Atmospheric Environment 80 (2013) 31–40

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Black carbon mass size distributions of diesel exhaust and urban aerosols measured using differential mobility analyzer in tandem with Aethalometer

Zhi Ning [a,b,c,*], K.L. Chan [a], K.C. Wong [a], Dane Westerdahl [b], Griša Močnik [d], J.H. Zhou [e], C.S. Cheung [e]

[a] School of Energy and Environment, City University of Hong Kong, Hong Kong
[b] Ability R&D Energy Research Centre, City University of Hong Kong, Hong Kong
[c] Guy Carpenter Asia-Pacific Climate Impact Centre, City University of Hong Kong, Hong Kong
[d] Aerosol d.o.o., Ljubljana, Slovenia
[e] Department of Mechanical Engineering, The Hong Kong Polytechnic University, Hong Kong

HIGHLIGHTS

- A new method is described to efficiently determine BC size distributions.
- Time resolved, automated mass size distribution measurements of black carbon from 20 to 600 nm are presented.
- Reports BC size distributions of diesel engine exhaust emission at different loadings.
- Reports BC mass size distribution of roadside and urban ambient aerosols.
- Fast mixing of black carbon was observed from fresh and ambient aerosols.

ARTICLE INFO

Article history:
Received 21 May 2013
Received in revised form
10 July 2013
Accepted 15 July 2013

Keywords:
Black carbon
Mass size distribution
Urban atmosphere
Diesel emissions

ABSTRACT

Black carbon (BC) is the dominant component of the light absorbing aerosols in the atmosphere, changing earth's radiative balance and affecting the climate. The mixing state and size distribution of atmospheric BC are largely unknown and cause uncertainties in climate models. BC is also a major component of diesel PM emissions, recently classified by World Health Organization as Category I Carcinogen, and has been associated with various adverse health effects. This study presents a novel approach of direct and continuous measurement of BC mass size distribution by tandem operation of a differential mobility spectrometry and a refined Aethalometer. A condensation particle counter was deployed in parallel with the Aethalometer to determine particle number size distribution. A wide range of particle sizes (20–600 nm) was investigated to determine the BC modal characteristics in fresh diesel engine tailpipe emissions and in different urban environments including a typical urban ambient site and a busy roadside. The study provided a demonstration of a new analytic approach and showed the evolution of BC mass size distribution from fresh engine emissions to the aged aerosols in the roadside and ambient environments. The results potentially can be used to refine the input for climate modeling to determine the effect of particle-bound atmospheric BC on the global climate.

1. Introduction

Black carbon (BC) is a component of particulate matter that has gained recognition in recent years for the effect on the climate (Jacobson, 2001), and the association with adverse health effects (WHO, 2012). It plays a role in influencing monsoon patterns and cloud formation; increasing snow and ice melting rates (Ramanathan and Carmichael, 2008); and raising the average sea level (Hu et al., 2013). Fossil fuel combustion, including coal and diesel, and biomass burning are major contributors to atmospheric BC (Bond et al., 2004). BC is an excellent marker for these combustion sources, especially for diesel exhaust, which has been listed as a human carcinogen (WHO, 2012) as well as known to link to acute vascular dysfunction and increased thrombus formation

* Corresponding author. School of Energy and Environment, City University of Hong Kong, Hong Kong.
E-mail address: zhining@cityu.edu.hk (Z. Ning).

1352-2310/$ – see front matter
http://dx.doi.org/10.1016/j.atmosenv.2013.07.037

(Tornqvist et al., 2007; Lucking et al., 2008). BC in urbanized areas, such as Hong Kong, originates from both local emission sources (Ning et al., 2012) and may also be regionally transported from more distant regions (Tornqvist et al., 2007).

Once BC is emitted from sources it undergoes physical changes but is considered chemically stable. BC from diesel fuel combustion originates in the form of small spherules often reported to be between 15 and 30 nm, which quickly form up agglomerate chain structure of soot particles once released from tailpipe (Kittelson, 1998). These aged particles have been shown to consist of primary carbonaceous particles together with volatile organic and inorganic constituents. The size of carbon containing particles that originate from diesel combustion may differ from those generated by biomass combustion or from coal burned in power/heating plants and for residential cooking and heating (Schwarz et al., 2008; Kondo et al., 2011). Knowing the size of BC particles present in urban and regional air is of considerable significance. The climate forcing potential of BC is influenced by particle size and mixing state (Ramanathan and Carmichael, 2008); and both atmospheric fate and deposition in the human lungs are also impacted by PM size (Lippmann and Albert, 1969; Lin et al., 1994).

