Atmospheric Research 97 (2010) 335–342

Contents lists available at ScienceDirect

Atmospheric Research

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

Inter-comparison of thermal and optical methods for determination of atmospheric black carbon and attenuation coefficient from an urban location in northern India

Kirpa Ram [a], M.M. Sarin [a,*], S.N. Tripathi [b]

[a] *Physical Research Laboratory, Ahmedabad, India*
[b] *Department of Civil Engineering, Indian Institute of Technology, Kanpur, India*

ARTICLE INFO

Article history:
Received 1 June 2009
Received in revised form 4 January 2010
Accepted 14 April 2010

Keywords:
Aerosol
Elemental carbon
Attenuation coefficient
Attenuation cross-section
Northern India

ABSTRACT

The simultaneous measurements of black carbon (BC, based on Aethalometer) and elemental carbon (EC, using thermo-optical EC–OC analyzer) in airborne particles collected from an urban location (Kanpur) in northern India are reported here. The strategy for site-selection is most relevant in order to assess the relative dominance of emissions from coal-fired industries, fossil–fuel combustion and biomass burning on the seasonal variability of EC (BC) concentrations. An inter-comparison of the analytical data ($n=32$) suggests that BC mass concentration is ~20% higher than that of EC. However, attenuation coefficient (b_{ATN}) measured by the two analytical instruments shows good agreement (slope = 0.97, $n=27$), establishing the validity of b_{ATN} derived from thermo-optical EC–OC analyzer. Furthermore, slope (20.7 m^2 g^{-1}) of a linear-fit to the data ($n=48$, $R^2=0.86$) for surface EC concentration ($\mathrm{EC_s} \leq 8$ µg C cm^{-2}) and optical-attenuation (ATN ≤ 180) measured at 678 nm on thermo-optical analyzer provides an independent and novel way of determining the "site-specific" attenuation cross-section (σ_{ATN}).

1. Introduction

Black carbon (BC), also referred as elemental carbon (EC) or light absorbing carbon (LAC), is one of the key species of the atmospheric aerosols contributing to positive radiative forcing (warming) at top of the atmosphere (TOA) and negative radiative forcing (cooling) at the surface level (Ramanathan et al., 2001). The determination of LAC mass (µg C m^{-3}) based on optical and thermal methods is referred as BC and EC, respectively. However, its measurement by two different methods suffers from large degree of uncertainty. An absolute method for the accurate determination of LAC by optical method is still lacking (Reisinger et al., 2008), and difference in the mass concentration by a factor of two to four (or even more) is not very uncommon (Hitzenberger et al., 2006).

The optical methods rely on measuring the change in attenuation of light (ΔATN) at a given wavelength through the filter embedded with aerosols and use of a constant factor (referred as attenuation cross-section, σ_{ATN}) to infer the BC mass concentration. These online methods are based on the basic assumption that absorption is solely due to LAC and σ_{ATN} remains constant during the course of measurements (Bond and Bergstrom, 2006; Snyder and Schauer, 2007); however, none of these assumptions are strictly valid. The absorption at a given wavelength may be sensitive to aerosol species other than LAC mass (Bond and Bergstrom, 2006; Snyder and Schauer, 2007). A number of studies reported in the literature invoke that σ_{ATN} is variable on a spatial scale, even shows diurnal variation (Snyder and Schauer, 2007) and changes from sample to sample (Liousse et al., 1993). More importantly, the data on σ_{ATN} reported in the literature are based on absorption measurements via optical method and

---

* Corresponding author. Tel.: +91 79 26314306; fax: +91 79 26301502.
E-mail addresses: kirpa@prl.res.in (K. Ram), sarin@prl.res.in (M.M. Sarin), snt@iitk.ac.in (S.N. Tripathi).

0169-8095/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.atmosres.2010.04.006

EC from a thermal method (Allen et al., 1999; Bond and Bergstrom, 2006; Liousse et al., 1993; Snyder and Schauer, 2007). The variability in σ_{ATN} has been interpreted in terms of emission sources, mixing state of aerosols, their chemical-composition and use of more than one protocol for the determination of EC by thermal method.

In contrast, thermal–optical method relies on the chemical properties of organic and elemental carbon (OC and EC) to assess their atmospheric abundances. The oxidation of organic carbon to CO_2 is achieved by heating the aerosol sample in an inert atmosphere of He (used as a carrier gas); whereas refractory and chemically inert EC is converted to CO_2 in an oxidizing environment ($He + O_2$). The simulataneous use of a laser source for the measurement of optical-attenuation (ATN) helps in defining the split-point between OC and EC and in making correction for pyrolyzed carbon. The use of different protocols (involving different temperature steps) reported in the literature suggests that measurement precision ranges from 4 to 13% for OC and 6 to 21% for EC (Schauer et al., 2003). In the present study, we have further made use of optical-attenuation (ATN measured at 678 nm) for the determination of σ_{ATN} and attenuation coefficient (b_{ATN}). In order to validate this analytical approach, we have compared EC and b_{ATN} data with the simultaneous measurement of BC on Aethalometer.

2. Site description and aerosol sampling

The ambient aerosols with aerodynamic diameter less than 10 µm (PM_{10}) were collected over a period of 13 months, during Jan 2007–Feb 2008, from an urban sampling site (Kanpur: 26.5° N, 80.3° E, 142 m amsl) in northern India. A high-volume sampler was set-up at a height of ~12 m above the ground level (on the terrace of a three-story building) in the premises of the Indian Institute of Technology (IIT). The sampler was operated at a flow rate of $1.0 \pm 0.1\ \text{m}^3\ \text{min}^{-1}$ and PM_{10} samples were collected by drawing the ambient air through tissuquartz filters (PALLFLEX$^{\text{TM}}$, 2500QAT-UP; size: $20.0 \times 25.4\ \text{cm}^2$). Prior to their use in the field, filters were cleaned by heating them at a temperature of ~350 °C for ~6 h. In general, an aerosol sample was collected every 5th-day but the frequency was increased to two samples per week during summer months (April–June). The samples were generally collected during day-time (local time, from 8:00 AM to 6:00 PM) with a typical sampling time of 8–10 h in order to filter ~550 m^3 of air. Soon after sample collection, filters were wrapped in Al-foils and packed into polyethylene zip-lock bags and later stored in refrigerator at 4 °C until the time of analysis. Simultaneously, an Aethalometer was operated at the same site for the measurement of black carbon (BC). The sampling site is ~15 km downwind of the main city and is influenced by emissions from biomass burning (mainly wood-fuel and agriculture-waste) and anthropogenic sources (thermal power plants and vehicular emissions). For further details on site description, reference is made to (Tripathi et al., 2006).

