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## The comparison between thermal-optical transmittance elemental carbon and Aethalometer black carbon measured at multiple monitoring sites

Cheol-Heon Jeong<sup>a,b</sup>, Philip K. Hopke<sup>a,b,\*</sup>, Eugene Kim<sup>a,b</sup>, Doh-Won Lee<sup>a,b</sup>

<sup>a</sup>Department of Civil Environmental Engineering, Clarkson University, Box 5708, Potsdam 13699-5708, NY, USA <sup>b</sup>Department of Chemical Engineering, Center for Air Resources Engineering and Science, Clarkson University, Box 5708, Potsdam 13699-5708, NY, USA

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## Abstract

Continuous and semi-continuous measurements of organic carbon (OC), elemental carbon (EC) and PM2.5 were performed during the summer of 2002 in Rochester, NY and Philadelphia, PA. During the study period in Philadelphia, high concentrations of wood smoke from a Canadian forest fire were transported to the monitoring site. Two-hour integrated thermal EC (EC)/optical EC (BC<sub>s</sub>) using a Sunset Lab OC/EC analyzer and continuous Aethalometer optical EC ( $BC_A$ ) using a two-wavelength Aethalometer were compared in various environments. The weekdays diurnal average for EC peaked during the morning rush-hour and was much higher than the value during weekends, whereas the OC results showed no diurnal variation of OC during either weekdays or weekends at both sites. The diurnal variations of BCA were also strongly correlated with the rush-hour traffic. The correlation coefficient between EC and BC<sub>A</sub> in Rochester ( $r^2 = 0.84$ ) was higher than in Philadelphia ( $r^2 = 0.60$ ) while the BC<sub>A</sub>/EC slopes were 3.3 and 2.7 in Rochester and Philadelphia, respectively. The difference in the slopes indicates that the specific attenuation crosssection used for the optical carbon analysis depends on the physical and chemical characteristics of elemental carbon. During the Canadian forest fire, the  $BC_A/EC$  slope dramatically dropped to 0.4 with a correlation coefficient of 0.60. The decrease of the proportionality between EC and  $BC_A$  demonstrates the variability of the absorption coefficient. The level of UV absorbing organic compounds significantly increased during the fire aerosol episode suggesting the presence of abundant organic compounds in the forest fire smoke particles. © 2004 Elsevier Ltd. All rights reserved.

*Keywords:* Organic carbon; Elemental carbon; Black carbon; PM<sub>2.5</sub>; Sunset Lab OC/EC analyzer; Aethalometer; Specific attenuation cross-section; Canadian forest fire

## 1. Introduction

Carbonaceous aerosol is a complex mixture and one of the more abundant components in urban  $PM_{2.5}$ .

Carbonaceous particles are composed of two main fractions, organic carbon (OC) that is semivolatile and elemental carbon (EC) that is refractory and strongly light absorbing. EC is formed by incomplete combustion and is nonvolatile. Gas to particle conversion of hydrocarbon gases, exhaust from combustion process, boilers, residential wood burning, meat cooking, and

<sup>\*</sup>Corresponding author. Fax: +1-315-268-4410. *E-mail address:* hopkepk@clarkson.edu (P.K. Hopke).

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road dust (Pandis et al., 1992; Rogge et al., 1993a,b, 1997, 1998) are known to be major sources of OC in PM<sub>2.5</sub>. Also, emissions from diesel heavy trucks and diesel automobiles are known to be the main sources of EC in urban areas (Gray and Cass, 1998). Light absorption by PM<sub>2.5</sub> particles is also primarily due to the carbonaceous species in the particles. The mass related to light absorption is typically referred to as black carbon (BC). Often BC and EC are used interchangeably. However, as will be seen from the results presented in this paper, these quantities are not measures of the same properties of PM<sub>2.5</sub>. Thus, careful definition of these quantities are required to permit proper discussion of their sources and how they behave in the atmosphere.

These carbon fractions are typically defined operationally by their measurement protocols. Since OC and EC have thermally different properties, they are determined by using thermal optical protocols. One such protocol is the National Institute of Occupational Safety and Health (NIOSH) method 5040 with correction by the thermal-optical transmission (TOT) (Birch and Cary, 1996; Babich et al., 2000; Chow et al., 2001; Watson and Chow, 2002). The other protocol is the interagency monitoring of protected visual environments/thermal optical reflectance (IMPROVE/TOR) (Chow et al., 1993, 2001). Both of these protocols produce OC and EC values, but because of differences in these protocols described by Chow et al. (2001), different values are obtained. There are also variations in the measurement of BC depending on the wavelength of light and whether reflectance or transmission is used.

