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Size Distribution and Diurnal and Seasonal Trends of Ultrafine Particles in Source and Receptor Sites of the Los Angeles Basin

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ABSTRACT

This paper presents results from a study conducted in two urban areas of southern California, Downey and Riverside, to examine the effect of different sources and formation mechanisms on the size distribution and temporal trends of ultrafine particles. Near-continuous data were collected for 5 months at each location. Our data clearly identified Downey as a source site, primarily affected by vehicular emissions from nearby freeways, and Riverside as a receptor site, where photochemical secondary reactions form a substantial fraction of particles, along with local vehicular emissions. In Downey, the diurnal trends of total particle number concentration and elemental carbon (EC) appear to be almost identical throughout the day and irrespective of season, thereby corroborating the role of primary emissions in the formation of these particles. This agreement between EC and particle number was not observed in Riverside during the warmer months of the year, while very similar trends to Downey were observed during the winter months in that area. Similarly, the size distribution of ultrafine particles in Downey was generally unimodal with a mode diameter of 30–40 nm and without significant monthly variations. The number-based particle size distributions obtained in Riverside were bimodal, with a significant increase in accumulation mode as the season progressed from winter to summer. During the warmer months, there was also an increase in sub-100-nm particles in the afternoon hours, between 2:00 p.m. and 4:00 p.m., that also increased with the temperature. The differences observed in the ultrafine particle distribution and temporal trends clearly demonstrated that mechanisms other than direct emissions play an important role in the formation of ultrafine particles in receptor sites of the Los Angeles Basin.

IMPLICATIONS

There is a fundamental lack of information on the size and chemical composition of ultrafine particles, both of which are essential in understanding their formation mechanisms in different urban and rural areas. Direct emissions from vehicles and power plants have been considered the main sources of these particles. The present study, conducted in urban and rural areas of the Los Angeles Basin, illustrated that this is a common misconception. Significant differences were observed in the ultrafine particle distribution and temporal trends in these areas, thereby demonstrating mechanisms other than direct emissions play an important role in the formation of ultrafine particles in receptor sites of the Los Angeles Basin. Ultrafine particle size distribution and diurnal patterns are modulated by the following parameters: (1) the midday peaking of photochemically generated species during the summer months, (2) the trapping of overnight emissions by the nocturnal inversion, (3) the rush-hour activity peaks of vehicle emissions, and (4) downwind long-range transport of particles emitted originally in highly polluted urban or industrial areas and advected to rural receptor sites.

INTRODUCTION

Atmospheric ultrafine particles have recently received significant attention because some toxicological investigations have indicated their potential for eliciting adverse health.[1-3] Laboratory studies conducted by Donaldson and MacNee[3] and Ferin et al.[4] showed that, for deposition of the same amount of particulate matter in the lung, toxicity tends to increase as particle size decreases. More recently, findings in a study conducted by Dailey et al.[5] demonstrated that when epithelial cells from human airways were exposed to the different modes of atmospheric particles based on an equal mass basis, ultrafine particles caused a greater response. In addition to these toxicologic findings, there are growing epidemiologic data showing an association between fine particles and respiratory health in asthmatic adults and children.[6,7] The emerging findings from both toxicologic and epidemiologic studies

require a better understanding of the sources, formation mechanisms, and chemical composition of atmospheric ultrafine particles. This information will help construct a comprehensive and systematic database that will serve as the link between population exposure to fine and ultrafine particles and epidemiologic health effects attributed to particulate matter (PM).

Number-based concentrations and size distributions are often considered better representatives of ultrafine particles, given that the contribution of these particles to the overall atmospheric particle mass concentration is quite small. With the exception of a few studies, there are limited data available on the size distribution of ultrafine particles in urban areas.[8-10] Ruuskanen et al.[8] monitored number and mass concentrations simultaneously in ultrafine (0–0.1 μm) and accumulation (0.1–2.5 μm) mode particles of $PM_{2.5}$ in three European cities in an attempt to identify similarities and differences among these locations. Poor correlations between number concentrations (mainly determined by the contribution of ultrafine particles) and $PM_{2.5}$ mass concentrations (mainly determined by the accumulation PM mode) were found. Similarly, poor correlation was found by Woo et al.[10] between number and volume concentrations of particles less than 2 μm in particle diameter. In addition to number concentrations, precise determination of ultrafine particle mass concentration is important for toxicologic studies, especially when comparing the toxic potential of these particles on equal mass basis to larger size ranges of PM.

A recent study conducted by Shi et al.[9] showed an appreciable persistence of nanoparticles (<10 nm) emitted from road traffic and stationary combustion sources in the urban atmosphere. Of particular interest is the high degree of correlation between nanoparticle number concentration and the intensity of solar radiation in urban background air observed in that study. This temporal association between nanoparticles and solar radiation strongly suggests the formation of secondary nanoparticles as a consequence of photochemistry. A more comprehensive study conducted by Woo et al.[10] reported three types of ultrafine particle "events", defined as episodes during which the particle number concentrations increase by 5- to 10-fold, associated with peaks of NO_2 or SO_2 concentrations, thereby suggesting secondary particle formation due to gas-to-particle conversion processes.

Although these studies measured the number concentrations and size distributions of ultrafine particles at various urban sites, few attempts have been made to investigate the relative influences of both direct emission and secondary formation processes of ultrafine particles over a large metropolitan area. This approach is of particular interest in complex urban areas that are under the influence of both local sources (e.g., direct vehicular emissions) and remote sources (e.g., secondary aerosol precursors transported from nearby urban areas) such as the Los Angeles Basin. Earlier work by Pandis et al.[11] proposed a trajectory model that describes the fate of emitted particle precursors, such as gas pollutants, through advection and photochemical reaction and finally to the formation of secondary organic aerosols in the Los Angeles Air Basin. Based on the results of that study, formation of ultrafine particles by secondary reactions should be expected to have distinct diurnal, seasonal, and spatial characteristics in the complex Los Angeles urban airshed. The high degree of temporal and spatial variability of parameters such as degree of solar radiation, atmospheric mixing depth, humidity, and temperature affect the concentrations, reaction rate, and fate of gaseous precursors.

