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Concentration and Size Distribution of Ultrafine Particles Near a Major Highway

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ABSTRACT

Motor vehicle emissions usually constitute the most significant source of ultrafine particles (diameter <0.1 μm) in an urban environment, yet little is known about the concentration and size distribution of ultrafine particles in the vicinity of major highways. In the present study, particle number concentration and size distribution in the size range from 6 to 220 nm were measured by a condensation particle counter (CPC) and a scanning mobility particle sizer (SMPS), respectively. Measurements were taken 30, 60, 90, 150, and 300 m downwind, and 300 m upwind, from Interstate 405 at the Los Angeles National Cemetery. At each sampling location, concentrations of CO, black carbon (BC), and particle mass were also measured by a Dasibi CO monitor, an aethalometer, and a DataRam, respectively. The range of average concentration of CO, BC, total particle number, and mass concentration at 30 m was 1.7–2.2 ppm, 3.4–10.0 μg/m^3, 1.3–2.0 $\times$ 10^5/cm^3, and 30.2–64.6 μg/m^3, respectively.

For the conditions of these measurements, relative concentrations of CO, BC, and particle number tracked each other well as distance from the freeway increased. Particle number concentration (6–220 nm) decreased exponentially with downwind distance from the freeway. Data showed that both atmospheric dispersion and coagulation contributed to the rapid decrease in particle number concentration and change in particle size distribution with increasing distance from the freeway. Average traffic flow during the sampling periods was 13,900 vehicles/hr. Ninety-three percent of vehicles were gasoline-powered cars or light trucks. The measured number concentration tracked traffic flow well. Thirty meters downwind from the freeway, three distinct ultrafine modes were observed with geometric mean diameters of 13, 27, and 65 nm. The smallest mode, with a peak concentration of 1.6 $\times$ 10^5/cm^3, disappeared at distances greater than 90 m from the freeway. Ultrafine particle number concentration measured 300 m downwind from the freeway was indistinguishable from upwind background concentration. These data may be used to estimate exposure to ultrafine particles in the vicinity of major highways.

IMPLICATIONS

Although they constitute only 1–8% of the mass of particulate matter (PM) in ambient air, ultrafine particles have been suggested as a possible causative agent for increases in mortality and morbidity associated with increases in PM concentration. Motor vehicle emissions usually constitute the most significant source of ultrafine particles in an urban environment, yet little is known about their concentration and size distribution in the vicinity of major highways. The present study, conducted in the vicinity of Interstate 405, shows that particle number concentration near the freeway was ~25 times greater than that at background locations, and that the concentration of ultrafine particles drops to background levels within 300 m downwind of the freeway.

INTRODUCTION

Throughout the past decade, epidemiologic studies have reported a consistent relationship between increases in particulate matter (PM) exposure and contemporary increases in mortality and morbidity.[1-4] However, the underlying biological causes of the health effects of PM exposure and the correct measurement metric are unclear. For example, it is unclear whether the mass concentration[5] or the number concentration[6,7] is most important in causing these adverse PM health effects. The particle size of airborne PM controls where the inhaled particles deposit in the various regions of the human respiratory system by the complex mechanisms of aerosol deposition.[8] Recent toxicological studies have concluded that, at the same mass concentration, ultrafine particles (diameter <100 nm) are more toxic than larger particles with the same chemical composition.[9-15] Recent dosimetry studies have reported that the total deposition fraction of

ultrafine particles increases as particle size decreases,[16,17] with the greatest fractional deposition in the deep lung occurring between 5 and 100 nm.[17] Currently, however, only the mass of PM less than 10 μm (PM_{10}) and less than 2.5 μm ($PM_{2.5}$) in aerodynamic diameter are regulated. Information about ultrafine particles is usually not available, even though ultrafine particles represent 80% of the particle number concentration in an urban environment.[18] The less numerous but much heavier supermicrometer particles dominate mass concentration measurements. Thus, both number concentration and the size distribution of ultrafine particles are needed to better understand ambient air quality and its potential health effects.

In an urban environment, motor vehicle emissions usually constitute the most significant source of ultrafine particles.[19,20] Although traffic-related air pollution in urban environments has been of increasing concern, most studies have focused on gaseous pollutants and the total mass concentration and chemical composition of particulate pollutants.[21-26] Because the majority of particles from vehicle exhaust are in the size range of 20–130 nm for diesel engines and 20–60 nm for gasoline engines,[27,28] it is important and necessary to quantify ultrafine particle emission levels and to determine ultrafine particle behavior after emission as they are transported away from the emission source—busy roads and freeways. Previously, researchers have measured the horizontal and vertical profiles of submicrometer particulates (16–626 nm) near a major arterial route in the urban area of Brisbane, Australia.[29] They found that, with the exception of measurements in close proximity to the road (~15 m), the horizontal profile measurements did not show statistically significant differences in fine particle number concentration at ground-level distances up to 200 m away from the road.

Hitchins et al. examined particle size distribution and concentration in the size range from 15 nm to 20 μm at distances from a road ranging from 15 to 375 m at two sites in Australia.[19] They conducted measurements under different wind conditions and found that when the wind blew directly from the road, the concentration of the fine and ultrafine particles decayed to about half of their maximum at a distance of 100–150 m from the road.[19] Shi et al. measured ultrafine particle number concentrations and size distributions at a busy roadside and at nearby urban background sites in Birmingham, England.[20] They observed a faster decline of particle number concentration than of mass concentration and concluded that dilution with background air is the main mechanism for the rapid decrease in particle number concentration and changes in particle size distribution with distance from traffic. Recently, it was reported that the fraction less than 10 nm constitutes more than ~40% of the total particle number concentrations at 4 and 25 m from the curb.[30]

While recent studies have examined ultrafine particles from traffic in other countries, no comparable work has been done in the Los Angeles basin, home to more than 15 million individuals and 10 million vehicles. Two studies characterizing Los Angeles freeway aerosols date to the 1970s.[31,32] More recently, ambient ultrafine particles in Pasadena, a city in the Los Angeles basin, have been studied.[33] Despite considerable improvements in air quality over the past two decades, the Los Angeles basin continues to exhibit the most severe particulate air quality problem in the United States. Laboratory studies have found that new engine technology and fuel reformulation have decreased particle mass concentrations emitted from vehicles, but ultrafine particle number concentrations have remained unchanged or have even increased.[27,28,34,35] With the advance of aerosol instrumentation, ultrafine particles now can be characterized much better than they could be 30 years ago. Thus, it is necessary and timely to conduct a comprehensive study of ultrafine particles in the vicinity of freeways in the Los Angeles area.