Comparing optical differences among carbonaceous species, EC is generally characterized as black carbon (BC) (NARSTO, 2003). Because of its ability to absorb light, BC reduces visibility by both scattering and absorbance and is important with respect to the earth's radiative balance (Wolff et al., 1981; Cruntzen and Andreae, 1990; Jacobson, 2000, 2001). In terms of analytical methodology, EC can be classified by two categories, thermal EC and optical BC. While thermal EC can be determined by TOT analysis or TOR (thermal-optical reflection) analysis as mentioned before, optical attenuation methods such as an Aethalometer have been usually used to obtain BC (Hansen et al., 1984). At this time, there has not been many reports regarding the differences between thermal EC and optical BC concentrations. Even though reasonably good agreements were reported in a few intercomparison studies of the Aethalometer with other carbon analytical methods. The calculated specific absorption cross section ( $\sigma$ , attenuation coefficient) for the Aethalometer varied in different environments (Allen et al., 1999; Babich et al., 2000; Lim et al., 2003). In addition, the thermal, optical, and chemical characteristics that include variable attenuation coefficients of BC are

different (Jennings and Pinnick, 1980; Liousse et al., 1993; Lavanchy et al., 1999; Hitzenberger et al., 1999). Liousse et al. (1993) found that EC may exist both in external mixtures in which EC can constitute the shell or the core of aerosols and in internal mixtures. The various chemical and physical properties of EC may also cause changes in the optical BC concentrations measured using the optical attenuation method even if same measurement system is applied. The intercomparison of different analytical instruments at multiple sites can provide a better understanding of the potential variations of aerosol optical BC under various atmospheric conditions.

Currently, there are few high time resolution measurements of OC, EC, and BC collocated with other continuous chemical species measurements at various monitoring sites. Continuous OC, EC, and BC measurements with higher time resolution than filter-based measurements are one of the important steps for understanding aerosol behavior and supporting source apportionment studies since they could permit measurements to be on the time scale of dynamic atmospheric processes such as wind direction shifts that affect the concentrations of atmospheric carbonaceous aerosol. With the high-time resolution, it can be used for epidemiological studies to investigate the influence of carbonaceous materials on acute adverse effects of human health.

As parts of summer intensive Rochester PM study and the Philadelphia north east oxidant and particle study (NE-OPS) program, real-time  $PM_{2.5}$  mass, semicontinuous organic and elemental carbon, and continuous black carbon were measured sequentially at urban sites in Rochester and Philadelphia. Semi-continuous carbonaceous species and continuous  $PM_{2.5}$  mass were measured in two cities to determine the relationships for OC, thermal EC, optical EC (BC) and  $PM_{2.5}$  mass concentrations. This paper reports the results of the intercomparison conducted to determine temporal variations of carbonaceous aerosols and to evaluate the variation of measurements of thermal EC and optical BC in the various atmospheric conditions.

## 2. Experimental methods

Studies were conducted at the University of Rochester Medical Center (Latitude  $43^{\circ}$  07' 30" N, Longitude 77° 37' 14" W) located 5 km southeast of downtown Rochester, New York from 6 to 18 June 2002 and at the NE-OPS site (Latitude 40° 02' 10" N, Longitude 75° 00' 14" W), approximately 20 km northeast of downtown Philadelphia, Pennsylvania from 1 July to 2 August 2002. The monitoring site in Rochester was adjacent to a road with moderate traffic and located 5 km away from downtown Rochester. In Philadelphia, the monitoring site was located 500 m away from a light traffic road and 1 km to the east of a heavy traffic highway (I-95).

Continuous PM<sub>2.5</sub> mass concentrations were obtained with a 30°C tapered element oscillating microbalance (TEOM) (Rupprecht and Patashnick, Albany, NY) with a sample equilibration system (SES) dryer every 10 min (Meyer et al., 2000). The 1400a TEOM was configured with a PM<sub>10</sub> head, a PM<sub>2.5</sub> sharp cut cyclone (SCC), a SES dryer, and a TEOM that directly measures particle mass collected on a filter by drawing ambient air through a filter at a constant flow rate, continuously weighing the filter and calculating rolling 10-min smoothed mass concentrations. The sample equilibration system (SES) includes a Nafion dryer (Perma Pure Inc., Toms River, NJ) to condition the main and bypass sample streams to low humidity and fixed temperature. The SES is designed to reduce the possibility of PM mass concentrations being overestimated due to the moisture affinity of some types of particles.

Carbonaceous materials in  $PM_{2.5}$  were measured by using two analyzers, a semi-continuous Sunset Lab OC/ EC field instrument (Sunset Laboratory, Forest Grove, OR) for OC, thermal EC (EC), and Sunset Lab optical EC (BC<sub>S</sub>) and a two-wavelength Aethalometer, AE-20 (Magee Scientific, Berkeley, CA) for Aethalometer optical EC (Aethalometer BC, BC<sub>A</sub>). Samples introduced into the semi-continuous OC/EC field instrument were segregated by a PM<sub>2.5</sub> very sharp cut cyclone (VSCC) (BGI Inc., Waltham, MA). The sampled aerosol is then passed through a carbon impregnated filter (CIF) multichannel, parallel plate denuder to remove most of the gas phase organic materials (Eatough et al., 1993).