3. Analytical procedures

For the determination of EC mass concentration, filter aliquots (1.5 cm^2 rectangular punches) were analyzed on the EC–OC analyzer (Sunset Laboratory, Forest Grove, USA) using thermo-optical transmittance (TOT) protocol (Birch and Cary, 1996; Schauer et al., 2003). The details of the analytical protocol and uncertainty in the measurements of EC and OC have been described in our earlier publications (Ram and Sarin, 2010; Ram et al., 2008; Rengarajan et al., 2007). The optical-attenuation [ATN; $\text{ATN} = -\ln (I/I_0)$] of a laser beam (at 678 nm) through the sample filter is continuously monitored and is used to define the split-point between OC and EC on a thermograph obtained during different heating steps in an inert atmosphere (100% He) and under oxidizing conditions (10% O_2 + 90% He, vol/vol). Thus, ATN signal measured at 678 nm, through the sample filter, is attributed to the light absorbing carbon (i.e. EC) in ambient aerosols and is further used to calculate the attenuation coefficient ($b_{\text{ATN–ECOC}}$) according to Eq. (1).

$$b_{ATN-ECOC}\left(\text{Mm}^{-1}\right) = ATN^{*}\frac{A\left(\text{m}^2\right)}{V\left(\text{m}^3\right)} \tag{1}$$

The terms A and V represent effective filter area (here, $417 \times 10^{-4}\ \text{m}^2$) and volume of air filtered (units of m^3) respectively. The error in b_{ATN} mainly arises from the uncertainty associated with ATN measurement; whereas both A and V are measured with relatively better precision and have small errors. The ATN signal through the blank filter and EC concentration are zero, as determined based on large number of analysis ($n = 50$). The overall uncertainty in b_{ATN} is better than 10%. The experimental details for the determination of attenuation coefficient ($b_{\text{ATN–ECOC}}$) and associated uncertainties have been described in our earlier publication (Ram and Sarin, 2009).

The determination of BC mass concentration by Aethalometer is based on change in the attenuation of light (ΔATN) measured through the filter in a given time interval (Δt). The change in attenuation (ΔATN) is considered to be proportional to BC mass, assuming that BC is the only absorbing component present in aerosols (Bodhaine, 1995; Bond and Bergstrom, 2006; Snyder and Schauer, 2007). In this study, typical flow rate used in Aethalometer is 3 lpm (liters per minute) and attenuation signal is integrated for 5 min. The relevant details of the protocol for Aethalometer based measurements have been described elsewhere and uncertainty in BC mass concentration is ~10% (Tripathi et al., 2005). In case of Aethalometer, attenuation coefficient ($b_{\text{ATN–Aeth}}$) can be calculated by multiplying the measured BC mass concentration ($\mu\text{g C m}^{-3}$) at 880 nm and constant value of attenuation cross-section ($16.6\ \text{m}^2\ \text{g}^{-1}$), according to Eq. (2):

$$b_{ATN-Aeth}\left(\text{Mm}^{-1}\right) = BC\left(\mu\text{g m}^{-3}\right)^{*}16.6\left(\text{m}^2\text{g}^{-1}\right) \tag{2}$$

It is relevant to state that BC concentrations, recorded every 5 min on Aethalometer, are integrated for a total time-period of 8–10 h (similar to the total sampling time on a high-volume sampler) for the inter-comparison with EC. The simultaneous operation of both high-volume sampler and Aethalometer ensures sampling of the same ambient air. Further, b_{ATN} measured on EC–OC analyzer at 678 nm has been corrected to match with that on Aethalometer (at

880 nm) by assuming inverse dependence of attenuation coefficient on wavelength (Dey and Tripathi, 2007).

4. Results and discussion

4.1. Measurements based on the EC–OC analyzer

The ATN and EC_s concentration at an urban site (Kanpur) ranged from 17 to 244 and 0.7 to 31.2 µg C cm^{-2}, respectively. However, the linear relationship between the two parameters, establishing the validity of Beer–Lambert's law, is limited to ATN $\leq$ 180 and $EC_s \leq 8.0$ µg C cm^{-2} (Fig. 1). It is noteworthy that samples collected during wintertime (Dec–Feb) exhibit significantly higher ATN (range: 131 to 244) for corresponding ECs concentrations ranging from 8.4 to 31.2 µg C cm^{-2} (data shown by filled circles, Fig. 1). Similar to the results obtained in Fig. 1, Junker et al. (2006) had reported that ATN (measured on Aethalometer) shows a linear increase with EC_s (assayed by thermal method) but the linearity does not extend for ATN > 178. Likewise, Watson and Chow (2002) have described that the linearity ceases beyond EC > 5 µg C m^{-3} for the aerosol samples collected from Fresno Supersite, California.

