



Brown carbon and thermal–optical analysis: A correction based on optical multi-wavelength apportionment of atmospheric aerosols



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HIGHLIGHTS

- Aerosol absorbance due to brown carbon is measured by a multi- λ equipment.
- Brown carbon artifacts in thermo-optical OC/EC determination are considered.
- A correction methodology of the standard thermo-optical approach is introduced.
- A firmer EC/OC separation is obtained when aerosol samples containing brown carbon.
- An operative quantification of the brown carbon mass is obtained at $\lambda = 635$ nm.

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ABSTRACT

Thermo-optical analysis is widely adopted for the quantitative determination of total, TC, organic, OC and elemental, EC, Carbon in aerosol samples collected on quartz fibre filters. Nevertheless, the methodology presents several issues in particular about the artefacts related to the formation of pyrolytic carbon. It is usually neglected the uncertainty due to the possible presence of brown carbon (BrC) in the sample under analysis, i.e. the optically active fraction of OC produced by biomass burning and with characteristics intermediate between OC and EC. We introduce here a novel correction to the standard thermo-optical protocol based on the determination of the fraction of the sample absorbance due to the (possible) presence of BrC. This is achievable thanks to the coupled use of the Multi Wavelength Absorbance Analyser (MWAA) of the University of Genoa and a standard Sunset Inc. EC/OC analyser. Our correction provides a firmer OC/EC separation as well as an operative quantification of the BrC mass. The methodology has been validated against independent determination of the levoglucosan content in the same filters sent to the Sunset analysis. Corrections up to 23% in the OC and EC values, determined via the standard and new thermo-optical analysis, have been found in a set of PM₁₀ (i.e. Particulate Matter with aerodynamic diameter less than 10 μ m) samples collected wintertime at a mountain site in Northern Italy.

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1. Introduction

Carbonaceous aerosols play an important role in air quality, human health and global climate change. Although the classification of carbonaceous aerosol components is still under debate (Pöschl, 2003), total carbon (TC) is generally divided in elemental (EC) and organic carbon (OC) (Pöschl and Shiraiwa, 2015). Actually, when determined by optical methods the refractory carbon is

usually referred as black carbon (BC). Amongst atmospheric aerosols, BC is considered the most efficient light-absorber in the visible spectrum (Bond et al., 2013; and reference therein) with a weak dependence on wavelength (Bond and Bergstrom, 2006; Moosmüller et al., 2009). Another light-absorbing component of carbonaceous aerosols is the so-called brown carbon (BrC) (Andreae and Gelencsér, 2006; Pöschl, 2003) i.e. the fraction of organic carbon with increased absorbance in the blue and ultraviolet (UV) region of the solar spectrum (Moosmüller et al., 2011). Carbonaceous light-absorbing particles are typically emitted by incomplete combustion of fossil fuels related to traffic, industrial processes and domestic heating as well as by biomass burning. BrC

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consists in a fraction of carbonaceous material that presents characteristics intermediate between these two classes of pollutants. In general, carbonaceous aerosol can be subdivided following two different classifications: refractoriness and light absorption (Pöschl, 2003); this leads to different quantities that are operationally defined (EC, BC, OC, etc.). From the thermo-chemical point of view, BrC is quite refractory: it doesn't evaporate up to 400 °C in an inert atmosphere (Chow et al., 2015). From the optical point of view, it absorbs light at almost every visible wavelength but especially in the UV-blue range (Laskin et al., 2015; Olson et al., 2015).