In view of the growing concern about ultrafine particle exposure, the need to assess exposure for epidemiology studies, and the high traffic density in the Los Angeles basin, the aim of this article was to systematically evaluate ultrafine particles in the vicinity of a freeway, particularly as they are transported downwind from the freeway. Particle number concentration and size distribution ranging in size from 6 to 220 nm were measured along with CO, black carbon (BC), and PM concentration as a function of distance from Interstate 405, one of the busiest freeways in the United States.

METHODS

Description of Sampling Site

This study was conducted in the Los Angeles National Cemetery adjacent to Interstate 405 between May 15 and July 18, 2001. Freeway 405 runs generally north and south (actual orientation 330°) along the western boundary of the cemetery, with a 1% upgrade going north. In the immediate vicinity of the sampling site, the terrain is flat-mowed lawn with scattered mature trees about 10 m high and 6 m apart. This flat region extends 0.7 km to the east of the freeway and 1.3 km along the freeway with no significant local sources of PM emissions other than the freeway. Measurements were made along Constitution Avenue, which runs perpendicular to the freeway. It passes through a tunnel under the freeway, thereby providing access to upwind and downwind sides of the freeway. At the sampling site, the freeway is elevated ~4.5 m above the surrounding terrain.

The site lies 6.4 km east of Santa Monica Bay and the Pacific Ocean. During the sampling period, a consistent sea breeze (eastward from the ocean) developed each day,

beginning in the mid-morning, reaching its maximum in early to mid-afternoon, and dying out in the early evening. The region upwind of the freeway is a residential area with no industrial or other obvious PM sources. Background measurements were taken ~300 m upwind of the freeway.

The only other freeways or major roads nearby are Sepulveda Boulevard, which runs parallel and immediately adjacent to the freeway, and Wilshire Boulevard, which runs perpendicular to the freeway more than 0.8 km to the south. During the sampling periods, traffic on Sepulveda Boulevard was light, ~5% of that on the freeway. For the usual wind direction (from southwest to northeast), traffic on Wilshire Boulevard was more than 2 km away along the wind vector and had little influence on particle levels.

The freeway has nine lanes, five northbound and four southbound. It is ~30 m wide, including a 1-m-wide median strip. The location of each measurement site for this study was determined by measuring its distance from the center of the median strip. The distance from each of the five sampling locations to the nearest traffic lane was 15 m less than the indicated distance.

Sampling and Instrumentation

Wind speed and directions were measured 6 m above ground level 30 m downwind of the freeway, which also served as a particle number concentration control site. Wind data were averaged over 1-min intervals and logged into a computerized weather station (Wizard III, Weather Systems Company). Throughout each measurement, the traffic strength on the freeway, defined as the number of vehicles passing per minute, was continuously monitored by a video recorder (camcorder) located on top of a 10-m tower close to the main gate of the Los Angeles National Cemetery. The camcorder was high enough to capture all nine lanes on the freeway and on Sepulveda Boulevard. After each sampling session, the videotapes were replayed, and traffic density was counted manually. Three 1-min samples were randomly selected from every 10-min interval. The data then were averaged for cars, light trucks, and heavy-duty trucks to estimate the traffic strength by type of vehicle.

Particle number concentration and size distribution in the size range from 6 to 220 nm were measured by a condensation particle counter (CPC 3022A; TSI Inc.) and a scanning mobility particle sizer (SMPS 3936, TSI Inc.), respectively. The sampling flow rate of the SMPS was adjusted to 1.5 L/min to measure particles as small as 6 nm and to minimize the diffusion losses of ultrafine particles during sampling.[8] Flexible conductive tubing (Part 3001940, TSI Inc.) was used for sampling to avoid particle losses caused by electrostatic forces. The sizing accuracy of the SMPS was verified in the laboratory by means of monodisperse polystyrene latex spheres (PSL, Polysciences Inc.). Data reduction and analysis of the SMPS output were performed using Aerosol Instrument Manager software (version 4.0, TSI Inc.). Measurements were taken 30, 60, 90, 150, and 300 m downwind and 300 m upwind from the center of the freeway. The distances were chosen based on preliminary measurements and previously published literature.[19] At each location, three size distribution samples were taken in sequence with the SMPS. Scanning time for each was 180 sec.

In addition to size distribution and total number concentration, concentrations of BC, CO, and PM were monitored simultaneously at each sampling location. Before each measurement, all instruments were synchronized. Data were averaged later over the time periods corresponding to the scanning intervals of the SMPS. A dual-beam aethalometer (Model AE-20, Andersen Model RTAA-900, Andersen Instruments Inc.) was used to measure BC concentrations every 5 min. CO concentrations were measured by a near-continuous CO monitor (Dasibi Model 3008, Environmental Corp.) every minute. The CO monitor was calibrated by means of standard CO gas (RAE Systems Inc.) in the laboratory and automatically zeroed each time the power was turned on. A DataRam photometer (RAM-1, MIE Inc.) was used as a continuous PM monitor. Because the PM concentrations measured by the DataRam were not actual gravimetric measurements, these values were used as indicators of general trends in PM concentrations and overall changes with distance from the freeway.

