.,) in "AMT".

Accurate and precise measurements of aerosol light absorption remain the primary limitation towards reducing the uncertainty in direct radiative forcing brought about black carbon. To this end, the present manuscript brings together well-established instrumentation (AE-33 Aethalometer, single wavelength MAAP and a single wavelength PAX together) with new or prototype in situ measurements (3-wavelength (445 nm, 520 nm, and 638 nm) prototype photoacoustic sensor, a dual wavelength (1064 nm and 532 nm) photothermal interferometer (PTI) and a second single wavelength (532 nm)) to inter-compare and evaluate the performance of all measurement methodologies. Black carbon (BC) aerosol were generated using small burner outfitted with an oxidation chamber to produce secondary aerosols that could, in turn, coat the furnace-generated BC particles thereby enabling a comparison between uncoated and coated BC particles. By and large, the manuscript is clearly written save a few sentences - highlighted below - and the reported findings this manuscript are of value - especially the performance of the photothermal interferometers, which, have not been fully utilized towards the measurement of BC-containing particle light absorption. This said, there are a couple of nagging issues, discussed below, that this reviewer feels needs to be addressed before acceptance for publication can be rendered.

An important caveat with the present work is that there no "direct" measurement of amount of coating mass associated with the soot particles, such as might be procured from a BC particle mixing state analysis using the Single Particle Soot Photometer (SP2) or a measurement conducted on known soot particle diameters and where a mass classifier could then be used to analyze the amount of coating on the BC particle. Instead, there is only an indirect measure of the coating mass viz-a-viz a EC/TC measurement. This may be a subtle point, but it is quite important as the authors use estimated coating to core mass ratios on polydispersed size distribution to derive conclusions about the observed absorption properties.

A central issue with this manuscript is the attribution of absorption enhancement. A quick back-of-the-envelope Mie calculation, in the core-shell approximation limit, suggests that even a modest coating thickness of 25 nm of a non-absorbing coating on top a 100 nm BC core will lead to absorption enhancements of 1.4 at 550 nm, 1.3 at 870 nm, and even 1.26 at 1064 nm (and even with at 10 nm coating, the enhancements are all on the order of 1.17-1.13. So the observation of no enhancement at the longer wavelengths is a bit puzzling (unless one brings in particle diversity, which the authors do not bring up). Additionally, the authors do not discuss the potential impacts of measurement uncertainty on their analysis (in some cases the decrepancy among the in situ measurements approaches 75%). Instead, the authors suggest that the absence of observed absorption enhancement at 870 nm is consistent with that reported by Cappa et al.. This is a highly-glossed over argument. The Cappa work compared ambient urban emissions with ambient emissions that were passed though a denuded, from which absorption enhancements were derived. Even given the great care the authors exercised in the Cappa work, the authors acknowledged in a later reply, about the possibility that the denuder did not remove all the coating. So the authors are urged to exercise when using Cappa et al. observations to analyze their observations. Addiitonally, the authors are encouraged to consider the potential impacts of particle diversity on their observations (e.g., see Fierce, et al. Black carbon absorption at the global scale is affected by particle-scale diversity in composition. Nat Commun 7, 12361 (2016)). This said, given the very large discrepancies in the observations, the authors would be well served providing a discussion on the impacts of measurement uncertainty on their conclusions.

In their analysis described on lines 313-314, the authors used the NIR wavelengths to decouple the lensing effect. If different wavelengths are used, then the size parameters differ, and the amount of lensing changes. Using the NIR wavelengths, the authors propose that absorption enhancement observed at 670 nm and shorter is due to the production of brown carbon from the oxidation of a-pinene. The authors need to back up this assertion. What species do they think is responsible for light absorption all the way out to 670 nm? The authors might want to start by looking at the paper by Song, C., et al., (2013), Light absorption by secondary organic aerosol from α-pinene: Effects of oxidants, seed aerosol acidity, and relative humidity, JGR., 118, 11,741–11,749). Very few organic aerosols exhibit light absorption to such long wavelengths. Additionally, the variability among the in situ measurements of absorption enhancement is surly large enough to warrant a discussion on how this variability impacts the conclusions drawn from the observations as discussed above.

Specific comments:

The authors are strongly encouraged to be very pedantic when discussing the coated soot particles. For example, the authors should explicitly distinguish in their tables uncoated soot particles and soot-containing particles (i.e., coated soot). It took a few rereads for this reviewer to fully appreciate that the reported GMDs were for the polydispersed aerosol exiting the coating/mixing chamber, irrespective of whether the soot was coated or not, and not a more direct and meaningful comparison of "uncoated" soot with "denuded" coated soot. The authors are strongly encouraged to reword some of their sentences to reflect this. For example, on page 8 (lines 230 - 231) the authors write "….The GMDmod of the soot particles increased from 88 nm to 126 nm while the EC/TC

mass fraction dropped ….". A more precise communication would be "The GMDmod of the soot-containing particles increased from 88 nm for uncoated soot to 126 nm following coating in the OCU…." I push on this because the authors point out because absent explicit distinguishing between soot and soot-containing particles and how the authors report the size distributions, someone could easily misinterpret that the reported GMDs for the coated cases as being derived from denuded soot - which is clearly not the case.

It is clear that the filter-based measurements are biased quite high compared to the in situ techniques. Are the authors worried about relying on a filter-based technique to derive AAEs from which measurements at other wavelengths can be adjusted to a single wavelength?

On line 262 the authors state that R_BC=3.4 which corresponds to EC/TC of 0.1. From the authors definitions of R_BC, and M_tot/M_BC - which should be R_BC+1 - then EC/TC = 1/(R_BC+1). R_BC =3.4 does not give E/TC = 0.1. Please check on this.

While it is likely that the BC particles are fractal-like, to get an SSA of 0.03 (for m=(2,-1)) requires a diameter of 50 nm, yet their GMD - mobility diameter - is 90 nm. The authors should explain this discrepancy.

This reviewer found it interesting that under the more dilute conditions (setup 0.1) the soot-containing particles were more heavily coated - as inferred from the GMDs. Why is that? Is this simply a limitation of the coating chamber in the limit of very high seed aerosol concentrations?

Somewhat related to the above, given the very high concentrations (i.e., 10^7 cc^-1) of soot in the micro smog chamber during the Setup 1 experiments, are the authors worried about coagulation? Since coagulation goes as the square of number concentration, it is very likely that coagulation is competitive with condensation and the authors are encouraged to evaluate the impacts, if any, on their observations.

Lines 194 - 200. Introducing a filter media before discussing the measurement seems backwards, The authors are encouraged to combine and order the sentences in these two paragraphs.

This reviewer found the legends in figures 3 and 4 a bit confusing in that the wavelength listed by the instrument is its operating wavelength, yet the data presented in the plots is adjusted to allow comparison at a single wavelength (532 nm). The authors might was to clarify this a bit better in the figures.