The semi-continuous OC/EC field instrument is based on NIOSH Method 5040. The temperature program of the field OC/EC analyzer has only two steps instead of the basic NIOSH four steps during the OC analysis when the sample is heated under high purity He. The time/temperature steps for the OC and thermal EC analysis are given in Table 1. To correct for EC error produced by OC pyrolysis, the darkening of the filter was monitored by measuring the intensity of light

Table 1

Temperature and residence time protocol of the semi-continuous Sunset Lab OC/EC field analyzer for 2-h integrated samples in Rochester and Philadelphia

Step	Gas	Residence time (s)	Temperature (°C)
OC	He <sup>a</sup>	90	600
OC	He <sup>a</sup>	90	870
Cooling	He <sup>a</sup>	60	640
EC	$He + O_2^{b}$	90	870

<sup>a</sup>Ultra high purity grade, >99.99%.

<sup>b</sup>10% oxygen.

transmitted while it is being analyzed. The light transmittance monitored by the laser beam through the filter was used for determining the split point between the pyrolized carbon formed from the organic carbon that was originally in the sample (Turpin et al., 1990; Birch and Cary, 1996). During the oxidizing step, EC and pyrolytic carbon were oxidized and the light transmittance through the filter increased to the background levels for a clean quartz filter. The split point is the point in time during the analysis at which the laser value equals the initial signal. In order to reduce uncertainties due to low concentrations of elemental carbon, samples for the field OC/EC instrument were collected for 105 min and were analyzed for 15 min every 2h.

The semi-continuous Sunset Lab OC/EC instrument was externally and internally calibrated by using sucrose standard stock solution  $(4.21 \,\mu g \, C \,\mu l^{-1})$  and a 4.97%methane in helium mixture, respectively. Three sucrose standard samples, micropipette deposits on clean punched filters (2.73, 27.34 and 54.68  $\mu$ g C cm<sup>-2</sup>), were used for the external calibration of total carbon concentrations every 3 days. Measured concentrations of the standard samples were verified within 5% of the calculated values. The internal calibration used by the methane mixture was automatically repeated in a fixed volume loop at the end of every analysis to compensate the variability of the instrument's FID responses. Unfortunately, there is no standard reference material for EC that can be used as part of the quality assurance process.

Sunset Lab "optical EC" (BC<sub>S</sub>) was measured by the semi-continuous Sunset Lab OC/EC analyzer using a 680 nm laser. The laser transmittance when a sample is loaded and the final signal when the deposit has been analyzed and removed are measured to obtain absorbance (attenuation, ATN) during sampling. Based on the absorbance and the measured thermal EC concentrations, the apparent attenuation coefficient is estimated using a second degree polynomial fit of the specific absorption cross section ( $\sigma$ , attenuation coefficient) obtained automatically by the instrument. An example of the relationship between the attenuation coefficient and the extent of the deposit is shown in Fig. 1 based on data obtained from measurements made in this study. The attenuation coefficient is related to the loading of elemental carbon on an unit filter area. As the sample becomes darker, the attenuation coefficient decreases. At very low loadings, the attenuation coefficient is much higher. Using the absorbance measured every 2h, the mass concentration of BCs was calculated using an attenuation coefficient obtained from the equation developed by the instrument.

High time resolution Aethalometer optical EC (Aethalometer BC,  $BC_A$ ) concentrations measured by using a two-wavelength Aethalometer were obtained at



Fig. 1. Variations of the attenuation coefficients used for the determination of optical elemental carbon  $(BC_S)$  measured by the semi-continuous Sunset Lab OC/EC field analyzer.

both sampling sites. Aethalometer BC (BC<sub>A</sub>) was measured at  $\lambda = 880$  nm and UV-absorbing aromatic organic material (UV-BC) was measured at 370 nm. BC<sub>A</sub> mass was obtained by determining the attenuation of light transmitted through a sampled filter (Hansen et al., 1984). In contrast to the non-fixed attenuation coefficients of the Sunset Lab semi-continuous OC/EC analyzer, the attenuation coefficient of the Aethalometer used in this study for the calculation of BC<sub>A</sub> was  $16.6 \text{ m}^2 \text{ g}^{-1}$  as recommended by the manufacturer. The attenuation coefficient is the critical parameter to convert attenuation measurements (ATN) to BC<sub>A</sub> mass ([BC<sub>A</sub>]) using the relation:

$$[BC_A] = ATN/\sigma.$$

Thus, variability is the attenuation coefficient would result in errors in the estimated black carbon mass. The two-wavelength Aethalometer has UV wavelength ( $\lambda =$ 370 nm) to identify the presence of certain organic compounds such as polycyclic aromatic hydrocarbons (PAH) that strongly absorb UV wavelengths. The enhancement in the UV absorbing signal indicates the presence of additional quantities of non-black, UVabsorbing aromatic organic material.

