1. Introduction

Highly-absorbing carbonaceous aerosol forms during the incomplete combustion of carbon-containing fuels. Due to the diversity of matter in the atmosphere, black carbon aerosol (BC) has been delineated from other suspended carbonaceous nanomaterials and narrowly defined by its chemical, physical and spectroscopic properties. BC is composed of nearly-elemental carbon with extended sp2-bonding between carbon atoms arranged in multi-layered graphene-like sheets forming concentric, spherical nanoscale monomers aggregated into an open, lacy structure [1-2], see Fig. 1. The lacy aggregates may rearrange (collapse) into a compact, spherical, void-filled morphology after interaction with condensed- and/or gas-phase species [3-5]. Other similar carbonaceous nanomaterials can form under different conditions impacting the material’s physical and, potentially, spectroscopic properties. For example, graphene and reduced graphene oxide (rGO) form crumpled nanopaper-like structures [6-9], see Fig. 1, chemically analogous to BC but morphologically dissimilar. It is unclear how, or if, these properties impact light absorption.

BC is spectroscopically defined as a material with a mass-specific (mass-normalized) absorption cross-section of $7.5 \pm 1.2 \text{ m}^2 \text{ g}^{-1}$ at $\lambda = 550 \text{ nm}$, the solar transmission maximum [1]. From the Beer-Lambert Law, the absorption coefficient ($\alpha_{abs}$, m$^{-1}$) is the product of the number density of absorbers (N, m$^{-3}$) and their corresponding absorption cross-sections (Cabs, $\text{m}^2$)

$$\alpha_{abs} = N \times C_{abs} = N \times m_p \times MAC = M \times MAC$$ (1)

If particle mass ($m_p$, g), or the ensemble mass concentration ($M$, g m$^{-3}$) is known, it is possible to parameterize $\alpha_{abs}$ in terms of MAC (m$^2$ g$^{-1}$). In the small particle (i.e. Rayleigh regime) or optically-thin limits where absorption scales directly with mass (volume) [10,11], MAC represents the mass-specific absorption cross-section. Otherwise, MAC represents the mass absorption coefficient; in some studies, the mass absorption efficiency (MAE) is also used [12-15]. In comparison to solution-phase spectroscopy, the mass-specific absorption cross-section and the mass absorption

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**Perspectives**

**Measured in-situ mass absorption spectra for nine forms of highly-absorbing carbonaceous aerosol**

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**A R T I C L E   I N F O**

Article history:
Received 8 December 2017
Received in revised form 19 April 2018
Accepted 21 April 2018
Available online 23 April 2018

**A B S T R A C T**

Mass absorption coefficient spectra were measured between $\lambda = 500$ nm and 840 nm for nine forms of highly-absorbing carbonaceous aerosol: five samples generated from gas-, liquid- and solid-fueled flames; spark-discharge fullerene soot; graphene and reduced graphene oxide (rGO) crumpled nanosheets; and fullerene ($\text{C}_{60}$) assemblies. Aerosol absorption spectra were measured for size- and mass-selected particles and found to be dependent on fuel type and formative conditions. Flame-generated particles had morphologies consistent with freshly emitted black carbon (BC) with mass absorption coefficients (MAC) ranging between 3.8 m$^2$ g$^{-1}$ and 8.6 m$^2$ g$^{-1}$ at $\lambda = 550$ nm. Absorption Angstrom exponents (AAE) — i.e. MAC spectral dependence — ranged between 1.0 and 1.3 for flame-generated particles and up to 7.5 for C$_{60}$. The dependence of MAC and AAE on mobility diameter and particle morphology was also investigated. Lastly, the current data were compared to all previously published MAC measurements of highly-absorbing carbonaceous aerosol.

Published by Elsevier Ltd.

