Operation of SMPS and Low Temperature TEOM in locations of the USC Children's Health Study (CHS) and the Los Angeles Supersite

Contract Number: 01-300

Principal Investigator: Constantinos Sioutas, Sc.D.,
Professor,
Deputy Director Southern California Particle Center and Supersite

Co-Investigator: Manisha Singh, Ph.D, Research Associate

Civil and Environmental Engineering
University of Southern California
3620 S. Vermont Avenue
Los Angeles, CA 90089

4/29/05

Disclaimer

The statements and conclusions in this Report are those of the author and not necessarily those of the California Air Resources Board. The mention of commercial products, their sources, or their use in connection with material reported herein is not to be construed as actual or implied endorsement of such products

Acknowledgements

TABLE OF CONTENTS

List of Figures

Abstract

Continuous measurements of particle number, particle size-distribution (14-700 nm) and particle mass (PM_{10}) were obtained at thirteen sites (urban, suburban and remote) in Southern California during years 2002, 2003 and 2004 in support of University of Southern California Children's Health Study (CHS). We report the spatial and temporal variation of particle mass, numbers and number size distributions within these sites. Scanning Mobility Particle Sizer monitors were used to measure particle number size data and low temperature Tapered Element Oscillating Microbalance monitors were used for PM_{10} mass measurement. Higher average total particle number concentrations are found in winter (November to February), compared to summer (July to September) and spring (March to June) in all urban sites. Contribution of local vehicular emissions is most evident in cooler months, whereas effects of long-range transport of particles are enhanced during warmer periods. The particle size profile is most represented by a combination of the spatial effects, e.g. sources, atmospheric processes and meteorological conditions prevalent at each location. Afternoon periods in the warmer months are characterized by elevated number concentrations, suggesting the formation of new particles by photochemistry. The results presented in this report indicate that location and season significantly influence particle number and size distributions in locations within Southern California. Strong diurnal and seasonal patterns in number concentrations are evident as a direct effect of the sources, formation mechanisms, as well as meteorological conditions prevalent at each location during different times of the day and year. These results will be used in the CHS as a first order indicator of not only human exposure, but also inhaled dose to ultrafine PM. They will also be used for the development and validation of predictive models for population exposure assessment to ultrafine PM in complex urban environments, such as that of the Los Angels Basin.

Executive Summary
Background

The objective of this project was to deploy and operate the Scanning Mobility Particle Sizer (SMPS 3936, TSI Inc.) and low temperature Tapered Element Oscillating Microbalance (TEOM 1400A, R&P Inc.) in locations of the Children's Health Study (CHS) in Southern California and the Los Angeles Supersite. Both of these devices are near-continuous monitors and make it possible to measure the size distribution of ultrafine (0.01-0.1 μm) and the majority of fine (0.1 – 1.0 μm) particles (SMPS) and to determine PM_{10} mass, including its volatile species (TEOM). The basic reason for deployment of these new technologies was to provide supplementary air quality data for the CHS. However, there are many compelling additional uses for this data. It provides a unique opportunity to perform additional health studies to determine the acute responses to community exposures or as a database to evaluate other health impacts such as mortality. Ultrafine particle information is important to scientists and regulators who endeavor to understand freshly emitted particles, how they are transformed, and are transported throughout communities.

Methods

Concentrations of mass of particulate matter (PM) with aerodynamic diameters less than 10 μm (PM_{10}) and size resolved sub-micrometer particle numbers (14-700 nm) were continuously measured in several locations in Southern California as a part of the University of Southern California (USC) Children's Health Study, supported by the South Coast Air Quality Management District (SCAQMD) and the California Air Resources Board (CARB). Semi-continuous data were collected concurrently throughout the calendar years 2002 and 2003 and few months in year 2004. Thirteen sites were examined in this study, eight within the Los Angeles Basin (LAB): Long Beach, USC, Mira Loma, Upland, Riverside, Lake Elsinore, Lake Arrowhead and Glendora; and five sites at other areas of Southern California: Alpine, Atascadero, Lancaster, Santa Maria and Lompoc. Selection of the sampling sites was made on the basis of their location within Southern California and the presumed contrasting air quality (hence exposure) regimes in terms of PM and gaseous co-pollutants, which have differentially affected children's health. Due to the relatively western location in LAB and surrounding urban environment, Long Beach and USC are considered "source" sites where fresh particles are emitted primarily from vehicular sources. The easterly sites, Riverside, Upland, Glendora, Mira Loma, Lake Elsinore and Lake Arrowhead are designated "receptor" sites, which have comparatively less traffic density and experience advected, aged and photochemically processed air masses from Central Los Angeles. It should be noted here that the designation of these sites as "receptors" by no means precludes the impact of local traffic sources.

Number-based particle size distributions as well as PM_{10} mass were monitored at each site for 1-3 months duration during a warmer and a cooler period. Accordingly, two Scanning Mobility Particle Sizers (SMPS) were deployed by rotation at two sites during selected time periods to measure the size distribution of sub-micrometer aerosols (14-700 nm). Hourly PM_{10} mass concentrations at each site were measured by low temperature Differential Tapered Element Oscillating Microbalance monitors. Additionally, concentrations of carbon monoxide

(CO), ozone (O_3), total nitrogen oxide species (NO_x), were continuously measured in all these locations. The concentrations of CO were measured near-continuously by means of a trace level CO monitor. A continuous Chemiluminescence Analyzer was used for the measurement of concentrations of NO_x, while O_3 concentrations were monitored using a UV photometer.

Results

In this study we see enhanced contribution of local emission sources to airborne particulate numbers during cooler months with stagnant meteorological conditions at all sites. During winter, at source and receptor sites, number concentrations peak in the morning and evening across all particle size ranges. The diurnal profile of number concentrations coupled with mode and geometric mean diameters (diameters corresponding to the mode and geometric mean of the aerosol distribution, respectively) information indicates a traffic origin for these particles during winter. During warmer months, effects of long-range dispersal of aerosol are observed most clearly at the easterly receptor sites of Glendora, Riverside, Mira Loma and Lake Arrowhead. The increased wind speeds and onshore flow in the warmer months lead to increased advection of pollutant parcels from the polluted western areas of the Los Angeles Basin (LAB). Additionally, dry and hot summer conditions would limit ultrafine particle growth to accumulation mode during transport. Afternoon periods in the warmer months are characterized by elevated number concentrations, suggesting the formation of new particles by photochemistry. It is interesting to note in our field measurements that summertime levels of ultrafine particles at source sites, such as Long Beach and USC peaked in midday (i.e., noon to 1 pm), whereas ultrafine PM numbers peak slightly later (i.e., between 3-4 pm) in the inland receptor sites. The time delay in the peak concentrations observed at the receptor sites is possibly due to the transport time for polluted air masses to reach those sites.

The correlation between particle number concentrations and PM_{10} has been widely studied and weak-to-moderate correlations have been generally observed between the two (Morawska et al., 1998; Woo et al., 2001; Noble et al., 2003; Fine et al., 2004; Sardar et al, 2004). Since the fine to ultrafine particle counts are dominated by very small particles and the PM_{10} mass is dominated by fewer, much larger particles, low correlation should be expected, especially in air masses dominated by fresher particles (either primary emission particles or freshly formed secondary particles). In our study, we also found weak-to-moderate correlations between PM_{10} and number concentrations with no particular seasonal trend (described in detail in Appendix C). These findings are very important from a regulatory perspective because they imply that controlling ambient PM_{10} mass via national air quality standards may not necessarily reduce human exposure to ultrafine particles that dominate the particle counts and have recently been shown to have toxic effects (as discussed in the introductory part of the report).

The correlation between particle number (PN) and gaseous pollutants [carbon monoxide (CO), nitric oxide (NO), oxides of nitrogen (NOx), and ozone (O3)] was investigated (described in Appendix A). The degree of correlation between hourly PN and concentrations of CO, NO, and nitrogen dioxide (NO2) at each site over the entire year was generally low to moderate (r values in the range of 0.1–0.5), with a few notable exceptions. In general, associations between PN and O_3 were either negative or insignificant. Similar analyses of seasonal data resulted in levels of correlation with large variation, ranging from 0.0 to 0.94 depending on site and season. Summertime data showed a generally higher correlation between the 24-hour average PN concentrations and CO, NO, and NO2 than corresponding hourly concentrations. Hourly

correlations between PN and both CO and NO were strengthened during morning rush-hour periods, indicating a common vehicular source. Comparing hourly particle number concentrations between sites also showed low to moderate spatial correlations, with most correlation coefficients below 0.4. Given the low to moderate associations found in this study, we conclude that gaseous co-pollutants should not be used as surrogates to assess human exposure to airborne particle number concentrations.

During the period of September 30 to October 9, 2002, union workers at the port of Long Beach, CA went on strike. A detailed analysis of the effect of this strike on particulate characteristics of Long Beach was performed by a comparison of PM as well as co-pollutant characteristics from pre-, during and post-strike periods. Our statistical analysis revealed statistically significant increase in concentrations of gaseous co-pollutants- NO_x and CO during the strike compared to pre- as well as post-strike period (p < 0.001). We also found statistically significant increase in particle number concentrations in the 60 to 100 nm as well as 100-200 nm ranges during the strike period. The increases in particle numbers (60-200 nm) as well as gaseous co-pollutant concentrations during the strike are indicatives of contributions of emissions from the idling ships at port during the strike period.

In late October of 2003, 13 large Southern California wildfires burned more than 750,000 acres of land, destroyed over 3,500 structures, and displaced approximately 100,000 people. The fire episode was declared the deadliest and most devastating in more than a decade, and local media advised individuals to stay indoors to avoid exposure to excessive levels of PM, CO, VOCs, and ozone caused by the wildfires. We took this opportunity to examine the actual impact of these wildfires on air quality in urban Los Angeles using the air quality data generated from this study. As described in Appendix B, measurements of pollutant gases (CO, NOx, and ozone), particulate matter mass concentration (PM), particle number concentrations (PN) and particle size distributions at several sampling locations in the LA basin before, during, and after the fire episode are presented. In general, the wildfires caused the greatest increases in PM10 levels (a factor of 3-4) and lesser increases in CO, NO, and PN (a factor of up to 2). NO2 levels remained essentially unchanged and ozone concentrations dropped during the fire episode. Particle size distributions of air sampled downwind of the fires showed number modes at diameters between 100 and 200 nm, significantly larger than that of typical urban air. The particles in this size range were shown to effectively penetrate indoors, raising questions about the effectiveness of staying indoors to avoid exposure to wildfire emissions.

Conclusions

The results presented in this report indicate that location and season significantly influence particle number and size distributions in locations within Southern California. Strong diurnal and seasonal patterns in number concentrations are evident as a direct effect of the sources, formation mechanisms, as well as meteorological conditions prevalent at each location during different times of the day and year. These results will be used in the CHS as a first order indicator of not only human exposure, but also inhaled dose to ultrafine PM. They will also be used for the development and validation of predictive models for population exposure assessment to ultrafine PM in complex urban environments, such as that of the Los Angels Basin.

Body of Report

Introduction

A number of observational studies have demonstrated acute and chronic effects of ambient particles on human health (Dockery and Pope 1994; Zanobetti et al. 2000; Pope, 2000). To this date, however, there appears to be heterogeneity in particulate matter (PM) concentrations and PM-associated health effects between locations within an urban setting, which raises considerable uncertainties as to whether PM mass, number, size, bulk or surface chemistry are the appropriate metrics associated with PM toxicity. For example, recent studies have shown that atmospheric ultrafine particles (with physical diameter < 100 nm) have the potential for eliciting adverse health effect (Oberdörster and Utell, 2002; Li et al., 2003; Li et al., 2004; Xia et al., 2004). Recent epidemiological studies by Peters et al. (1997), have demonstrated association between health effects and exposures to ultrafine particles compared to accumulation mode or coarse particles.

In the complex environment of an urban atmosphere, there is great variability in the number and type of sources of particles as well as in the diurnal and seasonal patterns of their emission strengths, all of which affect human exposure. Traffic is without doubt one of the most dominate sources of particles in urban areas (Shi et al., 1999; Cyrys et al., 2003). Recent studies have shown a dramatic decrease of ultrafine number concentrations with increasing distance from busy freeways in Los Angeles, thereby demonstrating that vehicular pollution is a major source of ultrafine particles and that high number concentrations can be a localized phenomenon, on scales of 100-300 meters (Zhu et al., 2002a,b). In addition to their direct emission in the atmosphere, particles may be formed as a result of photochemical reactions from gaseous precursors, including particulate sulfate formed from precursor sulfur dioxide, and secondary organic aerosols, formed from oxidation of aromatic hydrocarbons (Derwent et al., 2000). The secondary aerosol formation is largely governed by meteorological factors (Mäkelä et al., 1997, Kim et al., 2002). The high degree of temporal variability of the meteorological parameters such as degree of solar radiation, atmospheric mixing depth, humidity, and temperature - all contribute to the temporal variation in particulate number concentrations at a location.

Understanding how the number concentrations of particles change as a function of particle size, time of the day, location and season may help characterize the sources of these emissions as well as refine human exposure parameters used in epidemiological studies that attempt to link particulate levels and health effects they induce.

Due to recent health concerns, particle size distributions and number concentrations in several cities have been measured. Some recent continental sampling campaigns that measured size distributions include the Pittsburgh Air Quality Study (Stanier et al., 2004), the Atlanta PM Supersite program (Woo et al., 2001), and sampling campaigns in Los Angeles (Kim et al., 2002; Fine et al., 2004), Northern Europe (Ruuskanen et al., 2001), Tennessee (Cheng and Tanner, 2002), Brisbane, Australia (Morawska et al., 2002), the UK (Harrison et al., 2000), Estonia and Finland (Kikas et al., 1996) and Central Europe (Birmili et al., 2001). Most of these studies were conducted in urban areas in which the vast majority of ultrafine PM originate from primary sources (Morawska et al., 1998; Harrison et al., 2000; Woo et al., 2001), thus their diurnal profiles match those of local vehicular sources. The majority of these studies were also intensive in nature, conducted for a period ranging from a few weeks to a few months.

Shi et al. (2001) measured temporally resolved number concentrations to examine periods of nucleation events. Lawless et al. (2001) used the near continuous data obtained from an SMPS

1

and an optical particle counter to distinguish between primary and secondary contributions to $PM_{2.5}$ in Fresno, CA. These studies were intensive in nature, focusing on one specific location and for a limited time period. The spatial aerosol characteristics at different locations of a city have also been examined. Kim et al. (2002) identified periods of photochemistry and long-range advection as sources of ultrafine PM at two sites in Los Angeles Basin in addition to local vehicular emissions. Fine et al. (2004) inferred sources of ultrafine particles at two different locations in the eastern portion of Los Angeles Basin. Buzorius et al. (1999) measured aerosol characteristics at a series of sites in Helsinki, Finland in order to investigate the transport of aerosol traveling from source sites to receptor sites. Ruuskanen et al. (2001) conducted monitoring in three different European cities using continuous monitors to describe differences among the sites as well as diurnal variations of particle mass and number concentrations. Little information has been reported on the seasonal patterns of size distributions due to the lack of long-term monitoring. Stanier et al. (2004) measured aerosol size distributions at one location in Pittsburgh for an entire year, providing one of the first data sets in Northern United States from which seasonal patterns can be described.

The work presented in this report is intended to provide more comprehensive information about spatial, seasonal as well as diurnal variations of atmospheric particle numbers and size distributions (14-700 nm) within Southern California. This report utilizes the data set generated in support of the University of Southern California (USC) Children's Health Study (CHS). The CHS, which began in 1993, is one of the largest investigations of the long-term consequences of air pollution on the respiratory health of children. The main goal of CHS is to identify chronic effects of ambient pollutants in Southern California by performing cross-sectional and longitudinal studies in school children in several communities with varying exposures to particulate matter, ozone, and acid vapors. In this report we present ambient particulate characteristics measured at thirteen sites classified as urban (source and receptor) and remote (suburban/ mountainous) sites in Southern California during the years 2002 ,2003 and 2004.

Material and Methods

Concentrations of mass of particulate matter with aerodynamic diameters less than 10 μm (PM_{10}) and size resolved sub-micrometer particle numbers (14-700 nm) were continuously measured in several locations in Southern California. With the exception of USC site these locations were monitoring sites in support of the University of Southern California (USC) Children's Health Study. Semi-continuous data were collected concurrently throughout the calendar years 2002 and 2003 and for a few months in year 2004. Thirteen sites were examined in this study, eight within the Los Angeles Basin (LAB): Long Beach, University of Southern California, Mira Loma, Upland, Riverside, Lake Elsinore, Lake Arrowhead and Glendora; and five sites at other areas of Southern California: Alpine, Atascadero, Lancaster, Santa Maria and Lompoc as shown in Figure 1. Selection of the sampling sites, discussed in greater detail by Künzli et al. (2003), was made on the basis of their location within the LAB and the presumed contrasting air quality (hence exposure) regimes in terms of PM and gaseous co-pollutants, which have differentially affected children's health. Additionally, concentrations of carbon monoxide (CO), ozone (O_3), total nitrogen oxide species (NO_x), were continuously measured in all these locations. The concentrations of CO were measured near-continuously by means of a trace level CO monitor. A continuous Chemiluminescence Analyzer was used for the measurement of concentrations of NO_x, while O_3 concentrations were monitored using a UV photometer.

Table 1. Sampling Schedule

Site No.	Site Name	Sampling Period
1	Glendora	Jan-Feb'02, May-Jun'04
2	Lompoc	Jan-Feb-Mar'03
3	Long Beach	Sep-Oct-Nov'02, Aug-Sep'03
4	Mira Loma	Dec'02-Jan-Feb'03, Jun'02
5	Santa Maria	Oct-Nov'03, Feb-Mar-Apr'04
6	Riverside	Mar-Apr'02, Sep-Oct-Nov-Dec'02
7	Lake Elsinore	Apr'03
8	Lake Arrowhead	Jul-Aug'02, Jun-Jul'03
9	Atascadero	Apr'02, Jan-Feb-Mar'03
10	Alpine	Apr-May'03, Dec'03-Jan'04
11	Lancaster	Jun-Jul'03, Mar-Apr'04
12	Upland	Aug-Sep-Oct'03, Nov-Dec'03-Jan'04, May-Jun-Jul'04
13	USC	Dec'02-Jan'03, Sep'03

Located near a busy surface street, the Long Beach station is about 0.5 km northeast of freeway I-405 and approximately 1.5 km east of freeway I-710. The Long Beach station is mostly downwind of these two freeways as well as the Long Beach port which is situated approximately 7 km south of the sampling station. The Upland site is located in a residential area inside a community trailer park about 100 m from San Bernardino road, and is within 2 km (mostly downwind i.e., north-east) of the freeway 210. The Mira Loma site (about 80 km east of downtown Los Angeles) is located in a building on the Jurupa Valley High School campus, directly southeast of the intersection of freeways 60 and 15. The site is surrounded by several major warehouse facilities with frequent heavy-duty diesel truck traffic (Sardar et al., 2004; Na et al., 2004) and near several major cattle feeding operations. The sampling location at Riverside is within the Citrus Research Center and Agricultural Experiment Station (CRCAES), a part of the University of California, Riverside. It is located about 20 km southeast of the Mira Loma site and is situated upwind of surrounding freeways and major roads (Phuleria et al., 2004). The Glendora station is located at 840 E Laurel Ave. in a residential area away from major roadways. Atascadero station is located in the parking lot of the local fire station on Traffic way. The Lompoc station is located at 4350 Constellation Rd., in the parking lot of Cabrillo High School. The desert site of Lancaster is located in the office of Mojave desert AQMD and is approximately 2 km away from the nearest freeway SR 14. The Lake Arrowhead monitoring station is located in the Rim of World High School near highway 18, at an elevation of about 1700 m. It is a purely serene mountainous site with very few local emission sources, but heavily impacted by transported, aged air pollutants. Lake Elsinore is a rural site that is upwind of the I-15 freeway in southeastern California. Santa Maria sampling site is located at 906 S Broadway, Santa Maria. The sampling site at USC is located near downtown Los Angeles, approximately 100 m downwind of freeway 110. The Alpine station is a remote suburban to rural site located approximately 50 km east of downtown San Diego (approximately 200 km southeast of downtown Los Angeles).

Due to their relatively western location in Los Angeles Basin (LAB) and surrounding urban environment, Long Beach and USC are considered "source" sites where fresh particles are emitted primarily from vehicular sources. The easterly sites, Riverside, Upland, Glendora, Mira

Loma, Lake Elsinore and Lake Arrowhead are designated "receptor" sites, which have comparatively less traffic density and experience advected, aged and photochemically processed air masses from Central Los Angeles. It should be noted here that the designation of these sites as "receptors" by no means precludes the impact of local traffic sources, as it will be discussed later in this report. The time for air masses to transport from source to receptor sites can vary from a few hours to more than a day (Sardar et al, 2004).

Number-based particle size distributions as well as PM_{10} mass were monitored at each site for 1-3 months duration during a warmer and a cooler period. Accordingly, two Scanning Mobility Particle Sizers (SMPS, Model 3936, TSI Incorporated, St. Paul, MN) were deployed by rotation during selected time periods, as shown in Table 1, to measure the size distribution of sub-micrometer aerosols (14-700 nm) using an electrical mobility detection technique. In this configuration, the Condensation Particle Counter (CPC, Model 3022/A, TSI Incorporated, St. Paul, MN) flow rate was maintained at 0.3 L min^{-1} (with the sheath flow of the SMPS set at 3 L min^{-1}), and size- segregated particle number concentrations were recorded. Continuous particle number concentrations were averaged over 1-hour intervals for the subsequent analysis. The size distributions obtained from SMPS were used to derive information about aerosol properties like number median diameter, mode diameter and geometric mean (geomean) diameter of the aerosol. These three diameters correspond to the particle diameter corresponding to median, mode and geomean values of the number based aerosol size distribution. The ambient aerosol distributions are more or less log-normally distributed. For such size distributions these three diameters are very close in value and can be used interchangeably.

Hourly PM_{10} mass concentrations were measured during the first two months (December 2001 and January 2002) of the project by 30^0 Tapered Element Oscillating Microbalance (TEOM 1400A, R&P Inc., Albany, NY). Glendora and Mira Loma sites were monitored during these two months. These TEOMs suffered from negative bias in measurements. The TEOM is known to under-report PM mass under many ambient air-sampling conditions because it operates at temperatures far in excess of ambient (Allen et al., 1997). Volatile organic and nitrogen compounds are largely not measured as part of the mass by these devices due to volatilization. To correct this problem, the 30^0 TEOM were replaced by low temperature Differential Tapered Element Oscillating Microbalance monitors (low temperature TEOM 1400A, R&P Inc., Albany, NY) for subsequent sampling periods. Jacques et al. (2004) have described the design and performance evaluation of this monitor in greater detail. Briefly, the system consists of a size-selective PM_{10} inlet, followed by a Nafion® dryer that reduces the relative humidity of the sample aerosol to 50% or less. Downstream from the Nafion dryer and ahead of the TEOM sensor is an electrostatic precipitator (ESP) to alternately remove particles from the sample stream or allow the particle laden sample stream to continue to the sensor. The ESP is alternately switched on and off, for equal time periods of about 10 minutes. This dual sampling channel design makes it possible to account for effects such as volatilization of labile species, adsorption of organic vapors and changes in relative humidity and temperature, all of which affected the previous TEOM signal. The study by Jacques et al. (2004) showed that the time averaged TEOM PM_{10} mass concentrations agreed within ± 10% with those of collocated Federal Reference Methods (FRM). During months of September and October 2002 when sampling was being conducted in Riverside and Long Beach sites a PM2.5 cyclone preceded the TEOM inlet. Thus PM data for these two months obtained from TEOM is PM2.5 mass concentration data instead of PM10 mass concentration data.

Results

    The section describing our results is divided into four parts: Number based size distributions-seasonal and spatial trends, diurnal trends- PM$_{10}$ Mass, Number Concentrations and Number based characteristics, Long Beach October 2002 strike analysis and Air quality impacts of the October 2003 Southern California wildfires The latter two parts are "opportunistic" studies focusing on the impact of the union workers strike at the port of Long Beach on air quality and on the wildfires episodes in Southern California.

Number based size distributions- seasonal and spatial trends

    Descriptive statistics (total counts of particles within 14-700nm diameter and number median diameter) of the measured particle size distributions are presented in Table 2. Figure 2 depicts the particle size distributions measured by the SMPS during different seasons at our sampling sites. Average number size distributions at USC in summer as well as winter are very similar and corroborate the hypothesis that this site is heavily influenced by fresh vehicular emissions. Particles in the 20 - 50 nm range, which could be attributed to traffic, are the most abundant at this site. Also, number concentrations of this size range increase during the winter period. USC has similar number median diameter(NMD) during both seasons, an indication of the consistency of the sources (i.e., the traffic emissions from the nearby freeway I-110) affecting PM characteristics in that location. During the summer period, although total particle counts are lower due to more vertical mixing, particles < 20 nm diameter appear to be more abundant than in winter months. These particles could be due to contribution of enhanced photochemical particle formation in the summer months. Such new particle formation depends strongly on the intensity of solar radiation (O'Dowd et al.1999; Wehner and Wiedensohler, 2003), but the exact mechanism by which nucleation occurs is yet to be understood (Zhang and Wexler, 2002; Kulmala et al., 2004).

    Similar to USC, at Long Beach which is also a site highly impacted by vehicular emissions, the average particle number concentrations are higher in winter than summer for the particles > 40 nm. However, summer months witness an increase in particles <40 nm diameters. The size distribution in summer supports the hypothesis that this site may be influenced markedly by photochemically generated particles. Given that this site is situated close to the ocean, with the only major upwind sources being the port and the nearby freeways 710 and 405, both of which are quite proximal (i.e., within 8 km or less) to the site, the contribution of long range transport to particle numbers can be ruled out. The number median diameter (NMD) of the aerosol is also lower in summer than in winter. Larger NMD in winter (79.9 nm) compared to summer (59.8 nm) may be due to high relative humidity in the winter months, which would contribute to growth of particles by condensation of water vapor in the air. It should be noted that the proximity of that site to the ocean results in higher relative humidity levels compared to the rest of the urban sites, with prolonged periods of nighttime and morning fog. The smaller summertime NMD could be due to the increased photochemical production of smaller particles, as observed by Kim et al. (2002) and Wehner and Wiedensohler (2003). During the first week of October, union workers at the port of Long Beach went on strike. A detailed analysis of the effect of this strike on particulate characteristics of Long Beach is discussed in later section of this paper.

    Riverside, Mira Loma, Upland and Glendora are receptor sites downwind of the high concentration of sources in the western part of LAB. In addition to the effect of few local emission sources, particle number concentration at these receptor areas is also influenced by

aged, advected aerosol from the west, especially in summer season. The Upland station was directly impacted by Southern California wildfires during late October 2003 because of its location some 3.5 km downwind of one of the 13 fires during that period. The impact of this fire on aerosol characteristics is discussed in a later section of this report and thus we do not present the analysis here. However, for our seasonal characteristics analysis, we have excluded the data from that period.

At Riverside, the particle number concentrations are higher in winter compared to spring for particles <100nm. It is interesting to observe that the particles >100 nm are slightly higher in the spring period. The increase in the peak median size in springtime may be due to the contribution of advected, thus aged aerosols, which are generally larger in diameter (Zhang and Wexler, 2002), from the western polluted regions of the Los Angeles Basin.

The size distribution of aerosols also shows some seasonal variation at Mira Loma. In addition to a decrease in particle number concentrations, the number size distribution shifted towards larger sizes in summer compared to winter. Decrease in particle counts of all size ranges in summer reflects the effect of more dilution with elevated mixing height in warmer months. As in Riverside, the NMD of the aerosol in Mira Loma is larger in warmer season (Table 2). This may be the result of the increased wind speeds and onshore flow in the warmer months, leading to increased advection of pollutant air parcels from the western LAB. This advected aerosol is generally larger in diameter as noted earlier and would lead to larger NMD of the summer/spring aerosols.

Average number size distributions at Upland in summer as well as winter are very similar and suggest that the major contributor of PM at this site is the fresh vehicular emissions from nearby freeway. Upland has similar number median diameter during both seasons, an indication of the consistency of the sources (i.e., the traffic emissions from the nearby freeway) affecting PM characteristics in that location. During the summer period, total particle counts are lower due to more vertical mixing.

At the suburban remote site Alpine, in contrast to all the receptor sites discussed above, the particle numbers <100 nm are markedly higher in warmer months than in comparatively cooler periods (Figure 2 h). The NMD also shifts from 79 nm in winter to 43 nm in spring (Table 2). This may be due to increased summertime advection and photochemical particle formation. The influence of summer advection and photochemical particle formation is supported by wind data, which indicates a change in wind direction at Alpine from easterly (offshore) to westerly (onshore). The westerly winds would bring the aging air-mass from the San Diego metropolitan area to the station. The afternoon peak of aged and photochemically-derived particles occurs several hours after the wind direction change, allowing time for the air mass to reach the station from San Diego.

Particle size distribution data is available for only a spring month at Lake Elsinore and only a winter month at Lompoc. Winter period data for site Lake Elsinore was lost due to computer theft at this station. The data collected for summer period at Lompoc had to be rejected due to instrument malfunction. Thus these sites have data for a single season only. Both these sites display generally much lower number concentrations than the urban sites, as one would expect. The number concentrations at Lake Arrowhead are also comparatively lower than the urban sites. Some seasonal variation in size distributions is witnessed at Lake Arrowhead. The summer months have comparatively lower number concentrations with higher NMD as compared to spring months. This could be attributed possibly to more vertical mixing in summer as compared to cooler spring period. At the remote sites Atascadero and Santa Maria, the NMD as well as

number size distributions are similar in colder and winter seasons, with warmer periods exhibiting lower concentrations as a result of more vertical mixing. Overall average particle numbers at these locations are also much lower than the urban source and receptor areas. At the desert suburban site Lancaster, some seasonal variation in size distributions is witnessed; the particles < 100 nm diameter are much more abundant in spring as compared to summer period, an indication of enhanced contribution from few local vehicular sources in cooler period for reasons discussed before for the urban sites.

Table 2: Summary statistics showing average total particle number concentration (PN) and number median diameter (NMD)

Site no	Site	Season	Period	PN (Particles/cc)		NMD (nm)	
				Grand Avg.	Std. Devn.	Grand Avg.	Std. Devn.
1	Glendora	Winter	Jan-Feb '02	6479	3998	68.7	16.8
	Glendora	Summer	May-Jun'04	7690	5384	55.9	15.9
2	Lompoc	Winter	Jan-Feb-Mar '03	3683	3025	53.0	16.9
3	Long Beach	Winter	Nov '02	11018	5213	79.9	18.8
	Long beach	Summer	Aug-Sep '03	8938	5718	59.8	18.3
4	Mira Loma	Winter	Jan-Feb '02	19717	22227	65.2	19.4
	Mira Loma	Spring	Jun '02	8790	2753	81.6	20.5
5	Santa Maria	Spring	Feb-Mar-Apr '04	2823	1965	71.4	20.1
	Santa Maria	Winter	Oct-Nov '03	4497	3720	68.1	20.1
6	Riverside	Winter	Nov '02	10248	6577	47.7	16.6
	Riverside	Spring	Mar-Apr '02	7668	4360	62.6	21.3
7	USC	Summer	Sep '03	12458	5617	45.9	11.2
	USC	Winter	Dec '02 - Jan '03	14271	7393	45.4	14.2
8	Upland	Summer	Aug-Sep-Oct '03	10913	4105	61.5	14.1
	Upland	Winter	Nov-Dec '03 - Jan '04	16034	8944	56.6	13.6
9	Alpine	Spring	Apr-May '03	5034	3202	42.9	14.4
	Alpine	Winter	Dec '03 - Jan '04	2492	2012	79.3	18.5
10	Atascadero	Spring	Apr '02	3849	2798	104.0	39.8
	Atascadero	Winter	Jan-Mar '03	3839	3530	95.4	28.4
11	Lancaster	Spring	Mar-Apr '04	10153	8596	46.2	13.9
	Lancaster	Summer	Jun-Jul '03	3209	2700	81.9	18.0
12	Lake Arrowhead	Spring	Jun-Jul '03	4968	3553	66.9	17.4
	Lake Arrowhead	Summer	Jul-Aug '02	3114	2482	77.9	16.7
13	Lake Elsinore	Spring	Apr'03	3616	2928	75.7	20.7

Diurnal profiles- PM Mass, Number Concentrations and Number based characteristics

This section describes our observations of diurnal trends in particulate matter characteristics, which, combined with the size distributions, may provide insights into sources and possible formation mechanisms of particulate matter in each of these sites.