## 3. Results and discussion

## 3.1. Variations of real-time PM<sub>2.5</sub> and semi-continuous carbonaceous compounds

OC/EC values in Rochester from 10 to 14 June were lost due to the unexpected malfunction of the semicontinuous OC/EC analyzer. For the initial discussion of these measurements, the unusual Canadian forest fire episode observed in Philadelphia in early June was excluded from the calculations. Mean concentrations of thermal OC and thermal EC (EC) in Rochester were 8.6 and  $0.4 \,\mu g \, m^{-3}$ , respectively while the values in Philadelphia were 5.2 and  $0.4 \,\mu g \, m^{-3}$  during the study periods. Sunset Lab optical EC (BC<sub>S</sub>) and Aethalometer optical EC (Aethalometer BC, BC<sub>A</sub>) concentrations in Rochester ranged from 0.1 to  $1.8 \,\mu g \, m^{-3}$  with a mean of  $0.3 \,\mu g \, m^{-3}$  and from 0.2 to  $2.4 \,\mu g \, m^{-3}$  with a mean of  $0.9 \,\mu g \, m^{-3}$ , respectively. In Philadelphia BC<sub>S</sub> values ranged from 0.1 to  $2.1 \,\mu g \, m^{-3}$  with a mean of  $0.9 \,\mu g \, m^{-3}$ .

The average mass ratios and ranges of OC, EC,  $BC_8$ , and BC<sub>A</sub> to PM<sub>2.5</sub> over the duration of field study are shown in Table 2 for each sampling site. The values in Table 2 are calculated based on the 2 h averages of each measurements as OC and EC were obtained using the Sunset Lab analyzer every 2h. As shown, average mass fraction of semi-continuous OC/PM2.5 in Rochester was much higher than the ratio in Philadelphia while there were no significant differences of EC fractions in PM2.5 between both sites. It clearly shows that the carbonaceous aerosol accounted for 70% of PM25 and OC is most abundant chemical species during the study period in Rochester. In Philadelphia, carbonaceous particles only constituted approximately 30% of the 2-h averaged PM<sub>2.5</sub> concentrations. However, cases when the semicontinuous OC concentrations exceeded the PM2.5 were observed at both sites. These appear to be either significant loss of semivolatile OC from the TEOM or a significant adsorption artifact on the quartz filter in the Sunset OC/EC instrument. Since monitoring room temperature exceeded 30°C, the TEOM was often operated at more than 30°C for the cases and thus, loss of mass from the TEOM is the preferred hypothesis for the lack of mass closure (Jeong et al., 2004). On average, the semi-continuous EC fractions were low at both sites and the contributions to PM2.5 mass were small. The ratio of BCA to PM2.5 in Rochester was somewhat

Table 2

Average mass ratios of 2-h average OC, EC,  $BC_8$ , and  $BC_4$  to  $PM_{2.5}$  concentration obtained during the period 6–17 June, 2002 in Rochester and during the period 1 July to 2 August, 2002 except the Canadian forest fire event in Philadelphia

		Rochester	Philadelphia
OC/PM <sub>2.5</sub>	Average	0.70	0.26
,	Range	0.32-1.36	0.10-1.39
EC/PM <sub>2.5</sub>	Average	0.04	0.02
	Range	0.01-0.14	0.01-0.12
$BC_S/PM_{2.5}$	Average	0.03	0.02
	Range	0.01-0.13	0.01 - 0.09
$BC_A/PM_{2.5}$	Average	0.08	0.04
	Range	0.02-0.29	0.01 - 0.27
Valid number		47	304

higher than the ratio in Philadelphia, whereas there was no significant difference of  $BC_S$  between Rochester and Philadelphia.

#### 3.2. Diurnal variations of carbonaceous aerosols

Mobile sources, diesel and gasoline engines, are known to be major sources of OC and EC. However, OC concentrations may arise from a variety of source types (Gray and Cass, 1998). Sources of OC and EC may be potentially identified by using the temporal trends of the concentrations. Diurnal variations of semicontinuous OC and EC during weekdays and weekends in Philadelphia are shown in Fig. 2. As expected, the EC concentrations for weekdays peaked during the morning rush-hour from 7 to 9 a.m. and were much higher than the EC concentrations measured on the weekends. These results strongly suggest that sources of EC were closely related to motor vehicles. There were no evening rushhour peaks during both weekdays and weekends, presumably because of the substantially higher boundary layer mixing depths during the late afternoon. The diurnal variation boundary layer mixing depths of obtained on the NOAA Air Resources Laboratory



Fig. 2. Comparison of diurnal variations of elemental carbon, organic carbon, and boundary layer depths in Philadelphia, PA, 10 July–2 August 2002.

(NOAA, 2003) web server was also shown in Fig. 2. As expected, the 3h average mixing depths in the evening rush-hour during July 2002 was approximately three time higher than the depths in the morning rush-hour.

