

Particle Size Relationships at the Fresno Supersite

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ABSTRACT

Aerosol size distributions are presented for a winter intensive study at the Fresno Supersite. The size distributions were consistent with and predictive for continuous $PM_{2.5}$ measured by beta attenuation. They varied temporally with respect to source type and intensity, with the smallest mean diameters associated with high NO_x concentrations during weekday morning rush hours. Conversely, small and large particle and black carbon (BC) concentrations were higher during Sunday and weekday evenings in response to traffic and residential wood combustion emissions. Ambient $PM_{2.5}$ light scattering (Bsp) was precisely but systematically underestimated during winter, probably because of heating in the sample shelter.

INTRODUCTION

The U.S. Environmental Protection Agency (EPA) Supersites program examines atmospheric measurement technologies, source contributions and control strategies, and the effects of atmospheric particles on human health.¹ A major research goal at the Fresno Supersite is to evaluate nonroutine monitoring methods.² Measurements include high-resolution meteorology, $PM_{2.5}$ and PM_{10} mass, black carbon (BC), NO, NO_2 , NO_x , NO_y , O_3 , PAH, particle NO_3^- , and dry $PM_{2.5}$ and ambient TSP light scattering (Bsp).² In addition, particle size distributions from 0.009 to 10 μm are measured continuously. These measurements are motivated in part by concerns that ultrafine (i.e., nanometer-sized) particles adversely affect human health.³ In this paper, aerosol size distributions at the Fresno Supersite and their relationships with various chemical

and physical parameters are described. Light scattering estimated from the particle size distributions is compared with measured Bsp. It is expected that long-term, continuous measurements will be of sufficient quality to address air-quality and public-health issues. The detailed characterization of the aerosol size distribution should be particularly useful in the latter regard.

METHODS

The Fresno Supersite is located at 3425 First Street. A four-lane road with residential areas lies to the east, and commercial facilities, schools, and office buildings lie to the west, north, and south. The sampler is located in a second-story room with inlets ~10 m above the ground. This paper focuses on the period from December 15, 2000, through February 3, 2001, when an intensive series of continuous gas and particle and filter-based measurements was made. Particle-size distributions are measured through a PM_{10} inlet with a TSI SMPS 3936L10 (scanning particle mobility particle sizer: 0.009–0.392 μm diameter in 52 channels) and a PMS Lasair (LAS) 1003 optical particle counter (0.1–2 μm in 7 channels). The SMPS sizes particles based on their mobility in an electric field. While the SMPS data were adjusted for the decrease in small-particle counting efficiency, no attempt was made to correct for particle losses in the sample stream. However, such losses are expected to be on the order of 10% for particles with diameters of 20 nm. The LAS counts and sizes individual particles according to the amount of light each scatters at 633 nm. The instrument was factory-calibrated for size with polystyrene latex beads (Duke Scientific) with a refractive index of 1.59, i0.0. Because the office is environmentally controlled, the measured sizes are assumed to represent “dry” particles during the winter intensive.

Hourly-average PM_{10} and $PM_{2.5}$ mass were measured with Met One 1020 beta attenuation monitors (BAM). Meteorological measurements [wind speed and direction, temperature, pressure, relative humidity (RH), and solar irradiance] were made on a 5-min time base. TEI 42, API 400, and McGee AE14U aethalometer monitors were used

IMPLICATIONS

Long-term, continuous measurements of particle size distributions at the Fresno Supersite exhibit consistent and reasonable relationships with gas and particle pollutant concentrations, source emissions, and light scattering. The results suggest that such measurements will be useful for addressing air-quality as well as human-health issues.

to determine 5-min average NO_x/NO , O_3 , and BC concentrations, respectively. "Dry" $\text{PM}_{2.5}$ particle light scattering was measured on a 5-min time base with a Radiance M903 nephelometer at 530 nm. Total (TSP) Bsp was also measured at ambient RH with an open NGN-2 nephelometer. All measurements were averaged on an hourly basis in the following analysis.

