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The Absorption Ångström Exponent of black carbon: from numerical aspects

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Abstract. The Absorption Ångström Exponent (AAE) is an important aerosol optical parameter used for aerosol characterization and apportionment studies. The AAE of black carbon (BC) is widely accepted to be 1.0, although observational estimates give a quite wide range of 0.6~1.1. With considerable uncertainties related to observations, a numerical study is a powerful method, if not the only one, to provide a better and more accurate understanding on BC AAE. This study calculates BC AAE using realistic particle geometries based on fractal aggregate and an accurate numerical optical model (namely the Multiple-Sphere T-Matrix method). At odds with the expectations, BC AAE is not 1.0, even when BC is assumed to have small sizes and a wavelength independent refractive index. With a wavelength independent refractive index, the AAE of fresh BC is approximately 1.05, and is quite insensitive to particle size distribution. BC AAE goes lower when BC particles are aged (compact structures or coated by other scattering materials). For coated BC, we prescribed the coating thickness distribution based on a published experimental study, where smaller BC cores were shown to develop thicker coating than bigger BC cores. Both Compact and Coated BC the AAE ranges, at realistic particle sizes. For both Compact and Coated BC, the AAE is highly sensitive to particle size distribution, ranging from approximately 0.8 to 1.0 for relatively large BC with wavelength-independent refractive index. When the refractive index is allowed to vary with wavelength, a feature with observational backing, the BC AAE shows a much wider range. We propose that the presented results herein serve as a comprehensive guide for the response of BC AAE to BC size, refractive index, and geometry.

1 Introduction

The Absorption Ångström Exponent (AAE) is an aerosol optical property, and describes the wavelength variation of aerosol absorption. Because aerosol absorption normally decreases exponentially with wavelength over the visible and near-infrared spectral region (Ångström, 1929; Bond, 2001; Lewis et al., 2008), the AAE is defined as:

$$C_{abs}(\lambda) = b_{abs}\lambda^{-AAE} \tag{1}$$

where λ, C_{abs} and b_{abs} denote wavelength, the aerosol absorption coefficient, a wavelength-independent constant (that equals to the absorption coefficient at the wavelength of 1μm). Instead of absorption coefficient, some studies use the absorption aerosol absorption optical depth in Eq. (1), because the two are proportional. The AAE describes absorption variation with respect to wavelength, and is significantly influenced by particle size, shape and chemical composition (Scarnato et al., 2013; Schuster et al., 2015; Li et al., 2016). The chemical composition of aerosol material determines the wavelength-dependent refractive index.

AAE has been widely used for aerosol characterization studies (Russell et al., 2010; Giles et al., 2012). The basis for the AAE use in aerosol characterization is that AAE is an intrinsic property of each aerosol species. For example, black carbon (BC) aerosols have an AAE of 1.0, and organic aerosols and dust have higher AAE values (Kirchstetter et al., 2004; Russell et al., 2010). Thus, the AAE of an aerosol sample close to 1.0 is considered as BC rich aerosols from fossil fuel burning, and much larger AAE values are understood to indicate aerosols from biomass/biofuel burning or dust (Russell et al., 2010). AAE has also been quantitatively used to separate brown carbon (BrC) absorption from BC absorption (Kirchstetter and Thatcher, 2012; Lu et al., 2015). In the studies of BC/BrC absorption separation, the BrC absorption from biomass burning aerosols is usually retrieved by assuming that BrC contributes no absorption at near-infrared wavelengths and that BC has an AAE of 1.0 (Ganguly et al., 2005; Kirchstetter and Thatcher, 2012; Lu et al., 2015). Lack and Langridge (2013) quantified the effect of a specified BC AAE value on the absorption apportionment between BC and BrC, demonstrating the importance of BC AAE. Additional uses of AAE include aerosol color. A recent numerical study done by Liu et al. (2016), for example, demonstrate that AAE largely controls the color of aerosols in the ambient atmosphere. They found that aerosols have a visual of brown color if the aerosol AAE is larger than approximately 2. In another use, aerosol spectral light absorption is an important parameter for the assessment of the radiation budget of the atmosphere (Schmid et al., 2006).

Does BC indeed have an AAE of 1.0? BC, also known as soot, is an important aerosol species emitted from incomplete combustion of fossil fuel, biofuel and biomass (Bond and Sun, 2005; Bond et al., 2013; Chakrabarty et al., 2014), and exhibits significant variations on its physical and chemical properties due to differences in fuels and combustion conditions (Schnaiter et al., 2006; Bahadur et al., 2012; Reddington et al., 2013). BC AAE is widely accepted and used as 1.0 when the particles exist alone (Bergstrom et al., 2002; 2003; Schnaiter et al., 2003; Lawless et al., 2004; Bond and Bergstrom, 2006). If BC particles are much smaller than the incident light wavelength and have a wavelength-independent refractive index, the Rayleigh approximation does theoretically derive an AAE of 1.0 (Moosmüller and Arnott, 2009). BC particles are generally small compared to the wavelengths of visible light, but it is uncertain that all the BC particles clearly fall into the Rayleigh category, let alone the uncertainty in the wavelength dependence of the BC refractive index. Actually, real BC aggregates in the ambient atmosphere may just fall at the edge of the Rayleigh region at visible and near infrared wavelengths. Figure 1 visualizes the extent to which the Rayleigh approximation holds for spheres by comparing the approximation with the exact Mie results. In Fig. 1, the x-axis represents the particle size parameter, defined as 2πr/λ with r and λ being radius and wavelength, respectively. We can see from Fig. 1 that the Rayleigh approximation is only valid for absorption if the size parameter is less than 0.2. To be more specific, an aerosol sphere with a radius of 20 nm corresponds to a size parameter of approximately 0.12 at a wavelength of 1000 nm, at which the Rayleigh and Mie results agree quite well. However, if the wavelength decreases to 300 nm, the size parameter of the same sphere increases to 0.42, and the Rayleigh approximation underestimates the absorption by over 10%. BC monomers may even have radii larger than 20nm, and the aggregation of BC monomers in the atmosphere makes the Rayleigh theory even less applicable to BC absorption calculation; BC size will be discussed in details in the next section.

