

We would like to thank Reviewer 1 for the feedback, which has helped us to improve the manuscript. Below we added the response to each comment/question as well as the sections of manuscript that were adapted.

Reviewer: Page 1. Title. It seems that the title captures only a part of the accomplishment of this work. As stated in the conclusions, one outcome is the demonstration of the aerosol generation system. Perhaps the title could be revised to reflect this.

Response: Thank you for this comment. We have revised the title to "[Comparing black carbon and aerosol absorption measuring instruments – a new system using lab-generated soot coated with controlled amounts of secondary organic matter](#)".

Reviewer: Page 5, paragraph starting at line 145. One goal of this study seems to be to evaluate new instruments with existing instruments. Since the 'PAS' is a new instrument, it would be good to give more details and a schematic. It seems that operation at such a high frequency (around 23 kHz) would result in a low pass filter response to light absorption, that heat transfer from the aerosol to the surrounding air would not all occur within the acoustic period so that the measurements would be strongly a function of aerosol size. Additional details about the motivation for, and design of, the prototype PAS would be useful, perhaps given in the supplemental section. The additional detail could explain how the instrument 'modulation frequency adapts...' (what measurements or theory are used to accomplish this).

Response: Thank you for pointing this out. We have added a detailed description of the PAS to the Supporting Information in Section S4 as follows:

S4 Description of the PAS

The measurement principle of the PAS is based on the photo-thermal effect of light absorbing particles in an acoustic resonator, as shown in Fig. S3. BC particles in the laser beam absorb light (1), which causes them to heat up (2). This heat is transferred to the carrier gas, releasing a pressure wave from the particle (3). This effect is enhanced if the light is modulated at the right frequency (4), building a standing wave within the resonator which is measured with a sensitive microphone (5). By matching the light intensity modulation frequency with the resonance frequencies of the chamber, the quality factor of the acoustic mode ($Q \sim 1000$ at 22.7 kHz) enhances the signal amplitude. The amplitude corresponds linearly to the amount of absorbed light.

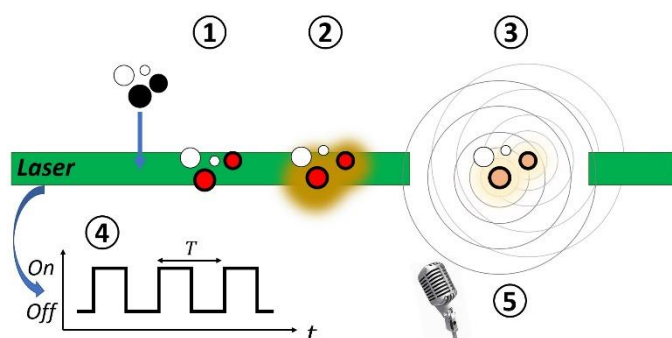


Figure S3. Illustration of the photothermal effect.

The photoacoustic instrument uses a novel resonator chamber with elliptical cross-section to enhance the photoacoustic, three lasers, a microphone, a loudspeaker, an amplifier and a signal-processing unit (lock-in amplifier). The three different wavelengths (445 nm with 700 mW, 520 nm with 300 mW, 638 nm with 300 mW power) of the diode-lasers allow us to measure wavelength-dependent optical properties of the aerosols.

The motivation for the elliptical cross-section is the possibility to separate the attenuation position from the measurement position of the microphone - at approximately the two focal points of the ellipse. The laser beam is guided by mirrors into the aluminium resonator along a focal point, which allows effective excitation of the transversal modes. The microphone is situated in the mid of the 24 cm long resonator case and can be moved transversally into the resonator, as indicated in Fig. S4. The microphone signal is then amplified and demodulated with a Stanford SR850 lock-in amplifier, which allows to measure amplitude and response delay of the photoacoustic signal at the excitation frequency, working currently at around 22.7 kHz. The measurements were performed with an integration time of 1sec therewith the mode can easily build up to a standing wave. The laser intensity modulation frequency is adapted periodically every 10 minutes, with the help of a loudspeaker and a frequency sweep, to match with the resonance frequency of the chamber.

