EDITOR

Thank you for your response to the initial review and the associated improvements to the manuscript. As you can see from the reviewer comments, they express some remaining concerns that should be addressed prior to publication. In particular, I find Reviewer #2's comments regarding the need to carefully quantify uncertainties and to make sure that the conclusions are robust in the face of these uncertainties compelling. I ask that you carefully consider the remaining concerns and suggestions made by both reviewers and modify the manuscript to address these issues. The revised manuscript will be sent to Reviewer #2 for further input.

This manuscript has many strong elements and represents an impressive experimental effort on a very important topic. Careful consideration of the robustness of the conclusions that can be drawn from imperfect data will make the scientific contribution only stronger. So I thank you for the efforts already made to address the reviewers' comments, and in advance for the additional changes they request.

Response:

Dear Editor

Thank you very much for your feedback. We completely agree that there is a need to quantify measurement uncertainties. The reason why we hesitated so far to provide the uncertainties of b_{abs} are the following:

1) Filter-based methods, such as the aethalometer and MAAP, suffer from systematic uncertainties which are difficult to quantify. To setup a robust uncertainty budget which takes into account the wavelength of the light-source and the particle-specific properties of the test aerosols (e.g. SSA), calibration against a reference method would be needed.

   For the AE33, the GAW recommendation for part of the systematic error relative to the filter multiple scattering parameter is 25% (WMO, 2016). The cross-sensitivity to scattering, which manifests as SSA dependence, should be smaller than ~20% estimated based on our measurements and the results from (Yus-Díez et al., 2021).

2) The uncertainties of prototype instruments, such as the PAS and MSPTI, are dominated by unexpected changes of the properties of the laser irradiation (e.g. modulation depth, frequency spectrum or beam cross-section) or pump performance which are impossible to rigorously quantify.

Nevertheless, we now provide an estimation of the measurement uncertainties related to b_{abs} in the manuscript text, section 2.2 "BC- and aerosol-absorption-measuring instruments".

Please find below a point-by-point response to the Reviewers' comments.

Thank you for your time and consideration.

Lack, D. A., Cappa, C. D., Covert, D. S., Baynard, T., Massoli, P., Sierau, B., Bates, T. S., Quinn, P. K., Lovejoy, E. R. and Ravishankara, A. R.: Bias in Filter-Based Aerosol Light Absorption Measurements Due to Organic Aerosol Loading : Evidence from Ambient Measurements, Aerosol Sci. Technol., 42(12), 1033–1041, doi:10.1080/02786820802389277, 2008.

Song, C., Gyawali, M., Zaveri, R. A., Shilling, J. E. and Arnott, W. P.: Light absorption by secondary organic aerosol from α-pinene: Effects of oxidants, seed aerosol acidity, and relative humidity, J. Geophys. Res. Atmos., 118(20), 11,741-11,749, doi:10.1002/jgrd.50767, 2013.

WMO: WMO/GAW Aerosol Measurement Procedures, Guidelines and Recommendations. [online] Available from: https://library.wmo.int/doc_num.php?explnum_id=3073, 2016.

Yus-Díez, J., Bernardoni, V., Močnik, G., Alastuey, A., Ciniglia, D., Ivančič, M., Querol, X., Perez, N., Reche, C., Rigler, M., Vecchi, R., Valentini, S. and Pandolfi, M.: Determination of the multiple-scattering correction factor and its cross-sensitivity to scattering and wavelength dependence for different AE33 Aethalometer filter tapes: A multi-instrumental approach, Atmos. Meas. Tech. Discuss., 29(March), 1–30, doi:10.5194/amt-2021-46, 2021.

REVIEWER 1

Review of revised paper: "Comparing black carbon and aerosol absorption measuring instruments – a new system using lab-generated soot coated with controlled amounts of secondary organic matter"

Manuscript

1. Pg 1 line 24. It may be useful to give the wavelength for the SSA observation range 0 to 0.7.

Response: We have modified the sentence, which now reads: … and single scattering albedo (SSA at 637 nm) from almost 0 to about 0.7".

2. Pg 6 line 145. Do the oscillations of the MAAP data correspond with filter spot changes?

Response: There seems to be a general consensus in the community on the source of the artifact being a non-disclosed internal averaging algorithm, but unfortunately there are no publications describing this artifact. We have amended the last sentence of the paragraph (Line 143) as follows: “While the exact reason for the variations is not known, they occur mid-range of the MAAP spot collection duration, and thus seem to be instrument-dependent and possibly related to a non-disclosed internal averaging algorithm.“.

We have now highlighted the filter spot times in figure S2 to support the discussion in the manuscript and we also added the following explanation (SI, section S3): "While the oscillations coincide with the frequency of filter spot changes, the actual spot change takes place during a steadier period of the oscillations. Therefore,

as stated in the manuscript chapter 2.2, the oscillations are not related e.g. to the spot-change related artefact described by (Hyvärinen et al. 2013)".

