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Effects of atmospheric water on the optical properties of soot aerosols with different mixing states

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ABSTRACT

Soot aerosols have become the second most important contributor to global warming after carbon dioxide in terms of direct forcing, which is the dominant absorber of visible solar radiation. The optical properties of soot aerosols depend strongly on the mixing mechanism of black carbon with other aerosol components and its hygroscopic properties. In this study, the effects of atmospheric water on the optical properties of soot aerosols have been investigated using a superposition T-matrix method that accounts for the mixing mechanism of soot aerosols with atmospheric water. The dramatic changes in the optical properties of soot aerosols were attributed to its different mixing states with atmospheric water (externally mixed, semi-embedded mixed, and internally mixed). Increased absorption is accompanied by a larger increase in scattering, which is reflected by the increased single scattering albedo. The asymmetry parameter also increased when increasing the atmospheric water content. Moreover, atmospheric water intensified the radiative absorption enhancement attributed to the mixing states of the soot aerosols, with values ranging from 1.5 to 2.5 on average at 0.870 μm. The increased absorption and scattering ability of soot aerosols, which is attributed to atmospheric water, exerted an opposing effect on climate change. These findings should improve our understanding of the effects of atmospheric water on the optical properties of soot aerosols and their effects on climate. The mixing mechanism for soot aerosols and atmospheric water is important when evaluating the climate effects of soot aerosols, which should be explicitly considered in radiative forcing models.

1. Introduction

Soot aerosols affect the energy budget of the Earth by absorbing solar radiation, influence cloud processes, and alter the melting of snow and ice cover [17,19,47]. Because the black carbon (BC) in soot aerosols dominates the absorption of visible solar radiation, soot aerosols are the second most important contributor of global warming after carbon dioxide in terms of direct forcing in the present-day atmosphere [21].

However, the uncertainties surrounding the net climate forcing from soot aerosols are substantial because little is known regarding the optical properties of soot aerosols. Comparing field and remote sensing observations with many climate models simulation indicates that the atmospheric absorption attributable to soot aerosols is too low in many climate models studies; these differences have not been extensively examined, nor are they well-understood [5].

The BC particles in soot aerosols are co-emitted with numerous other aerosols and aerosol precursor gases. Soon

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after emission, the BC particles mix with other aerosol components in the atmosphere [49,37,13]. The optical properties of soot aerosols depend strongly on the mixing mechanism of BC with other aerosol components ([48,6,30]), as well as its hygroscopic properties [53,56,55,28]. Based on modeling and laboratory studies, the strong absorption abilities of soot mixed with other aerosols enhance the radiative forcing of the aerosol by up to three times compared to the externally mixed scenarios [21,14]. However, based on in-situ measurements on urban plumes, the aerosol absorption enhancement for mixed soot may have been overestimated in models [8,22,9].

Determining and explaining the BC mixing state with other aerosol species is highly complex and remains unresolved to date. The optical properties of soot aerosols can depend strongly on the morphology [26,25,24,23,33,39,38]. The hygroscopicity of soot aerosols critically influences their optical properties [40,16,10]. How many ever climate models, the mixing mechanism of BC with other aerosol components and the water vapor in the ambient atmospheric remain largely unknown because the water and other semi-volatile species on the soot aerosol surface evaporate easily during the in-situ measurements performed under high-vacuum [51].

Due to the lack of reliable information on atmospheric water effects on soot aerosols optical properties and the critical importance of aerosols during radiative forcing assessments, this study aims to investigate the effects of atmospheric water on the optical properties of soot aerosols while determining the mixing mechanism for soot aerosols and atmospheric water. Theoretical simulations are required to quantify the mixing mechanism based on the volatile properties of water. The Multiple Sphere T-Matrix [35] was used to reconstruct the absorption properties and scattering properties of soot aerosols with different mixing states, extending the formulation to arbitrary configurations of spherical surfaces.

