Answers to RC1: 'general comments', Anonymous Referee #2

We strongly acknowledge the Referee for the valuable and precious comments and suggestions. In the following, a point-by-point reply to all the comments is given.

The aim of the paper should be better stressed in the abstract. Furthermore from the abstract it is not clear why the authors decided to use a different laser radiation. **It has to be specified**.

Following the Referee's advice we added in the abstract few sentences to better stress the aim of the paper and why we decided to use a different laser wavelength.

The text could be simplified in many points. For example at **line 64**: aerosol samples collected on filters made of refractory material (i.e. quartz fibre filters), should be: … made of quartz fibre filters (in fact there aren't other possibility).

Done

From line 69 to line 72 the text could be simplified since how TOT method operates is well known.

In our opinion, this very short paragraph could be useful to a reader not familiar with TOT measurements. So we prefer to keep it in the text.

At **line 85** of the introduction it should be mentioned that biomass burning contribution to PM could be also estimated by other methods such as AMS (aerosol mass spectrometry) which starting from mass spectral data is suitable for identification of biomass burning source. At this purpose I suggest to include the following reference:

Daellenbach, K.R., Bozzetti, C., Křepelová, A., Canonaco, F., Wolf, R., Zotter, P., Fermo, P., Crippa, M., Slowik, J.G., Sosedova, Y., Zhang, Y., Huang, R.-J., Poulain, L., Szidat, S., Baltensperger, U., El Haddad, I., Prévôt, A.S.H. Characterization and source apportionment of organic aerosol using offline aerosol mass spectrometry (2016) Atmospheric Measurement Techniques, 9 (1), pp. 23-39.

A short statement and the suggested reference have been added in the text

Somewhere in the introduction, it **should be mentioned that levoglucosan is the marker for BB**. At this purpose together with the reference Piazzalunga 2010, I suggest to include for example the following reference:

Vassura, I., Venturini, E., Marchetti, S., Piazzalunga, A., Bernardi, E., Fermo, P., Passarini, F. Markers and influence of open biomass burning on atmospheric particulate size and composition during a major bonfire event (2014) Atmospheric Environment, 82, pp. 218-225.

A short statement and the suggested reference have been added in the last part of section 3.2

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

Answers to RC2 Anonymous Referee #3

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-□ 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.

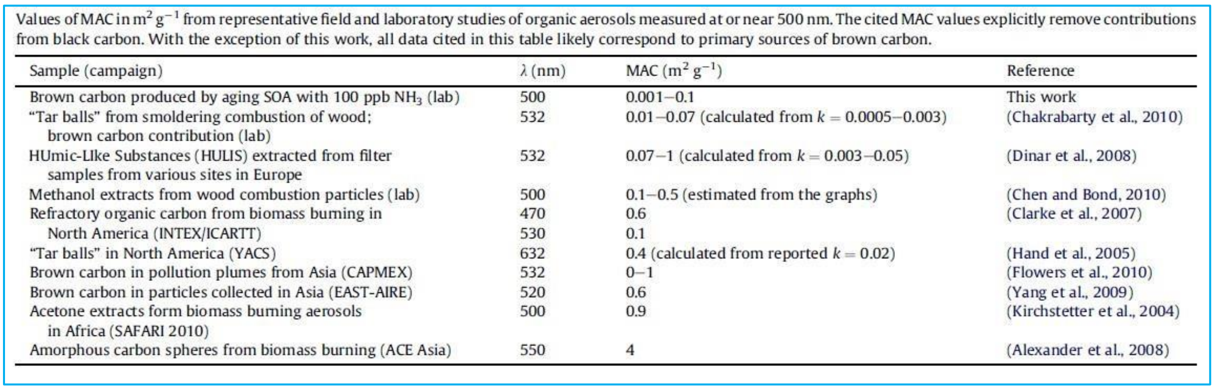
The Referee is right, we forgot to mention the secondary formation of BrC. It has been inserted in the text.

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 ± 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 m^2g^{-1} @635 nm and 23 m^2g^{-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 $MAC_{BrC}<1$ m^2g^{-1}. The author should explain why their results are significantly different from previous studies.



Values of MAC in $m^2\,g^{-1}$ 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)	λ (nm)	MAC ($m^2\,g^{-1}$)	Reference
Brown carbon produced by aging SOA with 100 ppb 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 $k = 0.0005–0.003$)	(Chakrabarty et al., 2010)
HUmic-LIke Substances (HULIS) extracted from filter samples from various sites in Europe	532	0.07–1 (calculated from $k = 0.003–0.05$)	(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 form 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 $MAC(OC_{WB}) \approx (0.4 \pm 0.1)$ $m^2\,g^{-1}$ for the red and $\approx (2.3 \pm 0.2)$ $m^2\,g^{-1}$ 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 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 µgC m^{-3}). If so, BrC reported using this approach is overinterpretation of the data.

The limit of quantification of OC (LOQ) is 0.1 µgC cm^{-2} that corresponds, in our sampling conditions, to about 0.009 µgC 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.

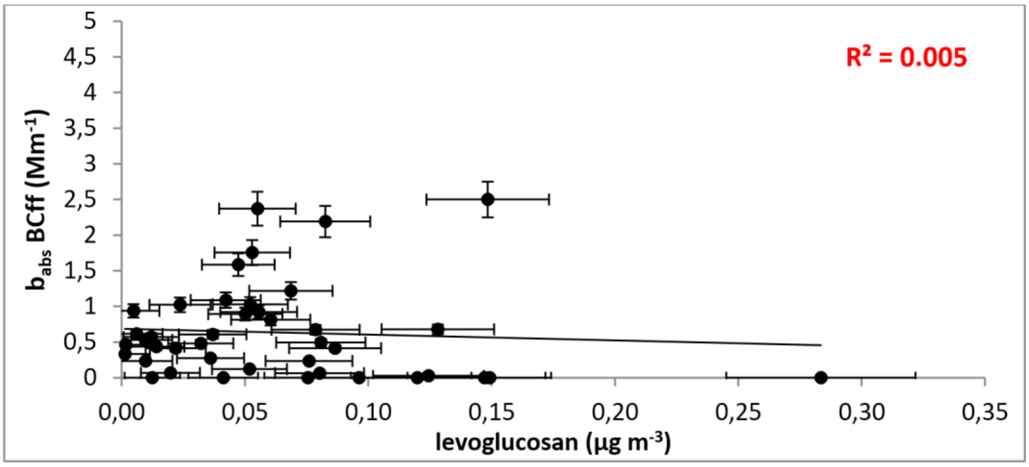
The paper Massabò et al. 2016 has been already evaluated and revised in a full peer-review process. Even if we think that the revision should be limited to this paper and not to others in the literature, we appreciate the interest of the Referee and we would like to reply at his/her specific comments. 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.

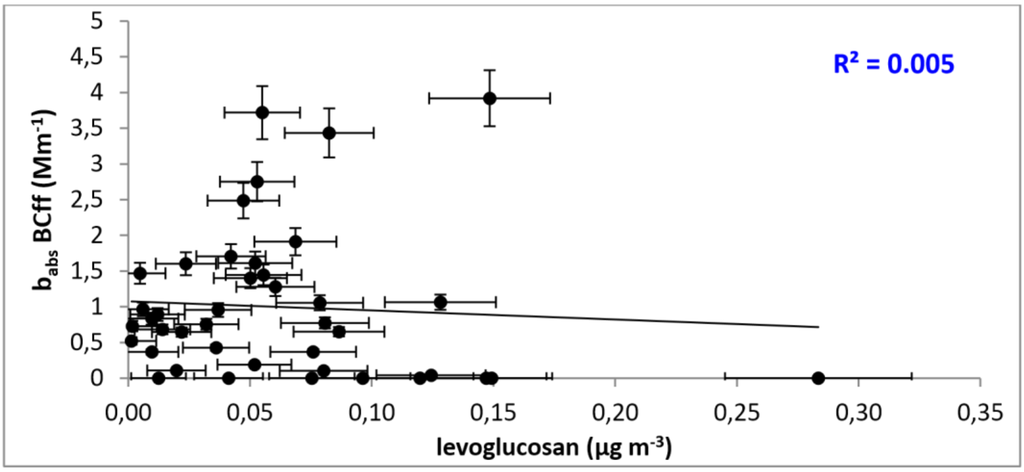
A considerable amount of works in the literature deals about the assumptions at the basis of the TOT/TOR technique, mostly pointing out that often they are critical or unacceptable (and we were aware of them, see §6 of that paper). But, in the absence of a definitive solution of these criticisms, these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

References

Chen, L. W. A., Chow, J. C., Wang, X. L., Robles, J. A., Sumlin, B. J., Lowenthal, D. H., Zimmermann, R., and Watson, J. G.: Multi-wavelength optical measurement to enhance thermal/optical analysis for carbonaceous aerosol, Atmos. Meas. Tech., 8, 451-461, doi: 10.5194/amt-8-451-2015, 2015.

Chow, J. C., Wang, X., Sumlin, B. J., Gronstal, S. B., Chen, L. W. A., Trimble, D. L., Kohl, S. D., Mayorga, S. R., Riggio, G., Hurbain, P. R., Johnson, M., Zimmermann, R., and Watson, J. G.: Optical Calibration and Equivalence of a Multiwavelength Thermal/Optical Carbon Analyzer, Aerosol. Air. Qual. Res., 15, 1145-1159, doi: 10.4209/aaqr.2015.02.0106, 2015.

Chow, J. C., Watson, J. G., Green, M. C., Wang, X., Chen, L. W. A., Trimble, D. L., Cropper, P. M., Kohl, S. D., and Gronstal, S. B.: Separation of brown carbon from black carbon for IMPROVE and Chemical Speciation Network PM2.5 samples, J. Air Waste Manage. Assoc., 68, 494-510, doi: 10.1080/10962247.2018.1426653, 2018.

Hadley, O. L., Corrigan, C. E., and Kirchstetter, T. W.: Modified Thermal-Optical Analysis Using Spectral Absorption Selectivity To Distinguish Black Carbon from Pyrolized Organic Carbon, Environ. Sci. Technol., 42, 8459-8464, doi: 10.1021/Es800448n, 2008.

Jung, J., Kim, Y. J., Lee, K. Y., Kawamura, K., Hu, M., and Kondo, Y.: The effects of accumulated refractory particles and the peak inert mode temperature on semi-continuous organic carbon and elemental carbon measurements during the CAREBeijing 2006 campaign, Atmos. Environ., 45, 71927200, doi: 10.1016/j.atmosenv.2011.09.003, 2011.

Massabò, D., Caponi, L., Bove, M. C., and Prati, P.: Brown carbon and thermal–optical analysis: A correction based on optical multi-wavelength apportionment of atmospheric aerosols, Atmos. Environ., 125, 119-125, doi: 10.1016/j.atmosenv.2015.11.011, 2016.

Subramanian, R., Khlystov, A. Y., and Robinson, A. L.: Effect of peak inert-mode temperature on elemental carbon measured using thermal-optical analysis, Aerosol. Sci. Technol., 40, 763-780, doi: 10.1080/02786820600714403, 2006.

Updyke, K. M., Nguyen, T. B., and Nizkorodov, S. A.: Formation of brown carbon via reactions of ammonia with secondary organic aerosols from biogenic and anthropogenic precursors, Atmos. Environ., 63, 22-31, doi: 10.1016/j.atmosenv.2012.09.012, 2012.

Yang, H. and Yu, J. Z.: Uncertainties in charring correction in the analysis of elemental and organic carbon in atmospheric particles by thermal/optical methods, Environ. Sci. Technol., 36, 5199-5204, doi: 10.1021/Es025672z, 2002.

Yu, J. Z., Xu, J. H., and Yang, H.: Charring characteristics of atmospheric organic particulate matter in thermal analysis, Environ. Sci. Technol., 36, 754-761, doi: 10.1021/Es015540q, 2002.

Review report AMT 2019-5 manuscript version 1

Answers to RC3 Anonymous Referee #1

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

The paper describes the application of a modified Sunset Lab Inc. EC/OC analyzer with a two wavelength set-up for analysis of ambient aerosol samples. It strongly relates to earlier work of the author which is described detailed in previous publications, nevertheless it extends to additional findings. The results derived from the comparison of two temperature protocols, NIOSH5040 and EUSAAR2, for the 405 nm wavelength as well as the reported MAC values are a valuable addition to the literature. However, the paper lacks in structure and suffers in use of proper scientific English which limits its potential. It is recommended that the text is reviewed with focus on syntax and vocabulary. Particular attention should be given in the first paragraph of the abstract and the first two paragraphs of the introduction. Further:

We tried to improve English for both syntax and vocabulary. In the following, a point-by-point reply to all the comments is given.

Sentence starting in line 115: “The hypothesis under such choice…” should be rephrased.

Done

The terms “real samples”, “real-world samples” and “real-world aerosol samples” are used throughout the text. The use of one term is recommended.

We changed using the form “real-world aerosol samples throughout the text.

