

Controlled generation of black carbon particles from a diffusion flame and applications in evaluating black carbon measurement methods

Thomas W. Kirchstetter*, T. Novakov

*Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory, One Cyclotron Road,
MS-70-108B, Berkeley, CA 94720, USA*

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Abstract

Measurements of black carbon (BC) concentration have long been uncertain. Neither a BC standard or a technique that provides a reliable measurement of BC exist, which precludes the evaluation and optimization of BC measurement methods. In this manuscript, we describe the generation of BC particles (mass absorption efficiency $\sim 8.5 \text{ m}^2 \text{ g}^{-1}$ and single scattering albedo ~ 0.2 at 530 nm) using an inverted diffusion flame. This flame is remarkably stable and can be used to generate a wide range of nearly constant concentrations of BC particles for many (e.g., 10+) hours. The particles contain essentially no organic carbon (OC), so the quantification of BC mass using any of the thermal or thermal–optical analysis (TOA) methods is straightforward instead of highly uncertain. In this case, the TOA measurement of BC can be used to evaluate the accuracy of other BC measurement methods. In this paper, we demonstrate the application of the diffusion flame in evaluating BC measurements made with filter-based light transmission methods, and in particular the aethalometer. We show that the amount of light attenuated by a BC-laden filter increases in less than constant proportion to the BC mass loading, and thus the effective BC attenuation coefficient decreases with increased BC mass loading. When sampling BC at constant concentration, the aethalometer erroneously reports decreasing concentrations of BC as its filter becomes increasingly loaded because it treats the attenuation coefficient as a constant. A simple method to correct erroneous aethalometer data when sampling aerosols with low single scattering albedo is presented. Another application of the diffusion flame considered in this paper is the development of BC standards for TOA. We envision the preparation of filter samples with known amounts of BC mixed with other aerosol constituents, which may help in understanding the uncertainty in and optimizing TOA measurements, and may be of use in future TOA method comparison studies. Toward this end, we demonstrate that the diffusion flame can be used to replicate filter samples with known amounts of BC. Additionally, we show that the combustion temperature of BC during TOA depends on sample composition, which suggests that the temperature-defined carbon fractions of some thermal and TOA methods may be of limited value.

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*Corresponding author. Tel.: +510 486 5319; fax: +510 486 7303.

E-mail address: twkirchstetter@lbl.gov (T.W. Kirchstetter).

1. Introduction

Black carbon (BC) is a major component of the soot produced during the combustion of fossil fuels, principally diesel and coal, and from biomass burning. Concern about BC in the environment arises from its role in air quality degradation and climate change. BC is a component of ambient fine particulate matter that is a public health concern because it is small enough to be inhaled and deposited directly in the lungs, where it can cause health problems. BC has been used as an indicator of exposure to diesel soot (e.g., [Fruin et al., 2004](#)), which has been classified as a toxic air contaminant ([CARB, 1998](#)) and a suspected carcinogen ([Cal EPA, 2005](#)). BC is the primary sunlight absorbing aerosol species and contributes to human induced climate change in several ways. The heating of the atmosphere due to absorption of solar radiation by BC exerts a direct global warming forcing that may be comparable to the forcing of the greenhouse gas methane ([Jacobson, 2001](#)). It has also been suggested that BC light absorption alters precipitation patterns and cloud lifetime ([Menon et al., 2002](#); [Ackerman et al., 2000](#)), and decreases the reflectivity and increases the melting of snow and ice ([Hansen and Nazarenko, 2003](#)).

Despite the importance of BC in the environment, quantifying BC has long been and remains an uncertain practice. BC concentrations are most commonly measured by analysis of quartz filter samples using thermal or thermal–optical analysis (TOA)¹ methods or with filter-based light transmission methods, such as the one employed in the widely used aethalometer. Several variations of the TOA method have been developed ([Watson et al.,](#)

2005). In general, TOA involves raising the temperature of a sample of particulate matter to evolve the carbonaceous material (i.e., volatilize, decompose, combust). The number of moles of evolved carbon is quantified, and an estimate is made of the relative amounts of organic carbon (OC) and BC that were present in the sample.

The long standing uncertainty in TOA measurements is illustrated by numerous comparison studies (e.g., [Countess, 1990](#); [Shah and Rau, 1991](#); [Schmid et al., 2001](#)). These show that when a particulate matter sample is analyzed using different TOA methods, the result is a range of BC estimates that sometimes vary by almost an order of magnitude ([Watson et al., 2005](#)). Even when the analyzed sample is supposed to be a reference material, different TOA methods yield a wide range of BC estimates ([Currie et al., 2002](#); [Klouda et al., 2005](#)).

While effectively demonstrating the uncertainty of the TOA BC measurement, these comparison studies cannot evaluate the accuracy of any of the TOA measurements because the mass of BC in the prepared samples and reference materials is unknown. Also, when employing samples of unknown composition in comparison studies, it is not possible to systematically explain how sample composition affects the TOA measurement. As [Watson et al. \(2005\)](#) noted, it is possible to observe differences, but it is not possible to explain why.

In general, the TOA measurement of BC is most uncertain when the mass fraction of BC is small compared to OC. A number of studies have demonstrated that the uncertainty in BC is due in large part to the pyrolysis of OC and resultant formation of light absorbing char, as well as the co-evolution of OC and BC (e.g., [Subramanian et al., 2006](#); [Conny et al., 2003](#)). In addition, the catalytic lowering of the combustion temperature of BC due to inorganic materials such as sodium or potassium present in some particulate matter samples ([Grosjean et al., 1994](#); [Lin and Friedlander, 1988](#); [Novakov and Corrigan, 1995](#)) may introduce uncertainty when employing thermal methods that attempt to distinguish OC from BC based solely on evolution temperature. Understanding the physical and chemical processes that take place during TOA is an important step in optimizing TOA methods for accurate measurements. In addition, the optimization of TOA methods would be aided by the development of a reproducible, well characterized BC reference material.

¹In this paper, we use the acronym TOA when referring generally to all variations of the thermal or thermal–optical analysis methods and are more explicit when referring to a particular method. The refractory, light-absorbing carbonaceous material measured by TOA is usually referred to as elemental carbon (EC) rather than BC, and the equivalence of the two terms is debatable. TOA does not truly identify elemental carbon, rather EC is operationally defined by the TOA method. The same could be said of BC, and it has been proposed that the more general term light absorbing carbon (LAC) be used instead of BC. We prefer using BC since it excludes other light-absorbing carbonaceous material, such as that emitted from biomass fires, which has a lower mass absorption efficiency at visible wavelengths and absorbs light with a stronger spectral selectivity than BC. In this manuscript, we do not seek to focus on the definitions of EC and BC or their equivalence. It is unlikely that these issues will be resolved unless the measurement methods are improved, and that is the direction of this manuscript.