In contrast to the diurnal trend of EC, semicontinuous OC slightly decreased for weekdays while OC slightly increased on the weekends. In general, although OC measured on weekdays was somewhat higher than the concentrations on weekends, the overall difference between weekdays and weekends was negligible in the afternoon. It might be expected that sources of OC were less related to traffic sources and they would be linked with a variety of sources such as stationary sources and formation of secondary organic aerosol in the afternoon.

Similar to the diurnal trends shown in Fig. 2, the diurnal variations of EC and OC measured in Rochester are also shown in Fig. 3. Note that due to limited data, the differences between weekdays and weekends were not compared. The results strongly support the diurnal patterns of carbonaceous aerosols that show clear morning peaks of EC occurred during rush-hour whereas there was no significant temporal variation of semi-continuous OC concentrations. This lack of variation also suggests significant levels of transported OC.

Diurnal variations of Aethalometer BC (BC<sub>A</sub>) obtained during weekdays (13 days for Rochester and 18 days for Philadelphia) and weekends (6 days for Rochester and 7 days for Philadelphia) in Rochester and Philadelphia are shown in Fig. 4. In Rochester, BC<sub>A</sub> concentrations on weekdays peaked around 9 a.m., and broad peak was found around 3-5 p.m. However, during the weekends, there was no peak as a function of time of day. It is assumed that the first peak was related to the morning rush-hour. The second broad peak also appeared to be traffic related, but reduced because of the greater dilution in the afternoon periods. In Philadelphia, the peak was observed during the morning rush-hour and the highest concentration occurred at 6 a.m.



Fig. 3. Diurnal variations of elemental carbon and organic carbon measured in Rochester, NY, 6–18 June 2002.



Fig. 4. Weekday and weekend diurnal variations of Aethalometer BC (BC<sub>A</sub>) in Rochester, NY and in Philadelphia, PA.

for weekdays. There was no significant diurnal variation of  $BC_A$  during weekends. Thus, the variations of  $BC_A$  were strongly related to motor vehicles combined with lower mixing height in the morning similar to the observed EC concentrations.

In comparing the two morning peaks of BCs in Rochester and Philadelphia, the peak time at the Philadelphia site occurred earlier than the peak at Rochester site. This is likely due to a result of near by surroundings of the sampling sites. As noted in the description of two monitoring sites, the Rochester site is located in the University of Rochester Medical Center, which is adjacent to a medium volume of traffic road. It is expected that most traffic sources might be concentrated in the late morning rush-hour, around 9 a.m. In contrast, the immediate surroundings of the Philadelphia site consisted of the suburban outskirts of Philadelphia and the busy I-95 highway, approximately 1 km from the site. It would be expected that the morning rush-hour on the highway in Philadelphia may start earlier than at the Rochester site. The difference in the morning rush-hour at two sites likely results in slight peak offsets in Fig. 4. Similar feature was also found in the diurnal trends of EC in Philadelphia and Rochester as shown in Figs. 2 and 3.

## 3.3. Comparison of thermal elemental carbon and optical elemental carbon

Fig. 5 show the correlations of 2-h average Sunset Lab thermal EC obtained in Rochester from 7 to 19 June 2002 and in Philadelphia from 1 July to 2 August 2002 and Sunset Lab optical EC ( $BC_S$ ) and Aethalometer BC ( $BC_A$ ) concentrations, respectively. The number of pairwised valid samples were 60 and 281 measurements in Rochester and Philadelphia, respectively. Since a strong and distinct impact of the Canadian forest fire from 6 to 9 July in Philadelphia was observed, these data that will



Fig. 5. Comparison between Sunset Lab thermal EC and Sunset Lab optical EC ( $BC_8$ ) in Rochester and Philadelphia during the summer of 2002.

be discussed in the next section were excluded in these figures.

As presented in Fig. 5, EC in Rochester values were strongly correlated with BCs values with a high correlation coefficient,  $r^2 = 0.95$  and the slope was  $0.89 \pm 0.02$ . Similar good agreement was also observed in Philadelphia although the correlation coefficient  $(r^2 = 0.73, \text{ and slope} = 0.99 \pm 0.07)$  was somewhat lower than the value in Rochester. In the bottom of Fig. 5 for Philadelphia, two extreme outliers were observed around in the early morning of August 2 with high BCs concentrations. Simultaneously with the peaks, the high concentrations of Aethalometer BC were also observed. It was probably due to unidentified particles having quite different attenuation coefficients compared to typical carbonaceous materials. The unusual cases with significantly high optical EC concentrations were mostly found during the Canadian forest fire episode.

