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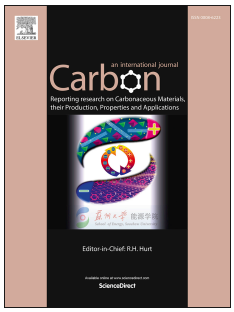


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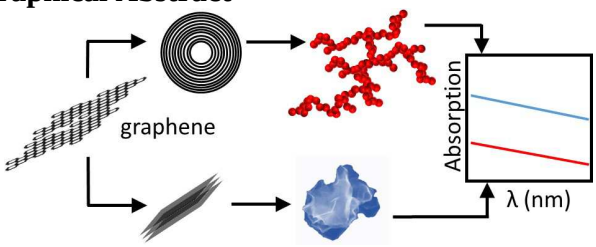
**Graphical Abstract**



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All authors have given approval of the final version of the manuscript.

data were compared to all previously published *MAC* measurements of highly-absorbing carbonaceous aerosol.

## 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 $sp^2$-bonding between carbon atoms arranged in multi-layered graphene-like sheets forming concentric, spherical nanoscale monomers aggregated into an open, lacey structure [1, 2], see Figure 1. The lacey 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 Figure 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 ± 1.2 $m^2\ g^{-1}$ at $\lambda$ = 550 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 ($C_{abs}$, $m^2$)

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

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 coefficient approximate the linear and non-linear regimes in absorption as a function of absorber number density (e.g. dilute and high concentration limits), respectively. For the remainder of this manuscript, *MAC* is used to refer to the mass absorption coefficient as the measured values of highly-absorbing carbonaceous particles may be size (mass) dependent (see Figure 5a and corresponding discussion). The wavelength dependence of *MAC* can be described by the absorption Ångström exponent (*AAE*)

$$MAC_{\lambda} = MAC_{\lambda,0}\left(\frac{\lambda}{\lambda_0}\right)^{-AAE} \quad (2)$$

where $\lambda$ and $\lambda_0$ are an arbitrary wavelength and a reference wavelength, respectively [16, 17].

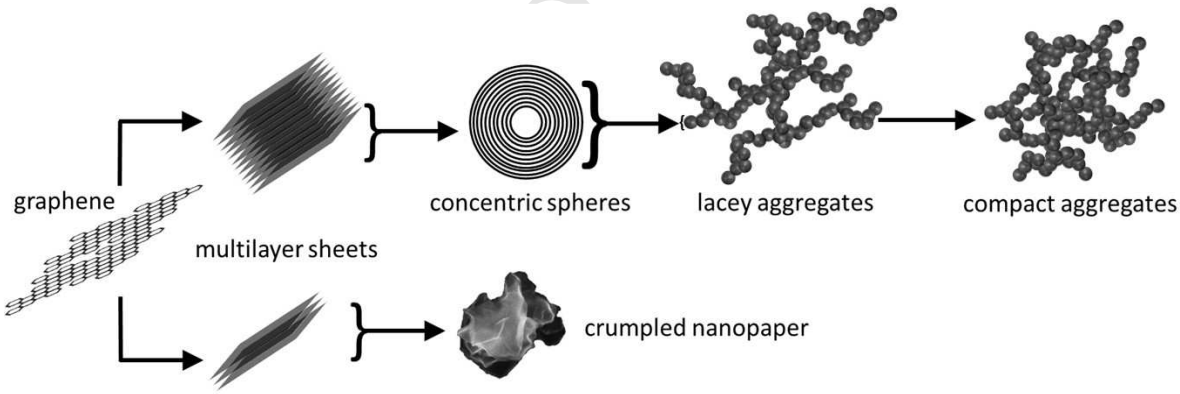


**Figure 1.** Schematic of formation for graphene-based highly-absorbing carbonaceous nanomaterials. Top shows graphene-like sheets stacking and forming nanoscale concentric spheres that aggregate into lacey structures resembling freshly formed BC. Aggregates may become compacted upon interaction with gaseous or condensed phase materials. Bottom shows graphene-like material in single or multilayer sheets forming a nanoscale crumpled-paper morphology.

