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The application of a multi-wavelength Aethalometer to estimate iron dust and black carbon concentrations in the marine boundary layer of Cape Verde

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HIGHLIGHTS

- Two-component model was used to decouple the light attenuation of aerosol constituents.
- Model provided a reliable estimate of black carbon in the presence of iron oxides.
- Iron in the fine aerosol was estimated due to negligible "brown" carbon concentrations.

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ABSTRACT

The two-component model (Fialho et al., 2006) was used to decouple the contributions of black carbon (BC) and iron oxides, present in dust, to the aerosol attenuation coefficient, measured with a multi-wavelength Aethalometer. The model results were compared with the elemental carbon (EC) and iron concentrations determined in the laboratory from the analysis of aerosol particles collected with conventional samplers. The comparison was based on one year of data obtained at Praia, Santiago Island, Cape Verde, after side by side operation of the aerosol monitoring instruments. The linear regression equation that best describes the relationship between BC concentrations, derived from the Aethalometer, and EC concentrations, derived from a PM_{10} high-volume sampler after filter analysis with a thermal optical method, presents a slope of 1.01 ± 0.05 and a correlation coefficient (r) of 0.90, showing that the model worked as intended to describe BC concentrations without interferences from iron dust. On the other hand, the linear regression equation that best describes the relationship between the iron concentrations derived from the Aethalometer and elemental iron concentrations, derived from a PM_{10} low-volume sampler after filter analysis by k_0 – Instrumental Neutron Activation Analysis, presents a slope of 0.495 ± 0.014 and a correlation coefficient (r) of 0.96. These results show that the two-component model underestimated the iron concentrations in dust aerosol, which was explained by differences in the size range of particles sampled with the Aethalometer and the PM_{10} low-volume sampler together with differences in the size distribution of iron oxides.

1. Introduction

The African continent is an important source of mineral dust and biomass burning particles to the global atmosphere (Prospero et al., 2002; Langmann et al., 2009). These particles are known to affect the Earth's radiative budget (Satheesh and Krishna Moorthy, 2005; Langmann et al., 2009), to influence cloud formation and

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precipitation (DeMott et al., 2003; Lin et al., 2006; Petters et al., 2009) and to play an important role in biogeochemical cycles (Crutzen and Andreae, 1990; Mahowald et al., 2005). The radiative effects of these particles are strongly related with their chemical composition (Haywood and Boucher, 2000; Satheesh and Krishna Moorthy, 2005). Iron oxides and black carbon (BC) are major light absorbing constituents, at visible wavelengths, of dust and combustion particles, respectively, (Bohren and Huffman, 1998; Bond and Bergstrom, 2006; Linke et al., 2006), thus contributing to the aerosol attenuation coefficient and affecting the radiative transfer within the atmosphere.

BC in atmospheric sciences is operationally defined as the light absorbing fraction of carbonaceous aerosols and is usually determined through the measurement of light attenuation by particles collected on a filter. However, optical techniques can provide erroneous estimates of BC, due to the presence of mineral dust. Previous studies dealing with this effect have shown that the contribution of dust aerosol to optical absorption can be as great as 30% (Jennings et al., 1996; Pinnick et al., 1993; Coen et al., 2003; Bodhaine, 1995; Hansen et al., 1993).

Previously, Fialho et al. (2005) proposed a two-component model to decouple the contribution of BC and dust from the aerosol attenuation coefficient measured with the Aethalometer.

$$\sigma_{\mathrm{ATN-aerosol}}(\lambda,t) = \sigma_{\mathrm{BC}}(\lambda,t) + \sigma_{\mathrm{dust}}(\lambda,t) \quad (1.1)$$

where $\sigma_{\mathrm{ATN\text{-}aerosol}}(\lambda,t)$ is the Aethalometer aerosol attenuation coefficient, $\sigma_{\mathrm{BC}}(\lambda,t)$ and $\sigma_{\mathrm{dust}}(\lambda,t)$ are, respectively, the BC and dust Aethalometer attenuation coefficients.