RESULTS AND DISCUSSION

The average winter intensive SMPS and LAS size distributions are plotted in Figure 1. The distributions were approximately lognormal and were similar to those found in other urban environments.^{4,5} Hourly-average integrated particle number concentrations averaged $22,000 \text{ cm}^{-3}$ and ranged from 2700 to $89,000 \text{ cm}^{-3}$. The number-weighted mean diameter (MD) averaged $0.066 \mu\text{m}$ and ranged from 0.021 to $0.109 \mu\text{m}$. Figure 2 compares SMPS and LAS integrated particle number concentrations for overlapping size channels of the two instruments (0.1 to $\sim 0.4 \mu\text{m}$). The LAS particle concentrations were systematically higher by $\sim 20\%$, on average. For 965 of 1161 hourly periods with $\text{SMPS} < 10,000 \text{ cm}^{-3}$, the average ratio of LAS/SMPS was 1.28 ± 0.29 , while for 196 cases with $\text{SMPS} > 10,000 \text{ cm}^{-3}$, the ratio was 0.89 ± 0.01 .

The differences between the LAS and the SMPS may be related to evaporative losses in the heated sample shelter. Based on the instrument flow rates and their locations in the shelter, it is estimated that particles sampled by the SMPS spend ~ 5 times longer in the heated shelter than particles sampled by the LAS. This could result in an apparent loss of SMPS particles from the region of overlap with the LAS. However, the relative responses of the two instruments appear to be very stable, suggesting that these measurements are well suited to evaluating relationships with other parameters. For example,

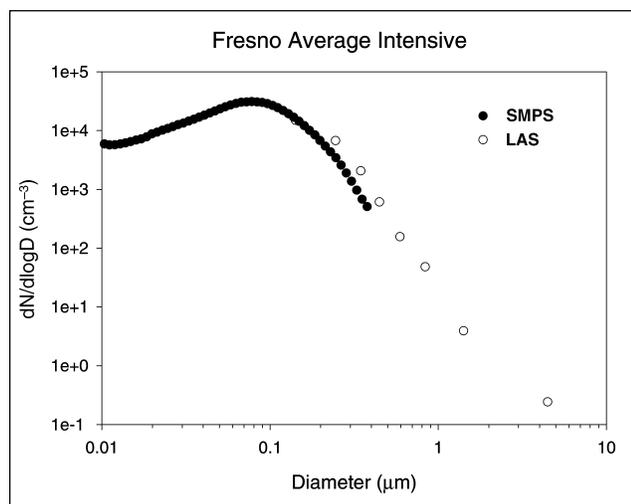


Figure 1. Average SMPS and LAS size distributions during the winter intensive study at the Fresno Supersite.

