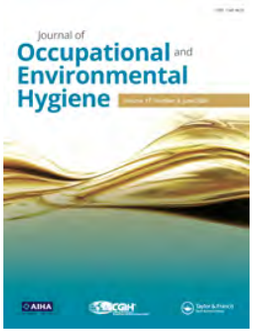

Journal of Occupational and Environmental Hygiene

ISSN: 1545-9624 (Print) 1545-9632 (Online) Journal homepage: https://www.tandfonline.com/loi/uoeh20

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To cite this article: Patrick O'Shaughnessy, Adrianne Stoltenberg, Craig Holder & Ralph Altmaier (2020) Laboratory evaluation of a personal aethalometer for assessing airborne carbon nanotube exposures, Journal of Occupational and Environmental Hygiene, 17:6, 262-273, DOI: 10.1080/15459624.2020.1740237

To link to this article: https://doi.org/10.1080/15459624.2020.1740237

Published online: 14 Apr 2020.

JOURNAL OF OCCUPATIONAL AND ENVIRONMENTAL HYGIENE
2020, VOL. 17, NO. 6, 262–273
https://doi.org/10.1080/15459624.2020.1740237

Laboratory evaluation of a personal aethalometer for assessing airborne carbon nanotube exposures

Patrick O'Shaughnessy, Adrianne Stoltenberg, Craig Holder, and Ralph Altmaier

Department of Occupational and Environmental Health, College of Public Health, The University of Iowa, Iowa City, Iowa

ABSTRACT

Aethalometers are direct-reading instruments primarily used for measuring black carbon (BC) concentrations in workplace and ambient atmospheres. Aethalometer BC measurements of carbon nanotubes (CNTs) were compared to measurements made by other methods when subjected to high (>30 μg/m^3) and low (1–30 μg/m^3) CNT aerosol concentrations representing worst-case and typical workplace concentrations, respectively. A laboratory-based system was developed to generate carbon black, as an example of a nearly pure carbon, micron-sized aerosol, and two forms of multi-walled carbon nanotubes (CNTs): small-diameter (<8 nm) and large-diameter (50–80 nm). High-concentration trials were conducted during which a scanning mobility particle sizer (SMPS) was used to track particle count concentrations over time. Relative to the behavior of the SMPS counts over time, aethalometer readings exhibited a downward drift, which is indicative of aethalometer response subjected to high BC loading on the receiving filter of the instrument. A post-sample mathematical method was applied that adequately corrected for the drift. Low-concentration trials, during which concentration drift did not occur, were conducted to test aethalometer accuracy. The average BC concentration during a trial was compared to elemental carbon (EC) concentration sampled with a quartz-fiber filter and quantified by NIOSH Method 5040. The CB and large-diameter CNT concentrations measured with the aethalometer produced slopes when regressed on EC that were not significantly different from unity, whereas the small-diameter CNTs were under-sampled by the aethalometer relative to EC. These results indicate that aethalometer response may drift when evaluating CNT exposure scenarios, such as cleaning and powder handling, that produce concentrations >30 μg/m^3. However, aethalometer accuracy remains consistent over time when sampling general work zones in which CNT concentrations are expected to be <30 μg/m^3. A calibration check of aethalometer response relative to EC measured with Method 5040 is recommended to ensure that the aethalometer readings are not under sampling CNT concentrations as occurred with one of the CNTs evaluated in this study.

KEYWORDS

Aethalometer; carbon nanotubes; elemental carbon

Introduction

Carbon nanotubes (CNTs) are a type of engineered nanomaterial produced for a variety of applications in engineering, material science, and medicine (Milne et al. 2008; Lu et al. 2012). Either single-walled CNTs, with diameters of 1–4 nm, or multi-walled CNTs, with diameters up to 100 nm (NIOSH 2009), are manufactured. Due to their small size and needle-like shape, CNTs may cause adverse health effects as an inhalation hazard. In fact, numerous toxicological studies have demonstrated the potential negative impact of CNTs on human health (Aiso et al. 2010; Nagai et al. 2011; Morimoto et al. 2012; Shvedova et al. 2012; Xu et al. 2012).

Based on documented adverse health effects associated with CNT inhalation, regulatory agencies have proposed occupational exposure limits (OELs) for CNTs. The U.S. National Institute for Occupational Safety and Health (NIOSH) published guidance for evaluating exposures to CNTs along with a Recommended Exposure Limit (REL) of 1 μg/m^3 measured as a respirable 8-hr time-weighted average (TWA) mass concentration of elemental carbon (EC) (NIOSH 2013). Researchers in Japan's National Institute of Advanced Industrial Science and Technology (AIST) and other agencies have recommended a respirable 8-hr TWA mass concentration of 30 μg/m^3 (Nakanishi 2015). Although different, the very low magnitude of these OELs attest to the need for highly sensitive instruments and analytical methods to measure CNT concentrations in workplaces.

NIOSH guidance (NIOSH 2013) recommends the use of NIOSH Method 5040 (NIOSH 2003) to determine

CONTACT Patrick O'Shaughnessy patrick-oshaughnessy@uiowa.edu Department of Occupational and Environmental Health, College of Public Health, 100 CPHB, S320, The University of Iowa, Iowa City, IA 52242, USA

CNT aerosol concentrations. NIOSH Method 5040 uses a thermal-optical analysis method that incorporates a flame ionization detector to quantify the amount of EC on a filter (NIOSH 2009). The stated limit of detection (LOD) of Method 5040 is 0.3 μg/filter punch, where the area of a filter punch is typically 1.5 cm^2. This LOD translates into the precision needed to measure a 2 $\mu g/m^3$ aerosol concentration when sampled using a 2-L/min cyclone and 37-mm cassette over 8 hr, or 1 $\mu g/m^3$ using a 4-L/min cyclone and 25-mm cassette over 8 hr.