Thermo-optical analysis (Birch and Cary, 1996; Watson et al., 2005; Hitzenger et al., 2006) is widely adopted for the quantitative determination of TC, OC and EC in aerosol samples collected on quartz fibre filters. This approach suffers of artefacts linked to the production of pyrolytic carbon during the thermal evolution (Yang and Yu, 2002; Chow et al., 2004) in an inert atmosphere, which limits the reliability of the methodology. As a matter of fact, a standard methodology for EC/OC discrimination is still missing as several thermal protocols are currently in use like NIOSH5040 (Birch and Cary, 1996), IMPROVE A (Chow et al., 2007) and EUSAAR2 (Cavalli et al., 2010). During the thermal evolution, a laser beam is sent through the sample and the transmitted (TOT) and/or reflected (TOR) light is collected and used to monitor and correct the undesired formation of pyrolytic carbon and hence to separate OC and EC. Basically, a “split point” is introduced and defined as the moment of the thermal evolution in which the laser transmittance/reflectance returns to the initial value: this way, the formation of pyrolytic carbon which makes the sample darker during the evolution in the inert atmosphere, is corrected. In both the TOT and TOR analyses, the basis assumption is that EC only can absorb the light, while OC is fully transparent at least at the wavelength of the adopted laser beam (typically in the red region). Actually, the presence of BrC, that is part of OC but also a light absorbing species at $\lambda = 635$ nm, shifts this separation towards EC, resulting in overestimated EC values and underestimated OC values (Bond and Bergstrom, 2006; Chen et al., 2015). In the standard thermo-optical approach, the initial value of the sample transmittance/reflectance is assumed to be directly proportional to the EC content in the sample under analysis, but this is no more true when BrC is also present inside the organic fraction of the aerosol. This issue was first addressed by Chen et al., 2015 by a multi-wavelength TOT/TOR instrument (Thermal Spectral Analysis – TSA). Actually, their results clearly demonstrated the role of BrC in the thermo-optical analysis, but were not conclusive since they could not disentangle the fraction of the sample absorbance due to BrC.

We have recently introduced a novel laboratory instrument, the Multi-Wavelength Absorbance Analyser, MWAA (Massabò et al., 2013), which measures both light attenuation and absorption of aerosol particles collected on a quartz fibre filter. Processing the 5- λ MWAA data by a new algorithm for optical apportionment (Massabò et al., 2015), we can estimate the fraction of light absorbed by both BC and BrC at any wavelength and in particular at $\lambda = 635$ nm. Exploiting the MWAA capabilities in the reduction of the data provided by a commercial Sunset EC/OC analyser[®], we are able to correct the OC/EC split point in the Sunset thermograms, to obtain a firmer determination of both OC and EC and to measure the BrC concentration directly in the samples under analysis. The description of such methodology and its comparison with independent chemical tracer of biomass burning (i.e. Levoglucosan, Simoneit et al., 1999; Piazzalunga et al., 2011), are the subject of the present work.

2. The aerosol absorption coefficient and the MWAA

The aerosol absorption coefficient, b_{abs} , was measured by the

Multi-Wavelength Absorbance Analyser (MWAA). The MWAA (Massabò et al., 2013, 2015) is a home-made laboratory instrument developed and installed at the Physics Department of the University of Genoa. The MWAA main features are here briefly summarized.

The MWAA is composed by 5 light emitting sources (laser diodes, $\lambda = 375, 407, 532, 635$ and 850 nm), an automatized sample-changer, and 3 low-noise UV-enhanced photodiodes. The first photodiode is placed beyond the filter in analysis for transmittance measurements (forward hemisphere), while the other two PDs are disposed at specific angles between the laser beam and the loaded filter to perform reflectance measurements (backward hemisphere). To derive the b_{abs} at each measured λ , the MWAA partially follows the approach reported by Petzold and Schönlinner (2004) and implemented in the MAAP (Multi-Angle Absorption Photometer): from the measurement of the light transmitted and back-scattered, the light angular distributions in both the forward and back hemispheres are retrieved using analytical functions. Once the light distribution is obtained in both hemispheres (Massabò et al., 2013), a radiative transfer model which takes into account the multiple scattering effects occurring within the particle-filter system, is applied (Hänel, 1987, 1994). The model returns the two parameters needed to calculate the sample absorbance (ABS – the fraction of light absorbed by the loaded filter), i.e. the total optical thickness (τ) and the aerosol-filter layer single scattering albedo (SSA). These parameters are linked to ABS through the relationship:

$$\text{ABS} = \tau (1 - \text{SSA}) \quad (1)$$

Finally, b_{abs} is given by Eq. (2):

$$b_{\text{abs}} = \text{ABS} \cdot \frac{A}{V} \quad (2)$$

where A is the active surface filter area and V is the volume of sampled air.