Figure 3 shows diurnal profile of particle number and mass for the month of December, 2001 in Glendora and Mira Loma. The error bars indicate the standard error calculated based on sampling size.   Particle mass concentration is calculated based on the particle number concentration measured by the SMPS, assuming perfectly spherical particles with a density of 1.6 g/cm3. The Glendora sampling station is not near any major roadways. There are no major emission sources near the sampling site. As the day progresses, the particulate matter emitted from Los Angeles eventually reaches the area of the Glendora sampling station. The temperature also drops as the day progresses in late afternoon causing the mixing layer to decrease in height. These factors cause the concentration of particles in the $PM_{0.5}$ (particulate matter < 500 nm in diameter) range to increase in the later hours of the day in Glendora. The sampling location in Mira Loma is different from Glendora in that it is located near the intersection of freeway 60 and freeway 15. Morning traffic emissions are clearly reflected in the profile shown in figure 3b. As the day progresses, temperature decreases beginning late in the afternoon and emissions from Los Angeles accumulate, and the particle concentration peaks in the late evening.

Figure 4 shows the correlation between number and surface area for December 2001 in both sites. There is very good correlation between number and surface area in both locations with R^2 of 0.8 and 0.86 for Glendora and Mira Loma, respectively. Figure 5 shows the diurnal profile of particle number and mass concentration measured by SMPS for January 2002 in both sampling sites. Similar trends as in December were observed.

Figure 6 shows the particle number and surface area correlation in both sampling sites for the month of January 2002. Very high correlation was again observed in Glendora with $R^2=0.88$. For Mira Loma, two distinct trends of particle formation were observed as shown in figure 6b, which possibly may indicate two separate sources during this period.

Figure 7 shows the daily profile of particle number concentration measured by SMPS and the particle mass concentration measured by 30˚C TEOM. Particle number concentration is measured for $PM_{0.5}$, while TEOM measure particle mass concentration for PM_{10}. During morning traffic hours, 6am to 8am, fresh emissions from motor vehicles generally contain high concentration of volatile organics. Temperature during this traffic period is also relatively low during the month of December and January. Therefore, when the air sample is heated to 30˚C, a large portion of the volatile compounds may have been lost. A significant fraction of particle mass concentration data collected by TEOM during this traffic period was shown to be negative. Similar problem was observed for the TEOM data during midnight. This problem is especially pronounced in Mira Loma, since a large portion of its particle concentration in the morning is generated by the nearby freeways. This can be seen in figure 7a . During the morning traffic hour, the particle number increases while particle mass measured by TEOM decreases. This problem was remedied when the newer versions of TEOM, operating with dual channel Electrostatic Precipitators were installed at this site in following months

Figure 8 shows the estimated geomean diameter during December 2001 and January 2002 in both sites. Little change was found in Mira Loma from December to January. Geometric mean (hereafter referred to as "geomean") diameter of the aerosol in Glendora, however, was much lower in January as compared to December .

Figures 9 and 10 show the profile of particle number concentration and surface equivalent diameter in Riverside during March and April 2002, respectively. The Riverside station is very similar to Mira Loma. Particle number concentration peaks during morning traffic period. Advection from Los Angeles also increases the particle number concentration as the day

progresses. The total number concentration at Riverside is much lower than Mira Loma. The surface equivalent diameters for both sites are also comparable.

Atascadero is a unique site because it is located in the rural region of Central California. There are no immediate sources of local emissions other than the fire station traffic and traffic on a rural portion of Hwy 101 approximately 0.3 km west of the station. The particle number concentration as a function of the time of the day during April 2002 is shown in figure 11 (a). The peak at 7 am could be presumably related to small local traffic coupled with the depressed mixing depth of the atmosphere at that time of the day. There is also an increase in particle number concentration at around noon time, which may be a result of photochemistry. The poor correlation between surface area and number concentration (Figure 11b) suggests that the high concentration of particles may be a result of several different formation mechanisms in the site during the sampling period.

Figure 12 present the general particulate matter characteristics observed in Mira Loma in summer of 2002. Consistent with measurements made in January 2002, the particle number concentration at Mira Loma is the highest among receptor sites in Los Angeles Basin (Figure 12a). The significant increase in number concentration observed during morning traffic hours in the previous months was not as pronounced in the June 2002 data. This may be due to the fact that the high school is out of session during this month. The high school traffic represents a significant local source since the station is located in the parking lot of the school. Gradual increase in number concentration as the day progresses is still observed as a result of advection of PM from urban LA sites located west (hence upwind) of Mira Loma. This is consistent with observations made in January 2002. Mode diameter and geomean diameter fluctuate significantly throughout the day ranging from 60nm to 125 nm at noon. The two indications of distribution characteristics agree well, indicating that in general, the particles in Mira Loma have unimodal distribution. The fluctuation during the day could be a result of local traffic emissions (from Freeway 60 and 15) and advection from Downtown area. The correlation between number and surface area concentration is approximately 0.5. This could also indicate that there maybe more than one source of particulates in Mira Loma during the months of June 2002.

Lake Arrowhead is located at an elevation of approximately 1700 m. During early morning and night, the inversion layer is generally below the station location. This is clearly observed in Figures 13-14a with low number concentration measured by the SMPS. As the day progresses, the warmer temperature cause the inversion layer to rise. Eventually, the station is under the inversion layer. The site is then significantly affected by advection from Los Angeles area. During the month of July 2002, Rim of the World High School is out of session. There is very little local emission. The mode diameter and geomean diameter remain relatively constant through out the day (Figure 13b). The high correlation between particle number and surface area concentration further reaffirm the hypothesis that there maybe only one source of particulate in the area – advection from Los Angeles area.

Figures 15 and 16 show the particulate matter characteristics found in Long Beach during the months of September and October 2002, respectively. During the period of September 30 to October 9, 2002, union workers at the port of Long Beach, CA went on strike. The impact of this strike on aerosol characteristics is discussed in detail in a subsequent section of this report thus we do not present the analysis here. However, for our seasonal characteristics analysis, we have excluded the data from that period. The diurnal profile of the particle numbers during both these months is very similar. The highest number concentration occurs during the middle of the day. Additionally comparatively smaller peaks are observed in morning and

evening periods. During warmer months, secondary aerosol formation is favored and new ultrafine particles may form as a result of the condensation of low-volatility products of photochemical reactions (largely organic compounds) onto stable, nanometer-size particles (O'Dowd et al 1999; Kim et al., 2002; Sardar et al., 2004). Secondary aerosol formation is the most likely explanation for the diurnal trends in PN during the summer period at Long Beach in which the peak particle concentrations during the afternoon period. The smaller morning and evening peaks of these pollutants correspond to morning and evening vehicular commutes on nearby freeways as well as Long Beach Blvd.

Figure 17 shows the PM characteristics found in Long Beach during the month of November 2002. The number concentration profile (Figure 17 a) exhibits a diurnal profile that is consistent with the pattern of traffic found on Long Beach Blvd and nearby freeways, with the number concentrations peak during early morning period (6-10 a.m.) and decrease during the day peaking again in the evening and nighttime periods. Possible explanation for these observations is that ultrafine PM, which mostly originate from vehicular emissions at Long Beach, become maximized during the early morning period when traffic peaks and atmospheric mixing depth is at a minimum. The number concentrations reach a minimum during afternoon period, because of decrease in traffic, and increase in mixing depth (which tends to dilute the vehicular emissions). The contribution of secondary aerosol processes during afternoon witnessed in September and October is not evident in the comparatively cooler month of November. The number concentrations increase again during the nighttime, mainly due to contributions of the evening traffic as well as depression of atmospheric mixing depth. Figure 17b shows the geomean diameter and mode of particulate matter at Long Beach during the month of November 2002. The figure suggests that particulates observed in the morning hours are different than those measured in the afternoon. PM appears to have a steady mode diameter between 85-90 nm from midnight to around 10 a.m. suggesting the condensational growth of existing particles due to fog during nighttime and morning hours. As the day progresses, temperature tends to increase, RH decreases, and both these factors reduce condensational growth leading to decrease in mode diameter of the aerosol during daytime.

Figures 18 -21 show the PM characteristics observed in Riverside, California during September-December 2002. In general, morning traffic may be the major contributor of particulate matter between 5-8am as shown by the peak in number concentration observed at 8am in all months (Figures 18a -21a). This time period also corresponds to decreases in mode diameter as shown in Figures 18b - 21b. As the day progresses, particle number concentration reach a minimum at noon when the inversion layer is the highest and mixing is the greatest. Particles were also observed to have the highest mode diameter at noon, indicating that these particles are stable. In the afternoon the particle number concentration continues to increase, reaching a peak at 8pm, which lasts through the night. This may be the result of long-range advection of particles from Los Angeles, combined with some local evening traffic; as the temperature cools and the mixing level decreases, particle concentration increases. Atmospheric mixing is low in the evening in receptor sites similar to Riverside, which causes the particles to remain in Riverside overnight. This helps to explain the steady number concentration at night. In general, the trends observed in Riverside during the months of September -December 2002 was consistent with observations made in March, April and May 2002.

The diurnal trends of PN at USC during the winter sampling period are shown in Figure 22a. As mentioned before, USC is close to vehicular sources and traffic is expected to be primary source of these particles at this site. The number concentrations have also been observed to be

higher during winter months. The morning and evening peaks of particulate numbers correspond to morning and evening commutes, which suggests that local traffic is the major contributor to ultrafine PM at this site during winter.

During summer months, secondary aerosol formation is favored and new ultrafine particles may form as a result of the condensation of low-volatility products of photochemical reactions (largely organic compounds) onto stable, nanometer-size particles (O'Dowd et al 1999; Kim et al., 2002; Sardar et al., 2004). Secondary aerosol formation is the most likely explanation for the diurnal trends in PN during the summer afternoon periods at USC (Figure 22b) in which the particle concentrations peak during the afternoon period, in addition to the usual morning and evening periods of commute.

Data from the second monitoring phase at Atascadero is presented in Figures 23-24. The particle number concentration as a function of the time of the day in the months of January, February and March 2003 are shown in figures 23 (a)-(c) respectively. The average diurnal profile is very similar for the three months. The peak at 7 am could be presumably related to small local traffic coupled with the depressed mixing depth of the atmosphere at that time of the day. There is also increase in particle number concentration during evening peaking at around 8 p.m., which may again be attributed to local evening traffic. This observation is further supported by the fact that geomean diameters (figures 24 a-c) of the ambient aerosol decrease during morning and evening time, approximately coinciding with the peak in number concentrations.

The Lompoc station is located 200 km from downtown Los Angeles. It is in a rural area with very little local emission, and no advection form Los Angeles area The particle number concentration as a function of the time of the day in the months of January, February and March 2003 are shown in figures 25 (a)-(c), respectively. Number concentrations peak during the morning and evening periods probably due to the contribution of few local traffic emissions combined with the depression of atmospheric mixing depth. In the month of January an additional midday peak in particle number concentrations is observed. This peak needs to be further investigated, as it is unlikely to be attributed to photochemical reactions, given the time period of the sampling. The geomean diameter (figure 26a) of the aerosol during the midday period in January is approximately 40 nm suggesting fresh emissions as the probable source of PM during this period of the day.

Lake Elsinore is a rural site that is upwind of the I-15 freeway in southeastern California. The site is downwind of the lake with no other nearby significant PM sources. The predominant southwesterly winds blow from the relatively clean beach cities to this site, so no urban plume affects it. Local traffic and wind blown dust are the primary sources of PM and peak during morning rush hour. The particle number concentration as a function of the time of the day in the month April 2003 is shown in figure 27 (a). We see a trend similar to the two sites discussed before, with a more predominant morning traffic peak and another peak during late evening and nighttime. During these periods the atmospheric mixing height is low which when combined with local emissions lead to high number concentrations.

Alpine is a suburban site north of the I-8 freeway. This site is impacted by very few local traffic emissions and is largely a receptor site of the San Diego metropolitan area. The diurnal profile of particle number concentrations for the months of April and May 2003 is shown in Figures 29-30(a). Both months show similar characteristics. An afternoon peak of particles of possibly secondary origin occurs several hours after the change of wind direction from easterly to westerly. There is a surge in particle numbers in the afternoon, which implies photochemical

formation of these particles and air mass advection, as seen at the urban receptor sites discussed earlier.

Observations on particulate characteristics at Lake Arrowhead during the second monitoring phase were very similar to the previous sampling period. Both samplings were conducted during relatively warmer months of the years 2002 and 2003 due to logistical reasons. Figures 31 and 32 depicts PM_{10} mass concentrations and number concentrations observed as a function of time of the day at Lake Arrowhead during the months of June and July 2003, respectively. During early morning and night, the inversion layer is generally below the station location. This is clearly observed in Figures 31a and 32a with low number concentration measured by the SMPS. As the day progresses, the warmer temperature cause the inversion layer to rise. Eventually, the station is under the inversion layer. The site is then significantly affected by advection from Los Angeles area. There are very little local emissions at this site. The mode diameter and geomean diameter remain relatively constant through out the day (Figures 31b and 32b).

Figures 33 and 34 show the particulate matter characteristics observed in Lancaster in the months of June and July 2003, respectively. The number concentration profile during the day shows possible influence from local traffic with the peak at morning traffic hours of 6-7am (Figures 33a and 34a). The number concentration decreases as local emission decreases and inversion layer rises, and begins to increase again at about 2 pm to reach a maximum at 3-4 pm, possibly due to advection bringing aged and photochemically processed aerosol to this site. In the month of June, the geomean and mode diameters range from 65-95 nm (Figure 33b). The geomean diameter and mode diameter agree very well through out the day ranging from 75 to 110 nm during July (Figure 34b).

Figures 35 and 36 show the PM characteristics found in Long Beach during second phase of sampling in the months of August and September, 2003. Similar diurnal trends that were observed during September-October 2002 are observed. The highest number concentration occurs during the middle of the day, additionally comparatively smaller peaks are observed in morning and evening periods. The surge in particle numbers in afternoon could be attributed to the formation of particles by photochemical reactions in the atmosphere , which would be more pronounced when solar radiation is maximum. The smaller morning and evening peaks of these pollutants correspond to morning and evening vehicular commutes on nearby freeways as well as Long Beach Blvd.

Figures 37,38 and 39 show the particulate matter characteristics found in Upland during the months of August, September and October 2003. The number concentration profile (37a - 39a) exhibits a diurnal profile that is consistent with the pattern of local traffic. Figures 37-39a show that the number concentrations peak during early morning period (6-10 a.m.) and decrease during the day peaking again in the evening and nighttime periods. The number concentrations reach a minimum during afternoon period, because of decrease in traffic, and increase in mixing depth (which tends to dilute the vehicular emissions). The number concentrations increase again during the nighttime, mainly due to contributions of the evening traffic as well as depression of atmospheric mixing depth. Figures 37b-39b show the geomean diameter and mode of particulate matter at Upland during the months of August to October 2003.

Figures 40, 41 and 42 show the particulate matter characteristics found in Upland during the months of November, December 2003 and January 2004, respectively. The number concentration profile is similar to that observed during September-October 2003. Figures 40-42a show that the number concentrations peak during early morning period (6-10 a.m.) and decrease during the day peaking again in the evening and nighttime periods. The geomean diameter

(Figures 40-42b) of the aerosol witnesses a dip during the morning period and evening periods, corroborating the theory that fresh emissions from vehicles is the probable source of aerosol during these periods.

The diurnal profiles of particle number concentrations for the months of October and November 2003 at Santa Maria are shown in Figure 43-44 (a). We see a small peak in number concentrations during morning time around 7 a.m. Additionally a predominant increase in number concentrations is observed during late morning to early afternoon period (around 11 am and noon.). Particulate matter concentration witnesses another small peaks in the evening time. The geomean diameter (figure 43-44b) of the aerosol witnesses a dip during the late morning and early afternoon period, suggesting fresh emissions as the probable source during this period.

The diurnal profile of particle number concentrations for the months of December 2003 and January 2004 at Alpine is shown in Figure 45 (a) and 46 (a), respectively. During both these months, higher numbers are observed in the morning, when the mixing height of the atmosphere is low. As the day progresses, the temperature increases and mixing height rises, correspondingly the particle number concentrations drop due to dilution and dispersion, and they increase again in evening and night when the mixing height depresses. The geomean diameter (figure 45-46b) of the aerosol witnesses a dip during the morning, suggesting fresh emissions as the probable source. Due to reduced photochemical activity and reduced dispersal from polluted metropolitan areas during winter period, the total counts are less than those experienced during warmer months discussed previously.

The diurnal profile of particle number concentrations for the month of February 2004 at Santa Maria is shown in Figure 47 (a). We see a peak in number concentration during morning time between 7 and 10 A.M. A small peak is observed around noon. Again a predominant peak is observed at 7 P.M. in the evening. The geomean diameter (Figure 47 b) of the aerosol witnesses a dip during the morning hours and during afternoon, suggesting fresh emissions at this site during that period.

Figures 48 and 49 show the particulate matter characteristics observed in Santa Maria in the months of March and April 2004, respectively. The number concentration profile during the day shows possible influence from local traffic with peaks during morning traffic hours of 7-11 am (Figures 48a and 49a). The number concentration decreases as local emission decreases and inversion layer rises. It begins to rise again at about 4 pm to reach a maximum at 7-8 pm, possibly due to evening traffic. In the month of March, the geomean diameter ranges from 65-90 nm (Figure 48b), while in the month of April the geomean diameter ranges from 65-80nm (Figure 49b). Local emissions are contributing factors to particulates in the site during these months.

The diurnal profile of particle number concentrations for the months of March and April 2004 at Lancaster are shown in Figures 50 (a) and 51 (a). We see a predominant peak in number concentrations during morning time around 7-8 A.M for both the months. Additionally a small increase in number concentrations is observed during late evening period (around 8-9 P.M). The PM_{10} follows the PN fairly well. The geomean diameter (Figure 50b, 51b) of the aerosol witnesses a dip during the morning, confirming fresh emissions as the probable source during this period. The geomean diameters during these months range between 40-60nm.

The Glendora sampling station is not near any major roadways or any other major emission source. Figures 52 and 53 depict the particulate characteristics at Glendora site during second phase of sampling in May and June 2004, respectively. During both these summer months, the particle numbers peak in afternoon (2-3 PM). As the day progresses, the particulate

matter emitted from the traffic- congested areas west and south of downtown Los Angeles reaches the area of Glendora. Additionally photochemical reactions in the atmosphere contribute to secondary aerosol formation at this site.

Figures 54, 55 and 56 show the PM characteristics found in Upland during the months of May, June and July 2004, respectively. The number concentration profile (54a, 55a and 56a) exhibits a diurnal profile that is consistent with the pattern of local traffic. The number concentrations peak during early morning period (7-9 a.m.) and decrease during the day peaking again in the late afternoon and early evening (3-5 PM) periods. The number concentrations increase again during the late afternoon, due to contributions of advected, aged and photochemically processed aerosol from Los Angeles, in addition to evening local traffic.

Long Beach October 2002 strike analysis

During the period of September 30 to October 9, 2002, union workers at the port of Long Beach, CA went on strike. The port which is located upwind to the sampling site is considered a major contributor to PM at Long Beach as a result of emissions from ships (Isakson et al., 2003), but perhaps more so because of the heavy-duty truck traffic associated with the port (Chow et al., 1994). It was interesting to determine whether significant changes in particle and co-pollutant characteristics were observed due to this strike. In order to understand the effects of this strike, we present the PM as well as co pollutant characteristics from pre-, during and post-strike periods in this section. Unfortunately, we do not have the SMPS data from September 25 to October 1, 2002, due to calibration and maintenance performed on the instruments at that time, therefore PM characteristics for the pre-strike period are studied from September 16-24, 2002 and for the strike period from October 2-9, 2002. Gaseous co-pollutant data are available throughout the pre-, during- and post-strike periods.

During the strike period, the following three major changes occurred that might have influenced air pollution in that area. First, there was a significant decrease in diesel truck traffic both on the nearby freeways 710 and 110 as well as local surface streets (Figure 57a). Second, about 200 ships were idling off the coast, immediately upwind of the Long Beach throughout the strike period (CNN, 2002). Third, there were significant changes in weather conditions during that period. While in September the weather in Long Beach was warm with the exception of the morning hours, it changed in early October (coincidentally with the strike) to cooler with mostly overcast days (Figure 58c). These weather conditions continued after the strike period. This change may be expected to increase particle concentration by enhancing gas to particle condensation and also to increase particle size by condensational growth.

Figure 58a shows the 24-hour averaged concentrations of particle number (14-700nm) and PM_{10} during the strike and non-strike period. The results of Figure 58a as well as our statistical analysis did not reveal any statistically significant impact of the strike on particle number as well as PM_{10} concentrations ($p > 0.05$). The corresponding concentrations of gaseous co-pollutants during the strike/non-strike period are presented in Figure 58b. There is a statistically significant increase in NO_x and CO concentrations during the strike compared to pre- as well as post-strike period ($p < 0.001$). High amounts of NO_x and CO emissions from ships have been observed in previous studies (Corbett and Fishback, 1997; Sinha et al., 2003; Cooper, 2003; Saxe and Larsen, 2004). These emissions have been reported to be more pronounced when the ships are at berth and idling (Cooper, 2003). An additional explanation for the elevated CO levels during the strike may be related to the increase in light duty traffic, shown in Figure 57. It can be seen that the total volume of traffic on both the freeways 110 and 710 was approximately

the same during the strike and non-strike periods (Figure 65b), while the diesel traffic was substantially reduced by more than 40% on 710 and about 25% on 110 freeways (Figure 57a), which implies that the gasoline vehicle traffic may have increased by 10-20%, leading to some elevation in CO concentrations. We believe, however, that the majority of the increase in CO levels must be attributed to emissions from the idling ships.

Emissions from diesel engines operating in ships contribute significantly to sub-micrometer range particles and typically have bimodal size distributions, with a dominant mode in the sub-40 nm and a weaker mode in the range of 70-100 nm (Isakson et al., 2003). Figure 59 shows the particle number concentrations in different size ranges through the strike/non-strike period. Particle concentrations below 30 nm seem unaffected by the strike. Even if a large number of these particles were emitted by ships, it is conceivable that a substantial fraction of them did not reach the sampling station due to coagulation, possible hygroscopic growth and-or volatilization processes that may have occurred during their transport. Particle numbers concentrations in the 60 to 100 nm as well as 100-200 nm ranges were, however, significantly elevated during the strike ($p < 0.001$), which may be indicative of the contributions of emissions from the idling ships.

The average size distributions of the particle number concentrations before, during and after the strike are shown in Figure 60. It can be seen that particle concentrations in the size range 60-300 nm were higher during the strike, as discussed above ($p < 0.001$). Also, the mode before and after the strike is smaller compared to the strike period, further supporting the argument for the larger-sized particles originating from ship emissions compared to those from heavy and light duty vehicles.

Air Quality Impacts of the October 2003 Southern California Wildfires

In late October of 2003, 13 large Southern California wildfires burned more than 750,000 acres of land, destroyed over 3,500 structures, and displaced approximately 100,000 people. The fire episode was declared the deadliest and most devastating in more than a decade, and local media advised individuals to stay indoors to avoid exposure to excessive levels of PM, CO, VOCs, and ozone caused by the wildfires. Our coincidental air pollution sampling campaign proved valuable in determining the impacts of this wildfire episode on pollutant levels in the Los Angeles Basin Appendix B (Phuleria et al., 2004) presents measurements of pollutant gases (CO, NO_x, and ozone) as well as PM concentrations and characteristics at different sampling locations in the LA basin before, during, and after the October 2003 fire episode. In addition, the effect of fire on indoor particle concentrations and size distributions is also investigated and presented.

In general, the wildfires caused the greatest increases in PM_{10} levels (a factor of 3-4) and lesser increases in CO, NO, and PN (a factor of up to 2). NO_2 levels remained essentially unchanged and ozone concentrations dropped during the fire episode. Particle size distributions of air sampled downwind of the fires showed number modes at diameters between 100 and 200 nm, significantly larger than that of typical urban air. The particles in this size range were shown to effectively penetrate indoors, raising questions about the effectiveness of staying indoors to avoid exposure to wildfire emissions**.**

15

Discussion

Particle number concentrations and size distributions in complex urban environments can be seen to be highly variable on temporal scales, from diurnal to seasonal, and spatially, from local scale influences, such as distances from highways, to regional scale influences, such as long range transport across air basins. Seasonal difference in solar intensity, temperature, and relative humidity can also strongly influence the diurnal size profile.

In this study we see enhanced contribution of local emission sources to airborne particulate numbers during cooler months with stagnant meteorological conditions at all sites. During warmer months, effects of long-range dispersal of aerosol are observed most clearly at the easterly receptor sites of Riverside, Mira Loma, Glendora and Lake Arrowhead. The increased wind speeds and onshore flow in the warmer months, lead to increased advection of pollutant parcels from the polluted western areas of the LAB (Fine et al., 2004). Additionally, dry and hot summer conditions would limit ultrafine particle growth to accumulation mode during transport (Kim et al., 2002).

In addition to the contribution of vehicular emissions to particle concentrations in Los Angeles, photochemical formation by secondary reactions in the atmosphere appears to be a major source of PM during the afternoon periods in the warmer months at all sites. Current studies by a number of groups have investigated and confirmed the photochemical formation of ultrafine particles in urban atmosphere. In addition to our observations in Los Angeles, secondary particle formation events have been observed in urban areas, including Pittsburgh (Stanier et al., 2004), St. Louis (Shi and Qian, 2003), and Mexico City (Baumgardner et al., 2004). An excellent review of this topic is given by Kulmala et al. (2004). The actual formation mechanism of nanoparticles in the range of 1-3 nm remains largely unknown and has recently become the subject of intensive research in the field of atmospheric science. Current hypotheses on the composition of these fresh nuclei include the binary nucleation of water and sulfuric acid (Kulmala, 2002), ternary nucleation of ammonia-sulfuric acid-water (Weber et al., 1997), and ion-induced nucleation (Yu and Turco, 2001). There is also general consensus that the species responsible for further growth of these nanoparticles to the > 10 nm range are different than the nucleating species (Stanier et al., 2004). Our current understanding of atmospheric nanoparticle processes suggests that growth of these particles to larger sizes within the ultrafine PM mode occurs by condensation of low volatility organic species. These species are products of photochemical oxidation of volatile organic precursors on these pre-existing nuclei (O'Dowd et al., 1999; Kulmala et al., 2004). In fact, recent studies by Zhang et al. (2004) showed that nucleation rates of sulfuric acid are greatly increased in the presence of organic acids (including products of atmospheric photochemical reactions), by forming unusually stable organic-sulfuric acid complexes, thereby reducing the nucleation barrier of sulfuric acid.

It is interesting to note in our field measurements that summertime levels of ultrafine particles at source sites, such as Long Beach and USC peaked in midday (i.e., noon to 1 pm), whereas ultrafine PM numbers peak slightly later (i.e., between 3-4 pm) in the inland receptor sites. A time delay in the peak concentrations observed at the receptor sites is possibly due to the transport time for polluted air masses to reach those sites.

The correlation between particle number concentrations and PM_{10} has been widely studied and weak-to-moderate correlations have been generally observed between the two (Morawska et al., 1998; Woo et al., 2001; Noble et al., 2003; Fine et al., 2004; Sardar et al, 2004). Since the fine to ultrafine particle counts are dominated by very small particles and the PM_{10} mass is dominated by fewer, much larger particles, low correlation should be expected,

especially in air masses dominated by fresher particles (either primary emission particles or freshly formed secondary particles). In our study, we also found weak-to-moderate correlations between PM_{10} and number concentrations with no particular seasonal trend (described in detail in Appendix C). These findings are very important from a regulatory perspective because they imply that controlling ambient PM_{10} mass via national air quality standards may not necessarily reduce human exposure to ultrafine particles that dominate the particle counts and have recently been shown to have toxic effects (as discussed in the introductory part of the report).

The overall lack of significant associations between hourly and 24-hour particle number versus gaseous co-pollutant concentrations at locations in LAB found in this study (described in Appendix A) can be attributed to the differences in the sources and formation mechanisms that are responsible for generating these pollutants in the environment of the Los Angeles Basin. These associations may become stronger for specific pollutants and time periods, for example, between PN, CO, and NO during traffic rush hours. However, if examined on a yearly or even on a seasonal basis, the results from this study suggest that co-pollutants such as CO, O3, or NOx cannot be used as surrogates to assess human exposure to particulate numbers in epidemiologic studies. These findings also imply that potential confounding effects of co-pollutants will not affect epidemiologic analysis seeking to link ultrafine particles to health effects because of the general lack of associations between particulate numbers and co-pollutant concentrations.

Summary and Conclusions

This report presents novel data, generated over a 2.5-year period, related to atmospheric particle numbers and size distributions (14-700 nm) at thirteen sites within Southern California generated in support of the University of Southern California Children's Health Study (CHS). The urban site (classified as source and receptor) and remote site (classified as suburban and mountainous) PM size distributions measured during CHS form an excellent data set for research on particle sources and aerosol processes.

In all urban sites we see higher average total particle number concentrations in winter (November to February), compared to summer (July to September) and spring (March to June). Contribution of local vehicular emissions is most evident in cooler months, whereas effects of long-range transport of particles are enhanced during warmer periods. Afternoon periods in the warmer months are characterized by elevated number concentrations, suggesting the formation of new particles by photochemistry. Our results show no meaningful correlation between particle number and mass, indicating that mass based standards may not be effective in controlling ultrafine particles (described in Appendix C).

The correlation between particle number (PN), particle mass (PM10), and gaseous pollutants [carbon monoxide (CO), nitric oxide (NO), oxides of nitrogen (NOx), and ozone (O3)] in LAB locations was investigated (described in Appendix A). The degree of correlation between hourly PN and concentrations of CO, NO, and nitrogen dioxide (NO2) at each site over the entire year was generally low to moderate (r values in the range of 0.1–0.5), with a few notable exceptions. In general, associations between PN and O3 were either negative or insignificant. Similar analyses of seasonal data resulted in levels of correlation with large variation, ranging from 0.0 to 0.94 depending on site and season. Summertime data showed a generally higher correlation between the 24-hr average PN concentrations and CO, NO, and NO2 than corresponding hourly concentrations. Hourly correlations between PN and both CO and NO were strengthened during morning rush-hour periods, indicating a common vehicular source. Comparing hourly particle number concentrations between sites also showed low to moderate

spatial correlations, with most correlation coefficients below 0.4. Given the low to moderate associations found in this study, we conclude that gaseous co-pollutants should not be used as surrogates to assess human exposure to airborne particle number concentrations.

Later part of the report discusses an "opportunistic" study on the impact of the union workers strike (October 2002) at the port of Long Beach on air quality. A comparison of PM as well as co-pollutant characteristics from pre-, during and post-strike periods helped us understand the effects of strike. Our statistical analysis revealed statistically significant increase in concentrations of gaseous co-pollutants- NO_x and CO during the strike compared to pre- as well as post-strike period ($p < 0.001$). We also found statistically significant increase in particle number concentrations in the 60 to 100 nm as well as 100-200 nm ranges during the strike period. The increases in particle numbers (60-200 nm) as well as gaseous co-pollutant concentrations during the strike are indicatives of contributions of emissions from the idling ships at port during the strike period.

In late October of 2003, 13 large Southern California wildfires burned more than 750,000 acres of land, destroyed over 3,500 structures, and displaced approximately 100,000 people. As described in Appendix B, the greatest impact was observed on PM_{10} concentrations which increased by factors of three or four depending on location. CO and NO levels increased to a lesser extent (a factor of approximately two), most likely due to the different relative emission rates of these pollutants from wildfires compared to typical urban sources such as traffic. Particle number concentrations and NO_2 were essentially unchanged, except at the sites nearest the fires where PN levels almost doubled. Ozone levels during the fires were observed to be lower during the fires at some sites, a possible result of light scattering by the smoke plume reducing photochemical activity levels. Particle number distributions downwind of the fires displayed number modes with diameters between 100 and 200 nm, larger than typical urban aerosol and explaining the larger increases in PM_{10} and $PM_{2.5}$ mass concentrations than that for ultrafine particle mass and particle number. These particles were also shown to penetrate effectively indoors, calling into question the prevailing advice to the public to remain inside to avoid exposure to harmful wildfire emissions.