The two-component model was further developed by Fialho et al. (2006), after experimental determination of the calibration coefficient for elemental iron (used as an indicator of light attenuation due to the presence of iron oxide in dust aerosol and considering that dust colour is the result of the overwhelming abundance of haematite, Fe_2O_3 (red), and goethite, FeO(OH) (yellowish brown), in soils with low concentrations of organic matter, such as deserts (Torrent et al., 1983).

$$\sigma_{\mathrm{ATN-aerosol}}(\lambda,t) = 14.625 \times \lambda^{-1} \times C_{\mathrm{BC}}(t) + 0.234 \times \lambda^{-4} \times C_{\mathrm{Fe}}(t) \quad (1.2)$$

Where, $C_{\mathrm{BC}}(t)$ and $C_{\mathrm{Fe}}(t)$ are, respectively, the concentrations of BC and elemental iron, and the numbers are the calibration constants for BC (14.625 μm m^2 g^{-1}, used by the Aethalometer (Hansen, 2003)) and elemental iron (0.234 μm^4 m^2 g^{-1}, estimated in Fialho et al. (2006)).

The purpose of this work is to test the two-component model described above by comparing the BC and iron concentration results obtained with a multi-wavelength Aethalometer with the elemental carbon (EC) and elemental iron concentrations determined in the laboratory from the analysis of aerosol particles collected with conventional high and low volume filter samplers. Although the operational definition of BC is different from that of EC, which is the aerosol carbon fraction that is oxidized in combustion analysis above a certain temperature threshold (Andreae and Gelencsér, 2006), both terms are often used interchangeably and are commonly well correlated (Allen et al., 1999; Park et al., 2002). Therefore EC is assumed to be an appropriate parameter to evaluate the Aethalometer performance.

This comparison study is based on one year of data obtained at Santiago Island (Cape Verde), within the framework of CV-Dust research project, after side by side operation of the aerosol monitoring and sampling instruments. Aerosol in the Cape Verde area has very often been observed to be a mixture of dust particles transported from the Sahara desert and carbon particles resulting from biomass burning practices in the region south of the Sahel (Lieke et al., 2011; Tesche et al., 2011) and from local traffic emissions (Gonçalves et al., 2014), and therefore the islands are ideally located to explore the two-component model capabilities.

The present work assumes that the enhancement of the aerosol attenuation coefficient with the wavelength was solely the result of iron in aerosol particles. Atmospheric "brown" carbon, which is also known to enhance the Aethalometer attenuation signal (Andreae and Gelencsér, 2006), was neglected considering the very low concentrations of levoglucosan (an acknowledged biomass burning tracer) reported by Gonçalves et al. (2014) during the CV-Dust field experiment (2–10 ng/m^3).

2. Experimental setup and working equations

2.1. Sampling site

Aerosol sampling was performed from January 12 through December 30, 2011, at the former airport of Praia, in the south-eastern edge of Santiago Island, Cape Verde (14° 55′ N; 23° 29′ W; 98 m a.s.l.). The site is located to the east of the urban settlement of Praia and prevalent winds are north-easterlies (trade winds) transporting particles from mainland Africa. However, local anthropogenic influences on aerosol composition cannot be precluded.

2.2. Aerosol attenuation coefficient measurements

A seven wavelength Aethalometer (Magee Scientific, model AE31, $\lambda = 370, 470, 520, 590, 660, 880$ and 950 nm) equipped with a "high sensitivity" circular spot size chamber was used to measure the aerosol attenuation coefficient. Ambient air was sampled at a flow rate of 4.0 dm^3/min, measured with the internal Aethalometer mass flowmeter (Sierra Model 824), through a whole air inlet without any specific cut-off size. The inlet setup consisted of one tube (length: 1.5 m; internal diameter: 6.0 mm) extending horizontally from an open window, with the opening slightly falling down. The inlet efficiency was estimated with the aerosol calculator program developed by Baron (2001), assuming spherical particles with densities between 1 and 4 g/cm^3 and diameters between 1 μm and 10 μm, and isokinetic sampling conditions (Table 1).

Particulate matter accumulated in a quartz fibre filter tape (Q250F from Pallflex©) and the instrument was setup to automatically advance the tape whenever the ATN (370 nm) sign was higher than 50% to avoid significant overloading of the filter with aerosol. The impact of the loading effect correction will be discussed below, in Section 3.2. From January 12 to April 7, at 10 a.m., the sampling period was set to 5 min; after that, until the end of the experiment (December 30, at 12 a.m.) it was set to 2 min, in order to decrease the time gaps between the automatic Aethalometer filter changes. The Aethalometer was setup to report the mass in μg/m^3 of equivalent BC and the instrument detection limit was 0.1 μg/m^3.

Table 1
Inlet efficiency for an isoaxial horizontal tube and isokinetic sampling conditions (Baron, 2001).

Particle diameter (μm)	Particle density (g/cm^3)		
	1.0	2.0	4.0
1.0	0.97	0.96	0.93
2.5	0.91	0.85	0.76
5.0	0.77	0.64	0.47
10	0.48	0.29	0.12