“λ=” , “@λ” and “@λ=” are used to state wavelengths. Please consider using one form (λ=) for consistency. *Done*

Sentence starting in line 59 should be revised. “Standarized” should be replaced by standardized. Since 2017, when EN16909 was published, there is uniformity in OC/EC analysis methodology, at least for EU. *Done*

Paragraph starting in line 157: Any specific reason why this subset was analyzed with EUSAAR2 only?

After the first positive results with pure Aquadag samples and considering the slope close to one, we preferred to make a “reproducibility study” (i.e. we used 2 punches for each laser in each sample) by EUSAAR_2 protocol. We got a very good agreement and final results only have been reported in the text. We’ll make clear this point in the revised text.

Paragraph starting in line 165: PM10 samples are known to add complexity in OC/EC analysis due to minerals, refractory material and oxides present in coarse fraction. Did you consider sampling/analysis of PM2.5 samples and have you noticed any of the above interferences?

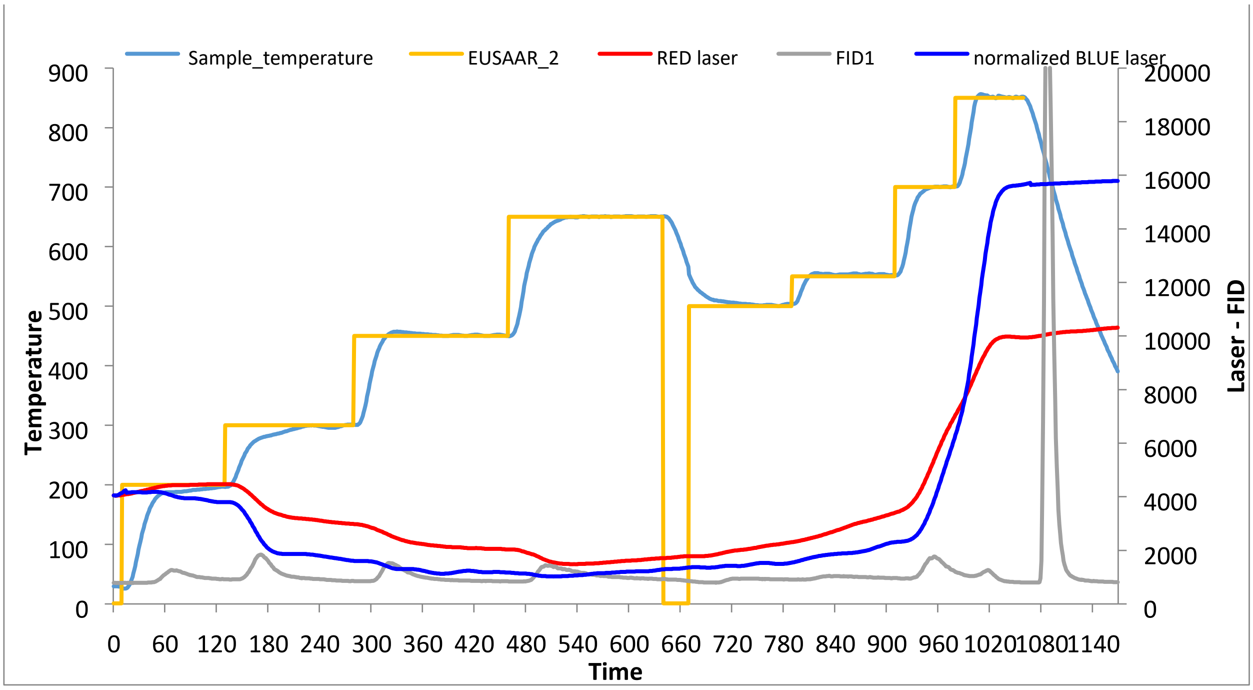
This point is very interesting, we thank the Referee for this valuable suggestion. Unfortunately, we had not the possibility to apply our methodology on PM2.5 samples but for sure we will try in the next future.

Line 174: It sounds like two different subsets were created, one for analysis with EUSAAR2 and one for NIOSH5040. If that is the case, why was that choice made instead of all samples being analyzed with both protocols?

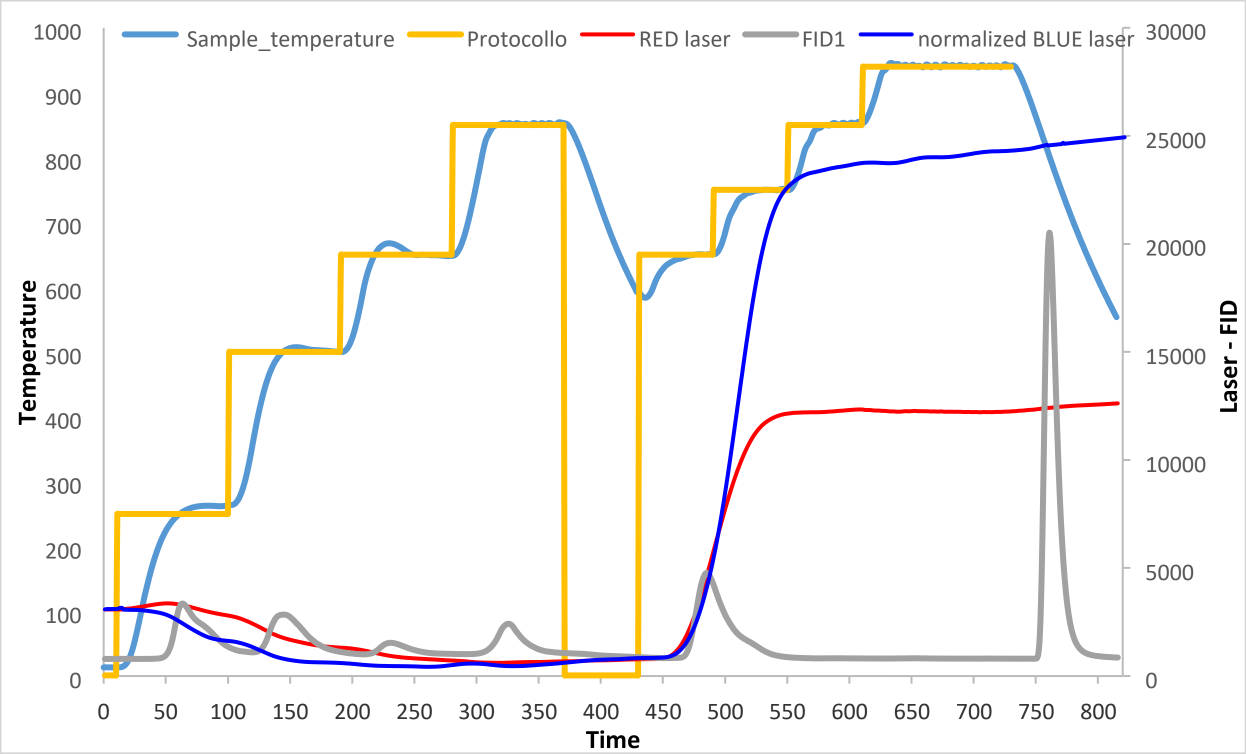
As explained above, we preferred to have a reproducibility check by measuring 2 punches for each laser in each sample.

Line 193: It is not clear to me why the discrepancy between EUSAAR2 and NIOSH5040 is mainly driven by charring. In a sense more pyrolytic carbon would result in a later split point and less EC reported. Further, since the blue laser diode resulted in later split points for EUSAAR2, wouldn't that rate it as less sensitive to charring instead of more, as mentioned in the text?

Actually, as shown in the example below (please note that the red and blue transmittance are normalized at the same initial value), in the EUSAAR_2 thermograms we observe a steeper decrease of the "blue" transmittance in the first phases (low temperatures). This corresponds to a higher sensitivity to pyrolytic formation when we use the blue laser diode.



EUSAAR_2

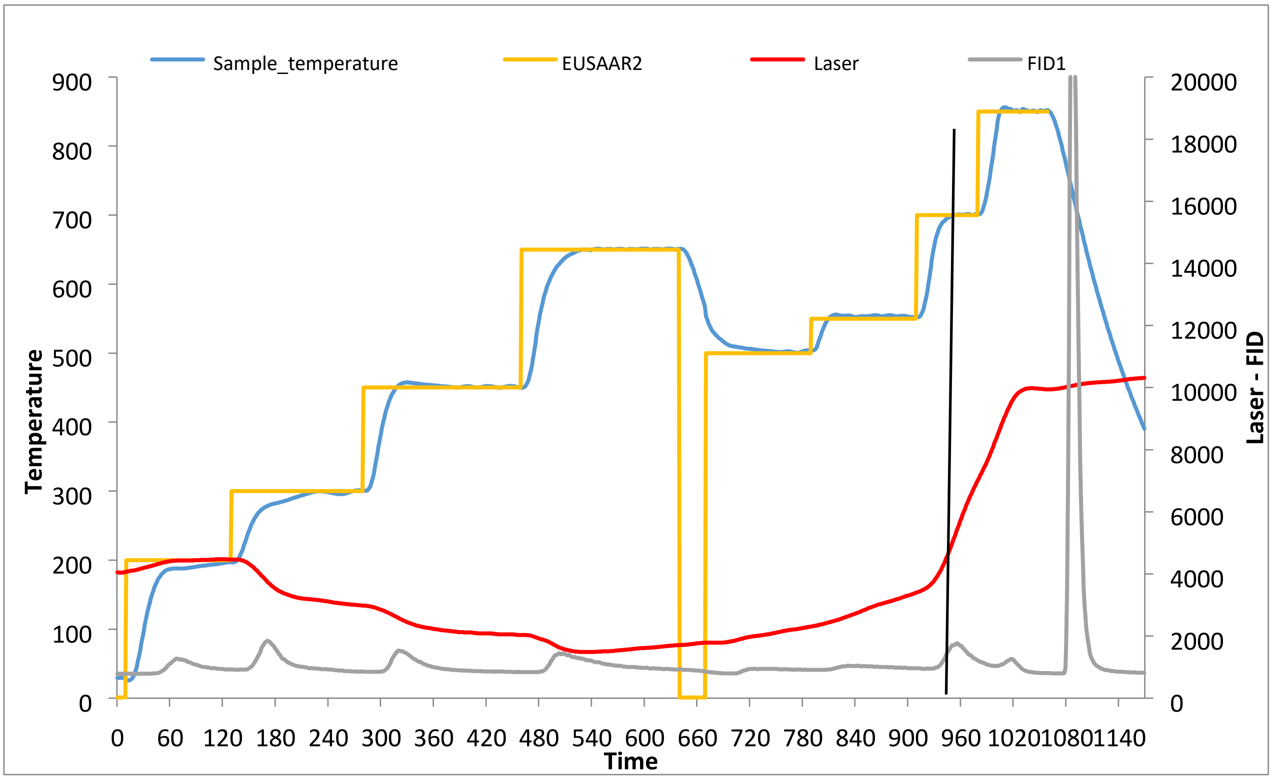


NIOSH5040

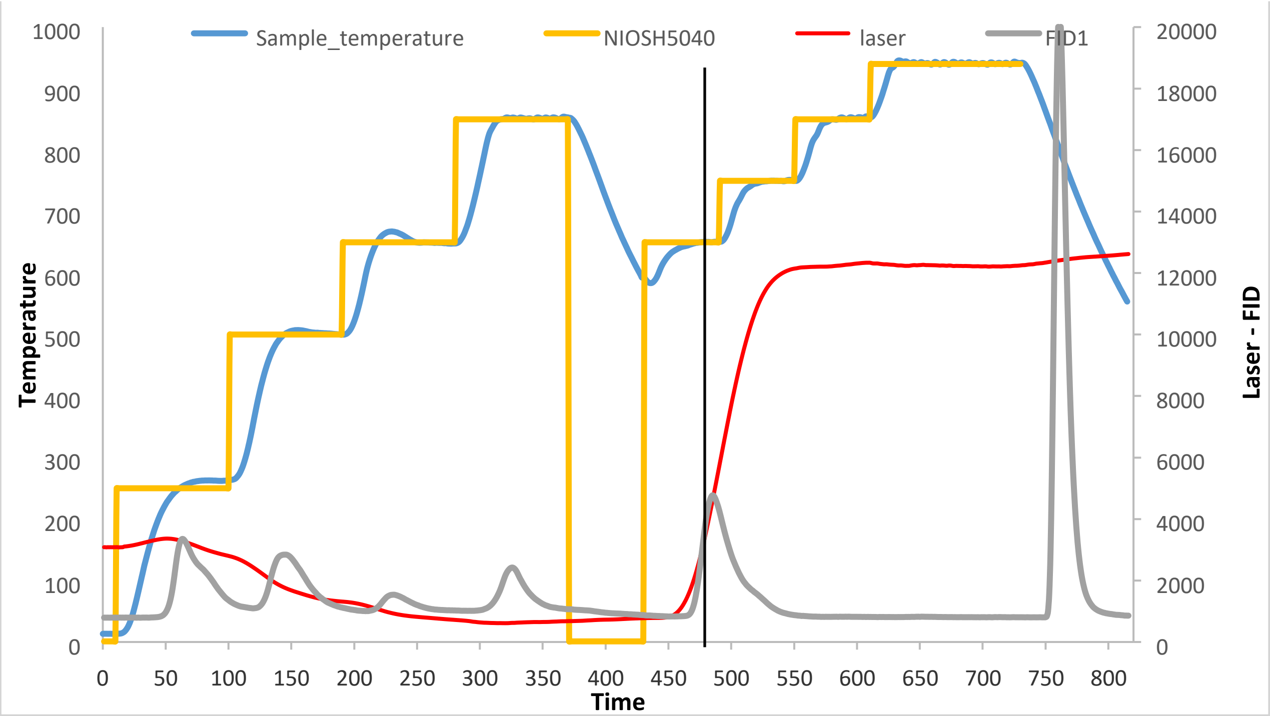
Is it possible to include a figure and/or representative thermograms that illustrate the consistent 40% discrepancy between EUSAAR2 and NIOSH5040?