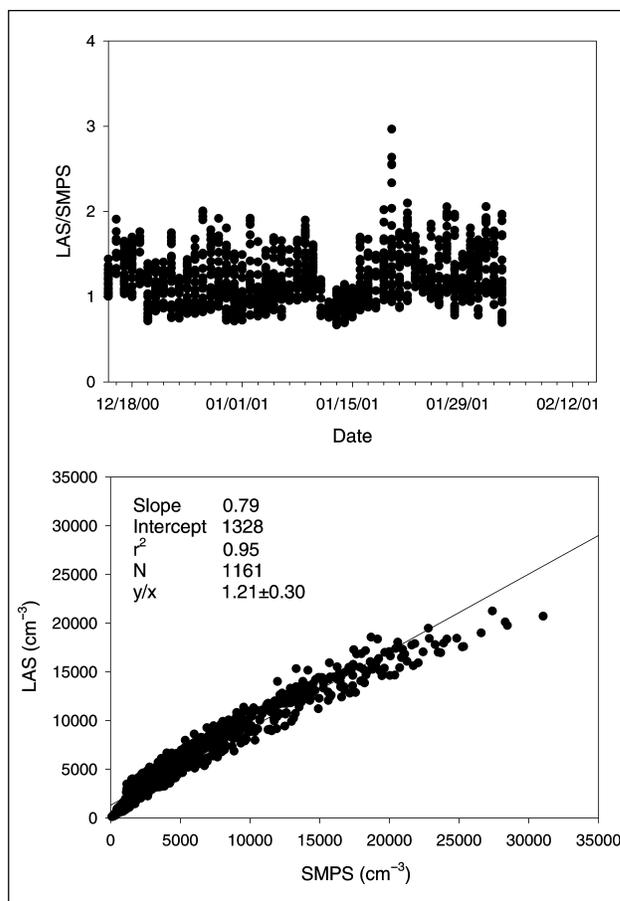


Figure 2. The relationship between LAS and SMPS concentrations for particles with diameters between 0.1 and $0.4 \mu\text{m}$.

Figure 3 shows that BAM $\text{PM}_{2.5}$ mass and LAS particle number concentrations for diameters greater than $0.3 \mu\text{m}$ were highly correlated ($r = 0.95$). Including particles smaller than $0.3 \mu\text{m}$ reduced the correlation to 0.87. This is reasonable because particle mass is dominated by the larger particles. Similar relationships between particle

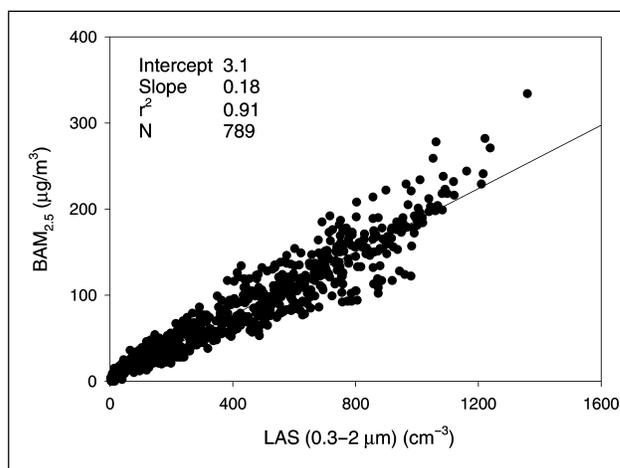


Figure 3. The relationship between BAM $\text{PM}_{2.5}$ and LAS particle concentrations ($0.3\text{--}2 \mu\text{m}$).

counts and $PM_{2.5}$ and PM_{10} mass were observed in Birmingham, England.⁴

In wintertime, the dominant sources of aerosol mass at the Fresno Supersite are emissions from motor vehicles, especially during rush hours, and residential wood combustion during the evening hours.^{2,6} Figure 4 shows hourly-average SMPS particle concentration from 0.009 to 0.392 μm , LAS particle concentration for diameters greater than 0.3 μm , the SMPS MD, and NO_x and BC concentrations over the average weekday diurnal cycle. During the morning rush hour [5:00–9:00 a.m. Pacific Standard Time (PST)], there were peaks in NO_x , SMPS, and BC concentrations accompanied by a minimum in the MD and a relative minimum in the LAS particle concentration. This suggests that fresh motor vehicle emissions in the morning were associated with the smallest particles. As pollutant and SMPS particle concentrations decreased thereafter, the MD increased from 8:00 to 11:00 a.m. PST. This increase may be related to the loss of small particles by coagulation. Pollutant and SMPS and LAS particle concentrations all increased from 4:00 to 9:00 p.m. PST, but during this period, the MD also increased. The increase in concentration is in part caused by the development of the nighttime inversion, but the concurrent increase in LAS and BC concentrations and the MD suggests the impact of residential wood combustion in addition to motor vehicle emissions.