3. Pg 16 lines 368-369. One issue with using the low-cost air quality sensor as a nephelometer is that it measures at close to ambient relative humidity (unless temperature controlled) so that it may not represent aerosol scattering that affects the AE33.

Response: Thank you for pointing this out. We believe that the relative humidity needs to be addressed explicitly as well. We have amended the text (Line 365) as follows: "By letting a low-cost nephelometer (temperature- and RH-controlled) run parallel to the AE33 at monitoring stations, …".

4. Pg 17 line 376. It may be useful to give the wavelength for the SSA range quoted.

Response: We have amended the text (Line 373) as follows: "… and optical properties (SSA almost 0 to 0.7 at 637 nm). ".

Supplemental Information

5. First sentence of section S4: There is a reference to an acoustic resonator in Figure S3, though the figure does not show a resonator.

Response: We have merged the pictures S3 and S4 and added a real picture of the setup. The resonator is now visible.

6. Line 45, 'photoacoustic' should be 'photoacoustic signal'.

Response: Thank you for spotting this. The sentence now reads: "The photoacoustic instrument uses a novel resonator chamber with elliptical cross-section to enhance the photoacoustic signal, …".

7. Line 46. How were the 3 lasers combined?

Response: We have added the following explanantion (Line 61, SI): "The laser wavelength is switched periodically every 60 seconds from blue to green to red, using only one wavelength at a given time. The three laser beam paths were combined inside the laser housing by way of dichroic mirrors".

8. Line 49. I'm not sure what is meant by the "attenuation position". Do you mean 'excitiation position."?

Response: Yes, we mean excitation. We have corrected the text accordingly.

9. In Figure S4, how are the aerosol put into the resonator? Is the ellipse a 1 D tube with elliptical cross section? What is the response time of the instrument to sudden aerosol inputs? What are the dimensions of the resonator?

Response: The new Figure S3 should be clearer now. We have also added: "Aerosols enter at one end of the resonator, and are drawn out at the other end using a pump. Response times to sudden aerosol inputs were in the order of three to four

minutes." Regarding the dimensions, we added the following explanation: 10 cm width, 8 cm height (see Line 58, SI).

10. Line 59. "…attenuates the acoustic modes …". Do you mean "… excites the acoustic modes …"?

Response: Yes, we apologise for this mistake. We have corrected the text (Line 77) accordingly.

11. Line 59. What kind of loudspeaker is used to generate sound at 22.7 kHz? How is it coupled to the chamber to excite the relevant mode?

Response: We now specify that it was a Balanced Armature Driver WBFK-30095-000 (Line 76), and added the following sentence (Line 67): "The loudspeaker and the microphone are both guided with the help of a rod into the resonator chamber."

12. Line 65-70. Since the phase delay was not measured, how is the aerosol light absorption made quantitative with this instrument?

Response: The PAS is calibrated with 1 ppm NO2 and the aerosol signal amplitude is compared to the signal amplitude from the NO2 measurements.

The PAS is a prototype instrument, which is still in the development phase. Further efforts are needed to improve the stability and repeatability of the measurements. Uncertainties are currently dominated by sporadic technical errors, which led to incomplete measurements for some data points.

We have now removed the PAS data from Figs. 3-4 of the main manuscript. The data are still listed in Tables S2 and S3 in the Supplemental Information.

REVIEWER 2

The revisions undertaken by the authors have strengthen their manuscript. However, this said, this reviewer still has an issue with the "definitive tone" taken by the authors with respect to attributing light absorption enhancement at the shorter wavelengths to coating absorption based on the absence of light absorption at the NIR wavelengths.

While DDA does predict a weaker light absorption enhancement relative to the simplistic core-shell model, the light absorption enhancement due to transparent coatings does not go to zero at the NIR wavelengths. Given the over all measurement uncertainty (which must include uncertainties associated with the light absorption measurements themselves, measurements of the aerosol mass concentrations and the derived mass ratios of coating to core, etc.) the conclusive tone that the light absorption enhancement observed at the shorter wavelengths is