The work presented in this paper is intended to add to the body of knowledge surrounding the size distribution and temporal trends of ultrafine particles in polluted urban areas. Sampling was conducted in two locations in southern California, Downey and Riverside. Ultrafine PM characteristics were compared over different time periods during which ultrafine PM is affected by different sources and formation mechanisms. The two sampling locations are representative of two distinct air pollution regimes in the Los Angeles Basin. The first site (Downey) is a typical urban area in the vicinity of downtown Los Angeles, in which primarily vehicular and to a lesser extent industrial sources are responsible for direct PM formation. The second site is located in the inland valleys of the basin, ~70 km east of downtown Los Angeles, and PM is primarily formed by secondary gas-to-particle reactions or by wind-blown dust from the nearby deserts. PM originally emitted in urban Los Angeles is also advected into this area after several hours of suspension in the atmosphere. It is therefore common to refer to the former air pollution regime as a "source" area and to the latter as a "receptor" area of the Los Angeles Basin.

METHODS

Sampling Locations, Frequency, and Instrumentation

Selection of Sampling Sites. A mobile aerosol laboratory, developed and supported by funding provided by the U.S. Environmental Protection Agency (EPA) under the Southern California Particle Center and Supersite, was deployed to collect the ultrafine ambient aerosol characterization data described in this paper. Near-continuous data were collected in both Downey and Riverside for a period of approximately 5 months at each location. Figure 1 shows the location of sampling sites in the Los Angeles Basin overlapped with overall wind direction during the day.

Downey is located near central Los Angeles along the "Alameda corridor." This location is associated with some

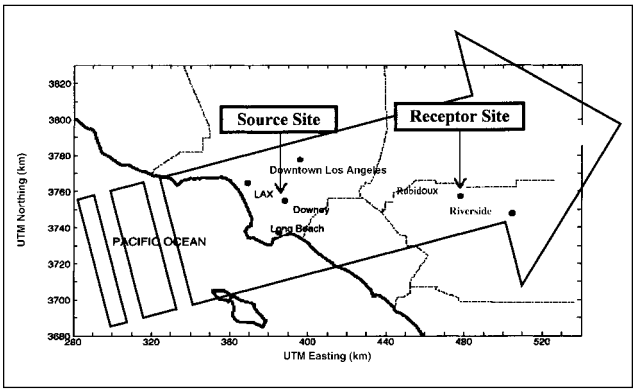

Figure 1. Locations of the source site (Downey) and the receptor site (Riverside) in the Los Angeles Air Basin. The large arrow shows the overall direction of wind during the daytime.

of the highest concentrations of inhalable particles (PM_{10}) in the United States, often exceeding the National Ambient Air Quality Standard of 150 μg/m^3. The Alameda corridor, named after Alameda Street, joins the coastal area of Long Beach with downtown Los Angeles. This unique geographical location places Downey ~10 km downwind from Long Beach, where large numbers of industrial plants and oil refineries operate, and ~2 km downwind of Interstate Highway 710 (I-710) and 5 km downwind of Interstate Highway 605 (I-605), both of which contribute to high concentrations of diesel emissions because of heavy diesel truck traffic.

Sampling in Riverside was conducted in the facilities of the Citrus Research Center and the Agricultural Experiment Station of the University of California. Riverside is a geographically different area from Downey. It is ~70 km directly east of downtown Los Angeles. Nearby dairy farms in the area of Chino (~10 km west, hence upwind of Riverside) contribute to very high concentrations of ammonia, which reacts with nitric acid to form particulate ammonium nitrate.[12] In addition, the aged particulate plume generated by the millions of vehicles mostly west of downtown Los Angeles is advected by the westerly winds to the Riverside area and contributes to a large portion of the local $PM_{2.5}$.[13] Because of the differences in the sources of the PM in each location, Downey is often considered to be the "source" site, impacted primarily by relatively fresh PM emissions, while Riverside is considered a "receptor" site, impacted primarily by aged aerosols transported to the region and by secondary particulates.[11]

Instrumentation. Ultrafine PM measurements in Downey were conducted near continuously from September 19, 2000, through January 31, 2001. Ultrafine PM measurements in Riverside were conducted during February 5–June 30, 2001. Several near-continuous and time-integrated instruments were employed in this study, which is part of the activities of the Southern California Supersite, funded by EPA. The scanning mobility particle sizer (SMPS 3936, TSI Inc.) was used to determine the number distributions of ambient particles in the size range of 14–500 nm. Data were acquired in time intervals of 15 min. A dual-beam aethalometer (Model AE-20, Andersen Model RTAA-900, Andersen Instruments Inc.) was used to measure the $PM_{2.5}$ elemental carbon (EC) concentration every 5 min. Wind speed and direction data were obtained every 5 min with a wind sensor (Met One Model 034A) mounted on a 10-m tower attached to the PIU trailer. Ambient temperature and relative humidity were measured by means of a temperature and relative humidity sensor (Vaisala Model MP113Y). All of the continuously measured data were logged onto an on-site data acquisition system (Automet 466A, Met-One Corp.), downloaded to a PC, and converted into digital format for storage.

Three collocated Microorifice Uniform Deposit Impactors (MOUDIs, Model 110 MSP Corporation) were used to obtain 24-hr averaged, size-fractionated particle mass and chemical composition data from each location. The three MOUDIs sampled for 24 hr, starting at 6:00 a.m., approximately once every week, during a weekday in each location. Each MOUDI operated at 30 L/min in rotating mode to achieve uniform particulate deposits over the substrate surfaces. The stages of the MOUDI collect particles in the size ranges of 0–0.10, 0.10–0.35, 0.35–1.0, 1.0–2.5, and 2.5–10 μm. The first size range (0–0.10 μm) represents the ultrafine PM mode. Depending on the type of chemical analysis, which is described in the following paragraph, Teflon (PTFE Teflon, 2-μm pore, Gelman Science) filters and prebaked aluminum foils were used as impaction substrates. Forty-seven millimeter filters were used as impaction substrates, whereas 37-mm filters were used as the MOUDI after-filter to collect the 0–0.10 μm particles.

Two of the MOUDIs were used with Teflon filters as impaction substrates. One set of MOUDI filters was used to determine the concentrations of inorganic ions such as SO_4^{2-} and NO_3^- by means of ion chromatography. The second set of filters was used to determine trace elements present in the ambient air through X-ray fluorescence. The third MOUDI employed prebaked aluminum foils as impaction substrates and prebaked quartz filters (Pallflex Corp.) as after-filters to determine the EC and organic carbon (OC) concentrations in the ambient air by thermoanalysis. This process is described in detail by Fung.[14] The Teflon filters used in these sampling procedures were weighed before and after each field test using a Mettler 5 Microbalance (MT 5, Mettler-Toledo Inc.), under controlled conditions of relative humidity (40–45%) and temperature (22–24 °C). To ensure removal of all particle-bound water before weighing, filters were stored in

the control humidity and temperature room for at least 24 hr prior to each weighing.