Available online 23 April 2018

https://doi.org/10.1016/j.carbon.2018.04.057

0008-6223/Published by Elsevier Ltd.
and normalized to data were corrected to account for presumed measurement biases data from peer-reviewed publications. The previously published average of 7.5 et al. (2013) [18] which focused on determination of BC and average particle mass and number density, ensemble absorption and average particle mass and number density, ensemble absorption cross-section and mass. Aerosol metrology, such as mass experimental parameters: e.g. ensemble absorption coefficients and mass concentration or single-particle absorption cross-section and mass. Aerosol metrology, such as mass selective and in-situ spectroscopies, has improved significantly since the 2006 BC MAC assessment enabling re-assessment. Newly developed techniques have highlighted the need for inter-comparability of laboratory methods and the development of aerosolizable materials for standards [22,23]. This investigation explores particle absorption for size- and mass-selected highly-absorbing carbonaceous aerosol. The goal is to establish the range of mass-normalized aerosol absorption for this important class of atmospherically relevant materials under controlled conditions and compare these data to other studies. MAC of nine types of highly-absorbing carbonaceous aerosol was determined from measurements of $a_{\text{abs}}, m_p$ and $N$ using a photoacoustic spectrometer coupled to a broad-bandwidth ($\lambda = 500$ nm–840 nm) light source, an aerosol particle mass analyzer and a condensation particle counter, respectively. Particles were generated from multiple sources to understand how aerosol formation conditions and material properties impact absorption. These data were compared to over four decades of published absorption data to aid in bounding the range of MAC measurements for this family of carbonaceous particles.

2. Materials and methods

A general experimental schematic is shown in Fig. 2. Aerosol generation was specific for each sample and is described below. Aerosol was dried and mobility- and mass-classified using a differential mobility analyzer (DMA) and an aerosol particle mass analyzer (APM), respectively, prior to measurements of absorption coefficients and number density using a photoacoustic spectrometer (PA) and condensation particle counter (CPC), respectively.

2.1. Aerosol generation

Carbon black (0.25 mg mL$^{-1}$, Cab-O-Jet® 200, Cabot Corp., Lot # 3404296) [24], graphene nanoplatelets (4 mg mL$^{-1}$, Graphene Supermarket #A-12) and fullerene soot (4 mg mL$^{-1}$, Alfa-Aesar #40971) particles were generated from aqueous solution in a constant-output liquid-jet cross-flow atomizer (TSI 3076) supplied with dry air (dew point $< -73 \, ^\circ C$) at 30 psig. Of the 2.2 L min$^{-1}$ of generated flow, 0.5 L min$^{-1}$ was sampled for measurements while the remainder was exhausted in a laboratory snorkel. For generation of thermally reduced graphene oxide (rGO) [25], graphene oxide (GO, 4 mg mL$^{-1}$, ACS Material, LLC) was atomized from aqueous solution. After drying, the aerosol stream was passed through a tube furnace (Lindberg-Blue Mini-Mite) at 320 °C to thermally reduce the GO. Any additional water produced during reduction was removed via passage through a secondary drying stage. For generation of graphene nanoplatelets and fullerene soot particles, the supply bottle was immersed in an ultrasonicator during atomization to mechanically suspend material in solution.

Fullerene (C$_{60}$) particles were generated through vaporization

![Fig. 1. Schematic of formation for graphene-based highly-absorbing carbonaceous nanomaterials. Top shows graphene-like sheets stacking and forming nanoscale concentric spheres that aggregate into lacey structures resembling freshly formed BC. Aggregates may become compacted upon interaction with gaseous or condensed phase materials. Bottom shows graphene-like material in single or multilayer sheets forming a nanoscale crumpled-paper morphology.](image-url)
and condensation of powdered C₆₀ (SES Research #600-9969) in a tube furnace maintained at 650 °C in a flow of Ar at 1.5 L min⁻¹ [26]. No drying elements were used. Of the supplied flow, 0.5 L min⁻¹ was sampled for measurements with the remainder exhausted in a laboratory snorkel.

Particles from ethylene fuel were generated from a Santoro diffusion flame [27]. Particles were aspirated into 5 L min⁻¹ of dry, HEPA-filtered air via a 1 mm diameter inlet on a sampling tube located 5 cm above burner centerline. An ejector pump located downstream mixed the particle stream with an additional 10 L min⁻¹ of dry HEPA-filtered air. Of this flow, 0.5 L min⁻¹ was sampled for measurements with the remainder exhausted in a fume hood.

Particles from kerosene and diesel fuel were generated from a simple wick lamp made in-house and modeled after typical sources used in developing countries [28,29]. The simple wick lamp was fueled with USA grade 1-K Kerosene (Klean Strip) or ultra-low sulfur diesel (NIST Emergency Services Facility fueling station, Gaithersburg, MD) using a 3.175 mm diameter braided cotton wick (Pepperell Braiding Company #1115-S) maintained at 1.5 mm above the lip of the lamp. The lamp was operated inside a 56 cm long, 8.25 cm I.D. glass shroud with a 20:1 parallel flow of dry, HEPA-filtered air located 5 cm above the lamp. An ejector pump located 7.5 cm above the wick terminus and drawing 0.5 L min⁻¹ of flow. Excess flow was exhausted in a laboratory snorkel.