In the aethalometer, the amount of light transmitted through a quartz filter is periodically measured while particles are collected, and the mass of BC on the filter ($\mu\text{g cm}^{-2}$) is calculated as (Hansen et al., 1984):

$$\text{BC} = \frac{\text{ATN}}{\sigma}. \quad (1)$$

Light attenuation is calculated from the measurements of transmitted light intensity, namely: $\text{ATN} = 100 \ln(I_0/I)$, where intensities I_0 and I correspond to initial and subsequent filter conditions, respectively (e.g., blank and particle-laden). Use of a constant proportionality constant, σ , also known as the attenuation coefficient, implies a linear relationship between the BC content and ATN of the particle-laden filter. The aethalometer estimates BC concentrations from intensity measurements in the infrared ($\sim 880\text{ nm}$) assuming an attenuation coefficient of $16.6\text{ m}^2\text{ g}^{-1}$, which was derived partly from the work of Gundel et al. (1984).

There are three main uncertainties in BC measurements made with the aethalometer. The first uncertainty pertains to the assumption that the attenuation coefficient, σ in Eq. (1), is constant as the filter darkens during the collection of light-absorbing particles. In this context, it is important to keep in mind that the attenuation coefficient is not a property of the BC particles only; rather it is a property of the particle-laden filter. Sadler et al. (1981) demonstrated the enhancement in the amount of light absorbed by BC particles when they are collected in highly scattering filter fibers. Using the aethalometer to measure aerosol absorption coefficient, Arnott et al. (2005) reported that the extent of this enhancement diminishes as the aethalometer's filter darkens and, thus, becomes less highly scattering. The filter loading effect reported by Arnott et al. is consistent with the results of similar studies on the measurement of aerosol absorption coefficient with the aethalometer (Weingartner et al., 2003), other light transmission instruments (Petzold et al., 2005) and measurements with the particle soot absorption photometer (PSAP) (Virkkula et al., 2005; Bond et al., 1999). These laboratory based results are supported by field observations indicating the tendency of BC readings to increase following the switching of the aethalometer's particle-laden filter with a pristine filter (e.g., LaRosa et al., 2002).

A second uncertainty is related to the influence of particle light scattering. By virtue of the scattering

of light by the filter fibers in which the particles become collected, the light transmission measurement is sensitive primarily to the fraction of particle light extinction that is absorption rather than scattering. In calculating BC concentrations solely with Eq. (1), the aethalometer neglects any influence of particle light scattering. However, others have reported that the particle scattering of light away from the aethalometer's detector is not negligible and is erroneously interpreted as particle light absorption (Arnott et al., 2005) or acts to minimize the particle loading effect discussed above (Weingartner et al., 2003). These reports are generally consistent with evaluations of other light transmission methods (Bond et al., 1999; Virkkula et al., 2005; Horvath, 1997), which indicate that the influence of particle light scattering increases as the BC mass fraction decreases.

A third uncertainty is related to whether or not the attenuation coefficient, σ , varies in response to changing aerosol properties. A number of studies report values of σ ranging from 5 to $25\text{ m}^2\text{ g}^{-1}$ (Liousse et al., 1993; Petzold et al., 1997; Martins et al., 1998; Lavanchy et al., 1999; Sharma et al., 2002; Schnaiter et al., 2003). The assertion is that the mass absorption efficiency of BC, and thus σ , depends on combustion source and atmospheric processing. Some have questioned the wide variability in σ because it is based in part on thermal or TOA measurements of BC, which, as discussed above, can be highly uncertain (Reid et al., 1998; Martins et al., 1998; Andreae and Gelencser, 2006).

Strictly speaking, none of the studies cited above relate directly to the influence of filter loading and particle light scattering on aethalometer measurements of BC. They evaluated measurements of aerosol absorption coefficient, not BC, using the aethalometer and similar instruments. However, BC is the primary light absorbing aerosol species and, therefore, these studies provide a strong indication that aethalometer measurements of BC are subject to the same sources of error as measurements of absorption coefficient.

It is quite telling that the aethalometer has been evaluated for measuring absorption coefficient (Weingartner et al., 2003; Arnott et al., 2005), but a similarly rigorous evaluation of the aethalometer for measuring BC has not been presented. The most obvious reason for this is the existence of a reference measurement of absorption coefficient (i.e., a measurement that is accepted as being reliable, e.g., the difference of in-situ extinction and scattering

coefficients) but the absence of an accepted reference measurement of BC concentration.

The purpose of this manuscript is to report on a recently developed BC source and demonstrate its utility in evaluating BC measurement methods. The BC source is an inverted diffusion flame that has two key attributes in this context: the particle production rate is nearly constant and the particles produced are composed only of BC. In this rather unique case, the measurement of BC by TOA is straightforward because OC does not interfere in the analysis and, therefore, can serve as the much needed reference measurement for evaluating other BC measurement methods, including but not limited to filter-based optical methods.

Below, we present data that characterize the stability of the diffusion flame and the physical and chemical properties of the BC particles it produces. In addition, we discuss two research applications of the diffusion flame that take advantage of its unique attributes: the evaluation of real-time measurements of BC using the aethalometer and the development of BC standards for thermal–optical analysis of carbonaceous aerosols. Admittedly, neither application is complete, and both are the subject of continuing research. The presentation of these applications is intended to demonstrate the utility of the diffusion flame in laboratory experiments where a stable source of well characterized particles is beneficial in addition to convey results meaningful to the measurement of BC.

2. Experimental

2.1. Diffusion flame

In our laboratory, BC aerosol is generated with a diffusion flame of methane and air in an inverted flow reactor. This method of particle generation is a slight modification of that developed by Stipe et al. (2005). A remarkable feature of this flame is its stability. There is no flickering or rotation a few seconds after ignition. Consequently, the particle generation rate and the concentration of particles produced are very stable, as illustrated below. The concentration of particles produced is readily varied by altering the fuel flow rate or the flow rate of particle-free dry air used to dilute the flame effluent. Whereas premixed methane/air flames are largely soot free, diffusion flames can be prolific sources of soot. As in a diesel engine, soot is produced due to a fuel rich environment in the diffusion flame. The

diffusion flame produces particle sizes in the range of those generated by modern engines, which makes it a good source of particles for air quality studies (Stipe et al., 2005). Additionally, Stipe et al. reported that the flame-produced particles do not have measurable C_2 or CH emission peaks when analyzed using laser fragmentation-fluorescence spectroscopy, which suggests that the particles do not contain significant amounts of OC.

2.2. Particle sampling

In our application, a portion of the diluted effluent was drawn through a sharp cut cyclone (or a two stage impactor) and into an anodized aluminum manifold that accommodated sampling with several instruments. We set the flame to produce different concentrations of BC depending on the type of experiment being conducted. We set the flame to produce constant BC concentrations at the $mg\ m^{-3}$ level to accommodate the collection of numerous quartz filter samples quickly, such as those referred to in Fig. 4. In all other cases, namely when sampling with common aerosol analyzers (listed below) to characterize the size and optical properties of the BC, when evaluating the aethalometer, and when preparing quartz filters to evaluate the effect of aerosol composition on the TOA measurement of BC, we set the flame to generate BC concentrations at the $\mu g\ m^{-3}$ level.