Electric power for the control site CPC and weather station was obtained by an extension cord to the cemetery office. Electric power for other sampling instruments at locations further downwind was supplied by a 1.2-kW gasoline-powered portable generator (Model EU 1000i, Honda Motor Co.). The generator was placed ~50 m downwind of each sampling location. Both total particle number and CO concentrations were measured at the control site while the generator was turned on and off. No detectable difference was observed.

Table 1 gives the sampling dates and times and summarizes the instruments that were used on each date. The weather station and the control CPC were placed at the 30-m downwind control site and sampled throughout the experiment. All other applicable instruments were moved together and sampled simultaneously at each sampling location. It took about 10 min to complete sampling at each location and 90 min to complete a set at all six locations. Three or four sets were performed on each sampling date.

RESULTS AND DISCUSSION

The measurements presented herein were conducted between May 15 and July 18, 2001. During the sampling

Table 1. Sampling dates and instruments used.

Date	Time	Weather Wizard III	Control CPC	SMPS	CO Monitor	Aethalometer	DataRam
05/15/01	10:30–15:30	×	×	×			
05/17/01	11:00–15:30	×	×	×			
05/30/01	11:00–16:00	×	×	×			
06/08/01	10:30–16:00	×	×	×			
06/20/01	10:30–15:30	×	×	×	×	×	×
06/21/01	11:00–16:00	×	×	×	×	×	×
06/22/01	10:30–16:00	×	×	×	×	×	×
07/17/01	10:30–15:30	×	×	×	×		×
07/18/01	10:30–16:00	×	×	×	×		×

period, traffic density ranged from 140 to 250 vehicles/min passing the sampling site in both directions. Average vehicle speed ranged from 2.5 to 30.0 m/sec (5–65 mph). Traffic primarily was dominated by gasoline-powered cars and light trucks, and less than 5% of vehicles observed were heavy-duty diesel trucks. The results presented in the next sections include measurements of total particle number concentrations by a control CPC and of wind velocity using a Weather Wizard III, both positioned at a fixed location 30 m downwind of the freeway; of CO, BC, and PM concentrations; and of ultrafine particle size distributions upwind and at five downwind distances from the freeway.

Wind Effects

Wind speed and direction were measured, averaged, and logged over every 1-min interval throughout each sampling period. Of more than 5000 observations from all the sampling dates, 100 wind data points were randomly selected and are plotted in Figure 1. The orientation of the freeway and the sampling road, Constitution Avenue, also are shown in the figure. Note that the Weather Wizard III instrument recorded wind direction at a 22.5° interval (e.g., 11.25° on either side of N, NNE, etc.) and wind speed at 0.4 or 0.5 m/sec intervals. In the figure, duplicate observations are spread out slightly in both directions to better illustrate how strong the wind was and how often the wind came from certain directions. Based on all 5000 observations, the percentage of sampling time that the wind came from each 22.5° segment also is shown in Figure 1. As shown in the figure, for most of the sampling time, the wind came directly from the freeway toward the sampling road with a speed of 1–2 m/sec. The consistency of observed wind direction and speed is a result of a generally low synoptic wind velocity and a reliable sea breeze in the sampling area. For this study, the consistency of the wind is important, because it allowed data from different days to be averaged together. Hitchins et al. found a completely different characterization of changes in total particle number concentration with increasing distances from a major road when the wind was blowing directly from, parallel to, or away from the sampling location.[19] They observed no trend when the wind was blowing away from the sampling location.[19]

In this study, we found that both wind direction and wind speed played an important role in determining the characteristics of ultrafine particles near the freeway. Figure 2 shows total particle number concentrations as measured by the control CPC, located 30 m downwind of the freeway, versus wind speed. A linear regression line, equation, and R^2 value also are included in Figure 2. The CPC was programmed to archive averaged total particle number concentrations at 1-min intervals in synchronization with the averaging time of the meteorological data. Only wind data within 45° of normal to the freeway are used in this figure. This range accounts for more than 80% of the total observations. In addition, Figure 2 includes particle number concentrations ranging in size from 15 to 697 nm, at 30 m, given by Figures 3a–c of Hitchins et al.,[19] for comparison. It can be seen that total particle number concentration measurements near the freeway are in general 2–3 times greater than those observed by Hitchins et al. at Tingalpa, Australia.[19] This is mainly because of the much heavier traffic density on the freeway, as discussed in the next sections. In addition, vehicle type,

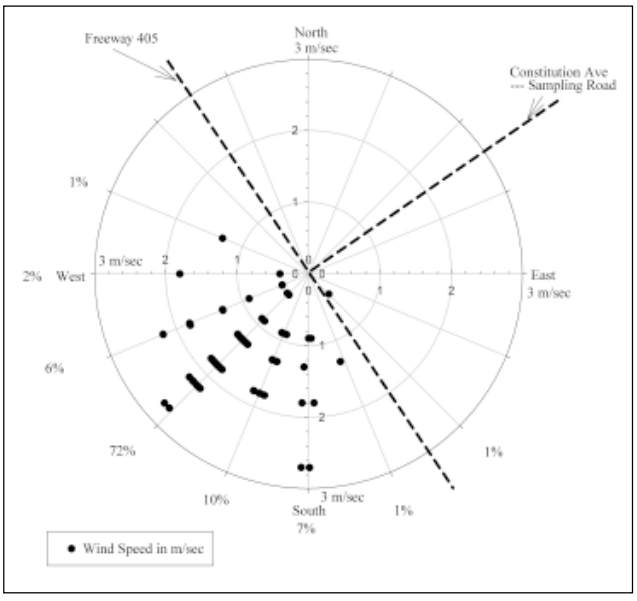

Figure 1. Wind direction and speed at the sampling site.