Looking from a different perspective, slope of a linear regression line in Fig. 1 ($m = 20.7$ m^2 g^{-1}) provides a direct measure of 'site-specific' attenuation cross-section (σ_{ATN}). In a recent study, Zhang et al. (2008) have reported that attenuation coefficient (b_{ATN}) measured using Aethalometer (at 660 nm) exhibits a linear relation (slope = 18.2 m^2 g^{-1}) with EC concentration (µg C m^{-3}) assayed by thermo-optical method. Likewise, attenuation coefficient measured on Particle Soot Absorption Spectrometer (PSAP) and EC concentration by EC–OC analyser is significantly correlated ($r = 0.95$) and the average value for σ_{ATN} is 24 m^2 g^{-1} (Hagler et al., 2007). More recently, Snyder and Schauer (2007) have obtained values of σ_{ATN} as 23.7 ± 0.4 and 18.3 ± 0.5 m^2 g^{-1} at 660 nm and 565 nm by comparing the attenuation coefficient measured by Aethalometer and PSAP, respectively, and EC via thermal method. The use of site-specific σ_{ATN} is, thus, suggested in view of the large variability (Liousse et al., 1993; Sharma et al., 2002). However, a constant value of 10 m^2 g^{-1} with PASP and 16.6 m^2 g^{-1} with Aethalometer is generally used in order to derive BC mass concentration (Sharma et al., 2002). Another likely cause for variability in σ_{ATN} can be attributed to the use of different protocols for the assay of EC by the thermal method. The value of σ_{ATN} (i.e. 20.7 m^2 g^{-1}) obtained in this study is similar to those reported in literature and demonstrate the usefulness of ATN measurements made on thermo-optical EC–OC analyzer.

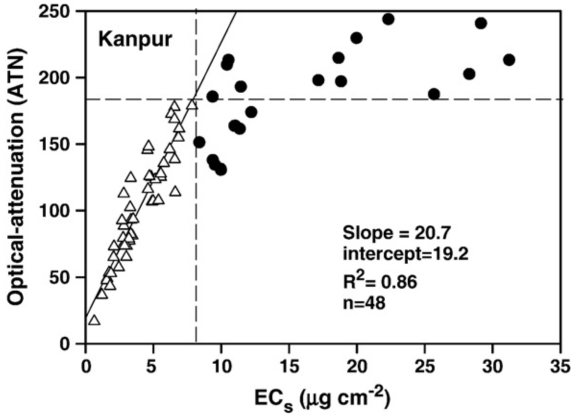

Fig. 1. Scatter plot between optical-attenuation (ATN) and EC_s concentration (µg C cm^{-2}) at Kanpur during the sampling period (Jan 2007–Feb 2008) indicating linear dependence of ATN on EC_s concentration. Data points (shown by filled circles) with EC_s > 8 µg C cm^{-2} (vertical dashed line) and ATN > 180 (horizontal dashed line) are not considered for the regression analysis.

The non-zero intercept in the linear regression plot (Fig. 1) suggests contribution from absorbing species other than BC. The mineral aerosols, with characteristic weak absorbing properties compared to BC, may be the possible cause for the non-zero absorption (Bodhaine, 1995). A recent study has suggested that mineral aerosols in northern India are non-absorbing at 670 nm even when hematite (Fe_2O_3) fraction is as high as 6%. However, a significant absorption by mineral dust at 440 nm has been reported (Mishra and Tripathi, 2008). The absorption by organic carbon, derived from biomass burning, can also be significant at lower wavelength (ultraviolet region) of the spectrum in particular when it contains humic-like substances (HULIS) and brown carbon (Andreae and Gelencser, 2006; Kirchstetter et al., 2004). Brown carbon (consisting of macro molecular compounds) is neither fully scattering nor absorbing; instead its absorption properties are between the two extreme values. These compounds are mainly derived from the smoldering combustion and residential coal combustion (Andreae and Gelencser, 2006; Graber and Rudich, 2006). In a recent study, Yang et al. (2009) have suggested that the mass absorption efficiency (MAE) of brown carbon (0.5 m^2 g^{-1}) is ~20 times lower than that of BC (10 m^2 g^{-1}). It is also reported that brown carbon (in coal-derived environment) can contribute to ~30% of total absorption and over 10% in mid-visible region of the spectrum. It is, thus, suggested that organic aerosols produced from biomass burning could be a significant source of absorption at the study site (Kanpur) and needs to be quantified in order to understand their contribution to the estimation of direct aerosol radiative forcing.

4.2. Temporal variability of chemical and optical parameters

The temporal variability in BC, EC mass concentrations, BC/EC ratio and optical parameters (b_{ATN} and σ_{ATN}) at an urban site (Kanpur) is shown in Fig. 2. The horizontal dash-line drawn at a value of 20.7 m^2 g^{-1} in Fig. 2(a) represents attenuation cross-section (obtained from Fig. 1); and that in Fig. 2(c) represents the equivalence line between BC and EC mass concentration. As evident from Fig. 2, the attenuation cross-section (σ_{ATN}) is significantly higher during summer and post-monsoon months (April to November) compared to that during wintertime (Dec to late Feb). The temporal variability in σ_{ATN} can be interpreted in terms of the mixing state of aerosols and its source from local biomass burning and vehicular exhausts (Martins et al., 1998; Schwarz et al., 2008). The lower values of σ_{ATN} could result from freshly emitted EC and external mixing of aerosols. The shallow boundary layer height decreases the vertical mixing of aerosols and, thus, leads to an external mixing during winter months (Dey et al., 2008). The internal mixing state of aerosols is favoured during summer and post-monsoon