The enhancement in absorption due to the mixing states has been discussed in several previous theoretical studies ([21,14]) and has been observed in both laboratory and field experiments [8,28]. In this study, the effects of atmospheric water on the optical properties (absorption coefficient, single scattering albedo (SSA), and asymmetry parameter (ASY)) of soot aerosols with different mixing states (externally mixed, semi-embedded mixed, and internally mixed) have been investigated using theoretical studies. These findings should improve our understanding of the effects of atmospheric water on the optical properties of soot aerosols and their effects on the climate.

2. Mixing states of soot aerosols with atmospheric water

The in-situ and laboratory measurements [49,1,13] indicate that the pure BC particles consist of small spherical primary particles combined into branched and often-hydrophobic aggregates. Pure BC particles tend to be coated with a thin layer of other aerosol components in the atmosphere through the coagulation and condensation of secondary aerosol compounds. With the aging of the light absorbing carbon particles, most BC particles are thickly coated and tend to be compact. Coating BC particles with water-soluble compounds changes their hygroscopic properties [41,44,45,55,27], which tend to be hydrophilic. For thinly coated light absorbing carbon aerosols, the BC particles are thinly coated by other aerosol components, and the morphology of the BC particles is still visible. For heavily coated light absorbing carbon aerosols, however, the BC particles are embedded into other aerosol components, and the morphology of BC particles is not visible.

To quantify the effects of water on the optical properties of soot aerosols in different mixing states, we assume that only three chemical compounds exist in the soot aerosols: black carbon (BC), sulfates, and water. Based on transmission electron microscopy (TEM) measurements [20,46,31,29,2] and the hygroscopicity of soot aerosols, the three mixing states of soot aerosols with and without water were modeled: externally mixed; semi-embedded mixed and internally mixed.

Fig. 1 shows a schematic image of the three mixing states. Fig. 1a shows the external mixture of pure BC and sulfate particles without water. Due to the hydrophilic properties of sulfate, in the wet condition, the sulfate tends to be coated with a water shell; the external mixture with water is shown in Fig. 1d. As the pure BC particles age, the aggregates can become semi-embedded (Fig. 1b) or internally mixed with the sulfate particles (Fig. 1c), and the corresponding hydrous mixing states are shown in Fig. 1e and f, which feature uniform water coatings.

The morphologies of the soot aerosols can be modeled using the parallel diffusion limited aggregation (DLA) algorithm [34]. The construction and morphology of the fractal clusters can be described by a well-known statistical scaling law:

$$N_s = k_0 \left(\frac{R_g}{a}\right)^{D_f} \tag{1}$$

$$R_g^2 = \frac{1}{N_s} \sum_{i=1}^{N_s} r_i^2 \tag{2}$$

where N_s is the number of monomers in the cluster, a is the mean radius of the monomer. k_0 is the fractal prefactor, D_f is the fractal dimension, R_g is the radius of gyration, which represents the deviation of the overall aggregate radius in a cluster, and r_i is the distance from the ith monomer to the center of the cluster.

For the sake of simplicity, the sulfate particles are treated as homogeneous spheres that are either coated or embedded within water. Water is treated as a uniform coating on the surface of sulfate particles. The radius of the sulfate particles (R_{su}) is used to reconstruct the sulfate particle, while the equivalent volume radius of water (R_w) is used to indicate the water content on the sulfate particles. For theoretical calculations, R_w is a multiple of the radius of the soot monomer (a). We chose three representatives R_w: $0a$ (0 μm), $12a$ (0.18 μm), $24a$ (0.36 μm).

To simulate these types of soot-containing mixtures, the surfaces of the soot-containing models do not overlap for the single scattering calculations, due to the limitations of the superposition T-matrix approach [36]. The external sulfate/water and soot aggregate mixtures can be modeled easily using a common DLA method. Moreover, the internal mixtures are modeled further based on the spherical constraints of the larger sulfate/water particle. The geometric center of