Several studies have used NIOSH Method 5040 to evaluate CNT exposures in occupational settings (Dahm et al. 2012, 2015). A study conducted in primary and secondary CNT manufacturing facilities found that detectable EC concentrations ranged from 0.68–7.86 $\mu g/m^3$ among personal samples and 0.47–4.62 $\mu g/m^3$ among area samples (Dahm et al. 2012). Eleven of the 14 personal samples from this study exceeded 1 $\mu g/m^3$. In their analysis of 14 CNT production sites, Dahm et al. (2015) found respirable EC concentrations < 3 $\mu g/m^3$ and inhalable concentrations <60 $\mu g/m^3$.

Method 5040 can be considered the most reliable method for assessing CNT exposures. However, a direct-reading instrument (DRI) is an attractive alternative method because its use does not require sending samples to a lab as is the case for Method 5040 analysis, and additional exposure information can be obtained from the time series of aerosol concentrations produced by a DRI. An aethalometer is an example of a DRI designed to measure the airborne concentration of black carbon (BC), which may also be suitable for measuring CNT aerosols. Black carbon is a term used to incorporate all black carbonaceous particles, including EC, that absorb light over a broad spectrum of visible light (Weingartner et al. 2003).

The operating principles of an aethalometer are well described by others (Hansen et al. 1984; Jimenez et al. 2007; Weingartner et al. 2003). In short, the BC mass concentration value reported by an aethalometer (C_{BC}) is a function of the change in light attenuation, ATN, through a collection filter from one reading to the next, ΔATN; the filter collection area, A; the sample flowrate, Q; the time between samples, Δt; and an attenuation efficiency, σ_{ATN}, (Jimenez et al. 2007):

$$C_{BC} = \frac{A \cdot \Delta ATN/100}{Q \cdot \Delta t \cdot \sigma_{ATN}} \quad (1)$$

Aethalometers are commonly used to measure BC concentrations in the ambient air (Jeong et al. 2004; Ahmed et al. 2009). Aethalometers have also been used to investigate CNT exposures in various workplaces. Han et al. (2008) measured very low BC concentrations except when fabrication equipment was opened, during which up to 200 $\mu g/m^3$ of MWCNTs were released. Lee et al. (2010) provide time series of aethalometer measurements made in three CNT workplaces where each varied between 1–4 $\mu g/m^3$. Kim et al. (2016) used an aethalometer to evaluate CNT levels in both background and workplace settings. They found background levels ranging from 0.36–2.64 $\mu g/m^3$ and only one of three worksites with BC levels above background.

Despite its promise as a suitable DRI for CNT exposures, aethalometers have been shown to produce a measurement artifact exhibited by a downward trend in readings when actual BC concentrations are stable (Kirchstetter and Novakov 2007; Virkkula et al. 2007). This measurement decay, or "filter loading effect," is principally attributed to a steady change in the value of σ_{ATN} as the filter is loaded and darkens with carbonaceous particles, rather than remaining constant as applied to Equation (1) to determine C_{BC} (Weingartner et al. 2003; Kirchstetter and Novakov 2007). This loading effect becomes more pronounced as BC concentrations increase. Several post-processing algorithms have been developed to eliminate the apparent decrease in concentration (Jimenez et al. 2007; Virkkula et al. 2007; Good et al. 2017). The method developed by Jimenez et al. (2007) is described in detail in the Methods section of this paper. For example, Kim et al. (2017) found relatively good agreement between BC concentrations measured with an aethalometer and particle mass concentration inferred from particle counts obtained with a scanning mobility particle sizer after employing the correction method described by Virkkula et al. (2007). Furthermore, the work by Hashimoto et al. (2013) demonstrated that the value of σ_{ATN} applied to an aethalometer may vary between CNT types and suggested that a correction factor be applied unique to the CNT type.

This review of the literature on the use of an aethalometer as a DRI for investigating CNT exposure levels suggested that their accuracy may be hindered by the loading effect and their accuracy may be CNT-specific. The purpose of this study, therefore, was two-fold: (1) determine the CNT concentration measured by an aethalometer below which the loading effect is not apparent; and (2) assess the accuracy of a portable aethalometer for measuring different CNT aerosols relative to their EC concentration measured using NIOSH Method 5040 in CNT atmospheres that did not produce a loading effect. An aethalometer was evaluated at the low concentrations expected in the

Table 1. Carbon black and CNT bulk powder properties[A]

Powder type	Tube diameter, nm	Tube length, μm	Specific surface area, m^2/g	Carbon purity, %	
				EDS[B]	TGA[C]
Carbon black	-	-	-	-	>98
Short CNT	10-20	0.5-2	>200	99.2	
Small CNT	<8	10-30	>500	97.5	96.8
Large CNT	50-80	10-20	>40	97.4	96.8

[A]Properties obtained from manufacturer's certificate of analysis
[B]Energy-dispersive X-ray Spectroscopy
[C]Thermogravimetric Analysis

breathing space of occupational settings and at high concentrations expected during some tasks (for example, reactor cleaning) to determine the usefulness of this DRI for evaluating the variety of workplace scenarios having potential CNT exposures.

Methods

Powder types

Three multi-walled CNTs (all from Nanostructured & Amorphous Materials, Houston, TX) and carbon black were evaluated in this study. The physical properties and percent of carbon content for each are shown in Table 1. Carbon black was used to demonstrate aethalometer performance when analyzing a traditional carbon-containing material expected to contain nearly 100% carbon (Thermax Powder Ultra-Pure N991, Continental Carbon, Houston, TX). The high concentration trials were performed with a multi-walled CNT with a relatively short tube length (Short-CNT, Stock No. 1236YJS) that was found to easily disperse as a suspension in water. The other two CNTs were multi-walled and with either a large (L-CNT, Stock No. 1233YJ) or small (S-CNT, Stock No. 1203YJ), diameter, but otherwise had similar compositions, including nearly identical carbon purity, that was important for making comparisons with NIOSH Method 5040. The powders were prepared by drying overnight in an oven (110 °C) to enhance powder aerosolization.