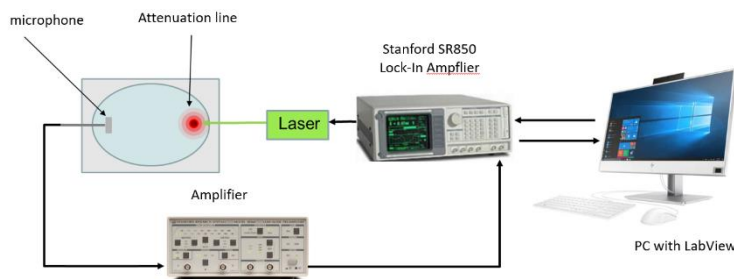


Figure S4: Schematic illustration of the PAS.

A loudspeaker (not shown in Fig. S4) is guided into the ellipse (parallel to the microphone) and attenuates the acoustic modes of the resonator chamber. These modes are independent of the light-absorbing particles in the chamber, but depend on the gas composition, temperature and pressure. The frequency of the loudspeaker is swept within a window where an acoustic resonance occurs. The frequency of the amplitude peak of this spectrum is then determined and its relative shift (to a reference measurement) is added to the laser intensity modulation frequency.

The motivation for the high frequency is on one hand to explore the response of the photoacoustic in the ultrasonic regime, as this was little explored in the past, and on the other hand to eventually measure the aerosol size distribution of the sample. At higher modulation frequencies it is easier to measure the phase delay between different aerosol size distributions, as the delay gets bigger for higher frequencies. At a fixed frequency, larger particle distributions could show a bigger phase delay than small particles, as the heat capacity rises with particle size. This phase delay was not yet measured and is still subject of investigation. Also measurements in the ultrasonic regime are expected to be less influenced by ambient acoustic noise.

Reviewer: Page 6, line 180. It's unclear to me how the babs values were normalized by total number concentration. Total number concentration seems potentially fraught with issues since light absorption of course depends on particle diameter in a complicated way.

Response: The total concentration is shown in the last column of Table 1.

Operation point	GMD_{mob} (nm)	$SS_{APAX,870}$ (-)	$SS_{Aneph/MAAP}$ (-)	AAE^1 (-)	AAE^2 (-)	EC/TC mass fraction ³ (%)	Total concentration ⁴ (cm^{-3})
1 – uncoated	91.7±0.1	0.027±0.001	0.0333±0.0002	1.14±0.01	0.875±0.014	91±7	25900±300
1 – coating 1	86.1±0.1	0.052±0.001	0.0749±0.0003	1.20±0.01	0.984±0.009	65±5	36500±100
1 – coating 2	83.4±0.1	0.12±0.01	0.148±0.001	1.28±0.01	1.05±0.01	48±3	35000±100
1 – coating 3	83.0±0.1	0.18±0.01	0.220±0.001	1.29±0.01	1.06±0.01	39±3	35500±100

GMD_{mob} (see column 2) does not change much throughout the experiment, therefore any artefacts arising from the dependence of light absorption on particle size are expected to be negligible.

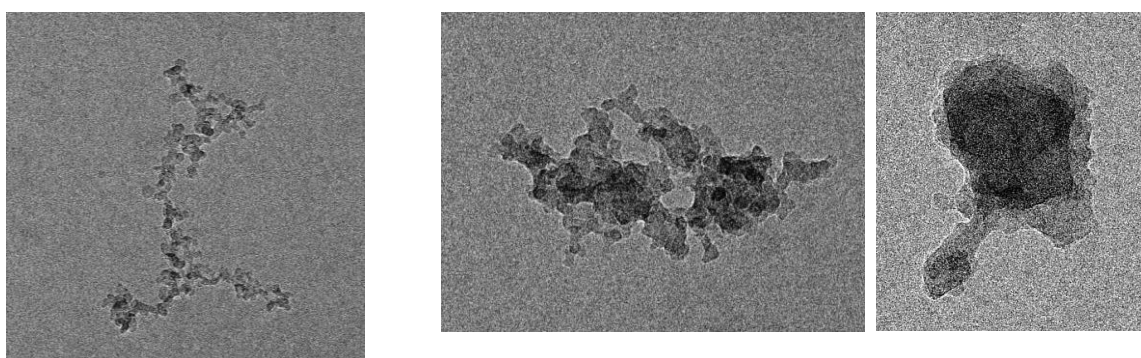
Example:

For "Operation point 1", the concentration of uncoated particles was taken as a reference value. The b_{abs} values of the coated points were adjusted by a correction factor equal to the ratio of the concentrations. For instance, for the first coating, b_{abs} was multiplied by $25900/36500 = 0.71$.

