Kousias et al.: Analysing the light-to-heat conversion of Black Carbon agglomerates to interpret results from different light absorption instruments (https://doi.org/10.5194/egusphere-2025-4498)

Review

General

The manuscript describes a new way of interpreting the signal of photoacoustic spectrometers when they are used for the measurement of light absorption by particles. It is interesting and potentially enlightening for both users and instrument developers. However, it was somewhat heavy to read and I found some errors and omissions in it, see the detailed comments below. I can recommend publishing the paper after making the respective corrections and modifications.

Detailed comments

P1L16: "... very well correlates ..." > ... correlates very well ...

Thank you for identifying this. It has been corrected.

P1: Nomenclature: give values and units when applicable

P2: Introduction. You cannot ignore filter-based absorption photometers in the introduction, they are by far the most used methods for measuring BC even though they have their uncertainties.

Thank you for your comment. The aethalometers were initially excluded from the study as the signal generation does not rely on particle absorption on a physical level. OA, OT and LII instruments rely on some heat dissipation mechanism to measure BC. Aethalometers estimate particle absorption based on purely optical properties. Thus, they cannot be modelled with the same approach. However, you re right that we cannot completely exclude them from the paper. We have added the following section at the end of the first paragraph in the introduction.

"In addition to the above technologies, instruments that employ filter-based absorption such as aethalometers are widely used, especially for ambient BC monitoring. Despite the wide use of aethalometers, they cannot be modelled with the same approach due to significant differences in their principle of operation. Thus, they will not be considered in the rest of the study."

P1L38-L44: The effect of humidity on OA signals and their interpretation is very relevant to the topic of the paper. The effect has been studied for instance by Raspet, R., Slaton, W. V., Arnott, W. P., and Moosmüller, H.: Evaporation-condensation effects on resonant photoacoustics of volatile aerosols, J. Atmos. Oceanic Technol., 20, 685–695, 2003. Cite also that and discuss possible consequences to your results later in the paper.

Thank you for your comment. Even though humidity is interesting, it is not considered by this work. It iw worth noting the difference of humidity effects on particle vs gas OA sensors. For particles, the absorbed light is translated to heat directly by the particle, without the need for molecular collisions and relaxation paths. For gases, humidity has a much stronger effect as it can be a key player in the translational to relaxation transition.

"For our entire analysis we assume dry conditions, so RH is outside the scope of the study. The presence of humidity can affect the OA signal generation in a number of ways. First, the heat conduction properties of the air surrounding the particle vary with humidity, with a tendency to improve heat conduction when RH increases. This effect is rather small, as it only affects the heat conduction from the particle to the air, and not the translation to relaxation transition, which is documented for OA gas detection. Second, for high relative humidity, water can condense on BC particles. The heat generated from light absorption can result to water evaporation from the surface of the particle, leading to reduced OA signal. Third, humidity can affect the acoustic transducer properties, leading to sub-optimal operation and sensitivity reduction (Walls 1988)."

P3L66-67: "In reality, the assumption of constant MAC is not valid for spherical particles larger than roughly 150 nm for visible light excitation (Jennings and Pinnick, 1980)."

MAC of BC particles is not size-independent constant for particles smaller than 150 nm either. It is approximately constant for particles much smaller than wavelength, then grows, reaches a maximum and then decreases strongly. It is easily shown with any Mie code, also yours, or by checking published articles, for instance Fig. 4 in Bond and Bergstrom, Aerosol Science and Technology, 40:27–67, 2006.

Thank you for this clarification. We have adjusted the phrasing accordingly. The new section is as follows:

"In reality, the MAC of spherical particles is approximately constant for particles much smaller than the excitation wavelength. For visible light excitation, this assumption is satisfied for particles smaller than 150 nm (Jennings and Pinnick, 1980)."

P4L90: "Radiation and sublimation are only relevant at higher temperatures, …"

Based on what? Justify the statement. Did you calculate that? How about at high RH?

Thank you for your comment . This is shown in the results section, and specifically in Figure 2. We have added a reference to this figure. RH is not relevant here as the key factor that determines the main dissipation mechanism is the particle temperature.

"As will be shown in Fig. 2, radiation and sublimation are only relevant at higher temperatures, which are typical for LII but which are not reached in OA and OT applications."

P5L112 "In Eq. (2), p is the pressure of the air surrounding the BC particle…"

Pressure must also depend on the altitude of the measurement site and the prevailing high or low pressure. So, I suppose this is the deviation from the ambient air pressure, right?