Whether BC AAE is exactly 1.0 or not is an issue we will address in this paper. Another issue is whether BC coated with scattering material would have the same AAE as uncoated BC. In the aforementioned BC/BrC absorption separation studies (Kirchstetter and Thatcher, 2012; Lu et al., 2015), the AAE for uncoated BC was implicitly assumed to be the same as that for coated BC. Lack and Cappa (2010) used a core-shell Mie code to investigate how BC changes its AAE value with respect to coating. At realistic particle sizes, they showed that the BC AAE increases to 1.4~1.6 after coated. They computed BC AAE using a group of BC particles where the cores were specified to have a lognormal size distribution. In their study, coating thickness was assumed to be linearly proportional to the core size by applying the same ratio of the entire particle diameter to the core diameter to all the particles – an assumption that has no experimental, observational or theoretical support. When BC particles grow in size by coating, the particle growth is governed by condensation. Theoretically, condensation reduces the diameter spread between big particles and small particles over time (Seinfeld and Pandis, 2016), on the contrary to the assumption by Lack and Cappa (2010). Schnaiter et al. (2005) coated BC particles with secondary organic aerosol material in a lab, and found that the coating increases particle sizes, while reduces geometric standard deviation (see Fig. 5 of their paper), as predicted by theoretical calculation of condensation process. Their work provided a meaningful experimental dataset to derive coating thickness of BC particles. Furthermore, Schnaiter et al. (2005) also measured the absorption of coated BC particles at 450, 550 and 700 nm (see Fig. 9 of their paper), and from these three wavelengths we do see that coating does decrease BC AAE (from approximately 1.1 to 0.8), thereby undermining the AAE results in Lack and Cappa's (2010) study.

When the true BC AAE is in doubt, one can alternatively investigate BC AAE by measuring the absorption of BC particles in the atmosphere, which turns out to be more challenging. BC AAE has been empirically estimated in numerous studies (e.g., Schnaiter et al., 2003; Kirchstetter et al., 2004; Bahadur et al., 2012; Chung et al., 2012). Schnaiter et al. (2003) found diesel soot to have an AAE of 1.1 and Palas soot to have an AAE of 2.1. Even if different soot particles would have different AAE values, the difference between 1.1 and 2.1 is quite significant. The particles measured by Schnaiter et al. (2003) may be not pure BC because BC particles always co-exist with other particles in the atmosphere. Non-BC particles can affect the total aerosol AAE by having BrC (which has higher AAE values) and also by coating BC and amplifying BC absorption, and the amplification of BC absorption is dependent on wavelength. Kirchstetter et al. (2004) measured the absorption of particles near a roadway or inside a tunnel, and, after extracting organic carbon (including absorptive BrC), found the AAE to be 0.6~1.3. The locations Kirchstetter et al. (2004) chose would have yielded AAE without much interference with BrC or coating. However, both Schnaiter et al. (2003) and Kirchstetter et al. (2004) used filter-based instruments to measure the absorption. Filter-based absorption instruments are susceptible to multiple artefacts such as optical interactions between the concentrated particle themselves and that of the particles with the filter substrate (Moosmüller et al., 2009). In addition, filter deposition may alter particle shapes and size distributions greatly (Subramanian et al., 2007), which affects aerosol absorption properties significantly (Li et al., 2016). Weingartner et al. (2003) and Arnott et al. (2005), for example, attempted to address these artefacts. The available correction schemes are not available for every type of BC and furthermore not optimized for adjusting AAE. Chow et al. (2009) showed that Particle Soot Absorption Photometer (PSAP) after an absorption artefact correction gives AAE values about 20% less than a filter-free photoacoustic instrument for the aerosols at Fresno, California. Gyawali et al. (2012) and Chakrabarty et al. (2013) generated BC dominated particles by burning oil, and measured the absorption using filter-free photoacoustic instruments. The estimated AAE ranged from 0.8 (kerosene soot) to 0.95~1.1 (mustard oil soot). Because there must have been some absorptive organic aerosols (e.g., BrC) in these aerosol samples that have a much larger AAE, the indication from these two studies is that BC AAE is lower than 0.8~1.1.

In addition, AAE values could differ due to differences in AAE calculations. For example, if the absorptions at two wavelengths are observed, the AAE can be approximated by:

$$AAE = -\frac{\ln(C_{abs1}/C_{abs2})}{\ln(\lambda_1/\lambda_2)} \tag{2}$$

where C_{abs1} and C_{abs2} are the absorption coefficients at the wavelengths of λ_1 and λ_2, respectively. Due to the variation on different ranges of wavelengths, the AAE approximated by Eq. (2) becomes quite sensitive to the choice of observational wavelengths.

Although observations do not give a clean value of BC AAE, it is safe to say that even accurate observations do not strongly support the theoretical constant of 1.0 for BC AAE. The fact alone that there are different types of soot particles (associated with different refractive indices) points to a range of BC AAE instead of a fixed value. Furthermore, it is not clear if the real BC AAE is 1.0 on the average. Despite all these uncertainties, BC AAE has been assumed to be 1.0 in many studies (Lack and Langridge, 2013; Moosmüller et al., 2009; Lack et al., 2008; Kirchstetter et al., 2004; Lewis et al., 2008). Meanwhile, numerical studies on BC AAE did not show systematic nor conclusive results to improve our understanding on them (Li et al., 2016; Lack and Langridge; 2013).

This study presents a systematic numerical investigation on the AAE of BC particles, and decomposes the AAE influence into that due to each particle microphysical property (e.g. size, shape, refractive indices and internal mixing). The paper is organized as follows. The microphysical properties of BC particles used for absorption simulations are discussed in Section 2, and Section 3 presents the AAE simulations and decomposes the AAE influences. Section 4 concludes this study.

2 BC properties

The absorption of a single particle or an ensemble of particles can be accurately calculated if the particle shape, size and refractive index are known. With a large amount of observations on BC microphysical and optical properties made in the past decades (Sorensen, 2001; Bond and Bergstrom, 2006), there is much less uncertainty in estimated shape, size and refractive index for BC compared with AAE estimation. The present study embarks on numerical calculations of BC optical properties. There have been numerious calculations of BC optical properties on a single wavelength (Sorensen, 2001; Liu and Mishchenko, 2005; 2007; Smith and Grainger, 2014), and the novelty of the present study is considering much wider but realistic ranges of BC properties (especially the particle shape and coating thickness) and focusing on its AAE systematically. The following subsections discuss BC geometry, size and refractive index, and explain how these properties are treated in the simulations herein.

2.1 BC geometry

BC particles exist in the form of aggregates with hundreds or even thousands of small spherical particles, called monomers. The concept of the fractal aggregate (FA) shows great success and wide applications on representing realistic BC geometries (Sorensen, 2001). The FA is mathematically described by the statistic scaling rule in the form of:

$$N = k_f \left(\frac{R_g}{a}\right)^{D_f} \tag{3}$$

where N is the number of spherical monomers in an aggregate, a the average radius of the monomers, R_g the radius of gyration, k_f the fractal prefactor, and D_f the fractal dimension. Based on Eq. (3), as k_f or D_f increases, a relatively small R_g is required, which corresponds to a relatively compact particle.