RESULTS AND DISCUSSION

Site Characteristics and Time-Integrated Data of Ultrafine Particles

Figures 2a and 2b show the change in wind speed and direction averaged over the 5-month sampling period at the two monitoring stations as a function of hour of the day. Wind speed and direction were reasonably consistent throughout the entire sampling period at both sites as indicated by relatively small error bars, which represent the standard error of individual measurements. In general, the average wind speed at both sites reaches a maximum in the afternoon, between 2:00 p.m. and 4:00 p.m., and decreases later in the evening and during the early morning hours. The increase in wind speed is due to the development of a persistent sea breeze during that time of the day, coming from the Pacific Ocean and directed inland, which transports aged aerosols and gas pollutants originally emitted in west and central Los Angeles to the Riverside area (see Figure 1).

Chemical Composition of Ultrafine Particles in the Two Sites

Table 1 shows the content of chemical species in ultrafine particles measured in Downey and Riverside over 24-hr sampling periods. The geometric mean mass concentrations of ultrafine particles are 4.12 and 1.34 μg/m^3 at Downey and Riverside, respectively. The mass concentrations in Downey are approximately 3 times higher on average compared with Riverside, because of the influence of the heavy traffic associated with the nearby freeways in this location. The relatively narrow range in the mass concentrations of EC at Downey indicates the consistency of diesel traffic sources of I-710 over a 24-hr time period.

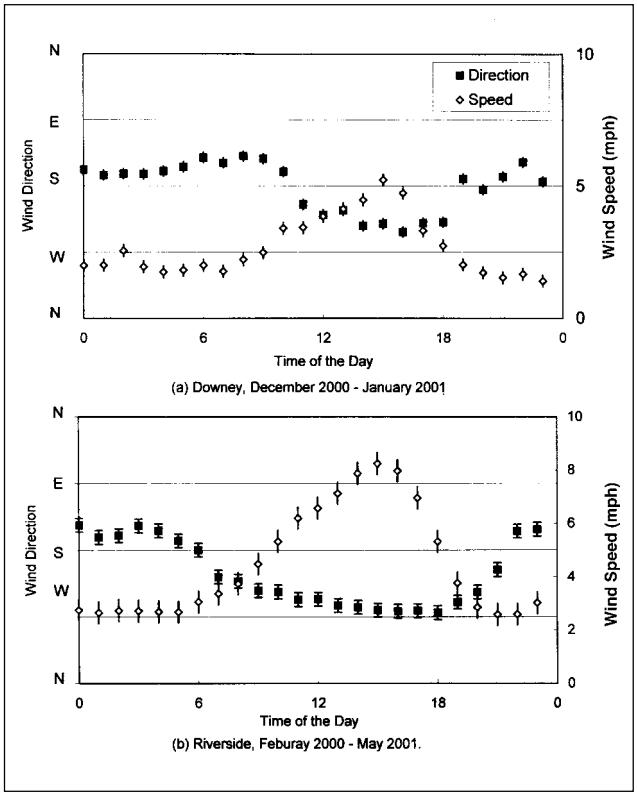

Figure 2. Diurnal trends of wind direction and wind speed at (a) Downey and (b) Riverside.

Table 1. Content of major chemical species in ultrafine particles measured at Downey and Riverside over 24-hr periods.

	Geometric Mean Mass Concentrations (Range), μg/m^3	
	Downey (9/17/00–1/31/01)	Riverside (2/5/01–6/30/01)
Total Mass	4.11 (1.12–8.89)	1.34 (0.42–3.65)
Elemental Carbon	0.67 (0.58–0.75)	0.13 (0.04–0.19)
Organic Carbon	2.75 (2.62–3.01)	1.35 (0.72–3.90)
Ammonium Nitrate	0.08 (0.02–0.14)	0.10 (0.33)[a]
Ammonium Sulfate	0.15 (0.078–0.11)	0.09 (0.05–0.20)

[a]Only the maximum value of the range is shown because the minimum value is below detection limit.

The fractions of chemical species in ultrafine particles in the two sites are displayed on pie charts in Figures 3a and 3b. The most abundant species in ultrafine particles at both sites is OC, followed by EC. Not surprisingly, the fraction of EC at Downey is higher than that at Riverside. EC is usually considered a marker of the combustion process and accounts for ~18% of the ultrafine particle mass concentration at Downey, an area that is largely affected by vehicular emissions. By contrast, the mass fraction of EC at Riverside is less than 10% of the ultrafine particle concentration.

The OC fraction of ultrafine PM at Riverside is somewhat higher than that at Downey. In addition to primary emissions from local traffic sources, OC at Riverside may originate from secondary reactions of gaseous precursors as well as from air parcels advected eastward from Los Angeles. Turpin and Hutzincker[15] suggested that the significance of secondary organic aerosol formation could be assessed by plotting OC against the EC concentrations measured in a given location. As shown in Figure 4, OC concentrations at Downey are strongly correlated ($R^2 = 0.89$) with concentrations of EC, which is a primary tracer of vehicular emissions. The average ratio of OC to EC at Downey, estimated from slope of the linear regression, is 3.5 (equivalent to 2.5 based on units of μgC/m^3) and very close to the reported value for ambient aerosols in Long Beach, an area located to the southeast of Downey by about 10 km and considered as another source site.[15] Figure 5

