Response to RC2

The authors thank the referee for the pertinent comments and the ideas to improve the manuscript. Our responses are presented below (in black the original comments from the referee and our responses in green).

GENERAL COMMENT

The study targets the measurement of absorption Ångström exponents (AAE) by filter-based multi-wavelength light absorption measurement methods. Light attenuation data from the widely used 7-wavelength Aethalometer are analyzed by applying two correction schemes according to Schmid et al. (2006) and Collaud Coen et al. (2010) and comparing the results to data from the filter-based offline Multi-Wavelength Absorbance Analyzer MWAA (Massabò et al., 2013; Massabò et al., 2015). Reference methods of the measurement of light scattering and light absorption were a 3-λ Integrating Nephelometer (Model Aurora 3000, Ecotech) and a single-wavelength Multi-Angle Absorption Photometer MAAP (Model 5012, Thermo Electron Group). Data have been collected at the ATTO site in Amazonia from the wet-to-dry transition season to the dry season in 2014.

The topic of the study is of relevance for the research area of determining black carbon (BC) and brown carbon (BrC) from the wavelength dependence of the light absorption coefficient, characterized by the AAE. The presented data is well suited for the study and of high importance and thus deserves publication in AMT. However, before being suitable for publication, the manuscript requires major revisions which are highlighted in the following.

> We agree with most of the comments presented by the referee. After a major revision of the manuscript, we consider we have addressed all of the referee concerns.

SPECIFIC COMMENTS

1. A more detailed description of the approaches in sections 2.3.1 and 2.3.2 is required. Particularly, the connections between Equations 8 to 14 need better explanation. Furthermore, the links between R_{meas} and R, and between C, and C_{ref}, as well as their respective wavelength dependencies need to be introduced. As an example, the authors say on lines 243 ff that “By applying a linear fit to Eq. (8) vs. ATN data, it is possible to obtain the shadowing factor as follows ...”. However, the connection of Eq (8) and Eq (9) via the claimed fit procedure is not clear. Then, on lines 248 ff, C is parameterized as a function of AAE, although the physically based relationship is on the wavelength. Again, the approach for this parameterization is not clearly described.

In Eq. (11), the wavelength dependence of the single-scattering albedo (SSA) is parameterized as a function of the AAE, although the physical-based relationship is on the wavelength. Furthermore, the parameters required for a direct determination of SSA as a function of λ are available: σ_{sca} is measured for 3 wavelengths and σ_{abs} is measured for one wavelength, so that SSA can be determined directly for one wavelength and extrapolated to the other wavelengths by the described iteration procedure. The direct approach would avoid the assumption that σ_{sca} and the scattering contribution of the SSA scale both with $å_{sca}$ and same for the absorption part. A comment is requested why this approach was chosen.

> We changed sections 2.3.1 and 2.3.2 to make the procedure clearer to the reader and fulfill the referee requests. Regarding the SSA parameterization expressed in Eq. (11) (now Eq. (12)), we used the presented approach to study the wavelength dependence on the multiple-scattering correction.

Changes to Section 2.3.1:

"Attenuation coefficients at 590 nm were interpolated to 637 nm assuming a power-law relationship as,

$$\sigma_{\mathrm{ATN}}(637\,\mathrm{nm})=\sigma_{\mathrm{ATN}}(590\,\mathrm{nm})\cdot\left(\frac{637\,\mathrm{nm}}{590\,\mathrm{nm}}\right)^{-\mathring{a}_{\mathrm{ATN}}} \qquad (7)"$$

"The compensated absorption coefficients, σ_{ap}, are calculated from attenuation coefficients, σ_{ATN}, by accounting for the different artifacts,

$$\sigma_{\mathrm{ap}}=\frac{\sigma_{\mathrm{ATN}}}{\left(C_{\mathrm{ref}}+C_{\mathrm{sca}}\right)\cdot R} =\frac{\sigma_{\mathrm{ATN}}}{\left(C_{\mathrm{ref}}+m_{\mathrm{s}}\frac{\omega_0}{1-\omega_0}\right)\left[\left(\frac{1}{f}-1\right)\left(\frac{\ln \mathrm{ATN}-\ln 10}{\ln 50-\ln 10}\right)+1\right]} \qquad (5)$$

where C_{ref} compensates for the scattering effects in comparison with a reference absorption measurement, C_{sca} accounts for the scattering effect of non-absorbing aerosol particles and R, for the filter-loading effect. The Schmid formulation uses the scattering factor m_{s} and ω_0 to calculate C_{sca} and the filter loading correction proposed by Weingartner et al. (2003), which takes ATN = 10 % as a reference point and includes the shadowing factor parameter, f, which describes the slope between σ_{ATN} and ln(ATN)."