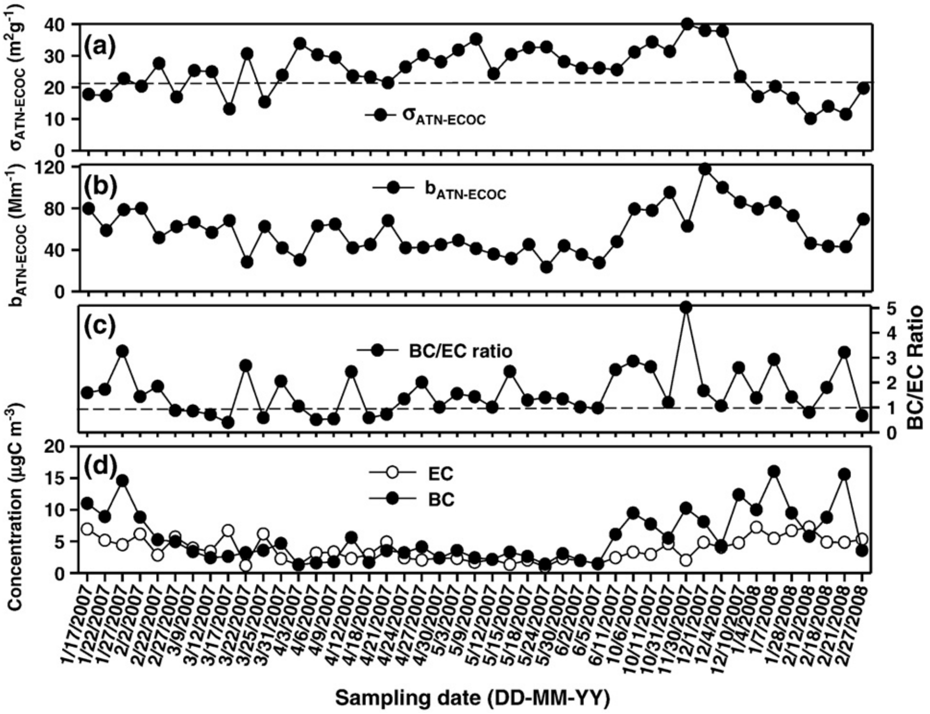

Fig. 2. The temporal variability in the chemical and optical parameters at Kanpur: (a) attenuation cross-section ($s_{ATN-ECOC}$) (b) attenuation coefficient ($b_{ATN-ECOC}$) (c) BC/EC ratio and (d) BC and EC mass concentrations. No samples were collected during the monsoon season (July–Sept). Note that the horizontal dashed-line in Fig. 2(a) represents the attenuation cross-section value of 20.7 m^2g^{-1} obtained from Fig. 1 whereas the equivalence line between BC and EC mass concentrations is shown in Fig. 2(c).

months (Dey et al., 2008). The formation of secondary organic aerosols (due to increase in photochemical activity) and enhanced vertical mixing are the likely causes for the internal mixing state of aerosols and, hence, resulting in higher σ_{ATN} during summer months.

The concentrations of EC and BC measured on EC–OC analyzer and Aethalometer are presented in Table 1. The EC concentration shows a large temporal variability and ranges from 0.7 to 14.4 μg C m^{-3} (Fig. 2d) during the sampling period (Jan 2007–Feb 2008). However, we restrict the discussion to the inter-comparison of EC and BC whenever simultaneous measurements have been made. The BC and EC concentrations show a linear trend ($R^2=0.62$, $n=32$); but BC concentration is ~20% higher compared to EC (Fig. 3a). The BC/EC ratio varied from 0.6 to 1.9, with an average value centering close to 1.1 ± 0.4 for these samples. Stone et al. (2007) have reported that EC concentrations are highly correlated with the Aethalometer BC ($R^2=0.968$), but the slope (i.e. EC/BC ratio) is less than unity. A number of studies report on EC concentrations to be lower than BC (Husain et al., 2007; Jeong et al., 2004). Likewise, EC concentrations higher than BC have also been reported in literature (Allen et al., 1999; Babich et al., 2000; Bae et al., 2007; Lavanchy et al., 1999).

4.3. Inter-comparison of the measured parameters based on thermal and optical methods

As stated earlier, the linear relationship between EC_s concentration (μg C cm^{-2}) and ATN measured on thermo-optical EC–OC analyzer sets the basis for the determination of attenuation coefficient ($b_{ATN-ECOC}$, Eq. (1)). The $b_{ATN-ECOC}$ varied from 23.4 to 117.8 Mm^{-1} (Fig. 2b; 1 $Mm^{-1}=10^{-6}$ m^{-1}) with higher values typical of wintertime (Dec–Feb) and lower values occurring during summer months (April–June). The Aethalometer and EC–OC analyzer based b_{ATN} data, for the sampling period (Jan–2007 to Feb–2008), are summarized in Table 1 and inter-comparison plot is shown in Fig. (3b). In case of Aethalometer, $b_{ATN-Aeth}$ is obtained by multiplying the BC mass concentration (at 880 nm) with σ_{ATN} (i.e. 16.6 m^2 g^{-1}) using Eq. (2); whereas $b_{ATN-ECOC}$ is derived from the measured ATN at 678 nm for every individual sample using Eq. (1). Also, $b_{ATN-ECOC}$ at 678 nm is corrected for 880 nm in order to make inter-comparison with Aethalometer based data. The b_{ATN}, as determined by the two analytical techniques, is well within the measurement uncertainties and observed difference is similar to those reported in the literature. For example, Snyder and Schauer (2007) have reported that absorption coefficient measured by the two widely used optical instruments, Aethalometer and Particle Soot Absorption Spectrometer (PSAP), shows a good agreement but Aethalometer based values are ~30% higher than those measured on PSAP. This study provides a direct method for the simultaneous determination of attenuation coefficient (b_{ATN}) and EC concentration in atmospheric aerosols. Also, the simultaneous measurements of ATN and EC concentration from EC–OC analyzer can be extended to other sampling sites in order to infer the 'site-specific' σ_{ATN} values on a regional scale, which in turn has implication to estimation of direct aerosol radiative forcing.

The difference between BC and EC mass concentrations (Fig. 3a) can be understood based on their definition and

Table 1
Measured values of EC and BC mass concentration during the sampling period (Jan 2007–Feb 2008) at Kanpur. The attenuation coefficient (b_{ATN}, 1 $Mm^{-1} = 10^{-6}$ m^{-1}) measured by two instruments are reported at 880 nm wavelength.