CNT aerosol generation

A CNT aerosol was produced using three aerosol generator types. Either a Collison nebulizer (CH Technologies, Westwood, NJ) or a dry powder disperser (Model SAG 410/U, TOPAS GmbH, Dresden, Germany) was used to produce high CNT concentrations. The nebulizer was found to more accurately produce concentrations $<50\,\mu g/m^3$, whereas the dry powder disperser was capable of producing a large range of concentrations with better reproducibility at concentrations $>50\,\mu g/m^3$. When nebulizing, a 0.5 mg/mL suspension was prepared in purified water (Q-Gard 1, Millipore, Billerica, MA) and sonicated for 5 min. Subsequent suspensions were prepared by serial dilution to obtain different aerosol concentrations. Pressurized air (138 kPa, 20 lb/in^2) to the Collison nebulizer was first conditioned with a desiccant air dryer to remove moisture and filtered with a high-efficiency particle air (HEPA) filter. A magnetic stirrer was used to ensure that the suspension remained well mixed during nebulization. The exiting droplet aerosol passed through a heated, 2.54-cm diameter brass tube and then through a water vapor condenser consisting of a 1-L glass jar surrounded by ice water. The dry disperser included a system for adding a consistent amount of dry powder to a knife-edged ring that rotates under a venturi aspirator. Adjusting the ring speed augmented the generation rate. Further details concerning the operating characteristics of this instrument when aerosolizing CNTs is given in O'Shaughnessy et al. (2014).

Low concentrations of CNT aerosol were developed with the use of an acoustic aerosol generator (Thorne 1994). The acoustic generator was composed of an open-ended aluminum cylinder (9-cm diam. x 30-cm long) covered on both ends with a flexible rubber sheet and positioned on top of a box containing a 7.6-cm speaker that projected sound upward toward the cylinder. A sound wave was produced with the use of a power amplifier (Model PCAU22, Pyle Audio, Inc., Brooklyn, NY) and a function generator operating at 200 Hz (Model 4010A, B&K Precision Corp., Yorba Linda, CA). Approximately 5–10 g of powder were placed inside the cylinder before commencing experimental trials. During operation, 5 L/min of filtered air flowed through the top portion of the cylinder.

Experimental setup and aerosol sampling

A schematic diagram of the experimental setup when using the acoustic generator is provided in Figure 1. The setup was similar when using the other two aerosol generating devices. As shown in Figure 1, the aerosol exited an aerosol generator and then entered a 4-L dilution chamber. Since the NIOSH REL relies on the respirable sampling concentration, a respirable

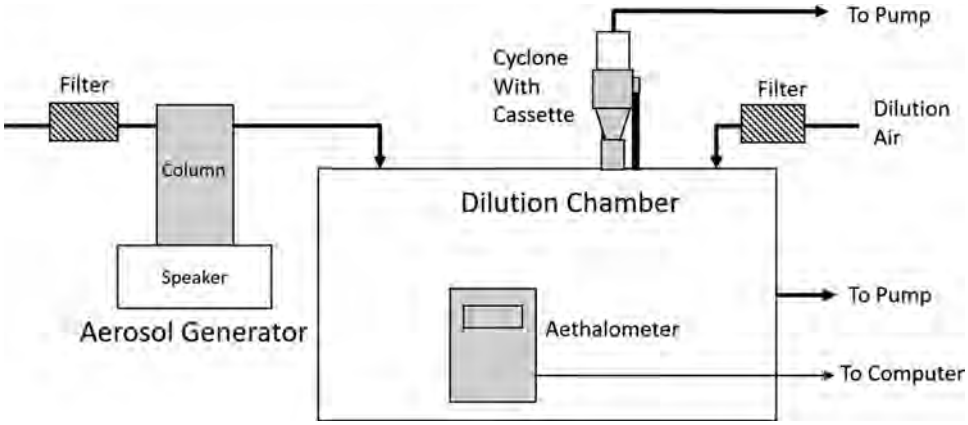

Figure 1. Schematic diagram of experimental setup with arrows indicating air flow direction.

cyclone (Model GK2.69, BGI Inc., Waltham, MA) was used to sample the CNT aerosol within the chamber. CNT samples for Method 5040 analysis were collected using a 25-mm cyclone operating at 4.2 L/min onto heat-treated quartz fiber filters for EC analysis (Cat. No. 225-1825, SKC Inc., Eighty Four, PA) during all trials. Due to the low concentrations being collected during this study, 25-mm filters were used to decrease the collection area to maximize the mass per filter area collected. The sample pump was pre- and post-calibrated with a primary standard air flow calibrator (Gilian Gilibrator-2, Sensidyne, LP, St. Petersburg, FL). Air pressure in the chamber was balanced to near atmospheric pressure by applying suction with a vacuum pump to ensure that the relatively weak internal pump of the aethalometer was not hindered by a low-pressure environment in the chamber. This process also brought filtered dilution air into the chamber that was used to control chamber concentrations near a desired level. Flow rates through the chamber therefore varied between approximately 5–10 L/min, which provided 1.25–2.5 air exchanges per minute (ACM). Our previous analysis of a small chamber indicated that ACM rates higher than 0.5 ACM provided mixing within a chamber by dilution air alone equivalent to that provided with a fan in the chamber (O'Shaughnessy et al. 2003). After terminating aerosol sampling through the cyclone and shutting off air through the aerosol generator, the trial end time was noted and the aethalometer was allowed to continue to run to sample the dilution air in the chamber until readings lowered to the detection limit of the instrument before opening the chamber to remove the aethalometer.