Particles from paraffin wax were generated from candles poured in-house using wax obtained from King of Heaven candles (Rok Ind. Ltd., Nairobi, Kenya) and a 3.175 mm diameter braided cotton wick (Pepperell Braiding Company #1115-S). Wicks were maintained at 1.25 cm during combustion and particles were sampled similarly to the liquid-fuel simple wick lamps.

2.2. Aerosol conditioning and classification

Water was removed prior to particle size- and mass-classification by passing the aerosol stream through a large-diameter Nafion drying tube (Perma Pure, LLC #MD-700-48F-1) with a 20:1 parallel flow of dry air (<5% relative humidity) and a pair of silica gel diffusion dryers (TSI #3062) prior to size (electrical mobility) selection by a DMA (TSI Long DMA #3081). The relative humidity inside the DMA was monitored to ensure it was stable (<10% relative humidity) for the duration of an experiment to avoid interferences from both gas and liquid water [16,30,31]. Sheath aerosol flow in the DMA was maintained at 10:1 by the recirculating pumps in the electrostatic classifier (TSI #3082). After size selection, particles were passed through an APM (Kanomax #3602), a PA and a CPC (TSI #3775S) in series. To ensure only particles bearing q = +1 were measured by the PA [32], we followed recommendations put forth in Radney and Zangmeister (2016) [33] for tandem DMA/APM measurements.

For C₆₀ (generated in Ar), the DMA was operated in a single-pass mode. Dry, HEPA-filtered air was supplied from a compressed air line and removed via vacuum pump with the sheath-aerosol volumetric flow maintained at 10:1 using a pair of mass flow controllers (MKS #1179C). The resulting sample airstream exiting the DMA contained ≈10% Ar.

2.3. Photoacoustic spectroscopy

MAC spectra spanning λ = 500 nm—840 nm were measured using a PA equipped with a supercontinuum laser and tunable wavelength and bandpass filter, as in Radney and Zangmeister (2015) [16] and the Supporting Information of Radney et al. (2017) [34]. Absorption coefficients (αabs), mass (mp) and particle number densities (N) were calculated from 1 Hz data and averaged to 30 s; wavelength regions were alternated at 30 s intervals. In total, 3 spectra were collected and averaged to a single replicate. For each replicate, MAC at each wavelength was then calculated through the second form of Eq. (1) (MAC = αabs/mpN). MAC values from a minimum of 3 replicates were averaged for all reported spectra; reported measurement uncertainties represent 2 times the standard deviation of all replicates at a given wavelength. From these measurements, material effective density (ρeff) was also determined (ρeff = 6mp/πDmp) where Dmp is the particle mobility diameter. Prior to measurement of C₆₀ aerosol, the frequency response of the acoustic resonator was measured to determine the resonant frequency, resonance half width and quality factor to account for changes in the speed of sound due to the higher Ar concentration; see Gillis et al. (2010) [35].

2.4. Particle imaging

For TEM imaging, particles were collected on lacy carbon grids using an electrostatic precipitator at 0.5 L min⁻¹ flow and 8 kV collection voltage. TEM images were collected at an accelerating voltage of 20 kV.