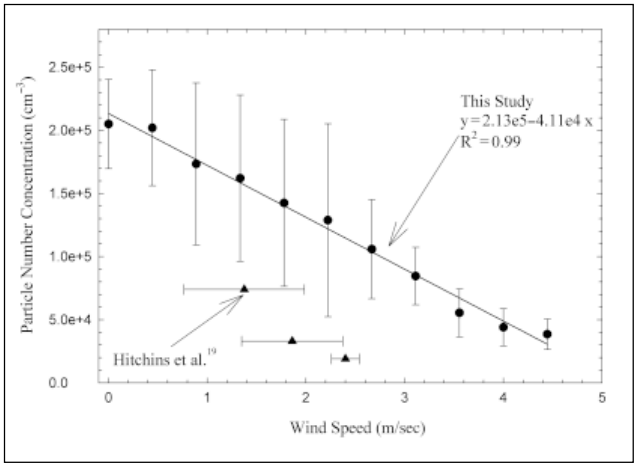

Figure 2. Total particle number concentration measured by a CPC located 30 m downwind from Freeway 405 vs. wind speeds. Bars indicate 1 standard deviation.

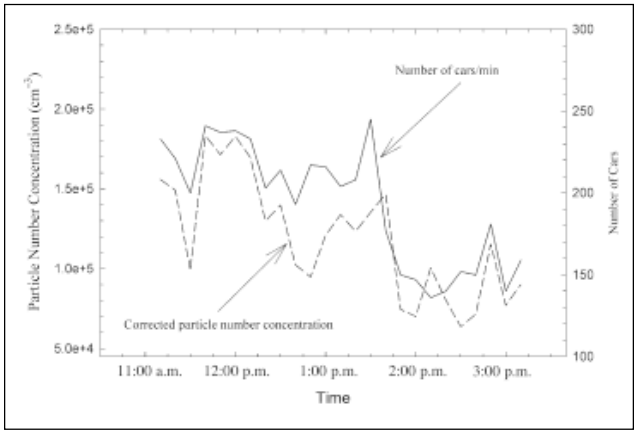

Figure 3. Correlation between traffic density and measured total particle number concentration, corrected for wind velocity, 30 m downwind from the freeway.

emission control equipment, and fuel type; utilization parameters such as age, accumulated mileage, inspection, and maintenance; operating modes such as average speed and fraction of cold/hot starts; and ambient parameters such as temperature and humidity also may contribute to the observed differences. Although the absolute particle number concentrations are quite different in these two studies, the relative particle number concentrations as a function of wind speed are quite similar. This indicates that atmospheric dilution of ultrafine particles by the wind is comparable for both cases.

Traffic Effects

Freeway 405 passing through west Los Angeles is considered one of the busiest freeways in the United States. The average traffic volume per hour during the measurement period was 13,000 cars, 350 light trucks, and 550 heavy trucks, totaling 13,900 vehicles. More than 93% of the vehicles passing by the measurement site on the freeway were gasoline-powered cars. This observed total traffic density was ~3 times higher than that reported by Hitchins et al. at Tingalpa, Australia,[19] and accounts for the higher observed total particle number concentrations.

Figure 3 shows the change in measured particle number concentration and the number of cars passing by the sampling site during those sampling periods when the wind was within 22.5° of normal to the freeway. Because wind speed played an important role in determining the total particle number concentrations, measured CPC readings were corrected to 1 m/sec by the following equation:

$$C_N^* = C_N \times \left(\frac{171{,}900}{213{,}000 - 41{,}100 \times V} \right) \quad (1)$$

where C_N^* is the corrected particle number concentration used in Figure 3, C_N is the CPC measured particle number concentration, 213,000 is the intercept of the regression line in Figure 2, 171,900 cm^{-3} is the particle number concentration at 1 m/sec velocity, –41,100 is the slope of the regression line, and V is the wind speed in m/sec as measured by the weather station. This correction will transform the measured particle number concentration to approximately a constant value at a relatively low wind speed (i.e., $V < 3$ m/sec). Because for most of the sampling time, average wind speed was in the range of 1–1.5 m/sec, this correction applies to more than 95% of the observations.

As shown in Figure 3, normalized particle number concentration tracked the traffic density very well, indicating that traffic is the major contributor to fine and ultrafine particles. A traffic slowdown on the northbound side of Freeway 405 usually developed on weekdays around 1:30 p.m., as indicated by the sharp drop of the solid curve in Figure 3. During this traffic slowdown, the average vehicle speed was usually less than 5 mph. The control CPC reading during that time period was observed to be much lower than normal, indicating that fewer ultrafine particles are produced during such traffic slowdowns. One possible explanation lies in the fact that nanoparticles produced by idling engines have longer residence times before they are exhausted from the tailpipe. Kittleson found that coagulation may reduce output number concentrations dramatically if engine exhaust is not diluted rapidly.[36,37]

Because both wind speed and traffic density affected the characteristics of ultrafine particles near the freeway and the control CPC reacted to these effects reasonably well, subsequent data for ultrafine particle analysis at increasing distances from the freeway were all normalized to the control CPC reading. An average CPC reading, $\overline{C_N}$, was obtained based on all the measurements. In Figures 4, 5, and 6, number concentration size distribution data were scaled to $\overline{C_N}$ by dividing each measurement by the ratio of the CPC reading for the period of measurement to $\overline{C_N}$.

Change in Ultrafine Particle Size Distribution with Increasing Distance

Figures 4a–f depict ultrafine particle size distribution at 30, 60, 90, 150, and 300 m downwind and at 300 m upwind of the freeway, respectively. The horizontal axis represents particle size on a logarithmic scale, while the vertical axis represents normalized particle number concentration. The normalized ultrafine particle size distributions, in the size range of 6–220 nm as measured by the SMPS, were averaged for all applicable sampling dates for each distance from the freeway. It is useful to describe the size characteristics of ultrafine particles near a vehicular source in terms of the parameters of a suitable distribution.[38-40] The number of modes for each ultrafine particle size distribution