In experiments designed to investigate the influence of catalytic materials on the combustion temperature of BC during TOA, BC from the flame was mixed with NaCl. A Collison nebulizer (BGI Inc, model CN24) was used to atomize solutions of NaCl. The atomized NaCl was injected into the air that diluted the diffusion flame effluent, which dried (to $RH = 22\%$) the atomized spray and created external mixtures of BC and salt without altering the production of BC from the flame.

Particle number size distributions were measured using a scanning mobility particle sizer (SMPS, consisting of a TSI model 3071A electrostatic classifier modified for recirculation of the sheath air and a TSI model 3022 condensation particle counter). Particle light absorption and scattering coefficients, respectively, were measured with a three wavelength PSAP (a modification of the Radiance Research PSAP operating at 467, 530 and 660 nm, as described by Virkkula et al., 2005) and a single wavelength integrating nephelometer (Radiance Research, 530 nm, model M903). The aethalometer

(Magee Scientific) was used to measure BC concentrations; BC concentrations presented in this manuscript are based on measurements using the standard 880 nm aethalometer channel. The SMPS sizing was verified using 300 and 500 nm polystyrene latex spheres and size distribution data was reduced using TSI software, and the nephelometer was calibrated using zero air and Freon-22. When operating the modified PSAP, the user chooses whether or not the reported absorption coefficients are corrected with the calibration derived by Bond et al. (1999). In this study, we occasionally chose to record “uncalibrated” absorption coefficients and to apply the calibration manually, as discussed below.

Particle samples were collected with quartz fiber filters (Pallflex 2500 QAT-UP) for subsequent measurements of BC content and ATN. Quartz filters were baked at 800 °C for 6 h prior to use to remove carbonaceous impurities.

2.3. Analysis of particle samples

The carbon content of quartz filter samples was measured using a variation of the TOA method originally described by Novakov (1981). In this study, filter samples were heated at a constant rate of 40 °C min⁻¹ from 50 to 700 °C in a pure oxygen atmosphere. The evolved carbon was fully oxidized over a platinum coated ceramic catalyst maintained at 800 °C, and the resultant carbon dioxide was measured with a nondispersive infrared analyzer (LI-COR, model 7000). The intensity of light transmitted through the sample was continuously monitored during analysis. The light source was a white light emitting diode (LED) and the detector was a spectrometer (Ocean Optics, model S2000). The recovery of our TOA instrument was determined to be 100 ± 5% by analysis of prepared samples of potassium hydrogen phthalate and glucose.

Our TOA protocol differs from the more common IMPROVE thermal–optical reflectance (TOR) and NIOSH thermal–optical transmission (TOT) protocols (Chow et al., 2001; Birch and Cary, 1996) which expose the sample to helium followed by a helium/oxygen mixture (as opposed to pure oxygen), raise the sample temperature stepwise (as opposed to at a constant rate), and measure optical reflectance or transmission at a single wavelength (as opposed to over a broad spectral region). Selected samples were analyzed according

to the IMPROVE TOR protocol in addition to our TOA protocol described above.

ATN was measured using a custom built optical spectrometer that allowed convenient placement of filter samples between the light source and detector. The light source was a collection of LEDs ranging from the near ultraviolet (375 nm) to the near infrared (940 nm) and the spectrometer (the same as that mentioned above) was equipped with a fixed grating and a linear CCD-array detector.

Selected samples of particulate matter were deposited onto lacey carbon coated grids and analyzed with a high resolution transmission electron microscope at NASA's Glenn Research Center (VanderWal et al., 2004).

3. Results and discussion

3.1. Characteristics of the diffusion flame particles

3.1.1. Particle morphology, size, and composition

Three transmission electron microscope images obtained at different levels of magnification are shown in Fig. 1. These illustrate that the particulate matter emitted from the diffusion flame consisted of aggregated primary spherules of approximately 20–30 nm in diameter, with an onion-shell nanostructure typical of diesel soot (Hays and VanderWal, 2006; Wentzel et al., 2003).

The average of 70 consecutively measured particle mobility number size distributions measured with the SMPS is shown in Fig. 2. The distribution is unimodal and approximately log normal with a peak mobility diameter of 130 nm. The small relative standard deviation of the size distribution (e.g., 3% at 130 nm) indicates that the size distribution was essentially constant over the (6.5 h) period of measurement. Stipe et al. (2005) described how the size distribution can be manipulated by adjusting the air to fuel ratio of the flame.

Carbon and optical thermograms, which show rates of evolved carbon and optical attenuation as the sample temperature is increased (i.e., dC/dT and dATN/dT) during TOA, are presented in Fig. 3 for a sample of particles from the diffusion flame. For the purpose of this illustration, ATN was computed such that a peak in the optical thermogram indicates the removal of light absorbing material. A single peak in the carbon thermogram at high temperatures indicates that all of the carbon in the sample is refractory. The complete overlap of the carbon and optical thermograms indicates that the carbon is

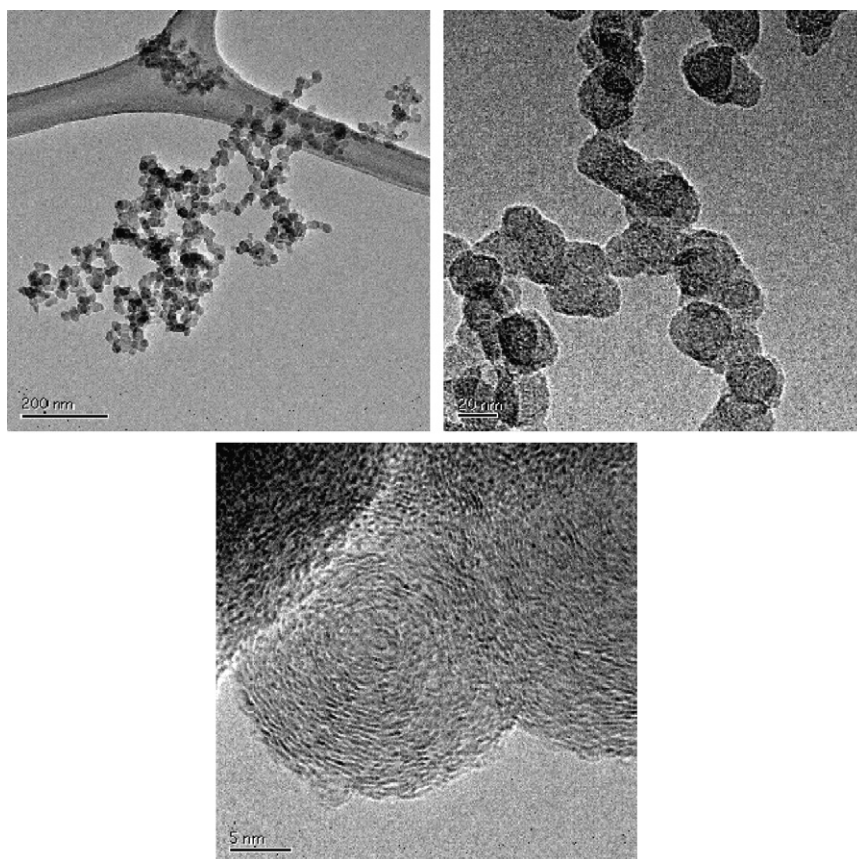


Fig. 1. Transmission electron microscope images of particulate matter generated with the diffusion flame and deposited on lacey carbon coated grids. Images are provided courtesy of Randy VanderWal's group at NASA's Glenn Research Center.