Immediately after emitted into the atmosphere, BC aggregates exhibit lacy structures with a small fractal dimension D_f, normally less than 2 (Sorenson, 2001; Chakrabarty et al., 2009). We refer to these lacy-structured BC aggregates as Fresh BC particles here. Over time, the structure and chemical composition of BC particles change, i.e. a process called “aging”. Aged BC particles normally have a structure of compact aggregates coated by other material (Moffet and Prather, 2009). We refer to these particles as Coated BC particles here. In some cases (such as humidified biomass burning aerosols), aged BC particles have a structure of compact aggregates without coating (Lewis et al., 2009). We refer to these uncoated aged particles as Compact BC particles. These three BC geometries are considered in the present study: lacy aggregates, compact aggregates and aggregates with coating, and are referred as the Fresh BC, Compact BC and Coated BC.

The optical properties of the Coated BC were investigated by a core-shell model with a Mie theory in the past, which assumes a spherical BC core in the center of coating sphere (Chung et al., 2012, Lack et al., 2012; Peng et al., 2016; Moffet and Prather, 2009), and this may introduce significant differences on BC optical properties. In this study, a compact aggregate is used for BC, and a spherical coating is added as the coating material following the ideal model developed by Liu et al. (2017). The coating is assumed to be non-absorptive sulfate, the wavelength-dependents refractive indices of which are obtained from the well-known aerosol optical property database OPAC (Hess et al., 1998). The real part of sulfate RI decreases slightly from 1.47 to 1.42 as the wavelength increases from 0.3 to 1.0 μm.

However, the amount of coating, the most important factor to determine the absorption enhancement, is one of the most poorly investigated issues for coated BC. The key issue here is to develop the relationship between core size and coating thickness for a group of different-sized BC particles. Here, we define coating thickness as the radius of a coated BC particle minus the radius of the core. As pointed out in section 1, Lack and Cappa (2010) assumed that coating thickness is linearly proportional to the core radius. On the other hand, if we apply aerosol condensation physics, we conclude that small core radii are associated with larger coating thicknesses, since condensation reduces the diameter differences between big and small particles.

To obtain a realistic relationship between core size and coating thickness, we choose to use the experiment results by Schnaiter et al. (2005). They coated diesel soot particles by secondary organic compounds in a chamber, and Figure 5 of their paper shows how the size distribution changes as coating progresses. A pair of typically BC size distributions before and after coating is shown in the left panel of Fig. 2, following Schnaiter et al. (2005). The lognormal size distributions were fitted based on the observations. The geometric mean diameters were observed to increase from 0.2 to 0.4 μm, whereas the geometric standard deviations decreased from approximately 1.7 to 1.2 in Fig. 5 of Schnaiter et al.'s (2005) paper. Assuming that both uncoated and coated BC particles have a lognormal size distribution, and big BC particles are still bigger than small BC particles after coating, we derive coating thickness as a function of core radius. The derived relationship is shown in the right panel of Fig. 2, where coating thickness is shown to be smaller with bigger cores. As coating progresses further, the geometric standard deviation of coated BC particles will fall further. The derived coating thickness Fig. 2 is considered as realistic one in present study to compute the AAE of Coated BC, and so further coating is not addressed here.

Figure 3 visualizes examples of BC particles with the three BC formats, i.e., geometries, considered in this study, and the BC aggregates in the figure all have 100 monomers. A tunable particle-cluster aggregation algorithm is applied to generate the FAs (Filippov et al., 2000; Liu et al., 2012), and the coating sphere is added with its center located at the mass center of compact FA. Three transmission or scanning electron microscope images of BC particles are also given in the figure for comparison (Burr et al., 2012; Lewis et al., 2009; Freney et al., 2010), and we can see that the numerically generated particles have similar structures to those realistic ones. Values that are close to the observed ones (Sorensen and Roberts, 1997; Sorensen, 2000; Brasil et al., 2000; Chakrabarty et al., 2014) have been widely used for numerical studies, and are applied here to represent realistic BC particles (Liu and Mishchenko, 2005; Smith and Grainger, 2014; Li et al., 2016). The diameter of the same-sized monomers is set to 30 nm, and the fractal prefactor of 1.2 is used. For the lacy aggregate, a fractal dimension of 1.8 is used, and both the Compact and Coated BC particles use a fractal dimension of 2.8. With the BC coating thickness distribution given above, the aggregate can be wrapped inside the coating sphere.

2.2 BC size distribution

Particle size distribution is one of the most commonly measured variables for aerosol studies. BC particles are not spherical and so the diameter (or radius) of the corresponding equivalent volume sphere is normally used to describe the size of each BC particle. Aerosol size measuring instruments (such as Scanning Mobility Particle Size Spectrometer) have repeatedly shown that a lognormal size distribution is a good fit for realistic BC size distributions (Bond et al., 2002; Chakrabarty et al., 2006; Reddington et al., 2013; Wang et al., 2015), and it is also widely used in numerical calculations of BC radiative properties and forcing (Moffet and Prather, 2009; Chung et al., 2012; Li et a., 2016). Observations for BC have shown equivalent volume diameters from 0.01μm up to 1.0μm (Chakrabarty et al., 2006; Reddington et al., 2013; Wang et al., 2015). To describe a lognormal size distribution, a mean size and a standard deviation are needed. Ambient data support geometric mean diameters (GMDs) between 0.10μm and 0.12μm for BC (Alexander et al., 2008; Coz and Leck, 2011; Reddington et al., 2013; Wang et al., 2015). The geometric standard deviation (GSD) values vary within a relatively narrow range. As a result, we consider BC with the GMDs between 0.05 and 0.2 μm for sensitivity purposes, and a fixed GSD of 1.5 is assumed.

With the concept of FA, the size of a BC aggregate is determined by both the size of monomers and number of monomers in the aggregate. Compared to the BC overall size distributions (i.e. distribution of monomer numbers), the monomers have a much narrower size distribution, and play a minor role in determining the optical properties of BC particles (Liu et al., 2015). Thus, we ignore the effects of monomer size distribution on BC absorption and fix the monomer size to a diameter of 30 nm, and the size of an aggregate is only determined by the number of monomers in the aggregate. With the equivalent diameter GMD between 0.05 ~ 0.2 μm, we consider aggregates with the number of monomers ranging from 1 to 2000. Numerical integrations can be easily carried out to obtain the averaged absorption of an ensemble of aggregates with a given size distribution. For Coated BC, the size distribution is applied for the BC core, and the overall effective volume diameter is larger than that of pure BC.

