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# Sensitivity of mixing states on optical properties of fresh secondary organic carbon aerosols

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ABSTRACT

At the beginning of the interaction of black carbon (or soot) and organic particles, fresh secondary organic carbon aerosols are generated by the dominant fractal aggregated soot monomers and the slight organic coatings. The complex morphologies and mixing states of these fresh secondary organic carbon aerosols significantly influence their optical properties. In this study, these heterogeneous particles were reconstructed using the fixed volume fraction model, and their optical properties are calculated using the discrete dipole approximation (DDA) method. For soot particles aged in a short time, the simulated absorption, scattering and single scattering albedo (SSA) showed a good agreement with the measurements. The amplifications of absorption and scattering between the thinly coated states (soot volume fraction equals 0.8, or the shell/core diameter ratio equals 1.08) and the freshly emitted states (bare soot with soot volume fraction equals 1) can reach to ~15% and ~35%, respectively. The simulations with these thinly coated states also indicated that the variations of morphologies may lead to the significant relative deviations on the absorption (up to ~15%) and scattering (up to ~100%) of these secondary aerosols. The effects of soot compactness and size on their optical properties were sensitive to the thickness of organic coatings, and larger organic refractive index may lead to larger absorption enhancements.



## 1. Introduction

Anthropogenic aerosols have modified the Earth's radiation balance by scattering and absorbing solar and longwave radiative transmission. Black carbon aerosols (BC, also called soot, or light absorbing aerosols) are primarily produced from incomplete burning of fossil fuel, biofuel, and biomass and are the dominant particle types having a strong warming effect on global climate [1]. It is observed that freshly emitted soot particles are aggregated by hundreds of tiny monomers. During the aging process, these fractal aggregated soot particles tend to be coated with organic materials, and generated the secondary organic carbon aerosols by heterogeneous reactions and photochemical oxidations [2–4]. Field studies showed that these organic coatings were growing thicker when the soot aging time continued. The mixing state of soot in the atmospheric aerosols approaches an internal mixture (coated soot particles) that leads to a much higher positive forcing than their external mixture [5,6]. The radiative forcing contribution of these light absorbing aerosols is still quite uncertain in climate forcing assessments because of the incomplete understanding of the radiative properties of these aerosols with complex morphologies and chemical compositions [7].

The effects of aggregation and heterogeneity on light scattering and absorption of these aerosol mixtures are remarkable. Previous laboratory experiments show that the coating of organic materials on soot particles leads to the significant enhancements of light absorption and scattering. The amplification of absorption cross section for soot internally mixed (or coated) with large organic materials was measured as ~150–200% [8–10]. In current climate models, these aerosols are commonly assumed to be a single homogenous or core-shell sphere, and their radiative properties are calculated using Mie theory. However, large discrepancies have been measured and simulated between these fractal aggregated heterogeneous aerosols and their equivalent simplification due to their complex morphologies, components, and mixing states [11–14]. The radiative forcing at the top of the atmosphere (TOA) was simulated as two times higher if freshly emitted black carbon is modeled as a fractal aggregate instead of a homogeneous sphere [15]. It is reported that the relative difference in the upward radiance due to the different mixing states can reach ~16%, whereas the relative difference of upward polarization can reach ~200% at TOA [16]. Soot coated with a concentric soluble shell yields radiative forcing estimates that are ~50% higher than those obtained with an external mixture model and ~40% lower than

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those with an internal mixture model [17]. Efforts to elucidate the morphology and mixing states of these secondary aerosols will reduce uncertainties when estimating their climate forcing on a regional and global scale.

Previous studies focus on the soot aggregates mixing with heavy coatings (large thickness), and showed remarkable absorption enhancements due to their internal mixing states [18,19]. For the heavily coated soot particles, the soot aggregates are fully embedded in the non-absorbing particles and hence the actual aerosol geometry approaches the coated sphere geometry, resulting in a closer agreement between measurements and simulations. However, previous models can hardly reproduce the optical properties of soot particles aged in a short time [8,20]. In this study, we tried to simulate and investigate the sensitivity of mixing states on optical properties of these secondary aerosols at the beginning of the interaction of freshly emitted soot and organic particles. In this mixing state, the freshly emitted soot aggregates may tend to be coated with a thin layer of organic materials, and still retain their fractal-like structures [21]. Fixed volume fraction model is applied for the reconstruction of these secondary organic carbon aerosols [22]. According to the given morphological and chemical parameters, soot monomers were aggregated and discretized into soot dipoles. Organic coating dipoles were further randomly coated on the soot dipoles. This model is able to explore the cases with high black carbon volume fractions (low organic-to-black carbon ratio) at the beginning of the interaction of freshly emitted soot and organic particles. Optical properties of these simulations with different morphological and chemical parameters are calculated using the discrete dipole approximation (DDA) method. The advantage of the DDA method is that it is applicable to arbitrary particle shapes and configurations [23,24]. The morphological and mixing states effects on their radiative properties are further investigated and discussed.

