

Interactive comment on “Spectral light absorption by ambient aerosols influenced by biomass burning in the Amazon Basin – I. Comparison and field calibration of absorption measurement techniques” by O. Schmid et al.

O. Schmid et al.

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We thank the anonymous referee #1 for carefully reading the manuscript and providing numerous helpful comments. Here we respond to these comments. For clarity, we have subdivided some of the referee's comments (a, b, etc.):

Referee's comment (R)

(R) 1a) The authors do not distinguish properly between light attenuation and light absorption which definitely describe different physical processes. In the Introduction

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Section and particularly in the Sections on Photoacoustic Spectrometry and on the Aethalometer, these terms are mixed.

Authors (A) response:

(A) 1a) While the terms attenuation and extinction have often been used synonymous in the literature, we acknowledge that in the interest of clarity it is better not to do so here. Therefore, we have carefully revised the manuscript and restricted the use of the terms 'extinction' and 'attenuation' to the mitigation of light passing through gas (with or without particulates) and through a filter substrate (with and without particulates), respectively.

(R) 1b) As an example, Eq. (2) states that light attenuation through the photoacoustic resonator is governed by the aerosol absorption coefficient. However, this is not true since also light scattering either by particles or by gas molecules contributes to light attenuation, or extinction, respectively, while the photoacoustic method is indeed only sensitive to light absorption.

(A) 1b) Referring to Eq. 2 the referee mentions that we erroneously state that 'light attenuation through the photoacoustic resonator is governed by the aerosol absorption coefficient', since 'also light scattering either by particles or by gas molecules contributes to light attenuation, or extinction'. While the latter is true, if the PAS is operated in the normal measuring mode, Eq. 2 refers to the PAS calibration, where no particles are present and the absorption coefficient of the calibration gas exceeds its scattering coefficient by 5 orders of magnitude, i.e., for this special case, the extinction of the laser beam is indeed governed by absorption of the calibration gas and therefore, Lambert-Beer's law as given in Eq. 2 can be used to calibrate the photoacoustic signal, that only depends on absorption too. In order to make this point more clear, we have revised the paragraph leading up to Eq. 2.

(R) 1c) In the same section, the authors plot extinction measured by an extinction cell against absorption measured by a photoacoustic spectrometer (Fig. 2). These are

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different quantities.

(A) 1c) Apparently, the referee got confused by our nomenclature. As stated on p.9366 (L-21-27) Sigma_LOPES represents the difference between extinction (Sigma_e) and scattering (Sigma_s), i.e., we are plotting the same quantities (absorption coefficient). In order to make this more clear we have replaced Sigma_LOPES by Sigma_e-Sigma_s as label of the y-axis in Figure 2 and we have reworded Sect. 2.3.3.

(R) 1d) Also in the last paragraph of Section 3.2.2, the authors state that light scattering may be interpreted erroneously as light attenuation. However, scattering contributes also to attenuation. The issue of absorption and attenuation requires careful revision of the manuscript.

(A) 1d) Of course the referee is correct in saying that scattering also contributes to attenuation. This was a typo, we meant that scattering could erroneously be interpreted as 'absorption' instead of 'attenuation'. This was corrected in the manuscript.

(R) 2a) Section 2.4 on the correction of the Aethalometer requires a clear definition of used properties. Symbols like Sigma_aeth and Sigma_aeth* are introduced without definition. Eq. (16) is obtained using the assumption that Sigma_aeth = Sigma_aeth*. Since Eq. (16) is widely used in the study, this assumptions requires explanation and discussion.

(A) 2a) Sigma_aeth and Sigma_aeth* represent the absorption coefficients Sigma_a derived from the Aethalometer data according to two different correction schemes introduced by Weingartner et al. 2003 (=W2003) and Arnott et al. 2005 (=A2005). Since both correction schemes derive the same quantity (Sigma_a), Sigma_aeth = Sigma_aeth*, if the correction schemes are accurate. We have reworded Sect. 2.4.3 to clarify this issue.

(R) 2b) The use of correction functions f and R(ATN) which describe the influence of filter loading on the measured absorption coefficient needs clarification. An additional

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figure showing the variation of attenuation ATN with wavelength for one example would be illustrative.

(A) 2b) We added a graph that shows a time series of Sigma_ATN and ATN for three different wavelengths. We added an interpretation of the parameter f and its effect on R based on the mathematical expression for R (Eq. 12). For a graphical illustration of R , we refer to Figure 5 and some clarifying remarks were added to the corresponding text in Sect. 3.2.1.

(R) 2c) In the concluding paragraph of Section 2.4 the authors adopt calibration factors f which are not given explicitly. Please quantify these calibration factors and define the method how they have been obtained. Again, a figure showing the factors f for different wavelength would be helpful. Such a figure would also justify the statement that the factors f are independent of the wavelength.

(A) 2c) We have now explicitly given the range of f values used here and a quantitative justification for the statement that f can be considered independent of wavelength. Considering the small magnitude of the correction due to f ($0.7 < R < 1$) and the clarifications made in the revised manuscript we do not believe adding a Figure (as suggested by the referee) is warranted (see Sect. 3.2.1).