"The slope of this relationship was given by the shadowing factor parameter, f. By applying a linear fit to the R_{meas} values obtained from Eq. (9) and the attenuation data, as shown in Eq. (10), the term $(1/f-1)$ can be obtained from the slope.

$$R_{\mathrm{meas}}=\left(\frac{1}{f}-1\right)\left(\frac{\ln \mathrm{ATN}-\ln 10}{\ln 50-\ln 10}\right)+1 \qquad (10)$$

Assuming f is wavelength independent, the averaged f is the used to calculate R at different wavelengths."

"In the next step, C, understood as the overall multiple scattering correction factor (C_{ref} + C_{sca}), is parameterized as a function of λ. The single scattering albedo, ω_0, at 637 nm is used in the following equation to calculate C as

$$C=C^{*}+m_s\frac{\omega_0}{1-\omega_0} \qquad (11)$$

where C^{*} corresponds to the multiple scattering effect by filter fibers and m_s to the aerosol scattering factor found by Arnott et al. (2005) (see Table S1). The implemented approach is useful to examine any wavelength dependence on C. The values of ω_0 are interpolated to the different Aethalometer wavelengths by using the Eq. (12), assuming that absorption and scattering coefficients follow a power-law wavelength dependence described by $\mathring{a}_{\mathrm{ABS}}$ and $\mathring{a}_{\mathrm{SCA}}$, respectively.

$$\omega_0(\lambda)=\frac{\sigma_{\mathrm{sp}}}{\sigma_{\mathrm{sp}}+\sigma_{\mathrm{ap}}} =\frac{\omega_{0,\mathrm{ref}}\left(\frac{\lambda}{\lambda_{\mathrm{ref}}}\right)^{-\mathring{a}_{\mathrm{SCA}}}}{\omega_{0,\mathrm{ref}}\left(\frac{\lambda}{\lambda_{\mathrm{ref}}}\right)^{-\mathring{a}_{\mathrm{SCA}}}+\left(1-\omega_{0,\mathrm{ref}}\right)\left(\frac{\lambda}{\lambda_{\mathrm{ref}}}\right)^{-\mathring{a}_{\mathrm{ABS}}}} \qquad (12)$$

Different $\mathring{a}_{\mathrm{ABS}}$ values (1; 1.25; 1.5; 1.75; 2) are then used to generate different correlation factors between ln(C) vs. ln(λ). The coefficients resulting from a quadratic fit are used to parameterize C as a function of $\mathring{a}_{\mathrm{ABS}}$ (see Fig. 4 in Schmid et al. (2006)). An iteration procedure is used to force the convergence of $\mathring{a}_{\mathrm{ABS}}$. In our calculations, the data converged after seven iterations."

Changes to section 2.3.2:

"In this study we implemented the Collaud Coen correction algorithm that resembles the Schmid correction (see eq. 14b in Collaud Coen et al. (2010)). This algorithm is different from the original Schmid algorithm in the calculations of the filter-loading effect and the multiple scattering correction factor. As shown in Eq. (6), the Schmid algorithm filters the data for ATN < 10 % in order to account only for the scattering by filter fibers in the C_{ref} calculation. On the other hand, Collaud Coen algorithm applies a prior filter-loading correction and then, by dividing the reference absorption data (MAAP) by the Aethalometer attenuation coefficients, they obtain C_{ref}, which accounts for both, scattering by filter fibers and scattering by embedded aerosol particles."