3. Results and discussion

This investigation focuses on the measurement of highly-absorbing carbonaceous aerosol absorption spectra with known electrical mobility diameter (Dm), mass (mp), and monomer diameters (Dmm, where appropriate). Water was removed prior to analysis and no coatings were added to the particles after they were formed [17]. The materials were generated from a variety of sources to quantitatively measure the variability in MAC spectra, as shown in Fig. 3. Nine forms of highly-absorbing carbonaceous aerosol were measured: two carbon allotropes (C₆₀ and crumpled graphene...
sheets) and seven types of amorphous carbon consisting of spark-discharge fullerene soot \[36\], thermally reduced graphene oxide (rGO), carbon black, and particles generated from gas (ethylene), liquid (kerosene and diesel) and solid (paraffin) fuel sources. Absorption spectra for each material were measured at the maximum absorption for each sample where the desired particles could be isolated from the polydisperse distribution \[33\]. Note that the spectral response of some of the measured materials may be dependent on particle size (electrical mobility), monomer size and/or sheet lateral dimensions, see discussion below. Particles from each sample were collected on lacey carbon grids for TEM imaging; see Fig. 3 insets. Additional TEM images are included in the Supplementary Data. Particles from ethylene, kerosene, diesel and paraffin fueled flames possessed lacy aggregate morphologies with low effective densities \(\rho_{\text{eff}} < 0.2 \text{ g cm}^{-3}\). The size and distribution of \(D_{\text{mon}}\) was determined from TEM images of each material and was fuel type dependent, see Table 1. Water-soluble carbon black particles were generated from combustion of carbonaceous fuels followed by rapid surface oxidization. The resulting particles consisted of well-defined aggregated monomers arranged into a nearly-spherical morphology with \(\rho_{\text{eff}} = 0.77 \text{ g cm}^{-3}\), similar in structure to compacted or aged flame-generated particles observed in the atmosphere and laboratory \[3–5,37,38\]. Fullerene soot was formed from the spark discharge of elemental carbon in the absence of O\(_2\) forming particles with comparable morphology and effective density to carbon black \[39\], but with oblong, necked, and poorly-defined monomers preventing the determination of \(D_{\text{mon}}\). Similar to previous studies \[6–9\], rGO was composed of multilayered graphene-like sheets with a crumpled nanopaper morphology. Graphene aerosol possessed a similar morphology to rGO with the addition of some soot-like aggregated monomers produced during the formation process. C\(_{60}\) aerosol was arranged into close packed spheres (packing density = 0.73) \[26\].

Mass absorption coefficient spectra were measured between \(\lambda = 500 \text{ nm}\) and 840 nm (see Fig. 3) using a photoacoustic spectrometer and a broadband supercontinuum laser source \[16\]. Particles atomized from aqueous solution had a factor of \(\approx 5\) lower uncertainty than particles generated from flames. All spectra possessed a minimum of 8 data points allowing for AAE to be fit using Eq. (2). The MAC at \(\lambda = 550 \text{ nm}\) ranged between 0.9 m\(^2\) g\(^{-1}\).
and 8.6 m² g⁻¹ (see Table 1). The measured MAC of carbon black, rGO and graphene were within 2σ of particles generated from lamp and wick sources at λ = 550 nm, however their measured AAE’s were not. Cₐ₀ had a MAC and AAE of 0.9 ± 0.5 m² g⁻¹ and 7.5 ± 0.9, respectively, that exhibited a statistically significant difference from all other materials.

The MAC of flame-generated particles (ethylene, kerosene, diesel, and paraffin) ranged between 3.8 m² g⁻¹ and 8.6 m² g⁻¹; the MAC of particles generated from ethylene were statistically different than the measured MAC of other flame-generated particles. The AAE of particles generated from diesel fueled simple wick lamps were also statistically different from the other flame-generated particles (p < 0.05).