Currently available methods for sizing carbon include size-fractionated filter sampling followed by carbon analysis, microscopy measurement, and recently by laser-induced incandescence method (Reddington et al., 2012), but with limitations (Moteki and Kondo, 2010; Gysel et al., 2012). The most important limitation is that automated BC sizing is limited to particles larger than approximately 70 nm thus making it somewhat unsuitable for the study of ultrafine BC (Moteki and Kondo, 2010). Filter based methods for sizing carbon containing PM are unable to provide necessary size and temporal resolution. This study presents a novel approach for the direct and continuous measurement of atmospheric BC mass size distribution by tandem operation of a differential mobility spectrometer and a refined Aethalometer. A wide range of particle sizes (20–600 nm) was investigated to determine the BC mass size distribution in diesel engine tailpipe emissions and roadside of a busy roadway and typical urban site, representing fresh, intermediate and aged aerosols, respectively. The results demonstrate the evolution of BC mass size distribution in different stages of lifetime in urban environment.

2. Methodology development

2.1. Scientific approach

The basic approach employed in this study was to pull sample air through a differential mobility analyzer (DMA) to select particles with different electrical mobility, in tandem with an Aethalometer to determine the BC mass size distribution based on the measured absorption coefficient and a condensational particle counter (CPC) to determine particle number size distributions. Modifications of the Aethalometer were required to increase sensitivity and to reduce measurement noise. The DMA was operated in a voltage stepping mode by programmed automation control to enable continuous measurement of a selected range of particle sizes. The method also went through intensive validation and evaluation. Furthermore, the tandem system was deployed in the field to determine BC mass size distributions of different samples, including fresh exhaust of a diesel engine, a near-roadway site and a typical urban site in Hong Kong.

2.2. Refinement and evaluation of Aethalometer

BC concentration was measured using an Aethalometer (Model AE51, Magee Scientific) with modifications to enhance the instrument sensitivity to low BC concentrations. The Aethalometer measures the attenuation of light from a LED light source array at a wavelength of 880 nm, through a PTFE-coated borosilicate glass fiber filter (Fiberfilm Filters, T60 material, Pall Corporation) while the air flow continuously accumulates BC onto the sample spot area. The attenuation of light is determined every second by the light intensities transmitted through a blank reference spot and the aerosol laden sample spot on the same filter, designated as I_0 and I, respectively:

$$\mathrm{ATN} = 100 \cdot \ln(I_0/I) \tag{1}$$

The BC mass loading on the filter is determined by:

$$\mathrm{BC(mass)} = \frac{A \cdot \mathrm{ATN}}{100 \cdot \sigma_{\mathrm{ATN}}} \tag{2}$$

where A is the sample spot area, σ_{ATN} (12.5 $m^2\ g^{-1}$) is the mass attenuation cross-section for the BC collected on the filter provided by the instrument manufacturer and verified in an ambient experiment (Ferrero et al., 2011). While BC aerosol is continuously loaded on the filter, the BC concentration is determined by the incremental increase of BC mass from Equation (2), divided by the air volume through the filter:

$$\mathrm{BC} = \left[\frac{A \cdot \Delta\mathrm{ATN}}{100 \cdot \sigma_{\mathrm{ATN}}}\right] \cdot \left[\frac{1}{Q \cdot \Delta t}\right] \tag{3}$$

Where Q is the flow rate, and ΔATN indicates the change of ATN during the time period Δt (Hansen et al., 1984).

The measurement precision of the Aethalometer is reported to be ±100 ng BC m^{-3} with one minute average at a flow rate of 150 ml min^{-1} as specified in technical specifications by the manufacturer, which is sufficient for ambient total BC concentration measurement with typical range of 1 μg m^{-3}–10 μg m^{-3} in urban environments. However, for this sizing application, much lower BC concentrations in size resolved bins are expected. Additionally, a shorter averaging time period is desired, requiring further improvement of the measurement sensitivity. Significant efforts were invested to evaluate the origins of the system noise and influencing factors of sensitivity in the aspects of light intensity (I), flow rate (Q) and averaging time (Δt) as determined in Equations (1)–(3).

2.2.1. Choices of power supplies

The attenuation is determined by comparing the measurements of light intensities below a reference part of the filter tape and below the part of tape where the sample is being continuously deposited. In order to optimize the sensitivity of the system, we performed a test to evaluate the stability of LED light source and the light detector with different power supply setups. A typical Aethalometer may be powered by the internal battery or an USB power supply. The criterion was the standard deviation of the measured BC concentration with particle free air flowing through the instrument. Fig. 1 shows the comparison of clean air measurement (a HEPA filter was installed in the sampling line) using power from a desktop PC via a USB port, 5 V DC supplied by an AC power adapter, as well as an external and an internal battery. The recorded BC data shows significant difference due to the quality of DC power among different supplies. The noise levels (expressed as the standard deviation of the data recorded with ten seconds time resolution) for external and internal batteries are 174 and 197 ng m^{-3}, respectively, compared with 1003 ng m^{-3} for AC power adapter and 245 ng m^{-3} for USB power supply from desktop PC. Following these observations, we chose to use batteries to power the Aethalometer. However, in order to allow continuous data