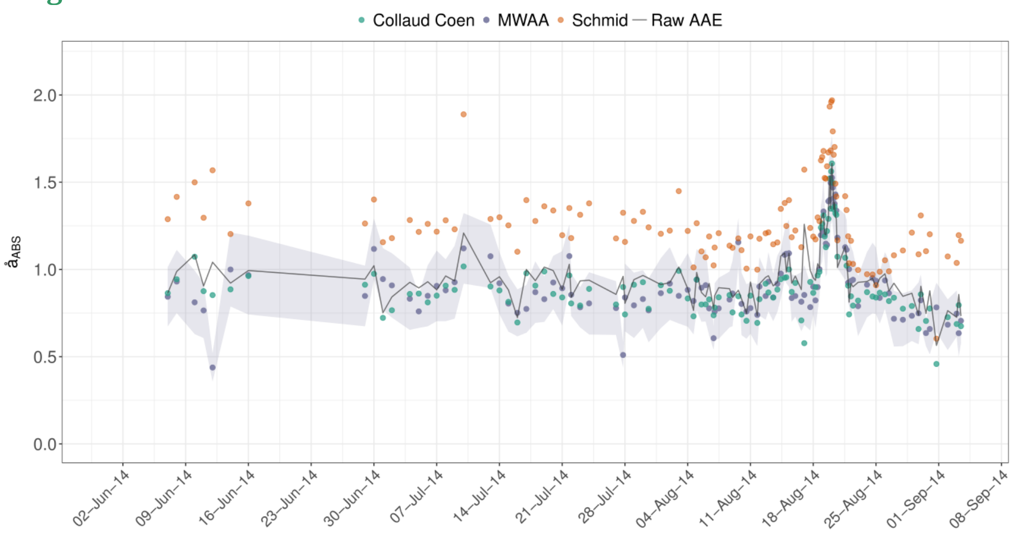
"Finally, the corrected absorption coefficients are calculated in a similar way to Eq. (5) but using m_s from Eq. (15) and averaging C_{ref}, m_s, ω_0 and R over a filter spot period; i.e., from a filter change time to the subsequent one."

Section 2.3.3 was merged with 2.3.2.

2. The authors have excluded the comparison of $å_{atn}$ from AE data to $å_{abs}$ from MWAA data; see Fig. 6, although they state that the original attenuation Ångström exponent was also found to fit very well the MWAA-retrieved AAE, see Fig. S4. I recommend to include the $å_{atn}$ values in the intercomparison and to discuss whether or not the wavelength-dependence of $å_{abs}$ is affected by the correction algorithms. The potential result that the original attenuation Ångström exponents may give reliable estimates of the wavelength dependence of σ_{abs} would be very important.

In the new version of the manuscript we give more relevance and discuss more about the comparison between the MWAA $å_{ABS}$ and $å_{ATN}$. The $å_{ATN}$ data shown in Fig. S4 is now added to Fig. 6.

New figure:



We added the following text to the manuscript:

Section 3.1

"The original attenuation Ångström exponent (without applying any compensation) was also found to fit quite well the MWAA-retrieved $å_{ABS}$, (Slope IQR: 0.89 – 1.10 with $R^2 = 0.75$, not shown). This finding is in accordance with Ajtai et al., 2011 who found a good agreement between 4-λ PAS measurements and the Aethalometer raw wavelength dependence at a sub-urban site."

Conclusions

"On the other hand, the Collaud Coen algorithm as well as the "raw" Aethalometer attenuation spectral dependence reproduced quite well the $å_{ABS}$ values obtained from MWAA measurements."

Abstract

"Additionally, we found that the wavelength dependence of uncompensated Aethalometer attenuation data significantly correlates with the $å_{ABS}$ retrieved from offline MWAA measurements."

3. The discussion of the results presented in Fig. 5 is critical. Here, the authors compare absorption coefficients obtained from MAAP and MWAA and found significant differences. When inserting the 1:1 line it becomes evident that σ_{abs} from MAAP are always larger than respective values from MWAA. Although the authors find a slope of 1.04 for the polluted period, there is a statistically significant offset of 1.18 Mm^{-1}. In the considered range of σ_{abs} values the offset can reach more than 10% of the total value. Furthermore, the data for the cleaner period with $\sigma_{abs} < 5\ Mm^{-1}$ are highly correlated which conflicts the argument, that the under-determination of σ_{abs} for low values may be explained by the proximity to the detection limit of the MWAA method. If this would be the case, I would expect a less linear relationship between the σ_{abs} values with arbitrarily scattered values from the MWAA method. A careful discussion of the results shown in Fig. 5 is recommended.