In conclusion, the results presented in this report indicate that location and season significantly influence particle number and size distributions in locations within Southern California. Strong diurnal and seasonal patterns in number concentrations are evident as a direct effect of the sources, formation mechanisms, as well as meteorological conditions prevalent at each location during different times of the day and year. These results will be used in the CHS as a first order indicator of not only human exposure, but also inhaled dose to ultrafine PM. They will also be used for the development and validation of predictive models for population exposure assessment to ultrafine PM in complex urban environments, such as that of the Los Angels Basin.

Recommendations

Despite abundant epidemiological evidence associating ambient particulate pollution with adverse health effects in humans, fundamental uncertainty and disagreement persist regarding which physical and chemical properties of particles (or unidentified confounding environmental influences) influence health risks, which pathophysiological mechanisms are operative, and what air quality regulations should be adopted to deal with the health risks. This lack of understanding stems in part from the paucity of reliable data linking population exposure to observed health. One way of

addressing these inadequacies is by performing large-scale epidemiological studies that research the relationship between population exposures to particulate matter and adverse health outcomes. A suggested direction of future work is the development of personal exposure models based on field measurements to predict the exposure of population to particulate matter in various environments impacted by different pollution sources. Size-specific information about PM will find use in the estimation of the fraction of PM from specific outdoor sources to which individuals are exposed, and determine the degree to which these disparate sources affect the incidence of cardiovascular/respiratory or other health effects. Size-segregated PM data may also be informative in using the inhaled dose, as opposed to the exposure concentration, as a possible metric for explaining a specific health outcome in these studies. Finally, the total particle number concentration, a parameter that is now monitored in several locations of selected urban areas of the US (including the current study) and Europe should be used as one of the independent variables in epidemiological studies. Although very few studies have already attempted to find a linkage of health effects and particle numbers (with some positive results), more studies of this nature in several areas will be needed to investigate the robustness of the association between ultrafine PM and health outcomes. In that respect, the results of the present study are very useful in that they will be used in the very near future by investigators at the USC Medical School to seek associations between respiratory effects of children, such as lung growth and exacerbation of asthma, and metrics such as particle size and number concentrations.

References

Allen, G.A., Sioutas, C., Koutrakis, P., Reiss, R., and Wilson, W. "Evaluation of the TEOM method for measurement of ambient particulate mass in urban areas." *Journal of Air and Waste Management Association*, 47:682-689, 1997.

Baumgardner D., Raga G.B., and Muhlia A. Evidence for the formation of CCN by photochemical processes in Mexico City. *Atmos Environ* 2004: 38(3): 357-367.

Birmili W., Wiedensohler A., Heintzenber J. and Lehmann K. Atmospheric particle number size distribution in central Europe: statistical relations to air masses and meteorology. *J Geophys Res* 2001:106 (D23): 32005-32018.

Buzorius G., Hameri K., Pekkanen J. and Kulmala M. Spatial variation of Aerosol Number Concentration in Helsinki City. *Atmos Environ* 1999: 33: 553-565.

Cheng M.D. and Tanner R.L. Characterization of ultrafine and fine particles at a site near the Great Smoky Mountains. *Atmos Environ* 2002: 36: 5795-5806.

Chow J.C., Watson J.G., Fujita E.M., Lu Z., Lawson D.R. and Ashbaugh L.L. Temporal and spatial variations of $PM_{2.5}$ and PM_{10} aerosol in the Southern California air quality study. *Atmos Environ* 1994: 28 (12): 2061-2080.

Cooper D.A. Exhaust emissions from ships at berth. *Atmos Environ* 2003: 37: 3817-3830.

Corbett J.J. and Fischbeck P. Emissions from ships. *Science* 1997: 278 (5339): 823-824.

CNN, Long Beach harbor strike, Internet, accessed August 24, 2004, http://money.cnn.com/2002/10/08/news/ports_longshoremen

Cyrys J., Stolzel M., Heinrich J., Kreyling W.G., Menzel N., Wittmaack K., Tuch T. and Wichmann H.E. Elemental composition and sources of fine and ultrafine ambient particles in Erfurt, Germany. *Sc Total Env* 2003: 305: 143-156.

Derwent R.G., Davies T.J., Delaney M., Dollard G.J., Field R.A., Dumitrean P., Nason P.D., Jones B.M.R. and Pepler S.A. Analysis and interpretation of the continuous hourly monitoring data for 26 C_2–C_8 hydrocarbons at 12 United Kingdom sites during 1996. *Atmos Environ* 2000: 34 (2): 297-312.

Dockery D.W. and Pope C.A. Acute respiratory effects of particulate air pollution. *Ann Rev of Pub Hlth* 1994: 15: 107-132.

Fine P.M., Shen S. and Sioutas C. Inferring the sources of fine and ultrafine particulate matter at downwind receptor sites in the Los Angeles Basin using multiple continuous measurements. *Aerosol Sci Technol* 2004: 18: 182-195.

Harrison R.M., Shi J.P., Xi S., Khan A., Mark D., Kinnersley R. and Yin J. Measurement of number mass and size distribution of particles in the atmosphere. *Phil Tran. R Soc Lond* 2000: 358: 2567-2580.

Isakson J., Persson T.A. and Lindgren E.S. Identification and assessment of ship emissions and their effects in the harbor of Goteborg Sweden. *Atmos Environ* 2003: 35: 3659-3666.

Jacques P.A., Ambs J.L., Grant W.L. and Sioutas C. Field evaluation of the differential TEOM monitor for continuous $PM_{2.5}$ mass concentrations. *Aerosol Sci Technol* 2004 (Suppl. 1): 38: 49-59.

Kikas U., Mirma A., Tamm E. and Raunemaa T. Statistical characteristics of aerosol in Baltic sea region. *J Geophys Res* 1996: 101 (D14): 19319-19327.

Kim S., Shen S., Sioutas C., Zhu Y. F. and Hinds W. C. Size distribution and diurnal and seasonal trends of ultrafine particles in source and receptor sites of the Los Angeles Basin. *J Air Waste Manage Assoc* 2002: 52: 297-307.

Kulmala M. How particles nucleate and grow. *Science.* 2002: 302: 1000-1001

Kulmala M., Vehkamäki H., Petäjä T., Dal Maso M., Lauri A., Kerminen V.M., Birmili W. and McMurry P.H. Formation and growth rates of ultrafine atmospheric particles: a review of observations. *J Aerosol Sci* 2004: 35: 143-176.

Künzli N., McConnell R., Bates D., Bastain T., Hricko A., Lurmann F., Avol E., Gilliland F. and Peters J. Breathless in Los Angeles: The exhausting search for clean air. *Am J Pub Hlth* 2003: 93(9): 1494-1499.

Lawless P.A., Rodes C.E. and Evans G. Aerosol concentration during the 1999 Fresno exposure studies as functions of size season and meteorology. *Aerosol Sci Technol* 2001: 34: 66-74.

Li N., Alam J., Eiguren A., Slaughter N., Wang X., Huang A., Wang M., Sioutas C. and Nel, A.E. Nrf2 is a Key Transcription Factor in Antioxidant Defense in Macrophages and Epithelial Cells: Protecting Against the Injurious Effects of Pro-oxidative Air Pollutants. *J Immunol* 2004: 173 (5): 3467-3481.

Li N., Sioutas C., Froines J.R., Cho A., Misra C and Nel A., Ultrafine Particulate Pollutants Induce Oxidative Stress and Mitochondrial Damage. *Environ Health Persp* 2003: 111 (4): 455-460.

Mäkelä J.M., Aalto P., Jokinen P., Pohja T., Nissinen A., Palmroth S., Markkanen T., Seitsonen K., Lihavainen H. and Kulmala M. Observations of ultrafine aerosol particle formation and growth in boreal forest. *Geophys Res Lett* 1997: 24: 1219-1222.

Morawska L., Jayarantne E.R., Mengersen K. and Thomas S. Differences in airborne particle and gaseous concentrations in urban air between weekdays and weekends. *Atmos Environ* 2002: 36: 4375-4383.

Morawska L., Bofinger N.D., Kocis L. and Nwankwoala A. Comprehensive characterization of aerosols in a subtropical urban atmosphere: particle size distribution and correlation with gaseous pollutants. *Atmos Environ* 1998: 32 (14-15): 2467-2478.

Na K.S., Sawant A.A., Song C. and Cocker D.R. Primary and secondary carbonaceous species in the atmosphere of Western Riverside County, California. *Atmos Environ* 2004: 38 (9): 1345-1355.

Noble C.A., Mukerjee S., Gonzales M., Rodes C.E., Lawless P.A., Natarajan S., Myers E.A., Norris G.A., Smith L., Ozkaynak H. and Neas L.M. Continuous measurement of fine and ultrafine particulate matter criteria pollutants and meteorological conditions in urban El Paso, Texas. *Atmos Environ* 2003: 37: 827-840.

Oberdörster G. and Utell M.J. Ultrafine particles in the urban air: To the respiratory tract- and beyond? *Environ Health Persp* 2002: 110 (8): A440-A441.

O'Dowd C., McFiggans G., Creasey D.J., Pirjola L., Hoell C., Smith M.H., Allan B.J., Plane J.M.C., Heard D.E., Lee J.D., Pilling M.J. and Kulmala M. On the photochemical production of new particles in the coastal boundary layer. *Geophys Res Lett* 1999: 26 (12): 1707-1710.

Peters A., Wichmann H.E., Tuch T. and Heinrich J. Respiratory effects are associated with the number of ultrafine particles. *Amer J Resp Crit Care Med* 1997: 155: 1376-1383.

Phuleria H.C., Fine P.M., Zhu Y. and Sioutas C. Characterization of Particulate Matter and co-pollutants during the fall 2003 Southern California fires. *J Geophy Res-Atmos* 2004 *(in press)*

Pope C.A. Review: epidemiological basis for particulate air pollution health standards. *Aerosol Sci Technol* 2000: 32 (1): 4-14.

21

Ruuskanen J., Tuch. Th., Ten Brink H., Peters A., Khlystov A., Mirme A., Kos G.P.A., Brunekreef B., Wichmann H.E., Buzorius G., Vallius M., Kreyling W.G. and Pekkanen J. Concentrations of ultrafine, fine and PM$_{2.5}$ particles in three European cities. *Atmos Environ* 2001: 35: 3729-3738.

Sardar S.B., Fine P.M., Hoon A. and Sioutas C. Associations between particle number and gaseous copollutants concentrations in the Los Angeles Basin. *J Air Waste Manage Assoc. vol 5, 4992-1005 (August 2004).*

Saxe H. and Larsen T. Air pollution from ships in three Danish ports. *Atmos Environ* 2004: 38: 4057-4067.

Shi J.P. and Qian Y. Aerosol size distributions (3 nm to 3 um) measured at St. Louis Supersite (4/1/01-4/30/02) *M. S. Thesis Department of Mechanical Engineering University of Minnesota Minneapolis MN, 55455.* 2003.

Shi J.P., Evans D.E., Khan A.A. and Harrison R.M. Sources and concentration of nanoparticles (<10 nm diameter) in the urban atmosphere. *Atmos Environ* 2001: 35:1193-1202.

Shi J.P.; Khan A.A. and Harrison R.M. Measurements of ultrafine particle concentration and size distribution in the urban atmosphere. *Sci Total Environ* 1999: 235: 51-64

Sinha P., Hobbs P.V., Yokelson R.J., Christian T.J., Kirchstetter T.W. and Bruintjes R. Emissions of trace gases and particles from two ships in the southern Atlantic Ocean. *Atmos Environ.* 2003: 37: 2139-2148.

Stanier C.O., Khlystov A.Y. and Pandis S.N. Ambient aerosol size distributions and number concentrations measured during the Pittsburgh Air Quality Study (PAQS). *Atmos Environ.* 2004: 38: 3275-3284.

Weber R.J., Marti J.J., McMurry P.H., Eisle, F.L., Tanner D.J. and Jefferson A. Measurement of new particle formation and ultrafine particle growth rates at a clean continental site. *J Geophy Res* 1997: 102 (D4): 4375-4385.

Woo K.S., Chen D.R., Pui D.Y.H. and McMurry P.H. Measurement of Atlanta aerosol size distributions: observations of ultrafine particle events. *Aerosol Sci Technol* 2001: 34: 75-87.

Wehner B., Wiedensohler A. A long-term measurement of submicrometer urban aerosols: statistical analysis for correlations with meteorological conditions and trace gases. *Atmos Chem Phys* 2003: 3: 867-879.

Xia T., Korge P., Weiss J.N., Li N., Venkatesen M.I., Sioutas C., and Nel A. Quinones and Aromatic Chemical Compounds in Particulate Matter (PM) Induce Mitochondrial Dysfunction: Implications for Ultrafine Particle Toxicity. *Environ. Health Persp.* 2004: 112 (14): 1347-1359.

Yu F. and Turco R.P. From molecular clusters to nanoparticles: Role of ambient ionization in tropospheric aerosol formation. *J Geophy Res* 2001: 106 (D5): 4797-4814.

Zanobetti A., Schwartz J. and Dockery D.W. Airborne particles are a risk factor for hospital admissions for heart and lung disease. *Environ. Health Persp.* 2000: 108(11): 1071-1077.

Zhang K.M. and Wexler A.S. A hypothesis for growth of fresh atmospheric nuclei. *J Geophy Res-Atmos* 2002:107 (D21): 4577.

Zhang R., Suh I., Zhao J., Fortner E.C., Tie X., Molina L.T., and Molina M.J. Atmospheric new particle formation enhanced by organic acids. *Science* 2004: 304: 1487-1490.

Zhu Y.F., Hinds W.C., Kim S., Shen S. and Sioutas C. Study of ultrafine particles near a major highway with heavy-duty diesel traffic. *Atmos Environ* 2002a: 36: 4323-4335.

Zhu Y.F., Hinds W.C., Kim S. and Sioutas C. Concentration and size distribution of ultrafine particles near a major highway. *J. Air Waste Manage. Assoc.* 2002b: 52: 1032-1042.

List of publications produced from this grant (attached as Appendices A-C)

1. Sardar S.B., Fine P.M., Yoon H. and Sioutas C. Associations Between Particle Number and Gaseous Co-Pollutant Concentrations in the Los Angeles Basin. *Journal of the Air and Waste Management Association. vol 5, 4992-1005 (August 2004)*

2. Phuleria, H., Fine, P.M., Zhu, Y. and Sioutas C. Characterization of Particulate Matter and co-Pollutants During the Fall 2003 Southern California Fires. *Journal of Geophysical Research*, In press(2004)

3. Singh M., Phuleria H., Bowers K., Sioutas C. Seasonal and spatial trends in airborne particle number concentrations and size distributions at the Children's Health Study sites in Southern California. Manuscript submitted to *Journal of Exposure Analysis and Environmental Epidemiology*, October 2004

Glossary of terms, abbreviations and symbols

California Air Resources Board	CARB
Carbon Monoxide	CO
Children's Health Study	CHS
Condensation Particle Counter	CPC
Number Median Diameter	NMD
Particulate Matter	PM
Particulate Matter with Aerodynamic Diameters less than 10 μm	PM_{10}
Particulate Matter with Aerodynamic Diameters less than 500nm	$PM_{0.5}$
Particle Number Concentration	PN

Relative Humidity   RH
Los Angeles Basin   LAB
Nitrogen Oxide   NO
Nitrogen Dioxide NO_2
Total Nitrogen Oxides   NOx
Ozone O_3
Pearson correlation coefficient   R
Scanning Mobility Particle Sizer   SMPS
South Coast Air Quality Management District   SCAQMD
Tapered Element Oscillating Microbalance   TEOM
University of Southern California   USC

Appendices

Appendix A: (Attached as pdf file)
Manuscript- Associations Between Particle Number and Gaseous Co-Pollutant Concentrations in the Los Angeles Basin.

Appendix B: (Attached as pdf file)
Manuscript-Characterization of Particulate Matter and co-Pollutants During the Fall 2003 Southern California Fires.

Appendix C: (Attached as pdf file)
Manuscript- Seasonal and spatial trends in airborne particle number concentrations and size distributions at the Children's Health Study sites in Southern California.

Figure 1   Locations of sampling sites in Southern California

Figure 2. Averaged number size distributions in winter and summer/spring periods at a) USC b) Long Beach c) Riverside d) Mira Loma e) Upland f) Glendora g) Lancaster h) Alpine i) Atascadero j) Lompoc k) Santa Maria l) Lake Arrowhead and m) Lake Elsinore
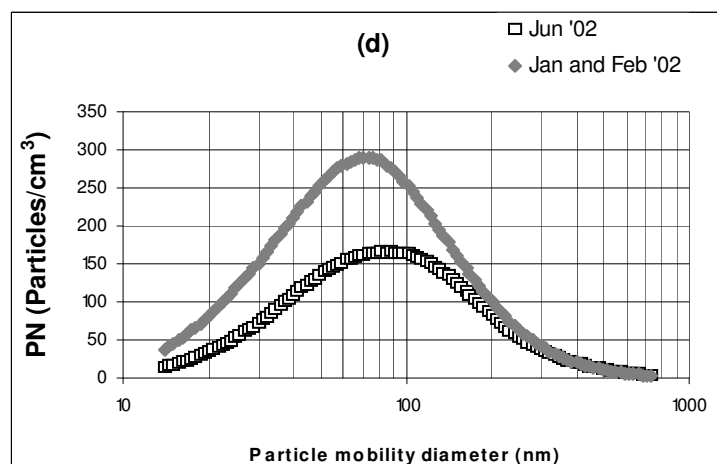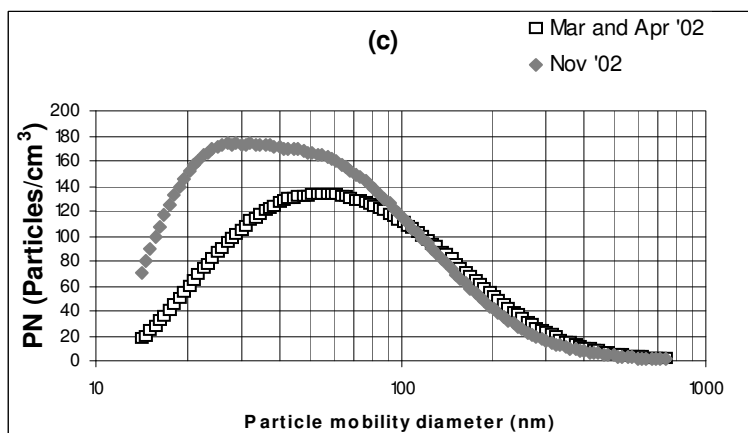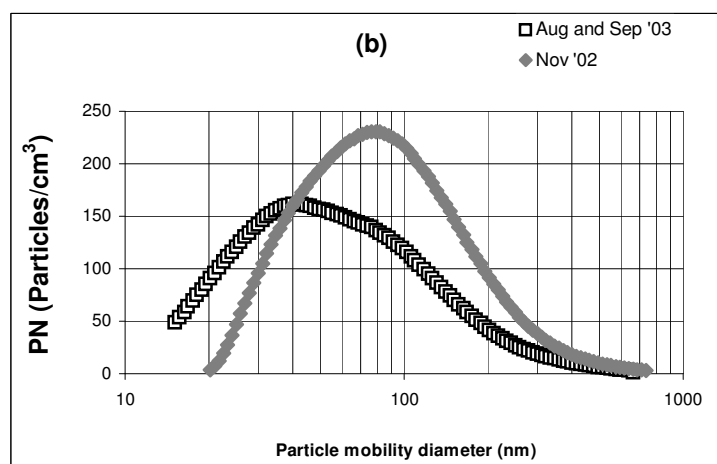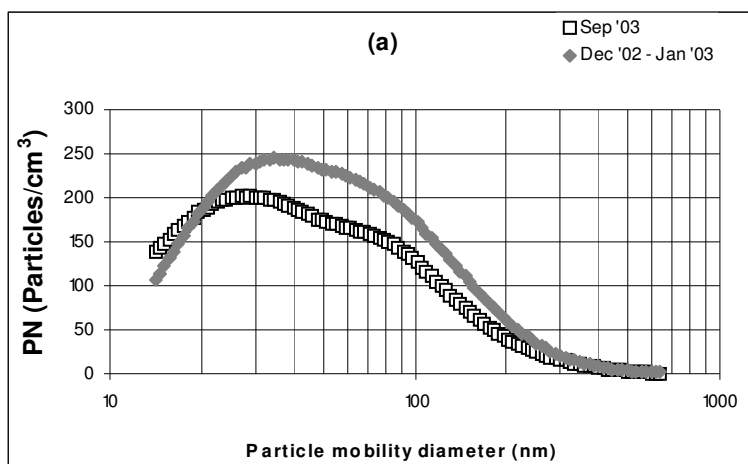
Figure 2 continued..

Figure 2 continued…

Figure 2 continued…

(m)

PN (Particles/cc) vs. Particle mobility diameter (nm)

April '03

(a)

(b)
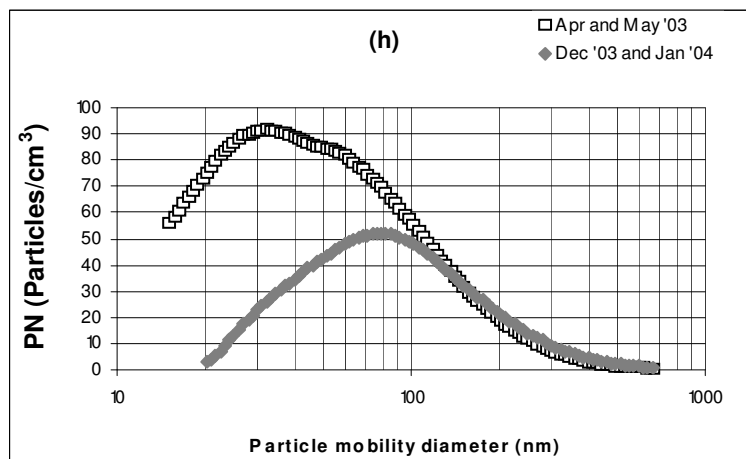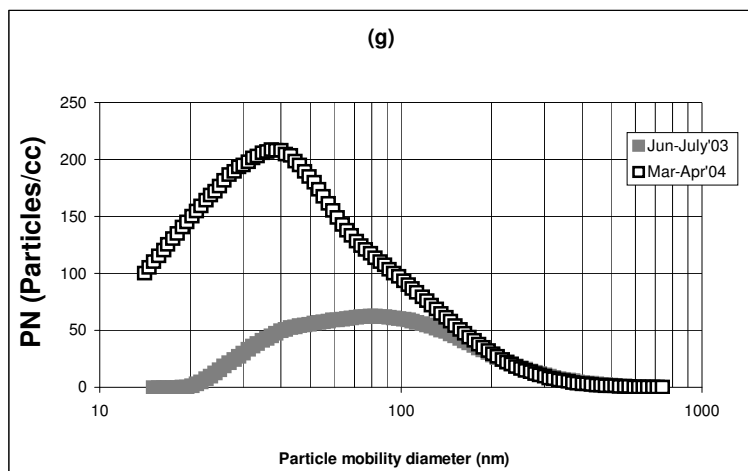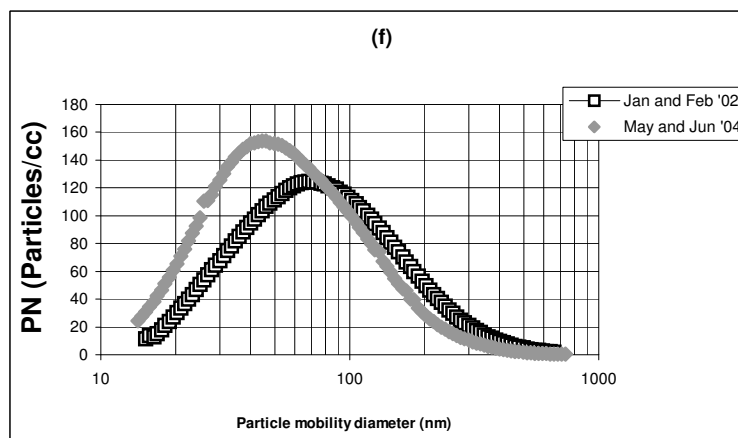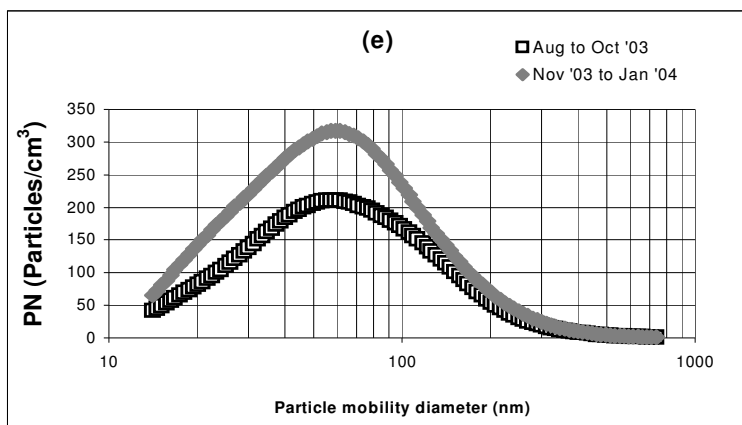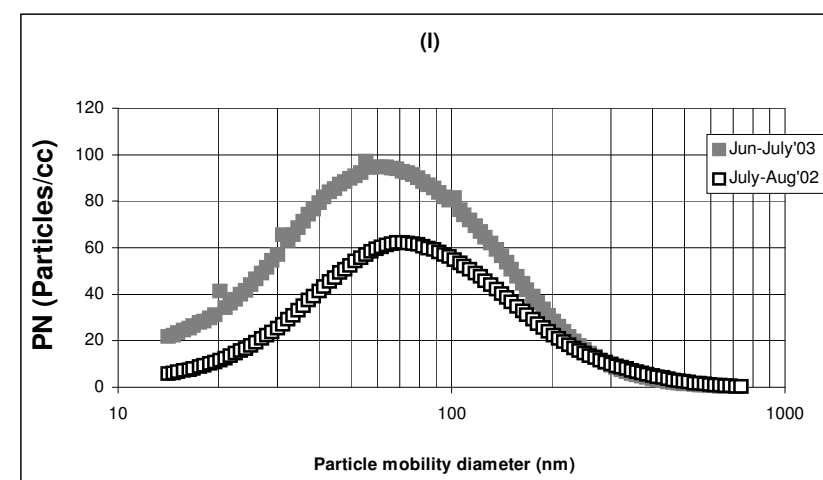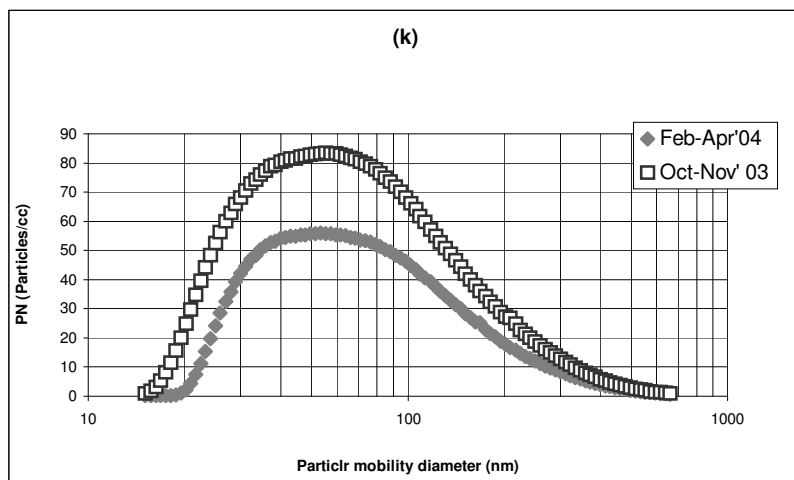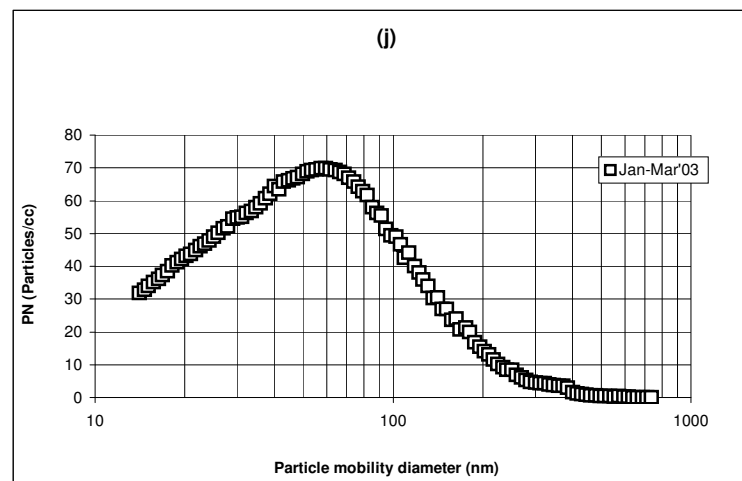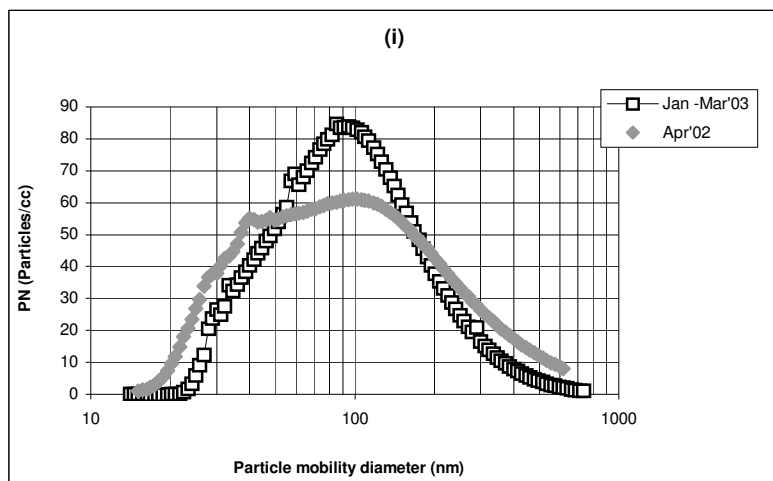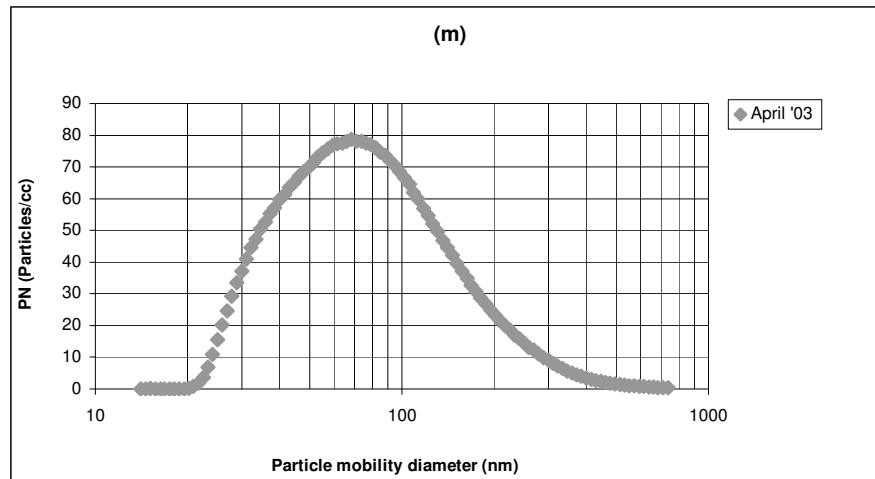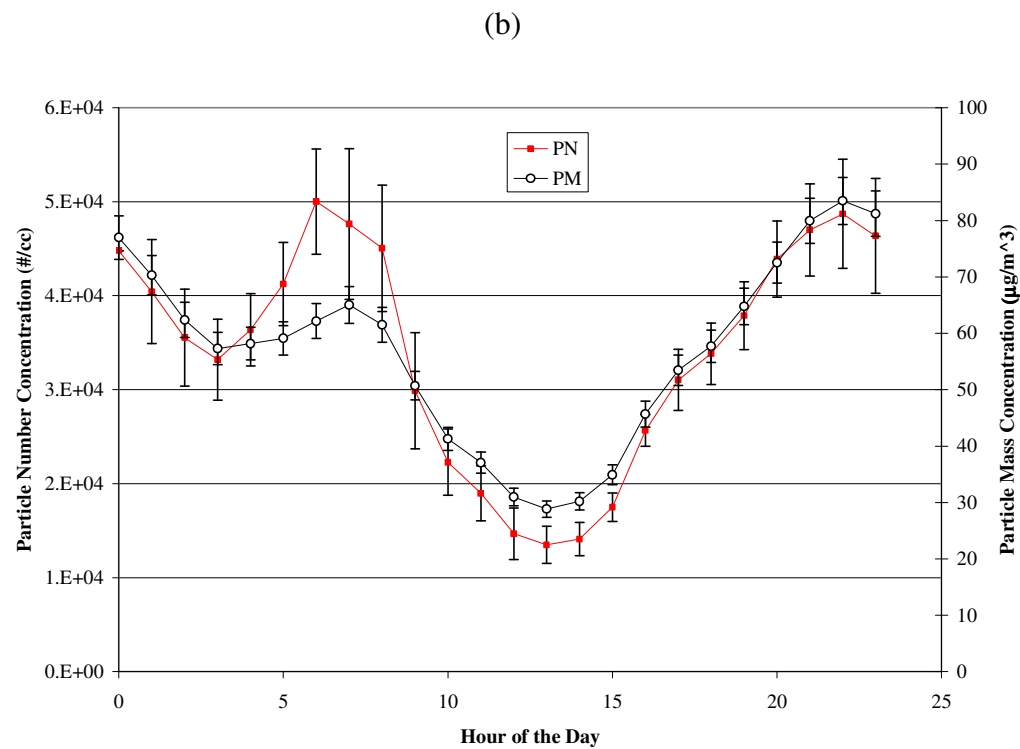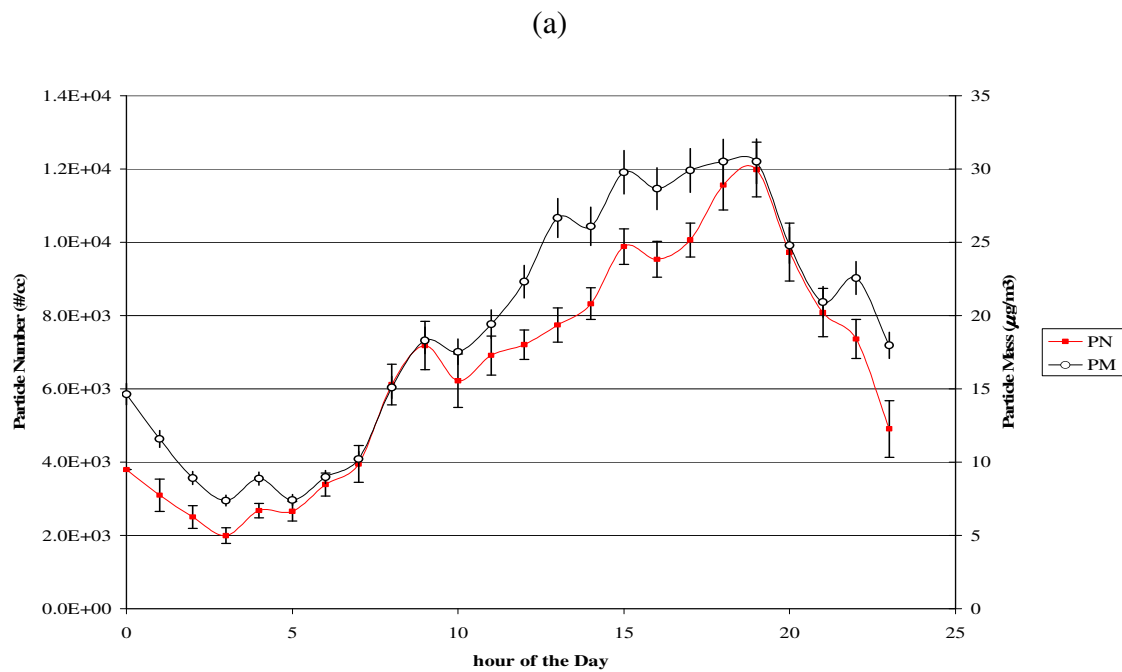
Figure 3. PN0.5 and PM0.5 mass concentrations for (a) Glendora and (b) Mira Loma in Dec 2001.