3. Field campaign and laboratory analyses

3.1. Samples collection

Aerosol samples used in the experiment were collected during a sampling campaign carried out in a small village (Propata, $44^{\circ}33'52.93''\text{N}$, $9^{\circ}11'05.57''\text{E}$, 970 m a.s.l.) situated in the Ligurian Apennines, Italy. PM10 aerosol samples were collected by a low-volume sampler (38.3 l min^{-1} by TCR Tecora, Italy) with filter change set every 48 h from midnight to midnight. This sampling time was chosen to collect a sufficient quantity of PM. In total, 28 PM10 samples were collected on quartz-fibre filters (Pall, 2500QAO-UP, 47 mm diameter), between November 7th, 2014 and January 7th, 2015. The rural site is characterized by consistent wood burning, especially during the cold season, as it is used for both domestic heating and cooking purposes.

Possible OC contamination of the quartz-fibre filters was assessed in each batch before sampling: maximum OC contamination was $1.5 \pm 0.3 \mu\text{g cm}^{-2}$. Due to this reason, we did no pre-fire the quartz fibre filters. Moreover, field blank filters were used to monitor any possible further contamination.

3.2. Laboratory analyses

All the samples were weighed before and after sampling in an air-conditioned room ($T = 20 \pm 1$ °C; R.H. = $50\% \pm 5\%$), after 48 h conditioning. The gravimetric determination of the PM mass was performed using an analytical microbalance (precision: $1 \mu\text{g}$) 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 analysed by MWAA to retrieve the absorption coefficient (b_{abs}) of PM at five different wavelengths. Thermal Optical Transmittance (TOT) instrument (Sunset Lab Inc.) for EC and OC determination was used adopting the EUSAAR_2 protocol (Cavalli et al., 2010). Finally, a portion of the same quartz-fibre filters underwent a chemical determination of the Levoglucosan concentration by High Performance Anion Exchange Chromatography coupled with Pulsed Amperometric Detection (Piazzalunga et al., 2010).

4. Multi-wavelength analysis and optical apportionment

The spectral dependence of the aerosol absorption coefficient (b_{abs}) can be generally described by the power-law relationship $b_{\text{abs}}(\lambda) \sim \lambda^{-\text{AAE}}$ where the AAE is the Ångström Absorption Exponent. Several works in literature show how AAE values are linked to 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). In many studies, the spectral dependence of the aerosol has been exploited to identify and apportion different sources of carbonaceous aerosol (e.g. Sandradewi et al., 2008; Favez et al., 2010; Lack and Langridge, 2013; Massabò et al., 2013, 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).

Fig. 1 shows the trend of the experimental AAE (AAE_{exp}) for the Propata dataset obtained fitting the b_{abs} values measured by the MWAA at 5 wavelengths: it ranges between 1.31 and 1.88 with a mean value of 1.55 ± 0.15 , thus indicating a substantial presence of wood burning in the sampling area. In Massabò et al. (2015), a new optical apportionment model (the “MWAA approach”) 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 ($b_{\text{abs}}^{\text{BrC}}$) at each measured λ . It is worthy to note that, at the basis of the MWAA approach, there is the assumption that BrC is produced by wood combustion only (see §4 in Massabò et al., 2015; Zheng et al., 2013). Here we focus on the optical apportionment at $\lambda = 635 \text{ nm}$ only, since this is the wavelength of the laser diode used

in the Sunset instrument. In Fig. 1, the optical apportionment at 635 nm is also reported: at this wavelength, light absorption resulted mainly due to BC from both fossil fuel (FF) and biomass burning (WB) while $b_{\text{abs}}^{\text{BrC}}$ values ranged between 4% and 10% (of total b_{abs}), with the notable exception of some days in which it reached values of ~20% in correspondence of $\text{AAE}_{\text{exp}} > 1.8$. The consistency of the calculated $b_{\text{abs}}^{\text{BrC}}$ values was checked by comparison with levoglucosan (*Levo*, in the following) concentration values. Fig. 2 shows the correlation study ($R^2 = 0.96$) between the two parameters which gave:

$$b_{\text{abs}}^{\text{BrC}} = (2.39 \pm 0.10) \text{Levo} + (0.05 \pm 0.01) \quad (3)$$

The average α_{BrC} value of the analysed samples turned out to be $\alpha_{\text{BrC}} = 3.8 \pm 0.2$, in agreement with previous literature works (Yang et al., 2009; Massabò et al., 2015; Chen et al., 2015). Actually, values of $\alpha_{\text{BrC-atn}}$ of 4.2–4.8 have been reported in Chen et al. (2015). However, such values have been obtained from attenuation data (this is the reason of the atn subscript in $\alpha_{\text{BrC-atn}}$): when we reduced in the same way the MWAA raw data of the Propata dataset we got $\alpha_{\text{BrC-atn}} = 4.4 \pm 0.2$.