due to coating absorption is not justified. The authors are strongly encouraged to review the work of Lack and Cappa (ACP, 10, 4207–4220, 2010) wherein those authors reported that "….BC cores coated in CClear can reasonably have AAE of up to 1.6, a result that complicates the attribution of observed light absorption to CBrown within ambient particles. However, an AAE < 1.6 does not exclude the possibility of CBrown; rather CBrown cannot be confidently assigned unless AAE > 1.6." (Lack and Cappa abstract) The reported AAEs contained in Table 1 range from 1.14 - 1.48 for the Aethalometer-derived values and from 0.875 - 1.36 for PTAAM-derived values, both of which fall well below the canonical 1.6 threshold cited by Lack and Cappa. This reviewer is not calling into the question the results, but rather the tone of certainty that the authors take with respect to either discussions of light absorption enhancement or attribution. Examples include: "As expected…" (line 270); "…the PAX which is insensitive to coating…" at 870 nm (line 263); or "These results suggest that the absorption enhancement….is dominated by light absorption by SOM" (lines 274-275). As alluded to above, the derived AAEs do not warrant such a conclusive tone. Additionally, the authors seem to have glossed over this reviewer's comment regarding the fact that the size parameter will differ for differing wavelengths and thus caution should be exercised when extrapolating the absence of light absorption at the longest wavelengths as evidence that light absorption observed at the shorter wavelengths IS due to light absorption by the coating. Indeed, this issue was also raised by Reviewer 1. The attribution issue needs to be addressed for fully before this manuscript can deemed as acceptable for publication. This reviewer believes that the work of Lack and Cappa along with the size parameter dependence on light absorption are likely the more robust explanations for the observed light absorption at shorter wavelengths versus coating absorption - based on the data presented in the manuscript.

Response: We thank the Reviewer once more for the valuable feedback. We apologise if the tone sounded too definitive, it was not in our intentions. Our intention was not to claim that the absorbing coatings would result in absorption enhancement and the text around line 270 was an oversight. We explicitly mention non-absorbing coatings in the replies to Reviewers and mention this only as a possible (general) mechanism in the manuscript text. We completely agree with the Reviewer and have modified the text and used a more reliable measurement of the AAE.

Indeed, now that we use the AAE values from the PTAAM (instead of the AE33) to convert b_{abs} of the PAX to 532 nm, the PAX also reports a weak absorption enhancement. We have now deleted the sentence: "…the PAX which is insensitive to coating…" at 870 nm (line 263) and have modified the text of the paragraphs as follows:

"In the visible and near UV region of the spectrum, the values of E_{abs} can include effects of both "lensing" and potential absorption by SOM. Absorption by α-pinene-derived SOM is very low with a MAC below 0.25 m^2g^{-1} (Nakayama et al., 2010) or even 0.01 m^2g^{-1} (Lambe et al., 2013) at 532 nm, depending on the oxidation state and experimental details. Instruments measuring in the wavelength region 520–637 nm all recorded an increase in $E_{abs,\,532}$ as a function of R_{BC} (Fig. 3c). At $R_{BC} \approx 3.4$, corresponding to an EC/TC

mass fraction of 10 % and an SSA of about 0.7, an absorption enhancement in the range 1.3 (PTAAM 532 nm) to ~ 2 (MSPTI 532 nm) was observed.

A weak absorption enhancement of about 1.1-1.3 at 532 nm was calculated from the PAX data (Figure 3c). We therefore interpret the absorption enhancement shown in Figure 3c to be due to a transparent coating by SOM on the absorbing BC core, as described by Lack and Cappa (2010). Moreover, as biogenic SOM is only expected to absorb light in the UV and near UV region (Nakayama et al., 2010, Lambe et al., 2013, Song et al., 2013), it is surprising that the MAAP indicates such a pronounced absorption enhancement at 637 nm. Apart from the lensing effect, one additional reason could be coating of BC in the filter by SOM or modification of the filter matrix optical properties by SOM (Lack et al., 2008).“

To return to the absorption of coatings, we would like to make a general observation that “browness” of BrC should not be interpreted as the absorption of the coating at the lower wavelengths, but rather the coated particles absorbing in this region – with the naming of BrC based on the properties of the whole particle, which is a coated soot core.

Concerning the measurement uncertainties:

3) The statistical uncertainty in R_{BC} was listed in Table S2 (as standard deviation). Here, we have made the following correction: we now provide the uncertainty as standard deviation of the mean in order to be in line with the rest of the manuscript. We also provide an estimation of the combined measurement uncertainties of the TEOM and R_{BC}, respectively:
4) (Line 197) TEOM measurements agreed within 1%-4% with the reference (manual) gravimetric method.
5) (Captions of Figs 3 and 4)The uncertainty (k=1) in R_{BC} is estimated to be about 5% (not shown).
6) We now provide an estimation of the measurement uncertainties related to b_{abs} in the manuscript, section 2.2 "BC- and aerosol-absorption-measuring instruments". We have revised Figures 3-5 accordingly. Note that the data points in panels b) and c) have been slightly shifted along the x-axis to improve the readability of the graph (the correct R_{BC} values are listed in Tables S2-S4). A clarification has been added in the caption of the figures.

