

We would like to thank Reviewer 2 for the valuable feedback and suggestions for improvement. Please find below the response to each comment/question as well as the sections of manuscript that were modified.

Reviewer: Accurate and precise measurements of aerosol light absorption remain the primary limitation towards reducing the uncertainty in direct radiative forcing brought about by 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) aerosols were generated using a 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 of 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 need to be addressed before acceptance for publication can be rendered.

Reviewer: An important caveat with the present work is that there is no "direct" measurement of the 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 an 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 a polydisperse size distribution to derive conclusions about the observed absorption properties.

Response: Thank you for your comment. The amount of coating mass associated with the soot particles was calculated based on gravimetric measurements by TEOM (direct method). This is explained in line 240: "In Fig. 3b, the absorption coefficient at 532 nm (k_{532}) is plotted as a function of RBC. $RBC = (M_{total} - M_{BC}) / M_{BC}$ is equal to the mass of organic coating over the mass of uncoated soot as measured by the TEOM". Also, in the captions of Figures 3 and 4 it is mentioned that "The total mass to BC mass ratio and RBC are based on TEOM measurements".

The Reviewer is absolutely right that additional measurements with a mass classifier would have been beneficial. The reason why we did not perform such measurements was the lack of availability of an APM or CPMA. Concerning the use of SP2 for deriving RBC mass, we believe that this method suffers from high uncertainties at such small particle sizes (GMD_{mob} 90 nm), which are at the limit of detection. Nevertheless, such measurements have been performed in an experiment conducted by some of the co-authors and are presently being analyzed (and will be featured in a future publication).

Reviewer: 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 of 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 discrepancy 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 through a denuder, 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. Additionally, 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.

Response: We thank the Reviewer for this valuable comment. We were not aware that the work by Cappa et al. might have been biased. We have now removed the sentence in line 262: "~~This is in good agreement with Cappa et al., who reported that BC emitted from large to medium-sized urban centres (dominated by fossil fuel emissions) does not exhibit a substantial absorption enhancement when internally mixed with non-BC material (Cappa et al., 2012). Eabs during both field campaigns exhibited minimal dependence on RBC, with Eabs, 532nm remaining close to 1 (absorption was measured by photoacoustic spectroscopy)~~".

We amended the text (Line 279) as follows: "A limitation of this study is that the relative humidity of the uncoated soot aerosols when entering the organic coating unit was low to very low (see subsection 2.1). No experiments were performed at high RH due to the presence of homogeneously nucleated SOA particles. It is known that the absorption by BC depends strongly on RH, and may lead to a factor of two increase in absorption at high RH compared with dry conditions (Fierce et al., 2016). This is one of the reasons why GAW (Global Atmospheric Watch) recommends measurements of light absorption at low RH (GAW report no. 226, 2016). Moreover, soot-containing particles generated in the laboratory under controlled conditions might have a more uniform composition compared to the aged soot particles in ambient air. In general, the range of absorption enhancement $E_{\text{abs}} = 1.1\text{-}1.3$ calculated based on the PAX and PTAAM agrees very well with (Fierce et al., 2016) who calculated a limited absorption enhancement ($E_{\text{abs}} = 1\text{-}1.5$) at low RH, when accounting for particle-level variation in composition of soot-containing particles. The dry conditions during and after ozonolysis of α -pinene may have also had an effect on the phase state of the SOM, leading most probably to a solid-state coating (Saukko, 2012)".

We also amended the section "Conclusions" (Line 390) as follows: "A limitation of this study was that the relative humidity of the uncoated soot aerosols when entering the organic coating unit was below 30%. More studies are needed at higher relative humidity in order to better simulate atmospheric processes".

When replying to a similar question from Reviewer 1, we noted that the enhancement (or lack of it at 870 nm) is dependent on two different issues. We repeat these two arguments here. It is important to note that Liu et al. (2016) ([10.1016/j.jqsrt.2015.08.005](https://doi.org/10.1016/j.jqsrt.2015.08.005)) show considerably less enhancement for the more realistic DDA models than for core-shell Mie model.

There are two issues: first, the wavelength dependence of absorption of coatings (or coated absorbing cores); second, the “loss” of the latent heat from the photo-thermal or photoacoustic signal due to the volatilization of coatings.