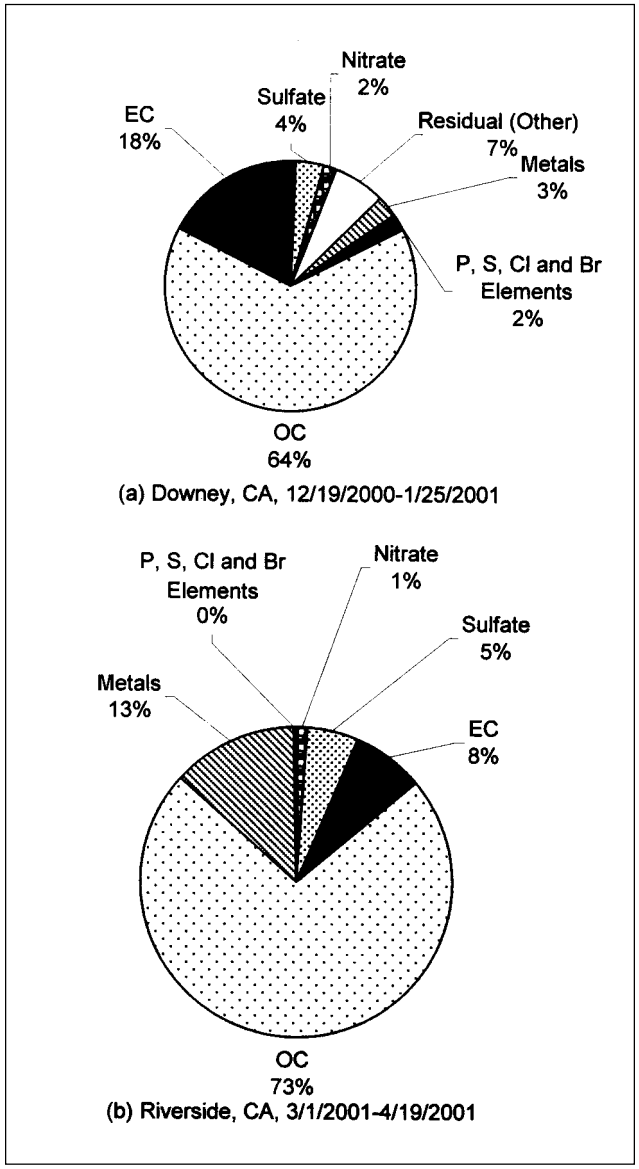

Figure 3. Twenty-four-hour averaged chemical compositions of ultrafine particles measured by MOUDI.

shows a rather weak association ($R^2 = 0.27$) between OC and EC concentrations at Riverside, indicating that a significant portion of OC in that area originates from sources that are unrelated to local vehicular emissions. The high average ratio of OC to EC concentrations (8.6 from the slope of linear regression) also implies the existence of secondary organic aerosols in ultrafine particles at Riverside.

It should be noted that the OC values measured by the MOUDI after-filter might be potentially biased by either positive or negative sampling artifacts related to adsorption of gas-phase organics or evaporative losses of particle-bound volatile compounds.[15] Given the high face velocity of the MOUDI after-filter (i.e., 65 cm/sec), the latter artifact may be more pronounced than the former. This argument is further supported by a recent methods

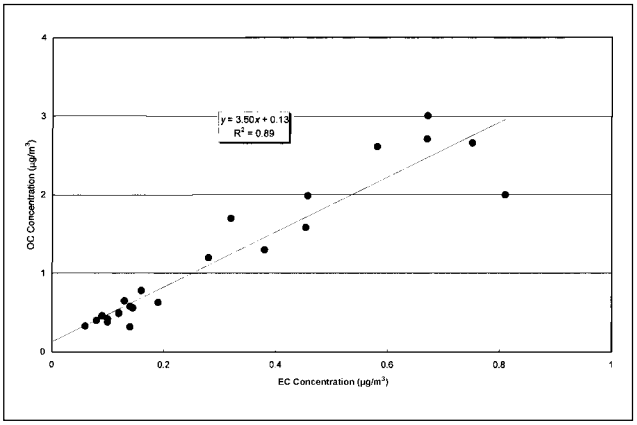

Figure 4. Twenty-four-hour averaged concentrations of OC and EC of ultrafine particles measured at Downey.

intercomparison study in Atlanta, GA, in which the MOUDI OC concentrations were systematically lower than those measured by collocated samples in which particles were collected on quartz filters preceded by diffusion denuders that were designed to remove gas-phase organics.[16] These artifacts are also a function of meteorological conditions, such as temperature and relative humidity.[15]

Considering that, in each location, sampling was conducted over a period of about 5 months, with varying meteorological conditions, we believe that the validity of correlations between the EC and OC concentrations in each location is not substantially affected by potential artifacts. Moreover, very similar correlations between the ultrafine particle EC and OC concentrations were obtained in Riverside and Downey during a smaller-scale intensive field study conducted in the spring of 2001, in which high-volume ultrafine PM collection in short time periods was accomplished by means of a combined ultrafine particle concentrator and a cascade impactor (NanoMOUDI, Model 110, MSP Corp.) capable of fractionating by size particles in four groups in the 10–100 nm range.[17] Collection of ultrafine PM by impaction instead of filtration

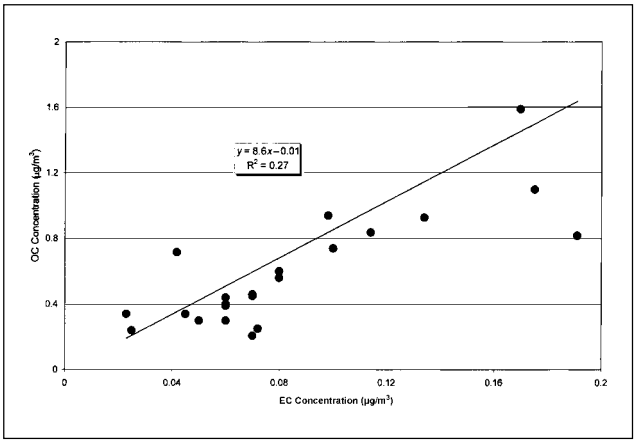

Figure 5. Twenty-four-hour averaged concentrations of OC and EC of ultrafine particles measured at Riverside.

eliminates positive artifacts. Furthermore, particle concentration enrichment has been shown to significantly reduce, if not eliminate, negative sampling artifacts.[18] The OC concentrations of the latter study are thus expected to be free of sampling artifacts. The high correlation between the EC and OC concentrations in Downey and the lack of correlation in Riverside observed in that study provides further corroboration to the findings of the work presented in this paper.

The concentrations of transition metals in atmospheric aerosols are of particular interest to toxicologists because of their catalytic function on oxidative reactions. Trace metals in ultrafine particles are mostly generated by vehicular emissions as well as emissions by industrial plants.[19] Table 2 shows the geometric mean trace metal concentrations in ultrafine particles measured at Downey and Riverside. Iron was the most abundant transition metal in both locations, followed by Cu and Zn. Other transition metals such as Cr, V, and Ni also showed relatively high mass concentrations. Vanadium, an element associated with petroleum combustion, was ~11 times greater at Downey than at Riverside. This is believed to reflect the contribution from traffic and refineries at Downey. Other ratios (Downey/Riverside) of transition metals concentration were slightly greater (3.7–5.4) than the overall mass concentration ratio (3.1).

Correlation between Number and Mass Concentrations

Ultrafine particles have distinct formation mechanisms, chemical composition, and physicochemical behavior in the atmosphere; consequently, they may affect human health differently than do fine and coarse particles, which are currently being regulated by air quality standards.[20] While the number concentration and size distribution have been considered as the most representative parameters to characterize ultrafine particles, mass concentrations may be a better health indicator of these particles, considering that toxicity of any compound is traditionally expressed per unit mass of that compound.

