

In-situ measurements of the mixing state and optical properties of soot with implications for radiative forcing estimates

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Our ability to predict how global temperatures will change in the future is currently limited by the large uncertainties associated with aerosols. Soot aerosols represent a major research focus as they influence climate by absorbing incoming solar radiation resulting in a highly uncertain warming effect. The uncertainty stems from the fact that the actual amount soot warms our atmosphere strongly depends on the manner and degree in which it is mixed with other species, a property referred to as mixing state. In global models and inferences from atmospheric heating measurements, soot radiative forcing estimates currently differ by a factor of 6, ranging between 0.2–1.2 W/m², making soot second only to CO₂ in terms of global warming potential. This article reports coupled in situ measurements of the size-resolved mixing state, optical properties, and aging timescales for soot particles. Fresh fractal soot particles dominate the measured absorption during peak traffic periods (6–9 AM local time). Immediately after sunrise, soot particles begin to age by developing a coating of secondary species including sulfate, ammonium, organics, nitrate, and water. Based on these direct measurements, the core-shell arrangement results in a maximum absorption enhancement of 1.6× over fresh soot. These atmospheric observations help explain the larger values for soot forcing measured by others and will be used to obtain closure in optical property measurements to reduce one of the largest remaining uncertainties in climate change.

aerosol | atmosphere | climate | composition

Soot particles represent the most strongly absorbing class of atmospheric aerosol at visible wavelengths and thus may warm the earth's surface directly by absorbing the incoming radiation from the sun. The direct forcing by soot depends not only on its optical properties but also on the altitude of the layer and the amount of reflection from below. Furthermore, when soot is deposited, it can accelerate the melting of ice and snow. Indirectly, soot can alter climate by heating the atmosphere and changing atmospheric dynamics, or by serving as nuclei for cloud formation, thereby changing cloud properties (1, 2). Not surprisingly, the importance of soot to climate change has been a major focus of many modeling, laboratory, and field studies (3–10). Recent investigations involving direct atmospheric measurements of soot particles suggest that they may have a global warming potential second only to CO₂ (11–13). The aforementioned modeling studies predicting higher radiative forcing values model soot particles as a core of strongly absorbing soot surrounded by a nonabsorbing shell. However, large uncertainties still exist in estimates of the radiative forcing of soot because of the lack of detailed in situ measurements of the mixing state and the associated optical properties as a function of particle size. These uncertainties limit our ability to quantify the relative impacts of soot on climate, thus limiting our ability to make effective policy decisions (14).

To reduce the uncertainties associated with atmospheric soot particles, direct measurements are required to quantify the chemical, physical, and optical characteristics of soot. The

optical properties of soot are very sensitive to the manner in which each particle is mixed with other species such as condensed organic carbon, sulfate, nitrate, and water. As soot particles age, they become coated by nonabsorbing species produced as a result of gas-phase oxidation reactions. Many studies suggest the use of a single particle optical model of an absorbing spherical core surrounded by a mantle of nonabsorbing material is appropriate for aged aerosol (5, 8, 14). Based on modeling and laboratory studies, a strongly absorbing soot particle surrounded by a nonabsorbing shell has been shown to enhance particle absorption by up to a factor of 3 (4, 15–18). In these cases, the use of the core-shell model serves as an excellent model system for aged aerosols. However, for fresh soot aerosols, such core-shell models may be unreliable for accurately predicting the optical properties of highly nonspherical particles with small coatings (5, 16, 19). Thus, it is crucial to determine how long it takes freshly emitted soot particles in an urban environment to convert to aged coated spheres to confidently predict atmospheric heating rates by using the core-shell assumption.

Measurements have been advancing so that it is possible to determine the detailed structure and chemical composition of soot particles. Using coupled incandescence and scattering at infrared wavelengths, coated soot particles can be inferred in real-time (20). Detailed measurements of the chemical composition and morphology of soot can be obtained with electron microscopy techniques (21, 22). These measurements support the use of modeling soot as an internal mixture with core-shell morphologies. However, microscopy techniques are performed in the laboratory and in a vacuum, which can change the morphology of the soot particles due to how they are impacted on the substrate; evaporation of water and other semivolatile species may also occur. Furthermore, the counting statistics provided by particle microscopy are often limited and thus may not be fully representative of ambient soot particles.