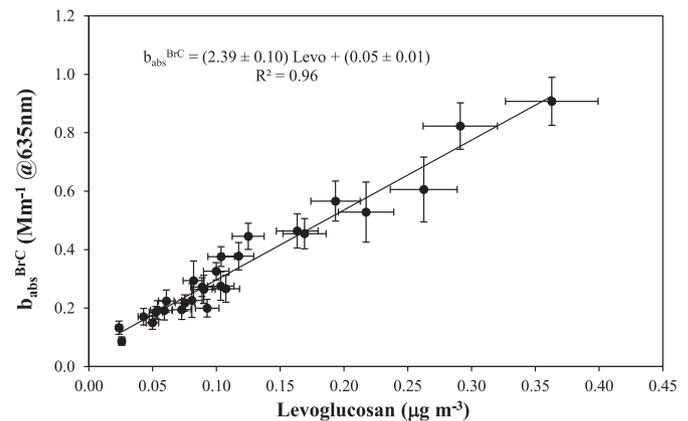


Fig. 2. Aerosol absorption coefficient apportioned to Brown Carbon ($b_{\text{abs}}^{\text{BrC}}$) @635 nm vs. levoglucosan concentrations.

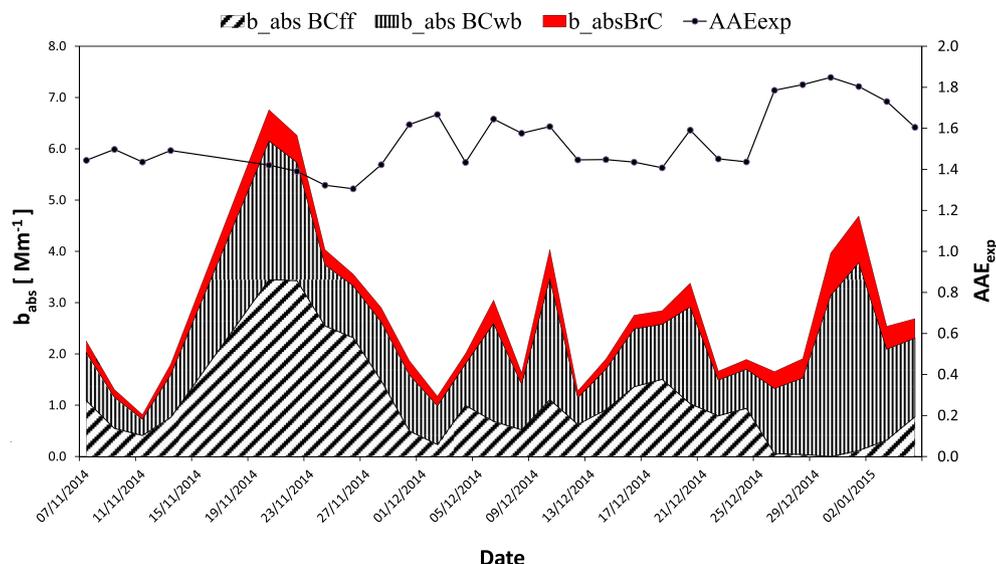


Fig. 1. Primary axis: Optical apportionment of the aerosol absorption coefficient (b_{abs}) @ $\lambda = 635 \text{ nm}$. Secondary axis: experimental AAE values obtained by fitting the measured b_{abs} values with a power-law relationship $b_{\text{abs}}(\lambda) \sim \lambda^{-\text{AAE}}$. The MWAA model attributed to BrC up to 21% of the total b_{abs} in correspondence of $\text{AAE} = 1.88$ (01/01–02/2015).