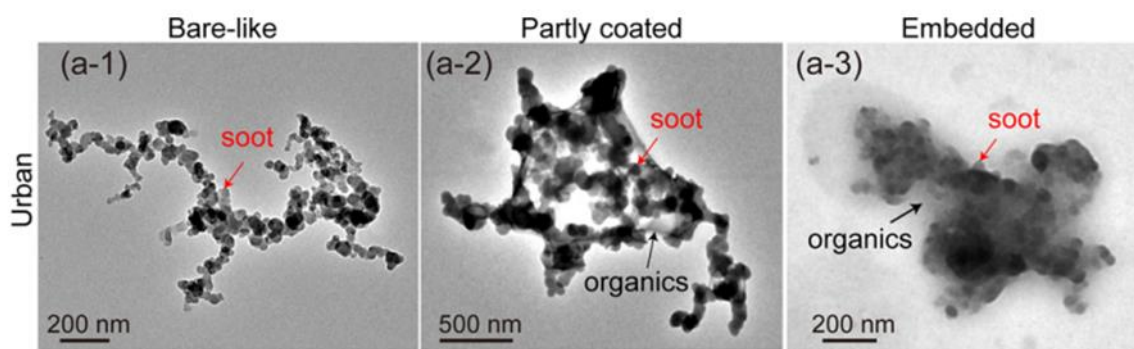
Reviewer: Page 8, line 215. Was electron microscopy performed to investigate soot core restructuring?

Response: This is indeed an important point. Cryo-TEM images of soot and coated soot particles were recorded during the study by (Ess et al., 2021) doi.org/10.1016/j.jaerosci.2021.105820.

The left panel below shows the TEM image of an uncoated (bare) soot particle, the middle panel is the image of a partly coated soot particle and the right panel the structure of a fully coated (i.e. embedded in the organic matter) soot particle. A gradual collapse of the soot core is observed as more SOA condenses on the soot core.



Our findings agree well with those reported by Wang et al. in the study "Fractal Dimensions and Mixing Structures of Soot Particles during Atmospheric Processing". Environmental Science & Technology Letters 2017 4 (11), 487-493, DOI: 10.1021/acs.estlett.7b00418 (see figure below):



Reviewer: Page 9, line 247. It seems that there is a contradiction in this paper to use the AE33 derived AAE to move the babs for other sensors (PAX for example) values all to 532 nm since the AE33 data is also described as being likely incorrect. What is the justification for doing this and what uncertainty enters the conclusions as a consequence?

Response: This is a valid concern. Figures 3 and 4 show b_{abs} at 532 nm. Two of the sensors (MSPTI and PTAAM) measured already at 532 nm, so no correction was applied. Three other sensors (AE33 520 nm, PAS 520 nm and MAAP 670 nm) measured at a wavelength close to 532 nm, therefore only a very small correction was needed. Any artefacts related to this correction are expected to be negligible compared to the systematic uncertainties of these instruments. The PAX is the only instrument that measured at 870 nm and would require a considerable correction for converting b_{abs} to 532 nm.

In Table 1, two sets of AAE values are calculated based on measurements by the AE33 and by the PTAAM. AAE as calculated based on AE33 is about 20 % higher than the AAE based on PTAAM. This difference is most probably a result of the artefacts related to the interaction between the particles and the filter matrix. Since the sample aerosol features very uniform diameters (Table 1), we believe the reason for this difference is the wavelength dependence of the multiple scattering parameter C in the AE33. The use of the AE33 derived AAE overestimates systematically the extrapolated absorption coefficients (from 870 nm to 532 nm) for PAX. Compared to the calculation using the PTAAM AAE, this overestimation is 10%-14%. 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: Page 9, lines 254-257. Which instrument(s) is (are) being considered reference methods for evaluating the results of these measurements? Which instruments provide the most and least correct measurements and how is that known?

Response: We believe that the AE33 is the instrument that suffers from the largest systematic errors. As discussed in this paper and in many previous publications, aethalometers assume a constant multiple scattering parameter C , which is not correct. C depends on the properties of the filter, design of apparatus and on the properties of the sample aerosol (e.g. particle size and SSA).