Sampling dates	EC	BC	$b_{ATN-ECOC}$	$b_{ATN-Aeth}$
	µg m^{-3}	µg m^{-3}	Mm^{-1}	Mm^{-1}
17-Jan-07	6.9	11.0	79.7	182.6
22-Jan-07	5.2	8.9	58.7	148.0
2-Feb-07	6.2	8.8	80.0	146.5
22-Feb-07	2.9	5.3	51.7	87.3
27-Feb-07	5.7	5.0	62.4	82.5
9-Mar-07	4.0	3.4	66.5	56.3
12-Mar-07	3.4	2.4	56.8	40.3
25-Mar-07	6.2	3.6	62.4	59.7
3-Apr-07	1.3	1.3	30.2	22.3
6-Apr-07	3.2	1.6	63.0	26.7
9-Apr-07	3.3	1.8	64.7	29.6
18-Apr-07	2.9	1.7	45.1	28.1
21-Apr-07	4.9	3.5	68.2	58.7
24-Apr-07	2.4	3.2	41.9	53.4
27-Apr-07	2.1	4.1	42.3	68.4
30-Apr-07	2.4	2.4	45.0	39.8
3-May-07	2.3	3.6	49.1	59.2
9-May-07	1.7	2.4	41.2	40.3
12-May-07	2.2	2.2	35.9	35.9
18-May-07	2.0	2.6	45.1	43.7
24-May-07	1.0	1.4	23.4	23.3
30-May-07	2.3	3.1	43.9	50.9
2-Jun-07	2.0	2.0	35.4	33.0
5-Jun-07	1.5	1.5	27.5	24.3
31-Oct-07	4.6	5.5	95.2	91.7
1-Dec-07	4.8	8.1	117.8	134.4
4-Dec-07	4.1	4.3	100.0	71.8
4-Jan-08	7.2	10.0	79.4	166.0
28-Jan-08	6.7	9.5	72.7	157.2
12-Feb-08	7.3	5.8	46.2	96.5
18-Feb-08	4.9	8.8	43.4	146.0
27-Feb-08	5.3	3.6	69.4	59.2

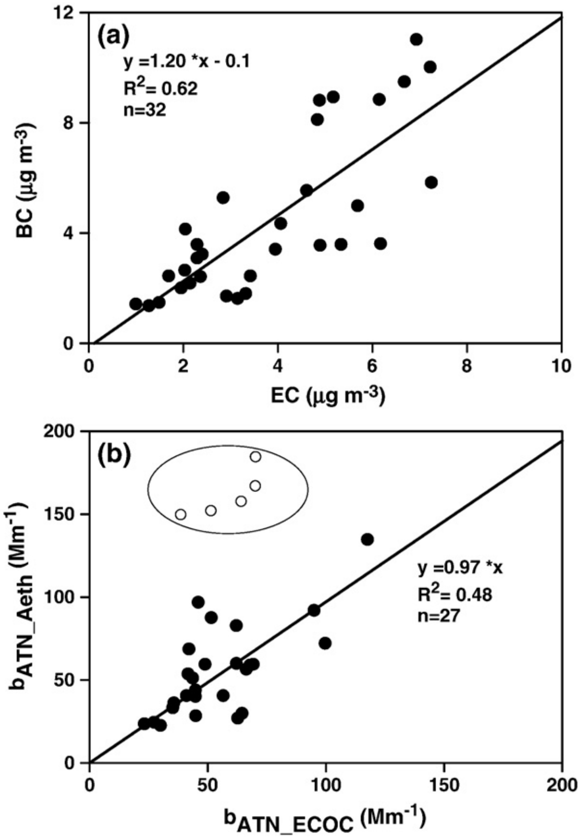

Fig. 3. (a) A comparison between BC and EC mass concentrations determined from the Aethalometer and the EC–OC analyzer and (b) represents inter-comparison of the attenuation coefficient derived from the optical (the Aethalometer, $b_{ATN-Aeth}$) and thermo-optical methods (the EC–OC analyzer, $b_{ATN-ECOC}$). The data points (open circles) collected during winter season (Dec–Feb) are not been considered in the regression analysis.

measurements using different analytical techniques. Also, the sources, composition, aging and mixing state of aerosols may lead to changes in the chemical and optical properties of aerosols and, hence, in the measurement of LAC mass concentration via optical methods. The EC fraction is chemically inert and is converted to CO_2 in an oxidizing medium during its measurement on EC–OC analyzer; whereas BC represents the absorbing component of aerosols and does not distinguishes the presence of any other absorbing species at a given wavelength (Andreae and Gelencser, 2006; Bond and Bergstrom, 2006). It is relevant to state that the measurement of EC by thermo-optical method may also lead to disagreement due to the difference in the analytical protocols (involving different temperature steps), type of aerosol particles and precise determination of the split-point between EC and OC. Schauer et al. (2003) had reported that the precision for EC measurement ranged between 6 and 21% when surface EC loading was in the range of 0.7–8.4 µg C cm^{-2} during ACE–Asia intercomparison study. Recently, Bae et al. (2007) have reported a good agreement (slope = 1.05 ± 0.15; $R^2 = 0.98$) between EC measurements performed using two different protocols (in one case use of six different temperature steps and in other case only two temperature steps are used for sample heating under oxidizing medium, 98% He + 2% O_2). Although EC and BC are defined on the basis of their chemical and optical properties respectively, both represent the LAC mass. The measurements reported in the literature show significant correlation and average BC and EC concentrations agree reasonably well within the standard deviation of the data (Reisinger et al., 2008).

The temporal variability in BC/EC ratio during the sampling period is presented in (Fig. 2c). The relatively high BC concentrations observed during wintertime (Dec–Feb) and post-monsoon (Oct–Nov) are attributed to the enhanced biomass burning activity. Badarinath et al. (2009) have reported on the transport of airborne BC from burning of agriculture-waste within the Indo-Gangetic Plain (IGP). It is suggested that biomass burning derived organic compounds containing humic-like substances (HULIS) and brown carbon can be an important absorber at lower wavelengths (Andreae and Gelencser, 2006; Kirchstetter et al., 2004). The measured BC and EC agree reasonably well for summer samples, with some of the BC values lower than that of EC (Tables 1 and 2). This is somewhat surprising as the abundance of mineral dust is relatively high in summer (Chinnam et al., 2006) and could result in higher absorption (Bodhaine, 1995). Recently, Zhang et al. (2008) have reported that absorption coefficient and EC shows a good correlation ($r = 0.96$) but BC values are ~20% higher than EC and have attributed excess absorption due to mineral dust.

Table 2
Monthly averaged values of EC and BC mass concentrations during the sampling period (Jan-2007–Feb 2008) at Kanpur. The attenuation coefficient (b_{ATN}, 1 $Mm^{-1} = 10^{-6}\ m^{-1}$) values measured by the two instruments are given at 880 nm wavelength whereas $\sigma_{ATN\text{-}ECOC}$ values are at 678 nm.