Fig. 6 shows the correlations between  $BC_A$  measured using the Aethalometer and thermal EC in Rochester and Philadelphia. Calculated BCA concentrations were significantly higher than EC at both sites although they were highly correlated ( $r^2 = 0.84$  in Rochester and  $r^2 =$ 0.60 in Philadelphia). In these intercomparison studies, the slopes of collocated BCA versus EC measurements were  $3.3 \pm 0.2$  and  $2.7 \pm 0.1$  in Rochester and Philadelphia, respectively. It should note that the slopes were much higher than the comparison between  $BC_S$  and ECwhile the correlation coefficients were relatively lower in the intercomparison of BCA and EC. As mentioned previously, the optical attenuation values measured by the Aethalometer were converted to Aethalometer BC mass concentration by using the specific absorption cross section, 16.6 m<sup>2</sup> g<sup>-1</sup> (Hansen et al., 1984; Hansen and McMurry, 1990). The obvious difference between the slopes at these sites suggests that the attenuation coefficient of BCA is variable with time and location and depends on the physical and chemical characteristics of light absorbing species that could include OC as well as EC.

Several studies found similar limitations for the Aethalometer and suggested that optical analysis for EC requires calibration for site-specific aerosol and optical properties since the attenuation coefficient depends on the size distribution, type of aerosol mixtures, and deposited mass per unit time (Horvath, 1993; Liousse et al., 1993; Petzold et al., 1997; Hitzenberger et al., 1999; Babich et al., 2000; Ballach et al., 2001). These results also suggest that the attenuation coefficients of the Aethalometer in Rochester and Philadelphia were larger than the manufacturer's value of  $16.6 \,\mathrm{m^2 g^{-1}}$ . Based on the thermal EC concentrations measured using the Sunset Lab OC/EC instrument, the fixed absorption coefficient for the Aethalometer can be modified as approximately  $54.8\,m^2\,g^{-1}$  in Rochester and  $44.2\,m^2\,g^{-1}$  in Philadel-

Fig. 6. Comparison between Sunset Lab thermal EC and Aethalometer optical EC (Aethalometer BC,  $BC_A$ ) in Rochester and Philadelphia during the summer of 2002.

phia, respectively. According to several measurements of the attenuation coefficients conducted in various locations (Jennings and Pinnick, 1980; Heintzenberg, 1982; Liousse et al., 1993), the attenuation coefficients were strongly related to the distance of the site from the black carbon sources. The attenuation coefficient at a remote site was low while the value near a street was higher. In Rochester, the sampling site was located about 3 m from a local road, and the very high attenuation coefficient might be due to the location of the Rochester sampling site.

The correlation coefficient of  $BC_A$  and EC concentrations in Philadelphia was lower than the value in Rochester. The somewhat poorer correlation in Philadelphia might have been due to the variable aerosol characteristics during several strong sulfate haze events



(Jeong et al., 2004). During the haze episode, BC<sub>A</sub> may become associated other particles as well as some water associated with the acid sulfate particles. There were five sulfate haze episodes in Philadelphia and the most severe haze episodes occurred from 2 to 4 July and from 17 to 19 July 2002 with the highest PM<sub>2.5</sub> mass concentrations of 92.8 and 95.4  $\mu$ g m<sup>-3</sup>. During the severe haze events, the differences between BC<sub>A</sub> and EC concentrations tended to increase because BC<sub>A</sub> sharply increased. The highest BC<sub>A</sub> concentration was observed on the morning of 3 July with a value of 8.0  $\mu$ g m<sup>-3</sup> whereas EC was 1.2  $\mu$ g m<sup>-3</sup>. It can be concluded that BC<sub>A</sub> concentrations in Philadelphia might be overestimated due to the hygroscopic behavior of carbonaceous materials during the sulfate haze events.

# 3.4. Influence of Canadian forest fire on carbonaceous compound measurements

A Canadian forest fire started on 2 July and severe smoke was transported to the monitoring site from 6 to 9 July 2002. Table 3 shows summary of real-time PM<sub>2.5</sub> mass and carbonaceous species measured in Philadelphia during the Canadian forest fire episode. PM2.5 concentrations ranged from 12 to  $164 \,\mu g \, m^{-3}$  with a mean of 79.8  $\mu$ g m<sup>-3</sup> with the highest PM<sub>2.5</sub> mass being observed around midnight on 7 July 2002 (local time). The mean PM<sub>2.5</sub> value during the forest fire was approximately 4 times higher than the mean during the rest of the measurement period 1 July to 2 August. The highest OC and EC concentrations were observed around midnight, 7 July and around 9 a.m. on 8 July 2002, respectively. Compared with the normal ambient conditions, the OC and EC concentrations dramatically increased by factors of 7 and 9, respectively. The mean concentration of BCA was approximately four times higher than the mean observed during normal days. The highest BCA value was also observed on the morning of 7 July 2002 with a value of  $8.0\,\mu g\,m^{-3}.$ 