We agree with the referee on his concerns about the interpretation of Fig. 5 and its implications. We have changed the discussion on section 3.2 as follows:

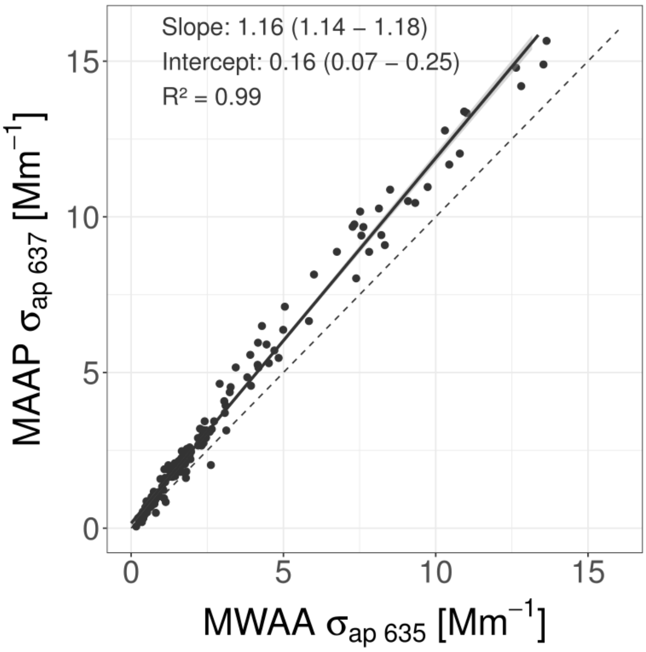
Original text:

The MWAA was used as a reference multi-wavelength measurement since it accounts for multiple scattering effects by means of a similar configuration to the MAAP. Light absorption coefficients obtained from the MWAA (at 635 nm) and from the MAAP (at 637 nm) were compared by applying an linear regression to both datasets after integrating the MAAP data over the filter total sampling times. The fit resulted in an MWAA underestimation by 14 to 18% when fitting the whole dataset. However, when comparing only data from the polluted period (18 – 23 August 2014), the MWAA underestimation was only ~5 %. A scatter plot, including the fits, can be seen in Fig. 5. The MWAA underestimation for low absorption coefficient samples might be related to the proximity to the instrument detection limits. The possibility of losing part of the BrC aerosol of medium volatility was also considered and all data with $\sigma_{ap} < 1\ Mm^{-1}$ were considered with caution when making any interpretation in the further analysis.

Replaced by:

"The MWAA was used as a reference multi-wavelength measurement since it accounts for multiple scattering effects by means of a similar configuration to the MAAP. Light absorption coefficients obtained from the MWAA (at 635 nm) and from the MAAP (at 637 nm) were compared by applying an linear regression to both datasets after integrating the MAAP data over the filter total sampling times, as shown in Fig. 5. The fit resulted in a MWAA underestimation of 14 to 18% when fitting the whole dataset. In general, all values measured by the MWAA at 635 nm were below the MAAP measurements at 637 nm with a decreasing offset towards lower absorption coefficients. This could be associated to a significant volatilization of the absorbing aerosol collected during the polluted period. The comparison Aethalometer – MWAA at different wavelengths was based on the assumption that these losses are wavelength-independent."

Updated figure:



4. A clear conclusion of the study is required. What have we learned from the presented work? Do the authors recommend the adapted Collaud Coen algorithm for future use, or one of the other two investigated approaches?

We agree with the referee and improved the conclusions and discussion of our results.

The conclusions were changed to:
"We applied two different correction algorithms to compensate for the various Aethalometer absorption measurement artifacts. The compensated data was compared to an offline multi-wavelength reference absorption measurement technique. This comparison allowed studying the effects of the correction schemes on the absorption at lower wavelengths and showed how this affects the $\mathring{a}_{ABS}$ retrieval. We found that both analyzed algorithms efficiently reproduce the reference MAAP absorption coefficients from Aethalometer data. However, the Schmid algorithm overestimates the $\mathring{a}_{ABS}$ compared to that obtained by the multiple wavelength measurement (MWAA). On the other hand, the Collaud Coen algorithm as well as the "raw" Aethalometer attenuation spectral dependence reproduced quite well the $\mathring{a}_{ABS}$ values obtained from MWAA measurements. The under- or overestimation of short-wavelength absorption coefficients by compensation algorithms is a factor that has to be considered when using corrected Aethalometer data to apportion the black and brown carbon contributions to total absorption. When comparing the absorption coefficients obtained from the different correction algorithms to the reference measurement at 370 nm, we found that the Collaud Coen algorithm is more appropriate to achieve the best comparison at this wavelength, especially for data with $\sigma_{ap} > 5$ Mm^{-1}. The Schmid algorithm resulted in high enhancements of the absorption coefficients at 370 nm over the sampling period."