Figures 6a and 6b show the relationship between daily number and daily $PM_{0.1}$ volume concentrations estimated from SMPS measurements, or mass concentrations obtained from MOUDI for $PM_{2.5}$, measured in Downey and Riverside. The correlation between the 24-hr average total number and $PM_{2.5}$ mass concentrations is very poor at both sites ($R^2 = 0.005$). A similar observation was reported by Woo et al.[10] based on yearlong measurements in Atlanta, GA. This lack of correlation should not be surprising because number concentrations are dominated by ultrafine particles while sub-2.5-µm mass concentrations are dominated by the contributions of the accumulation PM mode, which are generally affected by different sources and formation mechanisms. However, the number concentrations show a considerably higher correlation ($R^2 = 0.77$) with volume concentrations when restricted to particles less than 0.1 µm as shown in Figure 6b. It should be noted that this high correlation ($R^2 = 0.77$) was obtained by incorporating all data covering both sites and at different months of the year.

Table 2. Average ultrafine trace metal concentrations measured at Downey and Riverside over 24-hr periods.

Transition Metal	Geometric Mean Mass Concentrations (Range), ng/m³	
	Downey (9/17/00–1/31/01)	Riverside (2/5/01–6/30/01)
Ti	3.2 (0.2–9.1)	0.87 (0.22–2.9)
V	1.8 (0.2–15.9)	0.17 (0.16–0.33)
Cr	5.1 (0.2–37)	1.3 (0.17–6.7)
Mn	2.5 (0.3–5.7)	0.58 (0.3–2.03)
Fe	40.5 (10.4–133)	10.0 (1.23–33.8)
Ni	3.6 (0.1–12.3)	1.83 (0.13–13.6)
Cu	6.4 (0.6–24.6)	1.46 (0.18–9.54)
Zn	7.5 (1.4–38.6)	1.45 (0.11–6.11)

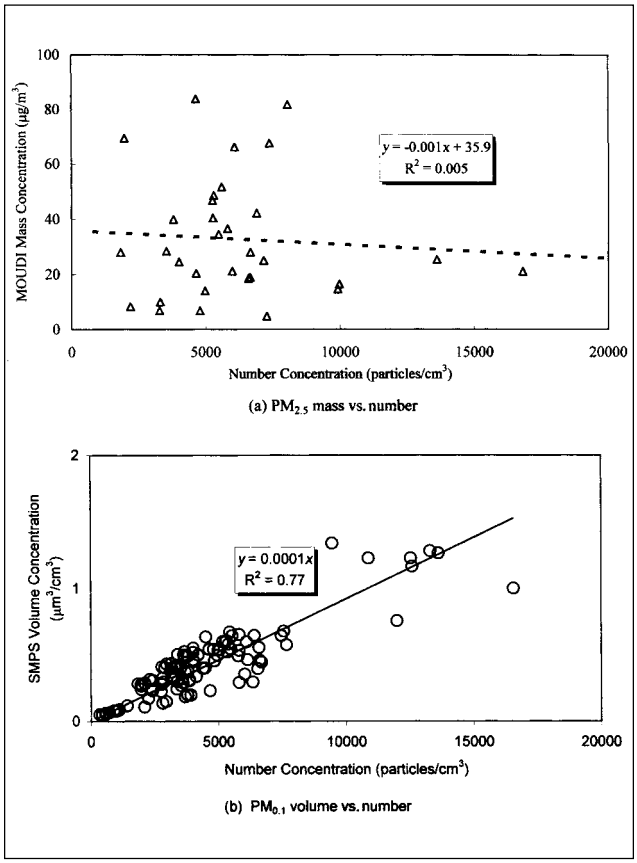

Figure 6. Correlation between the 24-hr average number and mass/volume concentrations measured in Downey and Riverside from October 2000 to May 2001.

To evaluate the validity of the SMPS data, the ultrafine mass concentrations determined gravimetrically by means of the MOUDI were compared with those estimated from the SMPS measurements. The mobility equivalent diameters determined by SMPS were converted to aerodynamic diameters[21] under the assumption that particles are perfect spheres with the density of 1.6 g/cm^3. Figure 7 shows the daily averaged mass concentrations estimated from SMPS data as a function of the ultrafine mass concentrations measured by MOUDI. As evident from the data plotted in Figure 7, ultrafine particle mass concentrations obtained from MOUDI and SMPS are in very good agreement and are highly correlated (R^2 = 0.91).

In addition to daily-averaged concentrations, a high correlation (R^2 = 0.74) was also observed between the hourly-averaged ultrafine number and volume concentrations, as shown in Figure 8. The correlation coefficient based on hourly concentrations is slightly lower than that based on 24-hr measurements, probably because of the larger number of data points. These findings suggest that number concentration can be a reasonably good indicator of ultrafine volume concentration, at least in the Los Angeles Basin.

Temporal Trends of Total Number Concentrations of Ultrafine Particles

Atmospheric parameters influencing ambient ultrafine particle concentrations, such as temperature, relative humidity, wind direction and speed, mixing height, and emission strength of particle sources fluctuate in substantially shorter time scales than 24 hr. Short-time measurements are thus essential to investigate the formation mechanisms and behavior of ambient ultrafine particles. Figures 9a–c show the diurnal pattern of total particle number concentrations in Downey and Riverside, averaged by the time of day. Hourly-average concentrations of EC are shown together on the *y* axis to illustrate the influence of primary sources such as vehicular emissions. Figure 9a demonstrates that ultrafine PM number concentrations in

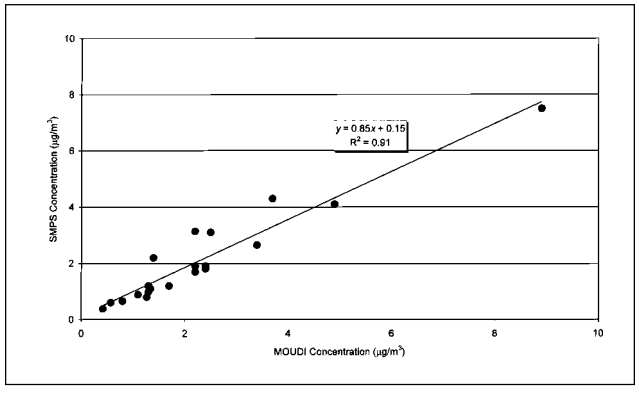

Figure 7. Comparison between daily mass concentrations ($PM_{0.1}$) estimated by SMPS and MOUDI.

