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Characterization of atmospheric black carbon and co-pollutants in urban and rural areas of Spain

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HIGHLIGHTS

- One-year black carbon (BC) experimental study at three different locations in Spain.
- Estimation of fossil fuel and biomass burning absorption Ångström exponents.
- Source apportionment of black carbon from fossil fuel and biomass burning.
- Dominance of fossil fuel at urban sites and biomass burning in winter at rural area.
- Relationship between BC with biomass burning tracers, organic and elemental carbon.

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ABSTRACT

A one-year black carbon (BC) experimental study was performed at three different locations (urban traffic, urban background, rural) in Spain with different equivalent BC (eBC) source characteristics by means of multi-wavelength Aethalometers. The Aethalometer model was used for the source apportionment study, based on the difference in absorption spectral dependence of emissions from biomass burning (bb) and fossil fuel (ff) combustion. Most studies use a single bb and ff absorption Ångström exponent (AAE) pair (AAE_{bb} and AAE_{ff}), however in this work we use a range of AAE values associated with fossil fuel and biomass burning based on the available measurements, which represents more properly all conditions. A sensitivity analysis of the source specific AAE was carried out to determine the most appropriate AAE values, being site dependent and seasonally variable. Here we present a methodology for the determination of the ranges of AAE_{bb} and AAE_{ff} by evaluating the correlations between the source apportionment of eBC using the Aethalometer model with four biomass burning tracers measured at the rural site. The best combination was AAE_{bb} = [1.63–1.74] and AAE_{ff} = [0.97–1.12]. Mean eBC values (±SD) obtained during the period of study were 3.70 ± 3.73 μg m^{-3} at the traffic urban site, 2.33 ± 2.96 μg m^{-3} at the urban background location, and 2.61 ± 5.04 μg m^{-3} in the rural area. High contributions of eBC to the PM_{10} mass were found (values up to 21% in winter), but with high eBC/PM_{10} variability. The hourly mean eBC_{ff} and eBC_{bb} concentrations varied from 0 to 51 μg m^{-3} and from 0 to 50 μg m^{-3} at the three sites, respectively, exhibiting distinct seasonal and daily patterns. The fossil fuel combustion was the dominant eBC source at the urban sites, while biomass burning dominated during the cold season (88% of eBC_{bb}) in the rural area. Daily $PM_{2.5}$ and PM_{10} samples were collected using high-volume air samplers and analyzed for OC and EC. Analysis of biomass burning tracers and organic (OC)

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and elemental (EC) carbon in the rural area indicate that biomass combustion is the main source, while OC and EC indicate a lower influence of this source at the urban site.

1. Introduction

Atmospheric aerosols influence the Earth's energy balance both directly, through absorption and scattering of solar radiation in the atmosphere (Shine and Foster, 1999; Haywood and Boucher, 2000; Satheesh and Krishnamoorthy, 2005; IPCC, 2007), and indirectly, by acting as cloud condensation nuclei or ice nuclei (Twomey, 1974; Albrecht, 1989; Lohmann and Feichter, 2005; IPCC, 2013). Some aerosol components (i.e. black carbon) may have a net warming impact, while others (i.e. nitrates, sulfates, organic carbon, etc.) may have a cooling effect (Chýlek and Coakley, 1974; IPCC, 2013). At the same time, aerosols reduce visibility, have an important impact on air quality, and also adversely affect human health (Dockery et al., 1993; Horvath, 1995; Beeson et al., 1998; Harrison and Yin, 2000; Pope et al., 2002; Wang and Christopher, 2003; Pope and Dockery, 2006).

The use of terms such as soot, BC, black smoke (BS), EC, light-absorbing aerosols, etc., has caused a great deal of confusion within the air quality monitoring and aerosol research communities. To avoid this, the Global Atmospheric Watch (GAW) Scientific Advisory Group (GAW/WMO, 2012; Petzold et al., 2013) recommended that when BC is measured using optical techniques, the term equivalent black carbon (eBC) should be used instead of BC to stress that the determined optical signal gives an equivalent mass concentration to the measured absorption.