		EC–OC analyzer		Aethalometer			
n	Months	$b_{ATN–ECOC}$	EC	$b_{ATN–Aeth}$	BC	BC/EC ratio	$\sigma_{ATN\text{-}ECOC}$
		Mm^{-1}	μg C m^{-3}	Mm^{-1}	μg C m^{-3}		$m^2\ g^{-1}$
3	Jan-07	72.3 ± 11.8	5.5 ± 1.3	191 ± 48	11.5 ± 2.9	2.2 ± 0.9	19.3 ± 3.0
3	Feb-07	64.7 ± 14.3	4.9 ± 1.8	105 ± 36	6.4 ± 2.1	1.4 ± 0.5	21.6 ± 5.4
6	Mar-07	54.0 ± 15.8	4.0 ± 2.2	55 ± 13	3.3 ± 0.8	1.2 ± 0.9	22.2 ± 6.6
9	Apr-07	49.2 ± 12.9	2.7 ± 1.0	47 ± 24	2.8 ± 1.4	1.1 ± 0.7	27.4 ± 4.1
7	May-07	38.6 ± 8.9	1.8 ± 0.5	44 ± 12	2.7 ± 0.7	1.5 ± 0.5	30.8 ± 3.6
3	Jun-07	36.9 ± 10.2	2.0 ± 0.5	53 ± 42	3.2 ± 2.5	1.5 ± 0.9	25.9 ± 0.3
3	Oct-07	84.6 ± 9.6	3.6 ± 0.9	126 ± 33	7.6 ± 2.0	2.0 ± 0.9	32.3 ± 1.8
3	Dec-07	101.2 ± 16	4.6 ± 0.4	137 ± 67	8.3 ± 4.0	1.8 ± 0.8	33.1 ± 8.3
3	Jan-08	79.2 ± 6.4	6.5 ± 0.9	196 ± 61	11.8 ± 3.6	1.9 ± 0.9	18.0 ± 2.0
4	Feb-08	50.5 ± 12.7	5.6 ± 1.1	140 ± 87	8.4 ± 5.2	1.6 ± 1.2	13.8 ± 4.2

The relatively high BC/EC ratios can result due to the use of lower σ_{ATN} in the Aethalometer based BC measurements. In fact, the value of σ_{ATN} (i.e. 20.7 $m^2\ g^{-1}$; Fig. 1) obtained in this study (based on EC–OC analyzer) is ~25% higher than that used in the Aethalometer at 880 nm (i.e.16.6 $m^2\ g^{-1}$). Although, linear regression plot between ATN and EC_s concentration yields a value of 20.7 $m^2\ g^{-1}$ for σ_{ATN} at Kanpur; the individual values calculated by dividing ATN with EC_s and R(ATN) show large variability (range: 10.1 to 38.0 $m^2\ g^{-1}$; Fig. 2a). The correction for shadowing effect, represented by R(ATN), is made using an equation described by Weingartner et al. (2003). Jeong et al. (2004) had reported that BC concentration measured (using Aethalometer) correlates well with that of EC (measured using Sunset Lab's EC–OC analyzer) for the samples collected from Rochester ($R^2 = 0.84$) and Philadelphia ($R^2 = 0.60$); but slope of the linear-fit for BC and EC data are 3.3 ± 0.2 and 2.7 ± 0.1, respectively. These studies suggest that the constant value of σ_{ATN} (i.e.16.6 $m^2\ g^{-1}$) used in Aethalometer needs to be modified to 54.8 $m^2\ g^{-1}$ for the measurements made at Rochester and to 44.2 $m^2\ g^{-1}$ at Philadelphia. In a similar study, Bae et al. (2007) have reported that EC concentrations are higher than BC and EC/BC ratio ranges from 1.23 to 1.6 and demonstrate that the observed disagreement arises due to the variability in σ_{ATN} of BC. The data reported in this study, as well as those reported in the literature (Bond and Bergstrom, 2006; Liousse et al., 1993), suggest that σ_{ATN} can vary from sample to sample as well as from site to site depending on the source and composition of aerosols. The use of 'site-specific' σ_{ATN} is, thus, necessary in order to assess the BC mass concentration from widely used optical methods (Sharma et al., 2002; Watson and Chow, 2002).

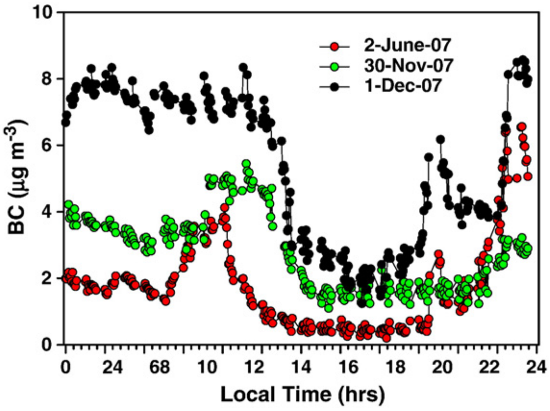

Fig. 4. The diurnal variability of BC mass concentration measured using the Aethalometer (at 880 nm) for the three selected days: 2-June-07 (summer), 31-Nov-2007 (post-monsoon) and 1-Dec-2007 (winter). No samples are collected during monsoon period (July–September).

4.4. Diurnal variability in Aethalometer based BC mass concentrations

The typical diurnal variability in BC mass concentrations for three selected days; 2-June-07 (summer), 31-Nov-2007 (post-monsoon) and 1-Dec-2007 (winter) is presented in Fig. 4. These data clearly points at two important results; the seasonal variability and the diurnal pattern of BC mass concentration. The BC mass concentrations during post-monsoon and wintertime are 2 to 4 times higher compared to those in summer. The seasonal variability in BC mass concentration (Fig. 4) can be understood in terms of variability in the source strength and boundary layer dynamics. The enhanced emissions from agriculture-waste and biomass burning during wintertime increase the organic aerosol loading (Ram and Sarin, 2010). Furthermore, relatively low ambient temperatures and shallow boundary layer height (typically 500 m) decrease the vertical mixing and help in efficient trapping of aerosols and thus, lead to an increase in the mass concentration of chemical species during winter season. In contrast, relative decrease in the biomass burning; higher temperatures and increase in the boundary layer height enhance the vertical mixing and lead to a decrease in the abundance of chemical species.

