

Response to RC2

We appreciate the reviewer's comments and suggestions, which helped to improve the manuscript. Our responses are presented below, including the original comments from the reviewer, which are presented with gray background.

REVIEWER

GENERAL

The paper presents analyses of aerosol optical properties measured at the ATTO site in Amazonia during several years. The authors have measured scattering and absorption coefficients, refractory BC (rBC), aerosol chemical composition as well as several supporting parameters. The wavelength dependence of absorption was used for estimating the contributions of black and brown carbon to light absorption, contributions of geographical source areas were estimated using transport analyses, mass absorption coefficients (MAC) by comparing independent absorption and rBC measurements. All this is important and valuable. The paper is mainly well written so I can recommend its publication after some clarifications and revision.

REVIEWER

The main point that bothers me is the way the contribution of brown carbon is calculated. It is the core of the paper so it should be presented clearly. I'll show the problem in the detailed comments.

AUTHORS

The details about how the BrC contribution was calculated are described later in this document when addressing the detailed comments of the reviewer.

REVIEWER

Another point that I miss is the size distributions of rBC. They were measured with the SP2 and used for MAC calculations but not shown anywhere. Why? The geometric mean diameters and geometric standard deviations of BC are useful and valuable as such for modeling purposes. Did they vary seasonally and with source areas? The size distribution

can also give hints of whether part of the BC remained undetected which would definitely affect the calculated MAC values, another important point in this paper. There should be some uncertainty analysis of the MAC.

AUTHORS

Agreed – the rBC size distributions and the instrumental counting efficiency are elemental for the calculations presented in this manuscript. Its revised version includes selected rBC size distributions (Fig. S5) and an estimate of the MAC uncertainty. These data will be the subject of a more detailed analysis in a future publication.

The rBC core size distributions included in the revised version are the following:

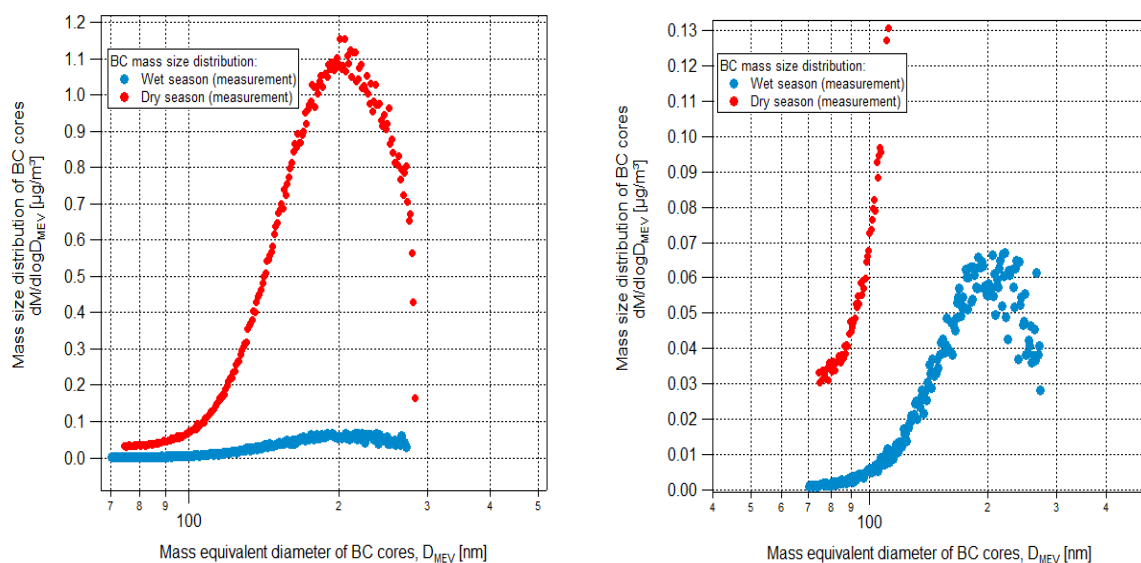


Figure S5. Refractory black carbon mass size distributions observed at the ATTO site on different characteristic days during the wet (blue dots) and dry (red dots) seasons in 2014. The right panel shows a zoom into the wet season size distribution.

REVIEWER

How about coatings? They can be obtained from the SP2 but not presented, why? It would be valuable for the analysis of absorption enhancement.

AUTHORS

The coating information is indeed relevant. However, a detailed SP2 data analysis would be beyond the scope of this manuscript and is the subject of a future study.

REVIEWER

DETAILED COMMENTS

L112 "(Womack et al., ref needed)." Write the ref.

AUTHORS

We apologize for the missing reference. It is included in the revised version.

REVIEWER

L221-227. I assume you corrected also the Aurora 3000 data for truncation, did you?

AUTHORS

Yes, the Aurora 3000 data was corrected according to Müller et al. (2011). This is clarified in the revised version of the manuscript.

REVIEWER

L234 "... instrument is able to provide absorption coefficients with a time resolution of 5 min."
The time resolution of the MAAP can be set not only to 5 min. Reword the sentence.