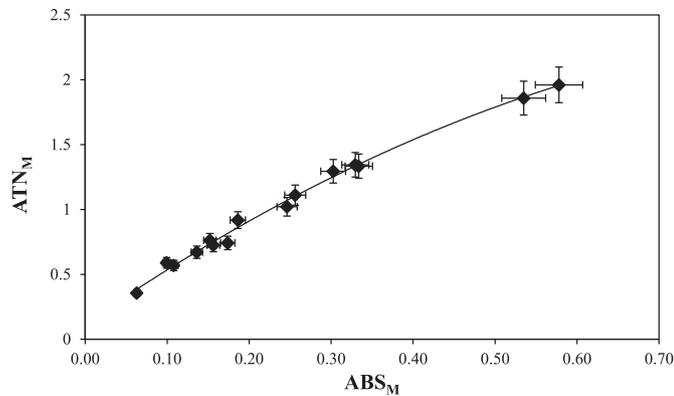


Fig. 3. Comparison between attenuation (ATN_M) and absorbance (ABS_M) values measured by the MWAA. The points are very well fitted by a polynomial curve of the second order ($R^2 = 0.99$).

5. Brown carbon and split point correction in TOT analyses

The rationale of the thermo-optical analysis of carbonaceous aerosol is well known; however, a brief summary deserves some space. TOT/TOR analysis generally includes two sequential thermal ramps performed by filling the oven with different gases (100% He and 90% He + 10% O₂, respectively). The pyrolytic combustion in the He-phase excludes the possibility of distinguishing OC and EC simply quantifying the carbon evolved in CO₂ during the He and He + O₂ phases, respectively. In fact, during the first thermal ramp, a fraction of OC gets charred becoming pyrolytic OC (OC_{pyr}), a compound with thermo-optical characteristics very similar to those of EC. Moreover, pyrolysis is favoured by the presence of metals and/or highly oxidized compounds on the loaded-filter (Chow et al., 2004); due to this effect the EC fraction would be overestimated. To solve this issue, the EC and OC_{pyr} optical properties are exploited. A laser beam is used to monitor the loaded-filter transmittance (or reflectance): during the He-phase, part of the non-light-absorbing OC transforms in highly-absorbent OC_{pyr}, causing a variation (decrease) in the sample transmittance/reflectance. The quantification of EC and OC is then carried out *a posteriori*, identifying the time during the He + O₂ phase in which the laser signal comes back to the original value measured at the beginning of the analysis. The quantity of Carbon evolved before this “split point” is thus operationally defined as OC, while the Carbon evolved afterwards is consequently considered to be EC. Finally both the split point position and OC/EC are quantities defined on an operational basis.

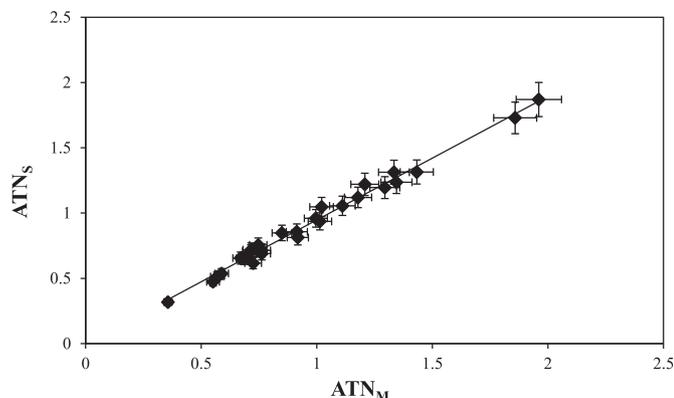


Fig. 4. Comparison between attenuation values measured by the MWAA (ATN_M) and by the Sunset (ATN_S).

This *modus operandi* relies on the hypothesis that at $\lambda = 635$ nm EC only can absorb light, while OC is considered to be completely transparent. Actually, BrC is an organic compound optically active in the visible range and its thermo-optical properties are intermediate between those of EC and OC. As pointed out in §4, BrC shows a steeper spectral dependence than EC and this leads to higher AAE values.