(a)

(b)
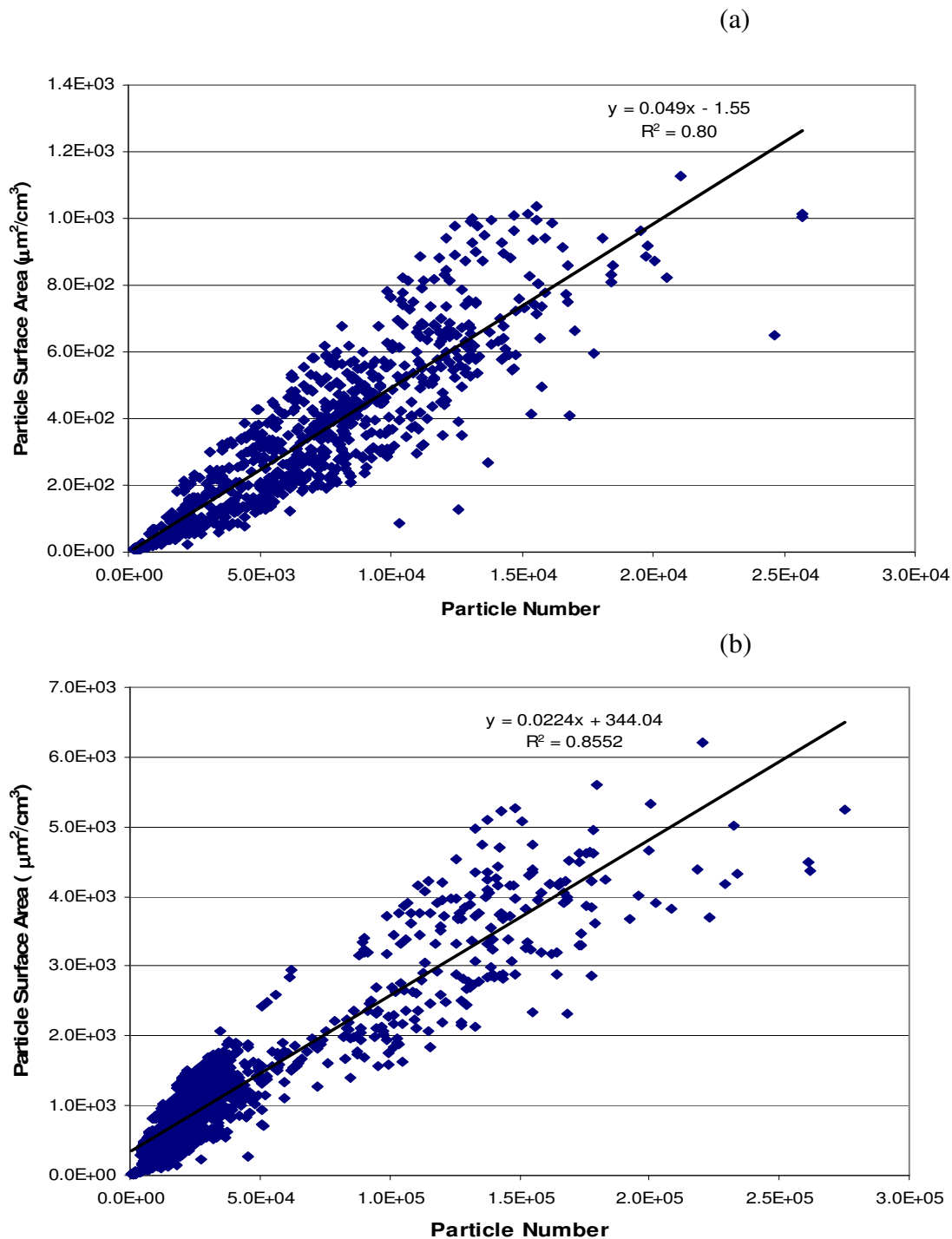
Figure 4. PN 0.5 and surface area comparison for (a) Glendora and (b) Mira Loma in Dec2001

(a)

(b)
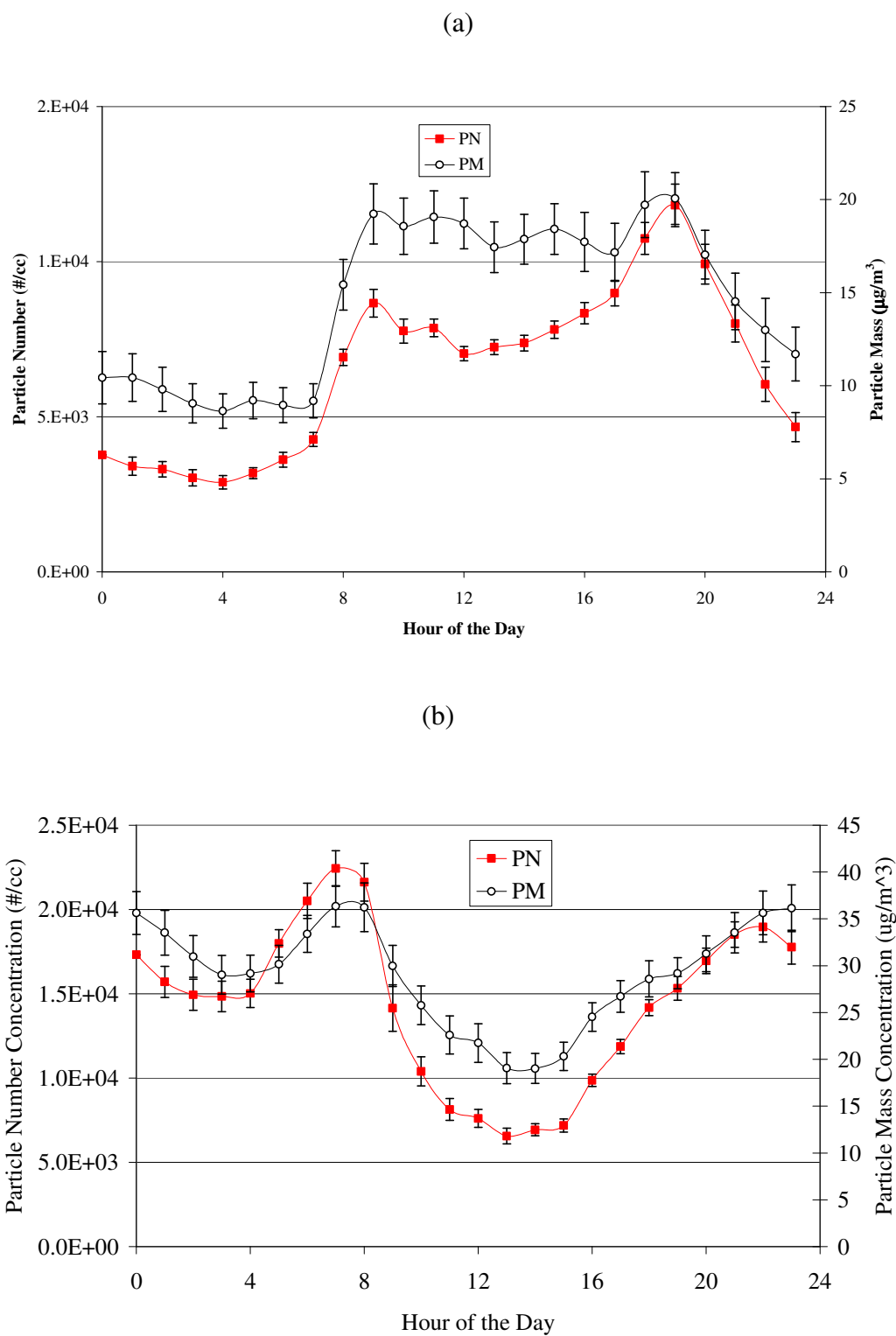
Figure 5. PN0.5 and PM0.5 ($\mu g/m^3$) mass concentrations comparison for (a) Glendora and (b) Mira Loma in Jan 2002.

(a)

$y = 0.0297x + 412.8$
$R^2 = 0.88$

(b)

$y = 0.0194x + 512.5$
$R^2 = 0.60$
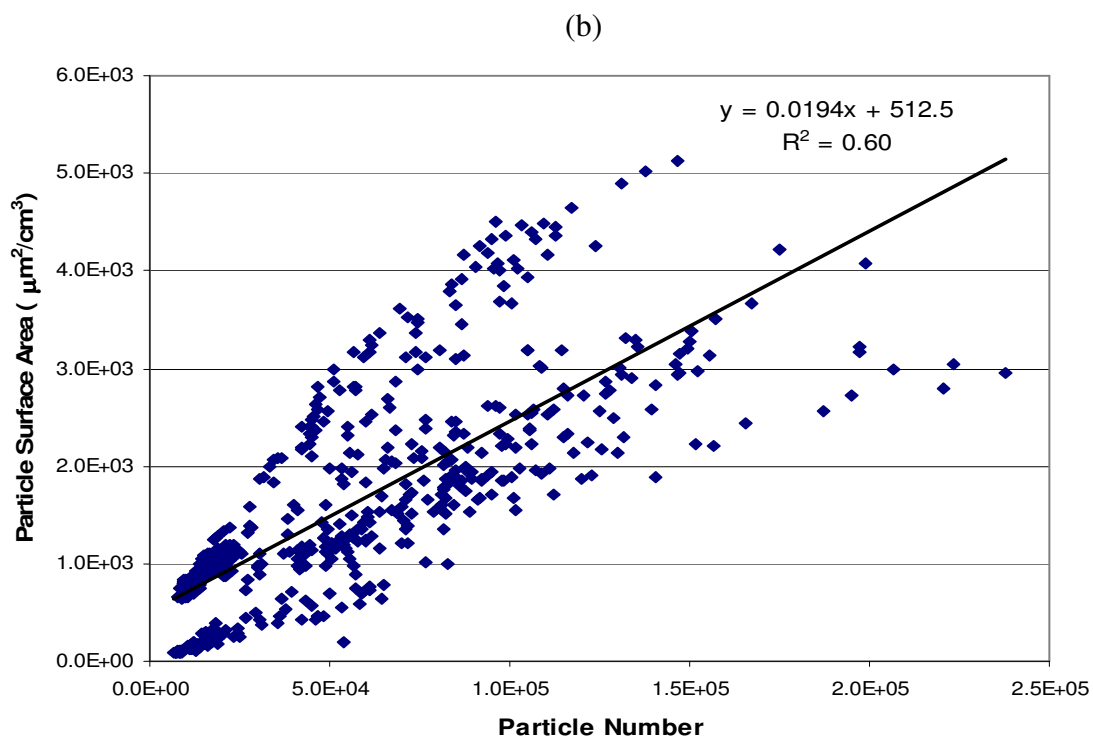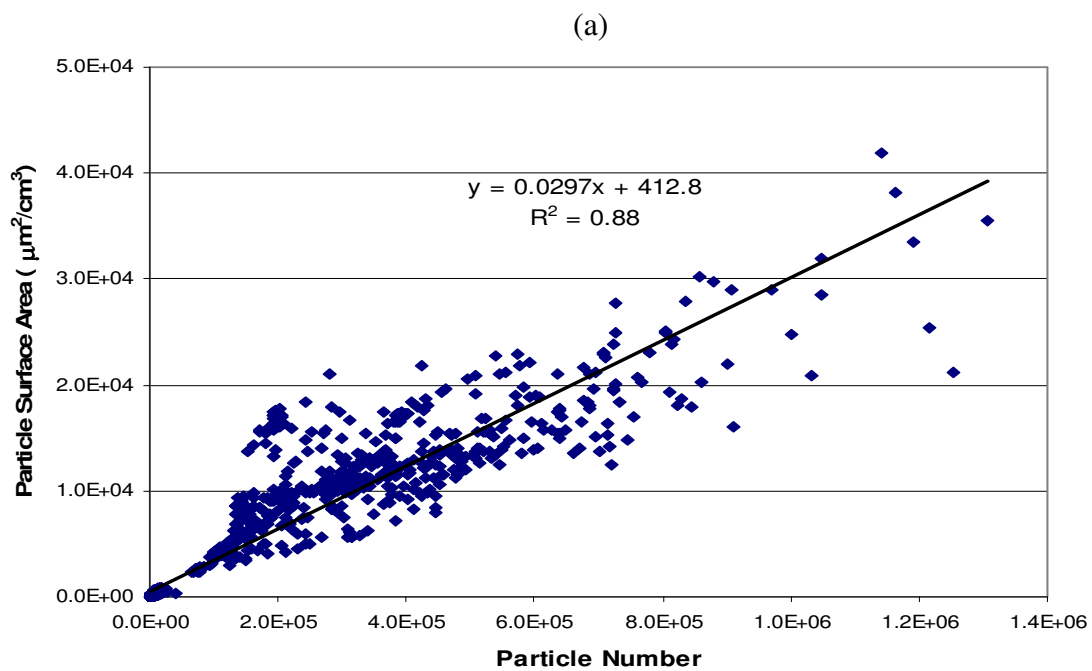
Figure 6. PN0.5 and surface area comparison for (a) Glendora (b) Mira Loma in Jan 2002
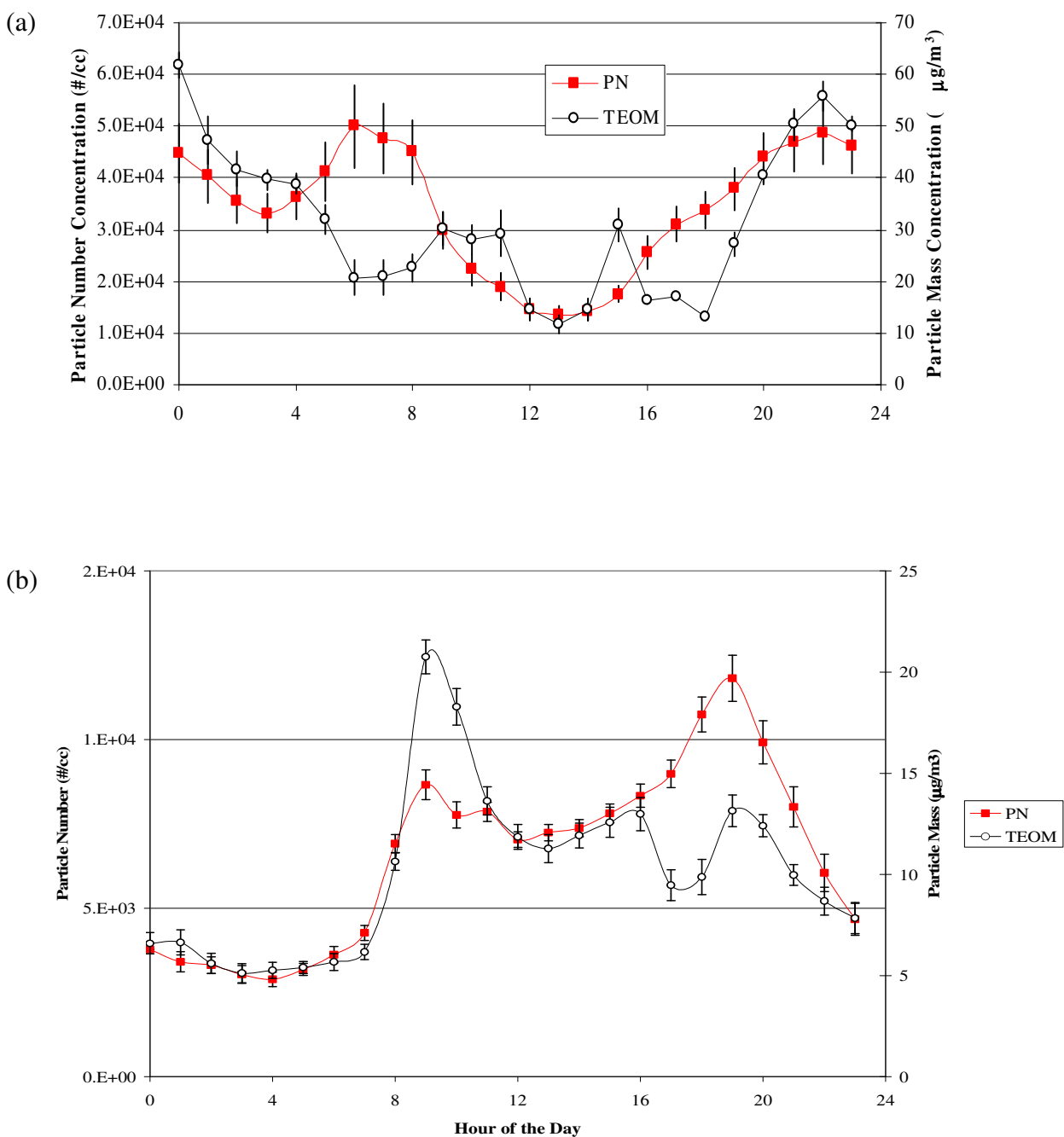
Figure 7. PN0.5 and PM10 mass concentration at
(a) Miraloma, Dec 2001
(b) Glendora Jan 2002
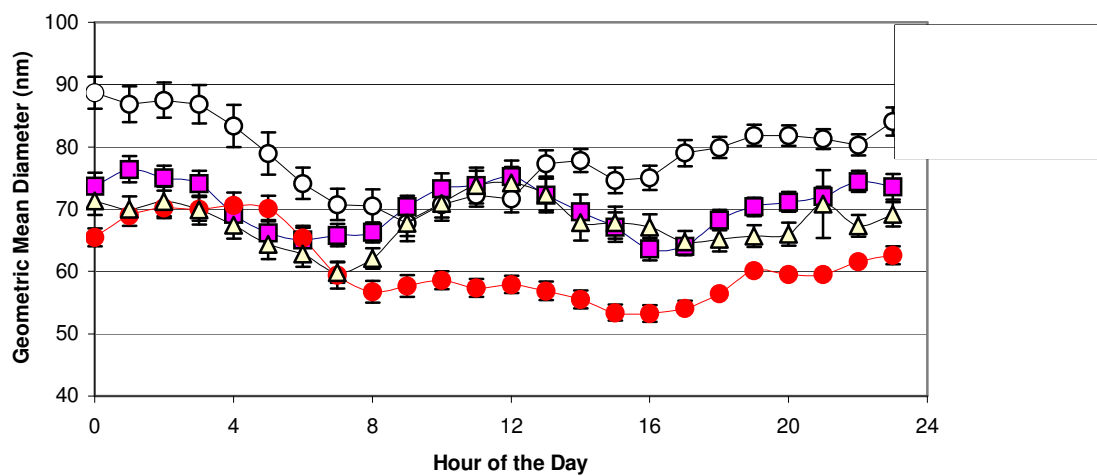
Figure 8. Geometric mean diameter in Mira Loma and Glendora for December 2001 and Jan 2002.

(a)
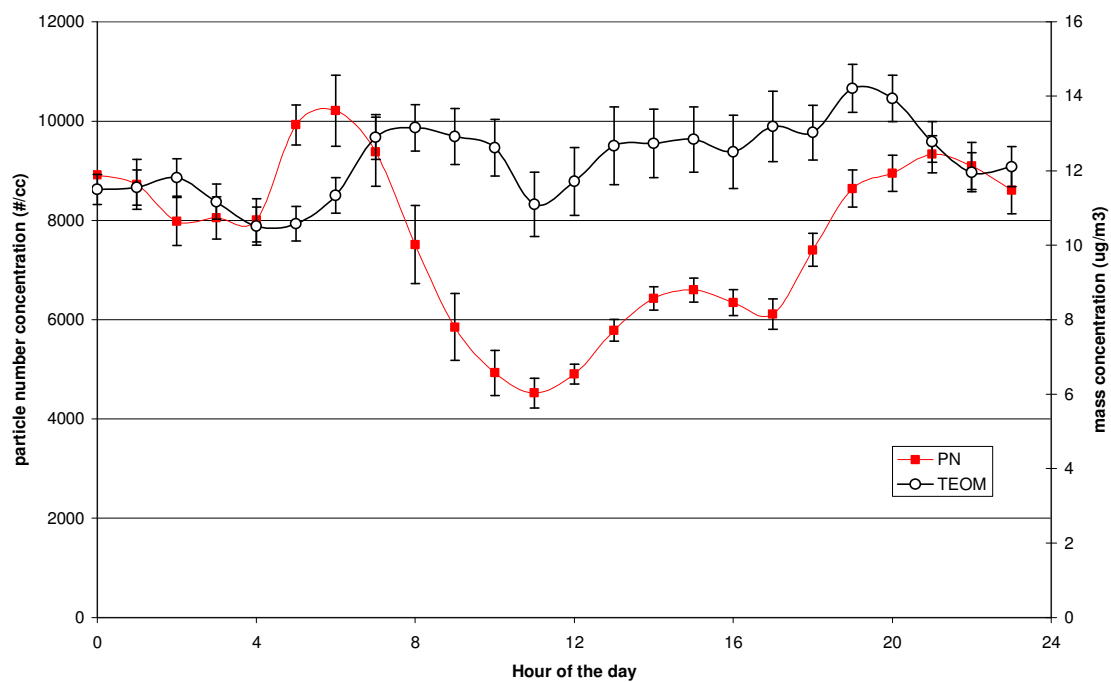
(b)
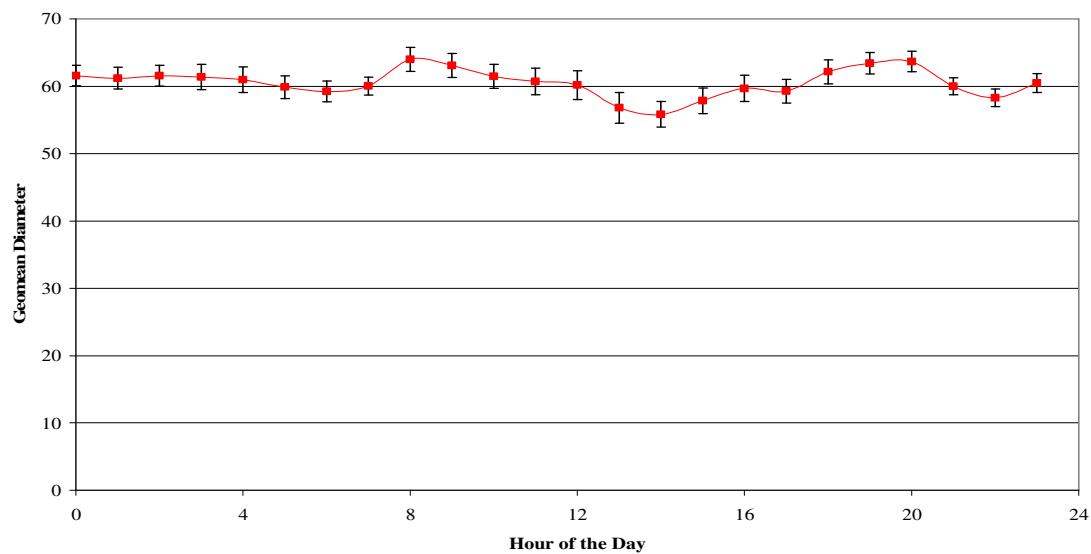
Figure 9. (a) Hourly PN0.5 Concentration and (b) geomean diameter   in Riverside during Mar 2002.

(a)

(b)
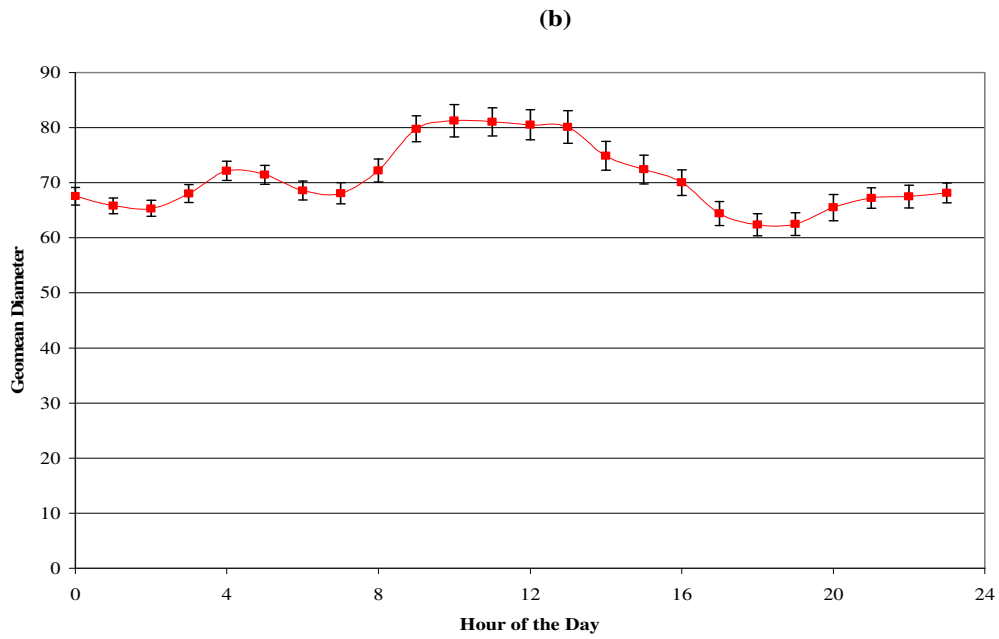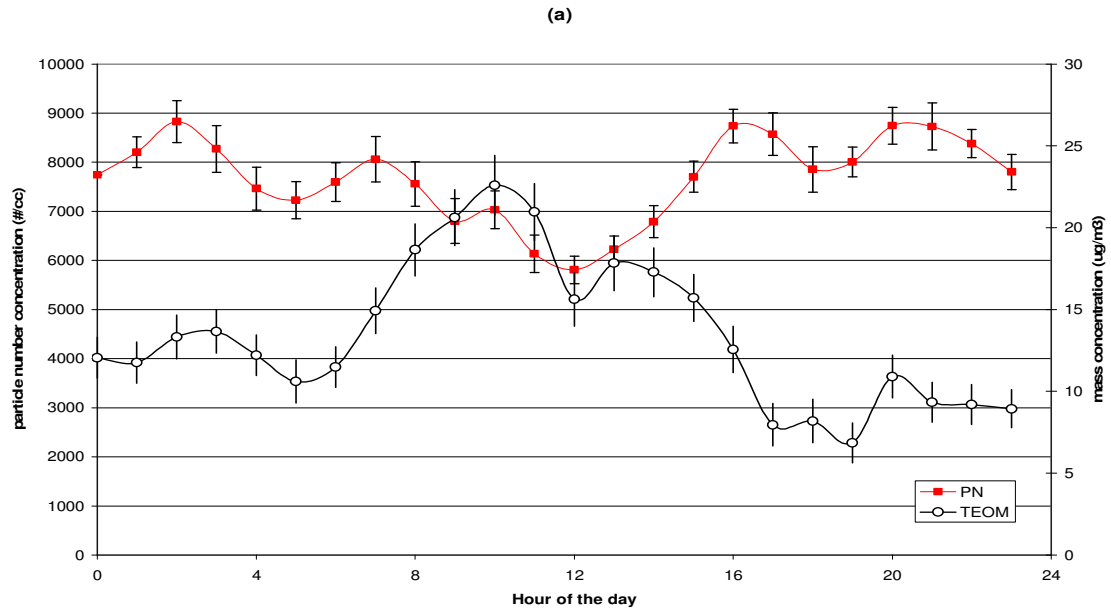
Figure 10. (a) Hourly PN0.5 Concentration (b) and geomean diameter in Riverside during Apr 2002.