As reported in the text we unfortunately had not the possibility to repeat the NIOSH and EUSAAR_2

protocols at the two different wavelengths on the same filters. This is why we based our discussion on the analysis of literature and previous results. We anyway include here two typical thermograms, NIOSH and EUSAAR_2, of the same urban samples batch and showing the typical transmittance trend linked to the quoted discrepancy.



Eusaar2, split point ≈ 950 s



Niosh5040, split point ≈ 480 s Line 267 and elsewhere in the text: The term "Sunset set-ups" could be altered to a more descriptive term.

Done

Line 289: What would be the value of 1σ? It seems that the difference between the two MAC values reported is substantially greater than the reported uncertainty.

The Referee is right, we did a material mistake in the text: the one sigma uncertainty is 0.4 m^2 g^{-1} (and this is right) but the discrepancy between the MAC values calculated in 2016 and the present work is slightly above 3 sigma (we change the text accordingly).

Line 316: “Brow carbon”

Done

Line 338: This sentence could be rephrased for easier comprehension.

We rephrased the sentence in this way: “We retrieved Brown Carbon concentration values directly from the Sunset thermograms following Massabò et al., 2016. Exploiting the synergic information provided by the Multi Wavelength Absorbance Analyzer, MWAA (Massabò et al., 2015) we could obtain the MAC(BrC) at the two wavelengths”.

Line 348: Same stands for this sentence.

We rephrased the sentences in this way: “In our findings, the ratio between BrC and Levo concentration values depends on the wavelength of the transmittance signal adopted during the thermo-optical analysis. This behavior could be due to 1) a better accuracy of the results in blue-light, more sensitive to BrC, or 2) the definition of BrC itself, which has to be considered wavelengthdependent. The present results do not allow any conclusive statement on this issue: actually, the label “Brown Carbon”, as well as the widely used “Organic and Elemental Carbon”, comes from an operative definition not without ambiguity.

Figure 4: It is not clear which relationship applies to which trendline.

Figure 4 has been amended.

Figure 6: It seems that 2 separate subgroups are formed, one equal and above the trendline and one below the trendline. Are those related to the specific sampling strategy or to any other parameter?

We noted this strange behavior with the formation of two separate subgroups. It doesn’t depend on different sampling strategy neither other evident parameter. Unfortunately, we didn’t find a reasonable explanation for this.

Two-wavelength thermo-optical determination of Light Absorbing Carbon in atmospheric aerosols

Dario Massabò[1,*], Alessandro Altomari[2], Virginia Vernocchi[1], Paolo Prati[1]

1: Dept. of Physics, University of Genoa & INFN, Via Dodecaneso 33, 16146, Genova, Italy
2: Dept. of Physics, University of Genoa, Via Dodecaneso 33, 16146, Genova, Italy

Abstract

Thermo-optical analysis is widely adopted for the quantitative determination of Total, TC, Organic, OC, and Elemental, EC, Carbon in atmospheric aerosol sampled by suitable filters. Nevertheless, the methodology suffers of several uncertainties and artefacts as the well-known issue of charring affecting the OC-EC separation. In the standard approach, the effect of the possible presence of Brown Carbon, BrC, in the sample is neglected. BrC is a fraction of OC, usually produced by biomass burning with a thermic behaviour intermediate between OC and EC. BrC is optically active: it shows an increasing absorbance when the wavelength moves to the blue/UV region of the electromagnetic spectrum. Definitively, the thermo-optical characterization of carbonaceous aerosol should be reconsidered to address the possible BrC content in the sample under analysis.

We introduce here a modified Sunset Lab Inc. EC/OC Analyzer. Starting from a standard commercial instrument, the unit has been modified at the Physics Department of the University of Genoa (IT), making possible the alternative use of the standard laser diode at λ = 635 nm and of a new laser diode at λ = 405 nm. In this way, the optical transmittance through the sample can be monitored at both the wavelengths. Since at shorter wavelengths the BrC absorbance is higher, a better sensitivity to this species is gained. The modified instrument also gives the possibility to quantify the BrC concentration in the sample at both the wavelengths. The new unit has been thoroughly tested, with both artificial and real-world aerosol samples: the first experiment, in conjunction with the Multi Wavelength Absorbance Analyzer (MWAA, Massabò et al., 2013 and 2015), resulted in the first direct determination of the BrC Mass Absorption Coefficient (MAC) at λ = 405 nm: MAC = 23 ± 1 m^2 g^{-1}.

Keywords: *carbonaceous aerosol, brown carbon, thermo-optical analysis, mass absorption coefficient*

---

[*] Corresponding Author: massabo@ge.infn.it

1. Introduction

Light absorbing carbon (LAC) is the fraction of carbonaceous aerosol, which can absorb electromagnetic radiation in the visible or near-visible range (Pöschl, 2003; Bond and Bergstrom, 2006; Moosmüller et al., 2009; Ferrero et al., 2018). A wide literature investigates and characterizes the optical properties of the inorganic-refractory LAC fraction, usually referred as Black Carbon, BC, (e.g. Bond et al., 2013; and reference therein) which is strongly absorbing from UV to IR, with a weak dependence on wavelength (Bond and Bergstrom, 2006; Moosmüller et al., 2009). Much less studied and understood is the organic LAC, often labelled as Brown Carbon, which appears to be optically active at wavelengths shorter than 650 nm and with an increasing absorbance moving to the blue and ultraviolet (UV) range (Pöschl, 2003; Andreae and Gelencsér, 2006; Moosmüller et al., 2011; Laskin et al., 2015; Olson et al., 2015). BrC can therefore be considered as the "optically active" part of the OC dispersed in the atmosphere. When considered from a thermo-chemical point of view, BrC also shows a refractory behaviour since, in an inert atmosphere, it volatizes at temperatures greater than 400 °C only (Chow et al., 2015). A discussion on the primary and secondary sources of atmospheric LAC is outside the scope of the present work; we simply remind that primary BrC is produced mainly by biomass burning even if, in some cases, also incomplete combustion of fossil fuels used in transport activities (i.e. terrestrial vehicles, ships and aircrafts) can generate this kind of compounds (Corbin et al, 2018). It is also worth to underline that carbonaceous aerosols impact on human health (Pope and Dockery, 2006; Chow et al., 2006; Mauderly and Chow, 2008), as well as on climate and environment (Bond and Sun, 2005; Highwood and Kinnersley, 2006; Chow et. al., 2010).

In the wider landscape of atmospheric carbonaceous aerosol, despite a worldwide diffused effort, the situation is not satisfactory and a standardized and conclusive approach is still missing. The quantitative determination of TC, OC and EC is often performed by a thermo-optical analysis (Birch and Cary, 1996; Watson et al., 2005; Hitzenberger et al., 2006) of aerosol samples collected on quartz fibre filters. However, thermo-optical analyses are affected by several issues and artefacts (Yang and Yu, 2002; Chow et al., 2004) and different laboratories/agencies adopt protocols which systematically result in discrepancies, particularly large in the EC quantification (Birch and Cary, 1996; Chow et al., 2007; Cavalli et al., 2010). A further issue arises when the effects of the possible presence of BrC in the sample are taken into account. So far, the monitoring of the sample transmittance during the thermal cycle, has been introduced to correct for the well know charring effect and the formation of pyrolytic carbon (Birch and Cary, 1996). This implies that BC is the sole absorbing compound at the wavelength implemented in the thermo-optical analyser (for instance at λ = 635 nm, the wavelength of the laser diode mounted in the extremely diffused Sunset Lab. Inc. EC/OC analyzer). Basically, with a sizeable concentration of BrC in the sample, one of the key assumptions of the thermo-optical methods fails and the EC/OC separation is even more unstable (to not say that, by design, the BrC quantification is not possible). This issue was preliminarily addressed by (Chen et al., 2015) by a multi-wavelength TOT/TOR instrument (Thermal Spectral Analysis – TSA) and further investigated in (Massabò et al., 2016). In the latter work, a method to correct the results of a standard Sunset analyzer and to retrieve the BrC concentration in the sample was introduced. The achievement was possible thanks to a synergy with the information provided by the Multi Wavelength Absorbance Analyzer, MWAA, (Massabò et al., 2015) developed in the same laboratory. A further step towards BrC quantification through the utilization of TSA was discussed in (Chow et al., 2018), where it was proved that the use of 7-wavelengths in thermal/optical carbon analysis allows contributions from biomass burning and secondary organic aerosols to be estimated. It is worthy to note that the biomass burning contribution to PM concentration can be also estimated by other methods such as Aerosol Mass Spectrometry, AMS (Daellenbach et al., 2016).

The MWAA approach allows the determination of the spectral dependence of the aerosol absorption coefficient (b_{abs}) which can be generally described by the power-law relationship $b_{abs}(\lambda) \sim \lambda^{-AAE}$, where the AAE is the Ångström Absorption Exponent. Several works reported AAE values which depend on the aerosol chemical composition (Kirchstetter et al., 2004; Utry et al., 2013) as well as its size and morphology (Lewis et al., 2008; Lack et al., 2012; Lack and Langridge, 2013; Filep et al., 2013; Utry et al., 2014). Furthermore, the spectral dependence of the aerosol has been exploited to identify different sources of carbonaceous aerosol (e.g. Sandradewi et al., 2008; Favez et al., 2010; Lack and Langridge, 2013; Massabò et al., 2013 and 2015). In general, AAE values close to 1.0 have been found to be related to urban PM where fossil fuels combustion is dominant, while higher AAE values, up to 2.5, have been linked to carbonaceous aerosols produced by wood burning (Harrison et al., 2013; and references therein) and therefore to the presence of BrC.

In the previous work by (Massabò et al., 2016) the effect of the BrC possibly contained in the sample on the thermo-optical analysis was quantified and exploited to retrieve the BrC concentration from the raw data provided by a standard Sunset Lab. Analyzer. This first step, suggested to modify/upgrade a Sunset unit adding the possibility to use a second laser diode in the blue range. This improves the sensitivity to the BrC and allows to check whether the BrC quantification depends on the adopted wavelength. We finally followed this route and we here introduce our modified Sunset Analyzer unit, the validation tests and the results of the first campaign in which the new unit was deployed.

2. Materials and Methods

2.1 The 2-lambda SUNSET analyzer

We have modified a commercial Thermal Optical Transmittance (TOT) instrument (Sunset Lab Inc.). This equipment had been originally designed (Birch and Cary, 1996) with a red laser diode (λ = 635 nm) to have the possibility to monitor and correct the well know problem of the formation of pyrolytic carbon by charring (Birch and Cary, 1996; Bond and Bergstrom, 2006; Chow et al., 2007; Cavalli et al., 2010). The assumption that OC is optically inactive at wavelengths greater than 600 nm is at the basis of the technique; therefore the laser beam attenuation is only due to the EC originally present or formed by charring in the sample under analysis. Actually, even at this wavelength, BrC can affect the reliability of the OC/EC separation and the standard methodology can be modified to quantify the BrC concentration (Massabò et al., 2016). Nevertheless, at λ = 635 nm the BrC Mass Absorption Coefficient, MAC(BrC), remains much smaller of the corresponding MAC(BC) and the modified procedure could/should be implemented at shorter wavelengths to gain in sensitivity.

We have modified our SUNSET unit making possible the alternative use of the standard laser diode at λ = 635 nm or of a World Star Technologies, 100 mW, laser diode at λ = 405 nm. This second laser diode can be mounted on the top of the SUNSET furnace by a homemade adapter (see Figure 1) and easily exchanged with the native red diode. With the new laser diode, the light detector placed at the bottom of the SUNSET furnace has to be changed too and we selected a photodiode (PD) THORLABS FDS1010 coupled with a bandpass filter THORLABS FBH405-10. The responsivity of the PD FDS1010 around λ = 400 nm is quite low (about 50 mA W^{-1}) but the high power delivered by the laser diode results in signals with an amplitude comparable to the values measured with the original SUNSET set-up (i.e. laser diode and PD). Furthermore, the FBH405-10 filter cuts all the light background produced by the high temperature of the SUNSET furnace, thus preserving the signal-to-noise ratio. Both laser and PD can be exchanged in about 10 min and no particular attention is requested but the proper alignment to maximize the PD output signal (i.e. the *transmittance* value displayed by the SUNSET control software). We have to note that the original configuration of the SUNSET instrument adopts a lock-in amplifier to improve the signal-to-noise ratio of the PD: we did not have the possibility to manipulate the parameters of the lock-in amplifier and to tune it to the new configuration.