Measurements were averaged for 2-hr periods in the weekday morning (7:00 and 8:00 a.m. PST) and weekday

evening (8:00 and 9:00 p.m. PST). The SMPS and LAS size distributions are plotted for both periods in Figure 5. Note that the morning distribution was broader and shifted to smaller sizes. The morning and evening mean diameters were 0.052 and 0.070 μm , respectively. While NO_x concentrations were similar for both periods, BC and LAS particle concentrations were higher by nearly a factor of 2 in the evening. Particle concentrations at 0.1 μm were nearly 4 times higher in the evening. Higher evening concentrations of both BC and large particles are consistent with wood burning, for which combustion occurs at lower temperatures and is thus less efficient than for motor vehicles. The peak evening SMPS particle concentrations occurred after 8:00 p.m. PST, which is somewhat later than the evening rush hour, and persisted until about 1:00 a.m. PST. Filter-based measurements also support higher concentrations of wood-smoke emissions during the evening. Average ratios of soluble K, a marker for vegetative burning,⁷ to $PM_{2.5}$ mass were 0.0065 and 0.0048 for sample periods from 4:00 p.m. to 5:00 a.m. and 5:00 a.m. to 4:00 p.m. PST, respectively.

The evolution of the particle size distribution over the diurnal cycle represents a complex interaction of meteorology, emissions, chemistry, and dynamics. In general, the evening and early morning hours are characterized by stagnant conditions under a strong surface inversion. As the mixed layer deepens during the day, particle concentrations are reduced by vertical and horizontal dispersion but also are influenced by more or less

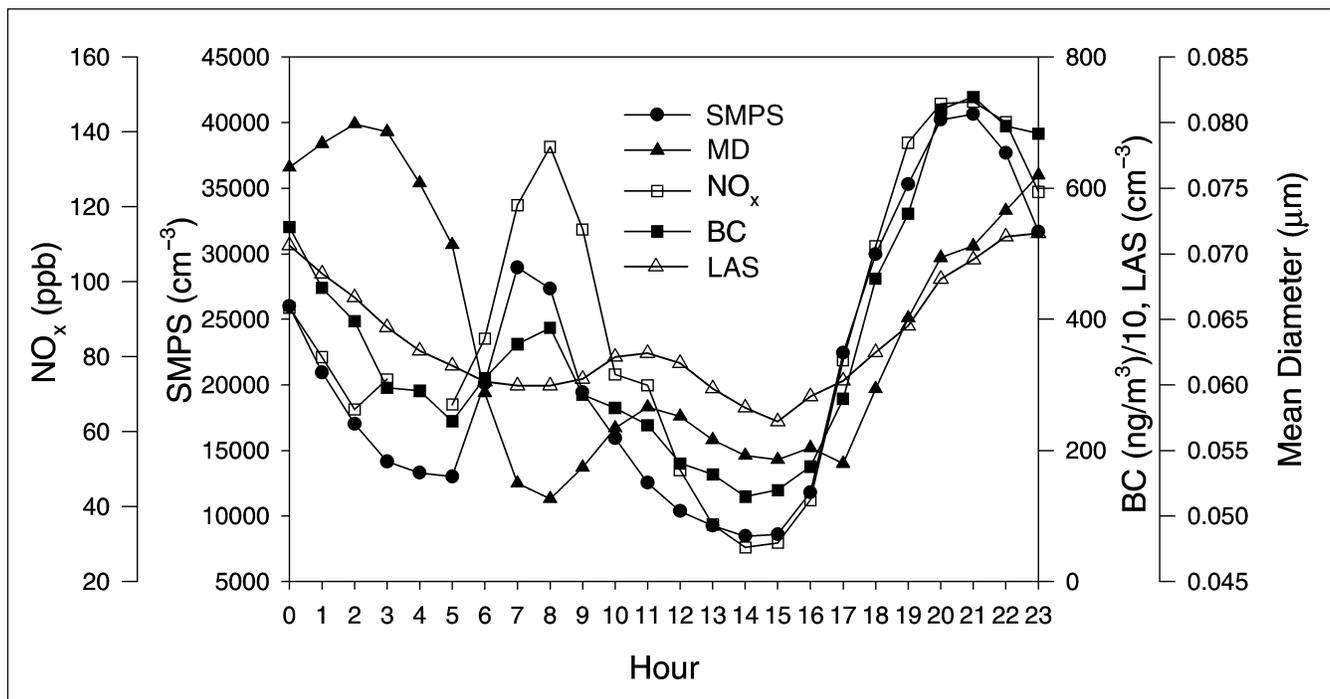


Figure 4. Average weekday diurnal variations of SMPS particle concentration (0.009–0.392 μm), MD, NO_x , BC, and LAS particle concentration (0.3–2 μm).