BC exhibits the second largest direct positive radiative forcing after $CO_2$ [1, 18, 19]. Quantitative assessment of an aerosol's radiative forcing requires its spectroscopic properties to

be well-known with minimal uncertainty across the ultraviolet to near-IR. The most comprehensive assessments of highly-absorbing carbonaceous aerosols were reviews by Bond and Bergstrom (2006) [1] and Bond, et al. (2013) [18] which focused on determination of BC *MAC* using data from peer-reviewed publications. The previously published data were corrected to account for presumed measurement biases and normalized to $\lambda$ = 550 nm assuming an *AAE* of 1 ($\lambda^{-1}$); i.e. particles in the Rayleigh regime with a wavelength independent complex refractive index ($m = n + ik$) over the desired wavelength interval [10, 11]. The studies used by Bond and Bergstrom (2006) [1] reported a BC *MAC* ranging from 1.6 $m^2$ $g^{-1}$ to 15.9 $m^2$ $g^{-1}$ with an average of 7.5 ± 1.2 $m^2$ $g^{-1}$ ($1\sigma$) at $\lambda$ = 550 nm. Notably, none of the studies used in the assessments directly measured *MAC* due to a lack, at the time, of reliable methods to measure aerosol mass *in-situ*. In addition to the determination of radiative forcing from BC, measured *in-situ* spectral properties, such as aerosol absorption and *AAE*, have also been used for aerosol identification and source apportionment [20, 21].

The most direct method of obtaining *MAC* is to measure all experimental parameters: e.g. ensemble absorption coefficients and average particle mass and number density, ensemble absorption coefficients and mass concentration or single-particle absorption cross-section and mass. Aerosol metrology, such as mass selectivity 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 $\alpha_{abs,}$ $m_p$ and $N$ using a photoacoustic spectrometer coupled to a broad-bandwidth ($\lambda$ = 500 nm to 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 Figure 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 concentration using a photoacoustic spectrometer (PA) and condensation particle counter (CPC), respectively.

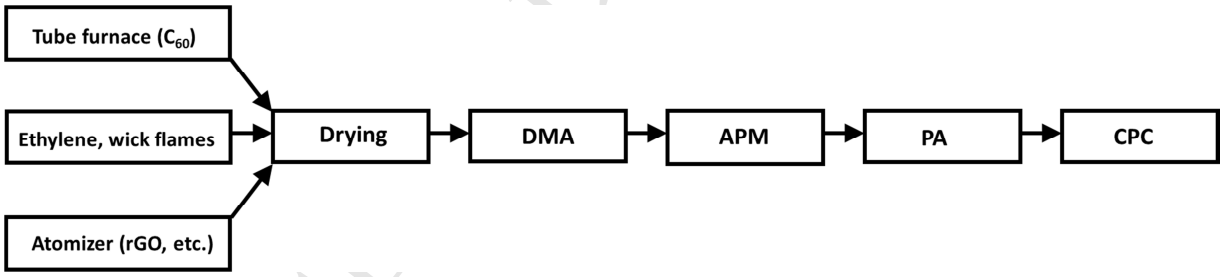


**Figure 2.** Experimental schematic for absorption measurements. Drying was used for flame- and atomizer-generated particles. A differential mobility analyzer (DMA) and aerosol particle mass analyzer (APM) were used for particle mobility- and mass-classification, respectively. Absorption spectra were measured using a broadband photoacoustic spectrometer (PA). Particle number concentration was measured using a condensation particle counter (CPC).

### *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 °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 and condensation of powdered $C_{60}$ (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

138 braided cotton wick (Pepperell Braiding Company #1115-S) maintained at 1.0 to 1.5 mm above
139 the lip of the lamp. The lamp was operated inside a 56 cm long, 8.25 cm I.D. glass shroud with >
140 50 L $min^{-1}$ of sheath flow. Under these conditions, the flame height was ≈ 1 cm. Particles were
141 sampled through an inlet 2.54 cm in diameter directed downward towards the flame, located ≈
142 7.5 cm above the wick terminus and drawing 0.5 L $min^{-1}$ of flow. Excess flow was exhausted in
143 a laboratory snorkel.