2.2 Test of the new configuration

The new blue-light set-up of the Sunset Analyzer was tested using both synthetic and real-world aerosol samples, collected on quartz fibre filters. Synthetic samples were prepared starting with a 5% (volume) solution of Aquadag, then nebulised by a Blaustein Atomizer (BLAM) and collected on quartz fibre filters. Aquadag is the trade name of a water-based colloidal graphite coating (particle diameters between 50 and 100 nm): these samples can therefore be considered to be composed by EC/BC only. The samples were first sent to an optical characterization by the MWAA instrument (Multi Wavelength Absorbance Analyzer, Massabò et al., 2015) which demonstrated that the optical absorption of Aquadag is independent on the wavelength. Actually, Aquadag particles tend to form conglomerates on the filter surface, with dimension about double of the longer wavelength implemented in the MWAA (i.e. the 850 nm of the infrared laser diode; Massabò et al., 2015). So, the comparison between the two Sunset set-ups was made with samples having the same absorption properties. EC and TC quantifications obtained at $\lambda = 635$ nm and $\lambda = 405$ nm resulted compatible adopting both the NIOSH5040 and EUSAAR_2 protocol (Cavalli et al., 2010), as shown in Figure 2 for the whole set of synthetic samples.

A second set of synthetic samples was prepared to mimic the behaviour of real-world aerosol samples: a 3% (weight) solution of ammonium sulphate $(NH_4)_2SO_4$ in Aquadag was prepared and nebulized with the BLAM. This way, a scattering compound is mixed to the absorbing Aquadag spherules. The optical absorption measured with MWAA resulted independent on wavelength with this second set of samples too. The results of the Sunset analysis with both the red and blue laser set-up are shown in Figure 3. This second set of samples was analysed through the EUSAAR_2 protocol only: we used two punches for each laser in each sample to have a reproducibility check. A strong correlation between the TC and EC values measured in red and blue light was obtained again with a slope close to unity.

A third and final test was performed using a set of daily PM10 samples collected by a low-volume sampler (TCR - Tecora, Italy) on quartz fibre filters (Pall-2500 QAO-UP, 47 mm diameter) in spring 2016 in the urban area of the city of Genoa (IT). A previous and long set of similar campaigns addressed to PM10 characterization (e.g. Bove et al., 2014 and references therein) in the same urban area could not identify sizeable contributes of biomass burning to PM composition, in particular during spring and summer. Such situation was confirmed by the determination of the Ångström exponent in the present samples by the MWAA. Actually, in the set of twenty PM10 samples, the values of the Ångström exponent ranged between 0.9 and 1.2, this confirming that Black Carbon is the sole or totally dominant light absorbing component in the local PM10 (Sandradewi et al., 2008; Harrison et al., 2013). Half of the samples was then sent to the Sunset analysis by the NIOSH5040 protocol while the EUSAAR_2 protocol was adopted for the remaining subset. The results are shown in Figure 4. The EC concentration values measured with the standard and modified Sunset analyzer are fully compatible when the NIOSH5040 protocol is adopted (basically, the split point position in the Sunset thermogram does not change with the two laser diodes). Instead, EC values determined by the EUSAAR_2 protocol resulted lower by about 30% when the blue laser diode was mounted. This corresponds to a shift of the split point position, which moves rightward and thus increases the amount of carbonaceous aerosol counted in the OC fraction. This effect is linked to the well-known issue of the formation of pyrolytic carbon during the thermal cycle in the inert atmosphere (i.e. in He). Several literature studies (e.g.: Cavalli et al., 2010; Panteliadis et al., 2015) indicated that the charring is smaller at the higher temperatures reached during the NIOSH thermal protocol. On the other way, standard thermo-optical analyses of urban PM samples often give higher EC values (up to 50%) when performed following the EUSAAR_2 instead of higher-temperature protocols (Subramanian et al., 2006; Zhi et al., 2008; Piazzalunga et al., 2011; Karanasiou et al., 2015; Panteliadis et al., 2015). Furthermore, as by-product of previous PM10 studies in the urban area of Genoa by a standard Sunset unit, we could observe a systematic and very reproducible 40% discrepancy between EC values determined in the same samples by EUSAAR_2 and NIOSH5040 protocols (with EC:EUSAAR > EC:NIOSH). Therefore, the thermo-optical analysis in blue light seems to be more sensitive to the charring formation during the EUSAAR_2 protocol and thus possibly more reliable in the EC/OC separation.

3. First field campaign and results

The modified Sunset instrument was used for the first time, in conjunction with the MWAA instrument and apportionment methodology (Massabò et al., 2015), to retrieve the MAC (Mass Absorption Coefficient) of Brown Carbon at the two wavelengths of $\lambda = 635$ nm and $\lambda = 405$ nm, in a set of samples collected wintertime in a mountain site.

3.1 Samples collection

Aerosol samples were collected in a small village (Propata, 44°33’52.93’’N, 9°11’05.57’’E, 970 m a.s.l.) situated in the Ligurian Apennines, Italy. Three different sets of PM10 aerosol samples were collected by a low-volume sampler (38.3 l min^{-1} by TCR Tecora): the first and the third sets had filter change set every 24h while the second set was sampled on a 48h-basis. In total, 41 (14+13+14) PM10 samples were collected on quartz-fibre filters (Pall, 2500QAO-UP, 47 mm diameter), between February 2nd and April 19th, 2018. Before the sampling, the filters were baked at T = 700°C for 2 hours to remove possible internal contamination. Field blank filters were used to monitor possible contaminations during the sampling phase. Wood burning is one of the PM sources around the sampling site, especially during the cold season, as it is used for both domestic heating and cooking purposes.

3.2 Laboratory analyses

All the samples were weighed before and after sampling in an air-conditioned room (T = 20 ± 1 °C; R.H. = 50 % ± 5%), after 48h conditioning. The gravimetric determination of the PM mass was performed using an analytical microbalance (precision: 1 μg) which was operated inside the conditioned room; electrostatic effects were avoided by the use of a de-ionizing gun.

After weighing, samples were first optically analyzed by MWAA to retrieve the absorption coefficient (b_{abs}) of PM at five different wavelengths. The EC and OC determination was performed adopting the EUSAAR_2 protocol (Cavalli et al., 2010) with both laser diodes at $\lambda = 635$ nm and at $\lambda = 405$ nm (two different punches were extracted from each filter sample).

Finally, the remaining portion of the same quartz-fibre filters underwent a chemical determination of the Levoglucosan (1,6-Anhydro-beta-glucopyranose) concentration by High Performance Anion Exchange Chromatography coupled with Pulsed Amperometric Detection (Piazzalunga et al., 2010). As well known in literature, this sugar is one of the typical marker of biomass burning (Vassura et al., 2014).

3.3 Optical apportionment

The MWAA analysis provided the raw data to measure the spectral dependence of the aerosol absorption coefficient (b_{abs}) which can be generally described by the power-law relationship $b_{abs}(\lambda) \sim \lambda^{-AAE}$ where AAE is the Ångström Absorption Exponent.

The time series of the resulting AAE values is shown in Figure 5: they range between 1.05 and 1.96 with a mean value of 1.55 ± 0.21. This figure indicates a substantial presence of wood burning in the sampling area. In (Massabò et al., 2015 and Bernardoni et al, 2017), an optical apportionment model (the "MWAA model") based on the measurement of b_{abs} at five wavelengths had been introduced to obtain directly the BrC AAE (α_{BrC}) and the BrC absorption coefficient (b_{abs}^{BrC}) at each measured wavelength. It is worthy to note that, at the basis of the MWAA model, there is the assumption that BrC is produced by wood combustion only (see §4 in Massabò et al., 2015; Zheng et al., 2013). In Figure 5, we report the optical apportionment at λ = 635 nm and at λ = 405 nm i.e. at the wavelength of the two laser diodes used in our modified Sunset instrument. At λ = 635 nm, light absorption resulted mainly due to BC from both fossil fuel (FF) and wood burning (WB) and the b_{abs}^{BrC} average value is 15% of total b_{abs}, with the notable exception of some days in which it reached values of ~ 30%, in correspondence of AAE > 1.9. Instead, at λ = 405 nm, the BrC contribute to light absorption rises up to 33% (average percentage of total b_{abs}), with a maximum value of 51%, again when AAE_{exp} > 1.9. The time series of b_{abs}^{BrC} values at both the wavelengths turned out to be well correlated (R^2 = 0.71) with the Levoglucosan (*Levo*, in the following) concentration values, as reported in Figure 6. The slope of the correlation curve increases by a factor 5.8 when moving from the red to the blue light.

The average α_{BrC} value turned out to be α_{BrC} = 3.9 ± 0.1, in very good agreement with a previous value (α_{BrC} = 3.8 ± 0.2) obtained in the same site and with the same approach (Massabò et al., 2016). The result is also in agreement with other literature works (Yang et al., 2009; Massabò et al., 2015; Chen et al., 2015).

3.4 Brown Carbon MAC

The methodology to extract the MAC value for BrC by the coupled used of MWAA and Thermo-Optical Analysis has been introduced in a previous work (Massabò et al., 2016). In that case, a standard (i.e.: with a red laser diode only) Sunset unit was used. The entire procedure is described in details in (Massabò et al., 2016), here we briefly summarize the main steps:

a) The fraction of light attenuation due to the BrC is first calculated in each sample with the MWAA raw data.
b) The empirical relationship between the light attenuation through the sample, observed in the MWAA and in the Sunset and at both wavelengths, is then determined. We remind

that in the Sunset measurement, the light attenuation is continuously recorded during the analysis; the value characteristic of each blank filter can be retrieved when all the light absorbing PM has been volatized (i.e. at the end of the thermal protocol).

c) The fraction of light attenuation due to the BrC in the sample is therefore calculated for the Sunset analysis and the initial transmittance value is corrected to estimate the attenuation value that it would have been found if BrC were not present in the filter sample.

d) A new split-point position is then determined taking into account the corrected value of the initial transmittance.

e) The OC and EC values determined with the standard and corrected split-point positions are then compared and the difference ($OC_{cor} - OC_{std} = EC_{std} - EC_{cor}$) is operatively assumed to be equal to the BrC in the sample. The corresponding BrC atmospheric concentration is finally calculated.

f) The correlation between the values of b_{abs}^{BrC}, provided by the MWAA analysis (see section 3.3) and BrC concentration, is studied to determine the MAC value.

In the present experiment, the procedure was adopted to analyse the thermograms produced with both the red and the blue laser diode mounted in the Sunset unit: the results are summarized in Figure 7. Despite a rather high noise in the data, the MAC(BrC) value at the two wavelengths can be determined and it turns out to be MAC(BrC) = 9.8 ± 0.4 $m^2 g^{-1}$ and 23 ± 1 $m^2 g^{-1}$, respectively at $\lambda = 635$ and 405 nm. This result deserves some comments:

- The MAC value at $\lambda = 635$ nm differs for about 3σ from the result reported in (Massabò et al., 2016) and obtained in the same site and in a similar season (i.e. November 2015 to January 2016; MAC = 7.0 ± 0.4 $m^2 g^{-1}$). Since differences in the type of wood burnt in the past and present campaign cannot be excluded, the two values can be considered to be in fair agreement.
- No comparison with previous or other literature values is possible for the MAC value at $\lambda = 405$ nm, given the substantial differences in adopted definitions and methodologies (Yang et al., 2009; Feng et al., 2013; Chen and Bond, 2010). However, the increase by a factor 2.3 with respect to the MAC at $\lambda = 635$ nm follows the expected behaviour.
- Under the assumption that the sole source of BrC is biomass burning, the MAC values can be referred to the total concentration of organic carbon (i.e. including the part not

optically active) produced by biomass burning. Adopting with the present data set the optical OC apportionment methodology reported in (Massabò et al., 2015), the BrC values determined at λ = 635 nm turn out to be about 4% of the OC produced by wood combustion, OC_{WB}, and consequently MAC($OC_{WB,}$ λ = 635nm) = 0.39 ± 0.06 m^2 g^{-1}. When the analysis is performed at λ = 405 nm, BrC results to be about 10% of OC_{WB} and MAC($OC_{WB,}$ λ = 405nm) = 2.3 ± 0.2 m^2 g^{-1}. Previous literature works (Feng et al., 2013; Laskin et al., 2015; and references therein) report MAC values of BrC and/or related OC ranging in a quite large interval.