(R) 2d) Related to this topic, Fig. 5 showing the fitting lines which are used to derive the factors f needs a more detailed discussion.

(A) 2d) Done (see also item 2b)

(R) 2e) Furthermore, the authors state in the Conclusions Section that the correction factors C and f are almost independent of the wavelength. This statement contradicts the calculations shown in Table 1 where the factor C varies by a factor of approx. 1.5 from 370 nm to 950 nm.

(A) 2e) The referee indicates that the potential wavelength-dependence of both f and C has to be addressed in more detail. For f , this issue was addressed in item 2c. To

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properly address this issue for C we have expanded our discussion on the estimated spectral dependence of C in Sect. 2.4.4. We now include the derivation of an expression (see Eq. 21 in the revised manuscript) describing the wavelength (λ) dependence of C for $370\text{ nm} < \lambda < 950\text{ nm}$ and for α_a values between 1 and 2.5. This covers the typical range encountered during atmospheric applications. Using this expression we find an absorption Angstrom exponent of about 1.9 for biomass burning aerosol, a value that is similar to previously reported literature values as discussed in the revised manuscript.

Based on the analysis described above we have weakened our statement in the conclusions. We are now stating that C can only be considered constant for λ between 450 and 660 nm (i.e. for 5 of the 7 wavelengths of the AE30), where the deviation of C from the reference value (C_{532}) is less than 12%. In addition, for the special case of soot-dominated aerosol (i.e. Angstrom exponent for absorption $\alpha_a = 1$; e.g. in urban areas) C can generally be considered constant, since the resulting deviation from C_{532} of up to +9% and -5.5% for 950 nm and 450 nm, respectively, is tolerable in light of an estimated 20% uncertainty of the Aethalometer.

(R) 2f) The entire issue of Aethalometer data correction needs clarification.

(A) 2f) As already indicated in items 2a through 2e we have substantially revised the section on Aethalometer data correction. The main changes are outlined here: 1. Eq. 9 was moved from Sect. 2.4.2 to 2.4.3. Now the entire discussion on the effect of aerosol scattering on attenuation is included in Sect. 2.4.3. 2. Eq. 14 and 15 were moved from Sect 2.4.2 to 2.4.4. Now the entire discussion on the spectral dependence of optical parameters is included in Sect. 2.4.4. 3. We have substantially revised the discussion on the effect of aerosol scattering on attenuation (Sect 2.4.3) 4. We have expanded the discussion on the spectral dependence of the calibration factors f and C (Sect. 2.4.4; see items 2c and 2e).

(R) 3a) The authors show an influence of relative humidity on the PSAP data analysis.

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The observed influence is largest for low relative humidities and vanishes for moderate RH values. These observations point in the opposite direction as expected from involved physical processes. The authors do not offer an explanation for their observation, but note that low RH data originate exclusively from night-time periods. Since it is known that the PSAP photodetector efficiency shows some dependence on the operation temperature of the instrument, the authors should check whether the RH effect does or does not translate into a temperature effect.

(A) 3a) In Sect. 3.1 we have added a Figure (new Figure 3b; the former Fig. 3b becomes fig. 3c) showing the dependence of the PSAP signal (normalized to the PAS) on temperature (T). This Figure also shows a correlation between the PSAP signal and T especially between 24 and 26C. Hence, it is conceivable that a T sensitivity of the PSAP photodetector plays a role, but the correlation of the PSAP bias with T is no stronger than with RH (for both $R^2 \sim 0.5$). Thus we cannot unambiguously identify either T or RH as the cause of this bias. In fact, any parameter with a pronounced diel variation is expected to correlate with this bias, since the bias itself displays a strong diel variation. As a consequence we have pointed out in the revised manuscript, that since T and RH are not two independently varying parameters, it is impossible to judge from our data whether T and/or RH or may be a third (as yet unidentified) parameter is responsible for the observed PSAP bias (Sect. 3.1, 4.1). However, for the purpose of this study, the most important aspect is that the PSAP bias shows a systematic dependence on RH (and T) that can be numerically described and, hence, can be corrected for. Since we have seen no advantage using the correlation with T instead of RH to correct for this bias, the correction algorithm for the PSAP was not changed and hence the PSAP related results remained unchanged.

(R) 3b) During the Reno Aerosol Optics Study (Sheridan et al., 2005) the corrected PSAP showed excellent agreement with a photoacoustic instrument for dry aerosol. Please discuss the discrepancies between the observations and results from previous studies.

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(A) 3b) While there are several publications indicating a sensitivity of the PSAP to RH (Guyon et al. 2004; Arnott et al., 2003), we are not aware of any publication mentioning a potential temperature sensitivity of the PSAP. The paper by Sheridan et al. (2005) (mentioned by the referee) and the more detailed companion paper by Virkkula et al. (2005) did not investigate a potential T and/or RH sensitivity of the PSAP and they do not even specify the operating RH and T except for stating that they were using 'dry' aerosol. Hence, it is difficult to perform a detailed comparison between our data and their results. However, we have expanded the already existing comparison to Virkkula et al., 2005 (p.9382 L.6-18) to discuss in more detail their outdoor calibration experiments that show good agreement with our (daytime) PSAP results for $RH > 30\%$ (see Sect 4.1).