Thank you for your comment. You are exactly right. We have added the following sentence to clarify this.

“Pressure p is used to calculate the deviation from ambient air pressure, due to the optoacoustic signal.”

P5L118-119: “Specifically, the refractive index of BC particles that was suggested by Bond & Bergstrom (2006), the particle size, and a wavelength range are inputs to the Mie Simulator GUI (2025).”

Give the values of the real and imaginary refractive indices so that readers don't have to dig them up from the original paper.

Thank you for your comment. We have added the respective values as shown below:

“the refractive index suggested by Bond & Bergstrom (2006) which is equal to 1.9 – 0.75i”

P6L158-163: “First, total absorption is equal to the absorption of a primary particle, based on the Mie theory (Hinds, 1999), multiplied by the number of primary particles ... This means that an agglomerate particle comprised of e.g. 100 primary particles, absorbs the same amount of light as 100 distinct spherical particles of the same size as the primary particles.”

It is not that simple. Check these, for example: Romshoo et al.: Significant contribution of fractal morphology to aerosol light absorption in polluted environments dominated by black carbon (BC). npj Clim Atmos Sci 7, 87 (2024). https://doi.org/10.1038/s41612-024-00634-0

Romshoo et al.: Importance of size representation and morphology in modelling optical properties of black carbon: comparison between laboratory measurements and model simulations, Atmos. Meas. Tech., 15, 6965–6989, https://doi.org/10.5194/amt-15-6965-2022, 2022.

Li et al.: Microphysical properties of atmospheric soot and organic particles: measurements, modeling, and impacts. npj Clim Atmos Sci 7, 65 (2024). https://doi.org/10.1038/s41612-024-00610-8

Typical methods include, for instance, T-matrix code or dipole-dipole approximation (DDA). They are heavier and more time-consuming methods, however, so if you don’t have such codes readily available I don’t require you repeat your calculations with them. But try to make some educated guess of how using them would change your conclusions.

Thank you for this comment. We have rewritten this section based on comments of both reviewers. The new section is as follows:

Agglomerate particle absorption is estimated using the RDG-FA method (Sorensen et al. 2018; Liu et al. 2010, Romshoo et al. 2022). For applying this method, we calculate the absorption coefficient of the primary particles that form the agglomerate using the Mie theory for spherical particles (Hinds, 1999), the refractive index suggested by Bond & Bergstrom (2006) which is equal to 1.9 – 0.75i, and a handy Mie Simulator GUI (2025). […] . However, Liu et al. (2010) and Bond et al. (2006) have demonstrated that this method may underestimate absorption by up to 30%.

P7L169-170: “The diameter of gyration is a proxy of the wetted surface of the particle, which is relevant for heat conduction”

Here you mention wetting. Condensed water has not been discussed anywhere else in the manuscript. It is definitely relevant so explain in more detail.

Thank you for your comment. We have modified this section to align with existing literature. The formula used for the agglomerate particle diameter has been reported to be a good proxy for the equivalent heat conduction diameter of the particle. A reference has been added. The term wetted surface was misleading and was removed.

"The diameter of gyration is a good proxy of the equivalent heat conduction radius (Liu 2008)."

P8L198-199: "One may conclude that laser intensities between 103.8 and 104 W/mm2 are suitable for LII applications, as a large share of the energy is dissipated through radiation."

That looks like quite a narrow range. How sensitive is it to particle properties? What do you mean by "a large share of energy is dissipated through radiation"? The red line in Fig. 2 looks zero to me.

How do you get Fig. 2? In Eq. (1) there is nowhere laser intensity. The graph is interesting and potentially useful but you have to justify it better so that the readers can reproduce the result. Step by step from Eq. (1). I get very suspicious when I see a straight constantvalue line like that of the heat conduction = 1 up to laser intensity of 103.8. as if there was some quantum state.

By the way, the y-axis title in Fig. 2 is most probably not correct, it cannot be percent: the highest line is 1%.

We improved the description of the Radiation term as follows:

"Radiation is never the main dissipation mechanism, with a small ad hardly distinguishable peak at ~4% of heat dissipation (0.04). Despite being very low as a percentage, is it large enough to be detected by LII instruments. One may conclude that laser intensities between $10^{3.8}$ and 10^{4} W/mm^{2} are suitable for LII applications, as the largest share of energy possible is dissipated through radiation. Intensities closer to $10^{3.8}$ W/mm^{2} should actually be preferred to reduce the destruction of particles due to sublimation. "

The term q(t) of eq. 1 included the light intensity and the excitation profile. We have modified Eq. (1) to explicitly show the laser intensity with the variable I_{laser} .