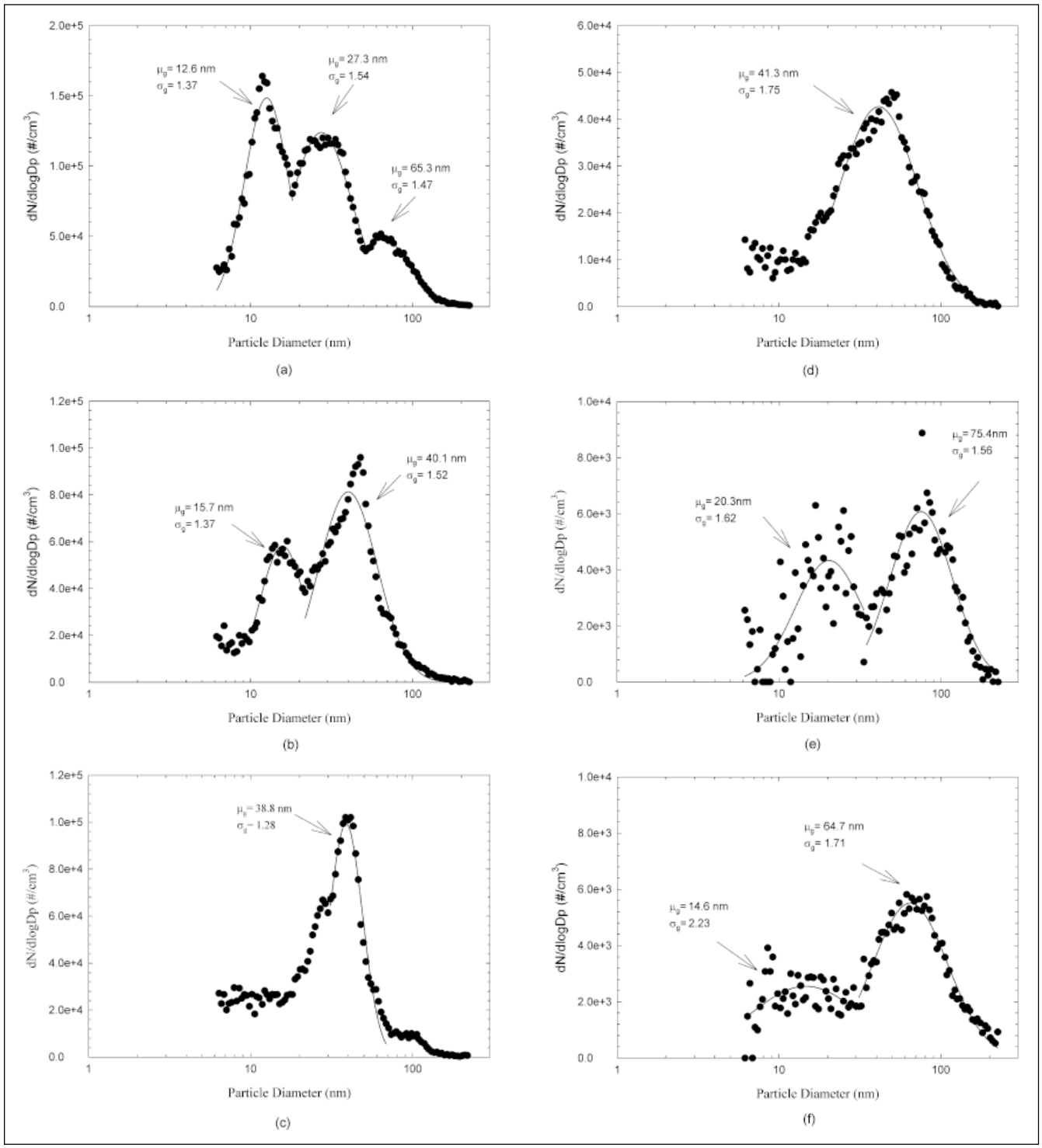

Figure 4. Fitted multimodel particle size distribution at different sampling distances from Freeway 405. (a) 30 m downwind, (b) 60 m downwind, (c) 90 m downwind, (d) 150 m downwind, (e) 300 m downwind, and (f) 300 m upwind. Size distributions were normalized to the control CPC's reading.

was determined by visual inspection of the size distribution graphs. Then, the full spectrum was subdivided into one, two, or three size-groups according to the number of modes. The data for each size-group then was fitted with a lognormal distribution using the SigmaPlot 2000 lognormal three-parameter fitting procedure.[41] The fitted distribution, the geometric mean diameter, μ_g, and the geometric standard deviation, σ_g, also are shown in Figures 4a–f for each observed mode.

As shown in Figure 4, ultrafine particle size distribution from the freeways changed markedly and its number concentration dropped dramatically with increasing distance. In Figure 4a, at the nearest sampling location, 30 m downwind from the freeway, three distinct modes were observed with geometric mean diameters of 13, 27, and 65 nm, respectively. The mode for the smallest particle sizes, with a peak concentration of $1.6 \times 10^5/cm^3$, was similar to that previously reported for direct laboratory measurement of vehicle emissions.[28] This mode shifted to a larger geometric mean diameter, 16 μm, and the modal number concentration dropped to one-third of the maximum concentration at 60 m downwind (see Figure 4b). This mode was not observed at greater downwind distances (see Figures 4c–e). The dramatic decrease in particle number concentration at ~10 nm likely was caused by several atmospheric aerosol particle mechanisms that enhanced small particle loss, diffusion to surfaces, evaporation, and coagulation. The smaller the particle, the greater its diffusion coefficient and its Brownian motion. Particles of 10 nm diffuse ~80 times faster than do particles of 100 nm. As particle size gets smaller, the Kelvin effect becomes more important, making it easier for molecules to leave the particle's surface by evaporation. In addition, when two small particles collide because of their Brownian motion (coagulate), they form a bigger particle. Thus, coagulation reduces number concentrations and shifts the size distribution to larger sizes.[8,32] The coagulation effect will be discussed in detail in the following paragraphs.