Table 1

<table>
<thead>
<tr>
<th>Species</th>
<th>Dₘₐₜ (nm)</th>
<th>mₚ (x10⁻¹⁷ g)</th>
<th>ρₑₒ (g cm⁻³)</th>
<th>Dₘₐₜ (nm)</th>
<th>MACMeasured (λ = 550 nm)</th>
<th>MACₐₐₑ (λ = 840 nm)</th>
<th>AAE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene soot</td>
<td>250</td>
<td>1.47</td>
<td>0.18</td>
<td>17 (3)</td>
<td>3.8 (0.5)</td>
<td>2.4 (0.2)</td>
<td>1.0 (0.3)</td>
</tr>
<tr>
<td>Kerosene lamp</td>
<td>700</td>
<td>21.0</td>
<td>0.12</td>
<td>42 (12)</td>
<td>8.6 (0.6)</td>
<td>5.5 (0.2)</td>
<td>1.0 (0.1)</td>
</tr>
<tr>
<td>Diesel lamp</td>
<td>700</td>
<td>21.0</td>
<td>0.12</td>
<td>26 (8)</td>
<td>7.5 (0.6)</td>
<td>4.6 (0.2)</td>
<td>1.3 (0.2)</td>
</tr>
<tr>
<td>Paraffin wick</td>
<td>700</td>
<td>23.6</td>
<td>0.13</td>
<td>28 (11)</td>
<td>8.2 (0.8)</td>
<td>5.2 (0.1)</td>
<td>1.1 (0.1)</td>
</tr>
<tr>
<td>Carbon black*</td>
<td>250</td>
<td>6.15</td>
<td>0.77</td>
<td>27 (7)</td>
<td>7.78 (0.06)</td>
<td>4.80 (0.04)</td>
<td>1.11 (0.03)</td>
</tr>
<tr>
<td>Graphene</td>
<td>450</td>
<td>23.5</td>
<td>0.51</td>
<td></td>
<td>7.5 (0.1)</td>
<td>5.35 (0.08)</td>
<td>0.74 (0.05)</td>
</tr>
<tr>
<td>Reduced GO</td>
<td>250</td>
<td>6.40</td>
<td>0.82</td>
<td></td>
<td>7.7 (0.1)</td>
<td>5.4 (0.1)</td>
<td>0.83 (0.07)</td>
</tr>
<tr>
<td>Fullerene soot</td>
<td>350</td>
<td>16.6</td>
<td>0.74</td>
<td></td>
<td>6.1 (0.4)</td>
<td>3.99 (0.06)</td>
<td>0.92 (0.05)</td>
</tr>
<tr>
<td>Cₐ₀</td>
<td>150</td>
<td>2.20</td>
<td>1.2</td>
<td></td>
<td>0.9 (0.5)</td>
<td>0.07 (0.02)</td>
<td>7.5 (0.9)</td>
</tr>
</tbody>
</table>

* H₂O soluble material. Does not meet operational definition of BC given in Ref. [18].

It has been noted that the MAC of particles produced from high-temperature flames, such as ethylene, are highly variable due to the quenching of particle oxidation by a rapidly flowing, cool gas at the flame terminus [3,16,40]. Small changes in particle formation conditions can greatly impact particle concentrations and spectral properties [3]. The MAC for ethylene presented in this study are comparable to previous reports in this laboratory using fuel and Wick sources at λ = 550 nm, however their measured formative conditions.

The effect of tertiary structure (i.e. morphology) on MAC for a collection of monomers is also significant. However, calculating MAC with elaborate particle geometries is a computational challenge best addressed using complex optical routines such as the discrete dipoles approximation and the superposition T-matrix method as described in studies by Mishchenko and Mackowski, among others [45–49].

These Mie theory calculations assume the simplest case using monodisperse spherical monomers, but help to capture the complexity and challenge of quantitative measurement, reporting, and comparison of highly-absorbing carbonaceous aerosol spectral data. In this investigation, the Dₘₐₜ of flame-generated particles ranged between 17 nm (ethylene soot) and 42 nm (kerosene lamp). Mie theory calculations over this range show that the MAC and AAE increase nearly linearly with Dₘₐₜ at constant refractive index (see Supplemental Data Fig. 53), with the MAC and AAE of 42 nm diameter monomers nearly 6% and 12% higher than 17 nm monomers, respectively. Thus, the difference in MAC and AAE between particles generated from ethylene fueled flames and wick lamps, with the only difference being the fuel used, cannot be explained solely by Dₘₐₜ. As all flame-generated particles had comparable morphology, the measured differences in MAC and AAE are likely due to differences in the refractive indices of each material under the measured formative conditions.

The definition of BC has 4 measurable properties [18]: 1) composed of aggregates of small carbon spheres, 2) MAC ≥ 5 m² g⁻¹ at λ = 550 nm, 3) refractory with a vaporization temperature near 4000 K, 4) insoluble in water and common organic solvents. Properties 1 and 2 were directly measured in this investigation. Despite some materials having formative conditions consistent with BC, only three of the nine samples met both the morphological and spectroscopic definitions of BC (particles generated from kerosene and diesel lamps, and the paraffin wax candle), see text in Table 1. The particles produced in this investigation from an ethylene fueled flame did not meet the spectroscopic definition for BC, whereas graphene and rGO did not meet the morphological definition. Carbon black met the morphological and spectroscopic definitions but its water solubility negates its inclusion.