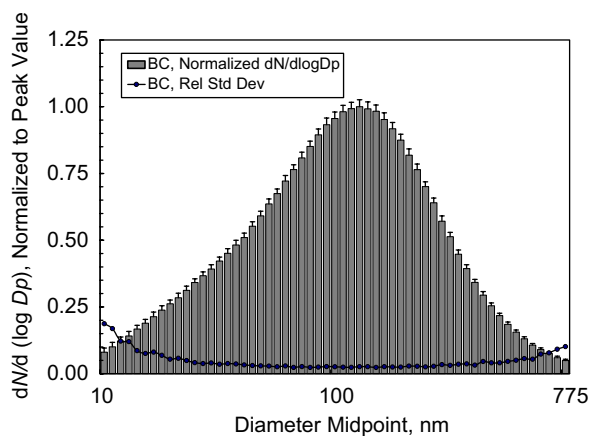


Fig. 2. Average (+1 standard deviation) of particle number size distributions of 70 consecutive SMPS scans when sampling BC from the diffusion flame. Each size bin of the distribution is normalized to the peak value of $dN/d \log D_p$ (at 130 nm). The small standard and relative standard deviations illustrate that the BC size distribution was not changing appreciably during the 6.5 h period of measurement.

entirely light absorbing and, thus, is composed entirely of BC. The optical thermogram does not drop below the baseline (i.e., $ATN \geq 0$) because char was not formed during the analysis. Furthermore, no carbon evolves and charring does not occur when the sample is heated in an inert helium atmosphere (not shown). These observations demonstrating that the soot emitted from the flame is composed entirely of BC are consistent with the results of Stipe et al. (2005). This is significant because without OC to interfere, the quantification of BC using any TOA method is straightforward. The mass of BC in the sample represented in Fig. 3 is obtained by integrating the carbon thermogram.

Carbon thermograms of filter samples increasingly loaded with BC from the diffusion flame are shown in Fig. 4a. Taking advantage of the constant emission rate of BC from the diffusion flame, this set of samples was collected simply by increasing the duration of sampling from 1 to 90 s. The combustion

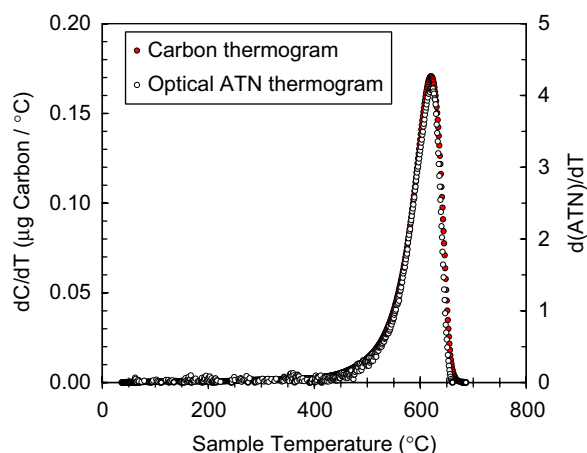


Fig. 3. Carbon, dC/dT , and optical, $d(ATN)/dT$, thermograms from the thermal–optical analysis of diffusion flame particles. A single carbon peak at high temperature evolves simultaneously with the disappearance in particle light absorbance. The overlap of the carbon and optical thermograms indicates that the carbon is entirely light absorbing BC. The flatness of the carbon and optical thermograms before the BC peak indicates that OC is not present in the sample and the sample does not char.

temperature of BC and the shape of the thermogram are essentially the same for all of the samples.

3.1.2. Absorption angstrom exponent, single scattering albedo, and mass absorption efficiency

The spectral attenuation of the quartz filter samples increasingly loaded with BC shown in Fig. 4a is shown in Fig. 4b. The increase in ATN with decreasing wavelength is well described by a power law, $ATN = \text{constant} \cdot \lambda^{-0.9}$, where the exponent near unity implies a weak absorption spectral selectivity that is typical of diesel soot (Schnaiter et al., 2003; Kirchstetter et al., 2005 and references therein).

Scattering and absorption coefficients measured during a 6 h sampling event wherein the BC concentration was changed in a step-wise fashion to achieve nine different BC concentrations are shown in Figs. 5a and b. (The calibration of the PSAP is discussed below.) The times series and the regression of the scattering coefficients against the absorption coefficients shown in Figs. 5a and b, respectively, demonstrate the linear correlation between scattering and absorption coefficients and indicate a single scattering albedo (SSA) of 0.15 for the diffusion flame BC particles. In the sampling event shown in Fig. 6a, comparison of BC concentrations ($\mu\text{g m}^{-3}$) measured by TOA and

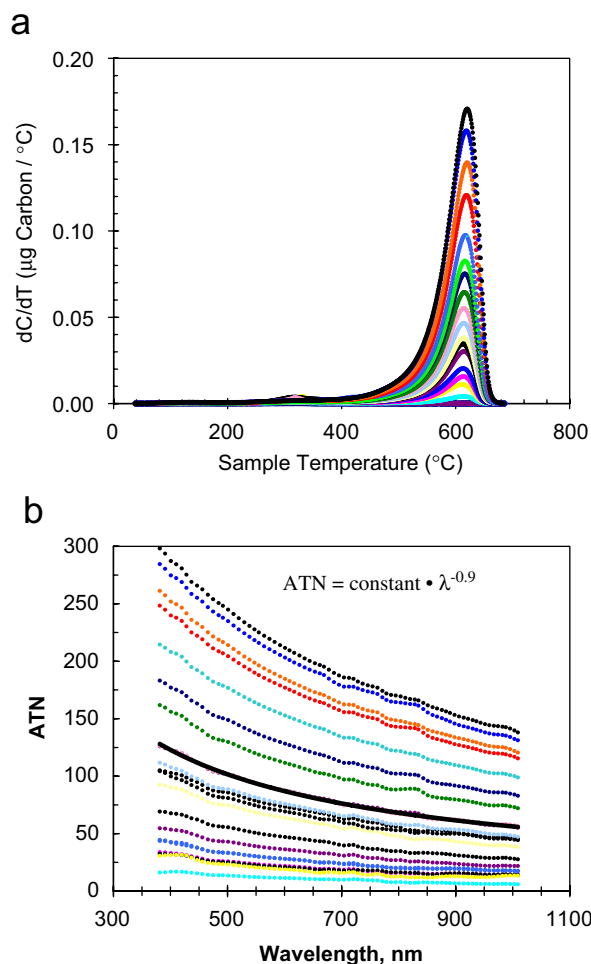


Fig. 4. (a) Carbon thermograms of filter samples increasingly loaded (up to $13 \mu\text{g cm}^{-2}$) with BC particles from the diffusion flame. (b) Spectral attenuation (ATN) measurements for the same set of filters. A weak spectral selectivity was observed; ATN varies approximately as λ^{-1} .

