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Absorption enhancement of aged black carbon aerosols affected by their microphysics: A numerical investigation

Xiaolin Zhang[a,b,c], Mao Mao[a,b,c,*], Yan Yin[a,b], Bin Wang[a,c]

[a] Earth System Modeling Center, Collaborative Innovation Center on Forecast and Evaluation of Meteorological Disasters, Key Laboratory for Aerosol-Cloud-Precipitation of China Meteorological Administration, Joint International Research Laboratory of Climate and Environment Change, Nanjing University of Information Science & Technology, Nanjing, 210044, China
[b] School of Atmospheric Physics, Nanjing University of Information Science & Technology, Nanjing, 210044, China
[c] International Pacific Research Center, University of Hawaii at Manoa, Honolulu, HI, 96822, USA

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ABSTRACT

An idealized spherical model with black carbon (BC) aggregates fully coated by sulfate is developed to study the absorption enhancement (E_{ab}) of polydisperse BC aerosols, which is numerically calculated by the multiple-sphere T-matrix method (MSTM). The aim of this study is to evaluate the effects of aerosol microphysics on the absorption enhancement of fully coated BC particles. The E_{ab} values of accumulation concentric coated BC aggregates with different BC fractal dimensions vary within 2%, while those of coarse coated BC aggregates can alter up to 20% depending on shell-core ratio D_p/D_c (spherical equivalent particle diameter divided by BC core diameter). The BC position inside coating can result in an E_{ab} decrease of fully coated BC aggregates up to approximately 15% and 20% in the accumulation and coarse modes, respectively. Compared with the concentric spherical structure, the off-center coated BC aggregates shows similar E_{ab} with a difference less than 9% in the accumulation mode, whereas it can lead to up to 31% reductions in E_{ab} in the coarse mode. The absorption enhancement of aged BC is sensitive to particle size distribution, and it decreases as particles becomes larger in accumulation mode, whereas the reverse is true in coarse mode. For BC aggregates fully coated with a very thin layer sulfate at different size distributions, E_{ab} values are generally in ranges of 1.5–1.8 and 1.3–1.4 in accumulation and coarse modes, respectively, while with coating reaching $D_p/D_c = 2.7$, their values range from 1.7–2.4 and 2.0–2.1 in accumulation and coarse modes, respectively. Our study indicates that, larger D_p/D_c with BC aggregates not close to the coating boundary, or BC position closer to particle geometric center enhance BC lensing effect, whereas BC aggregates near the boundary of heavy coating may not further enhance lensing effect significantly with increased coating fraction.

1. Introduction

Black carbon (BC) aerosols are largely generated due to fossil fuel demands, unless clean renewable energy sources [1,2] are widely utilized. Black carbon has been identified as the second most important anthropogenic global warming agent in the atmosphere by virtue of their strong absorption of solar radiation and their role in cloud formation [3,4]. The BC climate effects are significantly dependent on the mixing state (i.e., externally or internally mixing with other aerosol species) [5,6], and atmospheric aging by coating with secondary components induces BC absorption enhancement (E_{ab}) [7,8]. In light of the complex morphology and mixing structure, our understanding of BC properties, including the absorption enhancement of aged BC, is still limited, making BC one of the biggest uncertainties in the estimation of aerosol radiative forcing [9,10].

Freshly emitted BC aerosols are mostly hydrophobic and externally mixed with other particulates [11], and soon after, BC agglomerates to form aged BC aggregates due to multi-phase processes in the atmosphere [12]. The observations show that, during the aging process, BC becomes coated with other components, including heterogeneous reactions with gaseous oxidants [13], coagulation with preexisting particulates [14], and condensation of sulfate, organics and nitrate [15]. Meanwhile, BC aggregates may undergo considerable geometry restructuring and become compact after coated [11]. The coatings on BC can enhance the absorption above that of uncoated BC particles through the so-called 'lensing effect', which has been confirmed by theoretical calculations using Mie theory [5,16,17] and laboratory measurements under controlled conditions [18–21]. The enhancement of absorption can result in significant bias in ambient BC measurements [22,23],

* Corresponding author.
E-mail addresses: xlnzhang@nuist.edu.cn (X. Zhang), mmao@nuist.edu.cn (M. Mao).

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and further, lead to uncertainties in assessing the radiative effect [24,25].

Many field measurements have been carried out to reveal the variation of BC absorption during atmospheric aging processes. Knox et al. [26] observed an absorption enhancement up to 45% because of BC coating in downtown Toronto, Canada. Naoe et al. [27] presented that the coating enhance BC absorption by a factor of 1.1–1.4 with a larger enhancement for thicker coating at a suburban site in Japan. The absorption enhancements rising from 1.4 ± 0.3 in fresh combustion emissions to ~3 for aged BC aerosols are found in a regional rural site over the North China Plain (NCP) [28]. However, Cappa et al. [29] reported a negligible absorption enhancement of only 6% for ambient BC particles under a variable mixing state based on direct measurements over California, USA. This implies that the absorption enhancement of BC due to coating is rather complicated in ambient air, which may be dependent on particle size distribution, composition ratio, and coating morphology affected by emission sources and aging processes.