Even if the chemical composition of aerosols is characterized by large spatial and temporal variability (Moorthy et al., 2009; Mohr et al., 2011; Piazzola et al., 2012; Abdeen et al., 2014), carbonaceous aerosols typically comprise more than half of the submicron fraction of atmospheric particulate matter (PM) (Gelencsér, 2004; Putaud et al., 2004, 2010; Zhu et al., 2014). The major components of carbonaceous particulate matter in the atmosphere are organic carbon (OC) and a refractory (and also highly light absorbing) fraction resistant to oxidation at temperatures below 400 °C, known as elemental carbon (EC) (Penner and Novakov, 1996). When the elemental carbon is measured using optical methods relying on its strongly light absorbing character, it is called black carbon (BC). The carbonate or mineral carbon (CC) is usually a minor contributor to the total carbonaceous aerosol (Seinfeld and Pankow, 2003). OC can be directly emitted from sources as primary organic aerosol (POA) or can be produced by atmospheric reactions involving gaseous organic precursors forming secondary organic aerosol (SOA) (Seinfeld and Pandis, 2006). Although EC and BC have been often used indistinctly in the literature, refer to a similar fraction of the carbonaceous aerosol and are supposed to be comparable, they can have different thermal, optical, and chemical behavior and are distinguished by the measurement technique and protocol used.

BC is emitted during the incomplete combustion of fossil fuels, biofuels, and biomass burning and absorbs at all wavelengths of solar radiation (IPCC, 2013). It is always co-emitted with other organic compounds and inorganic gases, such as nitrogen oxides (NO_x) and sulfur dioxide (SO_2) (US EPA, 2012; Bond et al., 2013). BC is refractory (stability at very high temperatures, with a vaporization temperature near 4 000 K); insoluble in water and common organic solvents, and it exists in nature as an aggregate of small carbon spherules. These physical properties make it unique and distinguishable from other forms of carbon and carbon compounds contained in atmospheric aerosols (Bond et al., 2013; Petzold et al., 2013). BC, together with methane (CH_4) and tropospheric ozone (O_3), is one of the most important contributor to current global warming after carbon dioxide (CO_2) (UNEP-CCAC, 2014). UNEP and WMO (2011) have estimated that implementation of proposed BC and CH_4 control measures by 2030 could prevent up to 0.5 °C of additional warming by 2050.

Additionally, the review of the results of all available toxicological studies suggested that BC (measured as EC) may not be a major directly toxic component of fine PM, but it may operate as a universal carrier of a wide variety of, especially, combustion-derived chemical constituents of varying toxicity to sensitive targets in the human body such as the lungs, the body's major defense cells and possibly the systemic blood circulation (WHO, 2012). BC and co-pollutants make up for the majority of the fine particulate matter ($PM_{2.5}$), currently considered a major environmental cause of respiratory and cardiovascular diseases, with a global estimation of more than 6 million premature deaths annually from exposure to indoor and outdoor (Lim et al., 2012).

There are several available light-absorption based eBC measurement methods: (a) filter transmission measurements using instruments such as the Aethalometer (Hansen et al., 1984; Drinovec et al., 2015), the Particle Soot Absorption Photometer (PSAP; Bond et al., 1999), the Multi-Angle Absorption Photometer (MAAP; Petzold and Schönlinner, 2004) and the Continuous Soot Monitoring System (COSMOS; Miyazaki et al., 2008); (b) photoacoustic techniques: the absorption of the air suspended aerosol through the pressure fluctuation due to absorption can be measured for example by the Photo-Acoustic Soot Spectrometer (PASS) (Arnott et al., 1999); and (c) photo-thermal interferometry techniques (folded-Jamin interferometer; Jamin, 1856).

Sandradewi et al. (2008a; 2008b) suggested that the absorption Ångström exponent (AAE), characterizing the spectral dependence of aerosol light absorption (Kirchstetter et al., 2004; Moosmüller et al., 2011; Bond et al., 2013), can be used to quantify the contribution of fossil fuel and biomass burning to the total eBC mass concentration. For this purpose, they developed the so-called "Aethalometer model", a two-component method to apportion eBC to fossil fuel (eBC_{ff}) and to biomass burning (eBC_{bb}), which has been used extensively in the last recent years (Favez et al., 2009; Martinsson et al., 2017; Titos et al., 2017; Zotter et al., 2017).

As in other regions in Europe (Putaud et al., 2010) previous studies in Spain (Querol et al., 2004b) confirmed that carbonaceous aerosol was one of the main components of the aerosol in urban and rural areas. Source apportionment studies in Madrid, pointed to traffic emissions as the dominant source of carbonaceous aerosol (Plaza et al., 2011; Salvador et al., 2004, 2012) leading in many occasions to PM limit value exceedances.

PM_{10} limit values are also exceeded in other urban and rural areas of Spain (Querol et al., 2004a). One of these latter is the Andalusian olive groves region of Jaén, which in the last years has experienced both PM_{10} daily limit value and $PM_{2.5}$ annual limit value exceedances (Junta de Andalucía, 2015). High concentration levels are recorded during the autumn and winter months, and have been associated in principle to the increase of domestic biomass burning in these periods of the year (Salvador et al., 2016).