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Original article

Recommendations for calibration factors for a photo-reference method for aerosol black carbon concentrations

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ABSTRACT

Large measurement networks of Black Carbon (BC) aerosol are important for understanding its impacts on climate and health. PM2.5 filter samples were collected at three urban US locations and one India urban location and were analyzed for Elemental Carbon (EC) and Organic Carbon (OC) concentrations using thermo-optical analysis (TO) following the IMPROVE protocol for US samples and NIOSH protocol for India samples. Site and season-specific calibrations of an inexpensive photo-reference (PR) method were created with TO EC measurements of the US filter samples whereas method-specific calibration was prepared using India filter samples. Piece-wise calibration based on filter loading was also explored. Calibrations were applied across different sites, seasons and methods to determine Root Mean Square Error (RMSE) and average absolute error in each calibration by comparing with reference EC measurements. This paper investigates various calibrations of PR method to improve the agreement between PR method and TO EC measurements. Difference in BC estimated error remained within ±10% among three urban US site-specific calibrations, which suggests that site-specific calibrations are not necessary. Season based calibrations were found to perform best (least RMSE/Mean EC), when applied to same season test samples but resulted in large errors of up to 60% RMSE/Mean EC when applied to different seasons, thus warranting the use of season-specific calibrations of the PR method. RMSE relative to mean EC was 50% when calibration prepared from US samples (IMPROVE protocol) was used to test India samples (NIOSH protocol). However, method-specific calibration prepared from India samples reduced the error to 24%, showing the large dependency of PR method on reference BC measurement method. Calibration based on filter loading reduced the RMSE slightly for both US urban and India samples and indicated that filters with loadings higher than 20 μg cm^{-2} are not suitable for estimating BC by PR method.

1. Introduction

Large scale measurement of Black Carbon (BC), often referred to as Elemental Carbon (EC), is important for properly understanding its effects on global and regional climate change, and health. BC is formed primarily by incomplete combustion and directly absorbs sunlight, heating the particles and the immediate atmosphere (Schwartz and Buseck, 2000). It has been estimated that the direct effect of BC is the second most important contributor to global warming (Jacobson, 2001)and the climate forcing importance of BC has been underscored by numerous studies (Ramanathan and Carmichael, 2008; Grieshop et al., 2009; Ramanathan and Feng, 2009). BC also impacts health and visibility (Samet et al., 2000; Pope et al., 2002) with the inhalation of smoke containing BC responsible for an estimated 1.8 million deaths per year (Ezzati and Kamen, 2002).

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The measurement of BC is important for the evaluation of air pollution and climate models and to evaluate the effectiveness of BC mitigation programs. The use of terms BC and EC is dependent on the measurement method as the former is defined optically using aerosol light absorption whereas latter is defined thermally using its refractory properties. BC can be measured using different optical and mass based instruments (Cross et al., 2010), although results are method-specific and can differ widely (Hitzenberger et al., 2006). The Aethalometer (Hansen et al., 1984) and other filter based methods (Bodhaine, 1995) measure BC during or after loading on a filter through the attenuation of light of accumulating particles, whereas thermo-optical (TO) systems measure Elemental Carbon (EC) by combustion through a series of temperature ramps with an optical correction procedure for charring of organic compounds during pyrolysis (Schmid et al., 2001). Different protocols have been developed to determine the Elemental Carbon (EC) – Organic Carbon (OC) split point in TO analyzers. Two such methods, NIOSH and IMPROVE which are used in this study, have the same thermal evolution method but different temperature and optical monitoring methods (Chow et al., 2001). It has been shown that the two methods result in equivalent Total Carbon (TC) values whereas EC values obtained from NIOSH are typically less than half of those obtained from IMPROVE protocol. Primary difference between the two protocols as shown by Chow et al. (2001) is the allocation of carbon evolved at 850 °C in NIOSH to OC rather than EC, which when corrected results in good agreement between the two methods.