   We come to the following conclusion:

   (Line 262): Even when taking into account the expanded measurement uncertainties (k=2; 95% confidence interval), the measurements by the AE33 hardly agree with the measurements by the PAX and PTAAM. This indicates that the ~20% measurement uncertainty (k=1) assigned to the AE33 (see section 2.2) might be underestimated. Similar observations can be made for the MAAP at high R_{BC} ratios even though the deviations from the PAX and PTAAM are less pronounced.

We have also amended the text as follows:

(Line 277): The uncertainties in Figure 3c were calculated as the quadratic sum of the uncertainties in b_{abs} for the uncoated and coated soot. Note that this procedure is only a simplistic approximation. Ideally, the uncertainty in b_{abs} should be partitioned in type A (random) and type B (systematic) uncertainties and correlations between the different components should be taken into account. A robust uncertainty calculation was, however, not possible because the uncertainties of the instruments are not so clearly understood and, additionally, instruments such as the PAS and the MSPTI at times suffered from unexpected technical errors. In the case that b_{abs} is dominated by systematic uncertainties which remain the same when measuring the uncoated and coated soot particles, such uncertainties may cancel out, resulting in a much smaller combined uncertainty in E_{babs} than what presented in Figure 3c.

References:

1) Nakayama, T., Y. Matsumi, K. Sato, T. Imamura, A. Yamazaki, and A. Uchiyama (2010), Laboratory studies on optical properties of secondary organic aerosols generated during the photooxidation of toluene and the ozonolysis of a-pinene, J. Geophys. Res., 115, D24204, doi:10.1029/2010JD014387.
2) Andrew T. Lambe, Christopher D. Cappa, Paola Massoli, Timothy B. Onasch, Sara D. Forestieri, Alexander T. Martin, Molly J. Cummings, David R. Croasdale, William H. Brune, Douglas R. Worsnop, and Paul Davidovits: Relationship between Oxidation Level and Optical Properties of Secondary Organic Aerosol, Environ. Sci. Technol. 2013, 47, 6349−6357, dx.doi.org/10.1021/es401043j , 2013.
3) Lack, D. A. and Cappa, C. D.: Impact of brown and clear carbon on light absorption enhancement, single scatter albedo and absorption wavelength dependence of black carbon, Atmos. Chem. Phys., 10, 4207–4220, https://doi.org/10.5194/acp-10-4207-2010, 2010

Specific comments:

Line 150. The authors write: "….the FHNW group uses three different wavelengths (445 nm, 520 nm, 638 nm, ~300 mW each)…." Yet in the supplemental the authors cite - on line 47 - that the power level for the 520 nm is 700 mW, no where close to 300 mW. Which is it?

Response: Apologies for this typo, we meant 300 mW and we have corrected the text accordingly (SI, Line 60).

Line 218. The potential impacts of 10^7 /cc concentrations leading to coagulation. The rate of coagulation is proportional to the square of the number concentration. It is hard to imagine that coagulation is not occurring at such high concentrations, especially when coagulation has been observed in other studies at lower concentrations (~10^5 /cc). Perhaps the absence is due to transit time in the coating chamber? The authors are encouraged to at least speak to the possibility of coagulation and why they think it is not present.

Response: In Table S1 two different operation points for the miniCAST are listed. For Setup 1 (no diluter between the miniCAST and oxidation flow reactor), we had to slightly modify the settings of the miniCAST in order to still generate soot with GMDmob of 90 nm. Without modifying the setting, we would obtain particles with GMDmob > 90 nm due to coagulation. We believe,

however, that coagulation happens already in the outlet pipe of the miniCAST (and perhaps in the tube connecting the miniCAST with OFR). No further coagulation was observed in the OFR most probably because of the short residence time of the aerosols in the quartz tube (about 3 s). We have added an explanation in Section S1.

Line 268. This is where authors state that R_BC=3.4 which corresponds to EC/TC of 0.1. In their response the authors state that “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” The authors are encourage to put the response into the manuscript, because an interested reader with will the same simple calculation and discover ~ 2x difference between the MBC/MTotal derived form r_BC=3.4 and the reported EC/TC = 0.1.

Response: We have added this clarification in Line 247.

Line 344: The authors cite the modest enhancement in light absorption of ambient aerosols reported by Nakayama who conducted measurements at 781 nm. While this review is NOT a review of the Nakayama work, caution must always be exercised when comparing light absorption measurements using a denuder as denuders are known not to remove all the coating, yet making the assumption that the coating is all vaporized.

Response: The reason why we compared with the work of Nakayama et al. is because the authors studied aerosols with thin coatings. In our work, we also generated thin to moderate SOA coatings. But we agree with the Reviewer that it is quite difficult to compare laboratory with field studies because of the different conditions under which the aerosols are generated and processed. We have now removed the reference to Nakayama et al. from our manuscript.