Average OC fraction of PM2.5 mass concentration was 12% higher during the forest fire period than during the rest of the period. The increased OC/PM<sub>2.5</sub> ratio, 0.38, is similar to the values found by Patterson and McMahon (1984). They reported that OC/PM<sub>2.5</sub> ratios ranged from 0.41 to 0.61 for an open forest fire. In addition, OC was more highly associated with PM25 during the episode  $(r^2 = 0.95)$  than on the non-event days  $(r^2 = 0.68)$ . It clearly shows that OC strongly contributed to the increased PM2.5 mass during the forest fire event as expected. The mass ratio of EC/PM<sub>2.5</sub> slightly increased with a mean fraction of 4%, and the correlation coefficient between EC and PM<sub>2.5</sub> also moderately increased from 0.30 to 0.58 during the event. For the Aethalometer BC, the mass fraction BC<sub>A</sub> to PM<sub>2.5</sub> mass was around 3%. Although the mass fractions of EC and BCA were similar during the event, the correlation coefficient between  $BC_A$  and PM<sub>2.5</sub> decreased from 0.33 to 0.13 and was lower than the value between EC and PM<sub>2.5</sub>. There was a significant fluctuation of measured BCA values during the event, especially on 6 and 7 July 2002. High values of BCA were mainly observed around in the evening of 6 July and in the morning of 7 July whereas the strong peaks of PM<sub>2.5</sub> and EC were observed around midnight on 7 July and in the morning of 8 July 2002.

In order to better evaluate the effect of the forest fire on the carbon analysis methods for the determination of elemental carbon, the correlations between thermal EC and Aethalometer BC (BC<sub>A</sub>) during the severe haze events occurred around from 2 to 4 July and 18 to 19 July 2002, and during the Canadian forest fire episode in Philadelphia are shown in Fig. 7. There are two distinct slopes for the events in the figure. One slope plotted as closed circles is for the sulfate haze events when EC and BC<sub>A</sub> are highly correlated ( $r^2 = 0.68$ , slope =  $3.61 \pm 0.35$ ). The BC<sub>A</sub> values during the haze events were typically higher than EC concentrations with a good correlation as mentioned in the previous section. However, during the forest fire event, the trends

Table 3

Statistical summary of real-time PM<sub>2.5</sub>, semi-continuous OC/thermal EC, and continuous Aethalometer BC in Philadelphia during the Canadian forest fire, 6–9 July, 2002

	$PM_{2.5}^{a}$ ( $\mu g m^{-3}$ )	Organic carbon <sup>b</sup> (µg m <sup>-3</sup> )	Elemental carbon <sup>b</sup> (µg m <sup>-3</sup> )	Aethalometer black carbon <sup>a</sup> (µg m <sup>-3</sup> )
Mean	79.8	30.6	2.9	2.3
Standard deviation	36.2	16.2	1.6	1.5
Standard error	4.0	2.5	0.2	0.2
Minimum	12.0	3.1	0.1	0.3
Maximum	164.0	67.1	6.2	8.0
Valid number	82	41	41	82

<sup>a</sup>Averages of 1 h average samples.

<sup>b</sup>Averages of 2h integrated samples.



Fig. 7. Correlation between Sunset Lab thermal EC and Aethalometer BC ( $BC_A$ ) during the severe haze episodes and the Canadian forest fire event in Philadelphia, PA.

in EC and BCA changed dramatically on the afternoon of 7 July 2002 as is apparent in Fig. 7. The slope between EC and BCA also changed significantly from 3.61 to 0.35 while the correlation coefficient decreased somewhat  $(r^2 = 0.60)$ . Note that the data from afternoon 6 July to afternoon 7 July are in a transition region between two slopes and are not shown in the Fig. 7. The result of the proportionality between EC and Aethalometer BC shows clearly that there was a significant change in the attenuation coefficient in relation to the origin and the physical and chemical properties of carbonaceous aerosols during the Canadian forest fire episode. The variability of the attenuation coefficient is likely to be due to the presence of pyrolized organic matter and moisture emitted during the fire event (Liousse et al., 1993; Jacobson, 2000). In contrast to the correlation between EC and BC<sub>A</sub> in the normal urban atmosphere, BC<sub>A</sub> concentrations calculated by using a fixed attenuation coefficient were appreciably lower than the thermal EC values measured by the Sunset OC/EC analyzer in the heavily polluted atmosphere. Thus, this would result in an apparent underestimate of BCA mass for a given attenuation coefficient of the Aethalometer. Reported absorption coefficients for laboratory fires ranged from 0.04 to  $2.36 \text{ m}^2 \text{ g}^{-1}$  (Patterson and McMahon, 1984). Note that the values are significantly smaller than the  $16.6 \,\mathrm{m^2 g^{-1}}$  being used in the study. By comparison, data of Patterson and McMahon (1984) indicates that organic fraction during smoldering combustion pyrolysis was larger than the during flaming combustion.



Fig. 8. Correlation between Sunset Lab thermal EC and Sunset Lab optical EC during the severe haze episodes and during the Canadian forest fire event in Philadelphia, PA.