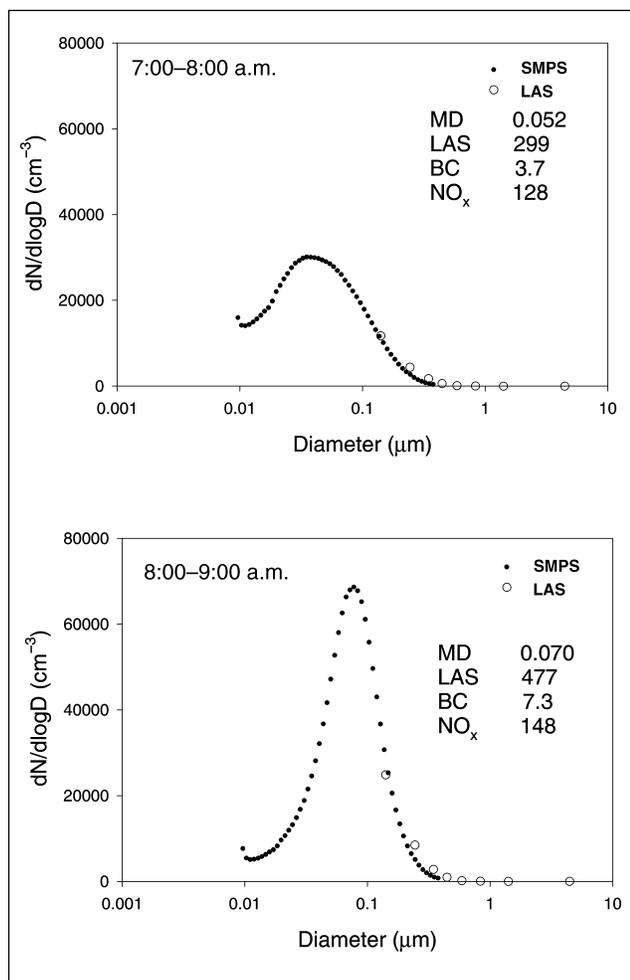


Figure 5. Average size distributions and chemical concentrations for weekday morning (7:00–8:00 a.m. PST) and evening (8:00–9:00 p.m. PST) periods. Units are MD (μm), LAS (cm^{-3} for 0.3–2 μm), BC ($\mu\text{g}/\text{m}^3$), and NO_x (ppb).

distant emissions advected to the site. New particles are produced and existing particles grow through photochemically mediated gas-to-particle conversion.^{8,9}

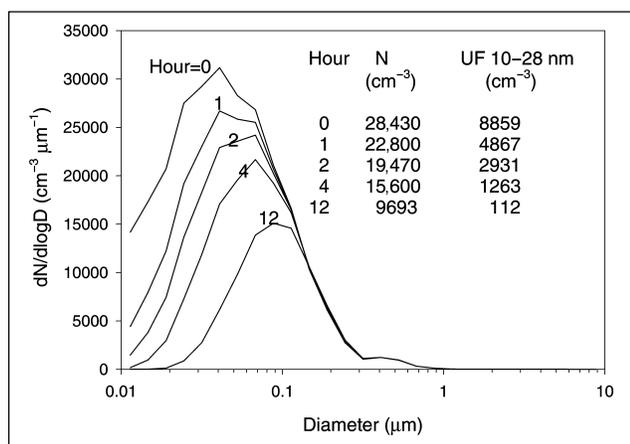


Figure 6. Estimated evolution of the average weekday morning size distribution through coagulation.

The evolution of the average 7:00–8:00 a.m. PST Fresno size distribution, with respect to coagulation, was examined using the multicomponent aerosol time evolution (MAEROS) model.¹⁰ The system was assumed to be static (i.e., no addition or removal of particles by advection or deposition and no gas-to-particle conversion). The model simulates the interaction of particles among a user-specified number of size bins. The results are shown in Figure 6 after 1, 2, 4, and 12 hr. Figure 6 shows the decrease in total (N) as well as ultrafine (UF—defined here as 0.010–0.028 μm) particle concentration over time resulting solely from coagulation. Note that while the half-life of the total particle number concentration is about 4 hr, that of the UF fraction is just more than 1 hr.