In our opinion, the PTAAM is probably the best candidate instrument to serve as reference method since the instrument can be calibrated at 532 nm with NO_2 . The calibration is transferred to the infrared (IR) channel using aerosolized nigrosin and its relative green-to-infrared absorption ratio determined using a Mie calculation based on size distribution measurements. However, since the PTAAM is a very recent development and the manuscript on the design and calibration of the instrument is still in preparation, we felt it might be premature to make such a strong statement in the current manuscript. Moreover, dedicated inter-comparisons between PTAAM and PAX are needed to understand the deviations between the two instruments. Such studies are already in progress and the results will be presented in due time.

Reviewer: Page 9, line 257, and later in the paper, page 10, lines 264-267. It still is not clear why the PAX 870 nm absorption measurements show no sensitivity to coatings. At what wavelengths are the coatings expected to be light absorbing to various degrees? It seems that the authors could readily evaluate the insensitivity to coating at 870 nm by using the

core/shell model for light absorption as a function of wavelength to theoretically evaluate light absorption enhancement at various wavelengths to confirm these results. Mass transfer is known to affect photoacoustic/photothermal measurements when the aerosol (or coating) has a high vapor pressure.

Response: This is an interesting and complex topic. 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 of 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-2020-438>) states that lensing effect is less pronounced at longer wavelengths using a Mie model. Liu et al. (<http://dx.doi.org/10.1016/j.iqsrt.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 (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 of 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 for the pump beam of the PTAAM to evaporate the soot coating. Increase of the measured AAE shows, however, 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 signals due to volatilization and recondensation are generated in the region 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.

Reviewer: Collectively the results shown in Figures 3b and 4b indicate that common aerosol light absorption measurement methods disagree by a factor of two, even in this case of laboratory-generated aerosol. If the measurements were given error bars that indicate precision and accuracy, would they overlap? It seems that the AE33 results are farthest from the rest, and that may be due to the choice of factors used to convert from filter-based to in situ light absorption. Assuming that the photoacoustic/photothermal measurements are closest to reality, can these measurements provide a suggested correction strategy for the AE33 light absorption calculation as a contribution to a growing literature on the subject?

Response: This is a very good question. Filter-based methods clearly suffer from systematic errors, which are much larger than the statistical ones. At the moment, we cannot give error bars for the combined uncertainties because the systematic errors can only be quantified by comparison to a reference method. Two methods which could serve as reference are the "extinction minus scattering method (EMN)" and photo-thermal interferometry (note that EMN suffers from large uncertainties at high aerosol SSA).

A correction strategy for the AE33 light-absorption calculation is discussed on pages 14-15 (Figure 4). We suggest, as others have done before us, to calculate new values for the aethalometer's C value as a function of SSA using the babs value of the PTAAM (or PAX) as a reference:

$$C_{SSA} = \frac{b_{atn,AE}}{b_{abs,ref}}$$

If the SSA of the ambient aerosol is known, then the calculated C(SSA) value can be used to post-correct the AE33 data. In well-equipped stations, this can be performed using an integrating nephelometer and a reference absorption measurement at a single wavelength (Yus-Diez et al., 2021, <https://doi.org/10.5194/amt-2021-46>), and can be extended using a multi-wavelength reference absorption measurement and a multi-wavelength scattering measurement in a representative campaign. Multi-wavelength absorption corrections and the determination of C can be derived from off-line filter measurements with a time resolution of hours to days (Bernardoni et al., 2021, <https://doi.org/10.5194/amt-14-2919-2021>). Moreover, a recent study suggests that "the low-cost and widely used PA monitors can be used to measure and predict the aerosol light scattering coefficient in the mid-visible nearly as well as integrating

nephelometers" (Ouimette et al., 2021, <https://doi.org/10.5194/amt-2021-170>). By letting a low-cost nephelometer run parallel to the AE33 at monitoring stations, an approximate SSA value (based on AE33 b_{abs} and low-cost sensor b_{scat}) can be calculated and the b_{abs} of the AE33 can be refined by implementing a new $C(SSA)$. Both b_{abs} by the aethalometer and SSA can be then refined in multiple steps in an iterative procedure.

We have amended Section 3 to include this information.

Reviewer: Minor issue: Page 15 line 333, 'of' is repeated.

Response: Thank you for spotting this error. We have removed the second "of".