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

148 *2.2 Aerosol conditioning and classification*

149 Water was removed prior to particle size- and mass-classification by passing the aerosol
150 stream through a large-diameter Nafion drying tube (Perma Pure, LLC #MD-700-48F-1) with a
151 20:1 parallel flow of dry air (< 5 % relative humidity) and a pair of silica gel diffusion dryers
152 (TSI #3062) prior to size (electrical mobility) selection by a DMA (TSI Long DMA #3081). The
153 relative humidity inside the DMA was monitored to ensure it was stable (< 10 % relative
154 humidity ) for the duration of an experiment to avoid interferences from both gas and liquid
155 water [16, 30, 31]. Sheath:aerosol flow in the DMA was maintained at 10:1 by the recirculating
156 pumps in the electrostatic classifier (TSI #3082). After size selection, particles were passed
157 through an APM (Kanomax #3602), a PA and a CPC (TSI #3775) in series. To ensure only
158 particles bearing $q$ = +1 were measured by the PA [32], we followed recommendations put forth
159 in Radney and Zangmeister (2016) [33] for tandem DMA/APM measurements.

For $C_{60}$ (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 $\lambda$ = 500 nm to 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 ($\alpha_{abs}$), mass ($m_p$) 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 ($MAC = \alpha_{abs}/m_pN$). *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 ($\rho_{eff}$) was also determined ($\rho_{eff} = 6m_p/\pi D_m^3$) where $D_m$ is the particle mobility diameter. Prior to measurement of $C_{60}$ 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 lacey 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 keV.

183

## 3. Results and discussion

This investigation focuses on the measurement of highly-absorbing carbonaceous aerosol absorption spectra with known electrical mobility diameter ($D_m$), mass ($m_p$), and monomer diameters ($D_{mon}$, 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 Figure 3. Nine forms of highly-absorbing carbonaceous aerosol were measured: two carbon allotropes ($C_{60}$ 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 $\alpha_{abs}$ (maximum $\alpha_{abs} = NC_{abs}$ for each sample) where the desired $q = +1$ 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 Figure 3 insets. Additional TEM images are included in the Supplementary Data. Particles from ethylene, kerosene, diesel and paraffin fueled flames possessed lacey aggregate morphologies with low effective densities ($\rho_{eff} < 0.2$ g cm$^{-3}$). The size and distribution of $D_{mon}$ 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 $\rho_{eff} = 0.77$ 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 $D_{mon}$. 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].

