Journal of Quantitative Spectroscopy & Radiative Transfer 161 (2015) 105–116

Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

journal homepage: www.elsevier.com/locate/jqsrt

The influence of different black carbon and sulfate mixing methods on their optical and radiative properties

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ARTICLE INFO

Article history:
Received 5 December 2014
Received in revised form
7 April 2015
Accepted 8 April 2015
Available online 18 April 2015

Keywords:
Internal mixing
External mixing
Black carbon
Sulfate
Aerosol optical properties

ABSTRACT

Three different internal mixing methods (Core–Shell, Maxwell-Garnett, and Bruggeman) and one external mixing method are used to study the impact of mixing methods of black carbon (BC) with sulfate aerosol on their optical properties, radiative flux, and heating rate. The optical properties of a mixture of BC and sulfate aerosol particles are considered for three typical bands. The results show that mixing methods, the volume ratio of BC to sulfate, and relative humidity have a strong influence on the optical properties of mixed aerosols. Compared to internal mixing, external mixing underestimates the particle mass absorption coefficient by 20–70% and the particle mass scattering coefficient by up to 50%, whereas it overestimates the particle single scattering albedo by 20–50% in most cases. However, the asymmetry parameter is strongly sensitive to the equivalent particle radius, but is only weakly sensitive to the different mixing methods. Of the internal methods, there is less than 2% difference in all optical properties between the Maxwell-Garnett and Bruggeman methods in all bands; however, the differences between the Core–Shell and Maxwell-Garnett/Bruggeman methods are usually larger than 15% in the ultraviolet and visible bands.

A sensitivity test is conducted with the Beijing Climate Center Radiation transfer model (BCC-RAD) using a simulated BC concentration that is typical of east-central China and a sulfate volume ratio of 75%. The results show that the internal mixing methods could reduce the radiative flux more effectively because they produce a higher absorption. The annual mean instantaneous radiative force due to BC–sulfate aerosol is about $-3.18\ W/m^2$ for the external method and $-6.91\ W/m^2$ for the internal methods at the surface, and $-3.03/-1.56/-1.85\ W/m^2$ for the external/Core–Shell/(Maxwell-Garnett/Bruggeman) methods, respectively, at the tropopause.

1. Introduction

Aerosols play an important role in the energy balance of the Earth–atmosphere system. Some aerosol species can absorb solar radiation and thus warm the atmosphere, whereas some other aerosols can scatter solar radiation and cause cooling of the atmosphere [1]. These interactions

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http://dx.doi.org/10.1016/j.jqsrt.2015.04.002
0022-4073/

between aerosols and radiation are known as aerosol direct radiative forcing (IPCC, AR5) [2].

Since the industrial era, the levels of aerosol species such as black carbon (BC), sulfate, and organic carbon (OC) in the atmosphere have increased continuously, making them the major anthropogenic aerosols. These three aerosol components have similar emission sources. BC and OC are mainly emitted by automobile exhausts, agricultural burning, forest fires, and petroleum-related industrial activities [1–4], while sulfate is usually generated by the chemical reactions of SO_2 and other components when they are mixed in the atmosphere [5,6]. Each of BC, sulfate, and OC can produce different direct radiative forcing. BC is an absorptive aerosol that can strongly absorb solar radiation from infrared to ultraviolet wavelengths, whereas sulfate and OC can significantly scatter solar radiation.