Two personal aethalometers (model AE51, AethLabs, San Francisco, CA) were used to obtain real-time concentrations of the mass concentration in the sampling chamber. The earlier high concentration trials were performed with a model AE51-S3 and the low concentration trials were performed after purchasing a model AE51-S6. Five preliminary trials were conducted during which both instruments were placed in the chamber to make simultaneous readings under various chamber concentrations ranging from 5–25 $\mu g/m^3$. A linear regression on the coincidental trial concentrations resulted in a slope of 0.991 ($r^2 = 0.998$), which was considered to indicate acceptable agreement between the two instruments. Furthermore, a t-test for autocorrelated sample sets (O'Shaughnessy and Cavanaugh 2015) resulted in no significant difference between the means of readings made by the two instruments ($p > 0.05$) during a 30-min trial.

The Teflon-coated borosilicate glass fiber filter strips (AE51-FS25, Aethlabs, San Francisco, CA) used by the aethalometer to determine the concentration of BC were changed before each trial. The manufacturer claims the instrument has a measurement range up to 1 mg/m^3 with a measurement precision of ±0.1 $\mu g/m^3$ when operating at 0.15 L/min with 1-min average time (Aethlabs, 2015). However, they recommend reducing the sample flow rate as the BC concentration is expected to increase. We therefore operated the aethalometer at a flow rate of 0.1 L/min and with a 5-min sample interval when performing high concentration experiments. The sample flow rate was further reduced to 0.05 L/min when conducting the low concentration experiments to compensate for an increased sample interval of every 30 s to obtain an accurate indication of the fluctuation in BC concentrations over time. Aethalometer flow rate was calibrated using software provided by the manufacturer prior to each use. Readings were zeroed whenever a blank filter was applied to the instrument. No corrections were made to instrument measurements other than to remove spurious negative values.

For both high and low concentration experiments, the aerosol particle size distribution was determined

using a scanning mobility particle sizer (SMPS, model 3080, TSI, Shoreview, MN) equipped with a long-differential mobility analyzer (model 3081, TSI, Shoreview, MN) and water-based condensation particle counter (model 3785, TSI, St. Paul, MN). The SMPS measured in size bins ranging from 7 to 290 nm while operating at a flow rate of 1.0 L/min. During high concentration experiments, this instrument was operated in tandem with the aethalometer and set to sample every 5 min in phase with the aethalometer recordings by sampling through a port in the chamber directly adjacent to the aethalometer. Transmission electron microscope (TEM) images were also obtained of the CNT aerosol with the use of a device specifically designed to capture particles onto a TEM stub by electrostatic precipitation (Model 100, ESPnano, Spokane, WA).

Experimental design

During high-concentration trials, the Short-CNT was sampled over a 50-min sample period. A Total of 18 trials were conducted that resulted in BC concentrations ranging between 30–110 μg/m^3. For low-concentration trials, six trials with targeted average mass concentrations of 1, 2, 6, 10, 15, and 20 μg/m^3 were conducted with carbon black, S-CNT and L-CNT. Sample duration was predetermined based on expected concentration to ensure that a sufficient mass of CNT was deposited on the sample filter to be above the laboratory's reporting limit of 0.76 μg EC/cm^2. This requirement resulted in sample durations ranging from 71 min to approximately 24 hr, with the longest time required for the lowest chamber concentration.

Sample analysis

The 25-mm quartz fiber filters were analyzed for EC using thermal-optical analysis and a flame ionization detector per NIOSH Method 5040. All samples were analyzed using the Sunset Laboratory Inc. (Tigard, OR) Organic Carbon/Elemental Carbon (OC/EC) instrument by a laboratory accredited by the American Industrial Hygiene Association Laboratory Accreditation Program. One blank for each powder type was submitted for analysis along with the samples collected. The EC mass per filter area determined by NIOSH Method 5040 was converted to a concentration based on the volume of sample air through the cyclone and the sampling surface area of the filter.

Data analysis

During high-concentration trials, the SMPS total count concentration per measurement was transformed into a mass concentration, C_S, assuming the particles measured were spheres with unit density (1 g/cm^3) to compare their fluctuations over time to the corresponding C_{BC} values. After a 50-min trial was completed, the relative difference between C_S at time period, k, ($C_{S,k}$) and the first C_{BC} measured at 5 min ($C_{BC,5}$) were compared to the relative difference between C_{BC} at time period, k, ($C_{BC,k}$) and the first measured concentration ($C_{BC,5}$) using the following equation:

$$\left[\frac{(C_{BC,k}-C_{BC,5})}{C_{BC,5}}-\frac{(C_{S,k}-C_{S,5})}{C_{S,5}}\right]100. \quad (2)$$

This comparison method, in which concentrations over time are compared on a relative basis, negated the need to know the actual density of the particles when transforming SMPS count concentrations to mass concentration.

The method to compensate for decay in aethalometer readings described by Jimenez et al. (2007) was applied under the assumption that a downward drift in concentration resulted from the filter loading effect. First, the difference in attenuation between successive ATN measurements, ΔATN(t), is computed for each sample time (0–50 min, by every 5 min). The ratio of these differences relative to the difference between the first two measurements, ΔATN(0), is then computed:

$$K(ATN)_m=\frac{\Delta ATN(t)}{\Delta ATN(0)}. \quad (3)$$

This ratio, based on measured (m) ATN values, is then regressed relative to the transmission value for each sample time, $T=\exp(-ATN/100)$, to determine $K(ATN)_r$, the $K(ATN)$ value resulting from the linear regression model:

$$K(ATN)_r=a+b(T). \quad (4)$$

The decay in instrument readings is then corrected by multiplying the aethalometer concentration readings, C_{BC}, by the inverse of $K(ATN)_r$.