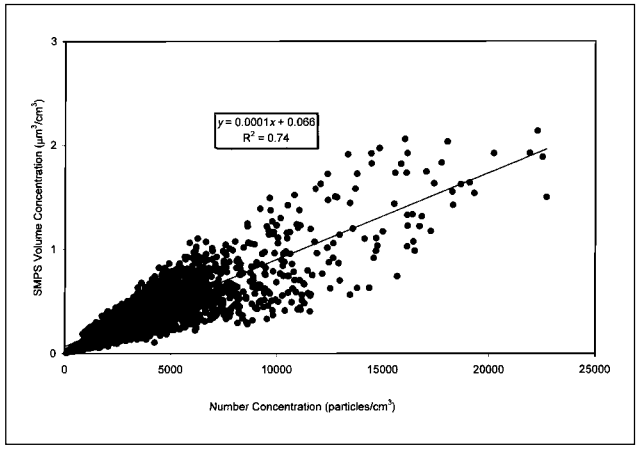

Figure 8. Correlation between hourly averaged number and volume concentrations of ultrafine PM measured in Downey and Riverside from October 2000 to May 2001.

Downey follow well the trends of EC concentration for the majority of the day, thereby indicating that most of the ultrafine particles are associated with primary emissions. The coincident peaks in the morning (6:00 a.m.–9:00 a.m. local time) are probably due to the increase in local vehicular emissions during morning traffic, combined with quasi-stagnant atmospheric conditions before the development of the sea breeze. The increase in EC concentrations after 6:00 p.m. may result from the

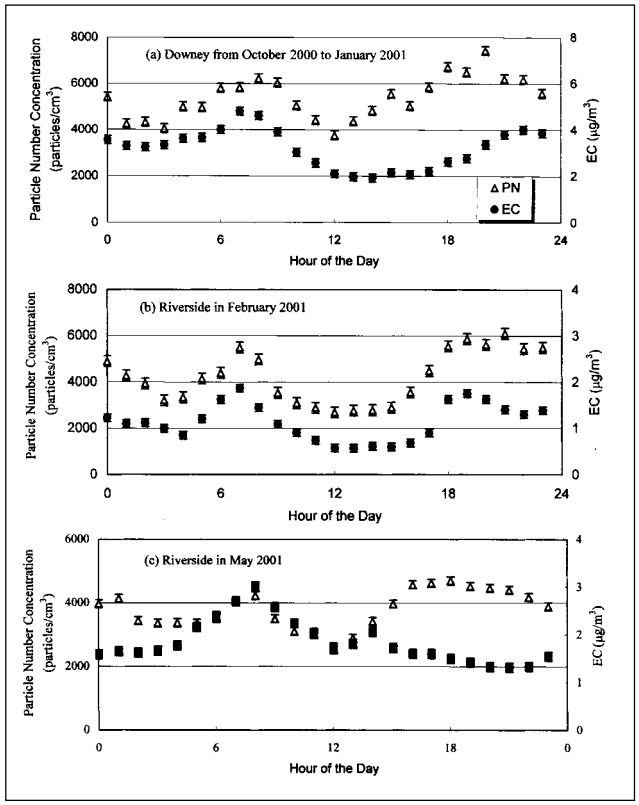

Figure 9. Diurnal pattern of particle number and EC concentrations averaged over time period (a) at Downey from October 2000 to January 2001, (b) at Riverside in February 2001, and (c) at Riverside in May 2001.

decrease in atmospheric mixing height combined with stagnant conditions during the night. A similar diurnal pattern of EC concentrations was reported by Allen and Koutrakis.[22] No substantial differences were observed in the ultrafine number and EC concentration diurnal trends between individual months in Downey.

Figures 9b and 9c show average ultrafine particle number concentrations as well as EC concentrations plotted against time of day in Riverside in February and June 2001. The diurnal pattern of the average number concentrations exactly follows that of EC in February, similarly to Downey. This suggests that ultrafine particles at Riverside during the winter months are mostly generated from the local primary sources without significant contribution from secondary sources. However, this strong correlation between number and EC concentrations in Riverside does not persist during the afternoon hours in warmer months. As shown in Figure 9c, ultrafine paricle number concentrations start to increase abruptly in the afternoon, while EC concentration gradually decrease. This observation strongly implies the presence of other sources and formation mechanisms of ultrafine particles during periods of intensive solar radiation, in addition to primary vehicular emission sources.

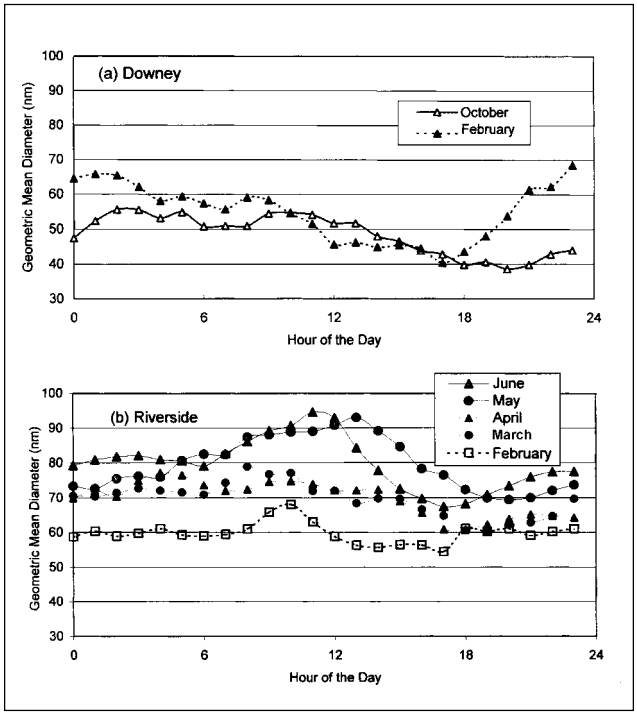

Figure 10. Monthly averaged aerosol geometric mean diameters plotted against hour of the day.

Particle Size Distribution: Seasonal Variation and Submodal Analysis

For a better display of the temporal variation of particle size distributions in both locations, the geometric mean diameters of sub-0.5-μm particles were averaged for a given month as a function of hour of the day. In Figures 10a and 10b, the monthly averaged geometric mean diameters in Downey and Riverside, respectively, are plotted against hour of the day. On average, geometric mean diameters of ultrafine particles in Downey are smaller than 60 nm during most of the day. The relatively constant traffic on I-710 and I-605 near the Downey site consistently provides fresh ultrafine particles, thereby maintaining the geometric mean diameters at less than 60 nm.