Over the past decade, mass spectrometers have been developed to measure the chemical composition and size of single atmospheric soot particles in real-time by using a combination of aerodynamic sizing and laser desorption ionization mass spectrometry. A most recent and promising advance in single particle mass spectrometry yields aerosol optical properties by measuring the intensity of scattered light as each particle passes through lasers originally used for aerodynamic sizing. These optical measurements have been applied to nonabsorbing ambient particles with different chemical mixing states and modeled by using Mie theory, thereby providing refractive index and density information (23). In this report, these in situ measurements of

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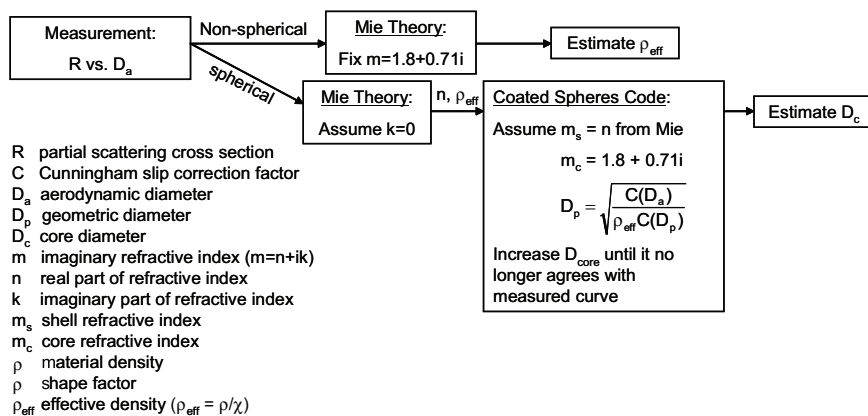


Fig. 5. A flow chart is showing the calculation steps used to estimate ρ_{eff} and D_c .

optical and atmospheric heating rate measurements (30) to derive accurate radiative forcings that can be used to predict the regional and global impacts of soot on future climate. Optical properties derived from such studies calculations are more physically based than models employing volume weighted refractive indices to represent atmospheric soot particles.

Conclusions

In this study, we have provided direct measurements of the optical and microphysical characteristics of atmospheric soot particles, showing how they can quickly evolve within an urban environment. Within 3 h after sunrise, photochemical activity results in the rapid conversion of fresh nonspherical soot to aged spherical coated soot particles, which become the dominant contributor to aerosol absorption in the middle of the day. By the time soot reaches rural and remote locations, it will acquire even more secondary material because of the longer time spent in the atmosphere. The aged soot measured in Riverside contained significant coatings acquired during transport across the Los Angeles air basin compared with relatively fresh soot particles at the center of Mexico City. It is well-documented that the Mexico City basin is flushed out on a daily basis by favorable meteorological conditions. Thus, differences in the meteorological conditions at the 2 urban locations resulted in both a larger absorption enhancement and a single scattering albedo for Riverside. Based on these in situ measurements, we conclude that for models to accurately describe soot in the ambient atmosphere, it is most appropriate to use a core size $\approx 100\text{--}200$ nm with age-dependent coatings composed of sulfate, nitrate, water, and organic carbon having refractive indices ranging from 1.44–1.49.