(R) 4a) The section on an influence of gaseous adsorption on the absorption measurement requires justification of the drawn conclusions. The data analysis builds exclusively on the assumption that the pollution of sampled air by azeous compounds correlates well with the pollution by particulate compounds which, however, must not be the case.

(A) 4a) Following the referee's suggestion we have reanalysed our data using gaseous components, namely NO₂ and CO (instead of aerosol absorption coefficient), as a proxy for gradients in gaseous pollution levels. While we do not suggest that either NO₂ or CO actually adsorb onto the Aethalometer filter matrix, these components serve as a proxy for pollution events driven by photochemistry and/or biomass burning, respectively. In contrast to our original result, we now find no significant correlation ($R^2 < 0.1$) of the gradient in multiple-scattering correction factor C with the gradient in pollution level. Hence, we withdraw our previous statement that there is evidence for a systematic effect of gaseous adsorption on the performance of the Aethalometer. However, we believe that this analysis and its (negative) result is still valuable enough to remain part of the manuscript. Nevertheless, in the interest of brevity we have substantially shortened this section by removing Fig. 8 and - of course - we changed the

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result of this section to ‘NO evidence for adsorption effects’. This new finding does not affect any of the other results of the paper.

(R) 4b) The observation that the deviation of the multiple-scattering correction factor C for high pollution levels from an average value is a function of the property Sigma_aeth may also be explained by having a look at Figs. 4 and 6a/b. The authors derive the factors C as arithmetic mean values from the respective data sets. However, Figs. 4 and 6a/b show that the scatter of $\text{Sigma_aeth}/\text{Sigma_PAS}$ is largest for absorption coefficients $< 10 \text{ Mm}^{-1}$. When excluding PAS data $< 10 \text{ Mm}^{-1}$ from the data analysis, the obtained factors C will be different. The authors should investigate to what extent these modified C factors influence their conclusion on an effect of gaseous adsorption on the Aethalometer performance.

(A) 4b) Since we now report no systematic dependence of the Aethalometer signal on the gradient in pollution level, this issue has become obsolete.

(R) 5) In the conclusions on a recommended practice for the correction of ethalometer data the authors define a “best practice” value of $C = 4.2$. This value deviates both from the value derived for the Amazonia aerosol and from the values reported by Weingartner et al. (2003) for coated and pure combustion particles. It seems more appropriate to use different C factors for different aerosol types, since following Eq. (20), the factor C contains the influence of the aerosol light scattering fraction.

(A) 5) With “best practice” we referred to ambient aerosol only as stated on p.9385 (L.5) and we implicitly assumed that this refers to internally mixed aerosol only, i.e., one can take the average of the available C values for internally mixed (and ambient) aerosol ($C = 4.2$) as reasonable estimate for ambient aerosols. However, we agree with the referee that it is desirable to be more specific and distinguish between pure/externally mixed soot and internally mixed soot. We now recommend a C value of 2.1 for pure and externally mixed soot (based on the calibration studies by Weingartner et al., 2003; Arnott et al., 2005) and 4.2 for internally mixed, aged ambient aerosol (Weingartner et al., 2003;

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Arnott et al., 2005; present study). Analogously, we have refined our recommendation for the calibration factor f using the parameterization provided by Weingartner et al. (2003).

SPECIFIC COMMENTS

(R) Entire manuscript: the frequent use of the word “relatively” should be restricted. It should be replaced by a more precise description wherever possible.

(A) Done.

(R) Introduction, 2nd paragraph: clarify the use of absorption, attenuation and extinction. State, that the difference methods relies on the relationship $\text{extinction} = \text{scattering} + \text{absorption}$; photoacoustic spectrometry uses the thermal expansion of light-absorbing particles caused by the transfer of radiative energy into thermal energy, please clarify.

(A) Done.

(R) Introduction, 3rd paragraph: Multi-angle absorption photometry is not an advanced Aethalometer but a totally different technique which uses radiative transfer methods for the data inversion, please revise the respective sentence.

(A) Done.

(R) Introduction, 4th paragraph: The difference methods needs an extinction cell plus an integrating nephelometer, which makes it difficult for field work, please add this clarification to the text.

(A) Done.

(R) Section 2.5: There is no Eq. 33.5, please correct.

(A) Done. We meant Eq. 21.

(R) Table 1: Specify values for C^* and m_s which were used for the calculation of C . The

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values may be given either in the text or in a footnote to Table 1.

(A) Done. We now list them as footnote to Table 1.

(R) Figure 2: Correct the label of the y-axis, it should read Sigma_e - Sigma_s.

(A) Done.

(R) Figure 8: Plot axis labels at the bounding frame of the figure.

(A) This figure has been removed from the manuscript (see item 4a)

REFERENCES

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Weingartner, E., Saathoff, H., Schnaiter, M., Streit, N., Bitnar, B., and Baltensperger, U. (2003), Absorption of light by soot particles: Determination of the absorption coefficient by means of aethalometers, *J. Aerosol Sci.*, 34, 1445-1463.

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