As shown in Fig. 4a, in addition to being dependent on material refractive index and Dₘₐₜ, MAC is also a function of morphology and/or Dₘₜ. It can be envisioned that particles with a lacey morphology – e.g. freshly-emitted flame-generated particles – with small Dₘₜ enables light to access the entire particle resulting from a spherical particle by changing monomer diameter (Dₘₐₜ) at a constant refractive index (m = 1.77 ± 0.08) and mass density (ρ = 1.65 g cm⁻³); see Fig. 4c. At λ = 400 nm the MAC increases by 1% between a Dₘₐₜ of 1 nm and 10 nm and 13% between 10 nm and 50 nm. For this refractive index, monomers >10 nm in diameter are outside of the volume absorption regime (constant MAC). The results also show AAE increasing from 1.0 to 1.2 for Dₘₐₜ between 1 nm and 100 nm. For Dₘₐₜ ≥ 100 nm, the spectral dependence may not be adequately captured by an AAE (Eq. (2)).

The effect of tertiary structure (i.e. morphology) on the measured formative conditions. In this case, a spherical particle by changing monomer diameter (Dₘₐₜ) at a constant refractive index (m = 1.77 ± 0.08) and mass density (ρ = 1.65 g cm⁻³); see Fig. 4c. At λ = 400 nm the MAC increases by 1% between a Dₘₐₜ of 1 nm and 10 nm and 13% between 10 nm and 50 nm. For this refractive index, monomers >10 nm in diameter are outside of the volume absorption regime (constant MAC). The results also show AAE increasing from 1.0 to 1.2 for Dₘₐₜ between 1 nm and 100 nm. For Dₘₐₜ ≥ 100 nm, the spectral dependence may not be adequately captured by an AAE (Eq. (2)).

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in absorption that scales linearly with particle mass (volume) for all $D_m$. In contrast, particles with a compacted morphology may only be in the volume absorption regime (constant $\text{MAC}$ and $\text{AAE}$) at very small mobility diameters ($D_m$) and transition to the Mie or geometric absorption regimes with increasing $D_m$, resulting in both parameters being a function of $D_m$. Fig. 5 tests this hypothesis by measuring the change ($\Delta$) in $\text{MAC}$ and $\text{AAE}$ as a function of $D_m$ between $\lambda = 532 \text{ nm}$ and $780 \text{ nm}$ for mass- and mobility-selected particles (21 samples) of multilayered crumpled sheets (rGO), compacted flame-generated particles (carbon black) and freshly formed, lacy particles generated from an ethylene flame with $D_{\text{mon}} \approx 20 \text{ nm}$. Particles generated from the ethylene flame were measured between $300 \text{ nm} < D_m < 550 \text{ nm}$ where it was assured only singly-charged particles were isolated from the distribution [3,33]. The $\text{MAC}$ of the crumpled sheets and compacted spherical particles decreases nearly monotonically with $D_m$, consistent with geometric absorption even for the smallest particles measured ($D_m = 150 \text{ nm}$). A similar dependence was measured for the change in $\text{AAE}$ with $D_m$ for crumpled and compacted particles, see Fig. 4b. For particles generated from an ethylene flame, the $\text{MAC}$ and $\text{AAE}$ are constant within measurement uncertainty for particles up to $D_m = 550 \text{ nm}$ and typical of particles in the volumetric absorption regime. These data confirm that particle morphology impacts the spectral properties of highly-absorbing carbonaceous particles. For flame-generated particles where $D_{\text{mon}}$ is small and the morphology is consistent with an open, lacy structure (fractal dimension, $D_f \approx 1.8$ [50]) it is reasonable to assume that the particle absorption scales directly with particle mass and $\text{MAC}$ and $\text{AAE}$ are invariant. For particles that fall outside of this narrow parameter space this assumption may not be valid.

Many studies have focused on the measurement and reporting of $\text{MAC}$ for highly-absorbing carbonaceous (BC-like) particles in the atmosphere since the first assessment of BC $\text{MAC}$ [1]. Fig. 6 shows the absorption spectra collected in this investigation, with the exception of $C_{60}$, and all the peer-reviewed $\text{MAC}$ data (1971–2018, 199 measured values) for materials reported as BC or soot, including 26 measurements of graphite and graphene allotropes of $C_{60}$.