After low-concentration trials, linear regression was used to examine the relationship between the average of aethalometer concentrations measured over a trial period and the associated time-integrated EC concentration resulting from Method 5040 over the span of concentration levels for each powder type. For each regression, a 95% confidence interval (CI) of the slope was calculated and compared to unity to determine if the two methods agreed. All statistical analyses were

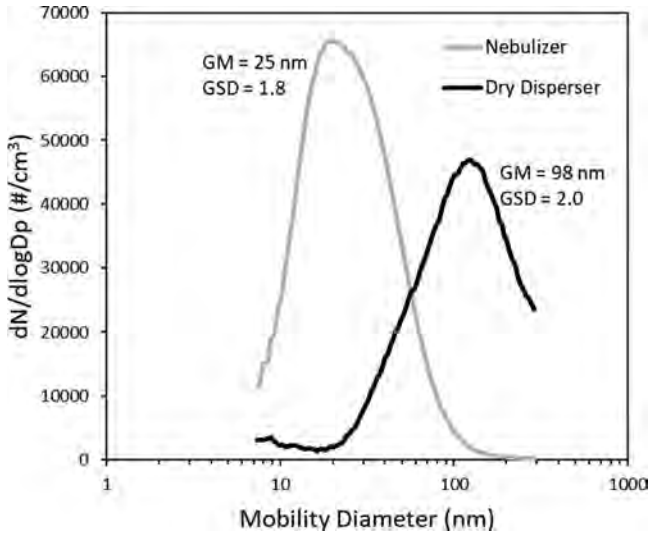

Figure 2. Typical MWCNT particle size distributions when generated using the nebulizer system and the dry disperser with associated geometric mean (GM) and geometric standard deviation (GSD).

conducted using Minitab (Version 17.1, State College, PA).

Results

Aerosol characteristics

The nebulizer system created a CNT aerosol with a geometric mean (GM) diameter of 25 nm and geometric standard deviation (GSD) of 1.8 (Figure 2). The dry disperser and acoustic generator created larger particles with a GM diameter near 100 nm and GSD of 2.0 (Figure 2). These size distributions indicate that the aerosols were primarily composed of agglomerates of CNT particles in the respirable size range ($< 4\,\mu m$) with the majority of the distribution being less than 700 nm. A photomicrograph of a multi-walled CNT aerosol is given in Figure 3. Given the true density of carbon nanotubes ($\sim 2.1\,g/cm^3$) the resulting aerodynamic diameter GM of 142 nm is well within the range of respirable particles in accordance with the NIOSH REL for CNTs.

High-concentration CNT trials

Results from a typical trial are shown in Figure 4 in which progressively lower C_{BC} values ("Original BC") are obtained relative to corresponding C_S values ("SMPS"). Application of Equation (2) to all 18 trials resulted in a downward trend in the average relative difference between C_{BC} and C_S from the first measurement as shown in Figure 5. This analysis indicates that the C_{BC} measurements were approximately 25% lower than expected after 50 min. However, the C_S values obtained over the same time period remained relatively stable, which justified the use of the decay compensation method described previously.

To determine whether the downward trend is dependent on CNT concentration, the slope of the relationship between C_{BC} and time was determined for each trial. A significant negative Spearman correlation (-0.70, $p = 0.001$) was found when these slopes were compared to the associated starting concentration, $C_{BC,5}$, of each trial (Figure 6). This analysis also indicated that C_{BC} readings below approximately 30 $\mu g/m^3$ did not decay appreciably over the 50-min time period of the trials (Figure 6).

A plot of $K(ATN)_m$ vs. transmission, T, with data derived from all trials is given in Figure 7. Applying the $K(ATN)_r$ value derived with use of Equation 4 adequately negated the drifting pattern for each trial as shown in Figure 4 for one trial ("Corrected BC"). However, a consistent relationship between $K(ATN)$ and T was not found between trials. The slope obtained varied between 0.417 and 2.445, and the intercept varied between -0.942 and 0.665. The regression line shown in Figure 7 is derived from the average of all slopes (1.418) and intercepts (-0.078) obtained from the 18 trials, which better represents the average association between $K(ATN)$ and T than does a regression fit through all of the combined data pairs.

Low concentration CNT trials

During low concentration trials, the aethalometer provided continuous, uninterrupted measurements that did not show evidence of the reading decay evident in the high concentration trials. A graph of aethalometer

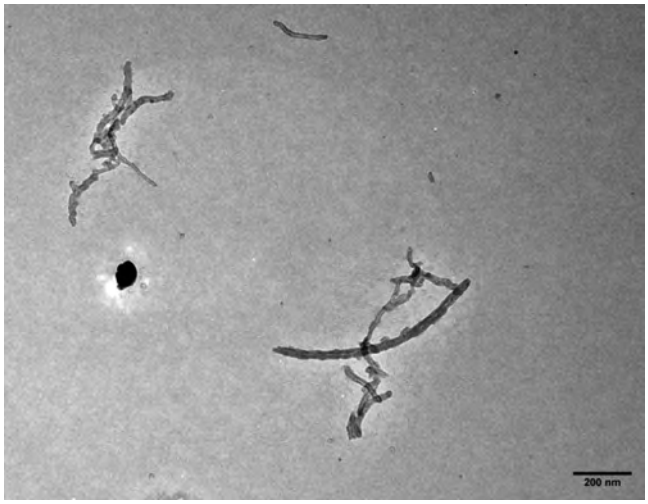

Figure 3. Transmission electron microscope image of MWCNT particles generated with the nebulizer system. Note scale bar of 200 nm.

