

## Review for amt-2019-5 “Two-wavelength thermo-optical determination of Light Absorbing Carbon in atmospheric aerosols” by Massabò et. al.

*We strongly acknowledge the Referee for the valuable and precious comments and suggestions.*

The manuscript reported a modified carbon analyzer with dual-wavelength configuration for the determination of Brown Carbon. Multiwavelength thermal-optical analysis had been reported using the DRI carbon analyzer (Chen et al., 2015; Chow et al., 2015; Chow et al., 2018), but multiwavelength applications on the Sunset analyzer remain limited (Hadley et al., 2008). In that sense, this study has the merit from the instrumental perspective. However, part of the data analysis suffered from overinterpretation, thus, revisions are needed.

*In the following, a point-by-point reply to all the comments is given.*

### General comments:

- 1) How this study can be beneficial to the carbonaceous aerosol research community? From the instrumental perspective, there is already a multiwavelength carbon analyzer that is commercially available (DRI2015), as noted by the authors. The modification described in this study might not be easy to be adopted and implemented by other research groups. The authors need to elaborate how this setup can be implemented by other researchers.

*The Referee is right, since a multi-wavelength carbon analyzer is commercially available, but, at least at the moment, it is not so widespread. Especially in Europe, the one wavelength Sunset EC/OC analyzer unit is by far the most common instrument for this kind of quantification. We think that the possibility to upgrade these “old” units to make possible 2- $\lambda$  measurements is a good chance to have more information on EC/OC separation and to study the effect of BrC (but not only) on TOT analysis. Moreover, the upgrade is easy and cheap since just a blue LED and a photodiode/bandpass filter system are needed. The basic information to implement this upgrade are detailed in the paper; for sure we are available to help anybody to carry out this operation but more technical issues should be given outside the present paper.*

- 2) Introduction. Beside primary BrC from biomass burning, the secondarily formed BrC should be mentioned.

*The Referee is right, we forgot to mention the secondary formation of BrC. It has been inserted in the text.*

- 3) The current modification only allows one laser to be used at each time, that means all samples need to be analyzed twice. As noted by the authors, the change of laser and PD require alignment to optimize the laser signal. Since laser and PD change would introduce further uncertainties into the OC/EC analysis, this point should be mentioned. Did the authors quantify the uncertainties in OC and EC determination that introduced by the change of laser and PD? For example, what's the standard deviations of OC and EC from multiple analysis for the same sample (identical laser and PD with mount-unmount cycles scenario vs. no laser and

PD change scenario)? The authors are encouraged to provide a estimation of uncertainty introduced.

*We have conducted several repetitions in order to evaluate uncertainties coming from the laser switching procedure. Uncertainties turned out to be of the same order of magnitude of the typical value characteristic of TOT measurements, i.e. about  $\pm 10\%$ , so we did not discuss uncertainties in the text. Anyway, the Referee is right since the procedure is simple but in principle effects due to different laser alignments cannot be excluded. For this reason, we do not change the lasers filter by filter, but we first perform the analysis of the whole samples batch with the red laser and then we repeat the analysis with the blue diode. In this way, we have only two alignments for each dataset. Anyway, we remind that, as reported in the text, we check the alignment at each laser change by maximizing its transmittance signal.*

- 4) The  $MAC_{BrC}$  reported in this study ( $9.8 \text{ m}^2\text{g}^{-1}$  @635 nm and  $23 \text{ m}^2\text{g}^{-1}$  @405 nm) seems to be one magnitude higher than the literatures values. An example is shown below. The following table was adopted from (Updyke et al., 2012). The author argued the difference is due to the operative defined BrC mass used in this study. It should be noted that literature studies applied different technical approaches for  $MAC_{BrC}$  determination as well, but most studies reported a  $MAC_{BrC} < 1 \text{ m}^2\text{g}^{-1}$ . The author should explain why their results are significantly different from previous studies.

Values of MAC in  $\text{m}^2 \text{g}^{-1}$  from representative field and laboratory studies of organic aerosols measured at or near 500 nm. The cited MAC values explicitly remove contributions from black carbon. With the exception of this work, all data cited in this table likely correspond to primary sources of brown carbon.