absorption coefficients (Mm^{-1}) measured with the PSAP indicate a mass absorption efficiency (MAE) of $8.5 \text{ m}^2 \text{ g}^{-1}$ for this BC.

Bond and Bergstrom (2006) noted that measurements of combustion aerosol SSA range from 0.15 to 0.28, including 0.17 for diesel soot (Scherrer et al., 1981). The SSA of the diffusion flame BC (0.15) is at the low end of this range, which is consistent with the absence of particulate OC (i.e., scattering aerosol). The value of the BC mass absorption efficiency ($8.5 \text{ m}^2 \text{ g}^{-1}$) is consistent with most values reported for freshly emitted light absorbing carbon ($7.5 \pm 1.2 \text{ m}^2 \text{ g}^{-1}$) (Bond and Bergstrom, 2006).

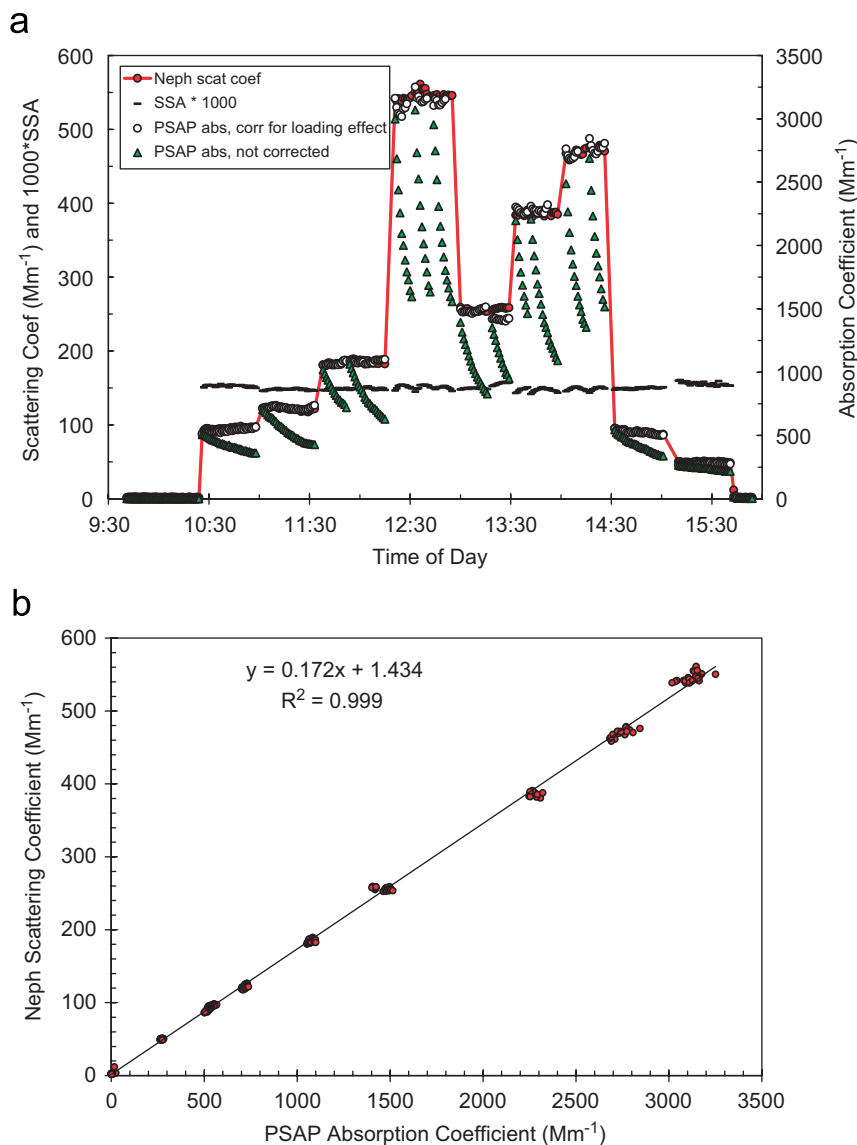


Fig. 5. (a) Measured scattering and absorption coefficients (at 530 nm) during a 6 h experiment where the BC concentration was changed in a stepwise fashion. Two sets of PSAP data are shown; the set that indicates constant absorption coefficients at each step of the experiment was corrected for the PSAP's nonlinear response to particle loading whereas the other set was not. (b) A linear regression of these data indicates a $\text{SSA} \sim 0.15$ for the flame BC.

3.2. Applications of the diffusion flame BC

The results presented above demonstrate that the diffusion flame produces controllable amounts of BC particles where the BC mass concentration can readily be quantified by TOA. This capability provides a good opportunity to evaluate instruments and methods that measure light absorbing BC particles. Two such applications of the diffusion

flame are discussed below. The first is an evaluation of the light transmission method for measuring BC, including its application in the aethalometer. The second application is the preparation of filter samples loaded with BC that can serve as standards for evaluating TOA measurements. These applications are the subjects of ongoing research efforts, which we plan to present more completely in forthcoming manuscripts.