5. Conclusions

The successful application of thermo-optical method, using EC–OC analyzer, for the determination of attenuation coefficient (b_{ATN}) and attenuation cross-section (σ_{ATN}) of airborne EC in an urban environment is reported here. Using EC–OC analyzer, attenuation cross-section ($\sigma_{ATN} = 20.7\ m^2\ g^{-1}$) at the sampling site (Kanpur in northern India) is about 25% higher than that used in the Aethalometer ($16.6\ m^2\ g^{-1}$) and BC concentration is also higher by same order compared to EC. The use of site-specific σ_{ATN} is also desirable for the systematic monitoring of BC concentration by Aethalometer. The significant difference in BC and EC mass concentrations requires systematic seasonal and spatial data in order to assess the nature of black carbon derived from coal-based industries, agriculture-waste burning and vehicular exhausts.

Acknowledgements

Authors would like to thank Mr. Sanjay Baxla for the help provided in the collection of aerosol samples at IIT-Kanpur and Ms. Jai Devi for providing the BC data. Authors acknowledge the financial support from the ISRO-GBP (Bangaluru, India).

References

Allen, G.A., Lawrence, J., Koutrakis, P., 1999. Field validation of a semi-continuous method for aerosol black carbon (aethalometer) and temporal patterns of summertime hourly black carbon measurements in southwestern PA. Atmos. Environ. 33, 817–823.

Andreae, M.O., Gelencser, A., 2006. Black carbon or brown carbon? The nature of light-absorbing carbonaceous aerosols. Atmos. Chem.Phys. 6, 3131–3148.

Babich, P., Davey, M., Allen, G., Koutrakis, P., 2000. Method comparisons for particulate nitrate, elemental carbon, and PM2.5 mass in seven U.S. cities. J. Air Waste Manage. Assoc. 50, 1095–1105.

Badarinath, K.V.S., Kharol, S.K., Sharma, A.R., Ramaswamy, V., Kaskaoutis, D.G., Kambezidis, H.D., 2009. Investigations of an intense aerosol loading during 2007 cyclone SIDR — a study using satellite data and ground measurements over Indian region. Atmos. Environ. 43, 3708–3716.

Bae, M.-S., Hong, C.-S., Kim, Y.J., Han, J.-S., Moon, K.-J., Kondo, Y., Komazaki, Y., Miyazaki, Y., 2007. Intercomparison of two different thermal–optical elemental carbons and optical black carbon during ABC-EAREX2005. Atmos. Environ. 41, 2791–2803.

Birch, M.E., Cary, R.A., 1996. Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust. Aerosol Sci. Technol. 25, 221–241.

Bodhaine, B.A., 1995. Aerosol absorption measurements at Barrow, Mauna Loa and the south pole. J. Geophys. Res. 100 (D5), 8967–8975.

Bond, T.C., Bergstrom, R.W., 2006. Light absorption by carbonaceous particles: an investigative review. Aerosol Sci. Technol. 40, 1–41.

Chinnam, N., Dey, S., Tripathi, S.N., Sharma, M., 2006. Dust events in Kanpur, northern India: chemical evidence for source and implications to radiative forcing. Geophys. Res. Lett. 33, L08803. doi:10.1029/2005GL025278.

Dey, S., Tripathi, S.N., 2007. Estimation of aerosol optical properties and radiative effects in the Ganga basin, northern India, during the wintertime. J. Geophys. Res. 112, D03203. doi:10.1029/2006JD007267.

Dey, S., Tripathi, S.N., Mishra, S.K., 2008. Probable mixing state of aerosols in the Indo-Gangetic Basin, northern India. Geophys. Res. Lett. 35, L03808. doi:10.1029/2007GL032622.

Graber, E.R., Rudich, Y., 2006. Atmospheric HULIS: how humic-like are they? a comprehensive and critical review. Atmos. Chem. Phys. 6, 729–753.

Hagler, G.S.W., Bergin, M.H., Smith, E.A., Dibb, J.E., 2007. A summer time series of particulate carbon in the air and snow at Summit, Greenland. J. Geophys. Res. 110, D21309. doi:10.1029/2007JD008993.

Hitzenberger, R., Petzold, A., Bauer, H., Ctyroky, P., Pouresmaeil, P., Laskus, L., Puxbaum, H., 2006. Intercomparison of thermal and optical measurement Methods for elemental carbon and black carbon at an urban location. Environ. Sci. Technol. 40, 6377–6381.

Husain, L., Dutkiewicz, V.A., Khan, A.J., Ghauri, B.M., 2007. Characterization of carbonaceous aerosols in urban air. Atmos. Environ. 41, 6872–6883.

Jeong, C.H., Hopke, P.K., Kim, E., Lee, D.W., 2004. The comparison between thermal–optical transmittance elemental carbon and Aethalometer black carbon measuredat multiple monitoring sites. Atmos. Environ. 38, 5193–5204.

Junker, C., Jennings, S.G., Cachier, H., 2006. Aerosol light absorption in the North Atlantic: trends and seasonal characteristics during the period 1989 to 2003. Atmos. Chem. Phys. 6, 1913–1925.

Kirchstetter, T.W., Novakov, T., Hobbs, P.V., 2004. Evidence that the spectral dependence of light absorption by aerosols is affected by organic carbon. J. Geophys. Res. 109, D21208. doi:10.1029/2004JD004999.

Lavanchy, V.M.H., Gaggeler, H.W., Nyeki, S., Baltensperger, U., 1999. Elemental carbon (EC) and black carbon (BC) measurements with a thermal method and an aethalometer at the high-alpine research station Jungfraujoch. Atmos. Environ. 33, 2759–2769.