(a)

(b)

$$y = 0.0312x + 152$$
$$R^2 = 0.306$$

(c)
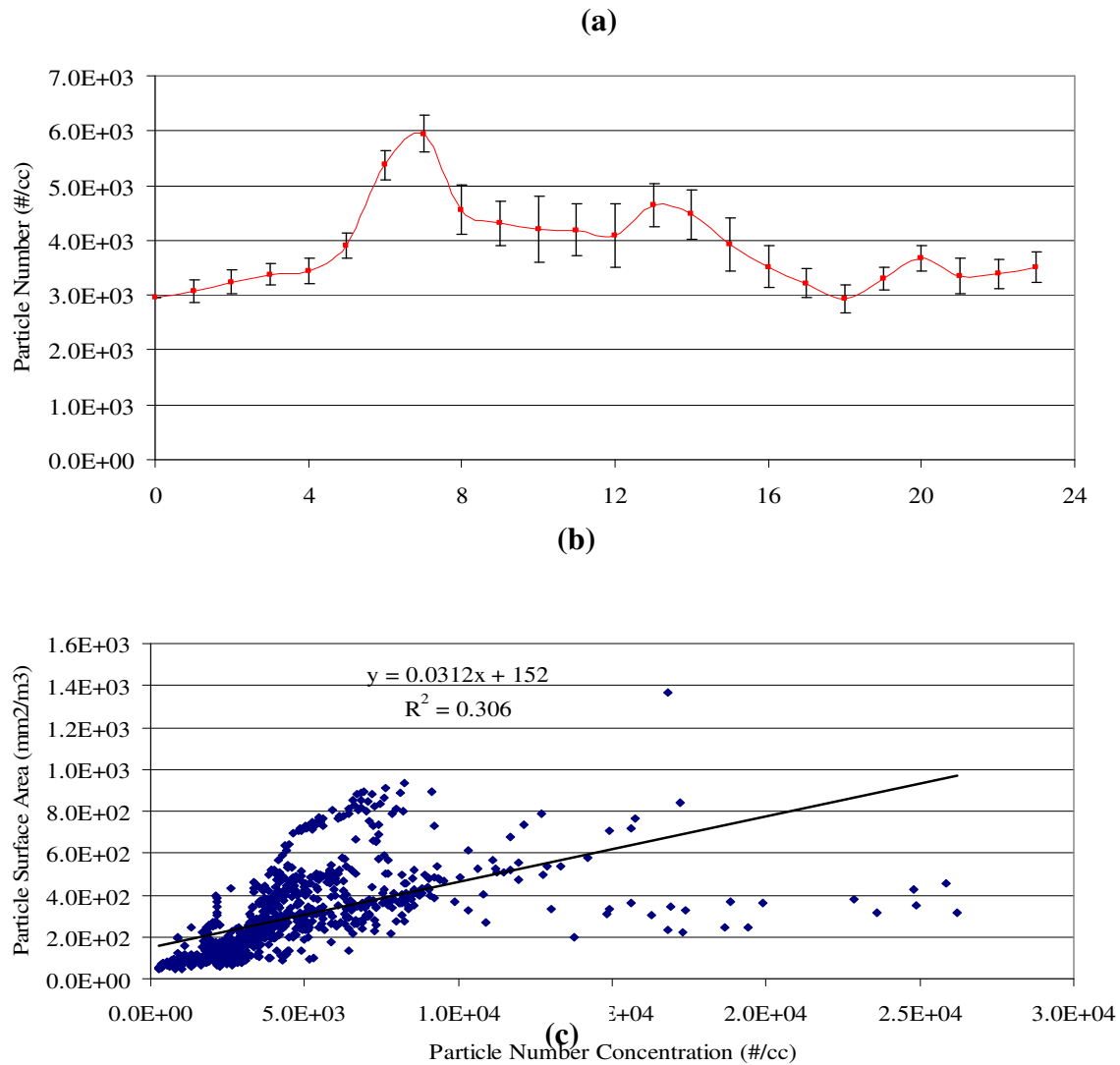
Figure 11. Atascadero Apr 2002
 (a) PN0.5 concentrations as a function of time of the day.
 (b) PN0.5 and surface area concentration correlation.

(a)

TEOM Mass Concentration and PM0.5 Number Concentration Measured by SMPS in Mira Loma (Jun 2002)

(b)

Mira Loma Geomean Diameter and Mode Diameter (Jun 2002)
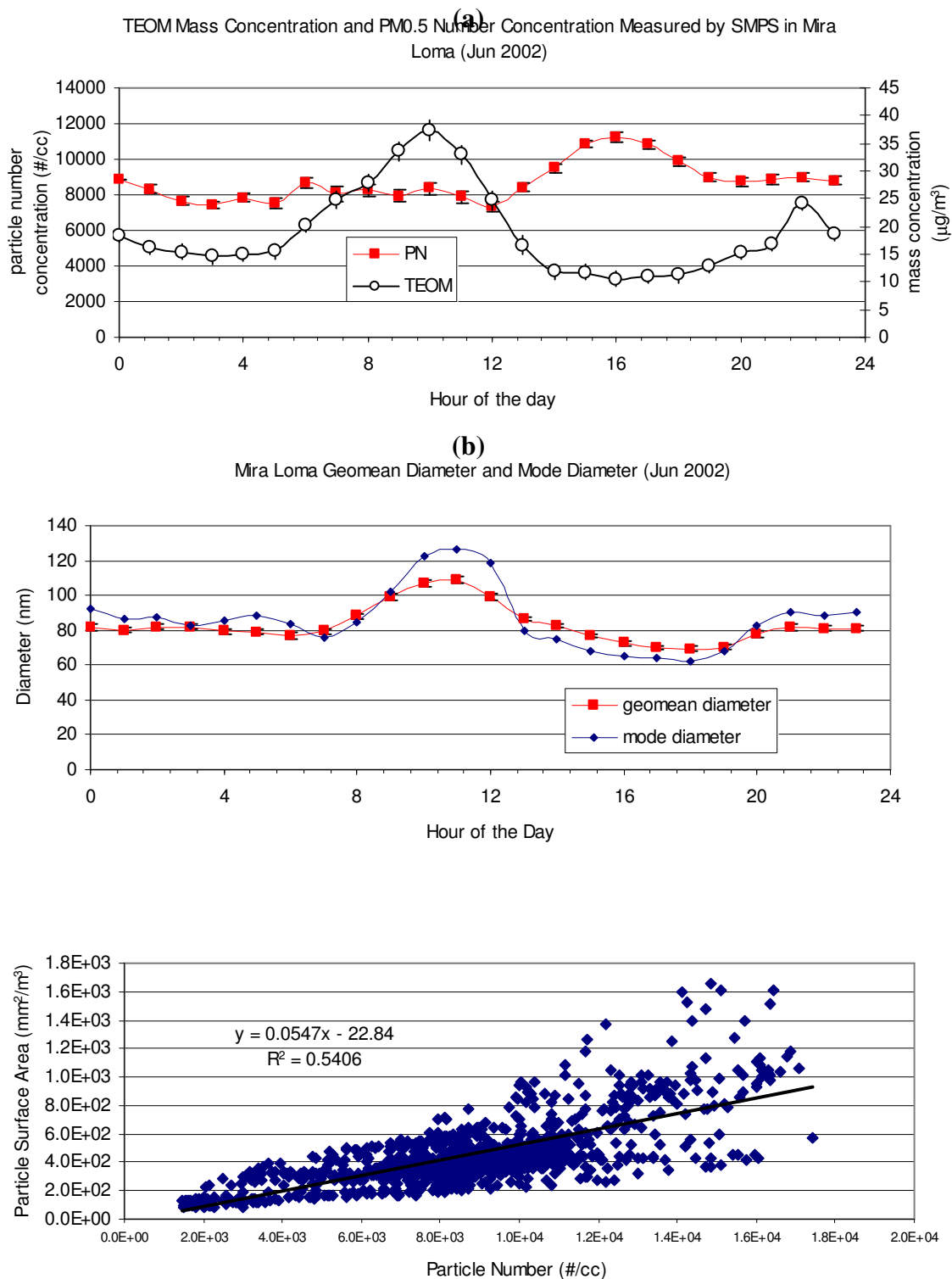
Figure 12. Particulate matter characteristics for Mira Loma, Jun 2002.
 (a) PN0.5 and PM10 mass concentrations as a function of hour of the day
 (b) Geomean and mode diameter
 (c) PN0.5 and surface area concentrations correlation

(a)

PM0.5 Particle Number and Mass Concentration measured by SMPS in Lake Arrow head
(Jul 2002)

(b)

Geomean Diameter and Mode Diameter in Lake Arrow head, Jul 2002

(c)

PM0.5 Particle Number and Surface Area Correlation in Lake Arrow head (Jul 2002)

$y = 0.048x$
$R^2 = 0.7786$
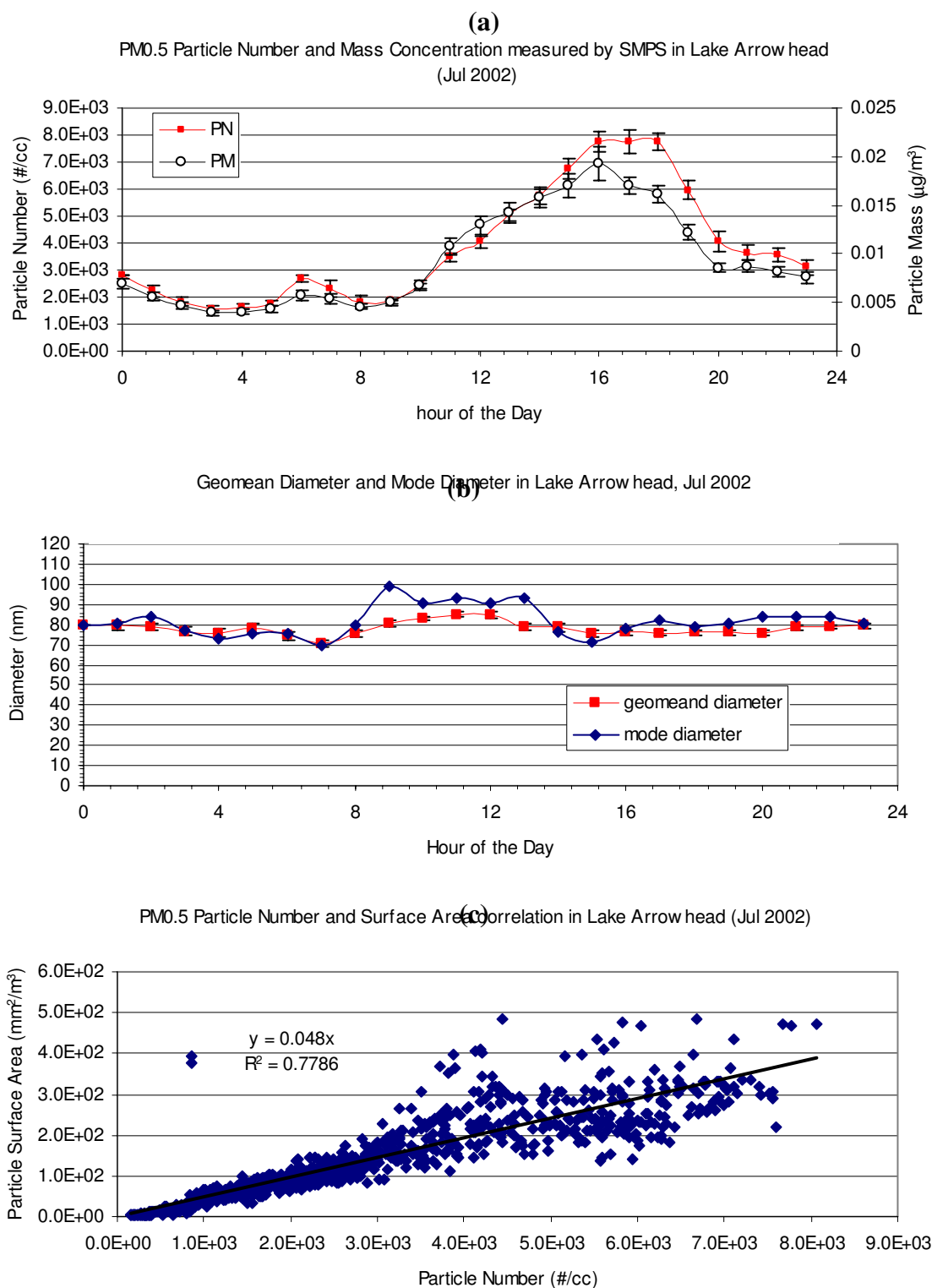
Figure 13. Particulate matter characteristics in Lake Arrowhead, Jul 2002
 (a). PN0.5 and PM10 concentrations as a function of hour of the day
 (b). Geomean and mode diameter
 (c). PN0.5 and surface area concentrations correlation
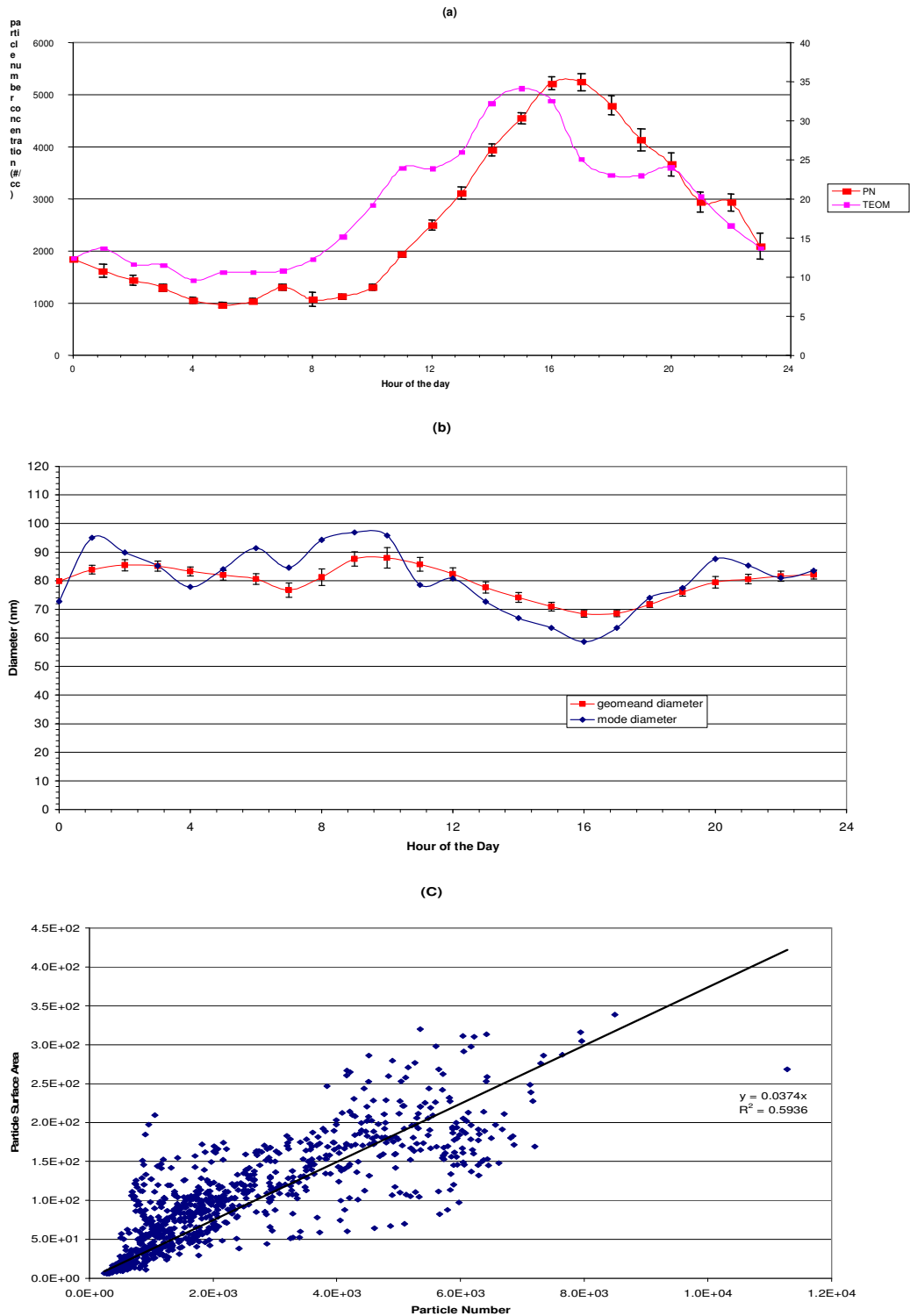
Figure 14. Particulate matter characteristics in Lake Arrowhead, Aug 2002
(a). PN0.5 and PM10 concentrations as a function of hour of the day
(b). Geomean and mode diameter
(c). PN0.5 and surface area concentrations correlation
 (c). PN$_{0.5}$ and surface area concentrations correlation

(a)

(b)

Figure 15. Particulate characteristics in Long Beach, California. (Sep 2002).
(a). PN0.5 and PM2.5 mass concentration as a function of hour of the day.
(b). Geomean and mode diameter.

(a)

(b)

Figure 16. Particulate characteristics in Long Beach, California. (Oct 2002).
(a). PN0.5 and PM2.5 mass concentration as a function of hour of the day.
(b). Geomean and mode diameter.

(a)

(b)
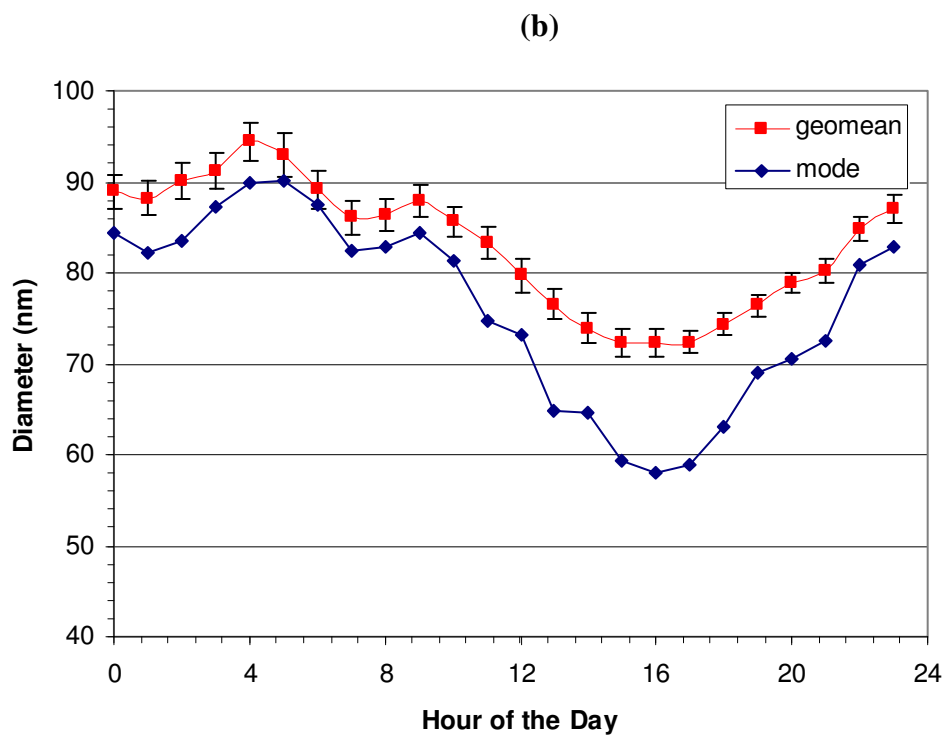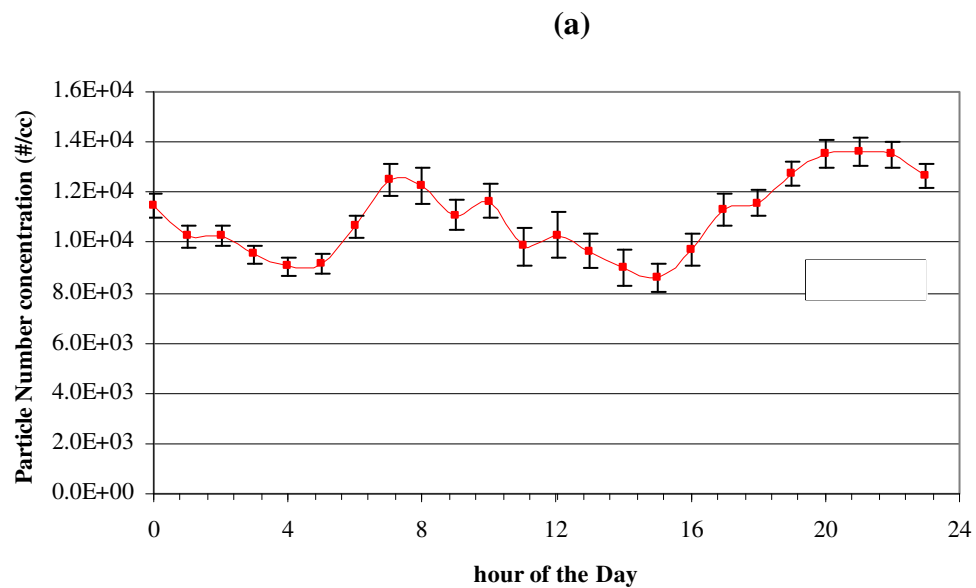
Figure 17. Particulate characteristics in Long Beach, California. (Nov2002).
(a). PN0.5 concentration as a function of hour of the day.
(b). Geomean and mode diameter

(a)

(b)
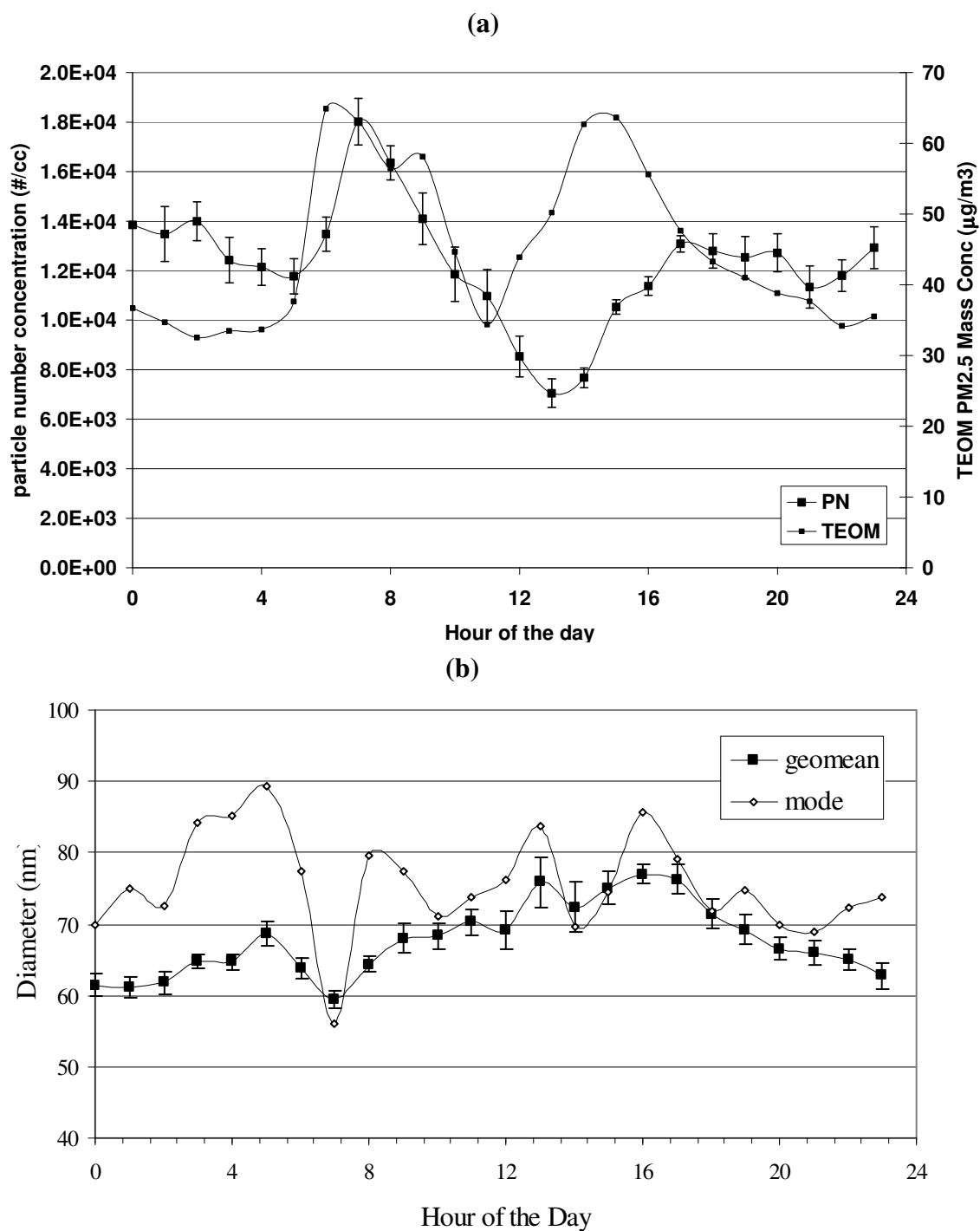
Figure 18 Particulate characteristics in Riverside, California. (Sep 2002).
(a). PN0.5 and PM2.5 mass concentration as a function of hour of the day.
(b). Geomean diameter and mode diameter.

(a)

Figure 19 Particulate characteristics in Riverside, California. (Oct 2002).
(a). PN0.5 and PM2.5 mass concentration as a function of hour of the day.
(b). Geomean and mode diameter.

(a)

(b)
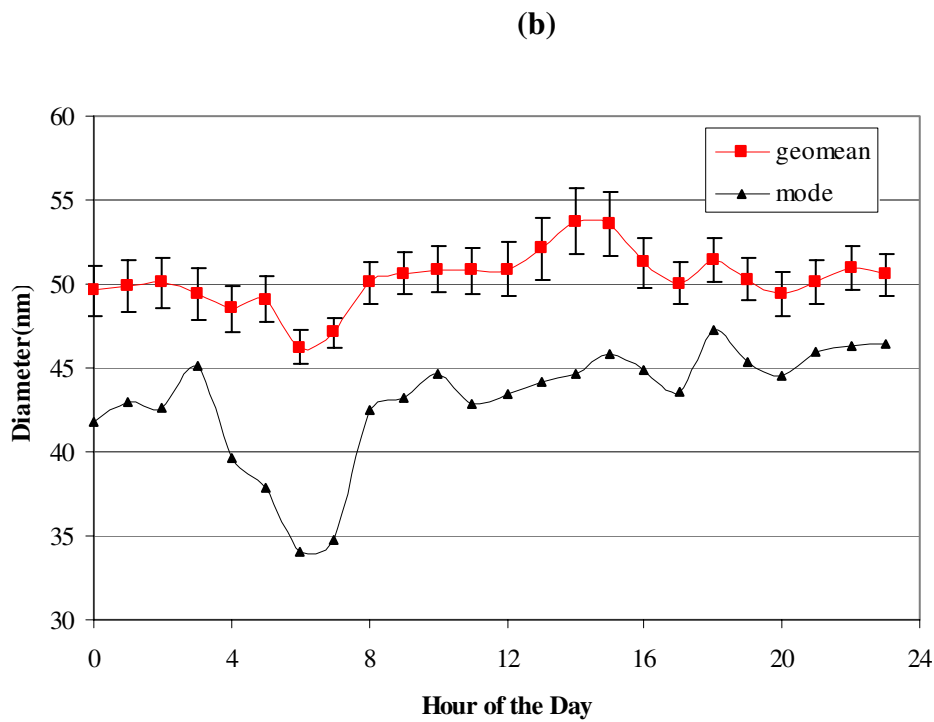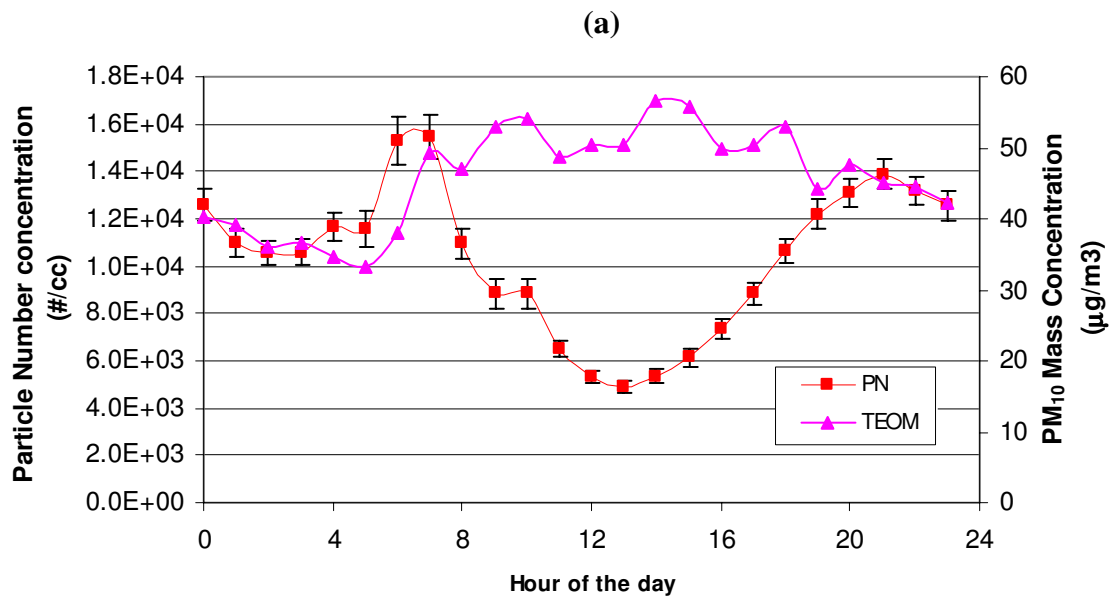
Figure 20. Particulate characteristics in Riverside, California. (Nov 2002).
(a). PN0.5 and PM10 mass concentration as a function of hour of the day.
(b). Geomean diameter and mode diameter.