2.3 BC refractive index

The refractive index (RI), a wavelength dependent complex variable, is one of the most important parameters to determine aerosol AAE, because the absorptions at different wavelengths are significantly influenced by both the real and imaginary parts of RI. However, it is also one of the most uncertain optical properties of BC particles, because it cannot be directly observed. Estimates of BC RI have been normally made from observed absorption, scattering (or extinction) and size distribution of suspended particles, or from reflectance of compressed BC solids, and the RI is inferred by obtaining a best fit to numerical simulations (either Mie theory by assuming spherical particle shape or the simple Rayleigh-Debye-Gans theory) (Chang and Charalampopoulos, 1990; Schnaiter et al., 2003; 2005; Kirchstetter et al., 2004; Dalzell and Sarofim, 1968; Stagg and Charalampopoulos, 1993; Vanhulle et al., 2002; Moteki et al., 2010). Some of those studies extend RIs at particular wavelengths into the whole spectrum by the dispersion equations or the Kramers-Krönig analysis (Dalzell and Sarofim, 1969; Querry, 1987; Chang and Charalampopoulos, 1990). These retrieval methods based on the unrealistic spherical shape assumption or inaccurate numerical modeling pose sizable errors on estimated RIs, let alone the error in aerosol optical property measurements. Furthermore, the BC materials from different combustions probably have different RIs, and this was discussed in the past (e.g., Sorensen, 2001; Bond and Bergstrom, 2006). There are also numerous datasets available with BC RIs over the entire solar spectrum to obtain its optical properties for radiative applications related to BC (d'Almeida et al., 1991; Krekov et al., 1993; Hess et al., 1998). More details on the BC RIs have been carefully reviewed and summarized by Sorensen (2001) and Bond and Bergstrom (2006).

Figure 4 compares BC RIs from those cited studies. Most observational based studies give RIs at some specific wavelengths, at which the observations are carried out, and some fitted results with continuous variations are also given. Both real and imaginary parts of the BC particles show quite wide ranges of variations, and we eliminated results with real part much larger than 2 and imaginary part much smaller than 0.5. The real part generally varies between 1.5 and 2.0. The imaginary part shows similar range of variation, and values from 0.5 up to 1.1 have been retrieved. Furthermore, none of these datasets show a wavelength-independent RI, and quite different variations over the wavelength are shown in the figure. The real part of RI generally increases as the wavelength becoming larger, whereas the slopes of the variations are quite different. However, both increasing and decreasing trends are noticed for the imaginary part of RI. The figure clearly shows the uncertainties and large variations on BC RI, which brings the most significant challenge on approximating its AAE.

In view of Fig. 4, it is difficult to find a single value to represent BC RI, whereas it is doable to give a reasonable range of variation for numerical investigation. We consider both wavelength-independent (i.e. constant) and wavelength-dependent RIs, and introduce two parameters to indicate the variation of real and imaginary part as wavelength, respectively. The real and imaginary part are defined as:

$$Re(\lambda) = Re_o + A(\lambda - 0.55) \tag{4}$$

$$Im(\lambda) = Im_o \times 10^{B(\lambda-0.55)} \tag{5}$$

where λ denotes wavelength in units of micron. A and B represent the wavelength dependence, and are defined independently. We use 0.55 μm as the reference wavelength, and Re_o and Im_o can be understood as the real and imaginary part of RI at 0.55 μm. If A=B=0, the BC RI becomes wavelength independent. The real part of RI is simply assumed to vary linearly with wavelength, and the imaginary part is linear in the logarithmic scale. Because the range of wavelength we consider is relatively narrow, i.e. visible and near infrared range, the simple assumption can capture the general variation of BC RIs. The corresponding A and B values for the RI shown in Fig. 4 are listed in Table 1, and both of them show quite different values from the various datasets. It should be noticed that Schnaiter et al. (2003; 2005) gives A and B much larger than those of other datasets, which may be due to the relatively coarse retrieval algorithm and the narrow spectrum range for the measurements. Besides Schnaiter et al. (2003; 2005), A and B values in the range of (0.0,0.25) and (-0.25, 0.0) respectively are enough to account for the RI wavelength-dependence of other datasets. In light of the RI estimates made by previous studies, both A and B are assigned to be in the range of -0.5 and 0.5 here, which gives a much wider range of variation that those shown in Fig. 4 (besides those from Schnaiter et al. (2003; 2005)). The shadow areas in Fig. 3 represent the large range of RIs that is considered in this study, and the areas clearly cover most previous BC RI estimates.

3 BC AAE

With the shape, size distribution and RI known, it becomes straight forward to calculate the corresponding optical properties at a given wavelength. Multiple numerical models are available to account for the light scattering properties of a cluster of spheres without overlapping, and the Multiple-Sphere T-matrix Model (MSTD) developed by Mackowski and Mishchenko (2011) is used in this study. The MSTM is a numerically exact model for light scattering by multiple spheres, and is widely used to study the scattering properties of BC particles. Due to the high accuracy and efficiency provided by the MSTM, it becomes convenient to consider the optical properties of BC as aggregates of small spherical monomers. It should be noticed that, using the MSTM, the BC particles are accurately treated as those shown in Fig. 3, and the errors can only be introduced by the uncertainties on particle microphysical properties, not the numerical model.

Because the AAE is widely approximated with the absorptions at two wavelengths using Eq. (2) (Utry et al., 2014; Li et al., 2016), BC also shows noticeable different AAE values over different ranges of spectrum. To obtain the most representative AAE value, we use BC absorptions at multiple wavelengths between 0.3 and 1.0 μm in steps of 0.05 μm, and the best AAE value to fit the absorptions over the spectrum is obtained by linear regression. Figure 5 illustrates an example of the AAE calculation, in which the averaged absorption cross sections are shown in the logarithmic scale as a function of wavelength. The red crosses in the figure are obtained from the MSTM for the Fresh BC, and a wavelength-independent RI of 1.8+0.6*i* over the entire spectral range and a GMD of 0.12 μm are used for the simulation. The absorption cross section shows a clear linear variation in the logarithmic coordinate, and the blue line is the linear fit from a linear regression. Thus, the slope of the line, i.e. 1.04 in this figure, is the AAE for BC with the corresponding microphysical properties. In this way, the bias introduced by considering absorptions at only two wavelengths can be avoided. It should be noted that the example in the figure shows an excellent linear relationship, which is not true for all cases, whereas linear regression still gives the best representation on the AAE values if the absorption doesn't accurately decrease exponentially.