- The ratio between BrC and Levo concentration values results to be BrC:Levo = 0.19 ± 0.02 and 0.42 ± 0.06, respectively when considering the BrC concentration determined by MWAA + Sunset at λ = 635 and 405 nm. In other words, the operative procedure, introduced in (Massabò et al., 2016), results in different BrC concentration values according to the considered/used wavelength. This fact can be interpreted in different ways: while the analytical sensitivity is higher at λ = 405 nm and the corresponding BrC values could be considered to be more firm, the category of compounds collected under the label "Brown Carbon" could be itself "wavelength dependent". The latter would imply that the BrC concentration cannot be defined separately from the wavelength and that its meaning is even more "operative" of the more widespread OC and EC fractions. As a matter of fact, while the b_{abs}^{BrC} values discussed in section 3.3, increase by a factor 5.8 moving from λ = 635 nm to λ = 405 nm, the corresponding variation of the MAC(BrC) values is by a factor 2.3 only. This is because the BrC concentration determined at λ = 405 nm doubles the value measured at λ = 635 nm. The purposes and the limits of the present study prevent any firm conclusion on the alternative explanation: BrC definition is wavelength dependent or the analysis in red light is not sensitive enough.
- When considering the OC_{WB}:Levo concentration ratio, the MWAA analysis at λ = 635 and λ = 405 nm give well compatible results, with a mean value of OC_{WB}:Levo = 4.5 ± 0.5.

4. Conclusions

We introduced a modified version of a commercial Sunset Lab. Inc. OC/EC Analyzer. We upgraded the standard instrument unit making possible the alternative use of a red (λ = 635 nm) or blue (λ= 405 nm) laser diode to monitor the light transmittance through the sample during the thermal cycle. The analytical performance of the new set-up has been tested both with artificial and real-world aerosol samples.

The new Sunset set-up was used to analyze a set of samples collected mostly wintertime in a mountain site of the Italian Apennines. We retrieved Brown Carbon concentration values directly from the Sunset thermograms following Massabò et al., 2016. Exploiting the synergic information provided by the Multi Wavelength Absorbance Analyzer, MWAA (Massabò et al., 2015) we could obtain the MAC(BrC) at the two wavelengths. The result at λ = 635 nm (MAC = 9.8 ± 0.4 m^2 g^{-1}) is in fair agreement with a previous study performed in the same site in winter 2015-2016. At our knowledge, the result at λ = 405 nm, MAC = 23 ± 1 m^2 g^{-1} is the sole direct observation at this wavelength.

In our findings, the ratio between BrC and Levo concentration values depends on the wavelength of the transmittance signal adopted during the thermo-optical analysis. This behaviour could be due to 1) a better accuracy of the results in blue-light, more sensitive to BrC, or 2) the definition of BrC itself, which has to be considered wavelength-dependent. The present results do not allow any conclusive statement on this issue: actually, the label “Brown Carbon”, as well as the widely used “Organic and Elemental Carbon”, comes from an operative definition not without ambiguity.

6. Acknowledgements

This work has been partially financed by the National Institute of Nuclear Physics (INFN) in the frame of the TRACCIA experiments.

References

Andreae, M. O. and Gelencsér, A.: Black Carbon or Brown Carbon? The nature of light-absorbing carbonaceous aerosol, Atmos. Chem. Phys., 6, 3131-3148, 2006.

Bernardoni, V., Pileci, R. E., Caponi, L., and Massabò, D.: The Multi-Wavelength Absorption Analyzer (MWAA) model as a tool for source and component apportionment based on aerosol absorption properties: application to samples collected in different environments, Atmosphere, 8, 218, 2017.

Birch, M. E. and Cary, R. A.: Elemental carbon-based method for occupational monitoring of particulate diesel exhaust: methodology and exposure issues, Analyst, 121, 1183–1190, 1996.

Bond, T. C. and Bergstrom, R. W.: Light absorption by carbonaceous particles: an investigative review, Aerosol Sci. Tech., 40, 27-67, 2006.

Bond, T. C. and Sun, H. L.: Can reducing black carbon emissions counteract global warming?, Environ. Sci. Technol., 39, 5921–5926, 2005.

Bond, T. C., Doherty, S. J., Fahey, D. W., Forster, P. M., Berntsen, T., De Angelo, B. J., Flanner, M. G., Ghan, S., Kärcher, B., Koch, D., Kinne, S., Kondo, Y., Quinn, P. K., Sarofim, M. C., Schultz, M. G., Schulz, M., Venkataraman, C., Zhang, H., Zhang, S., Bellouin, N., Guttikunda, S. K., Hopke, P. K., Jacobson, M. Z., Kaiser, J. W., Klimont, Z., Lohmann, U., Schwarz, J. P., Shindell, D., Storelvmo, T., Warren, S. G., and Zender, C. S.: Bounding the role of black carbon in the climate system: a scientific assessment, J. Geophys. Res.-Atmos., 118, 5380-5552, 2013.

Bove, M. C., Brotto, P., Cassola, F., Cuccia, E., Massabò, D., Mazzino, A., Piazzalunga, A., and Prati, P.: An integrated PM2.5 source apportionment study: positive matrix factorisation vs. the chemical transport model CAMx, Atmos. Environ., 94, 274-286, 2014.

Cavalli, F., Putaud, J. P., Viana, M., Yttri, K. E., and Gemberg, J.: Toward a standardized thermal-optical protocol for measuring atmospheric Organic and Elemental Carbon: the EUSAAR protocol, Atmos. Meas. Tech., 3, 79-89, 2010.

Chen, Y. and Bond, T. C.: Light absorption by organic carbon from wood combustion, Atmos. Chem. Phys., 10, 1773–1787, 2010.

Chen, L. W. A., Chow, J. C., Wang, X. L., Robles, J. A., Sumlin, B. J., Lowenthal, D. H., Zimmermann, R., and Watson, J. G.: Multi-wavelength optical measurement to enhance thermal/optical analysis for carbonaceous aerosol, Atmos. Meas. Tech., 8, 451-461, 2015.

Chow, J. C., Watson, J. G., Chen, L. W. A., Arnott, W. P., Moosmüller, H., and Fung, K. K.: Equivalence of elemental carbon by thermal/optical reflectance and transmittance with different temperature protocols, Environ. Sci. Technol., 38, 4414-4422, 2004.

Chow, J. C., Watson, J. G., Mauderly, J. L., Costa, D. L., Wyzga, R. E., Vedal, S., Hidy, G. M., Altshuler, S. L., Marrack, D., Heuss, J. M., Wolff, G. T., Pope, C. A. III, and Dockery, D. W.: Health effects of fine particulate air pollution: lines that connect, J. Air Waste Manag. Assoc., 56, 1368–1380, 2006.

Chow, J. C., Watson, J. G., Chen, L. W. A., Chang, M. C. O., Robinson, N. F., Trimble, D. L., and Kohl, S. D.: The IMPROVE_A temperature protocol for thermal/optical carbon analysis:

maintaining consistency with a long-term database, J. Air Waste Manag. Assoc., 57, 1014-1023, 2007.

Chow, J. C., Watson, J. G., Lowenthal, D. H., Chen, L. W. A., and Motallebi, N.: Black and organic carbon emission inventories: review and application to California, J. Air Waste Manag. Assoc., 60, 497–507, 2010.

Chow, J. C., Wang, X., Sumlin, B. J., Gronstal, S. B., Chen, L. W. A., Trimble, D. L., Kohl, S. D., Mayorga, S. R., Riggio, G., Hurbain, P. R., Johnson, M., Zimmermann, R., and Watson, J. G.: Optical calibration and equivalence of a multiwavelength thermal/optical carbon analyzer, Aerosol Air Qual. Res., 15, 1145-1159, 2015.

Chow, J.C, Watson, J. G., Green, M. C., Wang, X., Chen, L. W. A., Trimble, D. L., Cropper, P. M., Kohl S. D., and Gronstal, S. B.: Separation of brown carbon from black carbon for IMPROVE and Chemical Speciation Network PM2.5 samples, J. Air Waste Manag. Assoc., 68:5, 494-510, 2018.

Corbin J. C., Pieber S. M., Czech H., Zanatta M., Jakobi G., Massabò D., Orasche J., El Haddad I., Mensah A. A., Stengel B., Drinovec L., Mocnik G., Zimmermann R., Prévôt A. S. H., and M. Gysel: Brown and Black Carbon emitted by a marine engine operated on heavy fuel oil and distillate fuels: optical properties, size distributions, and emission factors, J. Geophys. Res-Atmos, 123, 6175–6195, 2018.

Daellenbach, K.R., Bozzetti, C., Křepelová, A., Canonaco, F., Wolf, R., Zotter, P., Fermo, P., Crippa, M., Slowik, J.G., Sosedova, Y., Zhang, Y., Huang, R. J., Poulain, L., Szidat, S., Baltensperger, U., El Haddad, I., and Prévôt, A. S. H.: Characterization and source apportionment of organic aerosol using offline aerosol mass spectrometry, Atmos. Meas. Tech., 9 (1), 23-39, 2016.

Favez, O., El Haddad, I., Piot, C., Boreave, A., Abidi, E., Marchand, N., Jaffrezo, J. L., Besombes, J. L., Personnaz, M. B., Sciare, J., Wortham, H., Geroge, C., and D’Anna, B.: Inter-comparison of source apportionment models for the estimation of wood burning aerosols during wintertime in an Alpine city (Grenoble, France), Atmos. Chem. Phys., 10, 5295-5314, 2010.

Feng, Y., Ramanathan, V., and Kotamarthi, V. R.: Brown carbon: a significant atmospheric absorber of solar radiation?, Atmos. Chem. Phys., 13, 8607-8621, 2013.

Ferrero, L., Močnik, G., Cogliati, S., Gregorič, A., Colombo, R., and Bolzacchini, E.: Heating rate of light absorbing aerosols: time-resolved measurements, the role of clouds, and source identification, Environ. Sci. Tech., 52 (6), 3546-3555, 2018.

Filep, Á., Ajtai, T., Utry, N., Pintér, M. D., Nyilas, T., Takács, S., Máté, Z., Gelencsér, A., Hoffer, A., Schnaiter, M., Bozóki, Z., and Szabó, G.: Absorption spectrum of ambient aerosol and its correlation with size distribution in specific atmospheric conditions after a red mud accident, Aerosol Air Qual. Res., 13, 49-59, 2013.

Harrison, R. M., Beddows, D. C. S., Jones A. M., Calvo A., Alves C., and Pio C.: An evaluation of some issues regarding the use of aethalometers to measure woodsmoke concentrations, Atmos. Environ., 80, 540-548, 2013.

Highwood, E. J. and Kinnersley, R. P.: When smoke gets in our eyes: the multiple impacts of atmospheric black carbon on climate, air quality and health, Environ. Int., 32, 560–566, 2006.

Hitzenberger, R., Petzold, A., Bauer, H., Ctyroky, P., Pouresmaeil, P., Laskus, L., and Puxbaum, H.: Intercomparison of thermal and optical measurement methods for elemental carbon and black carbon at an urban location, Environ. Sci. Technol., 40 (20), 6377-6383, 2006.

Karanasiou, A., Minguillon, M. C., Viana, M., Alaustey, A., Puaud, J. P., Maenhaut, W., Panteliadis, P., Močnik, G., Favez, O., and Kuhlbusch, T. A.: Thermal-optical analysis for the measurement of elemental carbon (EC) and organic carbon (OC) in ambient air, a literature review, Atmos. Meas. Tech. Discuss., 8, 9649-9712, 2015.

Kirchstetter, T. W., Novakok, T., and Hobbs, P. V.: Evidence that the spectral dependence of light absorption by aerosols is affected by organic carbon, J. Geophys. Res., 109, D21208, 2004.

Lack, D. A., Langridge, J. M., Bahreini, R., Cappa, C. D., Middlebrook, A. M., and Schwarz, J. P.: Brown carbon and internal mixing in biomass burning particles, Proc. Natl. Acad. Sci., 109, 14802-14807, 2012.

Lack, D. A. and Langridge, J. M.: On the attribution of black and brown carbon light absorption using the Ångström exponent, Atmos. Chem. Phys., 13, 10535-10543, 2013.

Laskin, A., Laskin, J., and Nizkorodov S. A.: Chemistry of atmospheric brown carbon, Chem. Rev., 115 (10), 4335–4382, 2015.

Lewis, K., Arnott, W. P., Moosmüller, H., and Wold, C. E.: Strong spectral variation of biomass smoke light absorption and single scattering albedo observed with a novel dual-wavelength photoacoustic instrument, J. Geophys. Res., 113, D16203, 2008.

Massabò, D., Bernardoni, V., Bove, M. C., Brunengo, A., Cuccia, E., Piazzalunga, A., Prati, P., Valli, G., and Vecchi, R.: A multi-wavelength optical set-up for the characterization of carbonaceous particulate matter, J. Aerosol Sci., 60, 34-46, 2013.