Coagulation by itself does not adequately explain the observed diurnal variation of the Fresno aerosol. This is illustrated by Figure 7, which plots average N and UF concentrations and the ratio of UF to N over the weekday diurnal cycle. On average, the UF accounted for 22.5% of the total. There were peaks in the UF at 7:00 a.m. PST and 5:00 p.m. PST, which roughly corresponded with the morning and evening rush hours. While the total particle concentration increased dramatically thereafter, the UF continued to decline. Assuming that the UF were characteristic of fresh motor vehicle emissions, their decline in the evening is consistent with a non-motor-vehicle source. The UF/N ratio peaked during the morning rush hour and then declined until about 11:00 a.m. PST. Although most of the decrease in UF from 8:00 to 11:00 a.m. PST was probably related to the concurrent decrease in the total particle concentration, the decrease in the UF/N ratio may also indicate losses caused by coagulation. The peak in the UF/N ratio occurred at about 3:00 p.m. PST, when the total was at its daily minimum. It is possible that this represents production of UF by gas-to-particle conversion rather than by primary emissions.

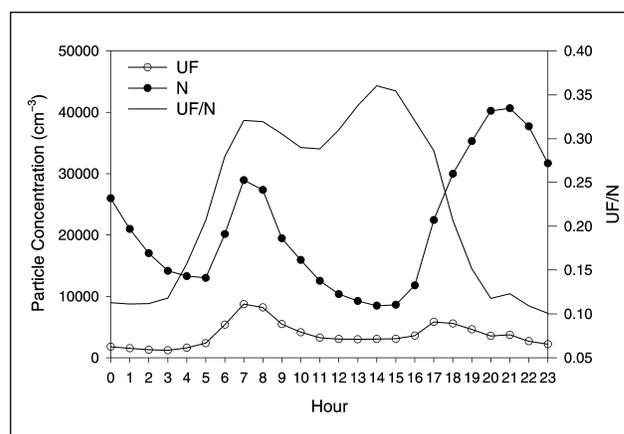


Figure 7. Average diurnal variation of the UF and N and the ratio of UF/N. N = total number and UF = number in the 0.01–0.028 μm range.

Finally, the consistency between the measured particle size distribution and light scattering was examined. The aerosol sampled with the Radiance PM_{2.5} nephelometer was dried to an average RH of 57%. The Bsp was estimated at 530 nm from the measured size distributions using Mie theory.¹¹ Hourly SMPS concentrations from 0.0093 to 0.392 μm were combined with LAS concentrations from 0.4 to 2 μm. The complex index of refraction of the Fresno aerosol was estimated from its average chemical composition [30, 4, 57, 8, and 1% NH₄NO₃, (NH₄)₂SO₄, organic carbon, elemental carbon, and geological dust, respectively] as 1.579, i0.05.¹² Measured and estimated Bsp are compared in Figure 8. While the r² was high (0.93), Bsp was systematically underestimated. A comparison of the Radiance and NGN-2 nephelometers for a limited number of cases at low ambient RH do not support a high bias in the Radiance measurement.

As noted previously, it is likely that Bsp was underestimated because of systematic undersizing caused by evaporation of particles in the sample shelter. The average difference between the temperature measured in the SMPS cabinet and the ambient temperature was 17 °C. It is likely that NH₄NO₃, a significant component of PM_{2.5}, and perhaps some organic material, were volatilized in the SMPS, reducing the size of the particles that most efficiently scatter light (e.g., >0.1 μm). Complete evaporation of the more numerous but smaller particles, whose optical scattering efficiencies are up to 4 orders of magnitude lower, would not have had an appreciable effect on measured Bsp. While some heating occurred in the Radiance nephelometer, it probably was not as much as that experienced by the aerosol in the SMPS. To test this hypothesis, these calculations were repeated for samples collected from June to August 2001, using the same refractive index. The results, shown in Figure 8, indicate little underestimation of Bsp. During summer, there was only a small difference between the SMPS and ambient temperatures (-2 °C).