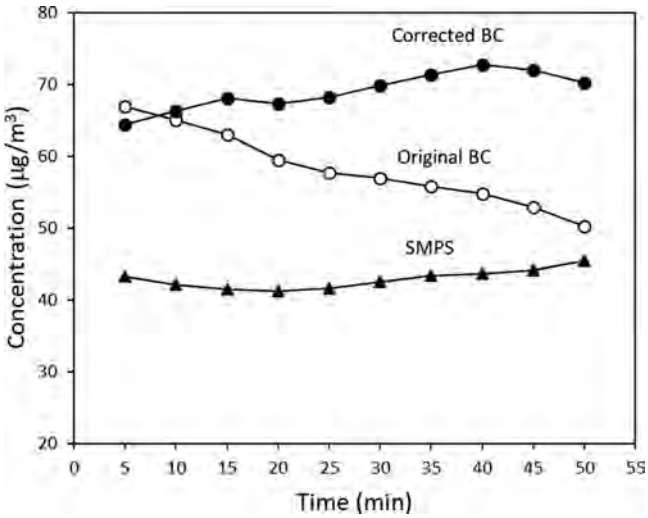

Figure 4. Example of aethalometer BC concentration measurements over time, original and corrected, relative to SMPS measurements.

readings from one of the longest trials (1,760 min) is shown in Figure 8. The shifts in concentration shown in Figure 8 were caused by adjustments made during the trial (primarily by adjusting the dilution flow rate) to maintain the concentration at the targeted value for the respective trial.

The paired data points and regression models for each powder type are shown in Figure 9. All blank samples were below the reporting limit for EC. All linear regressions resulted in insignificant intercepts ($p > 0.05$). The standardized residuals associated with each plot were < 2, which indicates that no point had statistical influence on the resulting linear relationship. For each powder type there was a strong positive linear relationship ($r^2 \geq 0.94$). The slopes for carbon black (1.182) and L-CNTs (0.941) vs. aethalometer averages were not significantly different from unity as indicated by the 95% confidence interval lines which span the 1:1 line. However, the slope for the S-CNT relationship (0.661) was significantly less than unity, which indicated under-sampling by the aethalometer for that aerosol.

Discussion

Aethalometer response was tested during this study relative to two potential uses for this instrument when evaluating CNT aerosol exposures in workplaces: high concentration scenarios associated with direct exposure to a CNT source, and low-concentration situations that may occur within the general space associated with CNT production areas. Results from the high concentration trials performed as part of this research suggest that the aethalometer used in this study can

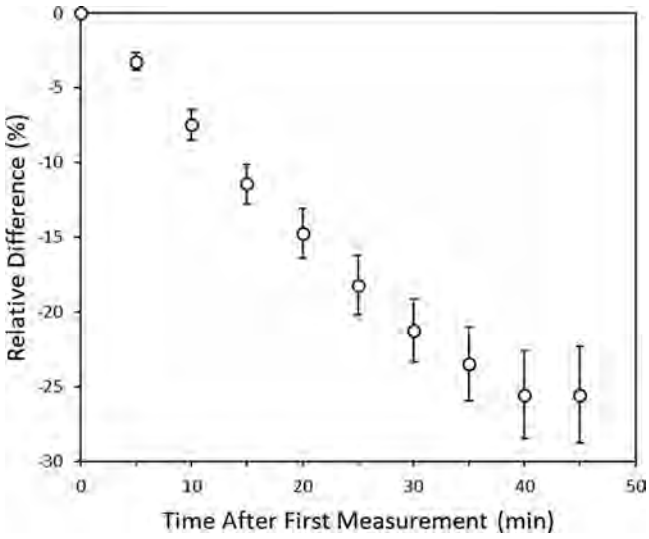

Figure 5. Average and standard deviations of the percent relative difference between BC concentrations measured after 5 min and subsequent 5-min measurements.

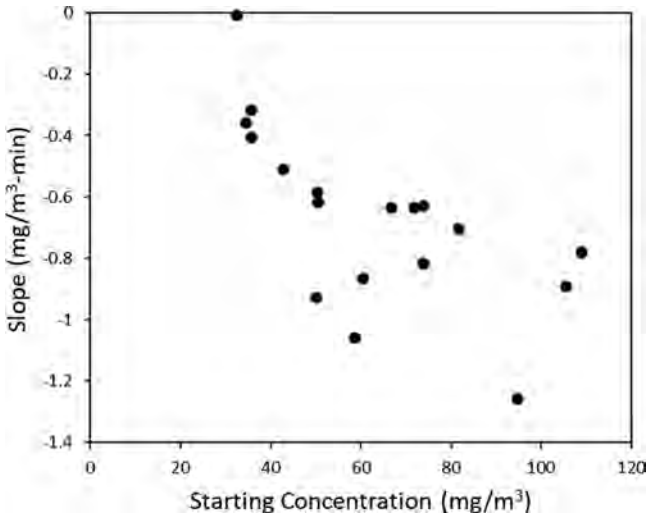

Figure 6. Slope of BC concentration and sample time relative to BC starting concentration indicating the lack of measurement decay when the aethalometer made measurements of BC less than approximately 30 mg/m^3.

exhibit an artificial decay in measurements over time for CNT concentrations exceeding 30 μg/m^3. However, the method described by Jimenez et al. (2007) employed during this study adequately compensated for instrument drift that may occur when using the instrument in high CNT concentration environments such as when handling raw powder or cleaning out a reactor (Methner et al. 2012). An average regression equation is provided in Figure 7 that could be used to compensate for that decay.

Personal aethalometers have been successfully used in other scenarios to measure personal BC exposures without obvious declines in concentration caused by the filter loading effect. Vilcassim et al. (2014) used a personal aethalometer in subway stations over relatively short 10-min sampling periods and found levels ranging from 5–23 μg/m^3 without mentioning the existence of decay in their readings. Likewise, Stapleton et al. (2018) measured diesel particulate matter emanating from older tractors in farming scenarios with a personal aethalometer and reported mean exposure levels up to 2.3 μg/m^3 over day-long sampling durations without experiencing instrument drift. Under most CNT production scenarios, levels above 30 μg/m^3 were rarely found during investigations of CNT exposure levels in the United States (Dahm et al. 2012, 2015), therefore, an aethalometer may not exhibit downward drift throughout a work day in most of these workplace scenarios. When measuring in low-concentration environments the primary issue then centers on instrument accuracy.