Massabò, D., Caponi, L., Bernardoni, V., Bove, M. C., Brotto, P., Calzolai, G., Cassola, F., Chiari, M., Fedi, M. E., Fermo, P., Giannoni, M., Lucarelli, F., Nava, S., Piazzalunga, A., Valli, G., Vecchi, R., and Prati, P.: Multi-wavelength optical determination of black and brown carbon in atmospheric aerosols, Atmos. Environ., 108, 1-12, 2015.

Massabò, D., Caponi, L., Bove, M. C., and Prati, P.: Brown carbon and thermal-optical analysis: a correction based on optical multi-wavelength apportionment of atmospheric aerosols, Atmos. Environ., 125, 119-125, 2016.

Mauderly, J. L. and Chow, J. C.: Health effects of organic aerosols, Inhal. Toxicol., 20, 257–288, 2008.

Moosmüller, H., Chakrabarty, R. K., and Arnott, W. P.: Aerosol light absorption and its measurement: a review, J. Quant. Spectrosc. Ra., 110, 844-878, 2009.

Moosmüller, H., Chakrabarty, R. K., Ehlers, K. M., and Arnott, W. P.: Absorption Ångström coefficient, brown carbon, and aerosols: basic concepts, bulk matter, and spherical particles, Atmos. Chem. Phys., 11, 1217-1225, 2011.

Olson, M. R., Garcia, M. V., Robinson, M. A., Van Rooy, P., Dietenberger, M. A., Bergin, M., and Schauer, J. J.: Investigation of black and brown carbon multiple-wavelength-dependent light absorption from biomass and fossil fuel combustion source emissions, J. Geophys. Res. Atmos., 120, 2015.

Panteliadis, P., Hafkenscheid, T., Cary, B., Diapouli, E., Fischer, A., Favez, O., Quincey, P., Viana, M., Hitzenberger, R., Vecchi, R., Saraga, D., Sciare, J., Jaffrezo, J. L., John, A., Schwarz, J., Giannoni, M., Novak, J., Karanasiou, A., Fermo, P., and Maenhaut, W.: ECOC comparison exercise with identical thermal protocols after temperature offset correction – instrument diagnostics by in-depth evaluation of operational parameters, Atmos. Meas. Tech., 8, 779–792, 2015.

Piazzalunga, A., Fermo, P., Bernardoni, V., Vecchi, R., Valli, G., and De Gregorio M. A.: A simplified method for levoglucosan quantification in wintertime atmospheric particulate matter by high performance anion-exchange chromatography coupled with pulsed amperometric detection, Int. J. Environ. An. Ch., 90, 934-947, 2010.

Piazzalunga, P., Bernardoni, V., Fermo, P., Valli, G., and Vecchi, R.: On the effect of water-soluble compounds removal on EC quantification by TOT analysis in urban aerosol samples, Atmos. Chem. Phys., 11, 10193-10203, 2011.

Pope, C. A. III and Dockery, D. W.: Health effects of fine particulate air pollution: lines that connect, J. Air Waste Manag. Assoc., 56, 709–742, 2006.

Pöschl, U.: Aerosol particle analysis: challenges and progress, Anal. Bioanal. Chem., 375, 3032, 2003.

Sandradewi, J., Prevot, A. H., Szidat, S., Perron, N., Rami Alfarra, M., Lanz, V., Weingartner, E., and Baltensperger, U.: Using aerosol light absorption measurements for the quantitative determination of wood burning and traffic emission contributions to particulate matter, Environ. Sci. Technol., 3316-3323, 2008.

Subramanian, R., Khlystov, A. Y., and Robinson, A. L.: Effect of peak inert-mode temperature on elemental carbon measured using thermal-optical analysis, Aerosol Sci. Tech., 40, 763–780, 2006.

Utry, N., Ajtai, T., Filep, Á., Dániel P. M., Hoffer, A., Bozoki, Z., and Szabó, G.: Mass specific optical absorption coefficient of HULIS aerosol measured by a four-wavelength photoacoustic spectrometer at NIR, VIS and UV wavelengths, Atmos. Environ., 69, 321-324, 2013.

Utry, N., Ajtai, T., Filep, Á., Pintér, M., Török, Zs., Bozóki, Z., and Szabó, G.: Correlations between absorption Angström exponent (AAE) of wintertime ambient urban aerosol and its physical and chemical properties, Atmos. Environ., 91, 52-59, 2014.

Vassura, I., Venturini, E., Marchetti, S., Piazzalunga, A., Bernardi, E., Fermo, P., and Passarini, F.: Markers and influence of open biomass burning on atmospheric particulate size and composition during a major bonfire event, Atmos. Environ., 82, pp. 218-225, 2014.

Watson, J. G., Chow, J. C., and Chen, L. W. A.: Summary of organic and elemental carbon/black carbon analysis methods and intercomparisons, Aerosol Air Qual. Res., 5, 65-102, 2005.

Yang, H. and Yu, J. Z.: Uncertainties in charring correction in the analysis of elemental and organic carbon in atmospheric particles by thermal/optical methods, Environ. Sci. Technol., 36, 5199-5204, 2002.

Yang, M., Howell, S. G., Zhuang, J., and Huebert, B. J.: Attribution of aerosol light absorption to black carbon, brown carbon, and dust in China - interpretations of atmospheric measurements during EAST-AIRE, Atmos. Chem. Phys., 9, 2035-2050, 2009.

Zheng, G., He, K., Duan, F., Cheng, Y., and Ma, Y.: Measurement of humic-like substances in aerosols: A review, Environ. Pollut., 181, 301-314, 2013.

Zhi, G., Chen, Y., Sheng, G., and Fu, J.: Effects of temperature parameters on thermal-optical analysis of organic and elemental carbon in aerosol, Environ. Monit. Assess., 154, 253–261, 2008.

FIGURE CAPTIONS

Figure 1: The new λ = 405 nm laser diode mounted by a steel adapter on the SUNSET furnace (top) and the comparison with the standard λ = 635 nm laser diode implemented by the manufacturer (bottom).

Figure 2: Quantification of TC (primary axis) and EC (secondary axis) at λ = 635 nm (red) and λ = 405 nm (blue) for the set of synthetic Aquadag samples. Top: NIOSH5040 protocol, bottom: EUSAAR_2 protocol.

Figure 3: Quantification of TC (primary axis) and EC (secondary axis) at λ = 635 nm (red) and λ = 405 nm (blue) for the set of synthetic Aquadag + Ammonium Sulphate samples by the EUSAAR_2 protocol.

Figure 4: EC concentration measured in two sub-sets of PM10 samples collected in consecutive days in the urban area of Genoa in late spring 2016. Values determined with the Sunset analyzer equipped with blue and red laser diodes, are compared.

Figure 5: Primary axis: Optical apportionment of the aerosol absorption coefficient (b_{abs}) at λ = 635 nm (top) and λ = 405 nm (bottom). Secondary axis: experimental AAE values obtained by fitting the measured b_{abs} values with a power-law relationship $b_{abs}(\lambda) \sim \lambda^{-AAE}$. FF and WB stand for Fossil Fuel and Wood Burning, respectively.

Figure 6: Aerosol absorption coefficient apportioned to Brown Carbon (b_{abs}^{BrC}) at λ = 635 nm (top) and at λ = 405 nm (bottom) vs. levoglucosan concentration.

Figure 7: Comparison between the aerosol absorption coefficient apportioned to Brown Carbon vs. the resulting operative BrC concentration values at λ = 635 nm (top) and at λ = 405 nm (bottom).

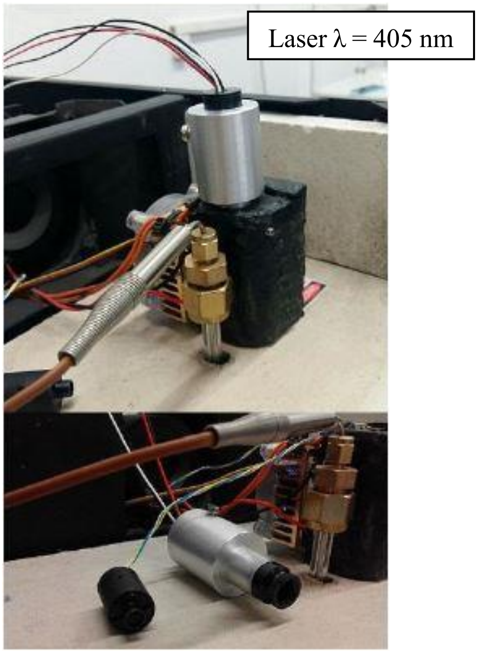
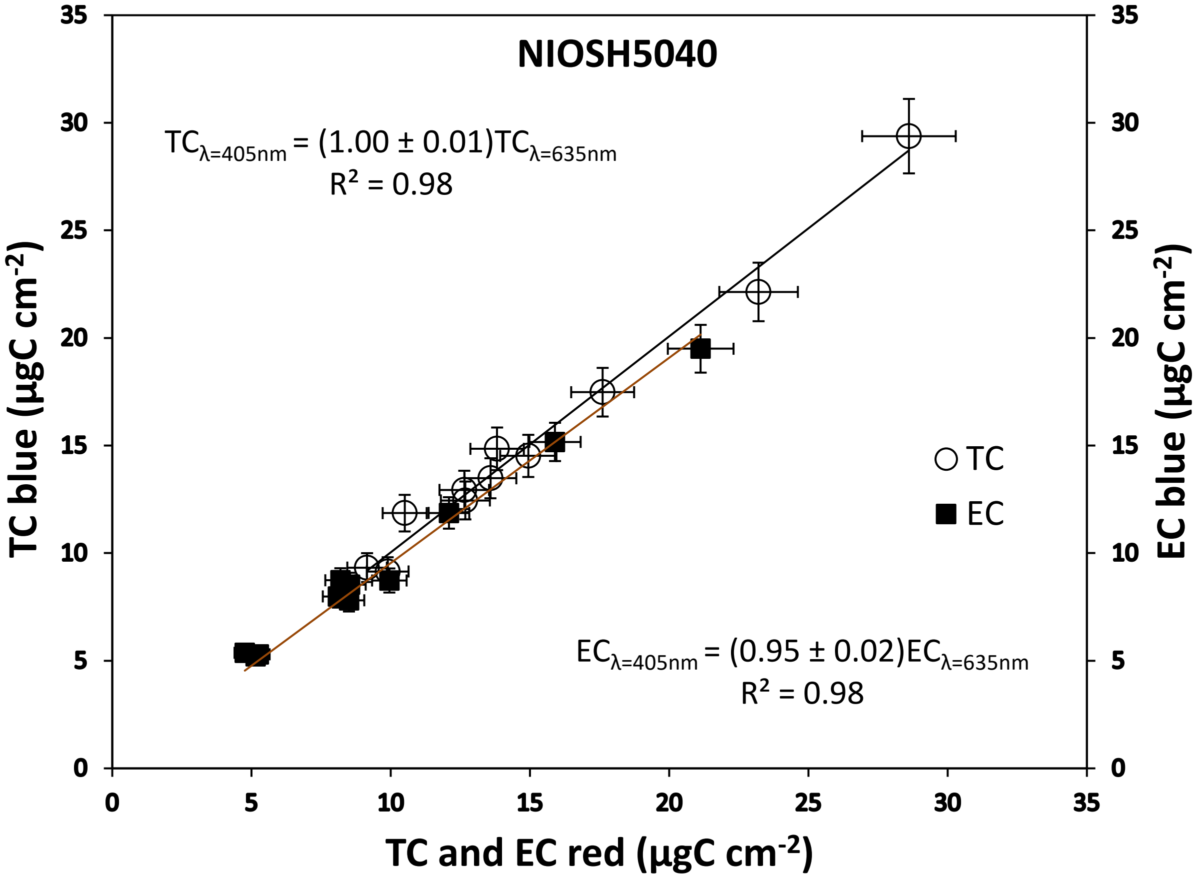
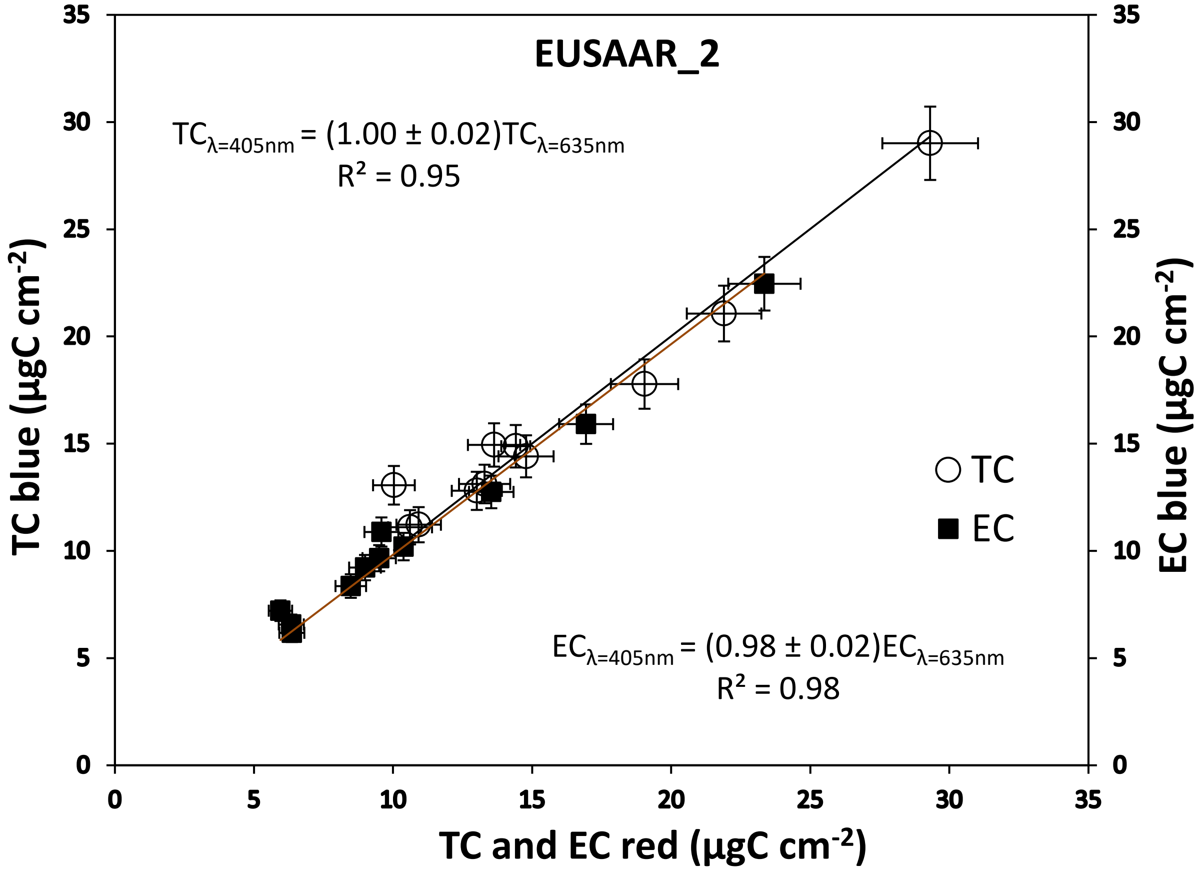