Figure 6 shows the calculated BC AAE with a wavelength-independent RI of 1.8+0.6*i* using the aforementioned numerical methods. The sensitivities of BC AAE to particle geometry and size are shown in this figure. Different BC conditions in the atmosphere, i.e. Fresh, Compact, and Coated BC, are represented by particles with different geometries. As evident in Fig. 6, even for those relatively small aerosols, geometry plays an important influence on the AAE. Moreover, particles with different geometries show different dependences on particle size. The AAE of the Fresh BC is approximately 1.05 and insensitive to particle size, because the interaction between monomers for lacy aggregates are relatively weak and the absorption per monomer does not change significantly as BC aggregate becomes larger. However, based on the Rayleigh theory, the AAE of small BC with a wavelength-independent RI should be 1.0 (*Moosmüller and Arnott*, 2009), because the Rayleigh absorption for small particles is proportional to λ^{-1}. Because, as wavelength becomes smaller, the Rayleigh approximation underestimates particle absorption for relatively small aggregates (see Fig. 1 and the corresponding discussion), especially those with aggregation structures, and, thus, accurate scattering simulations give AAE values a little bit larger than 1.0 for even small-sized particles with wavelength-independent RI. Meanwhile, the AAE of the Compact and Coated BC is highly sensitive to particle size, and decreases sharply with the GMD. The Compact BC has smaller AAE than Fresh BC, and shows AAE almost 0.8 as the GMD becomes close to 0.2 μm. For the Coated BC, the GMD of the mixed particle is larger than those of the homogeneous BC, and its AAE values are the most sensitive to particle size, decreasing from over 1.15 to 0.75. For BC with GMD larger than approximately 0.07 μm, aging would significantly decrease its AAE. Meanwhile, both those relatively small AAE values obtained for Compact and Coated BCs can potentially be used to explain observed small BC AAEs (Kirchstetter et al., 2004; Arnott et al., 2005; Gyawali et al.; 2012; Chakrabary et al., 2013). Compared with Fresh BC, the coating results larger AAE for small BC, whereas gives smaller AAE for relatively large BC particles. The AAE of Fresh BC with a GMD of 0.2 μm drops from approximately 1.05 to 0.75 after aging, both of which are close to the observed values and coincident with the changes (from 1.1 to about 0.8) of Diesel soot from Schnaiter et al. (2005), and the differences may be caused by uncertainties on the RI or coating amount. Even with non-absorptive coating material, the coating still amplifies BC absorption and changes the BC AAE. Considering the aging processes of BC aggregates, Figure 6 shows that, for relatively large BC particles, Compact BC has smaller AAE than those of the Fresh BC with lacy particle structure, and the AAE becomes even smaller after the compact aggregates mixed with other non-absorptive materials. The coating amount, structure or material may affect the absorption enhancement at different particle sizes and then the AAE, and this study considers a special but observation-based case. As a result, the conclusion for the Coated BC should be more carefully tested for further applications.

The influences of particle RIs on the AAE are illustrated in Fig. 7, and results for the Fresh, Compact and Coated BC are shown from top to bottom panels. Figure 7 considers only wavelength-independent RIs. The left column is for BC particles with a fixed imaginary part of 0.6 but real parts of 1.6, 1.8 and 2.0, and the right column is for those with the same real part (1.8) but different imaginary parts (0.4, 0.6, 0.8 and 1.0). The BC AAE increases as the real part increases or the imaginary part decreases. Although the imaginary part of RI is most directly related to particle absorption, real and imaginary parts affect BC AAE to similar degrees. Again, the sensitivity of BC AAE to its RIs is quite different for particles with different geometries. The AAEs of the Fresh BC is less sensitive to RI, and shows difference of < 0.1 for the RIs we considered. As the RI real part increases from 1.6 to 2.0, the AAE of the Compact BC increases by approximately 0.15, and the changes reach to as large as 0.3 for BC imaginary part between 0.4 and 1.0. However, after coating, the AAE becomes less sensitive to RI real part, but more sensitive to RI imaginary part. Considering the significant uncertainty in estimated BC RI due to differences on combustion fuels and conditions as well as whether BC is fresh or aged, it is highly questionable to use a fixed AAE value as in past studies (Lack and Langridge, 2013; Lack et al., 2008; Kirchstetter et al., 2004; Lewis et al., 2008). Even if a study aims to use an average BC AAE, we envision that the average BC AAE for aerosols from different combustion fuels would differ substantially, such as those from the biomass and fossil fuel.

All previous studies used a wavelength-independent RI over the entire spectrum, which may or may not be realistic for BC particles in the atmosphere. As explained in Section 2.3, parameters A and B are introduced to account for wavelength variance of the real and imaginary parts of RI, respectively. Because BC absorption increases as the real part of RI decreases or the imaginary part increases, it is simple to understand the influence of wavelength-dependent RIs on BC AAE. With simple variations assumed for both RI real and imaginary parts, it becomes possible to quantify the effects of RI wavelength variations. Previous simulations have given BC absorptions at some particular RI values (i.e. real part of 1.6, 1.8, and 2.0, and imaginary part of 0.4, 0.6, 0.8 and 1.0), and, to save computational time, BC absorptions at other RIs (that are obtained from Eqs. (4) and (5) with given A and B) are approximated by interpolation among those existing results. By comparing with accurate MSTD results, we find that the interpolation introduces relative errors of < 1% for the absorption, which is accurate enough for the AAE simulation.

Figure 8 illustrates the impacts of wavelength-dependent RIs on BC AAE, and three rows correspond to results for the Fresh (top), Compact (middle) and Coated (bottom) BC. Both A and B are assigned to change between -0.5 and 0.5. Figure 8 considers two examples for the reference RI at the wavelength of 0.55 μm, i.e. $Re_0+Im_0 i$ (1.8+0.6i and 1.8+0.8i), and they are marked by the solid and dashed curves, respectively. Meanwhile, three BC size distributions with the GMDs of 0.05 μm, 0.12 μm and 0.20 μm are used, and visualized by the red, blue and green curves. As expected, the AAE increases as A increases or B decreases, and quite different slopes are shown in different panels. Quantitatively, the AAE of BC with wavelength-dependent RIs for typical values of A=0.2 and B=-0.1 (Chang and Charalampopoulos, 1990; Krekov, 1993) would be approximately 0.15 larger than those with a wavelength-independent RI, and it becomes more difficult to understand the observed small BC AAE values (Kirchstetter et al., 2004; Gyawali et al., 2012). We focus on two features illustrated by the figure, both of which will be used later to decompose the influences of different BC properties on its AAE. First, for all cases, the AAEs show relatively linear variations as either A or B changes, and, thus, it becomes easy to quantify the influence of wavelength-dependent RIs on BC AAE. Secondly, different panels show very different AAE variation (slope) over A or B, whereas, for each panel, the slopes for different cases (i.e. different curves in a panel) are relatively similar, which means that the influence of both A and B dependent only on particle geometry. Figure 8 only shows six special but typical cases (two $\mathrm{Re_o}+\mathrm{Im_o}i$ by three GMDs), and more tests are carried out and show very similar results.