Because of atmospheric dilution, the number concentration for all sizes dropped dramatically with increased distance from the freeway. Number concentration dropped to approximately half its original value at 30 m somewhere between 90 and 150 m, as shown in Figure 4d. This result is in good agreement with Hitchins et al., who found that particle number concentrations decreased by 50% at 100–150 m.[19] Ultrafine particle concentration measured at 300 m downwind of the freeway (see Figure 4e) was comparable to what was measured at the background location 300 m upwind of the freeway (see Figure 4f). The maximum number concentration that was observed near the freeway was ~25 times greater than that at the background location. This suggests that people who live, work, or travel within 100 m downwind of major traffic sources will have much higher ultrafine particle exposure than those will who live farther from such sources. This result can be used in epidemiologic studies to evaluate the health effects of ultrafine particles.

The trend of size distribution and number concentration with increasing distances is shown in Figure 5, in which fitted lognormal distributions are used for each mode of the size distributions and shown together with a common scale for the vertical axis. According to Figure 5, number concentrations for smaller particles ($d_p < 50$ nm) dropped significantly with increasing distances from the freeway, but for larger ones ($d_p > 100$ nm), number concentrations decreased only slightly. This suggests that coagulation is more important than atmospheric dilution for ultrafine particles and the reverse is true for large particles. Researchers who have conducted experimental and theoretical studies on the transportation and transformation of vehicle particle emissions in the atmosphere often have concluded that the rapid dilution of the exhaust plume made coagulation insignificant.[20,42] However, in this study, the observed size distribution changes indicate that coagulation is not negligible.

Figures 6a–b show the decay of normalized total particle number and volume concentration, respectively, with distance along the wind direction from the freeway. Volume concentration was obtained from size-segregated SMPS data in the size range 6–220 nm. The horizontal axis represents the true distance as an air parcel travels from the freeway to the sampling locations. The total number and volume concentrations were normalized by dividing the averaged total number concentration by the control CPC concentration during each sampling period. Each data point in the figures represents an averaged value for all measurements with the same wind directions. The solid line is the best-fitting exponential decay curve, measured

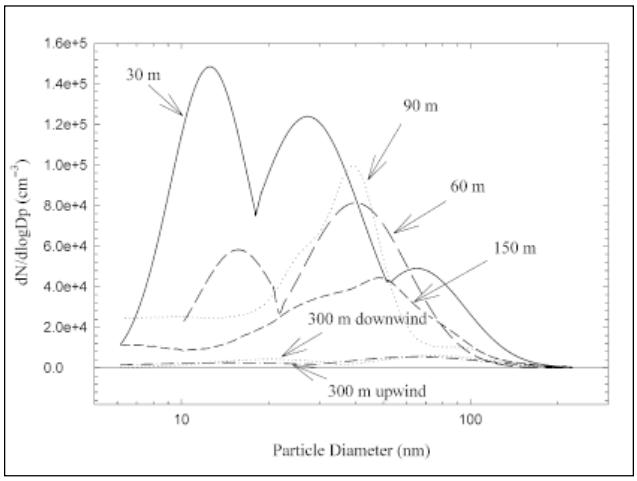

Figure 5. Ultrafine particle size distribution at different sampling locations near Freeway 405. Size distributions were normalized to the control CPC's reading.

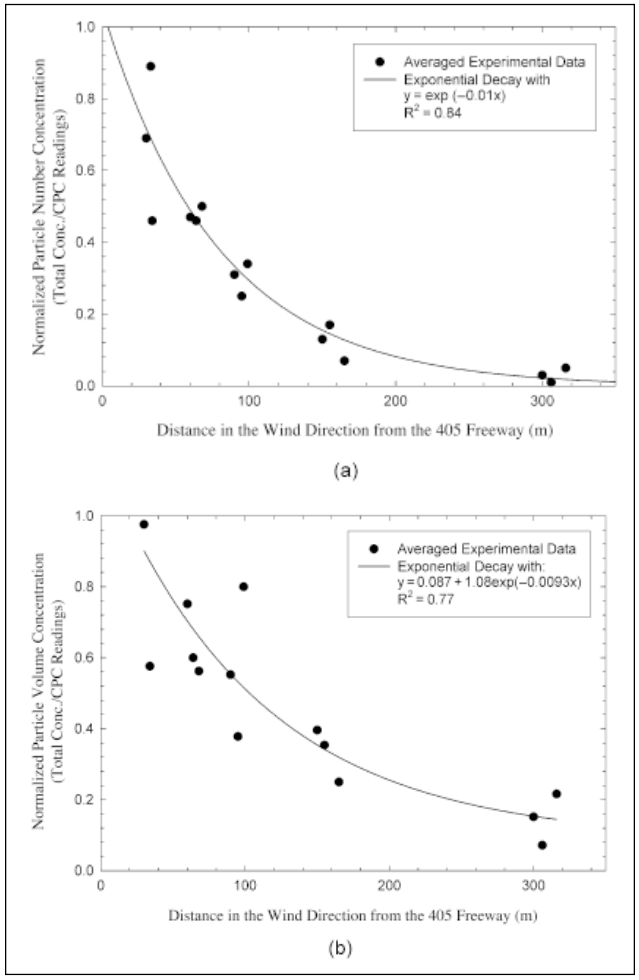

Figure 6. Normalized total particle (a) number and (b) volume concentration in the size range of 6–220 nm as a function of distance from Freeway 405.

