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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 μm) samples collected wintertime at a mountain site in Northern Italy.

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 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

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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; Hitzenberger 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:

$$\mathrm{ABS} = \tau\ (1 - \mathrm{SSA}) \tag{1}$$

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

$$b_{abs} = \mathrm{ABS} \cdot \frac{A}{V} \tag{2}$$

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°33′52.93″N, 9°11′05.57″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 $1.5 \pm 0.3\ \mu\mathrm{g\ cm}^{-2}$. 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 ± 1 °C; R.H. = 50% ± 5%), after 48 h 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 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