The slight increase in aerosol geometric mean diameters observed during the night, especially in colder months such as January, is probably driven by the growth of hygroscopic constituents of ultrafine PM such as NO_3^- and SO_4^{2-}. The relative humidity at night at Downey during that time of the year was in the 85–95% range, whereas the relative humidity at Riverside at night in the same time period was in the range of 65–75%. Overall, there is no substantial difference in the hourly averaged aerosol geometric mean diameters between individual months in Downey, regardless of season. The absence of temporal changes in geometric mean diameters supports the argument that ultrafine particles in Downey are mostly generated by primary emissions from near-constant local vehicular sources. In contrast, a distinguishable change in the diurnal trends of the geometric mean diameters of ultrafine aerosols was observed in Riverside as the season progressed from February to June. Figure 10b shows that the aerosol geometric mean diameter in Riverside increases from late February to June. In May and June, this increase is much more pronounced in the late-morning to early-afternoon period.

These changes in seasonal and diurnal trends of aerosol geometric mean diameters only in Riverside demonstrate the complexity and multitude of the source or formation mechanisms of particles in receptor areas of the Los Angeles Basin. The shift in size distribution in Riverside could be due to the following phenomena:

(1) advection of vapor species and consequent formation of secondary organic aerosols after in situ photochemistry in a short time (diurnal) scale; and
(2) rapid advection of aerosols originally emitted in upwind "source" areas of urban Los Angeles, such as Downey, after aging in the atmosphere for several hours during their transport eastward to the inland valleys.

The former scenario would affect the hourly (or diurnal) trends of the size distribution of mostly ultrafine PM, while changes in the accumulation mode in the receptor site would be indicative of the significance of the latter mechanism.

Figures 11 and 12 show typical particle size distributions in Downey and Riverside, respectively, measured on typical days with geometric mean diameters close to the

monthly averages. As shown in Figures 11a–d (October 10, 2000), particles measured in Downey consist of unimodal distributions with geometric mean diameters less than 60 nm. The overwhelming majority of these particles are generated by vehicular emissions from I-710 and I-605, both located upwind of the Downey site. A substantial fraction of vehicles on these two freeways are heavy diesel engines, which normally generate particles with modal diameters less than 50.[23] Apart from changes in the total particle number concentration, which are affected by meteorological factors, such as the atmospheric mixing depth or wind speed, there is little variation in the shape of the particle size distribution curves as well as in geometric mean diameters over the 12-hr period from 7:00 a.m. to 7:00 p.m. These observations illustrate the effect of the relatively constant vehicular emissions from nearby freeways in the area of Downey.

Compared with the unimodal size distributions in Downey, particles measured in Riverside show distinctly bimodal size distributions with one peak clearly less than and the other greater than 100 nm as seen in Figures 12a–d. Data from a typical day in May are presented, because a very clear decline in the average geometric mean diameter was observed in the afternoon during that month (see Figure 10). To distinguish between the actual contributions of each PM mode, measured size distributions were converted to submodes by means of multipeak curve fitting assuming that each submode follows a lognormal distribution. The modal diameter of the accumulation mode was set to 164 nm (i.e., the modal diameter at noon) because the data shown in Figure 12 indicate that the modal diameter did not change substantially during the noon–7:00 p.m. period. A striking feature of the data plotted in Figures 12a–d is the significant number of particles in Riverside found in the accumulation mode, compared with the results observed in Downey as well as numerous other studies conducted in urban areas and in locations mostly affected by vehicular emissions.[9,10,20,24]

These results also explain the relatively larger aerosol geometric mean diameters observed in Riverside than in Downey, shown in Figures 9 and 10. More importantly, Figures 12a–d demonstrate the evolution of the ultrafine mode as the day progressed from noon to early evening. The relative intensity of the ultrafine mode compared with the accumulation mode increased in the afternoon, reached a maximum between 3:00 p.m. and 4:00 p.m., and decreased after 4:00 p.m. The fraction of particles in the ultrafine mode is 32, 50, 65, and 59% of the total number concentration at noon, 2:00 p.m., 4:00 p.m., and 6:00 p.m., respectively. The increase of ultrafine PM during the afternoon period is of particular note, considering that factors

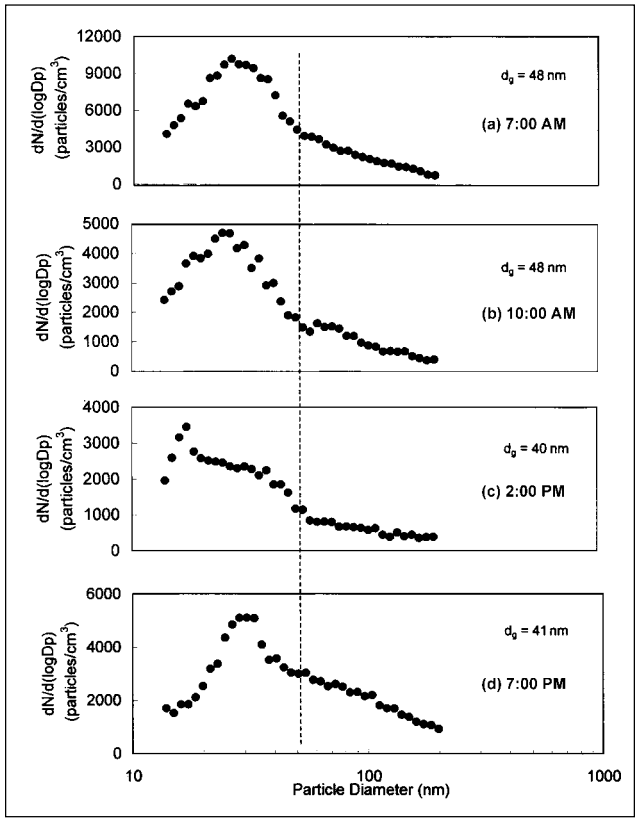

Figure 11. Size distributions of ultrafine particles at Downey, October 10, 2000 (d_g represents geometric diameter).