In the y axis 1 means 100 %. We clarified this.**P8L210: Model validation.** What particle diameter was used in the validation?

Thank you for this comment. We have specified the particle morphology that was used by the other models. The original section was changes to the following:

"The model is first validated by comparing the values of the individual terms of the energy balance model against the literature values of Hadef et al. (2010), who included all dissipation mechanisms for 20 nm spherical particles, and Snelling et al. (2004) who only considered conduction for agglomerate particles with primary particle size 29 nm, fractal dimension 2.2, and agglomerate particle diameter approximately 150 nm (Table 1).”

P9 Table 1. “… for the same input parameters.”

Give the input parameters and their values so that readers can repeat the calculations and possibly validate their own models.

Thank you for this comment. The input parameters are essentially the particle morphology that is mentioned in the text above. We have modified the table caption as follows to clarify this.

“Table 1: Comparison of the particle temperature and the intensity of dissipation mechanism as predicted by our model to the same metrics predicted by the models of Hadef et al. (2010) and Snelling et al. (2004) for the same particle morphology.”

P9L226-227: “…run simulations with 100 kHz modulation frequency and a rectangular pulse with the duty cycle varying between 1 % and 50 %.”

Please explain what “modulation frequency” and “duty cycle” mean for a non-engineer, as many readers of this journal are. And what does it mean that the cycle varies between 1% and 50%?

Thank you for your comment. We tried to clarify this. We added the section below:

“The modulation frequency defines the duration of the laser’s period, while the duty cycle defines the percent of the laser period that the laser is turned on”

P9L227: “The sample comprised 20 nm spherical BC particles”.

You write about 20 nm BC particles. Are they real? If so, how did you generate them? Describe the experimental setup in a figure and explanations.

Thank you for highlighting this shortcoming of the paper. We have used the same experimental setup that was presented in a previous publication, so we added a reference to this older publication. We have added the following section.

“The experimental setup uses a Planar 2D burner and custom dilution system. A detailed description as well as the characterization of the generated particles can be found in Stylogiannis et al. (2021).”

P10L240-244: You describe a real optoacoustic sensor and signals coming from it. The signals are even shown in Fig. 4. As far as I understand how a photoacoustic instrument works, it gives signals when light-absorbing particles flow into it. So, the same question must be repeated: how did you generate the particles? How were they lead to the sensor? Describe the experimental setup in a figure and explanations.

Thank you for your comment. Since we added a reference to the older publication for the previous comment no further changes are deemed necessary. The same publication is already referenced in these lines as well.

P11: Fig. 4. Why does the signal intensity decrease with increasing duty cycle? The y-axis title is "normalized". As far as I understand normalization, it is a division of any data population with the maximum value. Then the maximum value of the normalized data is 1. In Fig. 4 the max value is about 1.6. So, what does your normalization mean?

Thank you for your comment. We stated that we normalize the data by dividing with the intensity for a 50% duty cycle. To make the method clearer we modified the section to the following:

"A normalised response is calculated for each duty cycle by dividing with the response for the 50 % duty cycle. By definition, this normalised intensity is equal to 1 for a 50% duty cycle"

P11L253: "Heat flux (W)" Heat flux is mentioned here for the first time. Heat flux is a flow of energy per unit area per unit time. Its units are watts per square meter (W/m2).

Thank you for spotting this mistake. We replaced heat flux with heat flow.

P11L254-256: "Hence, to make the results easier to interpret, we present the ratio of heat conduction over particle mass (W/kg) for any particle, normalised over the same magnitude of a 20 nm spherical particle. This newly introduced metric is called normalised signal intensity."

Present this as an equation and explain it properly. This is important since you introduce here a new metric that you aim to use and obviously wish that so do others.