The MWAA provides the contribution of BrC to ABS at $\lambda = 635$ nm (see Eq. (2)) for each single sample. Even if the BrC absorbance increases dramatically in the blue-UV region of the electromagnetic spectrum, biomass burning aerosol can show a significant absorbance at $\lambda = 635$ nm too. Actually, in the samples collected during the experiment (see §4), up to 20% of the absorbed light was due to BrC (ABS_{BrC}). Although the MWAA has been originally designed for absorbance measurements, attenuation values can be easily deduced by the instrument raw data as:

$$ATN_M = -\ln\left(\frac{I_{M,L}}{I_{M,B}}\right) \quad (4)$$

where $I_{M,L}$ and $I_{M,B}$ are the light intensity measured by the MWAA photodiode (situated in the forward hemisphere) for the loaded and blank filter (i.e. before the sampling), respectively. Fig. 3 shows the correlation between the ABS_M and ATN_M (the subscript M stands for “MWAA”) values measured by the MWAA at $\lambda = 635$ nm with the 28 filter samples collected in Propata; data points were very good fitted ($R^2 > 0.99$) by a polynomial curve of the second order:

$$ATN_M = -2.08(ABS_M)^2 + 4.38(ABS_M) + 0.12 \quad (5)$$

Since ABS_{BrC} values and the relation between ABS_M and ATN_M were known, the value of ATN_M , free of the BrC contribution (in the following ATN_{M,BrC^c}), could be calculated as:

$$ATN_{M,BrC^c} = -2.08(ABS_M - ABS_{M,BrC})^2 + 4.38(ABS_M - ABS_{M,BrC}) + 0.12 \quad (6)$$

where $ABS_{M,BrC}$ is the absorbance apportioned by the MWAA model to the BrC content at $\lambda = 635$ nm. This correction could be done assuming that: 1) the effect of BrC on the not-light-absorbing properties of the particle-loaded filter is almost negligible and 2) ABS is an additive quantity (this assumption is anyway at the basis of the MWAA approach; for further details, see Massabò et al., 2015).

When the same samples were subsequently analysed by the EC/OC analyser, ATN values (ATN_S , the subscript stands for “Sunset”) could be extracted from the instrument raw data, considering the values of the laser transmittance measured at the beginning ($I_{S,L}$) and at the end of each analysis ($I_{S,B}$):

$$ATN_S = -\ln\left(\frac{I_{S,L}}{I_{S,B}}\right) \quad (7)$$

Fig. 4 shows the correlation between the ATN values measured, on the same Propata filters, by the Sunset instrument and the MWAA. The regression study showed a very good correlation ($R^2 = 0.99$) as well as a slope close to unity:

$$ATN_S = (0.95 \pm 0.01) ATN_M \quad (8)$$

With this relation and with the ATN_{M,BrC^c} extracted from the MWAA data, we could then calculate the values of ATN_S that it would have been found if BrC were not present in the filter samples, ATN_{S,BrC^c} . Finally, a new starting value of the laser transmittance was calculated for each single sample, as shown as an example in

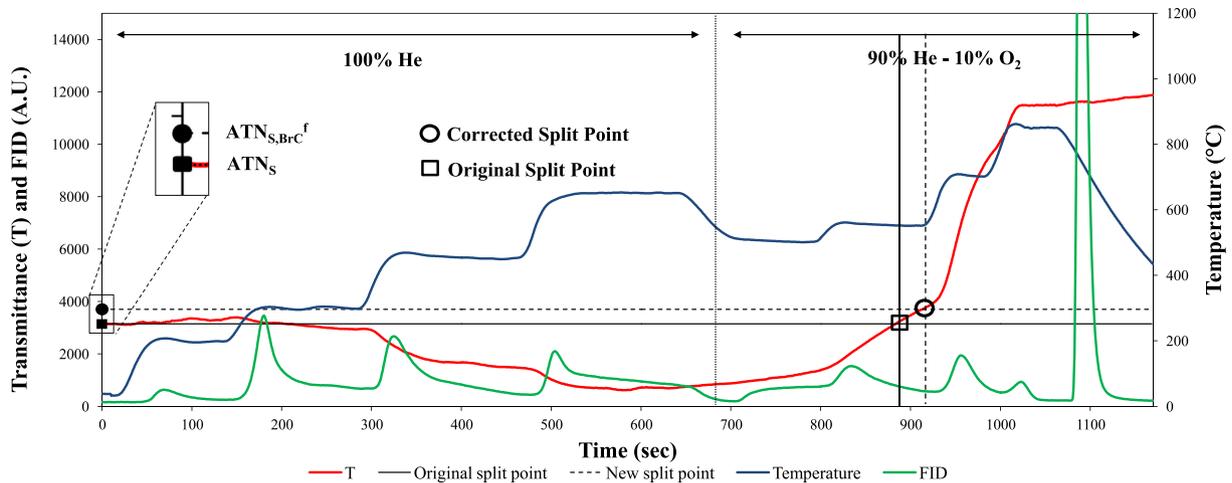


Fig. 5. Example thermogram showing the original split point – empty square dot (identified by the ATN_S value, i.e. non-corrected for BrC presence) and the new split point – empty round dot (identified by ATN_{S,BrC^f} , i.e. corrected for BrC presence). The new split point is rightmost of the original one leading to a new EC/OC separation.