Wavelength dependence

In this study, the soot coatings consisted of secondary organic matter from the oxidation of a biogenic precursor (α -pinene). According to the literature, biogenic SOA does not absorb as strongly as anthropogenic SOA. Light absorption is only observed in the UV and near-UV region:

<https://www.ncbi.nlm.nih.gov/pmc/articles/PMC7372712/>

[https://doi.org/10.1016/S0021-8502\(03\)00361-6](https://doi.org/10.1016/S0021-8502(03)00361-6)

Under certain experimental conditions, SOA from the ozonolysis of α -pinene showed negligible light absorption even at near-UV wavelengths:

<https://doi.org/10.1029/2010JD014387>

Therefore, it is not surprising that the PAX at 870 nm did not show any sensitivity to coatings. We also see the increase of the AAE with increasing thickness of the coating in the PTAAM (Table 1). We interpret this as the increase in absorption at lower wavelengths (532 nm) relative to the higher wavelengths (IR). Additionally, we see with PTAAM an enhancement of absorption at 532 nm for about a factor of 1.3 (Fig. 3) and no enhancement at 1064 nm (Fig. 5).

There are some differences between different modelled results regarding this effect. Virkkula (<https://doi.org/10.5194/amt-14-3707-2021>) states that the lensing effect is less pronounced at longer wavelengths using a Mie model.

Liu et al. (<http://dx.doi.org/10.1016/j.jqsrt.2015.08.005>) show (Figure 9) that the calculated lensing effect differs between the discrete-dipole approximation (DDA) and core-shell Mie models. The DDA model predicts lower lensing at longer wavelengths; core-shell model predicts a similar magnitude of lensing from the visible to the IR.

The differences between different models can be reconciled with measurements which we present using PTAAM.

Volatilization of coatings

We have evaluated the volatility of our SOA coating using a total carbon analyzer, developed by FHNW, during the increase of the sample temperature (manuscript in preparation). We do not have any evidence that the SOA coatings used in our study are more volatile than typical suburban aerosols. Had the coatings we produced been volatile, this would have been seen in the comparison between the PAX and PTAAM.

PTAAM measures absorption at 532 nm and 1064 nm on the same sample (retention time for aerosol in the pump beam is 1000-times longer compared to the modulation interval). In principle, it would be possible to evaporate the coating by the pump beam in PTAAM. Increase of the measured AAE shows

that at least part of the coating has not been removed. Estimated pump beam intensity in PTAAM is 2 W/mm² (PTAAM article in preparation – will be submitted shortly).

The recondensation of the possibly volatile coatings would occur during the off-phase of the pumping laser in the PAX and PTAAM. In the PAX, the acoustic wave, generated by absorption of light, moves away from the sample signal generation region by the time recondensation occurs. In the photo-thermal interferometer, the signal due to volatilization and recondensation are generated in the monitored probed by the probe beam, so the recondensation is measured and the latent heat is taken into account properly. We do not expect any absorption by the coating itself and no absorption enhancement by the coated absorbing cores (see arguments above). We would expect to measure the difference in the IR between the PAX and PTAAM if the SOA coatings had been volatile. We saw no differences (Fig. 5) in agreement with our total carbon measurements.

Considering other impacts of measurement uncertainty on the analysis, we provide statistical uncertainties in Figure 3 and 4 as well as the uncertainty of the splitter bias (1%, subsection 2.1). Other possible measurement uncertainties include diffusion losses in the connecting tubes. We have added the following text in subsection 2.1 (Line 110): "The PAX, PTAAM, PAS and AE33 have very similar sampling flows (1-2 L/min) and the difference in diffusion losses was compensated by adapting the length of the connecting tube to the flow of the instrument. For the MSPTI, which has a flow of 0.25 L/min, the connecting tube was kept as short as possible. Possible differences in the internal path length of the instruments (between the aerosol inlet and measurement cell) were not taken into account. In the case of the MAAP, which was operated at a flow of 12 L/min, it was challenging to compensate for the difference in the diffusion losses. We cannot rule out that the measurements by the MAAP are biased but we estimate that this bias is <5% and therefore much smaller than the systematic uncertainties of this filter-based instrument".

To conclude, we think that systematic measurement uncertainties due to splitter bias and diffusion losses have a small impact on our analysis. The discrepancy in the in-situ measurements seems to be instrument-dependent. Especially the prototype PAS and MSPTI instruments suffer from artefacts arising, for instance, from instabilities in the laser power (see Lines 306-308 and 325-327 for more details). These instruments are still under development. The reason we included the MSPTI and PAS in the study was not to suggest that these instruments are "mature" enough to be employed for BC monitoring, but to show how the combination of a miniCAST with the OCU can be used to test instruments based on different technologies. Commercialised instruments, such as the PAX and PTAAM, show in most cases a reasonable agreement. Figure 3b shows that the difference between the PTAAM and the PAX in babs is 10-20%, and the two instruments report practically the same Eabs (Figure 3c).