(a)

(b)

Figure 21. Particulate characteristics in Riverside, California. (Dec, 2002).
(a). PN0.5 (Dec 1-10,2002) and PM10 mass concentration as a function of hour of the
day.
(b). Geomean and mode diameter in Riverside (Dec1-10,2002)

(a)

(b)
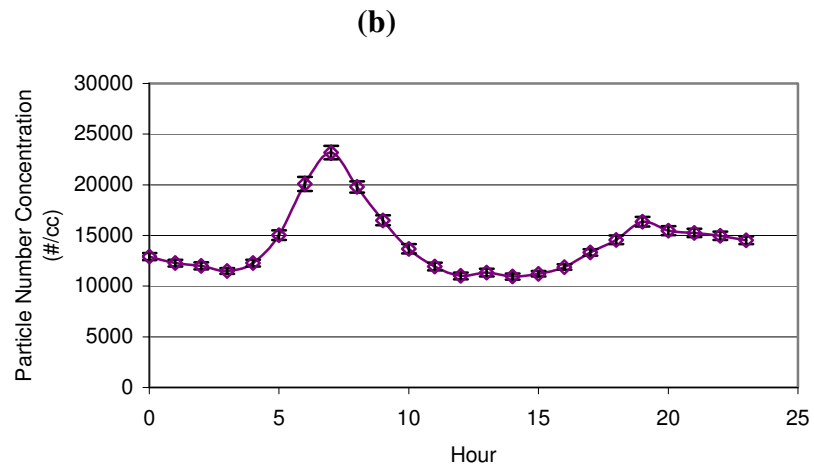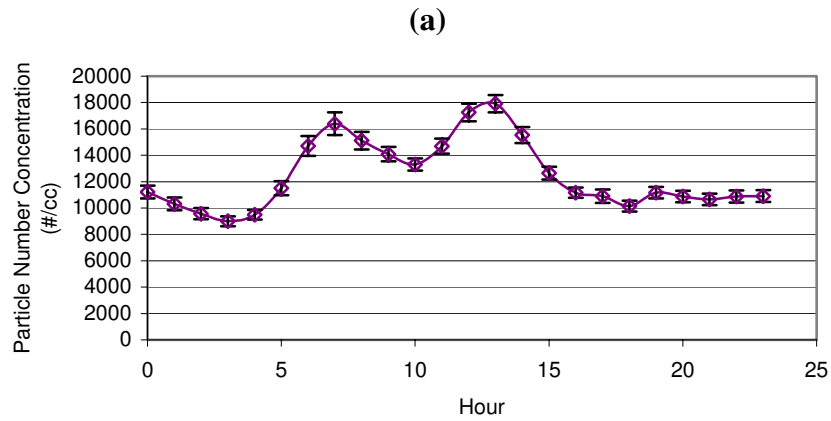
Figure 22.PN0.5 concentrations in USC, California. (a) Dec 2002-Jan 2003 (b) Sep, 2003
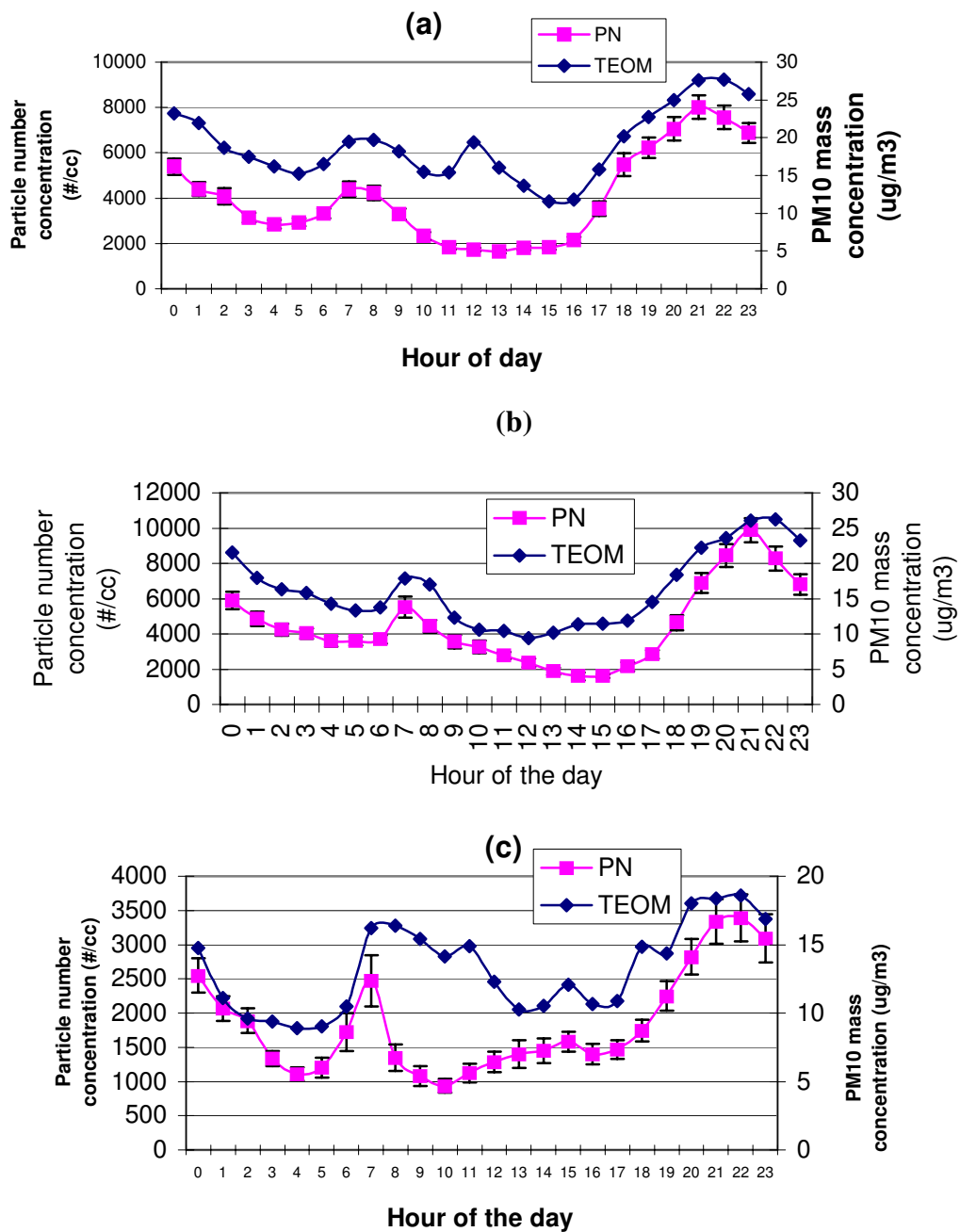
Figure 23. PN0.5 and PM_{10} mass concentration as a function of hour of the day. in Atascadero, CA for the months of (a) Jan, 2003 (b) Feb, 2003 (c) Mar, 2003.

(a)

(b)

(c)
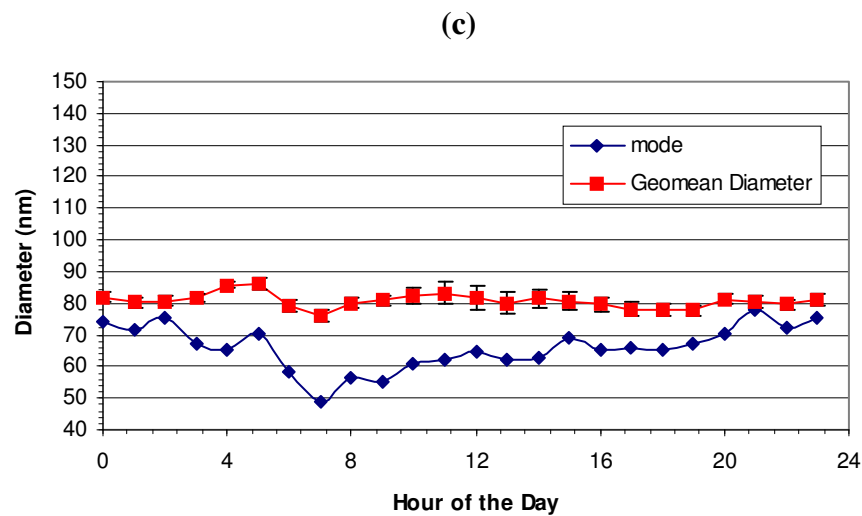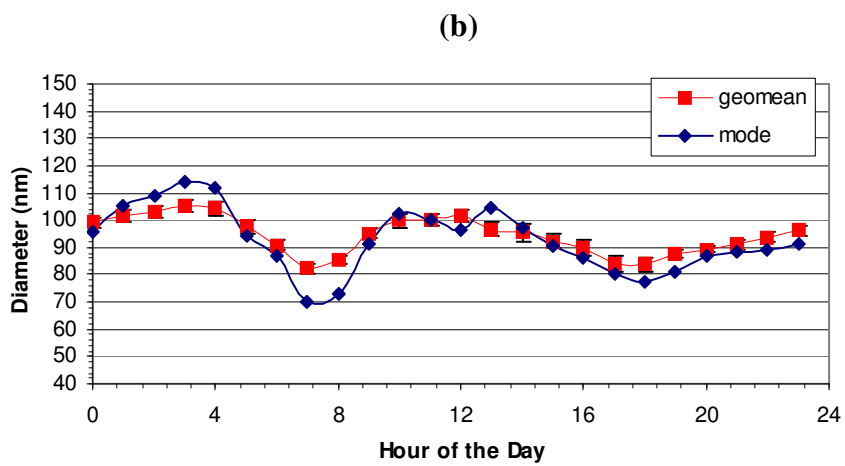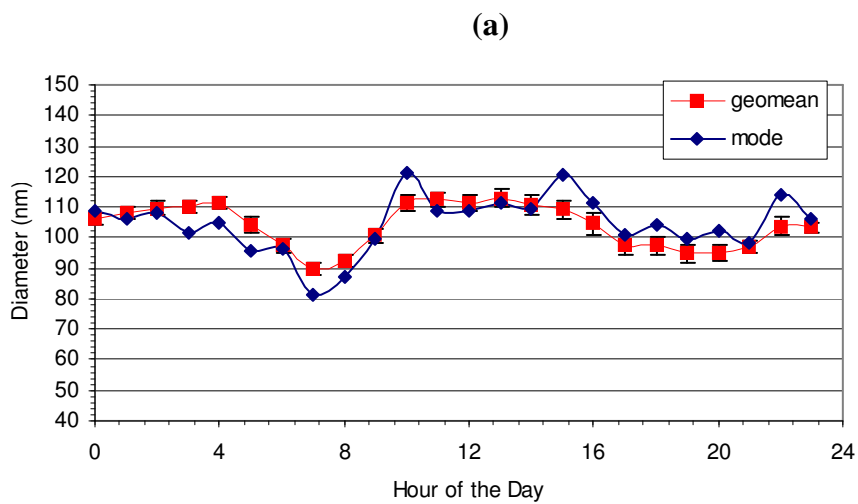
Figure 24.Geomean and Mode Diameters at Atascadero, CA in the months of (a) Jan,2003 (b) Feb, 2003 (c) Mar, 2003.
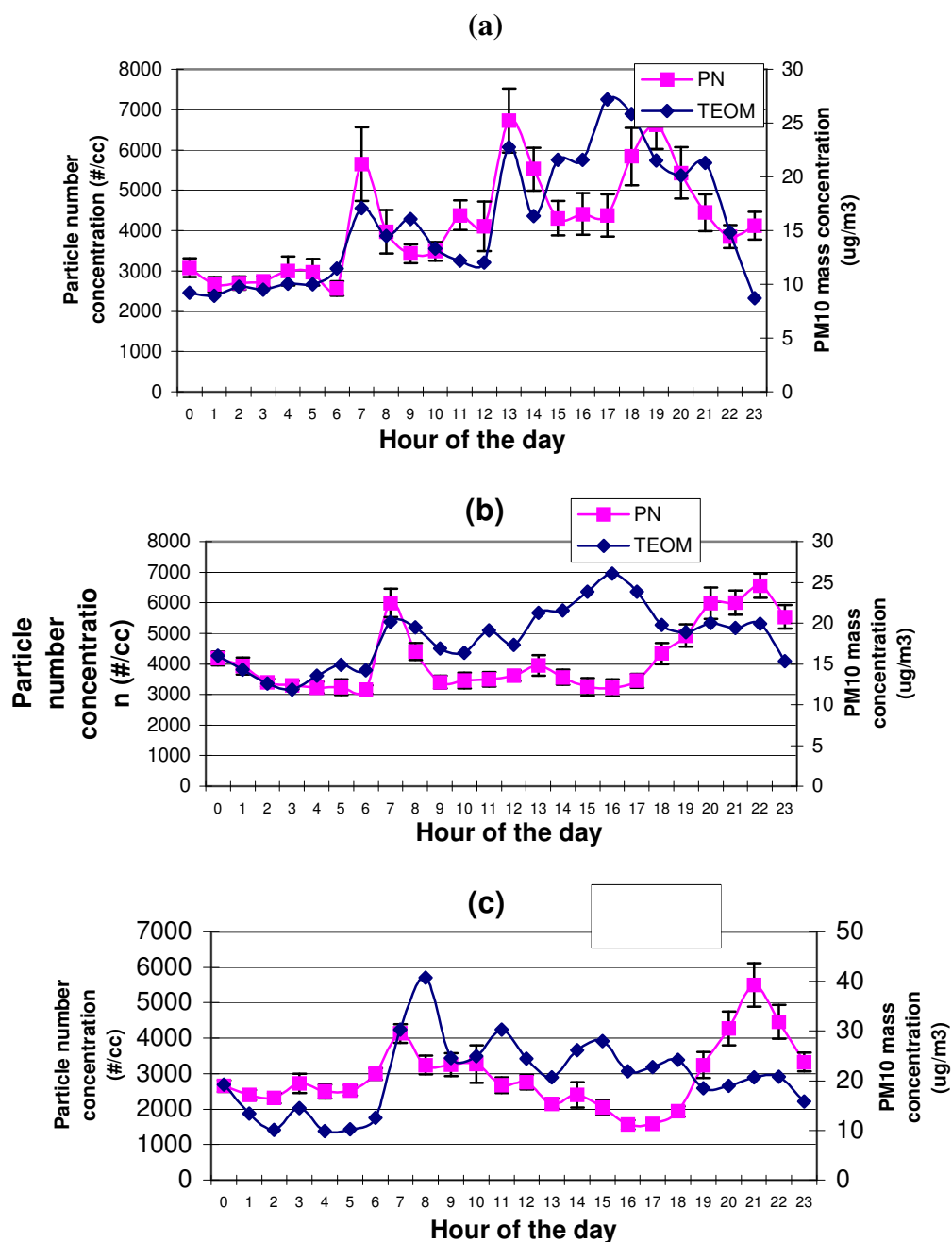
Figure 25. PN0.5 and PM_{10} mass concentration as a function of hour of the day. in Lompoc, CA for the months of (a) Jan,2003 (b) Feb, 2003 (c) Mar, 2003.

(a)

(b)

(c)
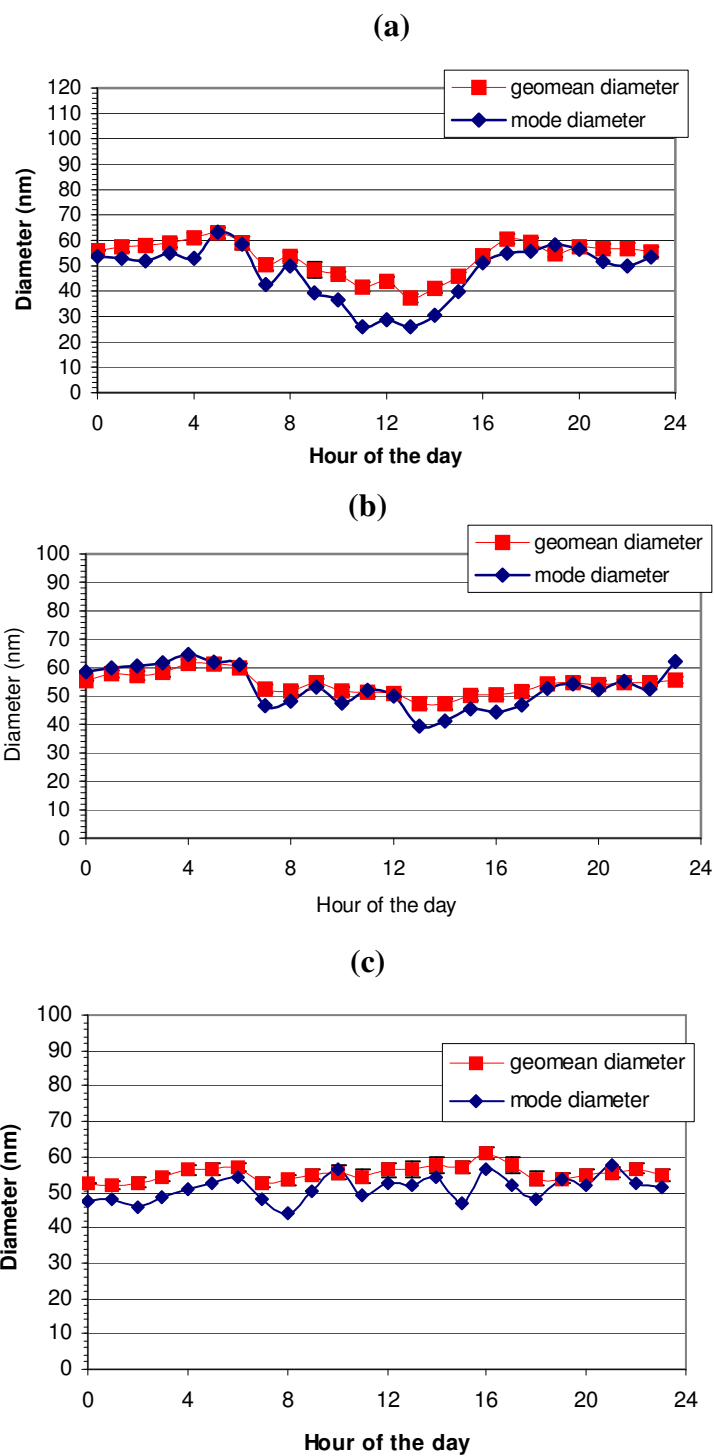
Figure 26.Geomean and Mode Diameters at Lompoc, CA in the months of (a) Jan,2003 (b) Feb, 2003 (c) Mar, 2003.

(a)

(b)

Figure 27. Particulate characteristics in Lake Elsinore, CA. (Apr 2003).
(a). PN0.5 and PM_{10} mass concentration as a function of hour of the day.
(b). Geomean diameter and mode diameters as a function of hour of the day

Figure 28. PM$_{10}$ mass concentration as a function of hour of the day in Lake Elsinor, CA. (May 2003).

(a)

Hour of the day

(b)

Hour of the day

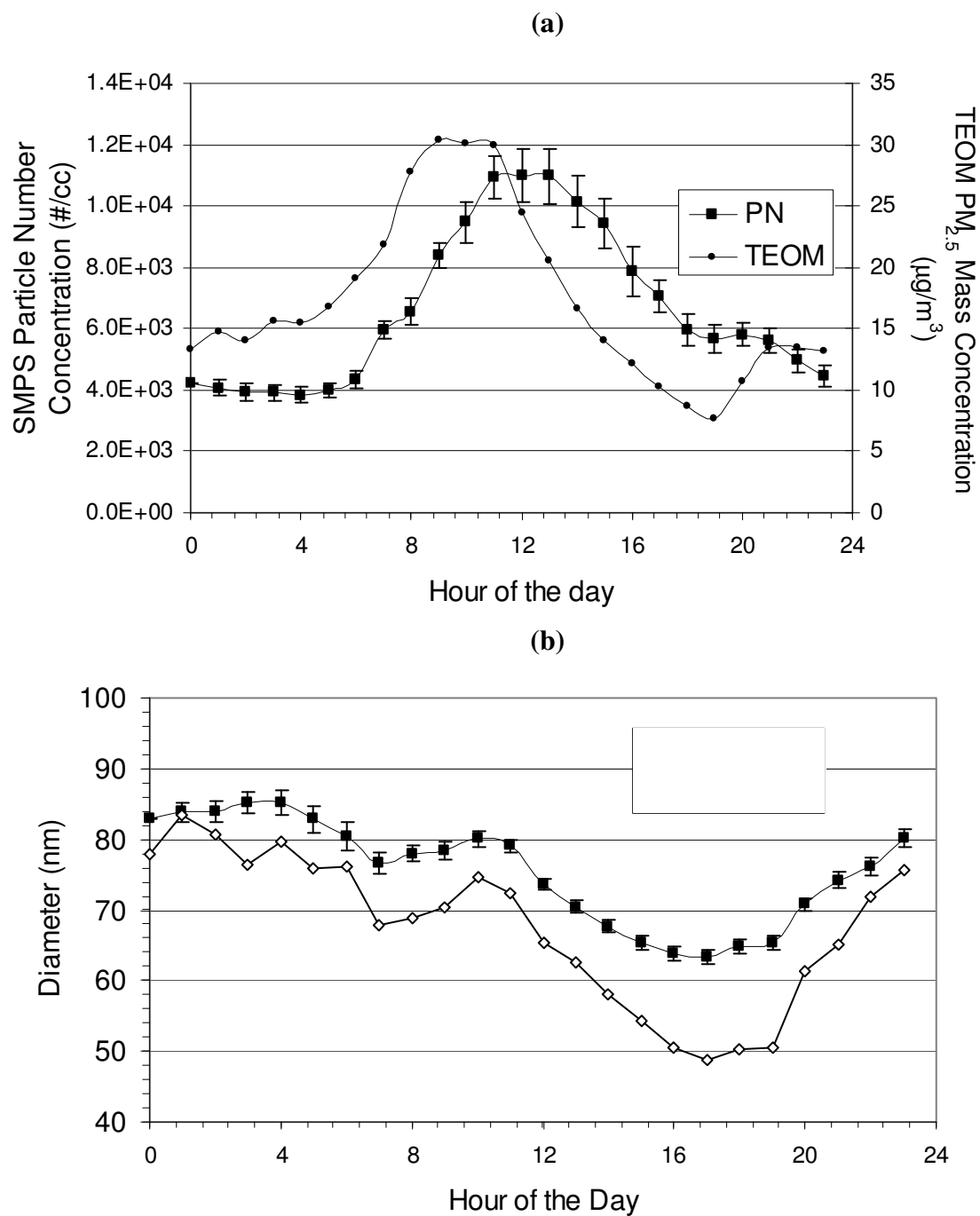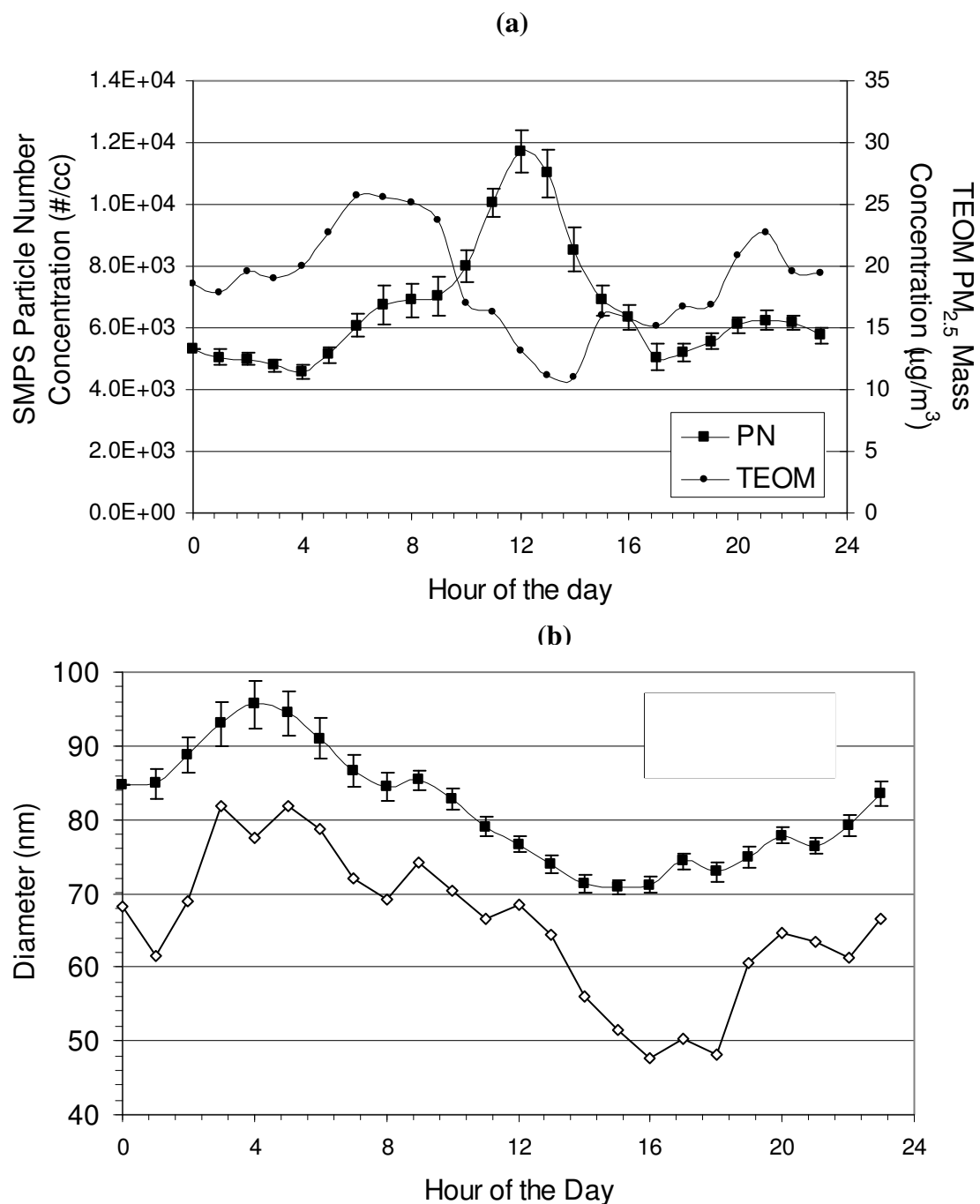Figure 29. Particulate characteristics in Alpine, CA. (Apr 2003).
(a). PN0.5 and PM_{10} mass concentration as a function of hour of the day.
(b). Geomean diameter and mode diameters as a function of hour of the day

(a)

(b)

Figure 30. Particulate characteristics in Alpine, CA. (May 2003).
(a PN0.5 and PM$_{10}$ mass concentration as a function of hour of the day.
(b). Geomean diameter and mode diameters as a function of hour of the day

(a)

(b)

Figure 31. Particulate characteristics in Lake Arrowhead, CA. (Jun 2003).
(a). PN0.5 and PM_{10} mass concentration as a function of hour of the day.
(b). Geomean diameter and mode diameters as a function of hour of the day

(a)

(b)
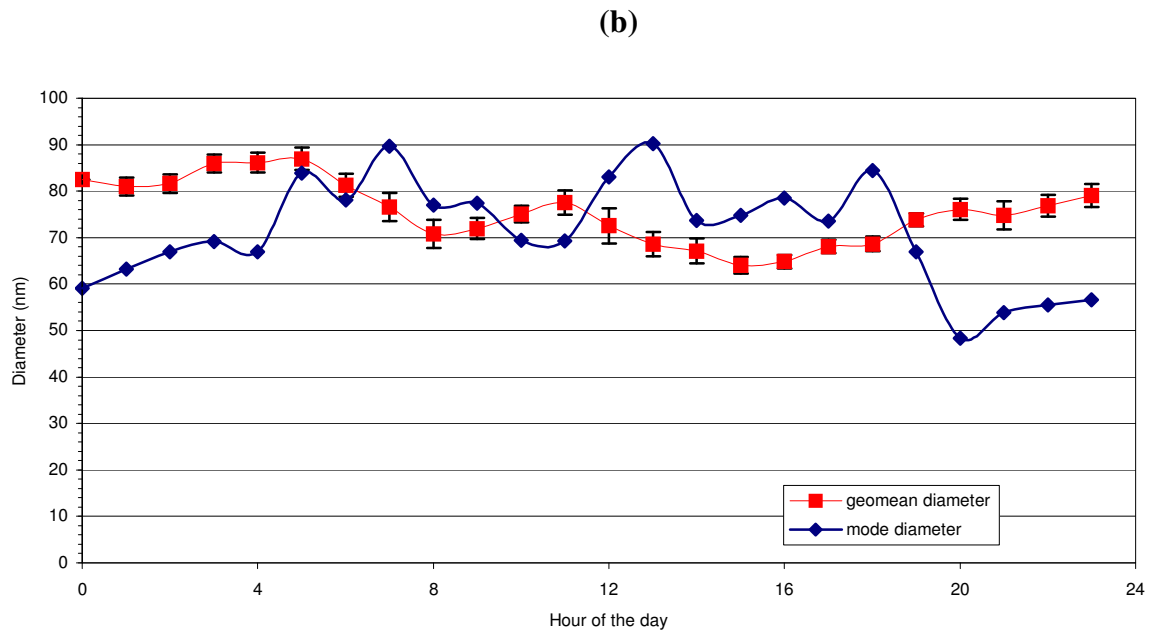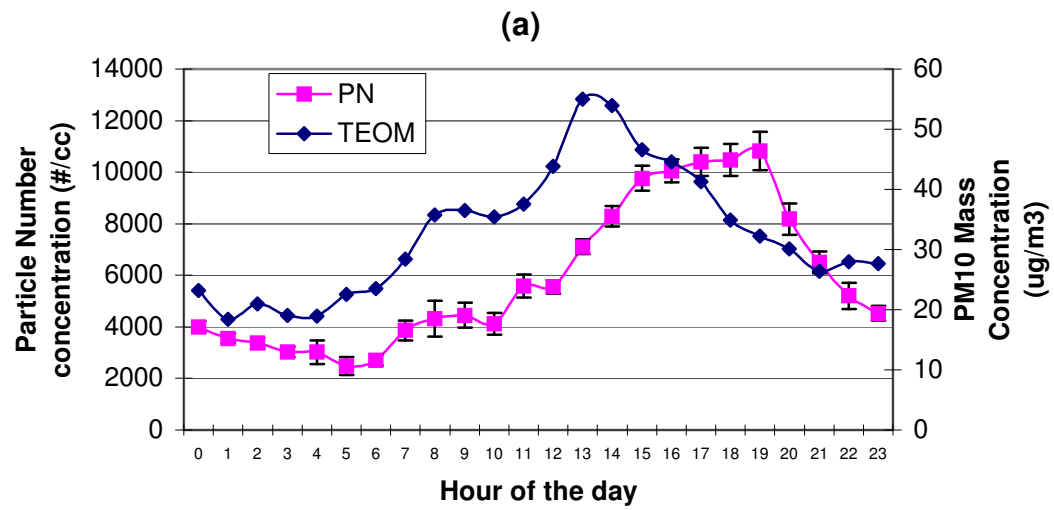
Figure 32. Particulate characteristics in Lake Arrowhead, CA. (Jul 2003).
(a). PN0.5 and PM_{10} mass concentration as a function of hour of the day.
(b). Geomean diameter and mode diameters as a function of hour of the day

(a)

(b)
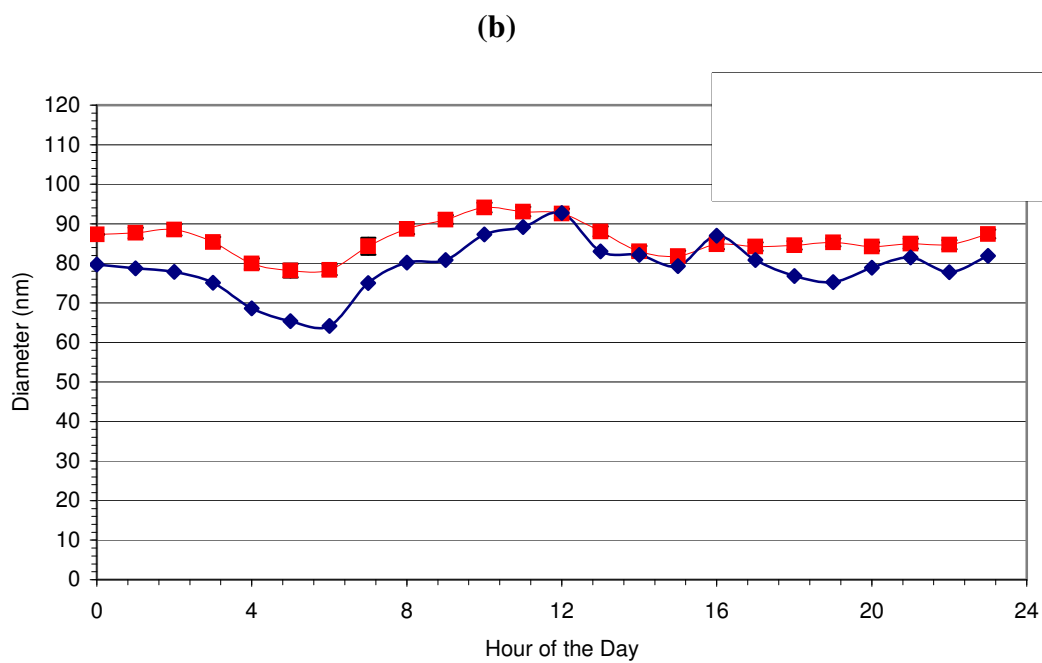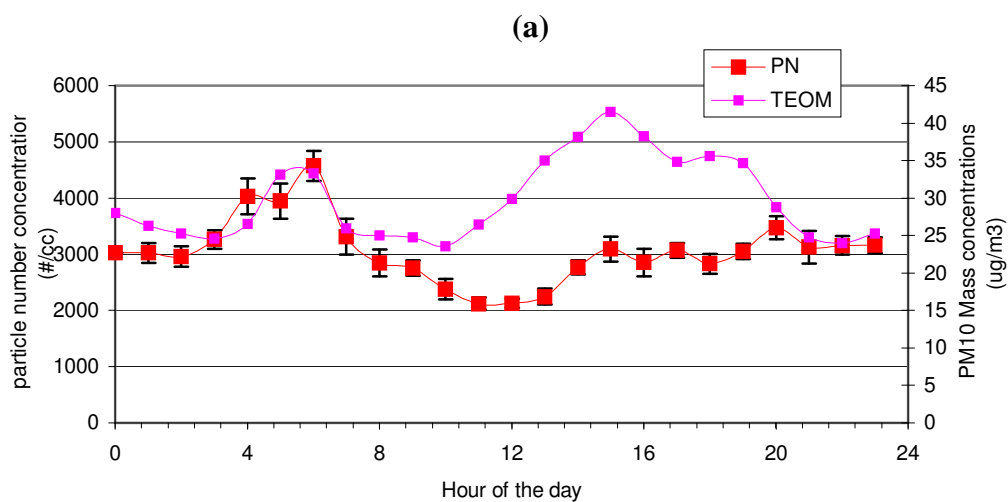
Figure 33. Particulate characteristics in Lancaster, CA. (Jun 2003).
(a). PN0.5 and PM_{10} mass concentration as a function of hour of the day.
(b). Geomean diameter and mode diameters as a function of hour of the day