Fig. 5. This led to a new position of the split point, rightmost of the original one, and consequently to lower EC and higher OC values. This new OC/EC separation is congruent with the BrC composition/origin: with the “standard” split point, BrC gets summed together with EC, while using the corrected split point it is correctly included in the OC fraction. Following the operative feature of the thermo-optical approach for EC/OC separation, an “operative” BrC mass (OC_{BrC}) was thus derived as:

$$OC_{BrC} = OC_{cor} - OC_{std} \quad (9)$$

where OC_{std} and OC_{cor} are the OC values returned by the thermo-optical analysis respectively in the standard and corrected way. **Fig. 6** reports a summary of the EC_{std} , EC_{cor} , OC_{std} , and OC_{cor} values

retrieved from the Propata data set. The differences in mass quantification were particularly consistent for EC with a maximum of 25% for sample 26 (corresponding to sampling days 01/01–02/2015). **Fig. 7a** reports the correlation study ($R^2 = 0.89$) between OC_{BrC} and $Levo$:

$$OC_{BrC} = (0.30 \pm 0.01) Levo \quad (10)$$

while **Fig. 7b** highlights the relationship found between OC_{BrC} and b_{abs}^{BrC} ($R^2 = 0.85$):

$$b_{abs}^{BrC} = (7.0 \pm 0.6) OC_{BrC} + 0.1 \quad (11)$$

Adopting the correlation study shown in **Fig. 7b**, the OC_{BrC} mass absorption cross-section, $MAC(OC_{BrC})$, was retrieved resulting in

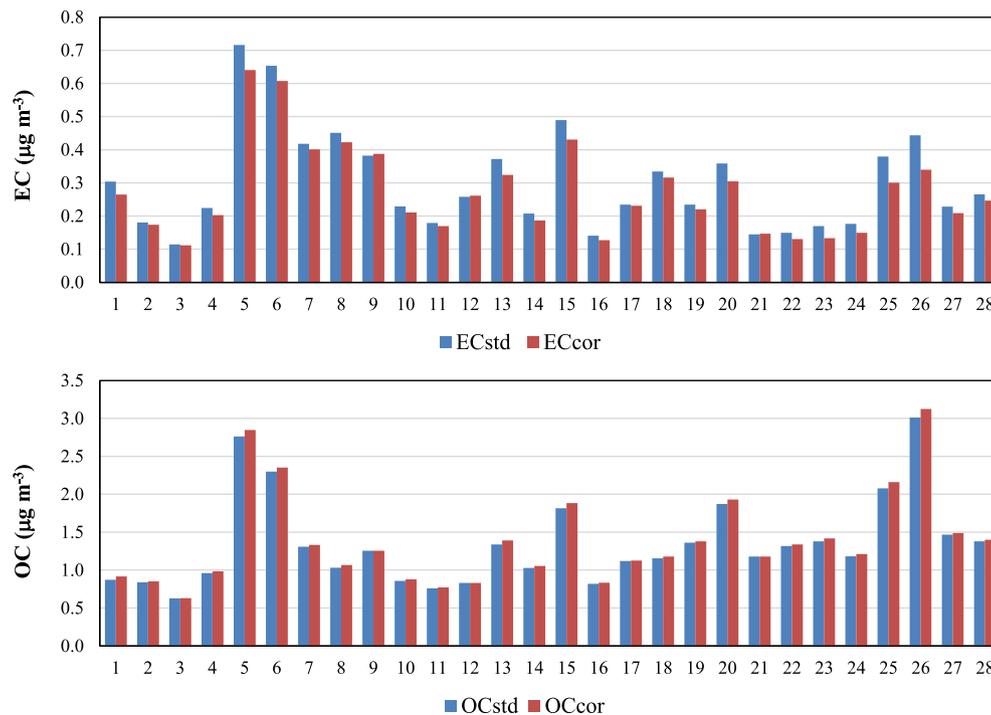


Fig. 6. Summary of the EC_{std} , EC_{cor} , OC_{std} , and OC_{cor} values retrieved for the 28 individual samples of the Propata data set.