Methods

In each of the field campaigns discussed in this study, an aerosol time-of-flight mass spectrometer (ATOFMS) with a converging nozzle inlet was used (31). For this article, it is important to note that this nozzle does not remove a measurable amount of semivolatile species or water from the particles (23). Measurements in Riverside, California ($33^{\circ}58'18.16\text{N}$, $117^{\circ}19'21.44\text{W}$) were carried out as part of the Study of Organic Aerosols in Riverside (SOAR-2) campaign from October 27 to November 21, 2005. Measurements in Mexico City ($19^{\circ}29'23.22\text{N}$, $99^{\circ}08'55.76\text{W}$) took place from March 7–31, 2006 as part of the Megacity Initiative: Local and Global Research Operations (MILAGRO) campaign. For each study, particle classification was carried out on single particle mass spectra by using the ART-2a algorithm (32). ART-2a was run with a vigilance factor of 0.80 and regrouped with a vigilance factor of 0.85. Soot clusters were isolated based on their mass spectral patterns before the light scattering analysis.

Details showing how refractive index and density were derived from Mie theory were described in detail in earlier work (33). The scattering data analysis procedure used herein is similar to that outlined in ref. 33, but has been refined (23). Because the soot particles considered in this study are internally mixed with nonabsorbing species and many have nonspherical shapes, not enough informa-

tion exists to determine both the refractive index and density of each component as was done for nonabsorbing spherical particles in our previous work (33).

To estimate effective density (ρ_{eff}) for nonspherical particles and core size (D_c) for spherical soot particles, we followed the steps shown in the flow chart in Fig. 5. Following the chart from left to right, we start from the measurements of the partial scattering cross section (R) and aerodynamic diameter (D_a). Based on the scattering pattern for a specific particle type, it is either classified as spherical or nonspherical. For nonspherical particles, it is assumed that the particles have an imaginary refractive index ($m = n + ik$) of pure soot ($m = 1.8 + 0.71i$) to retrieve the particle effective density (ρ_{eff}) by using the methodology of Cross et al. (34). For spherical particles, an inversion is first done by using Mie theory, assuming $k = 0$, to obtain a range of shell refractive index (m_s) and ρ_{eff} . This method was carried out at upper and lower 95% confidence intervals to retrieve estimates for m_s and ρ_{eff} . By using these bounds for m_s and ρ_{eff} from the Mie calculation, in addition to an assumed core refractive index of $m_c = 1.8 + 0.71i$, the core size is then varied to obtain a best fit constrained by the measurements.

For the measured scattering curves in Fig. 2, the large number of points that do not follow the theoretical upper limit represent particles that clip the laser beam because of the divergence of the particle beam. We have found that if the particles are nonspherical, a larger population will clip the laser beam because of lift forces perpendicular to the particle beam axis. In this way, by binning the particle intensity at a fixed size, we can tell whether or not the particles are statistically different from a sphere. We have found that the aged EC particles used in the core shell calculations here have pulse-height distributions that are not statistically different from those of a sphere. Thus, we have proven that the aged EC particles are spherical and have justified the use of our spherical model for aged particles.

To derive size distributions for the single particle types described herein, we have scaled up the ATOFMS counts to the measured size distributions. To further constrain the size distribution measurements, we have assumed that fresh soot was less efficiently detected by the ATOFMS than spherical soot because of particle beam divergence. We therefore scaled the counts of the fresh soot particles in the smallest size mode (≈ 150 nm) to match the total amount of soot measured with absorption measurements during the early morning periods. The resulting size distributions and log-normal fits for the fresh and aged types are shown in Fig. 3.

The soot size distributions and optical measurements were combined to calculate the absorption coefficient (β_{abs}):

$$\beta_{\text{abs}} = \int_{-\infty}^{\infty} \sum_{D_c} C_{\text{abs}}(D_c, D_s) f_c(D_c) \frac{dN}{d \log D_s} d \log D_s$$

where C_{abs} is the absorption cross section, N is the number concentration, D_s is the shell diameter, and f_c is the number fraction of particles having a core diameter D_c . C_{abs} was calculated by using the coated spheres code, which used the parameters obtained from the measurements described in *Methods* and listed in Table 1. The integrated single-scattering albedo was calculated as $\beta_{\text{sca}}/(\beta_{\text{sca}} + \beta_{\text{abs}})$, where β_{sca} is the scattering coefficient calculated in the same manner as β_{abs} .