Sample (campaign)	$\lambda$ (nm)	MAC ( $\text{m}^2 \text{g}^{-1}$ )	Reference
Brown carbon produced by aging SOA with 100 ppb $\text{NH}_3$ (lab)	500	0.001–0.1	This work
“Tar balls” from smoldering combustion of wood; brown carbon contribution (lab)	532	0.01–0.07 (calculated from $k = 0.0005\text{--}0.003$ )	(Chakrabarty et al., 2010)
HUMic-Like Substances (HULIS) extracted from filter samples from various sites in Europe	532	0.07–1 (calculated from $k = 0.003\text{--}0.05$ )	(Dinar et al., 2008)
Methanol extracts from wood combustion particles (lab)	500	0.1–0.5 (estimated from the graphs)	(Chen and Bond, 2010)
Refractory organic carbon from biomass burning in North America (INTEX/ICARTT)	470 530	0.6 0.1	(Clarke et al., 2007)
“Tar balls” in North America (YACS)	632	0.4 (calculated from reported $k = 0.02$ )	(Hand et al., 2005)
Brown carbon in pollution plumes from Asia (CAPMEX)	532	0–1	(Flowers et al., 2010)
Brown carbon in particles collected in Asia (EAST-AIRE)	520	0.6	(Yang et al., 2009)
Acetone extracts from biomass burning aerosols in Africa (SAFARI 2010)	500	0.9	(Kirchstetter et al., 2004)
Amorphous carbon spheres from biomass burning (ACE Asia)	550	4	(Alexander et al., 2008)

*All MAC values in the table refer the optical “effect” of BrC compared to the OC from wood burning. In this sense, they are not considering the BrC molecules only but their optical response normalized to all the  $OC_{WB}$  mass. Also in our case, if we plot  $b_{abs(BrC)}$  vs. the whole  $OC_{WB}$ , we get  $MAC(OC_{WB}) \approx (0.4 \pm 0.1) \text{ m}^2 \text{g}^{-1}$  for the red and  $\approx (2.3 \pm 0.2) \text{ m}^2 \text{g}^{-1}$  for the blue (see also the last part of the §5 of the Massabò et al 2016 paper).*

- 5) Line 277. Regarding the BrC mass determination using the method reported in Massabò et al. (2016), did the author considered laser-temperature correction (Jung et al., 2011)? Seen from Fig 5 in Massabò et al. (2016), the laser signal keep increasing during the  $\text{CH}_4$  stage, implying that laser-temperature correction was likely not performed. If that’s case, the BrC mass should be re-calculated.

*We thank the Referee for the suggestion. However, we are aware of the reported issue and we actually applied an operative correction similar to what proposed in the quoted paper. So, we think that no further corrections are needed in our dataset. Anyway, the Referee is rising an important issue often neglected in TOT/TOR analysis (the effect of temperature on transmittance signal affecting EC/OC separation).*

- 6) In addition, even if the laser-temperature correction is accounted, the laser uncertainty is simply too high for BrC mass determination. Please specify the limit of quantification (LOQ) for OC in the OC/EC analysis. The reviewer feels that  $LOQ_{OC}$  would be likely very close to the level of BrC reported in this study ( $0.005 - 0.14 \mu\text{gC m}^{-3}$ ). If so, BrC reported using this approach is overinterpretation of the data.

*The limit of quantification of OC (LOQ) is  $0.1 \mu\text{gC cm}^{-2}$  that corresponds, in our sampling conditions, to about  $0.009 \mu\text{gC m}^{-3}$ . So, except for few points, most of the BrC levels reported in the paper are well over this LOQ.*

- 7) The BrC determination approach described in Massabò et al. (2016) lacks physical meanings. The OC/EC split by the laser signal in the thermal optical analysis depends on two assumptions: (i) pyrolyzed organic carbon evolved before native EC during the oxygen stage. (ii) pyrolyzed organic carbon and native EC have the same MAC. However, both of these assumptions had been proved invalid (Yang and Yu, 2002; Yu et al., 2002; Subramanian et al., 2006). The approach that author used is a paradox: On one hand the authors report a  $MAC_{BrC}$  that is larger than  $MAC_{EC}$ . On the other hand, the laser correction process itself is based on the assumption that  $MAC_{BrC}=MAC_{EC}=MAC_{POC}$ . In that sense, the carbon fraction corresponding to the different laser split time cannot be considered as BrC mass.

*The paper Massabò et al. 2016 has been already evaluated and revised in a full peer-review process. Even if we think that the revision should be limited to this paper and not to others in the literature, we appreciate the interest of the Referee and we would like to reply at his/her specific comments. Furthermore, the referee's criticism directly address the basic assumptions of the TOT analysis since the first papers by Birch and Cary, 1996. We have to note however, that assumption (ii) makes not necessary the (i) one. From his point of view just the  $MAC_{EC}=MAC_{POC}$  assumption is part of the game.*