AUTHORS

Agreed – the corrected text reads:

Original version:

“... instrument is able to provide absorption coefficients with a time resolution of 5 min.”

Revised version:

“... the instrument is able to provide absorption coefficients. The instrument was set up to provide data at 1-min resolution”.

REVIEWER

L 303-304 "... . The 8-channel SP2 rBC mass measurement was underestimated by a factor of 5 % ..."

How was this 5% obtained?

Another thing is, how could you estimate missing BC if it were outside the size range detected by the SP2? In biomass burning smoke BC could be attached to larger particles as well.

AUTHORS

Agreed. The SP2 rBC counting efficiency drops significantly for particles smaller than 80 nm diameter. We have found the mentioned scaling factor by comparing SP2 counts vs. CPC size resolved counts of fullerene particles. Similar offset values have been found in the literature when comparing SP2 counts vs. condensation particle counters (Liu et al., 2017) or by fitting the SP2 rBC number or mass size distributions and calculating the missing mass fraction for the smaller particles (Wang et al., 2014). This estimation introduces uncertainties in the SP2 results, which in total, including those from the mass calibration, reach around 25 % uncertainty (Wang et al., 2014).

Regarding the BC attached to larger particles, we are aware of this kind of mixing and it can also occur over the Amazon rain forest. However, we have found no significant difference in the MAAP vs. SP2 offset when measuring particles below 1 μm (using a PM1 cyclone) vs. total particle measurements, which suggests that the fraction of BC attached to large particles is rather low.

We addressed the issue brought up by the referee by replacing the original section on page 12, line 303-304:

"The 8-channel SP2 rBC mass measurement was underestimated by a factor of 5 %, related to the size-dependent detection efficiency of the instrument, which is below 100 % in the 80 to 150 nm diameter range. Therefore, a scaling factor of 1.05 was applied to rBC mass concentration data to account for this systematic error".

by the following revised version:

"The 8-channel SP2 rBC size-dependent counting efficiency was obtained by comparing the counts of fullerene particles measured by the SP2 and a condensation particle counter (CPC). This way, an underestimation factor of 5 % was found to affect

SP2 rBC mass measurements and a scaling factor of 1.05 was applied to the data to account for this systematic error. Similar underestimation factors have been previously reported (Liu et al., 2017; Wang et al., 2014)”.

REVIEWER

L356-372, calculation of BrC. There is a problem here. I rewrite the equations and show it.

$$WDA = \dot{a}_{abs370-950} - \dot{a}_{abs660-950} \quad (3)$$

$$BC\dot{a}_{abs370-950} = \dot{a}_{abs660-950} + WDA \quad (4)$$

$$BC\sigma_{ap370} = \sigma_{ap950} \times \left(\frac{370}{950}\right)^{-BC\dot{a}_{abs370-950}} \quad (5)$$

$$BrC\sigma_{ap370} = \sigma_{ap370} - BC\sigma_{ap370} \quad (6)$$

Insert (3) to (4)

$$\Rightarrow BC\dot{a}_{abs370-950} = \dot{a}_{abs660-950} + WDA = \dot{a}_{abs660-950} + \dot{a}_{abs370-950} - \dot{a}_{abs660-950} = \dot{a}_{abs370-950}$$

Insert the result to (5)

$$\Rightarrow BC\sigma_{ap370} = \sigma_{ap950} \times \left(\frac{370}{950}\right)^{-BC\dot{a}_{abs370-950}} = \sigma_{ap950} \times \left(\frac{370}{950}\right)^{-\dot{a}_{abs370-950}} = \sigma_{ap370}$$

where the last step comes from applying (1) on line 342.

Insert finally the result to (6) and you get that $BrC\sigma_{ap370} = 0$.

This cannot be the idea, BrC being always zero. Rewrite the equations.

AUTHORS

We understand that the way the equations were written in the manuscript could be misleading because it was not clear whether the absorption Ångström exponents were modeled or measured. We have fixed it by including superscripts that indicate when \dot{a}_{abs} was modeled (superscript “BC”) or measured (no superscript).

The revised version is below:

$$\sigma_{ap370}^{BC} = \sigma_{ap950} \times \left(\frac{370}{950}\right)^{-\dot{a}_{abs370-950}^{BC}}, \quad (4)$$

$$\sigma_{ap370}^{BrC} = \sigma_{ap370} - \sigma_{ap370}^{BC}, \quad (5)$$

where $\dot{a}_{abs370-950}^{BC}$ is obtained from the Mie model calculations.

REVIEWER

Further on the same issue. On L361-362 it is written " Calculated BC WDA thresholds, presented in Fig. S5, were compared to the ambient data in order to retrieve the BrC contribution to light absorption. "

What do you mean by thresholds? Do you mean that if WDA is larger than a threshold then this is due to BrC? This is not clear at all. Looking at Fig S5 does not explain me, what these thresholds might be. And what is the reasoning for claiming that exceeding a threshold for WDA is due to BrC?