Results presented here suggest that the aethalometer used in this study provided readings that were

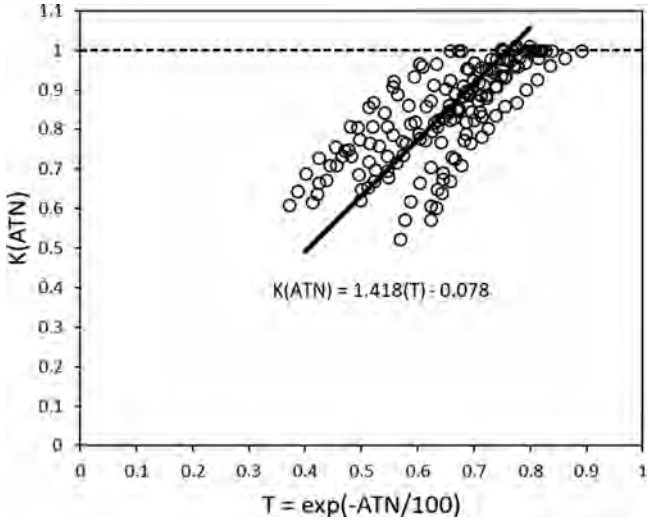

Figure 7. The relationship between K(ATN), the ratio of drop in attenuation between successive measurements (ΔATN) relative to the drop between the first two measurements, and transmission of light through the sample filter. A linear regression developed from the average slope and average intercept of those obtained from the 18 trials is also given.

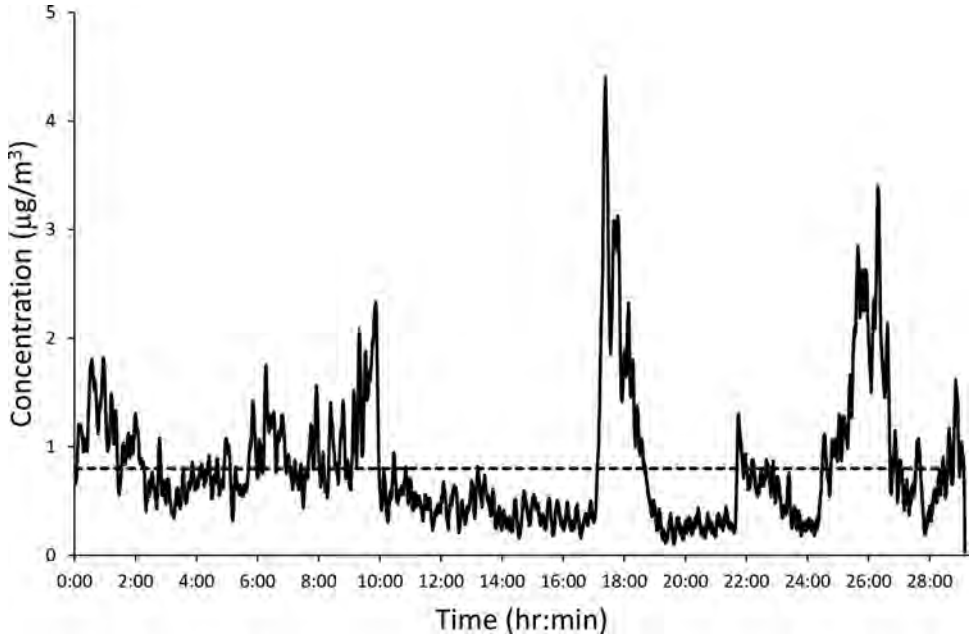

Figure 8. Example time series of BC concentrations made with the aethalometer during a low concentration trial. Sudden changes (10, 17, 22, 24, and 27 hr) resulted from operator changes in chamber flow rate to maintain concentrations near 1 µg/m^3.

strongly associated with EC values obtained by Method 5040 for two of the three CNT aerosols analyzed and undersampled one of the CNT aerosols. Hashimoto et al. (2013) evaluated a portable aethalometer and compared their results to NIOSH Method 5040 for various CNT types. They reported undersampling by the aethalometer for which they suggested correction factors ranging from 1.2–8.3 depending on CNT type. By comparison, the slope obtained from this research for L-CNT (Figure 9) results in correction factor of 1.5. The primary difference between our study and that of Hashimoto et al. (2013) is that the aerosol EC concentrations used in this study (1–30 µg/m^3) were much lower than those used by Hashimoto et al. (2013) (100–700 µg/m^3). This difference in concentrations suggests that the relative response is not constant over a large range of CNT concentrations but is, rather, close to unity at low concentrations then follows a diminished response pattern under high concentration conditions.

Regardless, our results agree with those of Hashimoto et al. in the respect that there may be differences in the relative response of the aethalometer with respect to CNT type. Hashimoto et al. (2013)