The implication of these observations for interpreting the winter intensive size distributions is that they may have represented mainly primary carbonaceous plus primary and secondary SO₄²⁻ particles. NH₄NO₃ that may have been volatilized would always have been secondary. It does not follow that the winter UF fraction was undercounted because of evaporation of NH₄NO₃ in the SMPS. Particle nucleation has been associated with sulfates in remote and urban environments.^{8,9} Shi et al. concluded that UF particles smaller than 50 nm in diesel exhaust were produced by homogeneous nucleation of H₂SO₄.¹³ However, while the total particle concentration was higher in winter than in summer (22,000 vs. 14,500 cm⁻³, respectively), the UF particle concentration was higher in summer (5000 cm⁻³) than in winter (3400 cm⁻³). This is

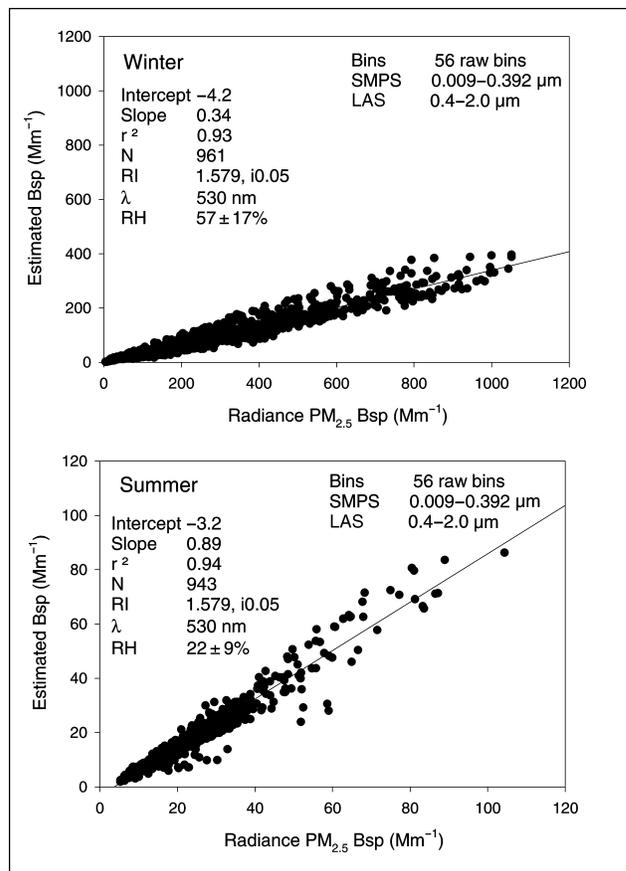


Figure 8. Comparison of estimated and measured dry Bsp in winter (top) and summer (bottom).

probably because of enhanced photochemical production during summer.

CONCLUSIONS

Continuous size distributions at the Fresno Supersite during winter are consistent with and predictive of PM_{2.5} mass. Measured particle sizes and concentrations varied diurnally with smaller particles associated with morning rush hour emissions. Higher large particle and BC concentrations and larger mean diameters during weekday evenings may be related to a combination of emissions from residential wood combustion and motor vehicles. The observed decrease in the ratio of UF to N particle concentration after the morning rush hour is consistent with losses expected from coagulation. The Bsp estimated using Mie theory from the measured size distributions was systematically lower than measured dry Bsp during winter, although the precision was very high (r² = 0.93). During the following summer, however, measured and estimated Bsp agreed much more closely. This is attributed to a reduction of particle size caused by evaporation of NH₄NO₃ and possibly organic material in the heated shelter during winter. Nonetheless, the results demonstrate systematic and consistent

relationships among particle concentrations and other chemical and physical parameters at the Fresno Supersite. Thus, long-term continuous particle size measurements are expected to be useful in evaluating air-quality and public-health issues.

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