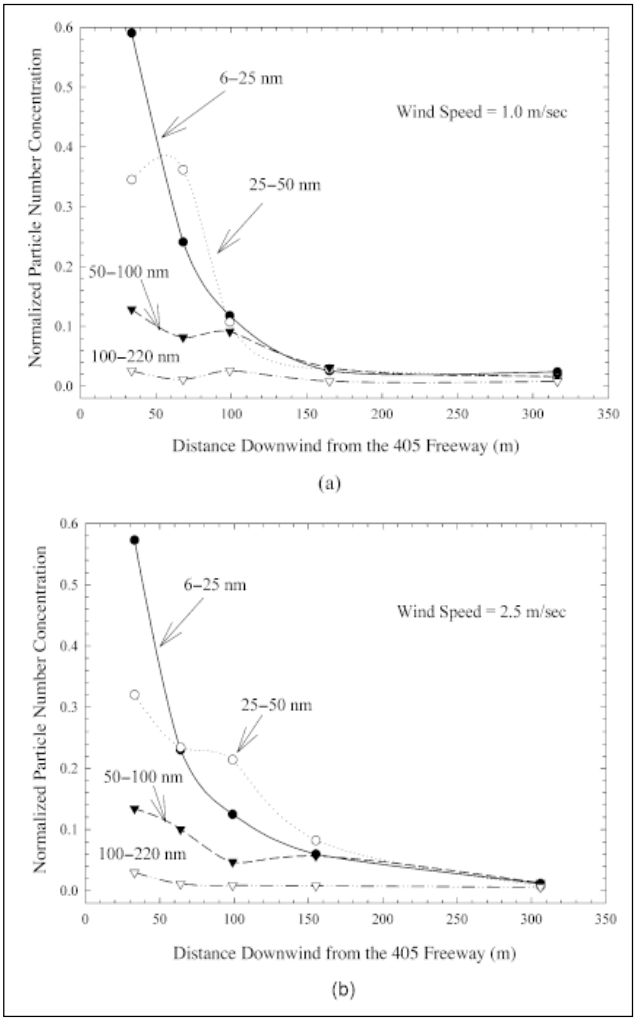

Figure 7. Normalized particle number concentration for different size ranges as a function of distance to the 405 freeway on (a) May 15, 2001, average wind velocity 1 m/sec, and (b) May 17, 2001, average wind velocity 2.5 m/sec.

using the SigmaPlot 2000 nonlinear curve-fitting procedure.[41] Exponential decay curves have been used previously to fit decreasing NO_2 concentrations with distance from a road[24] and were recently proposed by Hitchins et al. for ultrafine particle dispersion.[19] The best-fitting exponential decay equations and R^2 values also are given in the figures. Because coagulation will decrease only the total particle number concentration, not the volume, if coagulation is occurring, then total number concentration will decay faster than will total volume concentration, which is the case as shown in Figures 6a and 6b.

Based on Figures 4 and 5, it is clear that vehicle-emitted particles of different size ranges behave quite differently in the atmosphere. Thus, Figure 7 was prepared to illustrate the decay of particle number concentrations in four size ranges: 6–25 nm, 25–50 nm, 50–100 nm, and 100–220 nm. Two sampling days with different average wind speed were selected: May 15, at 1 m/sec, and May 17, at 2.5 m/sec. Particle number concentrations in each size group were obtained by adding the measured number concentrations in each SMPS size bin within the corresponding size range and normalizing to 1 and 2.5 m/sec, respectively. As shown in Figures 7a–b, the general trends of subgrouped ultrafine particle decay curves were quite comparable for the two dates. Total particle number concentration in the size range of 6–25 nm accounted for ~50% of the total ultrafine particle number concentration; it dropped sharply, ~80%, before 100 m, and leveled off after 150 m. Overall total particle number concentration decayed exponentially throughout the entire measured distance.

Number concentrations in the next two size ranges, 25–50 nm and 50–100 nm, all experienced a shoulder between 50 and 150 m. This can be explained by particles in smaller size ranges coagulating with these particles to increase their size and concentration, which partially compensates for the atmospheric dilution effects. Again, this result is consistent with the previous discussion, namely,

Table 2. Measured average concentrations at increasing distances from the freeway.

Measurement	Downwind Distance (m)				
	30	60	90	150	300
CO (ppm)	2.0 (1.7–2.2)	0.9 (0.7–1.0)	0.6 (0.5–0.7)	0.4 (0.3–0.5)	0.2 (0.1–0.3)
BC ($\mu g/m^3$)	5.4 (3.4–10.0)	3.2 (3.0–3.5)	2.5 (2.4–2.6)	1.6 (1.1–2.0)	1.3 (1.1–1.5)
Number Concentration ($\times 10^{-5}/cm^3$)	1.5 (1.3–1.7)	0.88 (0.77–0.96)	0.70 (0.61–0.85)	0.50 (0.42–0.58)	0.37 (0.30–0.39)
Mass Concentration ($\mu g/m^3$)	49.0 (30.2–64.6)	48.0 (37.1–55.0)	47.5 (29.5–63.4)	46.9 (30.1–65.5)	46.5 (30.0–58.9)

Note: Range given in parentheses.

that coagulation played a significant role in vehicle-emitted ultrafine particle atmospheric transportation and transformation. This observed result differs from model predictions by Shi et al.[20] and Vignati et al.[42] One reason is that the present study accurately measured freshly emitted particles down to 6 nm, while the previous models usually assumed a much lower particle number concentration for particles smaller than 15 nm.[20,42] As shown in Figure 7, only particles in the smallest size range coagulated with larger particle sizes. The number concentration of particles bigger than 100 nm did not change significantly as distance from the freeway increased. Because the wind speed was considerably stronger on May 17 than on May 15, one would expect that the atmospheric dilution effect also would be stronger. Thus, it was not surprising to see that those shoulders in Figure 7b occurred farther from the freeway and were not as significant as those shown in Figure 7a.