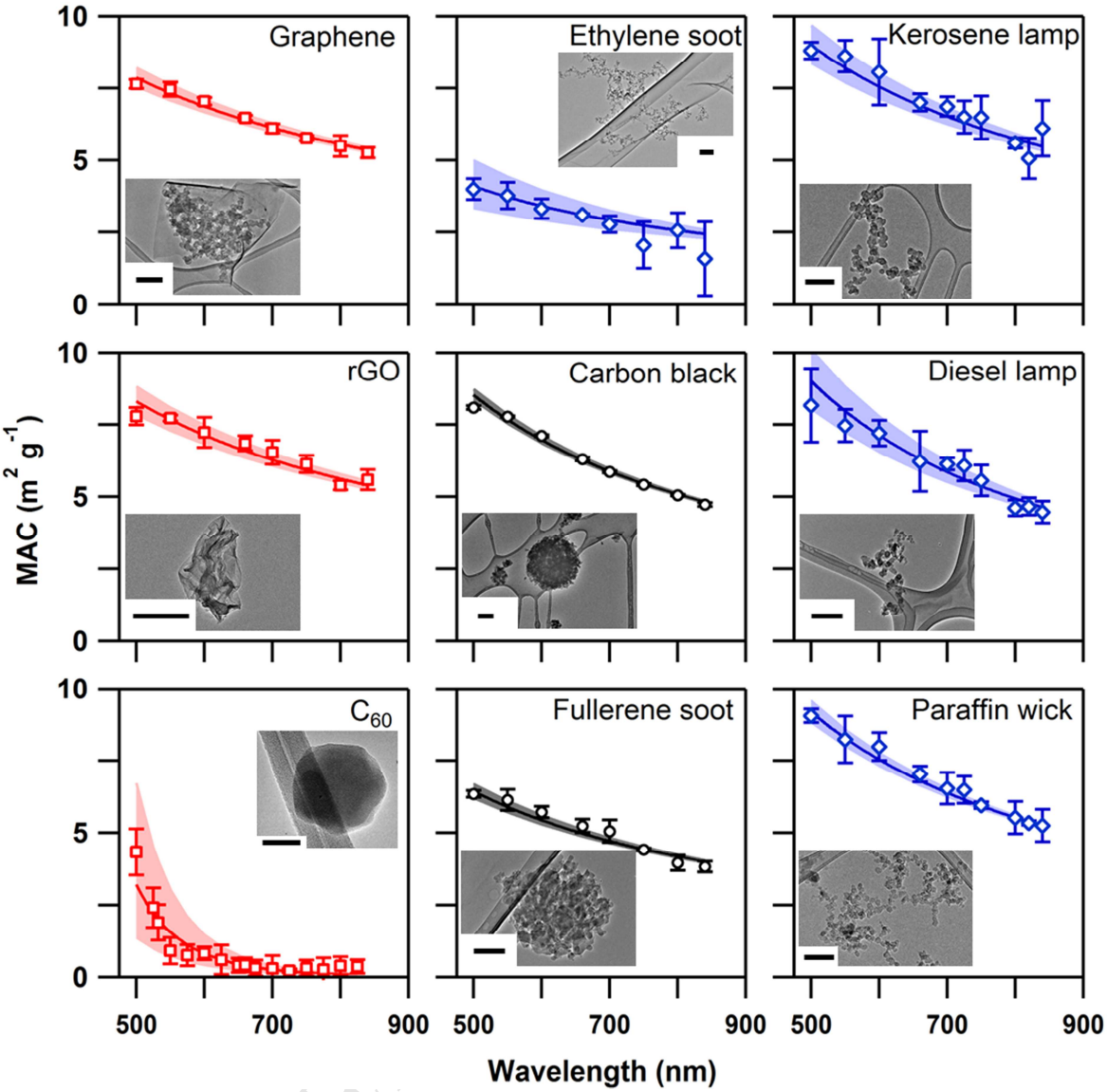


**Figure 3.** Plot of mass absorption coefficients (*MAC*) for the measured particles; corresponding mobility diameters ($D_m$) and mass ($m_p$) are shown in in Table 1. All plots have the same abscissa and ordinate axis ranges. Uncertainties are 2 times the standard deviation of a minimum of 3 replicate measurements. Red squares are carbon allotropes, black circles are commercially available materials, and blue diamonds are from laboratory generated particles from flames. Solid line is *AAE* determined from Eq. 2. Shaded areas represent fit uncertainties in $MAC_{\lambda,0}$ and *AAE*, see Table 1. Insets in each plot show the corresponding TEM images. Scale bars are 200 nm.

**Table 1**: Measured mobility diameter ($D_m$), mass ($m_p$), effective density ($\rho_{eff}$), mean monomer diameter ($D_{mon}$), measured *MAC* ($\lambda$ = 550 nm), fit $MAC_{\lambda,0}$ ($\lambda_0$ = 840 nm, see Eq. 2) and *AAE* for all particle types. Uncertainties shown in parenthesis are $2\sigma$. Green (red) text indicates species does (does not) meet definition for BC from Ref [18].

| Species | $D_m$ (nm) | $m_p$ ($x10^{-15}$ g) | $\rho_{eff}$ (g cm$^{-3}$) | $D_{mon}$ (nm) | $MAC_{Measured}$ ($\lambda$ = 550 nm) | $MAC_{\lambda,0}$ ($\lambda$ = 840 nm) | *AAE* |
|---|---|---|---|---|---|---|---|
| Ethylene soot | 250 | 1.47 | 0.18 | 17 (3) | 3.8 (0.5) | 2.4 (0.2) | 1.0 (0.3) |
| Kerosene lamp | 700 | 21.0 | 0.12 | 42 (12) | 8.6 (0.6) | 5.5 (0.2) | 1.0 (0.1) |
| Diesel lamp | 700 | 21.0 | 0.12 | 26 (8) | 7.5 (0.6) | 4.6 (0.2) | 1.3 (0.2) |
| Paraffin wick | 700 | 23.6 | 0.13 | 28 (11) | 8.2 (0.8) | 5.2 (0.1) | 1.1 (0.1) |
| Carbon black[a] | 250 | 6.15 | 0.77 | 27 (7) | 7.78 (0.06) | 4.80 (0.04) | 1.11 (0.03) |
| Graphene | 450 | 23.5 | 0.51 | -- | 7.5 (0.1) | 5.35 (0.08) | 0.74 (0.05) |
| Reduced GO | 250 | 6.40 | 0.82 | -- | 7.7 (0.1) | 5.4 (0.1) | 0.83 (0.07) |
| Fullerene soot | 350 | 16.6 | 0.74 | -- | 6.1 (0.4) | 3.99 (0.06) | 0.92 (0.05) |
| $C_{60}$ | 150 | 2.20 | 1.2 | -- | 0.9 (0.5) | 0.07 (0.02) | 7.5 (0.9) |