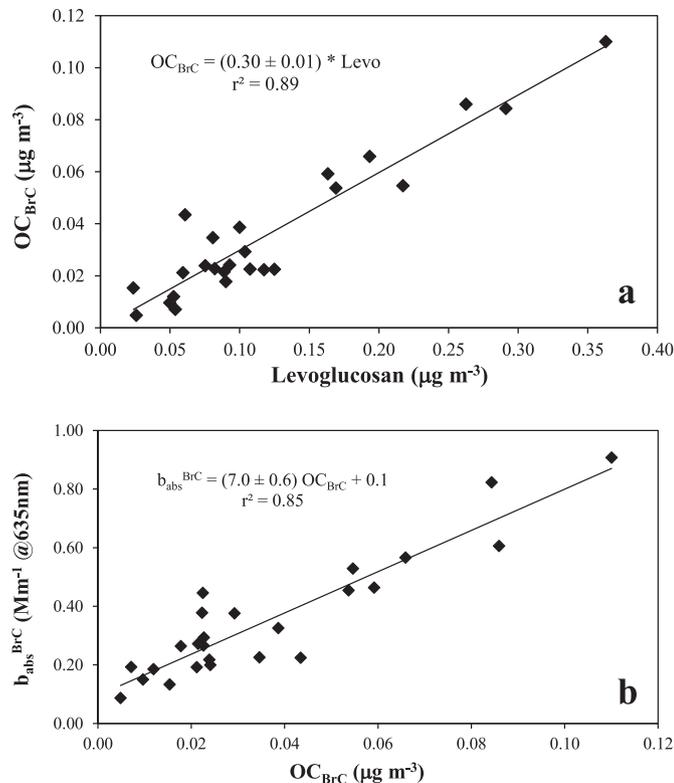


Fig. 7. a: Comparison between the resulting operative BrC mass ($OC_{BrC} = OC_{cor} - OC_{std}$) and levoglucosan concentrations. b: Comparison between the aerosol absorption coefficient apportioned to Brown Carbon ($b_{abs}^{BrC} @ 635nm$) and OC_{BrC} .

about $7.0 \text{ m}^2 \text{ g}^{-1}$. Finally, on the basis of the optical OC apportionment methodology reported in Massabò et al. (2015), the OC_{BrC} values turned out to be around 6% of the OC produced by wood combustion, OC_{WB} , and therefore $MAC(OC_{WB}) \approx (0.4 \pm 0.1) \text{ m}^2 \text{ g}^{-1}$. Previous literature works (Feng et al., 2013; Laskin et al., 2015; and therein cited literature) report MAC values of BrC and/or related OC ranging in a quite large interval. However, a comparison with previous results is complex given the substantial differences in adopted definitions and methodologies.

6. Conclusions

We introduced a correction of the standard thermo-optical analysis devoted to OC/EC quantification, to take into account the possible presence of BrC in the aerosol collected by quartz fibre filter. The correction is possible thanks to the use of the Multi Wavelength Absorbance Analyser, MWAA (Massabò et al., 2013, 2015), which provides the aerosol absorbance values at 5 different wavelengths from IR to UV. The fraction of the light absorbance and extinction due to the possible presence of BrC is measured in each single sample and used to correct the position of the split-point which usually divides OC from EC in the thermograms of the thermo-optical analysis. This way, a firmer OC/EC separation as well as a quantification of the BrC mass can be obtained. With a set of samples collected wintertime in the Italian Apennines, the mass absorption coefficient of OC produced by biomass burning was estimated to be around $0.4 \text{ m}^2 \text{ g}^{-1}$.

Finally, we underline that the novel methodology adopts the same operative approach of the thermo-optical analysis: the dependence of the results on the wavelength of the laser beam used to correct the charring effect needs to be further investigated, following the path tracked by Chen et al. (2015) and Chow et al.

(2015). Despite these possible limitations, our results point toward the development of a next-generation thermo-optical instrument equipped to provide multi-wavelength absorbance monitoring during the thermal cycle.

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