(a)

(b)
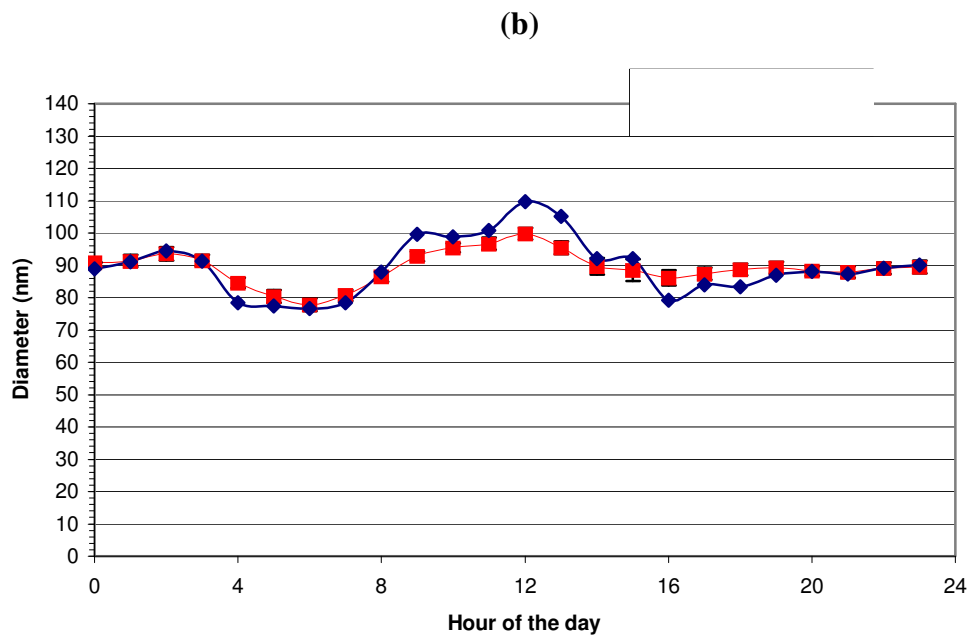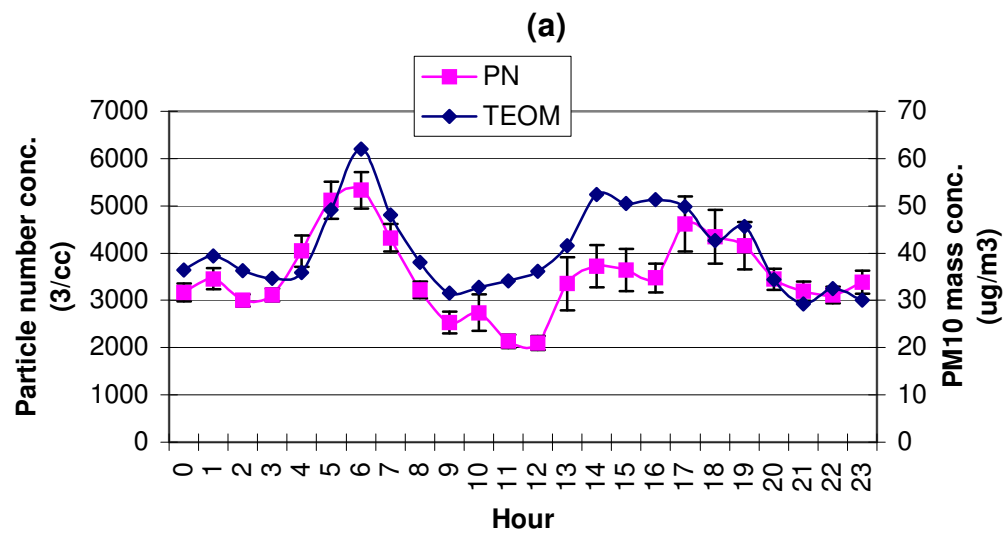
Figure 34. Particulate characteristics in Lancaster, CA. (Jul 2003).
(a). PN0.5 and PM_{10} mass concentration as a function of hour of the day.
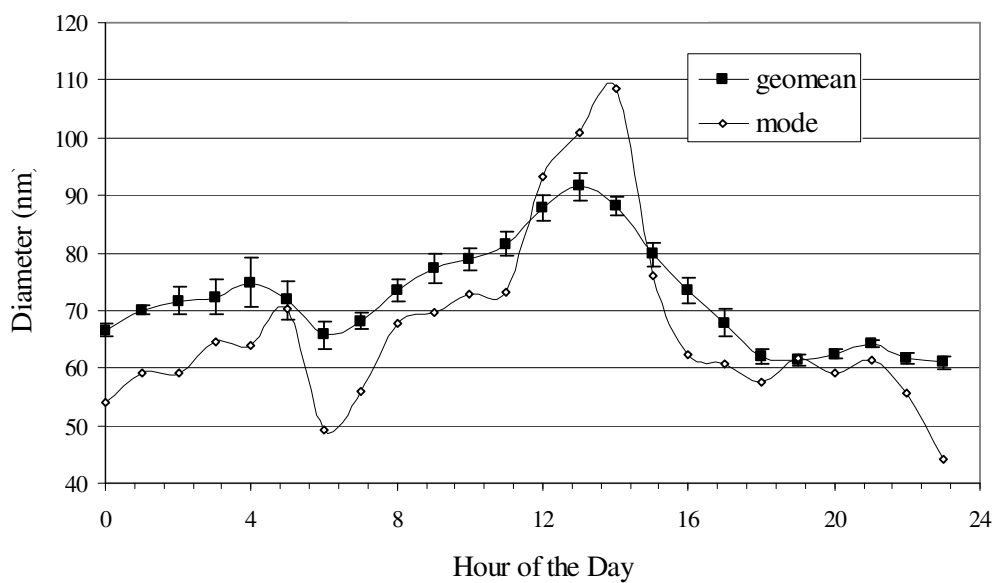(b). Geomean diameter and mode diameters as a function of hour of the day

(a)

(b)
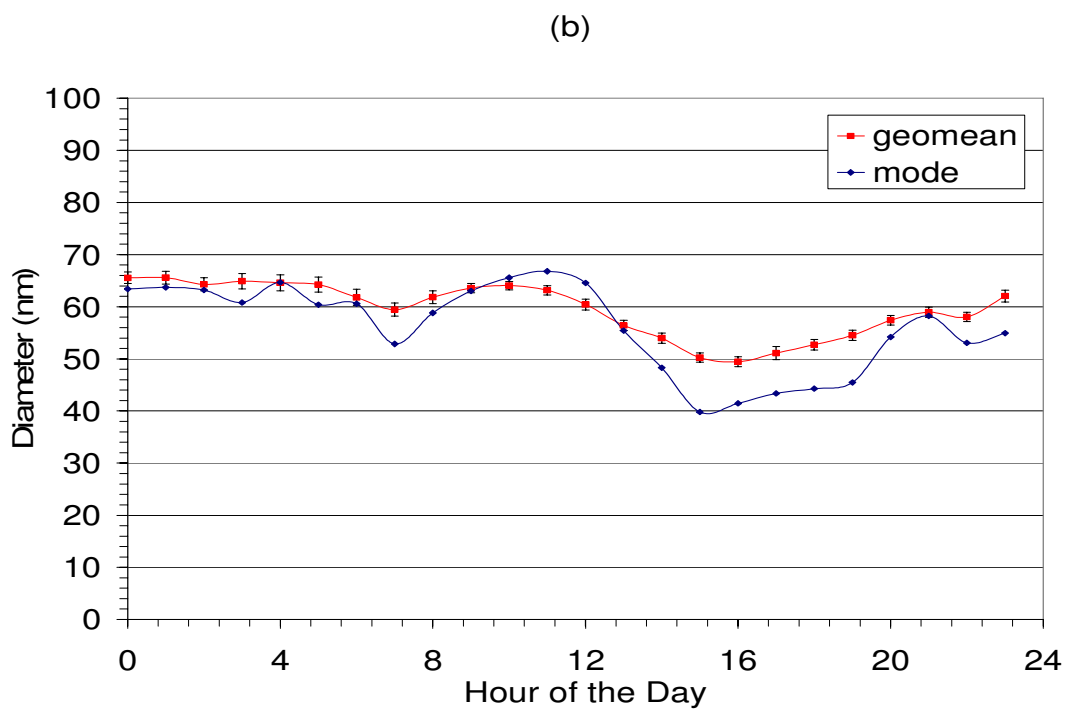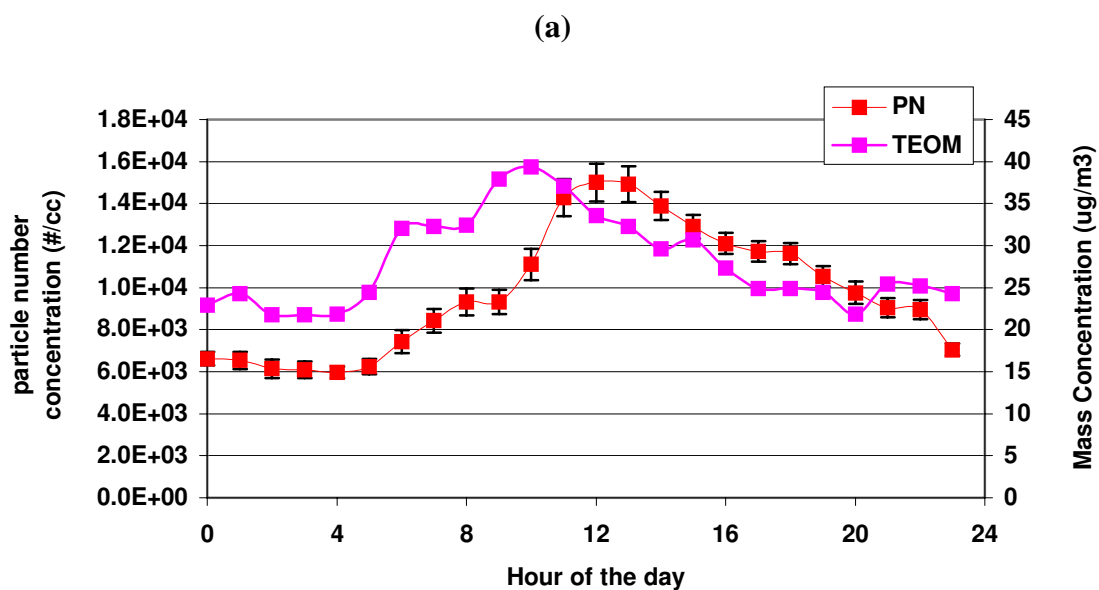
Figure 35. Particulate characteristics in Long Beach, CA. (Aug 2003).
(a). PN0.5 and PM_{10} mass concentration as a function of hour of the day.
(b). Geomean diameter and mode diameters as a function of hour of the day
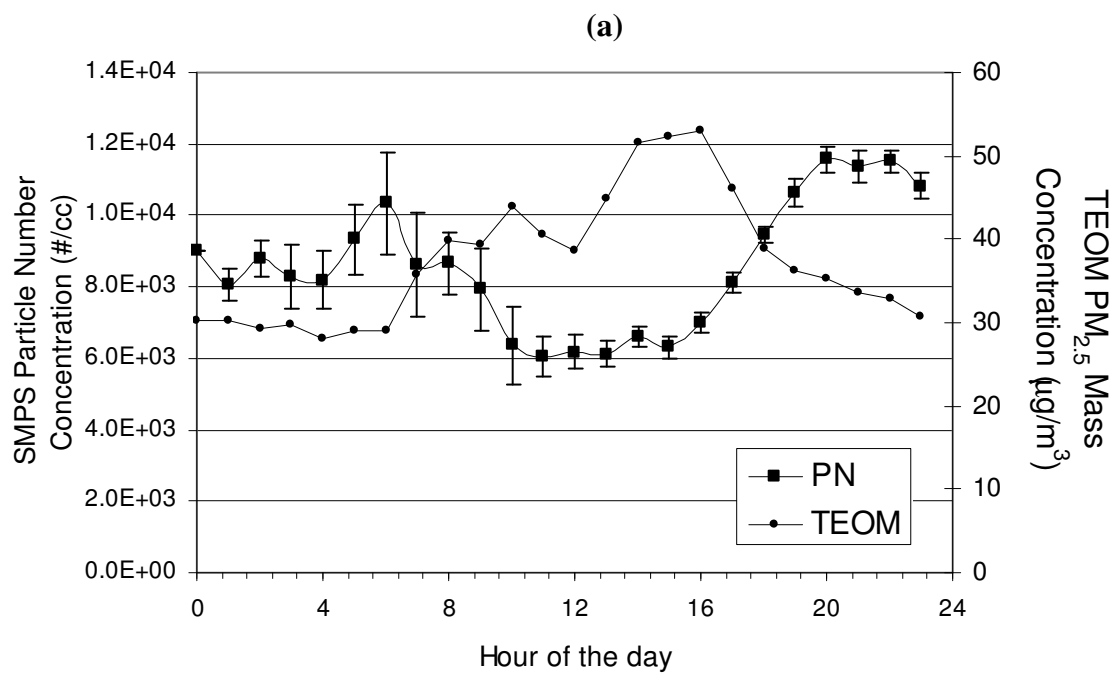
(a)

(b)
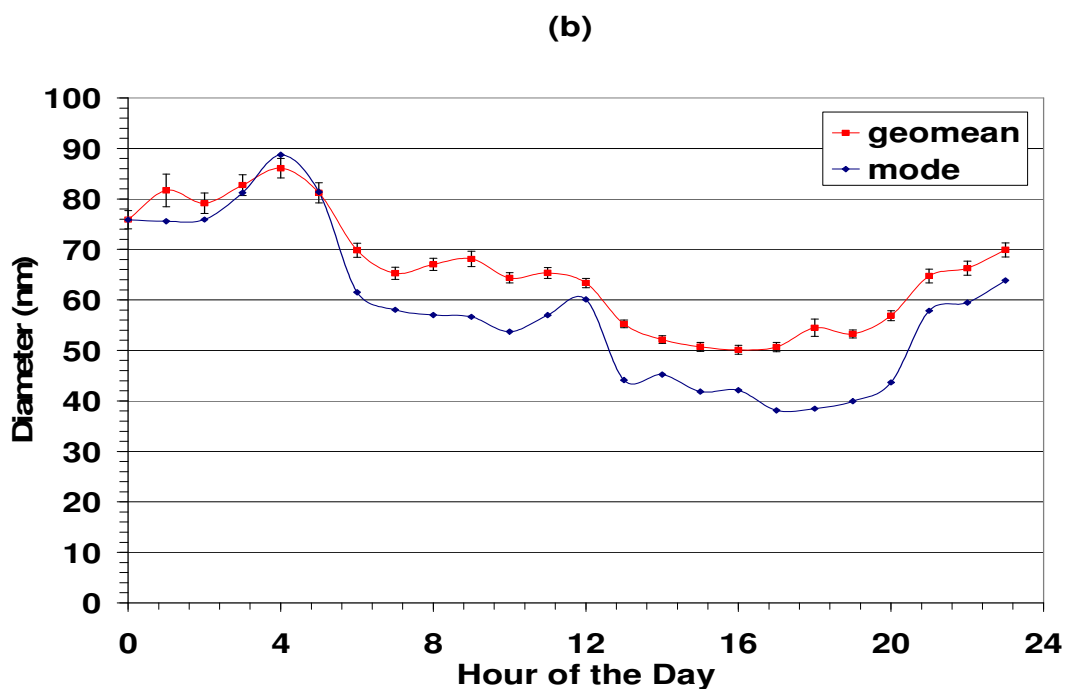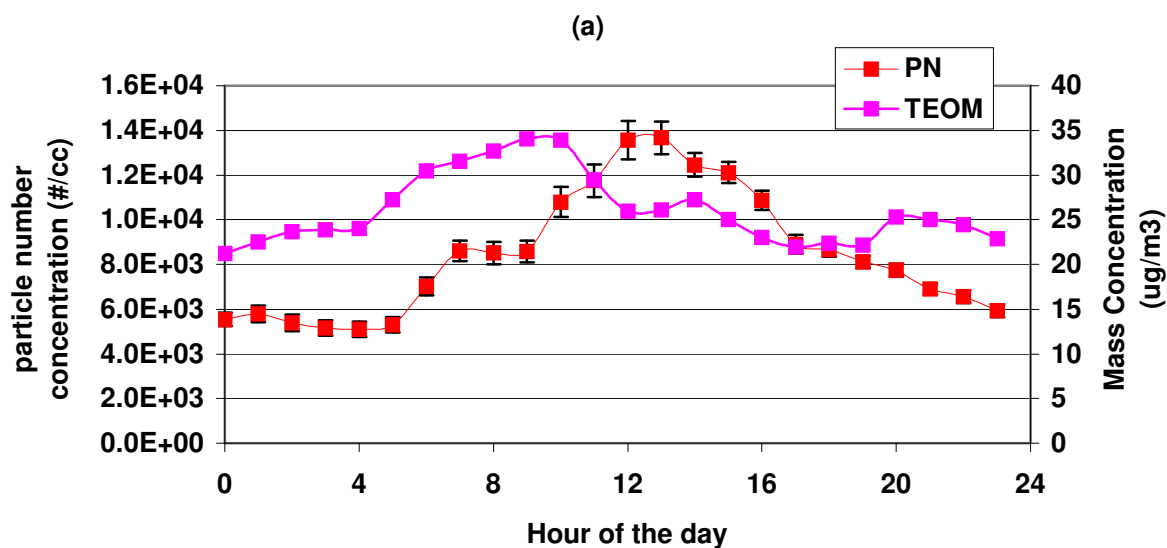
Figure 36. Particulate characteristics in Long Beach, CA. (Sep 2003).
(a). PN0.5 and PM$_{10}$ mass concentration as a function of hour of the day.
(b). Geomean diameter and mode diameters as a function of hour of the day

(a)

(b)
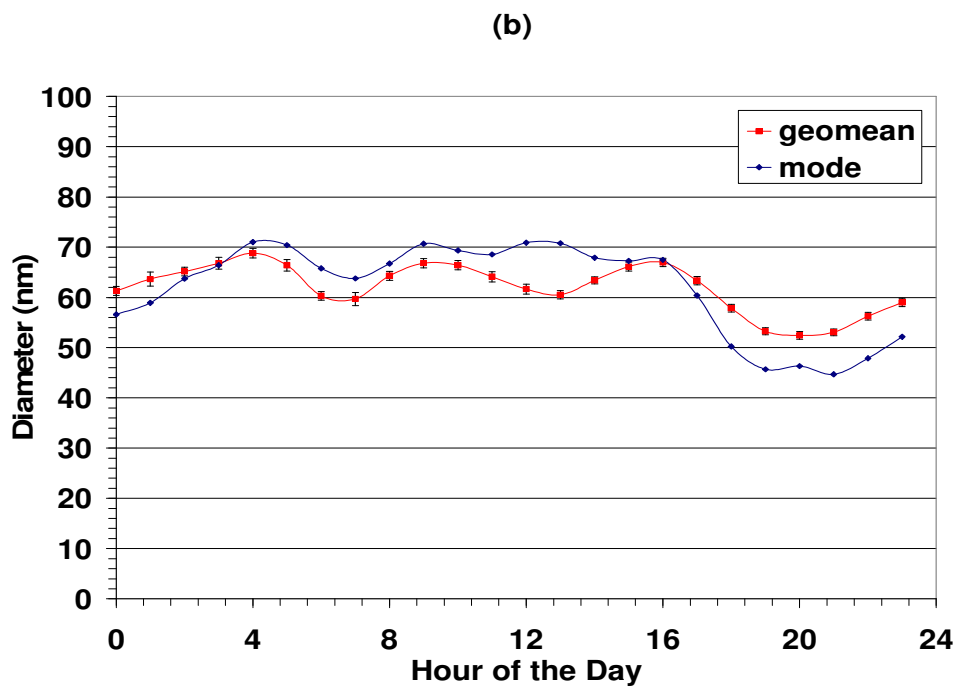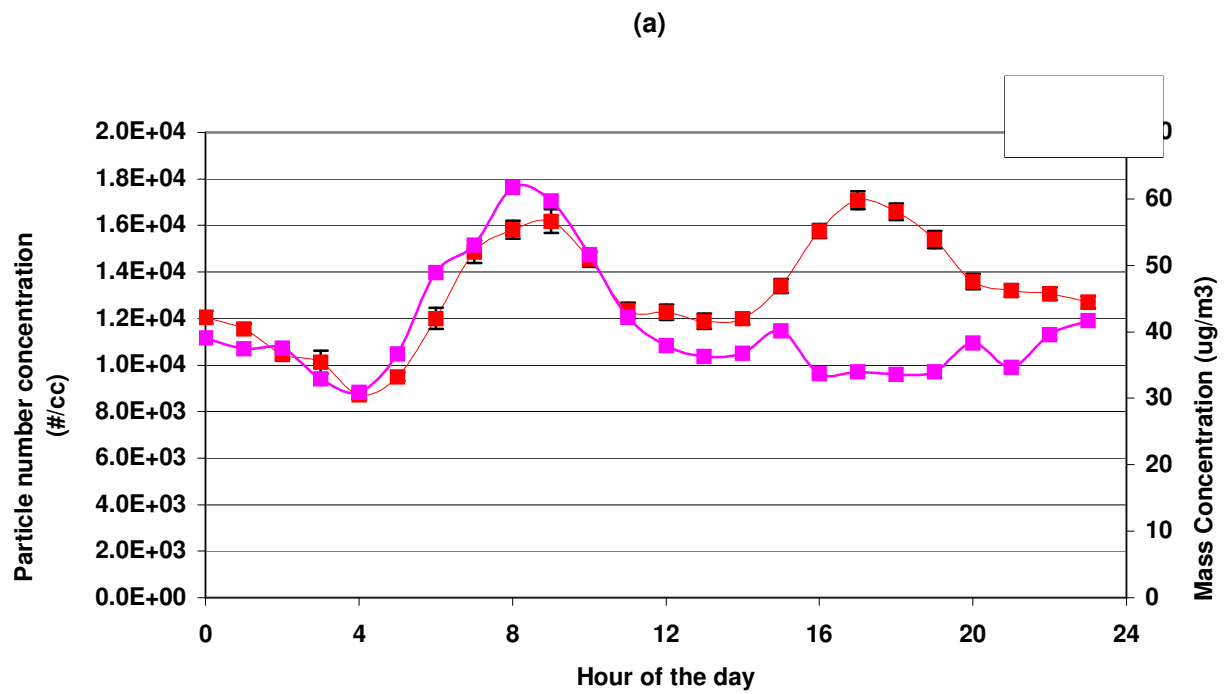
Figure 37. Particulate characteristics in Upland , CA. (Aug 2003).
(a). PN0.5 and PM_{10} mass concentration as a function of hour of the day.
(b). Geomean diameter and mode diameters as a function of hour of the day

(a)

(b)
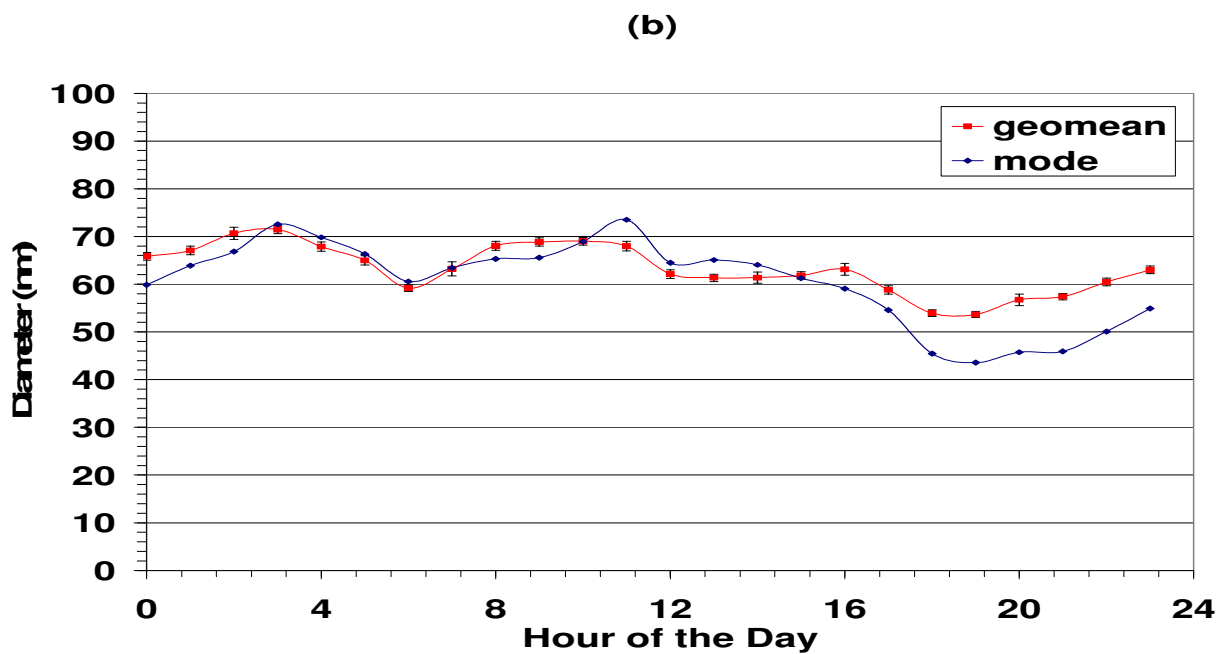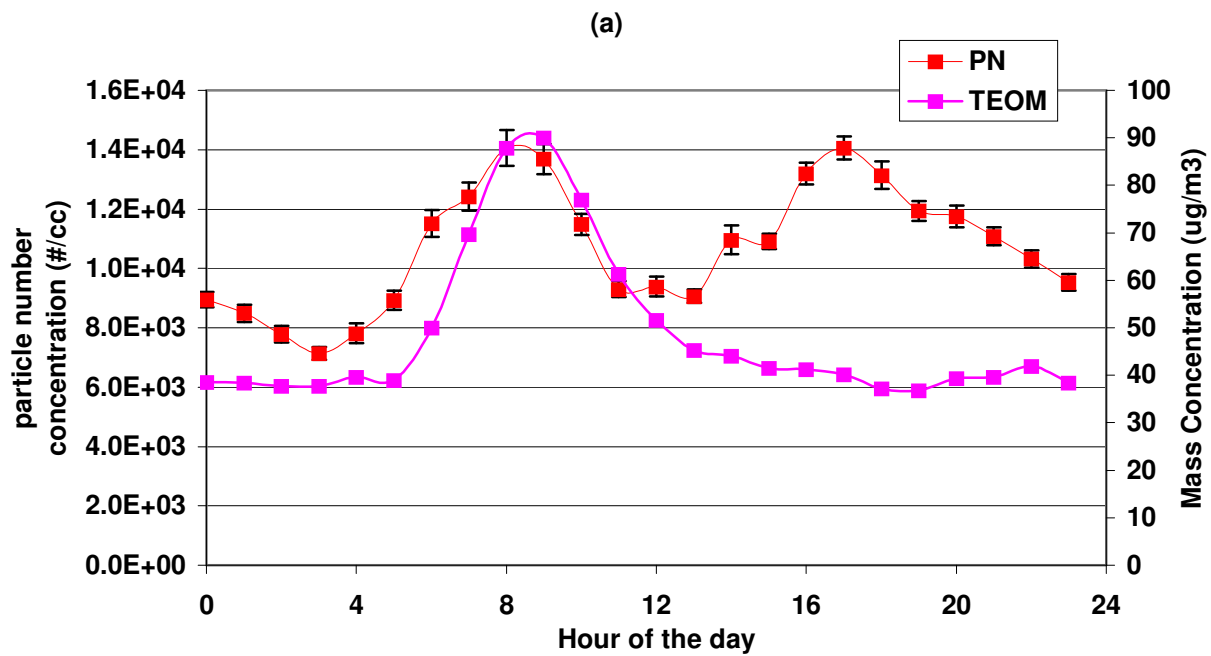
Figure 38. Particulate characteristics in Upland, CA. (Sep 2003).
(a). PN0.5 and PM_{10} mass concentration as a function of hour of the day.
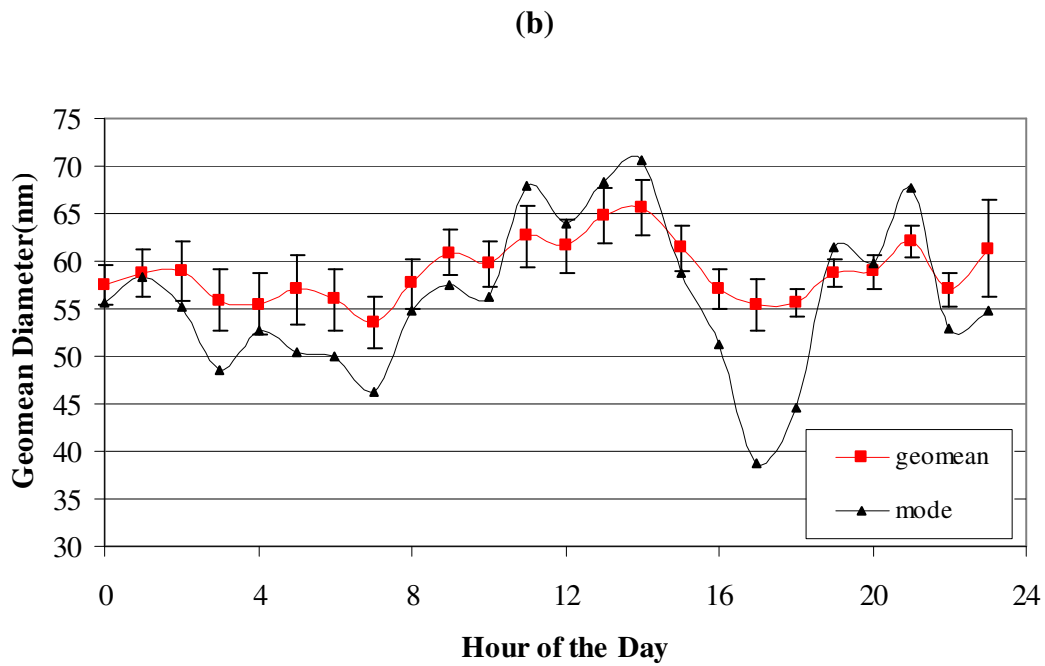(b). Geomean diameter and mode diameters as a function of hour of the day

(a)