[a] $H_2O$ soluble material. Does not meet operational definition of BC given in Ref [18].

Mass absorption spectra were measured between $\lambda$ = 500 nm and 840 nm (see Figure 3) using a photoacoustic spectrometer and a broadband supercontinuum laser source [16]. Particles atomized from aqueous solution had a factor of ≈ 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 nm ranged between 0.9 m$^2$ g$^{-1}$ and 8.6 m$^2$ g$^{-1}$ (see Table 1). The measured *MAC* of carbon black, rGO and graphene were within $2\sigma$ of particles generated from lamp and wick sources at $\lambda$ = 550 nm, however their measured *AAE*'s were not. $C_{60}$ had a *MAC* and *AAE* of 0.9 ± 0.5 m$^2$ 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 m$^2$ g$^{-1}$ and 8.6 m$^2$ 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 ($p < 0.05$).

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 flow conditions where particle concentration and $\alpha_{abs}$ were maximized and intra- and inter-day variability and uncertainty in *MAC* were minimized [3, 37].

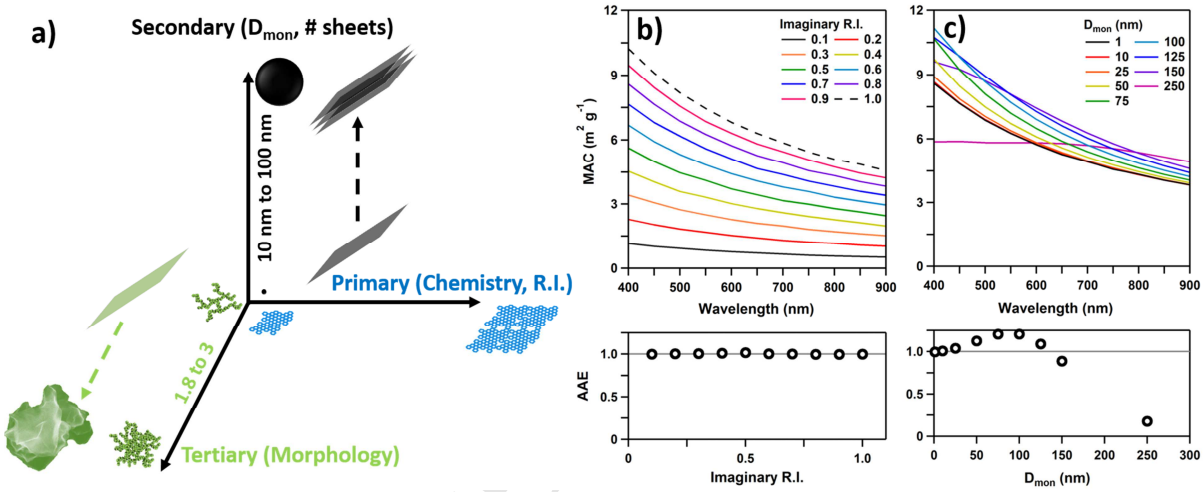


**Figure 4.** a) Mass absorption coefficients (*MAC*) of carbonaceous particles are a function of primary (refractive index), secondary (atomistic arrangement), and tertiary structures (particle morphology). b) *MAC* and absorption Ångström exponent (*AAE*) as a function of imaginary component of the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