With all previous factors considered, it becomes possible to decompose the influences of BC properties on its AAE. The AAE shows clear sensitivities on all properties to quite different degrees, whereas, for a particular particle geometry, all parameters show monotonic influence on the AAE. The relationships between the BC AAE and its properties are simply approximated with linear equations, and, thus, the BC AAE is expressed by:

$$AAE = AAE_o + k_1(GMD - 0.12) + k_2(Re_o - 1.8) + k_3(Im_o - 0.6) + k_4 \times A + k_5 \times B \tag{6}$$

The coefficients, from k_1 to k_5, are fitted to indicate the significance of the corresponding influence on BC AAE. The GMD should be given in unit of micron. Because the influence of BC properties on its AAE for particles with different geometries are completely different, we approximate the coefficients of the above equation for the Fresh, Compact and Coated BC separately. The fitted coefficients are given in Table 2. First three coefficients (k_1, k_2, and k_3) in the table are obtained by given the smallest root-mean-square relative errors for all AAE values calculated based on wavelength-independent RIs. Because Figure 8 shows that A and B have a quite clear and simple influence on the AAE, and the coefficients k_4 and k_5 are simply obtained by the averaged slopes given in each panel. The influence of BC properties on its AAE are clearly demonstrated by the coefficients in Table 2. Large absolute values mean to have more significant influence on the AAE, and the positive or negative sign indicates the sign of the correlation.

To demonstrate the performance of the simple expresses on approximating BC AAE, Figure 9 compares BC AAEs from accurate absorption simulations and Eq. (6). The left panel of the figure shows the cases in which the approximations give relatively accurate agreement to the simulations, whereas some of the poor cases are illustrated in the right panel. It is clear that the results for the Fresh BC show the best agreement because of the relatively weak influence of particle size on the AAE. The relatively poor agreements for the Compact and Coated BC are mainly because of the non-linear variation of the AAE on the GMD. The differences between the accurate simulations (solid curved) and the approximation (dashed lines) can reach even over 0.2 for small BC particles. However, considering that the BC are widely observed or considered to have a GMD larger than 0.10 μm, Figure 9 indicates that the simple linear approximation we obtained give a quite accurate estimation on BC AAE for BC of the three types.

Our results obtained here indicate that BC microphysical properties have a clear influence on BC AAE, and the influence can be quantitatively understood by Eq. (6) and the coefficients listed in Table 2. Considering the obvious variations obtained for BC particle sizes and geometries and the uncertainties on its RI, it is impossible to find a "best" AAE value for all BC aerosols. However, a range of reasonable AAE values can be obtained based on the observations of BC properties and the numerical results. For Fresh BC, the AAE are approximately 1.05, and aging makes AAE of typically sized BC particles to decreases by approximately 0.15 to 0.90. Furthermore, wavelength-dependent RIs makes the case much more complicated, and give wider ranges on the BC AAE. For Coated BC particles, the absorption can also be significantly affected by chemical composition, amount and geometry of mixing material (Li et al., 2016), and this study introduces a laboratory-based coating thickness distribution to reveal the significant effects of coating on BC AAE. With the help of Eq. (6), the BC AAE can be easily calculated if its properties (shape, size and RI) are known.

4 Summary and conclusions

We have numerically investigated the AAE of BC aerosols of three states in the atmosphere, i.e., fresh, compact and coated ones. The numerical computations conducted here have multiple controllable variables (such as BC size distribution) that all effect BC AAE, and we attempted to constrain these variables within the realistic ranges as determined by observational based studies. The MSTD was used to accurately compute the light absorption of non-spherical particles such as BC. The numerical results were analyzed to better understand the BC AAE values in relation to the controllable variables.

The results challenge conventional beliefs. With a wavelength-independent refractive index, our accurate numerical results show typical BC AAE values of 1.05 and 0.90, instead of 1.0, for fresh and aged BC particles respectively. In reality as revealed by many observational studies, the BC refractive index likely has sizable wavelength dependence, and BC is often coated by other aerosols. In these cases, BC AAE can even move beyond a range of 0.5~1.5. As a result, using a flat value of 1.0 for BC AAE could very likely introduce significant errors in aerosol absorption analysis studies.

Our results demonstrate that particle shape, i.e. the form of BC particles in the atmosphere, is the most influential factor in determining BC AAE. The AAE of fresh BC in the form of lacy aggregate is less sensitive to particle size, whereas, after aging process, the AAE of BC with compact or coated structures may significantly decreases as particle size increases. As the most uncertain particle property, the refractive index (RI) cannot be directly measured, and, thus, brings the most significant challenge on determining BC AAE. The BC particles with observational-based RI variations over wavelength may have an AAE value of 0.15 larger than corresponding ones with a wavelength-dependent RI. To quantify the complicated influences of different BC parameters on its AAE, linear approximations for BC AAEs in different conditions were obtained here. We propose that these approximations be applied to infer BC AAE with given BC properties in future studies.

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Table 1. Fitted values for the parameters A and B used to define the spectral variation of BC refractive indices.

Reference	A	B
Krekov, 1993	0.15	-0.09
d'Almeida et al., 1991	0.01	-0.05
C and C, 1990	0.23	-0.22
Schnaiter et al., 2003	0.63	0.36
Schnaiter et al., 2005	0.79	0.79
Kirchstetter et al., 2004		-0.05

Table 2. Fitted coefficients to show the sensitivities of BC properties on its AAE values. Two significant figures are kept for all coefficients except for k_4.

	AAE_o	k_1	k_2	k_3	k_4	k_5
Fresh BC	1.05	- 0.36	0.24	-0.13	0.3	-1.2
Compact BC	0.92	-2.5	0.40	-0.42	0.2	-1.1
Coated BC	0.90	-2.7	0.15	-0.53	0.05	-1.0

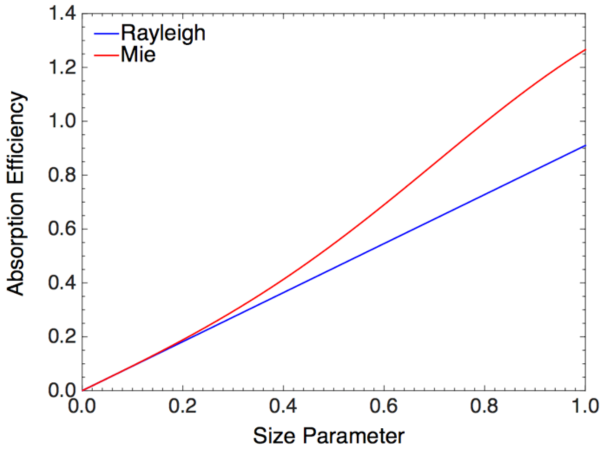

Figure 1. Comparison of the Rayleigh approximation and Mie theory for the absorption efficiency of spheres with a refractive index of 1.8+0.6*i*.