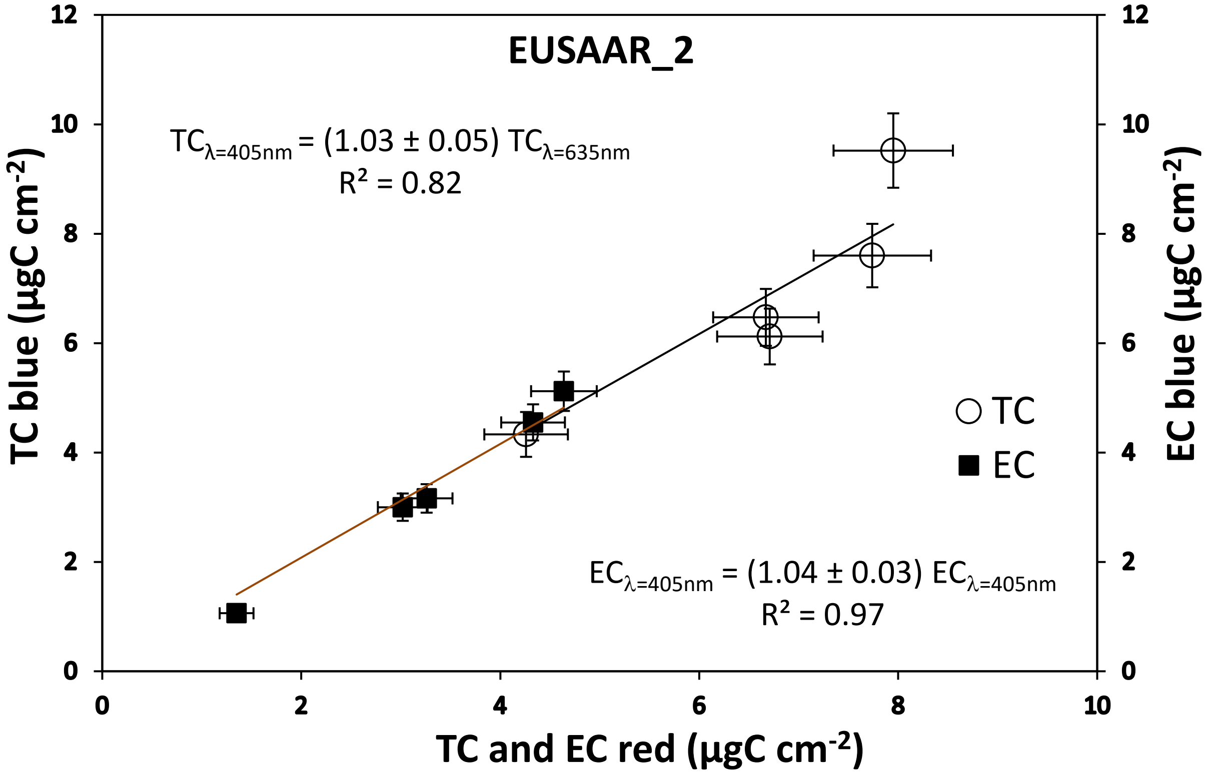
Figure 1

576 

577 

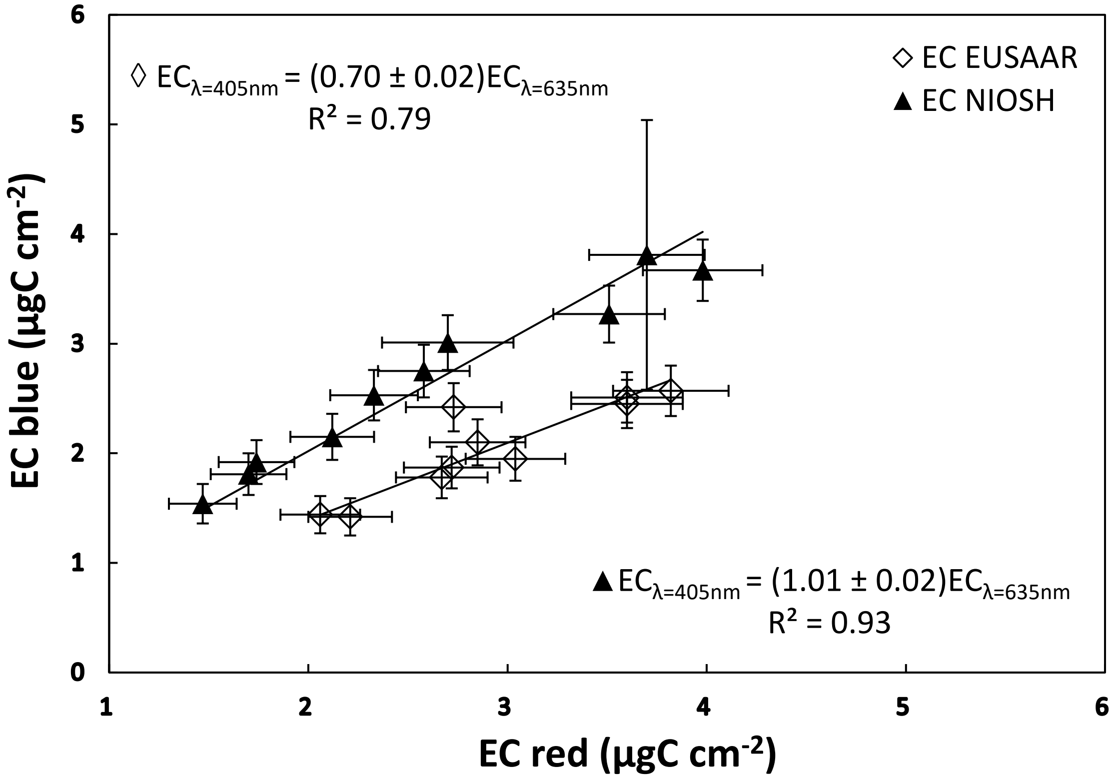
578 Figure 2

579



580

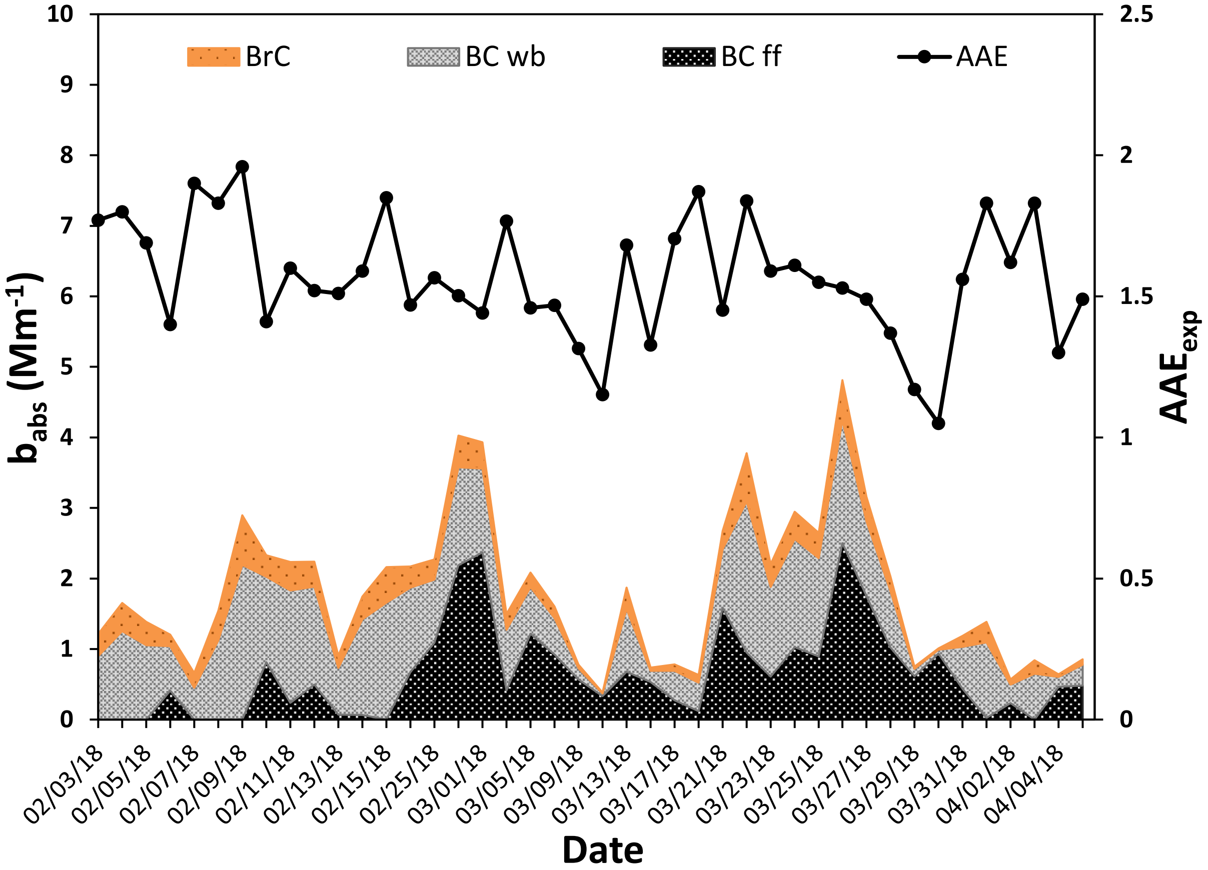
581 Figure 3



582

583 Figure 4

584


BrC
BC wb
BC ff
AAE
b_{abs} (Mm^{-1})
AAE$_{exp}$
0
1
2
3
4
5
6
7
8
9
10
0
0.5
1
1.5
2
2.5
02/03/18
02/05/18
02/07/18
02/09/18
02/11/18
02/13/18
02/15/18
02/25/18
03/01/18
03/05/18
03/09/18
03/13/18
03/17/18
03/21/18
03/23/18
03/25/18
03/27/18
03/29/18
03/31/18
04/02/18
04/04/18
Date