The parameters that influence the spectroscopy of graphene-like materials in spherical structures with a high imaginary component of the refractive index ($k$) has been previously described in detail by Moosmüller, et al. [10, 11]. It is important to note that the measured absorption per unit mass of highly-absorbing carbonaceous aerosol is a function the primary, secondary and tertiary structures of the material [41-44]; see Figure 4a. The intrinsic absorption strength of a material is a function of its chemical composition (i.e. refractive index); for

graphitic and graphenic materials, this refers to the extent of $sp^2$-bonding, surface imperfections and single sheet lateral dimension. Absorption by the primary structures can be enhanced or dampened depending upon their atomistic arrangement into secondary structure(s) as spheres, multilayered sheets, etc. The collection of secondary structures into a final tertiary morphology can further impact absorption strength. Figure 4b shows Mie theory calculations that simulate the effect of material primary structure (chemistry) on absorption strength per unit mass (*MAC*) by changing the imaginary component of the refractive index ($k$) with a constant real component ($n$ = 1.77); monomer diameter ($D_{mon}$ = 1 nm) and mass density ($\rho$ = 1.65 g cm$^{-3}$); this $D_{mon}$ and $\rho$ approximates a single $C_{60}$ molecule. In this case, *MAC* increases monotonically with $k$ and the spectral shape is invariant, *AAE* = 1.0, for all values of $k$.

The effect of secondary structure on *MAC* was also simulated for a spherical particle by changing monomer diameter ($D_{mon}$) at a constant refractive index ($m$ = 1.77 + 0.8$i$) and mass density ($\rho$ = 1.65 g cm$^{-3}$); see Figure 4c. At $\lambda$ = 400 nm the *MAC* increases by 1 percent between a $D_{mon}$ of 1 nm and 10 nm and 13 percent between 10 nm and 50 nm. For this refractive index, monomers $\geq$ 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 $D_{mon}$ between 1 nm and 100 nm. For $D_{mon} \geq$ 100 nm, the spectral dependence may not be adequately captured by an *AAE* (Eq. 2).

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 $D_{mon}$ 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 $D_{mon}$ at constant refractive index (see Supplemental Data Figure S3), with the *MAC* and *AAE* of 42 nm diameter monomers nearly 6 percent and 12 percent 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 $D_{mon}$. 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 spherules, 2) $MAC \geq 5$ m$^2$ g$^{-1}$ at $\lambda$ = 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 green 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.

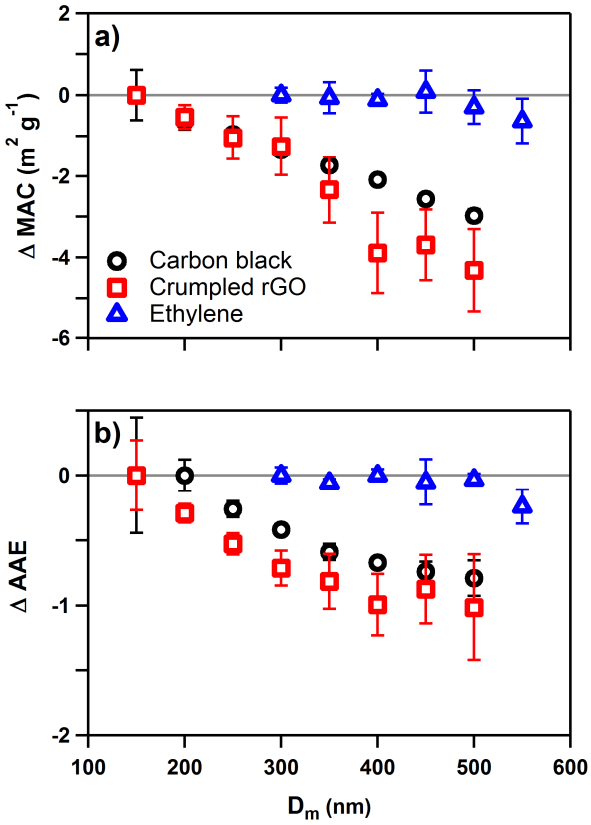


**Figure 5.** a) Change (Δ) in the mass absorption coefficient (*MAC*) at $\lambda$ = 532 nm and b) change (Δ) in absorption Ångström exponent (*AAE*) between $\lambda$ = 532 nm and 780 nm as function of particle mobility diameter ($D_m$) for compact carbon black (red squares), crumpled rGO (black circles), and fresh, lacey particles from ethylene flame (blue circles). Error bars are 1 standard deviation of a minimum of 3 replicate measurements.