Reviewer: 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 α -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 surely large enough to warrant a discussion on how this variability impacts the conclusions drawn from the observations as discussed above.

Response: This is a very good comment. We believe that the absorption enhancement reported by the MAAP might be an artefact. We amended the text (Line 270) as follows: "These results suggest that the absorption enhancement observed by the AE33, MAAP, PAS, PTAAM and MSPTI could be due to light absorption by SOM. Biogenic SOM is only expected to absorb light in the UV and near UV region (Song, 2013); thus, it is surprising that the MAAP indicates absorption enhancement at 637 nm. One of the possible reasons could be coating of BC in the filter by SOM or modification of the filter matrix optical properties by SOM (Cappa et al., 2008).

Specific comments:

Reviewer: 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 GMD_{mod} 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 GMD_{mod} 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.

Response: We apologise for the confusion. In Table 1, we do distinguish between uncoated and coated particles (see column 1), but we have now added the following clarification in the text (Line 216) to avoid any misunderstandings: "Note that the uncoated soot particles are "fresh" soot particles generated by the miniCAST burner (and not soot particles that have been coated and denuded)". We have also modified Figure 1 to show that the uncoated soot particles are delivered to the BC-measuring instruments through a line that bypasses the oxidation flow reactor.

We have also modified the text (lines 220 and 238) to make it clear whether soot is uncoated or coated: "The geometric mean mobility diameter (GMD_{mob}) of the soot particles gradually decreased from 92 nm (uncoated soot) to 83 nm (coated soot; coating 3) as shown in Fig. 2a" and "the GMD_{mob} of the soot particles increased from 88 nm (uncoated soot) to 126 nm (coated soot) while the EC/TC mass fraction dropped from ~85 % to ~10 % and the SSA increased up to ~0.7".

We agree with the Reviewer that a comparison of uncoated soot with denuded soot would be meaningful in order to better compare with atmospheric measurements. However, as the Reviewer noted in one of the comments above, denuding coated soot is not as straightforward as it sounds. Some SOA components are not volatile and might not be removed in the thermo-denuder or might be transformed by the heating, thus leaving a thin coating around the soot core. In our study, we made sure to avoid such artefacts by using fresh soot by the miniCAST burner.

Reviewer: 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?

Response: This is a valid concern, which was also raised by Reviewer 1. We have now revised Figs 3 and 4 of the manuscript by calculating b_{abs} based on AAE values from the PTAAM. We have also revised Tables S2 and S3 accordingly.

Reviewer: On line 262 the authors state that $R_{\text{BC}}=3.4$ which corresponds to EC/TC of 0.1. From the authors definitions of R_{BC} , and $M_{\text{tot}}/M_{\text{BC}}$ - which should be $R_{\text{BC}}+1$ - then $\text{EC/TC} = 1/(R_{\text{BC}}+1)$. $R_{\text{BC}} = 3.4$ does not give $\text{E/TC} = 0.1$. Please check on this.

Response: The values of R_{BC} , and $M_{\text{tot}}/M_{\text{BC}}$ are based on gravimetric measurements by TEOM as explained in the caption of Figures 3 and 4. It is true that the TEOM measurements do not agree so well with the EC/OC measurements. We believe that this is due to the high measurement uncertainties of the thermal-optical analysis and particularly with the difficulty to define the split point.

Reviewer: 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.

Response: The (uncoated) BC particles with $\text{GMD}_{\text{mob}} = 90$ nm are fractal-like as shown by TEM analysis (see Ess et al., 2021 main manuscript and supplemental information <https://www.tandfonline.com/doi/full/10.1080/02786826.2021.1901847>).

Reviewer: 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?

Response: As the dilution only affects the soot concentration and not the concentration of the VOC precursor, we have generally lower soot-to-VOC ratio, resulting in thicker coatings. When we do not dilute the soot aerosols, we have a higher number concentration of soot cores acting as seed particles (and therefore a larger surface area for the SOA to condense on), leading to thinner SOA coatings.

Reviewer: 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.

Response: We measured the size distribution of soot upstream and downstream of the micro smog chamber and found no difference when $\text{GMD}_{\text{mob}}=90$ nm (even at number concentrations of 10^7 cm^{-3}). We observe, however, coagulation when $\text{GMD}_{\text{mob}} < 50$ nm and care must be taken when working with soot in that size range.

Reviewer: 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.

Response: This is indeed a bit confusing. We have restructured the two paragraphs into a more logical order.

Reviewer: 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 want to clarify this a bit better in the figures.

Response: We apologise for the confusion. We have amended the text in the captions of Figures 3 and 4 as follows: "The legend below Figure 3c (Figure 4c) indicates the wavelengths at which the measurements were performed".