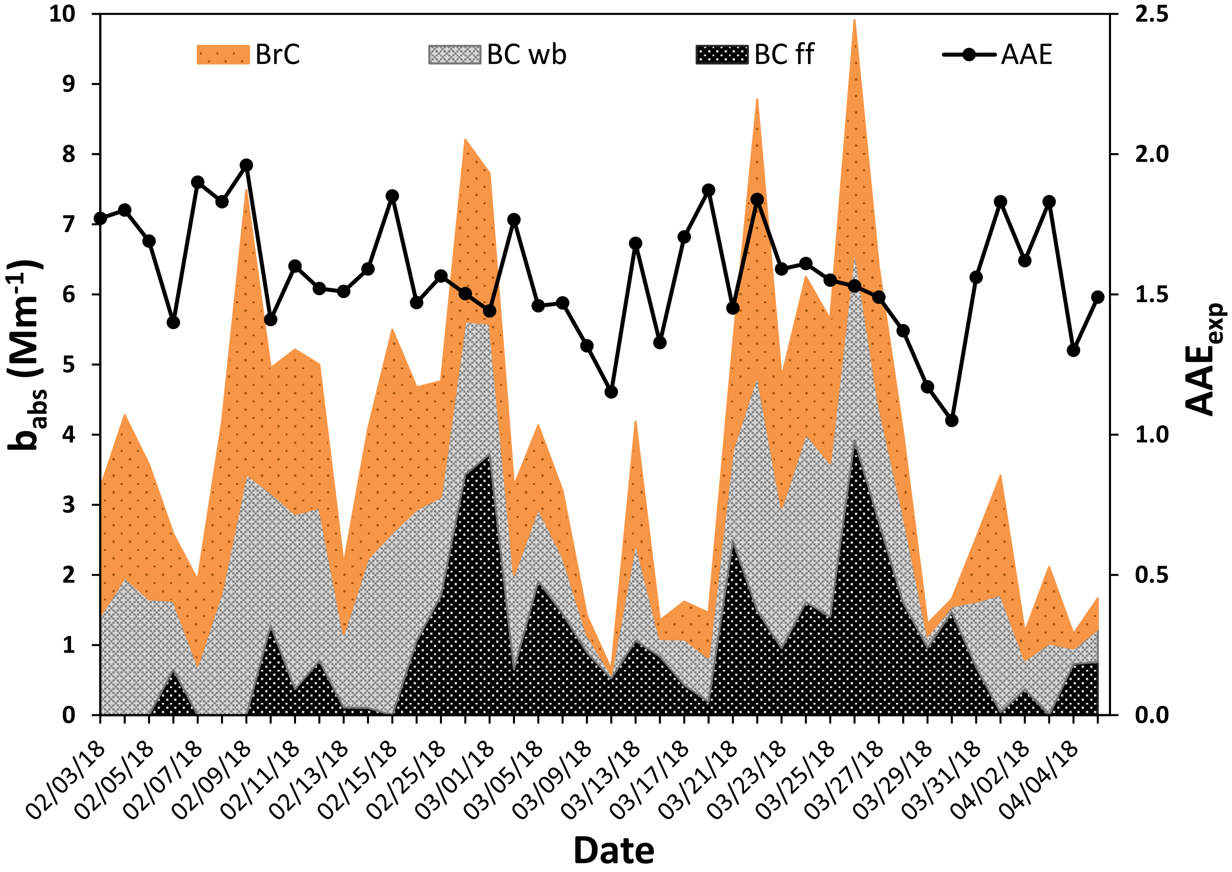
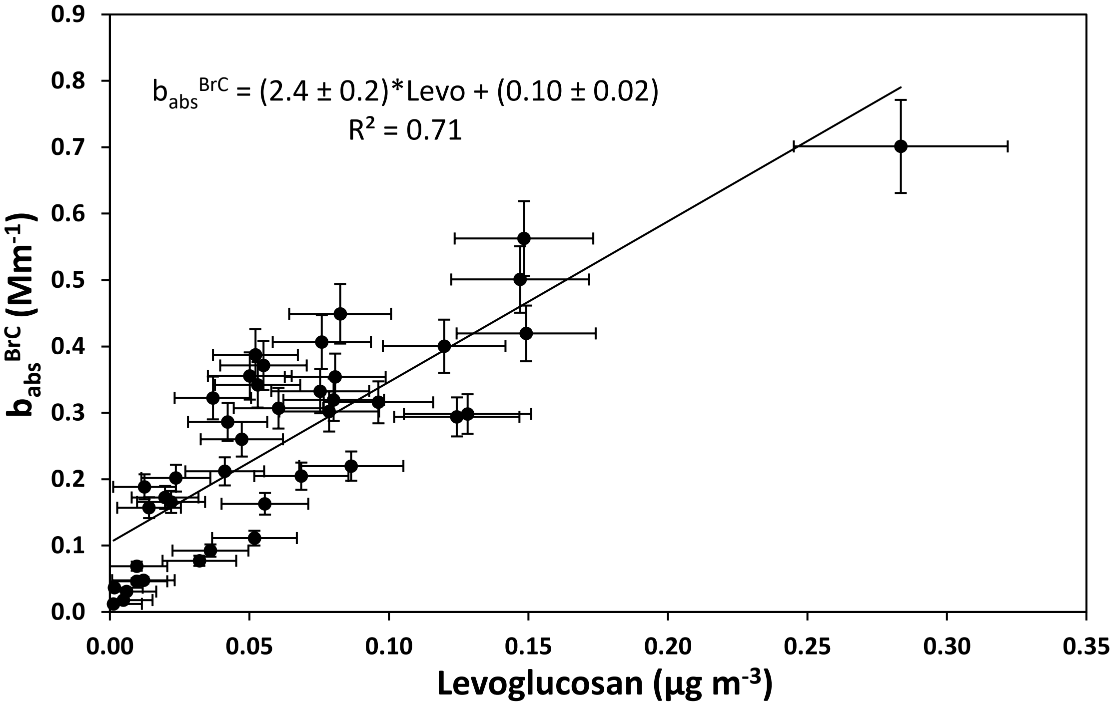

BrC
BC wb
BC ff
AAE
b_{abs} (Mm^{-1})
AAE$_{exp}$
0
1
2
3
4
5
6
7
8
9
10
0.0
0.5
1.0
1.5
2.0
2.5
02/03/18
02/05/18
02/07/18
02/09/18
02/11/18
02/13/18
02/15/18
02/25/18
03/01/18
03/05/18
03/09/18
03/13/18
03/17/18
03/21/18
03/23/18
03/25/18
03/27/18
03/29/18
03/31/18
04/02/18
04/04/18
Date

Figure 5


b_{abs}^{BrC} = (2.4 ± 0.2)*Levo + (0.10 ± 0.02)
R^2 = 0.71
b_{abs}^{BrC} (Mm^{-1})
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
Levoglucosan (µg m^{-3})

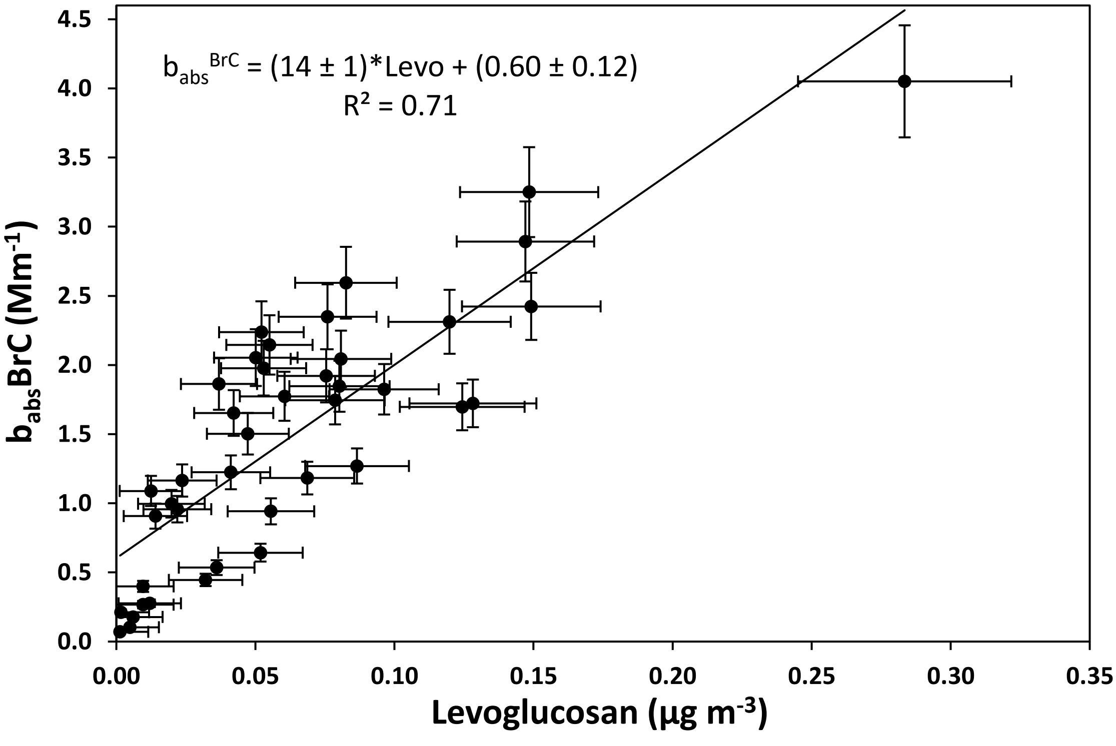

b_{abs}^{BrC} = (14 ± 1)*Levo + (0.60 ± 0.12)
R^2 = 0.71
b_{abs}BrC (Mm^{-1})
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
Levoglucosan (µg m^{-3})

Figure 6

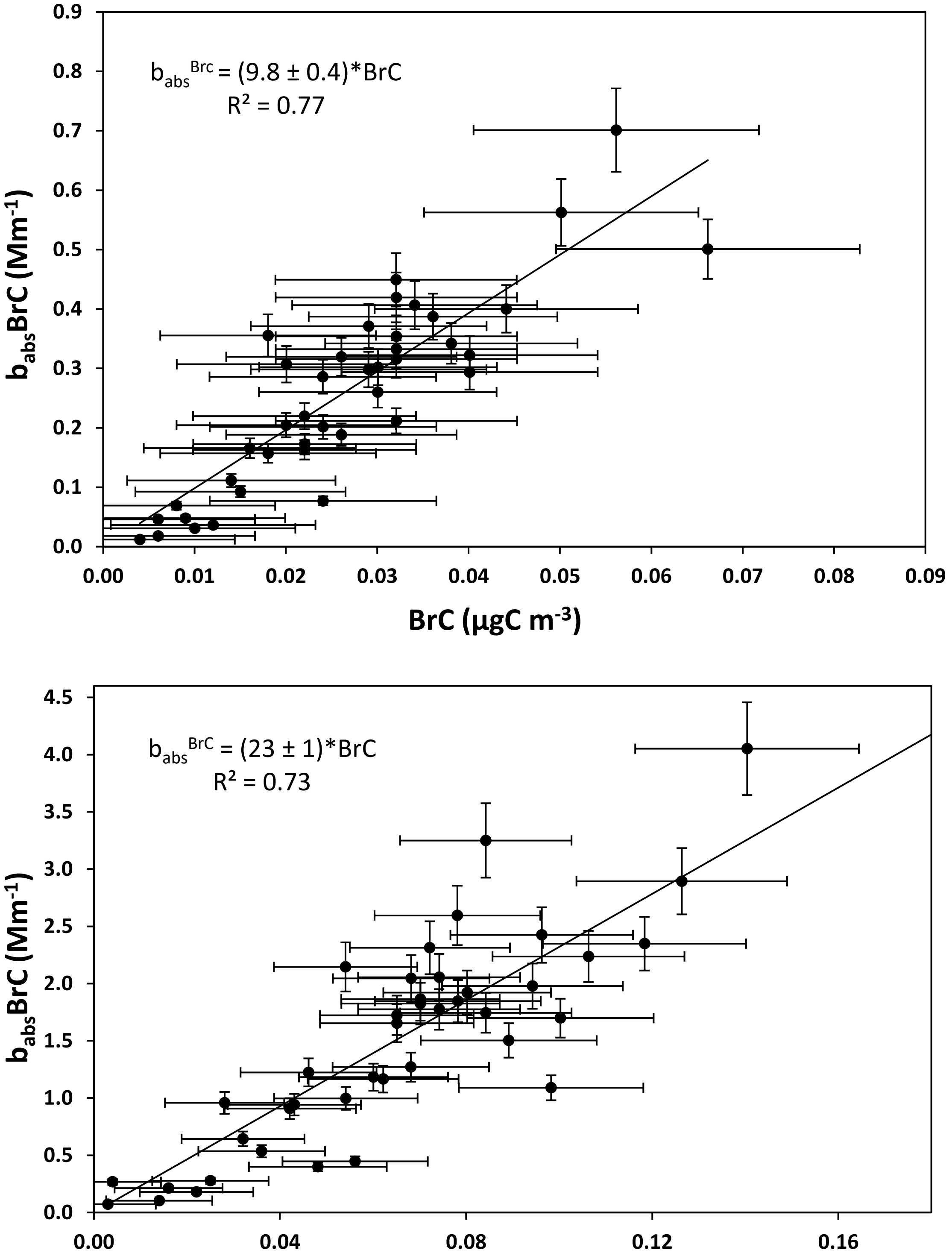

$b_{abs}^{Brc} = (9.8 \pm 0.4)*BrC$
$R^2 = 0.77$
$b_{abs}BrC$ (Mm^{-1})
BrC (µgC m^{-3})
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
0.00
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
$b_{abs}^{BrC} = (23 \pm 1)*BrC$
$R^2 = 0.73$
$b_{abs}BrC$ (Mm^{-1})
BrC (µgC m^{-3})
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
0.00
0.04
0.08
0.12
0.16

Figure 7