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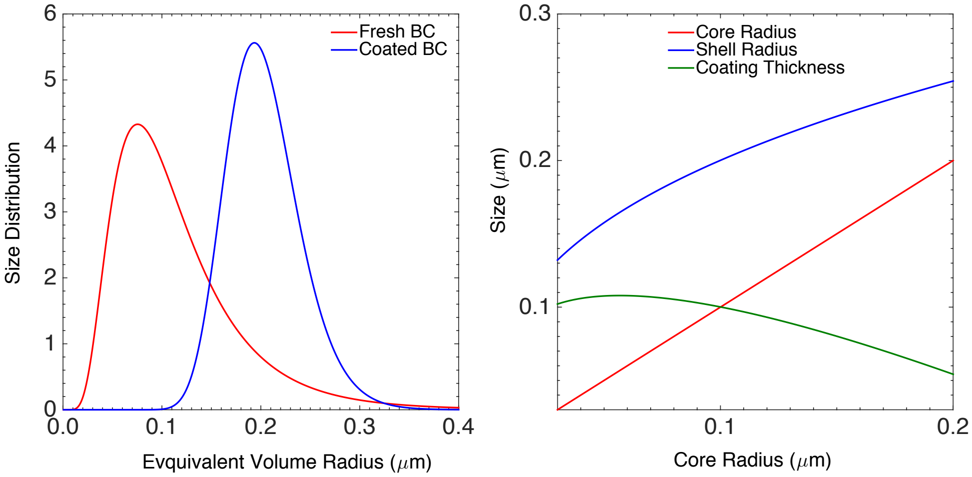

Figure 2. (a) Size distributions of fresh and coated BC based on the lognormal distributions and parameters from a laboratory study by Schnaider et al. (2005); see Fig. 5 of their study. (b). Shell radius and coating thickness as a function of BC core radius, as inferred from (a). Coating thickness is defined here as shell radius (i.e., radius of a coated BC particle) minus core radius.

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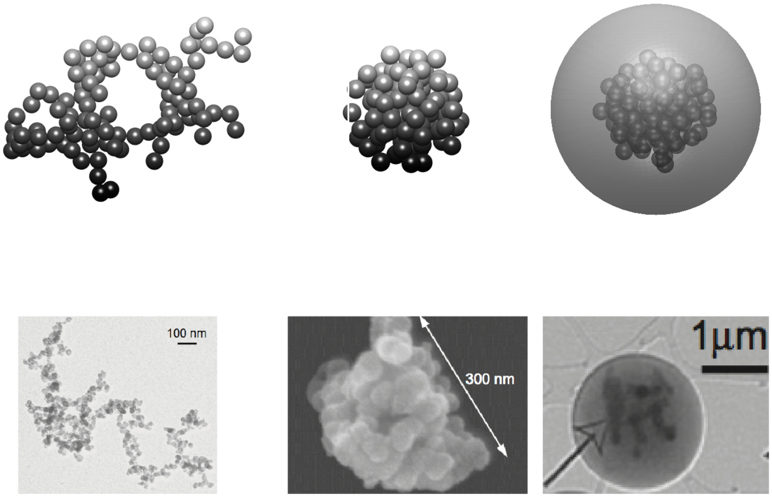

Figure 3. Geometries of numerically generated BC aggregates with different particle geometries, i.e. loose aggregate (left) for Fresh BC, compact aggregate (middle) for Compact BC, and coated aggregate (right) for Coated BC, and some examples of realistic BC images for comparison (Burr et al., 2012; Lewis et al., 2009; Freney et al., 2010).

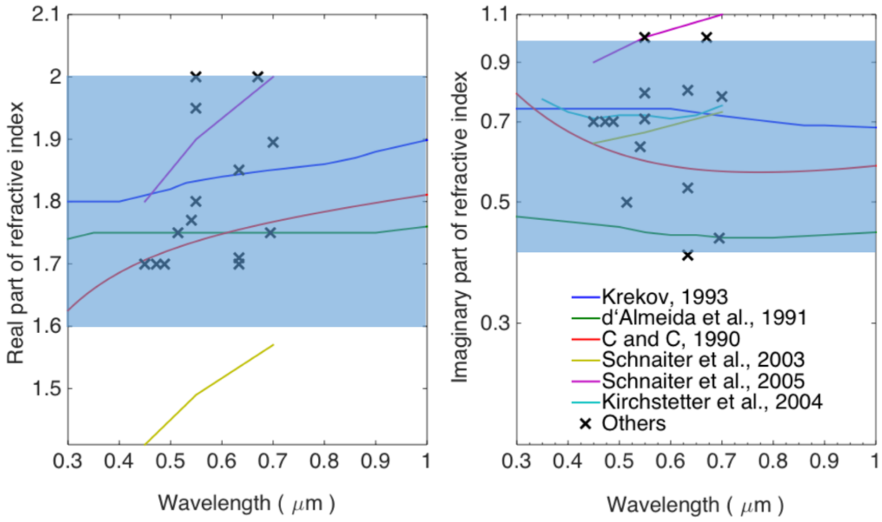

Figure 4. The real and imaginary parts of BC refractive indices from various observations. The blue shadow depicts the ranges considered in this study.

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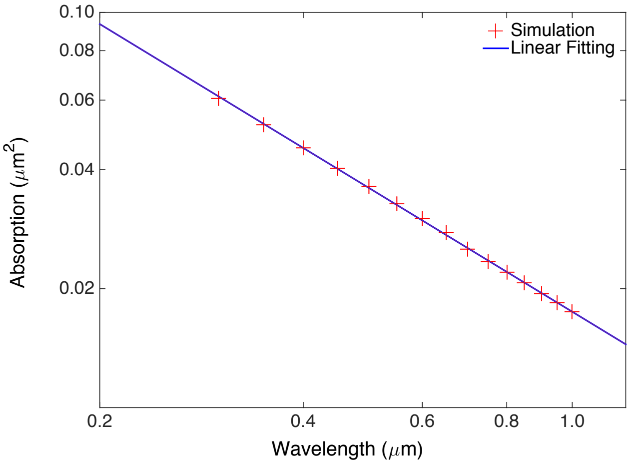

Figure 5. Absorption cross sections of Fresh BC with a wavelength-independent refractive index of 1.8+0.6i and a GMD of 0.12 µm as a function of wavelength.