As shown in Figure 4a, in addition to being dependent on material refractive index and $D_{mon}$, *MAC* is also a function of morphology and/or $D_m$. It can be envisioned that particles with a lacey morphology – e.g. freshly-emitted flame-generated particles – with small $D_{mon}$ enables light to access the entire particle resulting 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 *MAC* and *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 $D_m$. Figure 5 tests this hypothesis by measuring the change (Δ) in *MAC* and *AAE* as a function of $D_m$ between $\lambda$ = 532 nm and 780 nm for mass- and mobility-selected

particles (21 samples) of multilayered crumpled sheets (rGO), compacted flame-generated particles (carbon black) and freshly formed, lacey particles generated from an ethylene flame with $D_{mon} \approx 20$ nm. Particles generated from the ethylene flame were measured between 300 nm $\leq D_m \leq$ 550 nm where it was assured only singly-charged particles were isolated from the distribution [3, 33]. The *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 nm). A similar dependence was measured for the change in *AAE* with $D_m$ for crumpled and compacted particles, see Figure 4b. For particles generated from an ethylene flame, the *MAC* and *AAE* are constant within measurement uncertainty for particles up to $D_m$ = 550 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 $D_{mon}$ is small and the morphology is consistent with an open, lacey structure (fractal dimension, $D_f \approx 1.8$ [50]) it is reasonable to assume that the particle absorption scales directly with particle mass and *MAC* and *AAE* are invariant. For particles that fall outside of this narrow parameter space this assumption may not be valid.

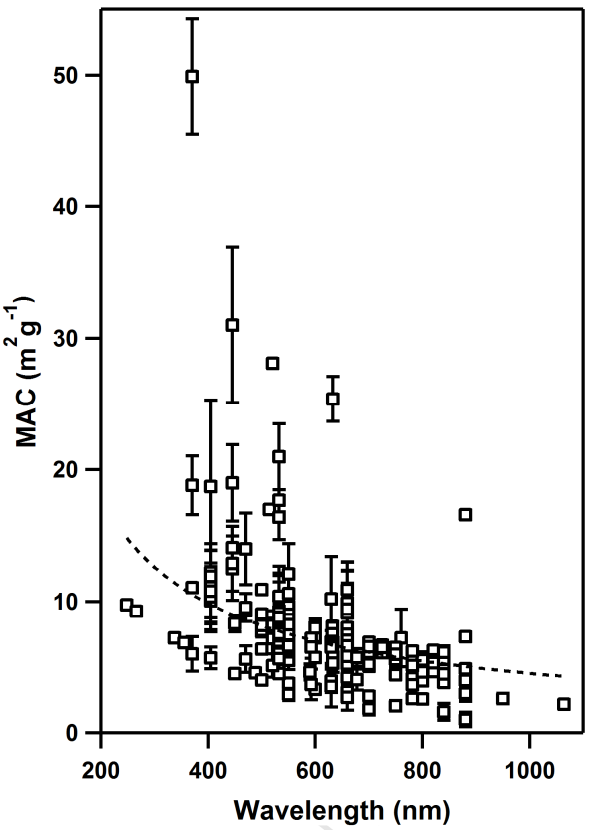


**Figure 6.** All published *MAC* data of BC, soot and allotropes of carbon between 1971 to current as a function of wavelength. Error bars are 1$\sigma$. Dashed line is fit to Eq. 2 – Data from refs. [3, 12, 36, 38, 51-77].

Many studies have focused on the measurement and reporting of *MAC* for highly-absorbing carbonaceous (BC-like) particles in the atmosphere since the first assessment of BC *MAC* [1]. Figure 6 shows the absorption spectra collected in this investigation, with the exception of $C_{60}$, and all the peer-reviewed *MAC* data (1971 to 2018, 199 measured values) for materials reported as BC or soot, including 26 measurements of graphite and graphene allotropes of carbon [3, 12, 36, 38, 51-77]. The reported data include both laboratory measurements of characterized systems from known sources such as coal combustion, kerosene wick lamps, diesel engines, diffusion flames, and spark discharge soot with known carbon-to-oxygen ratios and data from field-based observations from sites such as traffic tunnels and urban areas. The data are shown at the

wavelength reported in each study with 1σ uncertainty (if reported). The published data include 129 *MAC* values measured using photoacoustic spectroscopy (PAS), 36 reports from filter-based methods, and 29 reports which used extinction minus scattering. The range of data extends from 248 nm ≤ $\lambda$ ≤ 1064 nm, enabling the use of Eq. 2 to determine *AAE* and *MAC*.