Fig. 8 shows the correlations between EC and Sunset Lab optical EC  $(BC_S)$ . The correlation coefficients during the haze and during the Canadian forest fire episode were 0.82 with a slope of  $0.97 \pm 0.06$  and 0.80 with a slope of  $0.31 \pm 0.02$ , respectively. As noted previously, both EC and  $BC_S$  concentrations were obtained by a Sunset Lab OC/EC analyzer every 2h. As shown in Fig. 8, during the haze event the comparison showed a quite good agreement as expected, whereas during the forest fire event BCs values were around three times lower than EC even though the BCs values were calculated by flexible attenuation coefficients depending on the deposit loading of EC. The average attenuation coefficients applied during the haze episode and the forest fire episode were 51.3 and  $19.1 \text{ m}^2 \text{ g}^{-1}$ , respectively. The results indicate that fine particles emitted and transported from the Canadian forest fire resulted in the significant biases of the optical attenuation methods used to quantify EC. The absorptive capacity was probably underestimated since the attenuation coefficient used for the BCs varied as a function of the deposit loading. Based on the thermal EC values measured, the modified attenuation coefficient was 5.9 m<sup>2</sup> g<sup>-1</sup> on average during the Canadian forest fire episode.

As described previously, the AE-20 Aethalometer has two-wavelength sources, 880 and 370 nm, and the near UV wavelength is used for identifying the presence of UV absorbing organic compounds ( $BC_{UV}$ ) such as polycyclic aromatic hydrocarbons (PAH) even if the



Fig. 9. Comparison of Aethalometer BC ( $BC_A$ ) measured using 880 nm wavelength and Aethalometer UV absorbing organic matters detected using 370 nm wavelength in Philadelphia, PA.

values of components measured using this second wavelength cannot be quantified as real mass concentrations. The levels of  $BC_{UV}$  were typically less than or similar to  $BC_A$  concentrations during the normal measurement period. However, as shown in the Fig. 9, the UV absorbing organic compound concentration increased significantly to become much larger than  $BC_A$ concentrations during the fire episode period. It can be anticipated that some of the most abundant UV absorbing organic species were PAHs since burning of wood emits various hydrocarbons (McMahon and Tsoukalas, 1978; Jenkins et al., 1996). Thus, the instrument does respond to UV absorbing species and provides information that the mixture of sources of BC have changed.

## 4. Conclusions

The average semi-continuous OC/PM<sub>2.5</sub> in Rochester was approximately 0.70 and was much higher than in Philadelphia (0.26) while EC/PM2.5 in Rochester was slightly higher than in Philadelphia. The BC<sub>A</sub> ratio to PM<sub>2.5</sub> in Rochester was two times higher than the ratio in Philadelphia while BC<sub>S</sub> ratios to PM<sub>2.5</sub> at two sites were similar with a range from 0.01 to 0.13.

The diurnal patterns of OC and EC concentrations during weekdays and weekends suggest that the sources of EC were closely related with traffic sources whereas there were no significant trends in OC concentrations suggesting more effect of distant resources. The diurnal variations of the BC<sub>A</sub> obtained show that the variations of BC<sub>A</sub> were strongly correlated with motor vehicles analogous to the behavior of EC.

Two hour average EC and BC<sub>s</sub> values were quite well correlated in Rochester ( $r^2 = 0.95$ ) with a slope of

 $0.89 \pm 0.02$  while the correlation coefficient was 0.73 with a slope of  $0.99 \pm 0.07$  in Philadelphia. Comparing EC and BC<sub>A</sub>, the correlation coefficients at both sites were 0.84 with a slope of  $3.3 \pm 0.2$  in Rochester and 0.60 with a slope of  $2.7 \pm 0.1$  in Philadelphia. The attenuation coefficients of optical elemental carbon analyses may vary and depend on the sampling locations or atmospheric conditions. During severe haze events, the differences between BC<sub>A</sub> and EC concentrations tended to increase.

During the Canadian forest fire, PM2.5 mass ranged around from 12 to  $164 \mu g m^{-3}$  with a mean of 79.8  $\mu$ g m<sup>-3</sup> while OC, EC, and BC<sub>A</sub> increased by a factor of 7, 9, and 4, respectively. While the  $OC/PM_{25}$ ratio during the forest fire episode was 0.38, OC and  $PM_{2.5}$  was strongly correlated ( $r^2 = 0.95$ ). In addition, the proportionality between EC and BCA dramatically decreased from 3.61 to 0.35 while there was no significant change of the correlation coefficient during the Canadian forest fire episode. Similar behavior was also found in the comparison of EC and BCs. Although EC and  $BC_S$  calculated by using multiple attenuation coefficients showed a good agreement, the proportionality was also changed from 0.97 to 0.31 due to the influence of the forest fire. The UV absorbing organic compounds level significantly increased during the fire episode period.

It is clear from these results that there needs to be careful definitions of the operational carbon fractions. It is suggested that the term "black carbon" be reserved for optically based measurements and the term "elemental carbon" be reserved for thermal optical measurements. Even within each of these categories, it is essential to carefully define the measurement protocols since differences among the available protocols will produce differences in the measured concentrations. Future work may resolve these differences or lead to more uniform methodology, but in the interim, care is needed in describing and reporting OC, EC, and BC values.

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