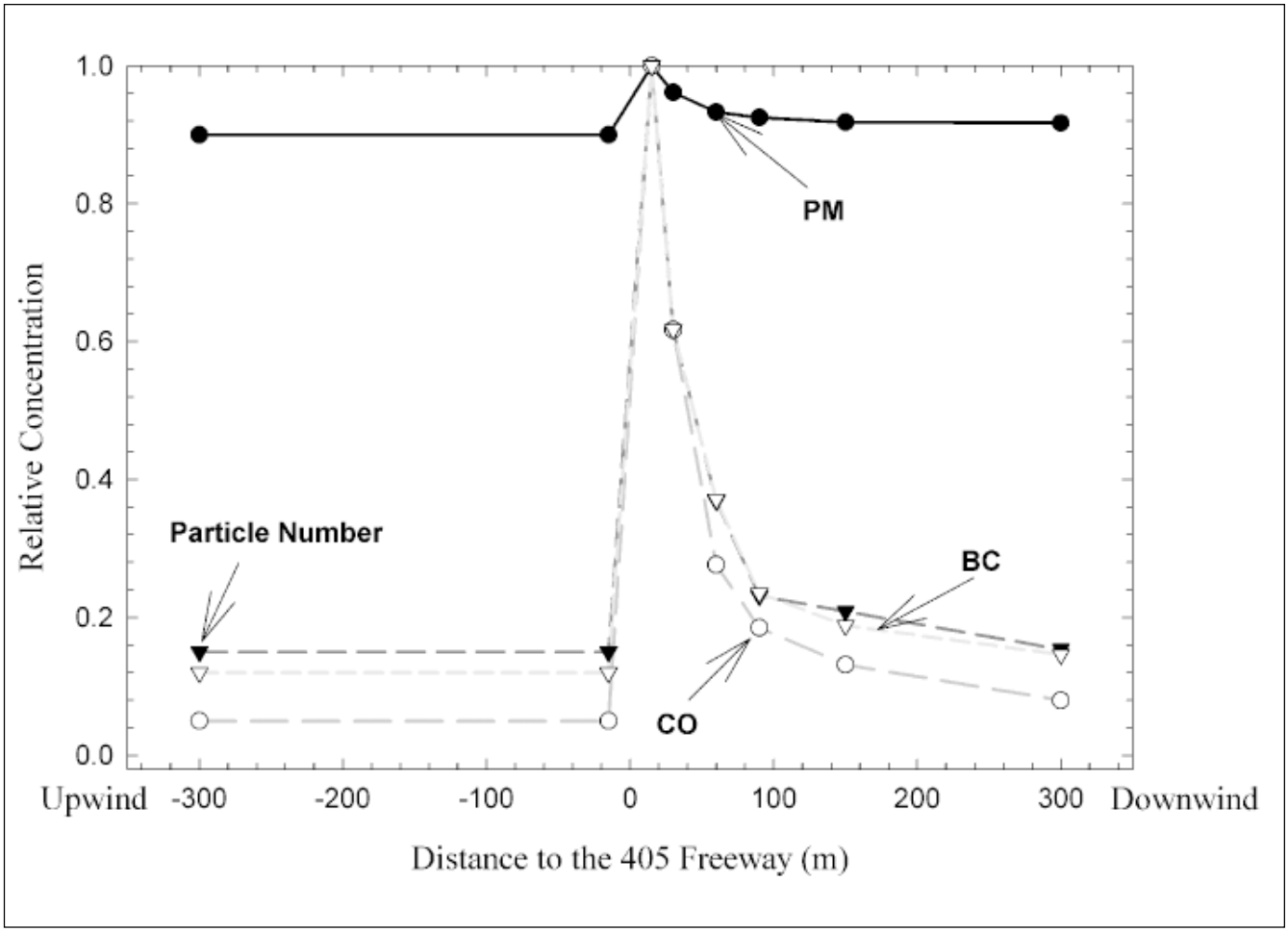

Figure 8. Relative mass, number, BC, and CO concentrations vs. downwind distance.

CO, BC, PM, and Particle Number

To make this freeway study more comprehensive, the concentrations of CO, BC, PM, and particle number also were measured at increasing distance from the freeway on certain days (see Table 1). CO and BC were intentionally selected because their ambient concentrations are related closely to vehicular emissions. Averaged concentration values at five distances from the freeway of each measured property are summarized in Table 2. Measured upper and lower limits also are given in Table 2. The CPC-measured total particle number concentration at the 30-m-downwind location was in good agreement with similar measurements by Shi et al. at 25 m downwind from the curb.[30] In general, the total particle number concentration found in this study is higher than that of urban ambient particles studied by Hitchins et al. in Tingalpa and Hughes et al. in Pasadena.[19,33] It can be seen in Table 2 that, except for the mass concentration measured by DataRam, all measured concentrations decreased noticeably when moving away from the traffic. The small change in PM concentration indicates that, although vehicular exhaust on one major freeway is the primary source of nearby ambient ultrafine particles, it contributes relatively little in terms of direct emissions to PM concentrations near freeways. Thus, regulation of vehicular emissions in terms of PM_{10} and $PM_{2.5}$ may have little effect on ambient particulate number concentrations.

Figure 8 shows the decay curves for CO, BC, total particle number, and mass concentration. The curves were normalized and extended to reach 1.0 at the downwind edge of the freeway. Background concentrations also are shown in the figure. The mass concentration measured by the DataRam decreased by only a few percent throughout the measured range, while CO, BC, and particle number concentration decreased ~60% in the first 100 m and then leveled off somewhat after 150 m. In fact, the CO, BC, and particle number concentrations tracked each other extremely well. This observed result confirmed the common assumption that vehicular exhaust is the major source of CO, BC, and ultrafine particles near a busy freeway. In addition, it suggests that, under the conditions of these measurements, the decreasing characteristics of any of these three pollutants can be used interchangeably to estimate the concentration of the other two pollutants near freeways.

CONCLUSIONS

Wind speed and direction are important in determining the characteristics of ultrafine particles near freeways. The stronger the wind, the lower the total particle number concentration. Total particle number concentration is related directly to traffic density and decreases significantly during a traffic slowdown. The average concentrations of CO, BC, particle number, and mass concentration at 30 m were in the range of 1.7–2.2 ppm, 3.4–10.0 $\mu g/m^3$, 1.3–$2.0 \times 10^5/cm^3$, and 30.2–64.6 $\mu g/m^3$, respectively. CO, BC, and particle number concentrations tracked each other extremely well as distance from the freeway increased. Exponential decay was found to be a good estimator for the decrease in total particle number concentration with distance along the wind direction. Measurements showed that both atmospheric dilution and coagulation play important roles in the rapid decrease of particle number concentration and the change in particle size distribution as distance from the freeway increases.

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