The *MAC* of the previously published data is highly variable. For example, at $\lambda$ = 532 nm (24 samples) the *MAC* of all published data ranges between 5.61 ± 0.46 $m^2 g^{-1}$ and 21.0 ± 2.5 $m^2 g^{-1}$, (average = 8.31 ± 0.89 $m^2 g^{-1}$) larger than the variability in *MAC* for the carbonaceous materials measured in this study. The published data was also examined by the source of the material. Aerosol generated from diesel engines represents the largest single source of reported *MAC* data (19 reported *MAC* values). The reported range in *MAC* from diesel engine generated aerosol for 514 nm ≤ λ ≤ 532 nm (7 samples) is 7.4 ± 0.5 $m^2 g^{-1}$ to 17 $m^2 g^{-1}$ (no reported uncertainty) with an average of 9.5 ± 3.3 $m^2 g^{-1}$.

The *AAE* of the all data shown in Figure 6 was calculated using Eq. 2 as 1.01 ± 0.15 (1$\sigma$), within uncertainty of 1.0 suggested in Bond and Bergstrom (2006) and in support of the $\lambda^{-1}$ dependence [1, 3, 10, 11, 18]. The *MAC* of the population using all the published data at $\lambda$ = 550 nm is 8.28 ± 0.34 $m^2 g^{-1}$, 10 percent higher than the previous assessment of BC *MAC*, with uncertainty reduced by a factor of 4, see Table 2.

**Table 2**. Fit parameters calculated from Eq. 2 of published carbonaceous aerosol *MAC* between 1971 and 2018. Fit parameters also reported for published PAS and filter-based measurements and after removal of outlier data > 5$\sigma$ from mean. Uncertainties are 1$\sigma$ and shown in parenthesis.

| | $k_0$ ($\lambda$ = 550 nm, $m^2 g^{-1}$) | *AAE* |
|---|---|---|
| All published measurements | 8.28 (0.34) | 1.01 (0.15) |
| All published PAS | 8.03 (0.31) | 0.84 (0.13) |
| All published Filter-based | 9.67 (1.50) | 1.83 (0.56) |
| All measurements – 5$\sigma$ outliers removed | 7.52 (0.18) | 0.85 (0.09) |
| PAS – 5$\sigma$ outliers removed | 7.39 (0.19) | 0.76 (0.19) |
| Filter-based – 5$\sigma$ outliers removed | 7.40 (0.53) | 1.31 (0.28) |

Some of the published *MAC* data was more than 5$\sigma$ from the mean, greatly increasing the uncertainty in both *AAE* and *MAC*, and are likely not physical (e.g. *MAC* = 50 $m^2 g^{-1}$ at $\lambda$ = 370 nm) based on *MAC* calculated from refractive indices and $D_{mon}$ using 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 $m^2 g^{-1}$ and *AAE* = 0.84 ± 0.13, whereas using data from filter-based studies results in *MAC* = 9.67 ± 1.50 $m^2 g^{-1}$ and *AAE* = 1.83 ± 0.56. Curation of all the data via elimination of data outside of the average *MAC* + 5$\sigma$ (9 points removed) results in a 50 percent reduction in the reported uncertainty for the *MAC*, with *MAC* = 7.52 ± 0.18 $m^2 g^{-1}$ and *AAE* = 0.85 ± 0.09, within 1$\sigma$ 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 + 0.79*i*, *MAC* = 7.5 ± 1.2 $m^2 g^{-1}$) [1], similar to other well-defined nanomaterials such as $SiO_2$ 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 $\lambda$ = 532 nm and 660 nm in Figure 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

405 known $D_m$, $D_{mon}$, $m_p$, and morphology it is likely the observed spectral variability in highly-
406 absorbing carbonaceous aerosol is due to the impact of material refractive index, $D_{mon}$, and, in
407 some cases, particle morphology that result from the diversity of formative conditions for this
408 family of materials.

409 **Acknowledgements**

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

412 **Appendix A. Supplementary Data**

413 Supplementary Data includes Mie theory calculations of *MAC* and as a function of $D_{mon}$, and
414 TEM images of particles.

415
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