The cost of such measurement systems can be prohibitive for multi-location, large scale experimental or monitoring efforts. Recently, a new photo-reference (PR) method has been developed for measuring black carbon based on photographs of exposed, aerosol loaded filters that have been placed on a calibration chart that contains reflectance standards associated with known BC concentrations. The method is based on the fact that Black Carbon loading on the filter is tightly correlated with red color pixel or red reflectance (R) value of the filter image, which decreases as the BC loading on the filter increases (Ramanathan et al., 2011). Red reflectance of a filter image is expressed in RGB (red-green-blue) color space and ranges from 0 (pure black) to 255 (pure white). The method works with any digital colorimeter or image-forming instrument, including inexpensive mobile phone cameras. The PR method has been calibrated to Aethalometer and TO instruments and is significantly less expensive than other BC measurement methods. The PR method is also relatively easy to follow in field conditions for personnel with a minimum amount of training and provides rapid BC measurements within about 20% of the calibrated standards (Ramanathan et al., 2011). As per our communication with the researchers in atmospheric science and air pollution assessment, the use of PR method is increasing where the access and resources for EC-OC analysis are not possible. The potential sources of error in the method are the digital imaging devices having different color correction algorithms and change in the lighting and exposure while creating the images, which can alter the actual darkness of the filter, and thus change the red reflectance value. To account for this, a reference scale having BC calibration standards is included in each image to calibrate for different ambient conditions, and is described in detail in our earlier publication (Ramanathan et al., 2011).

The objective of the present work is to examine the difference in the correlation of thermo-optical EC loading with the PR method using aerosol samples collected in different sites and seasons. It is hypothesized that site-, season- and method-specific calibrations would help in better understanding the correlation of red reflectance and EC loading, and thus could be used to reduce error of the PR method for large scale BC monitoring purposes. Calibrations based on the loading of the filters were also hypothesized to improve BC estimates. US samples were used to create site-, and season-specific calibrations and a combined calibration using all US samples following IMRPOVE protocol was used to predict BC for Kanpur samples and were tested with TO-EC measurements following NIOSH protocol. Finally, the calibration constructed from Kanpur samples following NIOSH protocol was used for predicting BC for the same samples to determine if a method specific calibration can reduce the error in prediction. Interactions between calibrations were not considered in order to minimize the complexity of analysis.

2. Methodology

2.1. Filter sampling

Two sets of aerosol loaded filters were used in this study: One at IIT Kanpur campus which is located in the industrial city Kanpur, India (26.5°N, 80.3°E) and the other from three US urban cities: Los Angeles (34.1°N, 118.25°W) and Riverside (33.9°N, 117.4°W), California, and Denver (39.7°N, 104.9°W), Colorado.

In IIT Kanpur, a locally designed impaction based PM2.5 sampler (Gupta et al., 2011) and a high volume sampler were used to collect PM2.5 samples on 47 mm diameter (Whatman, QMA) and A4 size quartz filters, respectively, during January 16, 2010 to February 20, 2010. Filters were preconditioned at 550 °C in an oven to evaporate any adsorbed carbon present in the filter prior to sampling. Flow rate of the sampling was 15 L per minute (Lpm) in case of 47 mm filters and 1000 Lpm in case of A4 size filters. A total of six samples were collected in a day: one in morning from 7:30 a. m. to 10:30 a. m., three in the day time from 11:00 a. m. to 11:30 p. m. (one every 2.5 h) with 30 min gap in between for filter change. Samples were sealed in plastic containers and refrigerated at 4 °C to avoid any loss of particles until the analysis was performed (Kaul et al., 2011).

Quartz filters from urban US locations were collected by stations maintained by the Environmental Protection Agency to collect urban BC aerosols. A total of 333 PM2.5 filter samples were collected which includes 116 from LA, 96 from Denver and 121 from Riverside. Samples were collected on 25 mm quartz filter, using a sampler made by URG (URG-3000N). The sampling was done from midnight to midnight, approximately every 3rd day for a year in 2011. Flow rate of the sampling was 22 Lpm. Filters were provided for analysis by the Desert Research Institute, Nevada System of Higher Education.

2.2. Measurement of BC

Filters from urban India (IIT Kanpur) were analyzed for EC and OC loadings using a TO analyzer (Sunset Laboratory) following NIOSH5040 TOT protocol (NIOSH, 1996). Filters from urban US were also analyzed using a TO analyzer (Sunset Laboratory) following the IMPROVE TOT protocol (Chow et al., 2001). EC and OC were reported as surface loading (μg cm^{-2}). Instrument detection limit for the analysis is ~0.05 μg cm^{-2}. EC loading (μg cm^{-2}) can be converted to EC concentration (μg m^{-3}) by the following equation:

$$\text{EC loading}\left(\mu g\ cm^{-2}\right) = \frac{\text{EC}\ \left(\mu g m^{-3}\right)\cdot F\cdot T}{A} \quad (1)$$

where F is the volumetric flow rate (m^3 min^{-1}), T is the time duration (min), and A is area of the filter (cm^2).