Thank you for your comment. We have added a new equation and tried to better describe the new metric. The final section is as follows:

"Next, we proceed to examine the intensity of the generated OA signal for various particle properties. The signal calculated by our model is proportional to the heat flux flow (W) from the particle to the surrounding air, which generally increases with particle size due to larger mass. In other words, if one tries to plot the signal from a 100 nm particle and a 10 nm particle as bar plots on the same axis, the signal from the 100 nm particle will be very large, and the signal from the 10 nm particle will be hardly visible. Small deviations are impossible to spot in such a plot. Hence, to make the results easier to interpret, we present the ratio of heat conduction over particle mass (W/kg) for any particle, normalised over the same magnitude of a 20 nm spherical particle, which is a typical size for primary BC particles (Bond, Olsen).. This newly introduced metric is called normalised signal intensity, and its calculation is shown in Eq. (11). We assume that all particles have the same mass absorption coefficient (MAC), thus any possible combination of particle morphology and laser modulation should in theory produce a value of one expressed in this normalised signal intensity. We will show that this is not always true.

$$S_{norm} = {S_{D_g}/m_{D_g}} \Big/ {S_{d_p=20nm}/m_{d_p=20nm}} \quad (11)$$ "

P12L269: and Fig. 5a,b: "The normalized signal intensity drops as the fractal dimension increases."

Very interesting! But please explain. Why is the normalized signal about 1 up to some fractal dimension and decreases then?Thank you for your comment. We have added the following to explain the result:

"The reason for this is that as particle become larger, and especially if they have large fractal dimension, they become worse at dissipating the absorbed heat. So, even though all particles absorb the same energy, they cannot all dissipate all that energy back to the surrounding air."

P12L272-274 and Fig 5c: "In Fig. 5c, the data for both diameters of gyration are plotted over the volume to surface ratio (V/S) of the agglomerate particle on the x axis. We observe that all particles fall in the same line, independently of their diameter of gyration and primary particle size".

Very interesting! Please explain. Why do the points fall on the same line?

We have provided a potential explanation as to why. We also added references to existing LII publications that have observed similar results. We were unaware of these publications, but they were suggested by the second reviewer.

"A possible explanation for this is that the volume of the particle is proportional to the amount of energy absorbed, while the surface calculated with the diameter of the agglomerate particle is a good proxy for the heat equivalent diameter of the particle. Thus, the V/S ratio is a good proxy to evaluate if the particle can conduct all the energy it absorbed. In LII particle cooling monitoring, a similar observation has been associated with the Sauter mean diameter of the particle, which is equivalent to the V/S ratio shown here and further affirms the validity of our model."

P13L291-292: "This way, BC can be distinguished from other absorbing particles of different properties, for example ash particles."

Sounds interesting but please explain how it could be done even theoretically.

We have added a short explanation here and a reference to the next section as this is better explained below.

"For example, a particle with very high heat capacity will absorb more energy than it can conduct to the surrounding air, leading to reduced normalised signal. However, physical properties alone cannot be used to normalize the signal from devices of different operation characteristics or to correct for different V/S ratios. Thus, we propose a better metric in section 3.6."

P14L299-L303 and Fig. 7: Very nice result! And even I understand this.

P15L318-320 and Fig. 8b: "Fig. 8b shows that when the dimensionless metric is used as independent variable, then all values fall in the same line, demonstrating the excellent predictive value of the proposed metric."

This is an impressive result! But explain more, I don't understand why all points are on the same line. Can you explain it?

Thank you for your comment. We tried to explain it. We added the following section:“Essentially, the modulation frequency (fmod) is the inverse of the modulation period. Thus, the dimensionless metric is the ratio between the relaxation time of the particle (how fast it dissipates energy through heat conduction) and the duration of the period (how much time it has to cool down to its initial temperature). Mathematically, TOA is the exponent of Eq. (8) at the end of the period when the light is turned on, and the temperature of the particle start to rise again.”

P16L345-347: “2019). A tarball of 150 nm, measured by an OA instrument with modulation frequency 100 kHz will be detected with an efficiency of 72 % compared to conventional BC particles that would be 100 % visible.”

How do you get these numbers? Do you calculate it using equations in this paper? If so, please do it properly in detail with initial values and used equations, not just throw numbers in the last section. Or if it comes from some other paper, cite it.

Thank you for your comment. We calculate this based on the shape of the tarball which is spherical and should lead to a high volume to surface ratio. We have clarified that we assume the tarball spherical.

P16L348-349: “An OA sensor that utilizes the findings of the current work, can accurately measure tarball concentration and potentially distinguish them from conventional BC particles.”

I don’t understand how. Please explain in more detail.

Thank you for your comment. We have tried to clarify this. We added the following:

“by estimating the reduction of the normalised signal intensity.”