3.2.1. Evaluation of the aethalometer: the effect of particle loading on attenuation coefficient

BC concentrations reported by the aethalometer when subjected to constant a concentration of BC from the diffusion flame are presented in Figs. 6a and b. The constant BC concentration during this 6 h experiment is indicated by the steady BC concentration measured by TOA, which in this

case serves as the reference measurement of BC, and the constant values of scattering coefficient and SSA. The repeating trend of decreasing BC concentrations erroneously reported by the aethalometer indicates a measurement artifact. The BC concentration reported by the aethalometer at the start of its measurement cycles was about 1.8 times larger than it was at the end of its

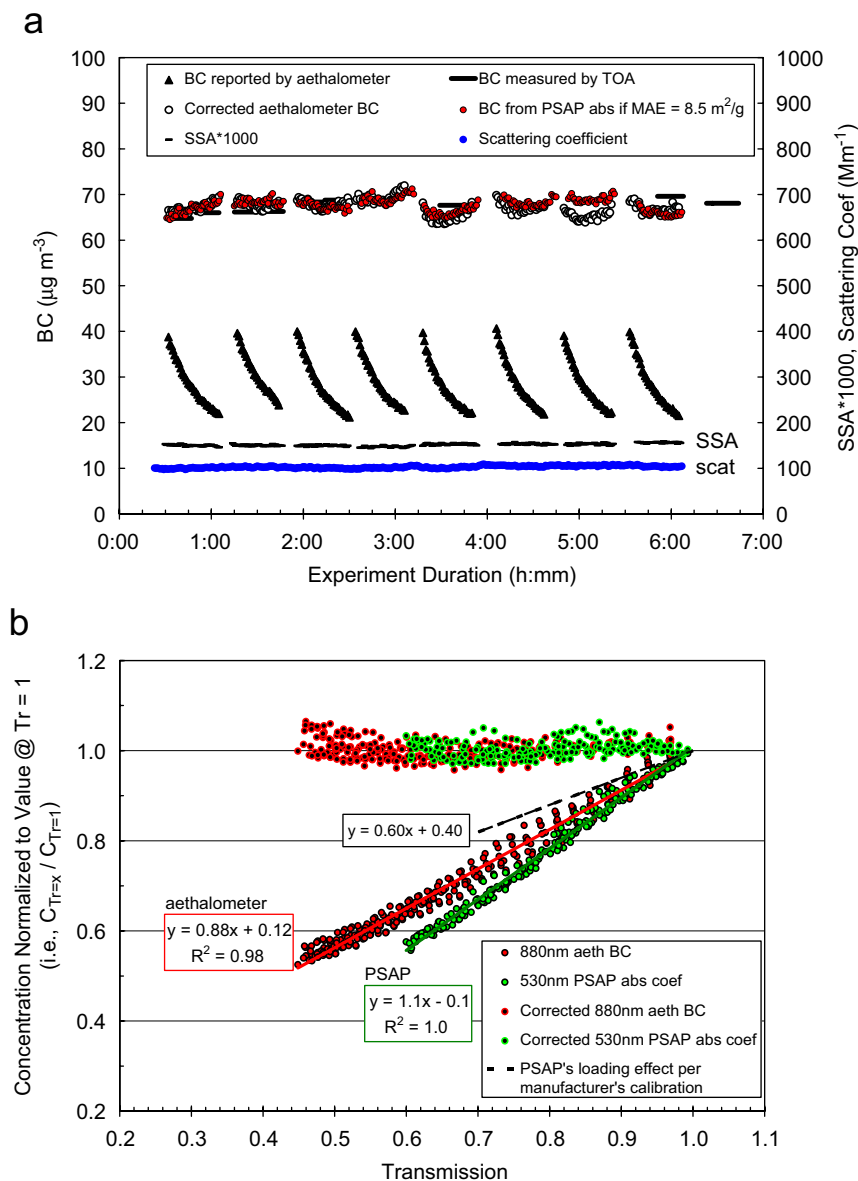


Fig. 6. (a) Measured aerosol properties during a 6 h experiment. The BC concentrations measured by TOA and derived from calibrated PSAP absorption coefficients, and the scattering coefficients and values of SSA, indicate a nearly BC concentration. In contrast, the BC concentrations reported by the aethalometer indicate a measurement artifact. (b) Normalized BC concentrations and absorption coefficients before and after correction for the measurement artifact, which is due to the reduction in instrument response as the sampling filters darken with BC. The corrected data indicate relatively constant aerosol concentrations.

measurement cycles (i.e., when $ATN_{880\text{ nm}} \sim 75$ or transmission ~ 0.47).

The aethalometer reported decreasing BC concentrations not because the concentration or the mass absorption efficiency of the BC was changing during the experiment, but because the attenuation coefficient of the collected BC decreased as the aethalometer's filter became increasingly darkened with these light-absorbing particles. One explanation of this effect is that as the filter becomes darker, the internal reflection of light diminishes and, thus, the extent of the enhancement in the amount of light absorbed by the collected BC particles diminishes. Arnott et al. (2005) reported the same phenomenon in similar terms. Weingartner et al. (2003) described the particle loading effect somewhat differently, namely as a particle shadowing effect, which we interpret as meaning that some particles physically block light from reaching other particles. We note that when aethalometer measurements in our experiments were extended beyond the default maximum $ATN_{880\text{ nm}}$ of 75, reported BC concentrations decreased only marginally more than is shown in Fig. 6a before leveling off. For example, when the measurement cycle was extended to $ATN_{880\text{ nm}} = 150$, we observed that the BC concentration at the start of the cycle was 2.2 times larger than the concentration at the end of the cycle. This factor of 2.2 is comparable to factor of 2.14, which is the amount that aethalometer's filter enhances particle light absorption (Weingartner et al., 2003), which gives credence to the phenomenological explanation of Arnott et al.

This particle loading effect is not specific to the aethalometer's measurement, rather it is common to all light transmission measurements using highly scattering filters. We observed the particle loading effect when analyzing quartz filters increasingly loaded with BC. The less than proportional increase in ATN with increased BC loading of these filters is clear, as is the decreasing attenuation coefficient with increasing ATN, as shown in Figs. 7a and b. Similarly, measurements with the PSAP and the more recently developed multi-angle absorption photometer have been calibrated to account for a nonlinear instrumental response to particle loading (Bond et al., 1999; Virkkula et al., 2005; Petzold et al., 2005).

As shown in Fig. 6b, the BC concentrations reported by the aethalometer decreased linearly with decreasing filter transmission. This suggests a simple means of correcting reported concentrations,

namely using Eq. (2):

$$BC = \frac{BC_o}{0.60(0.88 \text{ Tr} + 0.12)} \propto \frac{ATN}{10(0.88 \text{ Tr} + 0.12)} \quad (2)$$

In Eq. (2), BC and BC_o are the corrected and uncorrected BC concentrations (g m^{-3}), Tr is the measured filter transmission, and the constants 0.88 and 0.12 are the slope and intercept of the regression line shown in Fig. 6b. (The factor 0.60 reduces the manufacturer's attenuation coefficient ($\sigma_{880\text{ nm}}$) from 16.6 to $10 \text{ m}^2 \text{ g}^{-1}$, as discussed below.) Transmission can be computed directly from the