In recent studies, observational data have indicated that many aerosol particles form complex inhomogeneous structures, which is referred to as internal mixing [7,8]. Unlike external mixing, when considering internal mixing the influence of the micro-structure of aerosols on the radiative transfer must be taken into account. Pósfai et al. [9] found that soluble substances wrapping around BC may act as a lens that can focus radiation on the absorptive core, and increase the absorptive ability of mixed particles. Liu et al. [10] investigated four Effective Medium Approximations (EMAs) in modeling inhomogeneous particles with a homogeneous sphere, and calculated the optical properties of BC–sulfate aerosol. Lesins et al. [11] found that the magnitude of the differences in optical properties between externally mixed and internally mixed aerosols can reach 50% in a humid environment. Jacobson et al. [12] compared BC radiative forcing using different mixing methods and found that internal mixing methods can greatly enhance the positive radiative forcing of BC. The magnitude of enhancement was closely related to the coagulation and growth of aerosol particles. Many simulation results have also indicated that internal mixing can result in extra absorption by these aerosols, thereby leading to significantly higher direct forcing [13,14]. Furthermore, black carbon particles are usually in cluster forms, especial for those emitted from combustion sources, particle morphology take some impacts on the optical properties [15].

There are difficulties in applying internal mixing methods to climate simulations because of the need to ascertain the structure of internally mixed particles and the percentage of internally mixed particles among the total aerosol. Recent observations have suggested that the internal mixing rate is sensitive to both the hygroscopicity and the aging process of the substances involved. Based on BC aging process during one day, Riemer [16] indicated that BC inclined to form internally mixed particles as the aging process exacerbated. Ma et al. [17] investigated the diurnal variation of the mass ratio of the carbonaceous component extracted from mixed aerosol particles in North China, and found that the mixing states of carbonaceous aerosol was strongly affected by the diurnal changes of the mixed layer. They tend to form internally mixed particles during the nighttime and externally mixed particles during the daytime.

There are many methods to describe the internal mixing of aerosols, and the optical properties of aerosols calculated by these methods may be quite different. In this work, we calculated the optical properties of mixed BC and sulfate aerosol particles using four methods: three internal mixing methods (Core–Shell, Maxwell-Garnett and Bruggeman) and volume-weighted external mixing. Then, we compared differences in the optical properties between internally mixed and externally mixed aerosol particles, and their influences on radiative calculations.

In Section 2, we explain the methods used to calculate the optical properties of mixed aerosol particles, including the transformation of complex refractive indices at different relative humidities. In Section 3, we present the optical properties obtained for BC–sulfate aerosol using the different mixing methods at three typical spectral bands, and give a detailed discussion about the impacts of the volume fraction and relative humidity (*RH*) on their optical properties. We then entered the calculated optical properties into the Beijing Climate Center Radiation transfer model (BCC-RAD) and explained how the mixing methods affect radiative calculations in the atmosphere. Finally, Section 4 is a summary of this study.

2. Methods

2.1. The mixing states and treatments of aerosol particles

In this study, five optical properties of mixed particles were calculated: mass extinction/absorption/scattering coefficient ($Q_e/Q_a/Q_s$ [m^2/g]), single scattering albedo (ω), and the asymmetry factor (*ASY*).

In the external mixing state, each part of the mixed particle was treated as an independent sphere with no geometric contact with other parts of the particle (Fig. 1a). Furthermore, radiative transfer does not occur between each part of the mixture. Multi-phase scattering occurs inside the particle in the internal mixing state, therefore making the calculation of particle optical properties more complicated than in the external mixing state. The Core–Shell method is used when the particle is formed by an insoluble core with a soluble shell, and both parts share the same geometric center (Fig. 1b). The Maxwell-Garnett method is based on Maxwell-Garnett's equivalent medium theory, and is used when the position of the insoluble core is random in the mixed particle (Fig. 1c). The Bruggeman method assumes that each part of the particle retains a spherical shape and remains in contact with other parts of the particle at the surface (Fig. 1d). The mixing models presented in Fig. 1 are spherical approximations.

Mie scattering theory can be applied in three of the methods: external mixing, and the Maxwell-Garnett and Bruggeman internal methods. For the volume-weighted external mixing method, the optical properties of mixed particles were obtained by the optical properties of each part of the particle multiplied by its volume fraction (Eq. (1)).

$$\beta = \sum_i f_i \cdot \alpha_i. \tag{1}$$

Assuming the externally mixed particles contain i kinds of substances, f_i is the volume fraction of substance i and