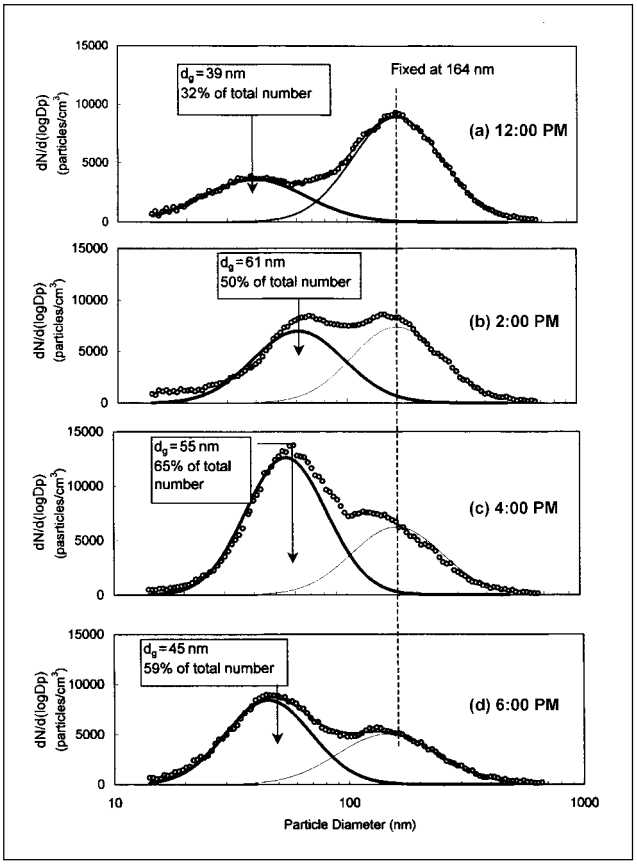

Figure 12. Simulated submodes of particles in the afternoon in Riverside, May 16, 2001.

such as wind speed, traffic, and atmospheric mixing layer all change in a direction that would tend to decrease the concentration of ultrafine PM if these were formed by primary emissions. Assuming constant emissions from the primary sources and based on the ultrafine PM fraction at noon, secondary aerosol formation accounts for more than half of the ultrafine PM by numbers at 4:00 p.m. A recent study conducted at the same location of Riverside in March reported that the ratios of OC to EC mass concentrations in ultrafine mode increased from the morning to the midday period.[17] The increase of the ultrafine mode is mostly due to heterogeneous nucleation processes initiated by secondary reactions that form low-vapor-pressure species.[11] These reactions are favored during periods of intensive solar radiation, as indicated in previous studies.[10,20]

The large number of particles found in the accumulation mode (see Figure 12) provides further evidence that Riverside is a "receptor" area, in contrast with Downey (see Figure 11). The evolution of accumulation mode in Riverside was more pronounced as the season progressed from February to June. Figure 13 shows the monthly averaged particle size distributions measured in Riverside at 6:00 a.m., a time period during which the size distribution is not affected by photochemistry. Averaged data from Downey during the same time period in February are also plotted in the same graph for comparison. Both the number concentration and the modal diameter of the accumulation mode increased as the season progressed from February to June. Considering that secondary aerosol formation due to photochemical reactions is impossible during this time of day, the increase in the accumulation mode in Riverside during the warmer season was at least in part due to the advection of particles of this size range originally generated, directly or via secondary reactions, in the source areas of urban Los Angeles.

The winter period in the Los Angeles Basin is characterized by surface temperature inversions in the coastal region and generally weak onshore flow. Hence, the highest

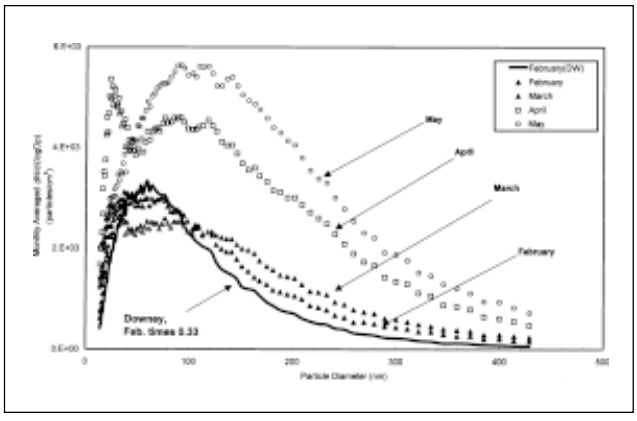

Figure 13. Monthly averaged particle size distributions in Riverside measured at 6:00 a.m.

ambient levels of primary pollutants such as ultrafine PM, CO, and NO_2 are generally observed in the coastal region during the winter months.[25] In contrast, the warmer period, typically ranging from May through late October, is characterized by higher temperature differences between the coastal regions and inland valleys of the basin, which result in strong temperature inversions aloft and a strong onshore flow. Together, these phenomena produce rapid transport of primary pollutants from the coastal and central region to the interior valleys. As the air parcels travel eastward, they pass over highly polluted areas in which ultrafine particle generation is enhanced by photochemical secondary reactions during the warmer seasons. By the time they reach the Riverside area, after a period on the order of 1 day,[11] the particles collected by the air parcel agglomerate to form more stable accumulation-mode particles. Additional rapid mixing in the atmosphere under high wind speed enhances the coagulation process.[19]

SUMMARY AND CONCLUSIONS

In this study, we investigated the physicochemical characteristics as well as diurnal and seasonal trends of ultrafine particles in a source (Downey) and a receptor (Riverside) site of the Los Angeles Air Basin. Data were obtained through both semicontinuous measurements and time-integrated sampling with the overall objective of understanding the processes that generate ultrafine PM in each location and their dependence on season as well as time of day. Overall, our experimental results clearly identified Downey as a source site, in which ultrafine particles are generated mostly by the near-constant vehicular emissions from nearby freeways. While primary emissions are important sources of ultrafine particles in Riverside during the colder months of the year, a substantial fraction of these particles is formed by photochemical secondary reactions as the season progresses toward the spring and summer. In Downey, hourly particle number concentrations followed very well the EC concentrations (a tracer of vehicular emissions) throughout 24 hr without significant monthly variation, thereby providing corroboration to the argument that these particles are directly emitted. By contrast, in Riverside, primary emissions are an important formation mechanism of ultrafine particles only in the colder months, whereas during the warmer period of the year (defined in Los Angeles as the period from May to October), the diurnal trends of ultrafine particle concentrations deviate substantially from those of EC concentrations.

Ambient particles in Downey displayed a consistently unimodal number-based size distribution, with modal diameters around 30–40 nm throughout the 5-month period from September 2000 to January 2001. The particle size distributions measured in Riverside indicated that, as the season progresses from winter to

spring, secondary reactions as well as advection of particles originally emitted in urban Los Angeles are important PM sources in that area. Secondary reactions are a short time-scale phenomenon, which affects only the diurnal pattern of the aerosol size distribution in Riverside by increasing the number of sub-100-nm particles in the afternoon hours. Advection of particles formed upwind of Riverside, a longer time-scale phenomenon, increases the accumulation mode of ambient PM throughout the day during the warmer months of the year. Our findings thus illustrated that mechanisms other than direct emissions play a significant role in the concentration of ultrafine particles found in receptor areas of the Los Angeles Basin.

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