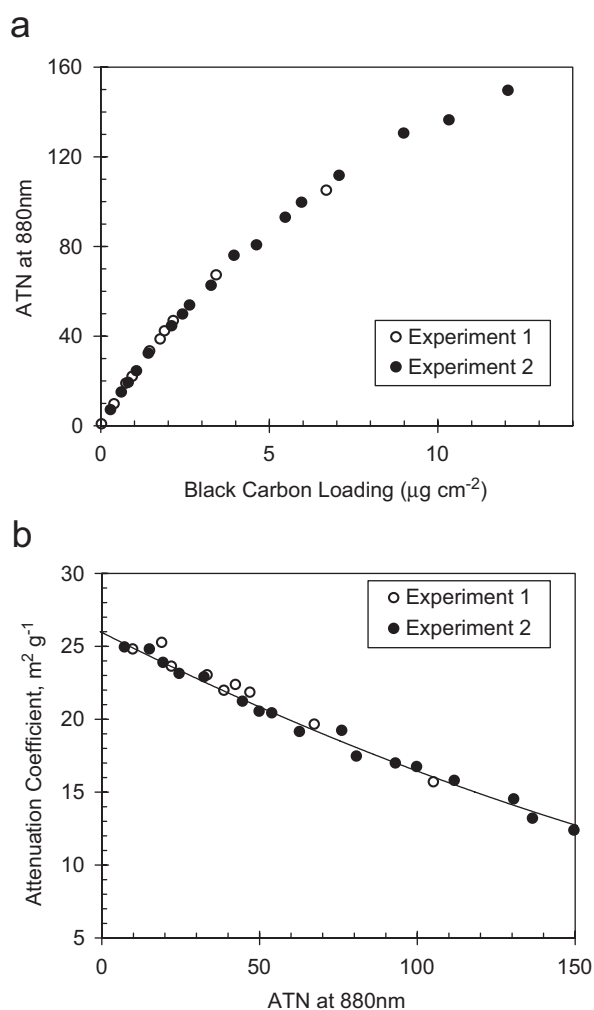


Fig. 7. (a) ATN versus BC loading and (b) attenuation coefficient versus ATN for quartz filter samples of BC particles generated with the diffusion flame. ATN increases in less than constant proportion to the BC loading of the filter and the corresponding attenuation coefficients (σ) decrease with increasing ATN.

ATN measured by the aethalometer: $Tr = \exp(-ATN/100)$. As the aethalometer's filter collects BC and Tr decreases from unity, the denominator of Eq. (2) decreases, which accounts for the decreasing attenuation coefficient. We applied Eq. (2) to the BC concentrations reported by the aethalometer (i.e., to BC_o), and the influence of particle loading on the attenuation coefficient was largely eliminated, as evidenced by the nearly constant corrected BC concentrations shown in Figs. 6a and b.

Note that at the start of a new aethalometer cycle when $Tr = 1$, Eq. (2) reduces to $BC = BC_o/0.60$. The factor 0.60 that reduces the manufacturer's attenuation coefficient (σ_{880nm}) from 16.6 to $10\text{ m}^2\text{ g}^{-1}$ was applied in order to increase the aethalometer BC concentrations to equal those determined by TOA, as shown in Fig. 6a. It is likely that the difference between the manufacturer's σ ($16\text{ m}^2\text{ g}^{-1}$) and the value derived in this study ($10\text{ m}^2\text{ g}^{-1}$) is at least partly due to the collection of BC when the aethalometer initialized its filter between measurement cycles. During this period of several minutes ($\sim 8\text{ min}$), the aethalometer continues to draw sample air through its filter. It is probable that in experiments like those conducted in this study, a significant loading of the filter can occur in this period of time, which begins to reduce the enhancement of particle light absorption before the aethalometer reports any measurements. Arnott et al. (2005) arrived at the same hypothesis. In our ongoing research, we are testing this hypothesis.

The observations discussed above suggest that aethalometer data is subject to a significant measurement artifact when the aerosol SSA is low, as it is for the BC from the diffusion flame. This may be relevant when close to combustion sources, such as diesel-fueled motor vehicles. The same aethalometer measurement artifact was observed when sampling diesel engine exhaust in an experimental chamber (Jiménez et al., 2006). However, the SSA of most ambient aerosols is in the range 0.80–0.95, which is much greater than that of the diffusion flame BC. Weingartner et al. (2003) and Sheridan et al. (2005) demonstrated that the particle loading effect is much less pronounced at higher SSA. Likewise, Turner et al. (2005) reported that the particle loading effect is not always evident in ambient data sets. Therefore, the modified aethalometer calibration presented above (i.e., Eq. (2)) should be applied to low SSA aerosol only. In

our continuing application of the diffusion flame, we are attempting to evaluate the influence of particle light scattering on the particle loading effect when the aethalometer is subject to aerosols characterized by values of SSA common to most ambient aerosols.

Before discussing the next application of the diffusion flame, we note that expressing the aethalometer's attenuation coefficient as a linear function of transmission (in Eq. (2)) is functionally consistent with the calibration of the PSAP, which compensates for decreasing instrumental response to increasing particle collection according to

$$B_{\text{abs}} = \frac{B_o}{2.18(0.60 Tr + 0.40)}. \quad (3)$$

In Eq. (3), B_{abs} and B_o are the calibrated and uncalibrated absorption coefficients (m^{-1}), respectively, the factor 2.18 was derived by Bond et al. (1999) to account for the enhancement of particle light absorption caused by the multiple scattering of light within the PSAP filter, and the linear function of Tr is the manufacturer's compensation for the effect of particle loading on this enhancement (i.e., the effect of particle loading on instrument response).

Further, we note that the PSAP's diminishing response to increasing particle loading was more pronounced in our experiments than suggested by the manufacturer's calibration, as illustrated in Fig. 6b. Therefore, the values of absorption coefficient (and SSA) presented above were not calculated using the manufacturer's correction for particle loading, rather we derived a new calibration:

$$B_{\text{abs}} = \frac{B_o}{2.18(1.1 Tr - 0.1)}. \quad (4)$$

The slope and intercept of the linear function of Tr in Eq. (4) were derived from a statistical regression of the PSAP data collected without application of Eq. (3) (i.e., from the "raw" PSAP data). The application of Eq. (4) to these "raw" data largely eliminated the influence of particle loading, as shown in Figs. 5a and 6b.

Last, we note that our observation of a more pronounced filter loading effect for the PSAP is consistent with Sheridan et al. (2005), who reported that the PSAP's filter loading correction was inadequate when sampling aerosol characterized by low values of SSA.

3.2.2. Towards the development of a BC standard for TOA

The ability to produce controlled amounts of BC with the diffusion flame can be applied to the replication of quartz filter samples with known amounts of BC, either alone or mixed with other aerosol components. In this study we prepared samples of BC and BC plus NaCl. The NaCl was mixed with the BC in the post combustion region to produce external mixtures, as described earlier. Fig. 8 shows the carbon thermograms of 11 prepared samples: nine of only BC and two of externally mixed BC and NaCl. The duration of each sample was 15 min and the 11 samples were collected over a 10 h period. The relative standard deviation (rsd) of the BC loading of these samples is only 2.8%. The BC concentration generated with the diffusion flame for the collection of these samples was at the $\mu\text{g m}^{-3}$ level. Even less variability in BC content (rsd = 1%) is exhibited by samples of shorter duration collected over shorter periods of time when sampling BC concentrations at the mg m^{-3} level. These results demonstrate that the stability of the diffusion flame facilitates the collection of repeatable amounts of BC onto quartz filters.