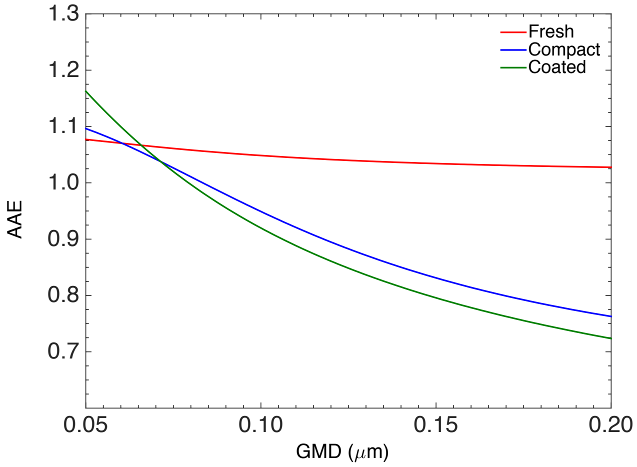

Figure 6. AAEs of the Fresh, Compact and Coated BC as a function of particle GMD.

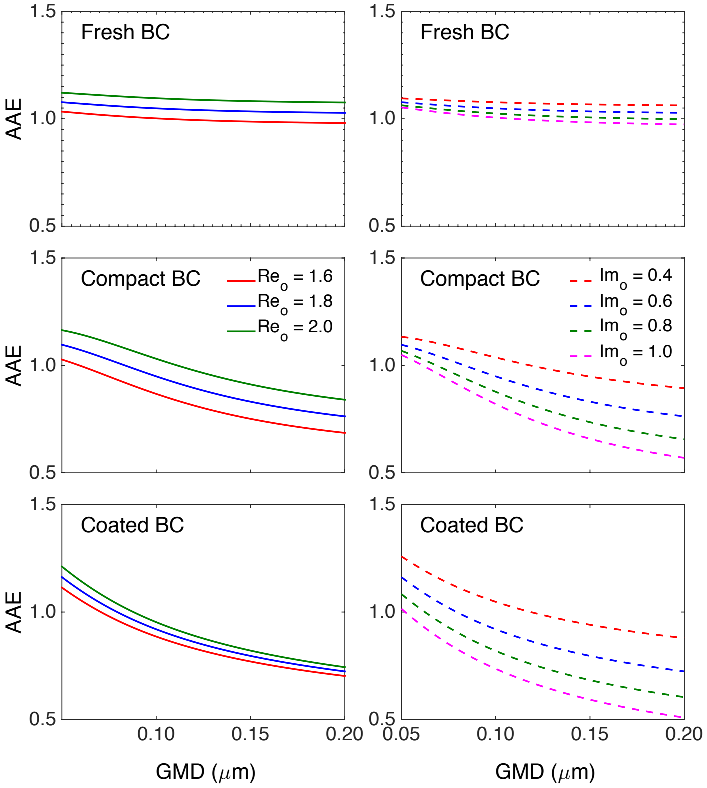

Figure 7. Influence of wavelength-independent refractive index on the AAEs of the Fresh BC (top penal), Compact BC (middle panel), and Coated BC (bottom panel). A fixed imaginary part of 0.6 is used for the left panel, and a fixed real part of 1.8 is used for the right panel.

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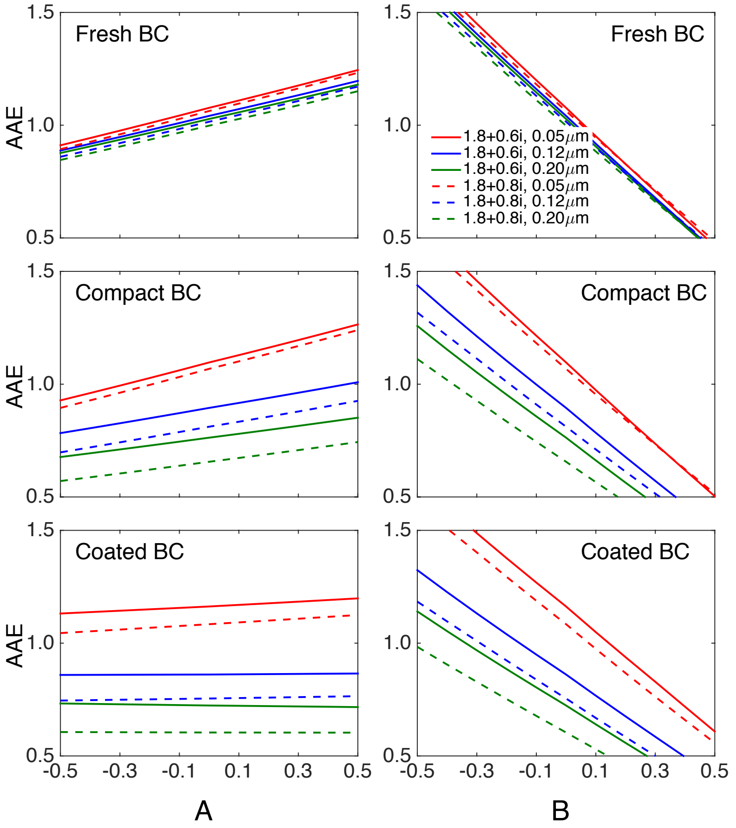

Figure 8. Influence of wavelength-dependent refractive indices on the AAEs of the Fresh BC (top penal), Compact BC (middle panel), and Coated BC (bottom panel).

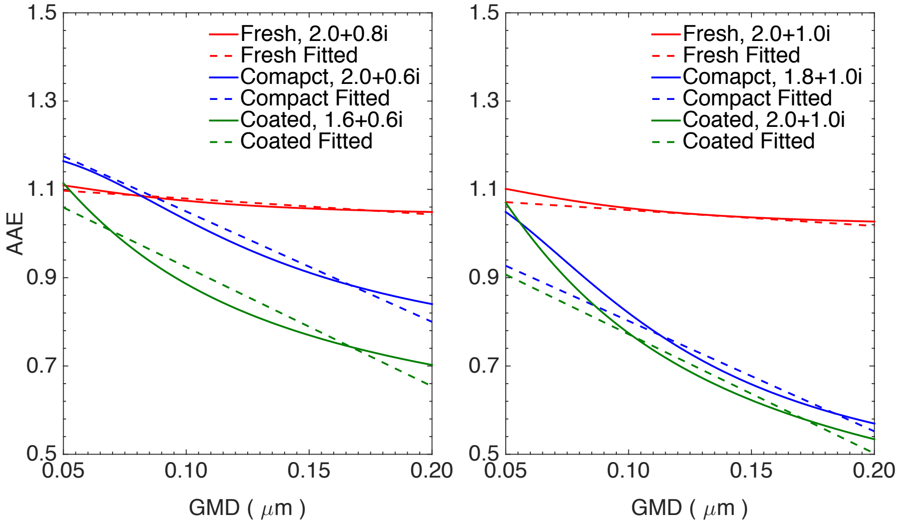

Figure 9. Comparison between the AAEs given by accurate numerical simulations (solid curves) and those approximated by Eq. (6) and the corresponding coefficients in Table 2. (dashed curves)

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