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Multi-wavelength optical determination of black and brown carbon in atmospheric aerosols

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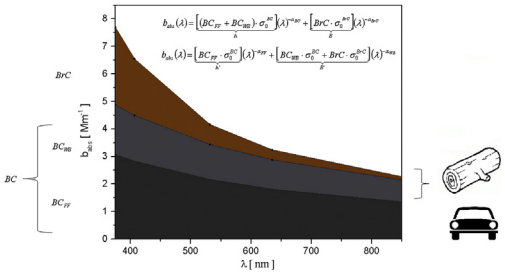
HIGHLIGHTS

- Aerosol light absorption at several λs due to Black and Brown Carbon is measured.
- The value of Ångström exponent of Brown Carbon is directly extracted by raw data.
- The new apportionment procedure disentangles fossil and wood burning contributions.
- Equivalent Black Carbon and Organic Carbon are separately apportioned.
- The procedure is validated against independent Levoglucosan and ^{14}C determination.

GRAPHICAL ABSTRACT



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ABSTRACT

In this paper, a new way to apportion the absorption coefficient (b_{abs}) of carbonaceous atmospheric aerosols starting from a multi-wavelength optical analysis is shown. This methodology can disentangle and quantify the contribution to total absorption of equivalent black carbon (EBC) emitted by wood burning (EBC_{WB}) and fossil fuel (EBC_{FF}) as well as brown carbon (BrC) due to incomplete combustion. The method uses the information gathered at five different wavelengths in a renewed and upgraded version of the approach usually referred to as Aethalometer model. Moreover, we present the results of an apportionment study of carbonaceous aerosol sources performed in a rural area and in a coastal city, both located in the North-West of Italy. Results obtained by the proposed approach are validated against independent measurements of levoglucosan and radiocarbon. At the rural site the EBC_{WB} and EBC_{FF} relative contributions are about 40% and 60% in winter and 15% and 85% in summer, respectively. At the coastal urban site, EBC_{WB} and EBC_{FF} are about 15% and 85% during fall. The OC contribution to the wood

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burning source at the rural site results approximately 50% in winter and 10% in summer and about 15% at the coastal urban site in fall. The new methodology also provides a direct measurement of the absorption Ångström exponent of BrC (α_{BrC}) which resulted $\alpha_{BrC} = 3.95 \pm 0.20$.

1. Introduction

Carbonaceous aerosols play an important role in environmental issues like 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 black carbon (BC), organic carbon (OC) and carbonate carbon (CC).

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 wavelenght (λ) (Moosmüller et al., 2009). Another light-absorbing component of carbonaceous aerosols is the so-called brown carbon (BrC) (Andreae and Gelencsér, 2006; Pöschl, 2003), 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.

It is worthy to note that beyond carbonaceous aerosols, also other aerosol components show strong light-absorbing properties like iron oxides in mineral dust particles (Linke et al., 2006).

The spectral dependence of the aerosol absorption coefficient (b_{abs}) is generally described by the power–law relationship $b_{abs}(\lambda) \propto \lambda^{-AAE}$ where the AAE is the Ångström absorption exponent (Moosmüller et al., 2011). In literature works AAE has been shown to be sensitive to aerosol chemical composition but also to particle size and morphology (e.g. Kirchstetter et al., 2004; Lewis et al., 2008; Utry et al., 2014). In a large number of cases, it has been exploited as a chemically selective parameter useful to identify the aerosol origin and apportion sources for different carbonaceous aerosols (Sandradewi et al., 2008; Ajtai et al., 2010; Favez et al., 2010; Flowers et al., 2010; Filep et al., 2013; Utry et al., 2013); nevertheless, Utry et al. (2014) claim that the assessment of aerosol microphysical properties is needed to retrieve more accurate results on the aerosol absorption properties. AAE values around 1 have been reported for BC and up to 9.5 for BrC (Lack and Langridge, 2013).

An advantage of the AAE determination in aerosol samples by multi-λ techniques is the possibility of performing on-line source apportionment studies as done by many authors in recent years to evaluate woodsmoke and traffic contributions adopting the so-called Aethalometer model (Sandradewi et al., 2008; Favez et al., 2010) thus avoiding time consuming laboratory analyses.

At the state of the art the measurement of light absorption is still challenging (Andreae, 2001; Moosmüller et al., 2011), notwithstanding filter-based on-line techniques (e.g. the Aethalometer; the Particle Soot Absorption Photometer; the Multi Angle Absorption Photometer, among others) are widespread but – with the exception of the Aethalometer – multi-λ analysis is generally not implemented. There are some important drawbacks to be addressed in order to get reliable values from these filter-based instruments as it is well known that they are affected by measurement and sampling artifacts (e.g. effects due to multiple scatterings, to particle shadowing due to filter loading, absorption of organics; Bond et al., 1999; Collaud Coen et al., 2010; Vecchi et al., 2014; among others). Although not very widespread yet, photacoustic spectroscopy operated at multi-λ (Lewis et al., 2008; Ajtai et al., 2010; Flowers et al., 2010) is currently the only method capable to overcome the above mentioned drawbacks in absorption measurements.

At the University of Genoa a Multi-Wavelength Absorbance Analyzer (MWAA) has been recently developed (Massabò et al., 2013) basing on the single-λ Multi Angle Absorption Photometer concept (MAAP, Petzold and Schölinner, 2004; Petzold et al., 2005). Such instrumentation measures both transmitted and scattered light in the forward and back hemispheres thus reducing the cross-sensitivity to aerosol scattering components and filter loading effects (Müller et al., 2011). This approach does not need a posteriori data corrections necessary when attenuation measurements only are performed (e.g. Collaud Coen et al., 2010): such corrections are typically composition dependent and prevent real-time accurate source apportionment.

In this work, we present a new apportionment methodology together with an original data reduction approach developed using an up-graded version of the MWAA serving reliable b_{abs} data at different wavelengths. From the direct apportionment of BC and BrC spectral absorption properties, the contributions of fossil fuels (FF) and wood burning (WB) to the carbonaceous aerosols concentration can be disentangled.

2. The Multi-Wavelength Absorbance Analyzer (MWAA)

2.1. Set-up

A detailed description of the original MWAA set-up is given in Massabò et al. (2013) and in the following only major changes and upgrades will be reported.

The MWAA is basically composed by light emitting sources, an automatized sample-changer, and 4 low-noise UV-enhanced photodiodes. In the original configuration three low-power laser diodes (λ = 407, 635, 850 nm) were displaced on a slide and manually aligned thanks to mechanical benchmarks. In the new configuration, two laser diodes with λ = 375 nm and 532 nm (World Star Tech) have been added. A motorized stage has been added to interchange the laser sources thus improving the system stability and reproducibility and facilitating the analysis of many samples.

The 5-λ b_{abs} measurements are exploited in the model proposed in this paper to retrieve more accurate results (see §3). In particular, measurement at UV wavelength is useful because the absorption properties of atmospheric aerosols at this λ are generally poorly known and brown carbon is expected to strongly absorb in this