The thermograms in Fig. 8 also illustrate that the combustion temperature of BC can be significantly

influenced by other aerosol constituents, consistent with earlier work demonstrating that common constituents of biomass smoke, such as Na and K, catalyze the combustion of BC (Novakov and Corrigan, 1995). In the current study, the addition of NaCl to the sample decreased the combustion temperature of BC by $\sim 150^\circ\text{C}$ when analyzed using our TOA method. When analyzed according to the more common IMPROVE TOR protocol that reports evolved carbon as the sample temperature is increased stepwise (i.e., EC1, EC2, EC2), a similar effect was observed. The sample without salt evolved as 80% EC2 and 20% EC3, whereas when mixed with salt it evolved as 20% EC1 and 80% EC2.

This demonstration emphasizes the need for caution when distinguishing between OC and BC solely on the basis of evolution temperature, as is done for example in the R&P 5400 carbon particulate analyzer (Rupprecht et al., 1995) and in the two-step thermal analysis methods (Cachier et al., 1989; Lavanchy et al., 1999). Similarly, because thermogram features are influenced by the aerosol composition, they may be of limited value. For instance, since they are not additive, the various temperature-defined carbon fractions of the IMPROVE and NIOSH protocols (i.e., EC1, EC2,

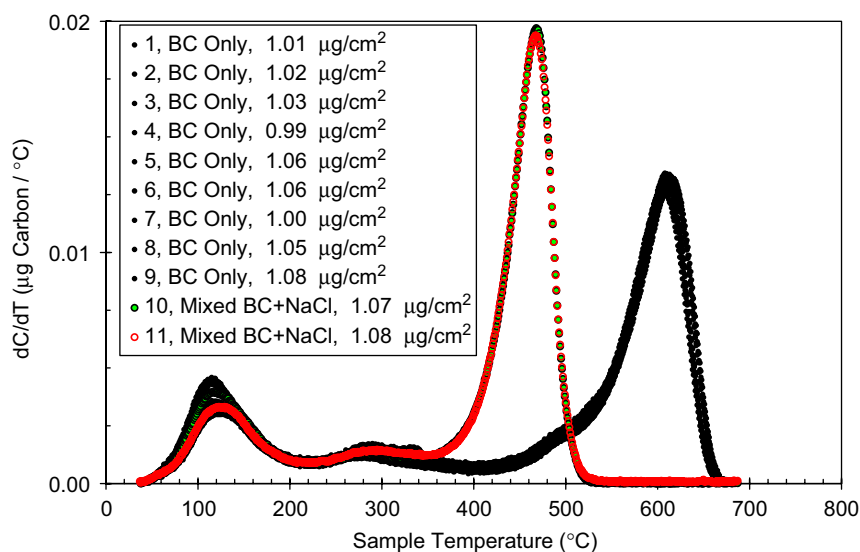


Fig. 8. Carbon thermograms of 11 quartz filters that sampled diluted exhaust of the diffusion flame. The duration of each sample was 15 min and the samples were collected over a period of 10 h. The small relative standard deviation (2.8%) of the BC loadings (reported in the legend) indicates the consistency of the BC generation rate and the ability to replicate filter samples with the same BC loading. The thermograms also indicate that the combustion temperature of BC was reduced by $\sim 150^\circ\text{C}$ when the NaCl was mixed with the BC. The lower temperature thermogram features, which do not appear in the thermograms shown in Figs. 3 and 4a, are due to the adsorption of organic vapors in the dilution air onto the quartz filters (see e.g., Kirchstetter et al., 2001). The use of an activated carbon denuder to scrub organic vapors largely eliminates these features.

EC3) may not be appropriate for use as source profiles (i.e., fingerprints) in source apportionment calculations (e.g., Kim and Hopke, 2004).

In this study, we prepared samples of BC and NaCl, but BC could be mixed with additional relevant aerosol constituents to develop BC standards that represent chemically simple to complex particulate matter in the environment. Mixtures could include inorganic compounds that affect BC combustion in addition to organic compounds that vary in their potential to pyrolyze, form char and co-evolve with BC during analysis. Organics that absorb light should also be considered. Smoldering biomass and atomizing solutions of humic acid are examples of methods of generating organic particulate matter that is both light absorbing and prone to charring during TOA. Standards containing light-absorbing, pyrolytic and catalytic materials in addition to BC could be produced to represent ambient particulate matter samples that typically yielded the greatest BC measurement uncertainty range in past TOA method comparison studies. Further, while externally mixed aerosols were generated in this study, internal aerosol mixtures, such as BC coated with organics, could also be prepared.

The BC standards described above may be useful in future studies attempting to understand uncertainty in and optimize the TOA measurement. While synthetic mixtures will not completely mimic the chemical complexity or the degree to which chemical species are internally versus externally mixed in ambient particulate matter, and they are likely not the answer for all accuracy problems in TOA, they may serve as a new tool for evaluating TOA measurement accuracy. Synthetic BC standards could be used to greater effect than current BC reference materials that contain unknown amounts of BC. In future TOA comparison studies, e.g., the BC standards could be used to assign measurement accuracy, and systematic application of BC standards with varying composition could be used to quantify the effects of sample properties on measurement accuracy. Past comparisons studies yielded wide ranges of BC estimates for most samples, which demonstrate uncertainty in TOA measurements, but could not assign accuracy to any TOA method and thus offered little benefit in the way of optimizing and reducing measurement uncertainty. BC standards could also be employed to understand how TOA responds optically during charring, and possibly to begin to understand to

what extent aerosol-mixing state is conserved when aerosols are collected on filters and to what extent aerosol mixing state affects TOA measurements.

Given the important role of BC in the environment, we recommend additional research aimed at improving BC measurements, and, further, we discourage the adoption of any BC measurement method as the “standard” method unless it can first be demonstrated that it accurately measures BC.

4. Conclusion

The stability of the inverted methane/air diffusion flame and the unique composition of the particles which it generates (BC only) make it a valuable research tool for evaluating BC and light absorption measurement methods. The absence of OC in the particles produced by the diffusion flame eliminates uncertainty in the TOA measurement of BC content, which allows the TOA measurement to serve as a reference measurement of BC. Two applications of the flame are presented: the evaluation of the aethalometer and the development of BC standards for TOA. We demonstrate the reduction of the attenuation coefficient, and thus the erroneous measurement of BC concentration, due to the reduction in the aethalometer’s response to particle light absorption as particles are collected and darken the aethalometer’s filter. We demonstrate the ability to repeat the preparation of filter samples with equal amounts of BC, and we demonstrate that the combustion temperature of BC during TOA is affected by sample composition. These applications of the diffusion flame will be discussed more completely in forthcoming manuscripts.

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