## 2. Method

### 2.1. Models of secondary organic carbon aerosols with various morphological and chemical properties

Freshly emitted soot particles consist of small spherical primary particles combined into branched aggregates, these soot monomers tend to be coated by a thin layer of organic materials. At the beginning of the interaction of freshly emitted soot and organic particles, the soot particles may retain their fractal-like structures, which can be described by the fractal law [25,26]. The equations were widely used in the simulations and measurements of fractal aggregated aerosols [27–29], as following:

$$Ns = k_0\left(\frac{Rg}{a}\right)^{Df} \tag{1}$$

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

where fractal dimension ( $D_f$), fractal prefactor ( $k_0$), number of monomers in an aggregate ($N_s$), and mean radius of the monomer ($a$) are used to reconstruct the morphology of the soot particles. For an aggregate $D_f$ describes its space-filling characteristic, while $k_0$ is strongly influenced by shape anisotropy (stringiness) and monomer packing density. $Rg$, called the radius of gyration, is a measure of the overall aggregate radius, $r_i$ is the distance from the $i$th monomer to the center of the cluster [30,31].

Soot volume fraction ($F_{soot}$) is applied for indicating the mixing states of soot particles and organic materials. Without organic coatings, the soot volume fraction of freshly emitted soot particles equals 1 ( $F_{soot} = 1$). During aging process, the secondary organic carbon aerosols were generated by the interaction of freshly emitted soot and organic particles, and coating more organic materials leads to smaller soot volume fraction. This study tried to investigate the optical properties of these secondary aerosols at the beginning of the aging, thus, the cases of $0.8 \le F_{soot} \le 1$ were considered. In previous studies, similar ratios were also presented for indicating the mixing states of soot and organic particles, including the organic-to-black carbon ratio $\left(F_{OA/BC} = \frac{1}{F_{soot}} - 1\right)$ [20].

In this study, the organic materials were simulated to be randomly and discretely distributed on the surfaces of soot monomers. The fixed volume model is applied for the modeling of secondary organic carbon aerosols with various morphological and chemical properties [22]. First, freshly emitted soot particle was simulated by aggregating hundreds of ( $N_s$) spherical monomers with constant radii ( $a$), and their morphologies were constrained by the fractal law. Further, these soot monomers were discretized into dipoles by a suitable D/d ratio (D: diameter of soot spherical monomers; d: dipole space). This D/d ratio was determined by the accuracy demand of the DDA method. More accurate results can be calculated with more dipole numbers, but computation time would be dramatically increased [32]. According to the numbers of soot discrete dipoles $\left(N_{soot}^{dipoles}\right)$ and the soot volume fraction ( $F_{soot}$), the exact numbers of organic dipoles $\left(N_{organic}^{dipoles} = N_{soot}^{dipoles} \times \frac{1-F_{soot}}{F_{soot}}\right)$ can be fixed. After that, to simulate the mixing process of the soot and organic aerosols [21,33], these organic dipoles were randomly adhered to the discrete dipoles in a continuous way, until the added organic dipoles reached to their given numbers $\left(N_{organic}^{dipoles}\right)$, as shown in Fig. 1.

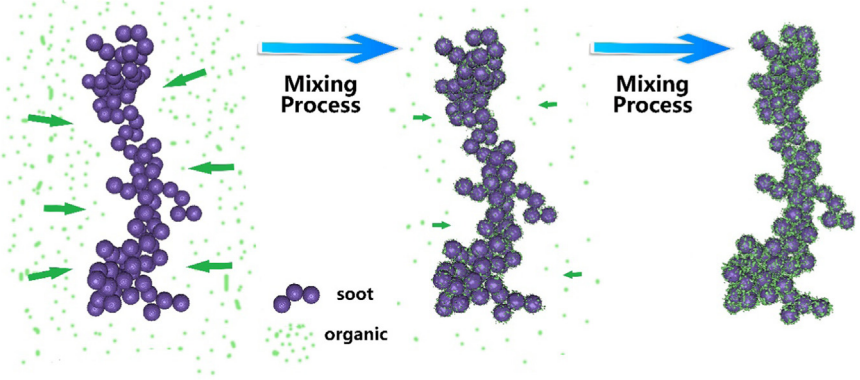


**Fig. 1.** Schematic diagram for the generation of secondary organic carbon aerosols composed of fractal aggregated soot particles and organic coatings.