Fig. 4. a) Mass absorption coefficients ($\text{MAC}$) of carbonaceous particles are a function of primary (refractive index), secondary (atomistic arrangement), and tertiary structures (particle morphology). b) $\text{MAC}$ and absorption Ångström exponent ($\text{AAE}$) as a function of imaginary component of the refractive index for particles with a real component of the refractive index $= 1.77$, $1 \text{ nm}$ monomer diameter ($D_{\text{mon}}$) and $1.65 \text{ g cm}^{-3}$ mass density. c) $\text{MAC}$ and $\text{AAE}$ as a function of $D_{\text{mon}}$ at constant refractive index ($m = 1.77 + 0.8i$).

Fig. 5. a) Change ($\Delta$) in the mass absorption coefficient ($\text{MAC}$) at $\lambda = 532 \text{ nm}$ and b) change ($\Delta$) in absorption Ångström exponent ($\text{AAE}$) between $\lambda = 532 \text{ nm}$ and $780 \text{ nm}$ as function of particle mobility diameter ($D_m$) for compact carbon black (red squares), crumpled rGO (black circles), and fresh, lacy particles from ethylene flame (blue circles). Error bars are 1 standard deviation of a minimum of 3 replicate measurements. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
The range of data extends from 248 nm to 550 nm (7 samples) is 7.4 ± 0.5 m² g⁻¹ to 17 m² g⁻¹ (no reported uncertainty) with an average of 9.5 ± 3.3 m² g⁻¹. The MAC of the population using all the published data at λ = 550 nm is 8.28 ± 0.34 m² g⁻¹, 10% higher than the previous assessment of BC MAC, with uncertainty reduced by a factor of 4, see Table 2.

Some of the published MAC data was more than 5σ from the mean, greatly increasing the uncertainty in both AAE and MAC, and are likely not physical (e.g. MAC = 50 m² g⁻¹ at λ = 370 nm) based on MAC calculated from refractive indices and D_m from Mie theory. The published data shows a dependence on the method utilized for analysis, see Table 2. For example, using only PAS data yields MAC = 8.03 ± 0.31 m² g⁻¹ and AAE = 0.84 ± 0.13, whereas using data from filter-based studies results in MAC = 9.67 ± 1.50 m² g⁻¹ and AAE = 1.83 ± 0.56. Curation of all the data via elimination of data outside of the average MAC + 5σ (9 points removed) results in a 50% reduction in the reported uncertainty for the MAC, with MAC = 7.52 ± 0.18 m² g⁻¹ and AAE = 0.85 ± 0.09, within 1σ of MAC but with a lower AAE than reported in the BC assessments [1,18].

4. Conclusions

The presented data highlight MAC variability of highly-absorbing carbonaceous aerosol. BC has been previously defined as a material with a well-defined refractive index and MAC that can be assigned defined values (e.g. BC refractive index = 1.95 + 0.79i, MAC = 7.5 ± 1.2 m² g⁻¹) [1], similar to other well-defined nano-materials such as SiO₂ or polystyrene spheres that have been used for standards. If a single MAC value exists for BC and other similar materials, it would be expected that its reported range would be narrow; see data at λ = 532 nm and 660 nm in Fig. 6 where adequate data exists for comparison between studies. The range in published MAC observations suggests that either: 1) the reported data is dominated by measurement errors and biases and that the MAC of BC and other similar materials is well-defined and invariant across formative conditions or 2) the reported data captures the spectral variability and that highly-absorbing carbonaceous aerosol exists within a range of chemical and physical properties that impact particle absorption. Based on the measurements presented in this study for particles with known D_m, D_mn, m_p, and morphology it is likely the observed spectral variability in highly-absorbing carbonaceous aerosol is due to the impact of material refractive index, D_mn, and, in some cases, particle morphology that
result from the diversity of formative conditions for this family of materials.

Acknowledgements

The authors thank Yang Yang at the University of Maryland for assistance in acquisition of TEM images of some samples.

Appendix A. Supplementary data

Supplementary Data includes Mie theory calculations of MAC as and a function of $D_{max}$ and TEM images of particles. Supplementary data related to this article can be found at https://doi.org/10.1016/j.carbon.2018.04.057.

References


Acknowledgements

The authors thank Yang Yang at the University of Maryland for assistance in acquisition of TEM images of some samples.

Appendix A. Supplementary data

Supplementary Data includes Mie theory calculations of MAC as and a function of $D_{max}$ and TEM images of particles. Supplementary data related to this article can be found at https://doi.org/10.1016/j.carbon.2018.04.057.

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