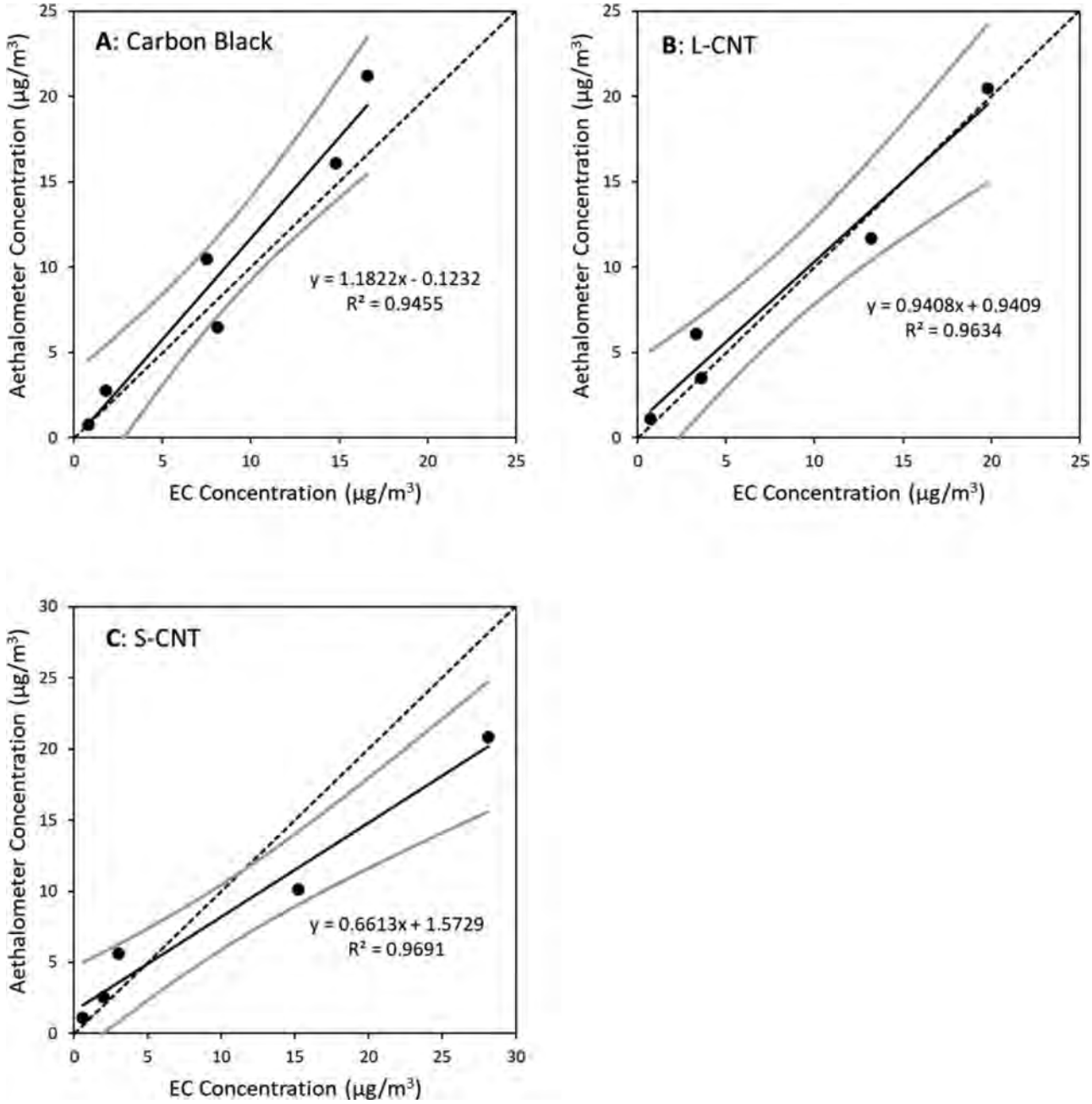

Figure 9. Plots of average aethalometer concentrations relative to EC concentrations by Method 5040 for (A) carbon black, (B) large-diameter CNTs, and (C) small-diameter CNTs. Dashed line is 100% agreement, solid line is regression line, grey lines are 95% confidence intervals.

suggest that σ_{ATN} values appropriate for measuring atmospheric aerosols may not be appropriate for nearly pure carbon aerosols such as CNTs. Weingartner et al. (2003) discuss the many factors that can influence the value of σ_{ATN} and report values ranging from 3.2–20 m^2/g depending on sampling location in ambient environments. Petzold et al. (1997) report $\sigma_{ATN} = 3.85$ m^2/g for a BC aerosol produced with a spark discharge generator, which would report C_{BC} values 3.25 times higher than when using $\sigma_{ATN} = 12.5$ m^2/g, the value applied to the aethalometer used in this study. Performing a pilot study within a manufacturing plant in which concurrent aethalometer and Method 5040 samples are taken would aid in determining whether a correction factor is needed.

Our results indicate that a personal aethalometer exhibited the sensitivity needed to measure CNT concentrations as low as the recommended REL for CNTs of 1 $\mu g/m^3$ and therefore has value for use during a health risk assessment of CNT workers and CNT process evaluations. As shown in Figure 9, there

is some error between the plotted data points and the regression line which can indicate some lack of sensitivity in the aethalometer. However, our measurement system was not precise enough to determine whether that error is associated strictly with the aethalometer or results from differences in aerosol concentration within the chamber between the ports used to sample for Method 5040 analysis and sampling with the aethalometer. Furthermore, our results suggest that a personal aethalometer can provide reliable BC measurements over extended time periods as long as CNT concentrations are below 30 μg/m^3, which is reasonable given reported measurements at CNT facilities within that concentration range (Dahm et al. 2012, 2015).

Conclusion

The findings of this study indicate that an aethalometer can detect and quantify carbon-containing nanoparticles such as CNTs at levels found in CNT manufacturing facilities. The BC measurements made with the aethalometer also demonstrated a strong positive association with EC measurements resulting from Method 5040, which indicates that the aethalometer can be used to evaluate CNT exposures relative to the NIOSH REL defined in terms of EC. When evaluating CNT concentrations in production situations that result in concentrations > 30 μg/m^3, aethalometer readings should be expected to drift downward and therefore require correction using the method described here or by others. When evaluating CNT concentrations < 30 μg/m^3, the aethalometer can provide reliable measurements over time periods sufficient to evaluate a workplace atmosphere. However, the instrument might *underestimate* concentrations depending on CNT type. Therefore, it is recommended that the aethalometer be periodically calibrated relative to EC measurements determined by using Method 5040. Otherwise, the aethalometer can be used to provide the real-time data needed to monitor workplace settings relative to a background location as a screening tool for quickly indicating CNT releases or for evaluating a new control measure.

Acknowledgments

The authors also wish to thank Steve Strebel of the Wisconsin Occupational Health Laboratory, for his aid with Method 5040 sample analysis and interpretation.

Funding

This research was supported by University of Iowa Center for Health Effects and Environmental Contamination, the University of Iowa Environmental Health Sciences Research Center (NIH P30 ES005605), and by the Heartland Center for Occupational Health and Safety, a NIOSH/CDC Education and Research Center (T42OH008491).

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