Numerical modeling is a powerful method to improve our understanding of the complex absorption enhancement of aged BC aerosols. Core-shell Mie theory calculations employed by many current climate models, assume coated BC particles with a concentric spherical configuration and indicate absorption enhancements up to 3 being plausible [16,17]. Thus, the state-of-the-art climate models typically either compute an absorption enhancement on the basis of simplified mixing-state assumptions or assume a constant value of ~1.5 for BC absorption calculations [30–33]. Nevertheless, the simple concentric spherical core-shell model cannot adequately represent realistic BC-containing particles in the atmosphere. He et al. [34] calculated the absorption enhancement of BC coated by sulfuric acid at three monodisperse sizes (i.e., mobility diameters of 155, 245 and 320 nm) with different morphologies to capture BC aging in laboratory experiments. Some other coated BC models representing more realistic morphologies are built to study their optical properties [e.g., 35, 36], while corresponding calculations relevant to absorption enhancement due to BC coating show generally qualitative results.

Recently, more and more observations related to the composition ratio and mixing structure of aged BC aerosols are presented. Based on the SP2 (single-particle soot photometer) measurements of BC spherical equivalent core diameter (D_c) and coating thickness, observed values of D_p/D_c (particle diameter divided by BC core diameter) are 1.1–2.1 in London [37] and 2.1–2.7 in Beijing [38]. Among aged BC coating materials, sulfates are found to be primary drivers of enhanced BC absorption in China [28], and the large sulfate formation rate is induced by the aqueous oxidation of SO_2 by NO_2 under polluted environments [39]. About 48.6% BC particles are observed to be coated with non-refractory materials during polluted period in northwestern China [40]. The observations from China et al. [41] quantify that ~50% BC aerosols emitted from biomass burning are heavily coated (embedded), ~34% are partly coated, ~12% have inclusions and ~4% are bare. Similar results with fully and partly coated morphologies dominated are observed for aged BC particles at a remote marine free troposphere site in Portugal, where often receives long-range transported air masses from North America, Africa or Europe [42]. Some studies show that BC aerosols externally attached to or partially encapsulated in weakly absorbing materials have E_{ab} of ~1, i.e., absorption showing no obvious increase relative to uncoated BC particles [34,43,44]. This is probably due to that externally attached and partially coated BC geometries lack of efficient lensing effect, and that weakly absorbing coating materials block the photons from behind BC, producing a shadowing effect [45]. Thus, BC particles fully coated with weakly absorbing materials account for the absorption enhancement significantly, which is still under discussion. With more recent observations shown, a more reliable and quantitative simulation of the absorption enhancement of aged BC aerosols becomes urgent, which will benefit our understanding of the mechanism responsible for the model-observation discrepancies.

Here, we build a simple model to systematically account for the impacts of aerosol microphysics of aged BC particles on their absorption enhancement based on our current understanding. The model representing aged BC particles, and the numerical method used to calculate their absorption properties and absorption enhancements are introduced in Section 2. Section 3 presents the effects of aerosol microphysics, including composition ratio, coating morphology and size distribution, on the absorption enhancement of coated BC particles. The sensitivity evaluations of aged BC absorption enhancement due to uncertainties of BC refractive index are also discussed in Section 3, and Section 4 concludes the work.

2. Methodology

2.1. Aged BC model

The observations indicate that freshly emitted BC particles usually exist as loose cluster-like aggregates, having numerous similar-sized spherical monomers [e.g., 46]. The fractal aggregates have been successfully utilized to construct these freshly BC aggregation geometry, obeying the well-known statistical scaling law [e.g., 47]:

$$N = k_f \left(\frac{R_g}{a} \right)^{D_f}, \tag{1}$$

where N is the monomer number of an aggregate, a is the monomer radius, and k_f and D_f are the fractal prefactor and fractal dimension, respectively, controlling the aggregate structure. The aggregate becomes more compact, as k_f or D_f increases. R_g is the gyration radius, measuring the overall spatial size of an aggregate, and is defined as

$$R_g = \sqrt{\frac{1}{N} \sum_{i=1}^{N} r_i^2}, \tag{2}$$

where r_i denotes the distance of the ith monomer from the whole aggregate mass center.

The observations also show that these freshly emitted BC aggregates tend to be coated with secondary aerosol compounds through coagulation and condensation with the time going [e.g., 48,49]. During this aging process, most BC particles are thickly coated, and their chain-like aggregates tend to collapse into more compact clusters [21,50]. The fractal dimensions for fresh BC aggregates are generally less than 2, while they are close to 3 for aged BC aerosols [51]. There is sufficient evidence that aged BC aerosols can be overall particle spherical, and some microscopic images do show this geometry [e.g., 21,52,53]. Meanwhile, the simple spherical coatings on BC have similar effects on optical properties to those based on more complicated coating structure [35,36]. BC coating components mainly consist of sulfate, nitrate, ammonium and organics [54], and we select sulfate as the weakly absorbing coating material, since it is the primary driver of enhanced BC absorption over China [28,39]. Therefore, the simple sphere with BC fractal aggregate coated with sulfate, is considered to build a realistic aged BC particle model for efficient optical simulation here. This study considers the aged BC particles with sulfate fully coated, which is illustrated in Fig. 1.

To construct this homogeneous internal-mixed particle, we first generate a BC fractal aggregate and then add a spherical sulfate coating. For the BC aggregates, the value of k_f is set to be 1.2 based on Sorensen [47]. The radius a of BC aggregate monomers varies over a range of about 10–25 nm [55], while the monomer number N is observed to vary up to approximately 800 [56]. Since