Liousse, C., Cachier, H., Jennings, S.G., 1993. Optical and thermal measurements of black carbon aerosol content in different environments: variation of the specific attenuation cross-section, sigma (σ). Atmos. Environ. A Gen. Top. 27A, 1203–1211.

Martins, J., Artaxo, P., Liousse, C., Reid, J., Hobbs, P., Kaufman, Y., 1998. Effects of black carbon content, particle size, and mixing on light absorption by aerosols from biomass burning in Brazil. J. Geophys. Res. 103 (D24), 32041–32050.

Mishra, S.K., Tripathi, S.N., 2008. Modeling optical properties of mineral dust over the Indian Desert. J. Geophys. Res. 113, D23201. doi:10.1029/2008JD010048.

Ram, K., Sarin, M.M., 2009. Absorption coefficient and site-specific mass absorption efficiency of elemental carbon in aerosols from urban, rural and high-altitude sites in India. Environ. Sci. Technol. 43, 8233–8239.

Ram, K., Sarin, M.M., 2010. Spatio-temporal variability in atmospheric abundances of EC, OC and WSOC over northern India. J. Aerosol Sci. 41, 88–98.

Ram, K., Sarin, M.M., Hegde, P., 2008. Atmospheric abundances of primary and secondary carbonaceous species at two high-altitude sites in India: sources and temporal variability. Atmos. Environ. 42, 6785–6796.

Ramanathan, V., Crutzen, P.J., Kiehl, J.T., Rosenfeld, D., 2001. Atmosphere: aerosols, climate, and the hydrological cycle. Science 294, 2119–2124.

Reisinger, P., Wonaschütz, A., Hitzenberger, R., Petzold, A., Bauer, H., Jankowski, N., Puxbaum, H., Chi, X., Maenhaut, W., 2008. Intercomparison of measurement techniques for black or elemental carbon under urban background conditions in wintertime: influence of biomass combustion. Environ. Sci. Technol. 42, 884–889.

Rengarajan, R., Sarin, M.M., Sudheer, A.K., 2007. Carbonaceous and inorganic species in atmospheric aerosols during wintertime over urban and high-altitude sites in North India. J. Geophys. Res. 112, D21307. doi:10.1029/2006JD008150.

Schauer, J.J., Mader, B.T., Deminter, J.T., Heidemann, G., Bae, M.S., Seinfeld, J. H., Flagan, R.C., Cary, R.A., Smith, D., Huebert, B.J., Bertram, T., Howell, S., Kline, J.T., Quinn, P., Bates, T., Turpin, B., Lim, H.J., Yu, J.Z., Yang, H., Keywood, M.D., 2003. ACE–Asia intercomparison of a thermal–optical method for the determination of particle-phase organic and elemental carbon. Environ. Sci. Technol. 37, 993–1001.

Schwarz, J., Gao, R., Spackman, J.R., Watts, L., Thomson, D.S., Fahey, D.W., Ryerson, T.B., Peischl, J., Holloway, J.S., Trainer, M.K., Frost, G.J., Baynard, T., Lack, D., DeGouw, J.A., Warneke, C., Negro, L.A.D., 2008. Measurement of the mixing state, mass, and optical size of individual black carbon particles in urban and biomass burning emissions. Geophys. Res. Lett. 35, L13810. doi:10.1029/2008GL033968.

Sharma, S., Brook, J.R., Cachier, H., Chow, J., Gaudenzi, A., Lu, G., 2002. Light absorption and thermal measurements of black carbon in different regions of Canada. J. Geophys. Res. 107 (D24), 4771. doi:10.1029/2002JD002496.

Snyder, D.C., Schauer, J.J., 2007. An inter-comparison of two black carbon aerosol instruments and a semi-continuous elemental carbon instrument in the urban environment. Aerosol Sci. Technol. 41, 463–474.

Stone, E.A., Lough, G.C., Schauer, J.J., Praveen, P.S., Corrigan, C.E., Ramanathan, V., 2007. Understanding the origin of black carbon in the atmospheric brown cloud over the Indian Ocean. J. Geophys. Res. 112, D22S23. doi:10.1029/2006JD008118.

Tripathi, S.N., Dey, S., Tare, V., Satheesh, S.K., 2005. Aerosol black carbon radiative forcing at an industrial city in northern India. Geophys. Res. Lett. 32, L08802. doi:10.1029/2005GL022515.

Tripathi, S.N., Tare, V., Chinnam, N., Srivastava, A.K., Dey, S., Agarwal, A., Kishore, S., Lal, R.B., Manar, M., Kanwade, V.P., Chauhan, S.S.S., Sharma, M., Reddy, R.R., Gopal, K.R., Narasimhulu, K., Reddy, L.S.S., Gupta, S., Lal, S., 2006. Measurements of atmospheric parameters during Indian Space Research Organization Geosphere Biosphere Programme Land Campaign II at a typical location in the Ganga basin: 1. Physical and optical properties. J. Geophys. Res. 111, D23209. doi:10.1029/2006JD007278.

Watson, J.G., Chow, J.C., 2002. Comparison and evaluation of in situ and filter carbon measurements at the Fresno Supersite. J. Geophys. Res. 107 (10.1029/2001JD000573), 8341. doi:10.1029/2001JD000573.

Weingartner, E., Saathoff, H., Schnaiter, M., Streit, N., Bitnar, B., Baltensperger, U., 2003. Absorption of light by soot particles: determination of the absorption coefficient by means of aethalometers. J. Aerosol Sci. 34, 1445–1463.

Yang, M., Howell, S.G., Zhuang, J., Huebert, B.J., 2009. Attribution of aerosol light absorption to black carbon, brown carbon, and dust in China — interpretations of atmospheric measurements during EAST-AIRE. Atmos. Chem. Phys. 9, 2035–2050.

Zhang, X.Y., Wang, Y.Q., Zhang, X.C., Guo, W., Niu, T., Gong, S.L., Yin, Y., Zhao, P., Jin, J.L., Yu, M., 2008. Aerosol monitoring at multiple locations in China: contributions of EC and dust to aerosol light absorption. Tellus 60, 647–656.