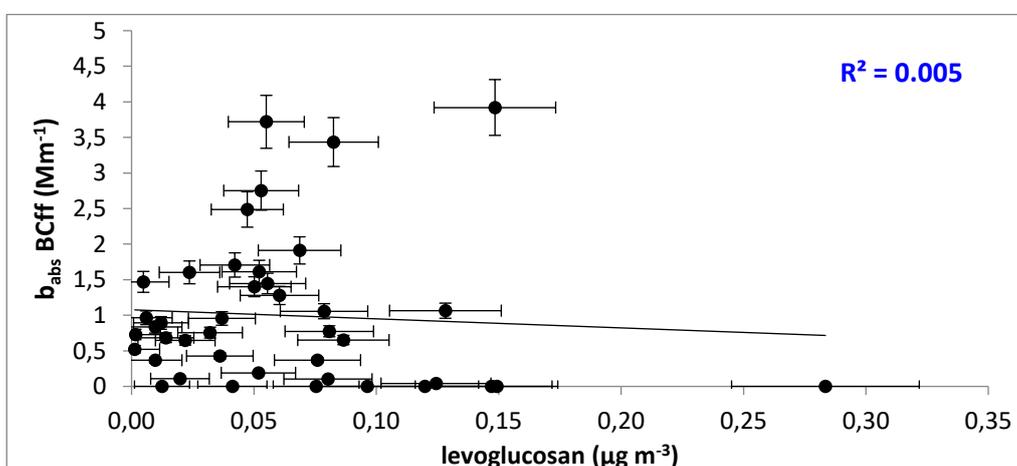
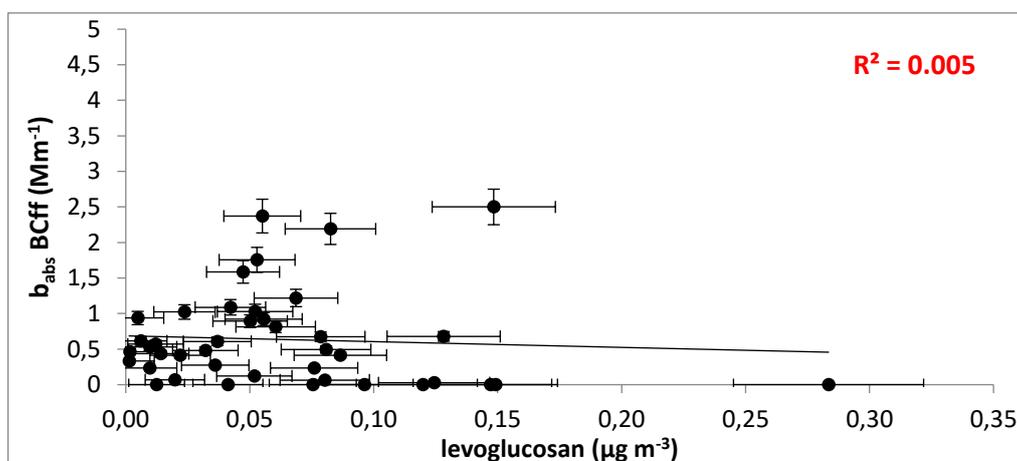
*A considerable amount of works in the literature deals about the assumptions at the basis of the TOT/TOR technique, mostly pointing out that often they are critical or unacceptable (and we were aware of them, see §6 of that paper). But, in the absence of a definitive solution of these criticisms, these assumptions are necessary to separate EC from OC, or we simply have to forget this analytical technique.*

*The previous paper (Massabò, 2016) started from these (questionable, we agree) assumptions, trying to gather information on BrC, and actually we don't see any paradox. About the reported  $MAC_{BrC}$ , this value turned out from the comparison of: 1) difference in mass between uncorrected/corrected EC values and 2) absorption coefficients apportioned with the MWAA model to BrC. About the "other hand assumption", we did not write in that text the statement  $MAC_{BrC}=MAC_{EC}=MAC_{POC}$ , and this assumption is never considered in that proposed methodology. Anyway, we underline that we defined the retrieved BrC mass as "operative BrC*

mass”, precisely to highlight its dependence on the specific methodology adopted and, from this quantity, we calculated the  $MAC_{BRC}$  (without the cited assumption  $MAC_{BRC}=MAC_{EC}=MAC_{POC}$ ).

- 8) The authors are encouraged to check the  $b_{abs,BCff}$  vs. levo scatter plot. If the  $R^2(b_{abs,BCff}$  vs. levo) is significantly lower than the  $R^2(b_{abs,BRC}$  vs. levo), that would be a useful evidence to confirm a successful split of  $b_{abs}$  into BrC,  $BC_{WB}$  and  $BC_{ff}$ .

As suggested, we checked the  $b_{abs,BCff}$  vs. levo scatter plot and, as expected, there is no correlation between the two parameters. In the following, we report the two scatter plots.



#### Technical comments:

- 1) The figure quality needs to be improved. For example, for comparison of the same quantity/parameter, the X and Y range should be the same and the aspect ratio of the plot should be 1:1.

*In the final version of the paper, a full (graphical) revision of the figures will be given.*

- 2) Figure 1. Please label the laser wavelength on the photo directly for easy reference.

*Done*

- 3) Figure 2-7. The font size is too small for the text in these figures. Please adjust accordingly.

*Done*

- 4) Figure 5 caption. “WW and FF stand for Fossil Fuel and Wood Burning, respectively.” Should be “FF and WB stand for Fossil Fuel and Wood Burning, respectively”

*Done*

- 5) Line 245. “and biomass burning (WB)” should be wood burning?

*Done*

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