This is much too descriptive way to explain how you calculated BrC. Give more details so that other people can use the same method and evaluate it. Recently many people have started using the so-called "Aethalometer model" (Sandradewi et al., 2008) and it would be good if the model presented in this work could be compared with it.

AUTHORS

Agreed. The WDA thresholds used in this study were the 25th and 75th percentiles of the modeled BC wavelength dependence and they are shown as dashed lines in Fig. S6 (Fig. S5 in the original version). These percentiles were calculated using data of particles from 100 to 275 nm diameter. As can be seen in Fig. S6, the inter-quartile range comprises internally mixed particles of the following diameters: 125, 150, 225, and 275 nm with coating thickness to core size ratio > 0.3, and part of the particles with 175 and 200 nm diameter. This range also includes most of the externally mixed particles in the size range from 100 to 225 nm diameter. When the 75th percentile threshold is exceeded, the particles are considered to include BrC additionally to BC. The sensitivity of this model was tested by changing the core size diameters and the refractive index of the coating material and the results were expressed as "relative overestimation" of the BrC carbon contribution to σ_{370} , as shown in Table S2.

We addressed the issue brought up by the referee by replacing the original section on page 14, line 361-362:

"Calculated BC WDA thresholds, presented in Fig. S5, were compared to the ambient data in order to retrieve the BrC contribution to light absorption."

by the following revised version:

“Calculated BC WDA thresholds (25th and 75th percentiles), shown in Fig. S6, were compared to the ambient data in order to identify BrC influenced periods. For a general analysis, data with WDA lower than the 75th percentile were considered to be in the *BC-only* regime. The presence of BrC, additionally to BC, occurred when the modeled BC absorption at 370 nm was exceeded.”

REVIEWER

L373-377, still about the same issue. How did you get the uncertainties? Give formulas. Writing that " The relative overestimation of the BrC contribution obtained by using different BC core sizes and different refractive indices in the Mie model calculations can be found in Table S2." is simply too qualitative and not understandable. People have to be able to reproduce the result.

AUTHORS

The results presented in Table S2 were actually a sensitivity evaluation of the model and not a real uncertainty analysis. Basically, the WDA thresholds were recalculated by changing different parameters in the model. This clarification is included in the revised version of the manuscript.

Revised version:

“A sensitivity study of this model was done by changing the refractive indices and the core size of the model input. These results are presented in Table S2 as relative overestimation of the BrC contribution to $\sigma_{ap, 370}$ ”.

REVIEWER

L472-473 " Rizzo et al. (2013), however, pointed out that this relationship is only evident for surface and volume mean diameters and was not clearly valid between σ_{sc} and count mean diameters. " Also Virkkula et al.: ACP, 11, 4445–4468, 2011 found the same.

AUTHORS

We thank the reviewer for pointing out about this reference and will include it in the revised version.

REVIEWER

L568 -> Where do you get the equivalent potential temperature from? Model, I assume, present in methods then.

AUTHORS

The potential temperature, θ_e , was calculated according to Stull (1988), as follows:

$$\theta_e = T_e \cdot \left(\frac{p_0}{p} \right)^{\frac{R}{c_p}} \approx \left(T + \frac{L_v}{c_p} r \right) \left(\frac{p_0}{p} \right)^{\frac{R}{c_p}}$$

where

T : Air temperature.

p : Atmospheric pressure.

p_0 : Reference pressure (1000 hPa).

R : Gas constant for air.

c_p : Specific heat constant for pressure.

L_v : Latent heat of evaporation.

r : Water vapor mixing ratio

The cited reference is included in the revised version of the manuscript.

REVIEWER

L672 Do you have a clear definition for "BC-only regime"?

AUTHORS

We thank the reviewer for asking about this because it was not clear in the submitted version of the manuscript. A comment has been included in the revised version, section 2.3:

“For a general analysis, data with WDA lower than the 75th percentile were considered to be in the *BC-only* regime”.

REFERENCES

Liu, D., Whitehead, J., Alfarra, M. R., Reyes-Villegas, E., Spracklen, D. V., Reddington, C. L., Kong, S., Williams, P. I., Ting, Y.-C., Haslett, S., Taylor, J. W., Flynn, M. J., Morgan, W. T., McFiggans, G., Coe, H. and Allan, J. D.: Black-carbon absorption enhancement in the atmosphere determined by particle mixing state, *Nat. Geosci.*, 10(3), 184–188, doi:10.1038/ngeo2901, 2017.

Stull, R. B.: *An Introduction to Boundary Layer Meteorology*, Springer Netherlands., 1988.

Wang, Q., Huang, R.-J., Cao, J., Han, Y., Wang, G., Li, G., Wang, Y., Dai, W., Zhang, R. and Zhou, Y.: Mixing State of Black Carbon Aerosol in a Heavily Polluted Urban Area of China: Implications for Light Absorption Enhancement, *Aerosol Sci. Technol.*, 48(7), 689–697, doi:10.1080/02786826.2014.917758, 2014.