MINOR COMMENTS

1. The nomenclature used in the manuscript requires careful cross-checking, particularly for the following issues:

- BC mass concentrations obtained from light absorption methods are referred to as equivalent BC (eBC). This acronym should be used throughout the manuscript whenever appropriate.
  We agree but prefer to use the most commonly used acronym BC_e, instead of eBC.

- The absorption Ångström exponent is referred to as AAE, as $å_{ABS}$, or as $å_{abs}$.
  We homogenized the manuscript to use always $å_{ABS}$.

- The light absorption coefficient is referred to as σ_{abs}, as σ_{ABS}, or as σ_{ap}. Consistency is requested.
  Light absorption coefficient is now represented as σ_{ap} throughout the text.

- The city of Genoa is referred to as Genoa or Genova, please check.
  All changed to "Genoa".

2. The complete reference (Kirchstetter et al., 2004) should be listed in the bibliography.
Corrected.

3. When referring to Virkkula's PSAP correction scheme (Virkkula et al., 2005), also the correction (Virkkula, 2010) should be referenced.
The reference to the correction has been included in the new version.

4. Line 66: The sentence "retrieving the wavelength dependence of ambient aerosol requires ..." is misleading. I assume the authors mean "retrieving the wavelength dependence of ambient aerosol optical properties requires ...".
Corrected.

5. Line 117: The acronym PAS should be introduced.
Corrected.

6. Line 169: The correct name of the MAAP is (Model 5012, Thermo Electron Group, Waltham, USA).
Corrected.

7. Line 204: The correct equation deduced from the Lambert-Beer law is $ATN = 100 \ln (I_0 / I)$ or $ATN = -100 \ln (I/I_0)$; see e.g. (Hansen et al., 1982; Petzold et al., 1997; Weingartner et al., 2003).
Corrected.

8. Line 211: The meaning of „ (14625/λ)" is not clear. If it should refer to the parameterization of α_{ATN} values as a function of wavelength, a clarification and the addition of units are needed.
We agree. Changed to: "α_{ATN} is the λ-dependent BC mass attenuation cross-section (14625 nm m^2 g^{-1} λ^{-1})".

9. Eq. (6). Why not inserting the MAAP wavelength value given one line above instead of using the variable λ_{MAAP}?
We agree. Changed to "637 nm".

10. Line 238: Please specify for which variable the parameter C_{ref} was averaged.

In this statement we refer to C_{ref} obtained from Eq. (5); i.e., the average is calculated using attenuation interpolated to 637 nm and absorption data from the MAAP. In order to clarify we added “averaged over the sampling period”.

11. The use of reference wavelengths of 637 nm or 880 nm is confusing; see Section 3.1. A short explanation may help to clarify why the specific wavelength is used as a reference.

We agree that using the 880 nm wavelength as a reference might be confusing. We decided to report R values at 660 nm, which is the Aethalometer wavelength that is closer to 637 nm. Moreover, when mentioning the wavelength dependence of R we now calculate it for the full Aethalometer spectral range (370 – 960 nm).

The manuscript was changed to:
“At 660 nm, the Aethalometer wavelength that is closer to the MAAP measurement wavelength, the filter-loading correction calculation resulted in R correction factors of 0.98 ± 0.02 and 1.01 ± 0.01 for June – July and August – September, respectively. A slight wavelength dependence was observed; the *R* values were up to 4% higher at 370 nm compared to those calculated at 960 nm during the cleanest period of this study (June – July).”

12. Line 436: On a statistical basis, the offset of the Collaud Coen algorithm of -0.07 − 0.30 is not slightly negative but indistinguishable from zero. This statement should be corrected.

We agree. Discussion has been updated after an update to Fig. 8. Details are included in our response to referee #1.

13. Figures: For all scatter plots, 1:1 lines and grid lines should be shown as guidelines to the reader. In Fig. 7, the range of x- and y-axes should be similar, it might be of advantage to show only the relevant AAE - range from 0.5 to 2.0.

Fig. 7 has been updated and the new y-axis range goes from 0.0 to 2.0. We included 1:1 lines in all scatter plots but Fig. 4.

 # End of referee comments and author responses #

References

Ajtai, T., Filep, Á., Utry, N., Schnaiter, M., Linke, C., Bozóki, Z., Szabó, G. and Leisner, T.: Inter-comparison of optical absorption coefficients of atmospheric aerosols determined by a multi-wavelength photoacoustic spectrometer and an Aethalometer under sub-urban wintry conditions, J. Aerosol Sci., 42(12), 859–866, doi:10.1016/j.jaerosci.2011.07.008, 2011.