(b)
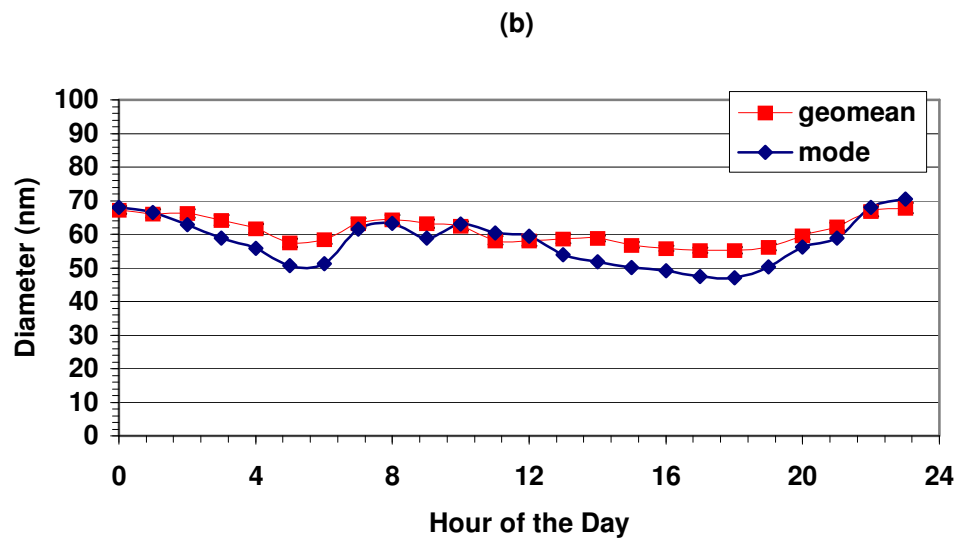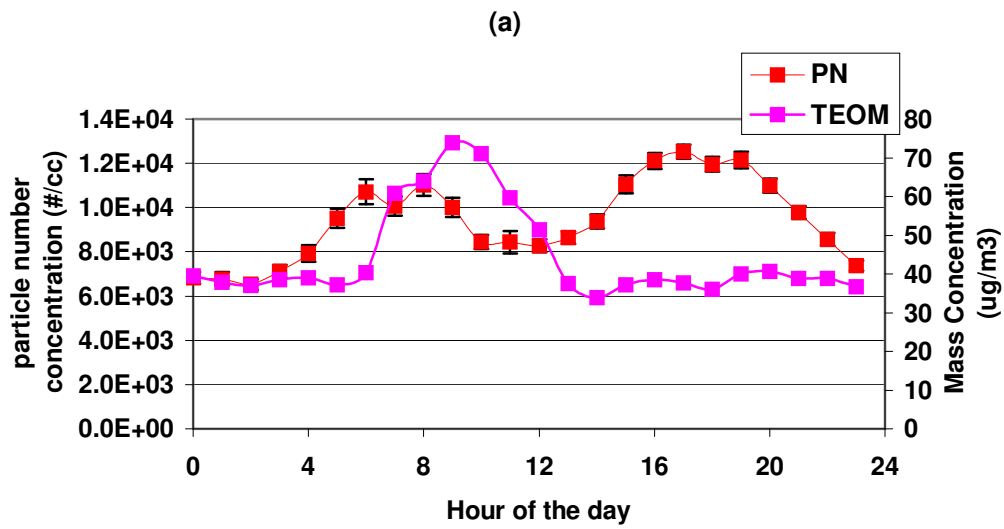
Figure 39. Particulate characteristics in Upland, CA. (Oct1-22,29-31 2003)Non-fire period.
(a). PN0.5 and PM_{10} mass concentration as a function of hour of the day.
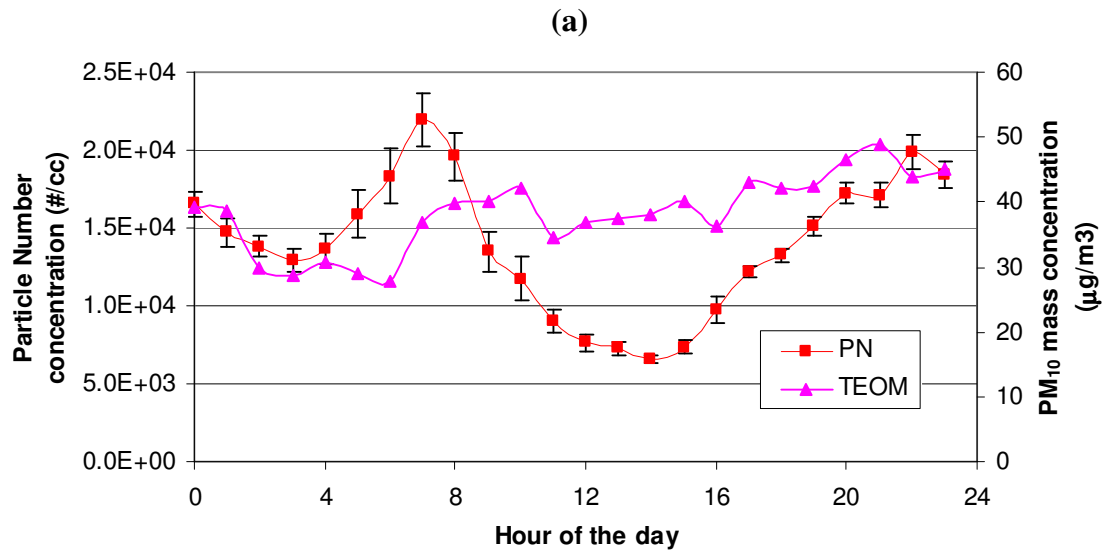(b). Geomean diameter and mode diameters as a function of hour of the day
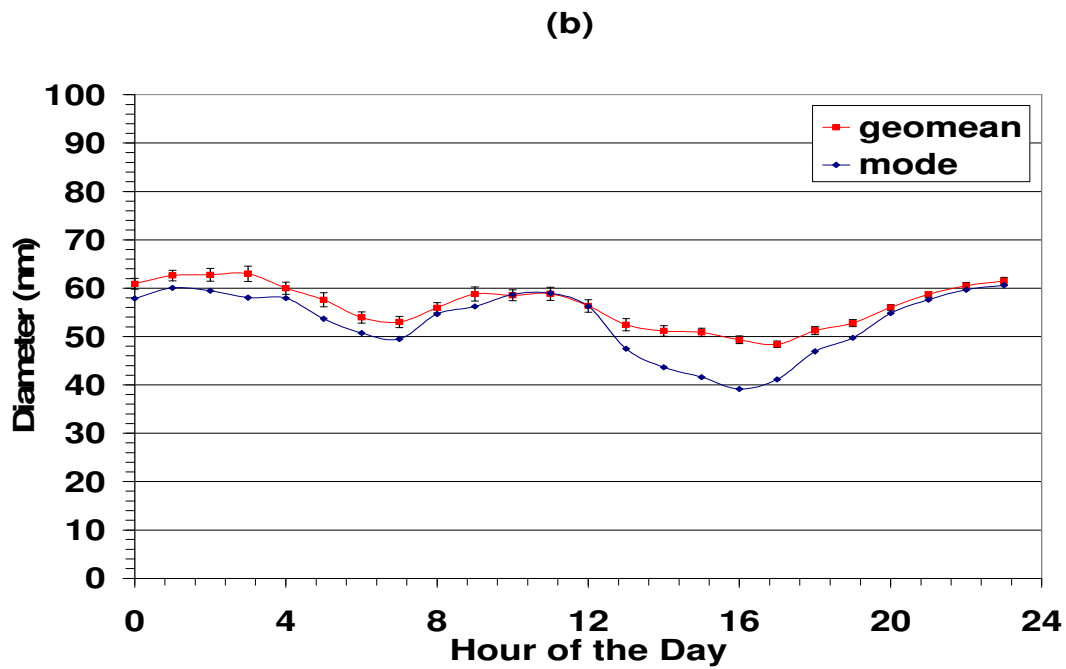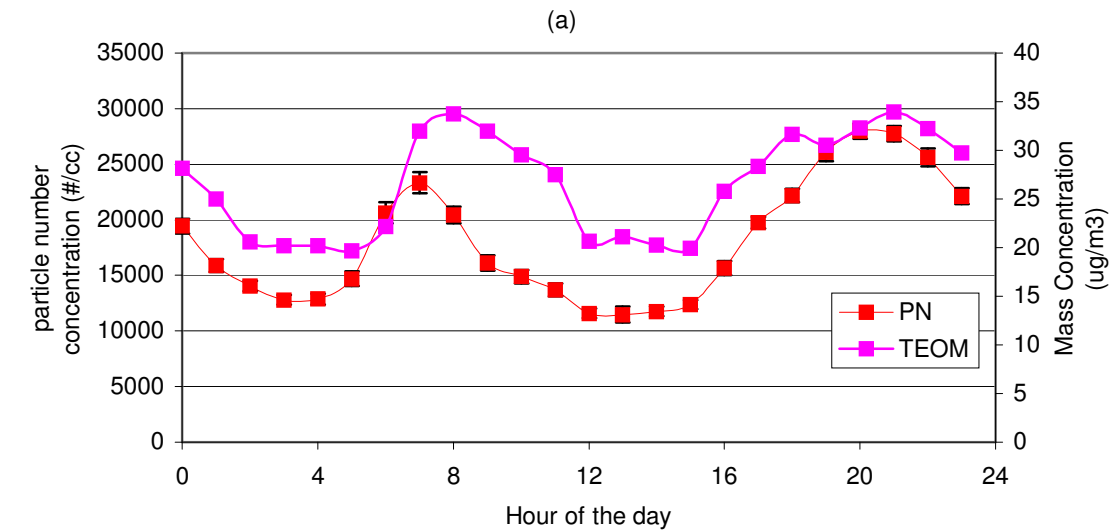
Figure 40. Particulate characteristics in Upland, CA. (Nov 2003).
(a). PN0.5 and PM$_{10}$ mass concentration as a function of hour of the day.
 (b). Geomean diameter and mode diameters as a function of hour of the day

(a)

(b)
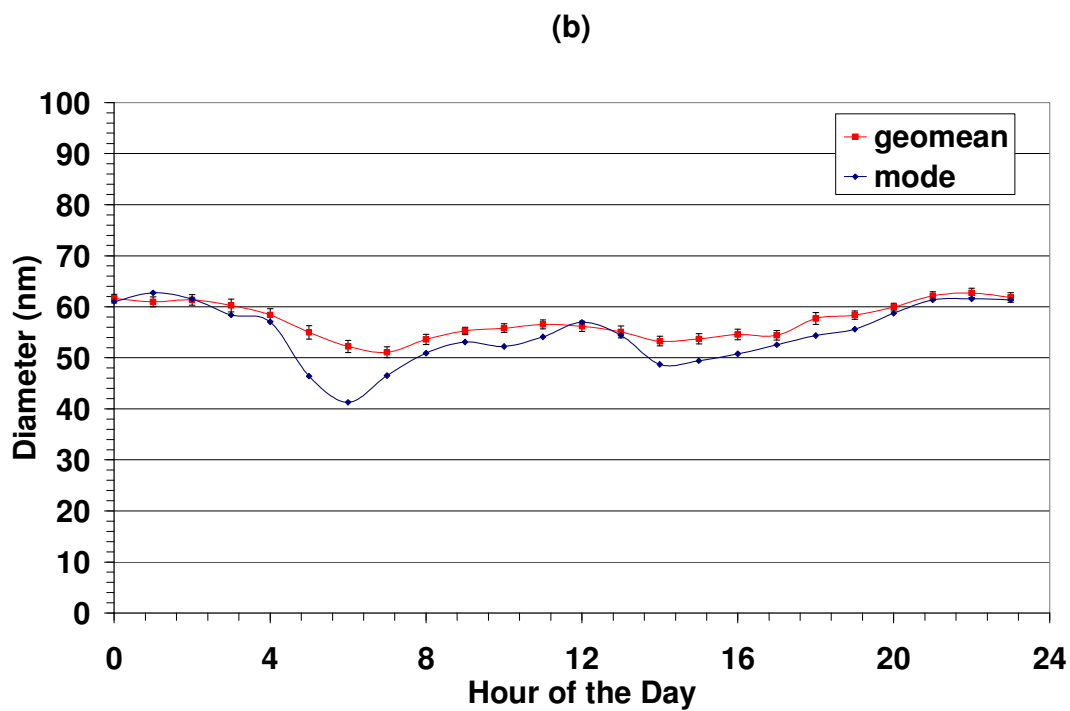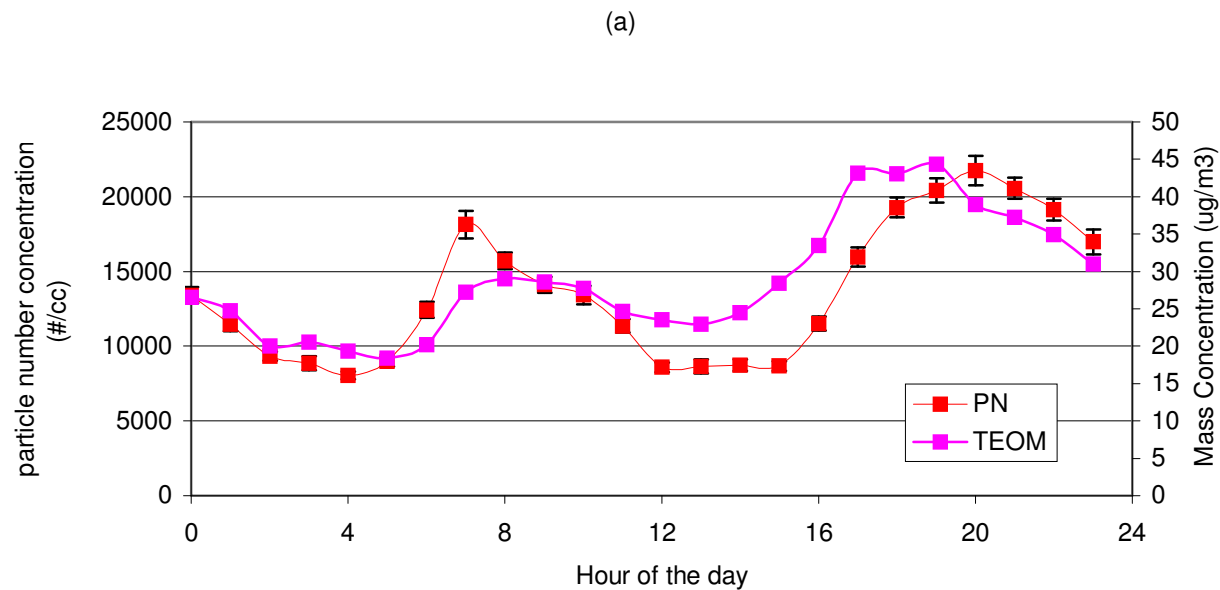
Figure 41. Particulate characteristics in Upland, CA. (Dec 2003).
(a). PN0.5 and PM$_{10}$ mass concentration as a function of hour of the day.
(b) Geomean diameter and mode diameter as a function of hour of the day.

(a)

(b)
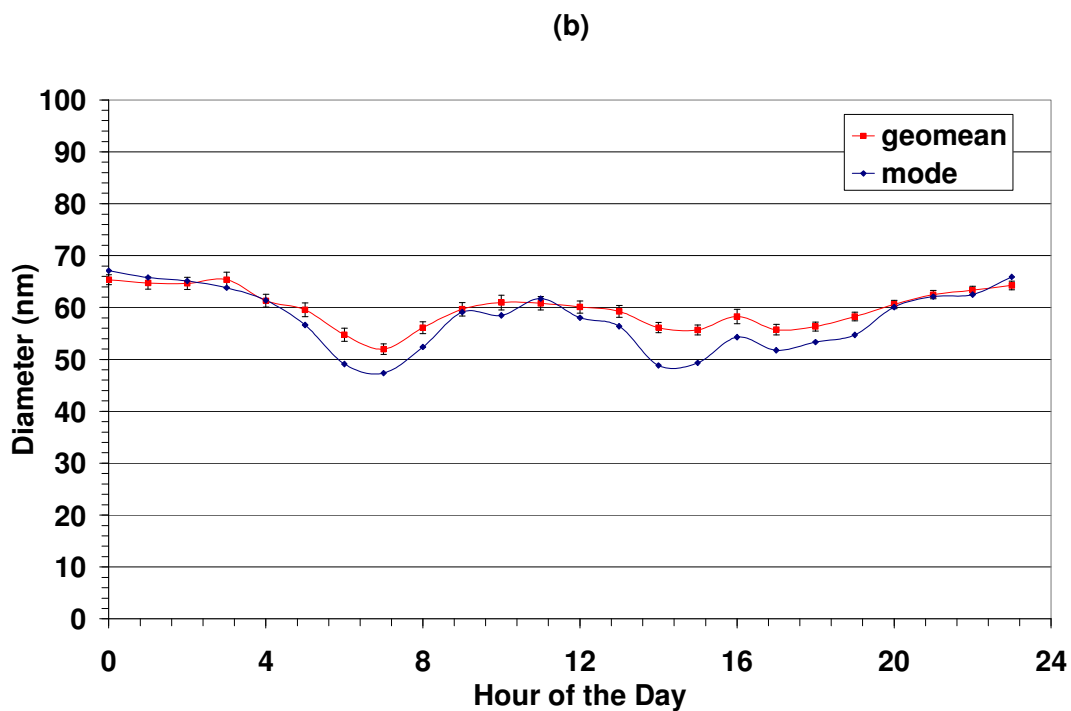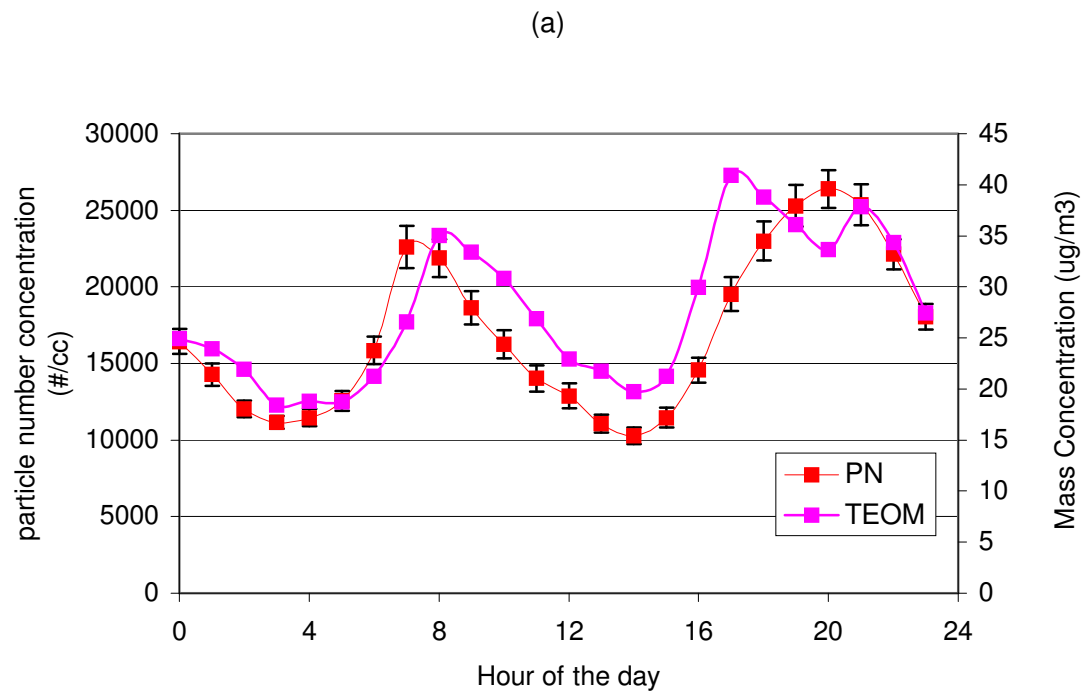
Figure 42. Particulate characteristics in Upland, CA. (Jan, 2004)
(a). PN0.5 and PM_{10} mass concentration as a function of hour of the day.
(b). Geomean diameter and mode diameters as a function of hour of the day
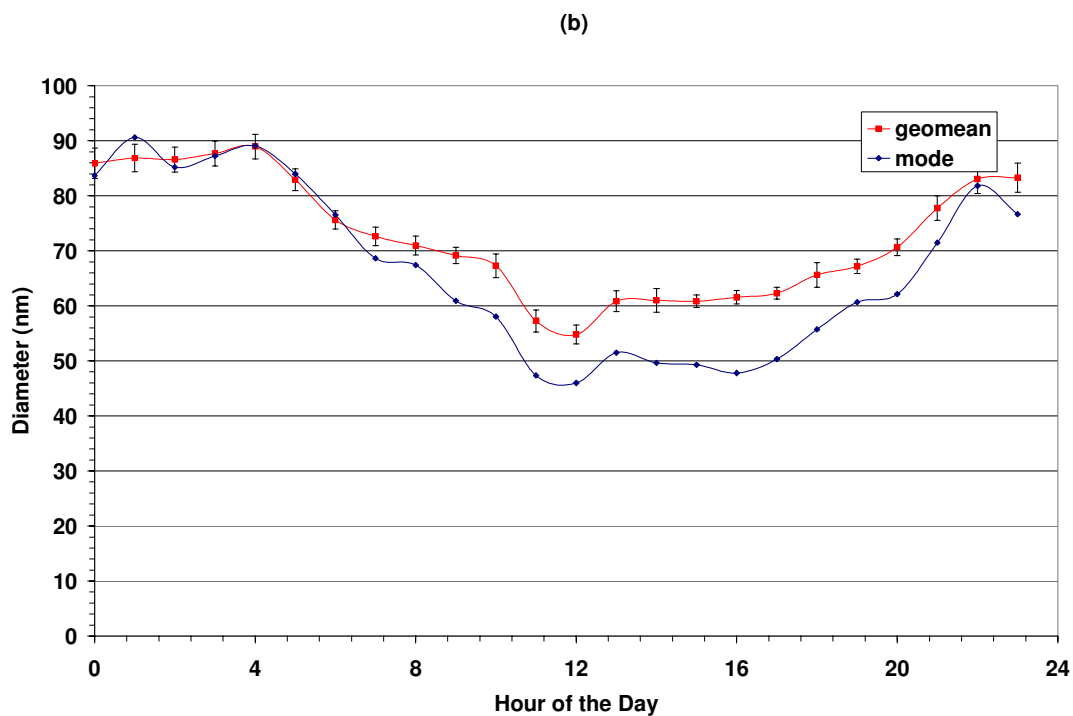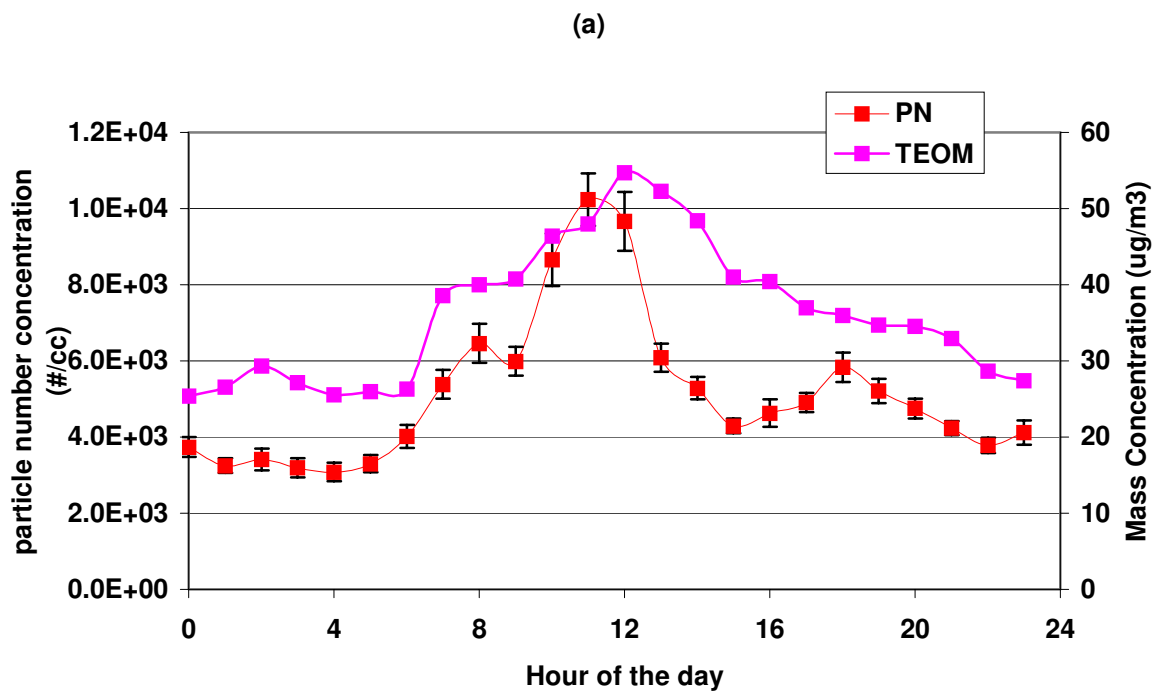
Figure 43. Particulate characteristics in Santa Maria, CA. (Oct 2003).
(a). PN0.5 and PM$_{10}$ mass concentration as a function of hour of the day.
(b). Geomean diameter and mode diameters as a function of hour of the day
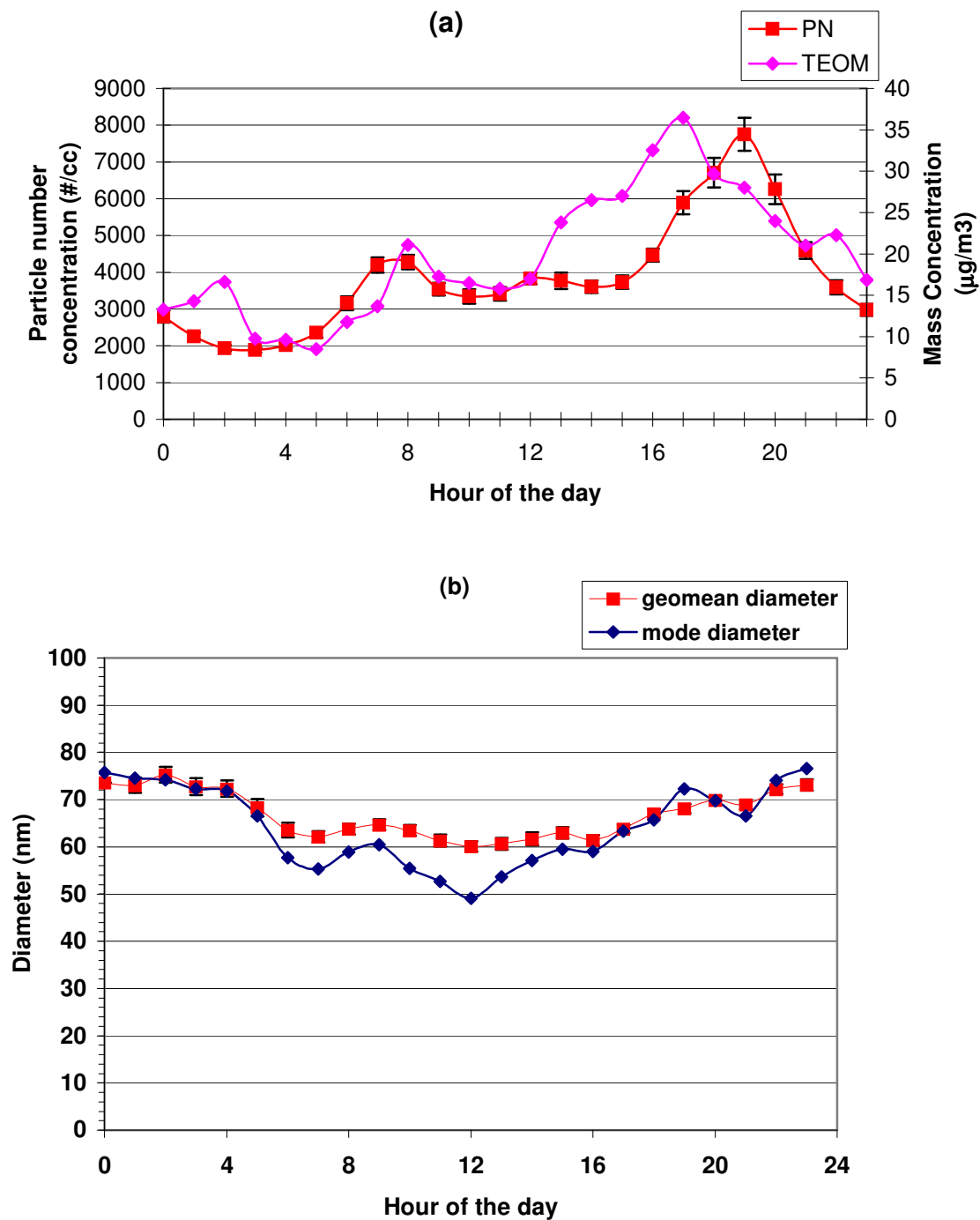
Figure 44. Particulate characteristics in Santa Maria, CA. (Nov 2003).
(a). PN0.5 and PM_{10} mass concentration as a function of hour of the day.
(b). Geomean diameter and mode diameters as a function of hour of the day
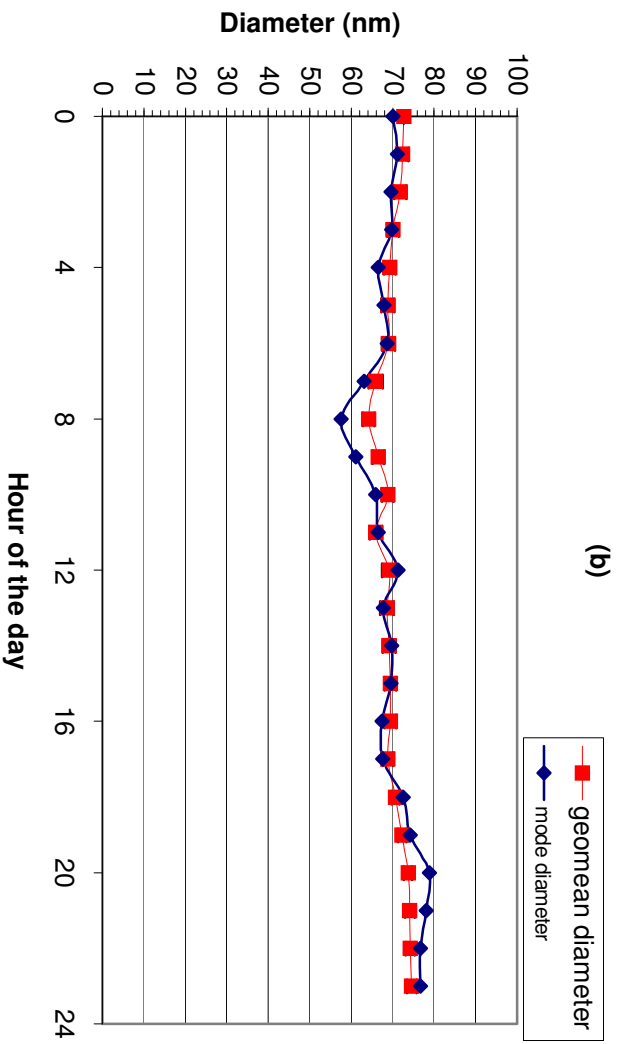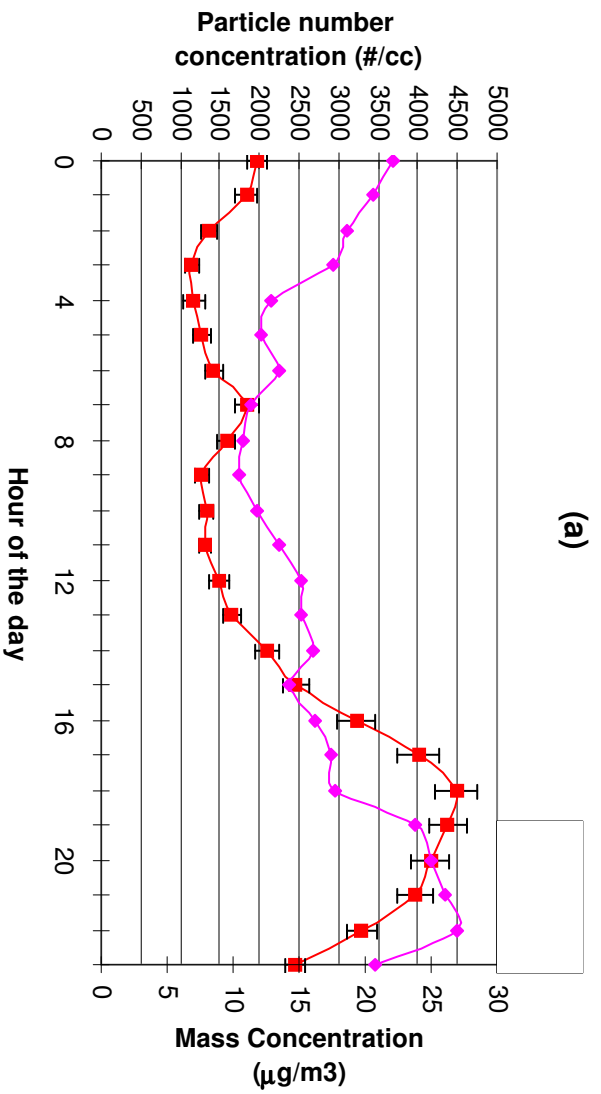
Figure 45. Particulate characteristics in Alpine, CA. (Dec 2003).
(a). PN0.5 and PM$_{10}$ mass concentration as a function of hour of the day.
(b). Geomean diameter and mode diameters as a function of hour of the day
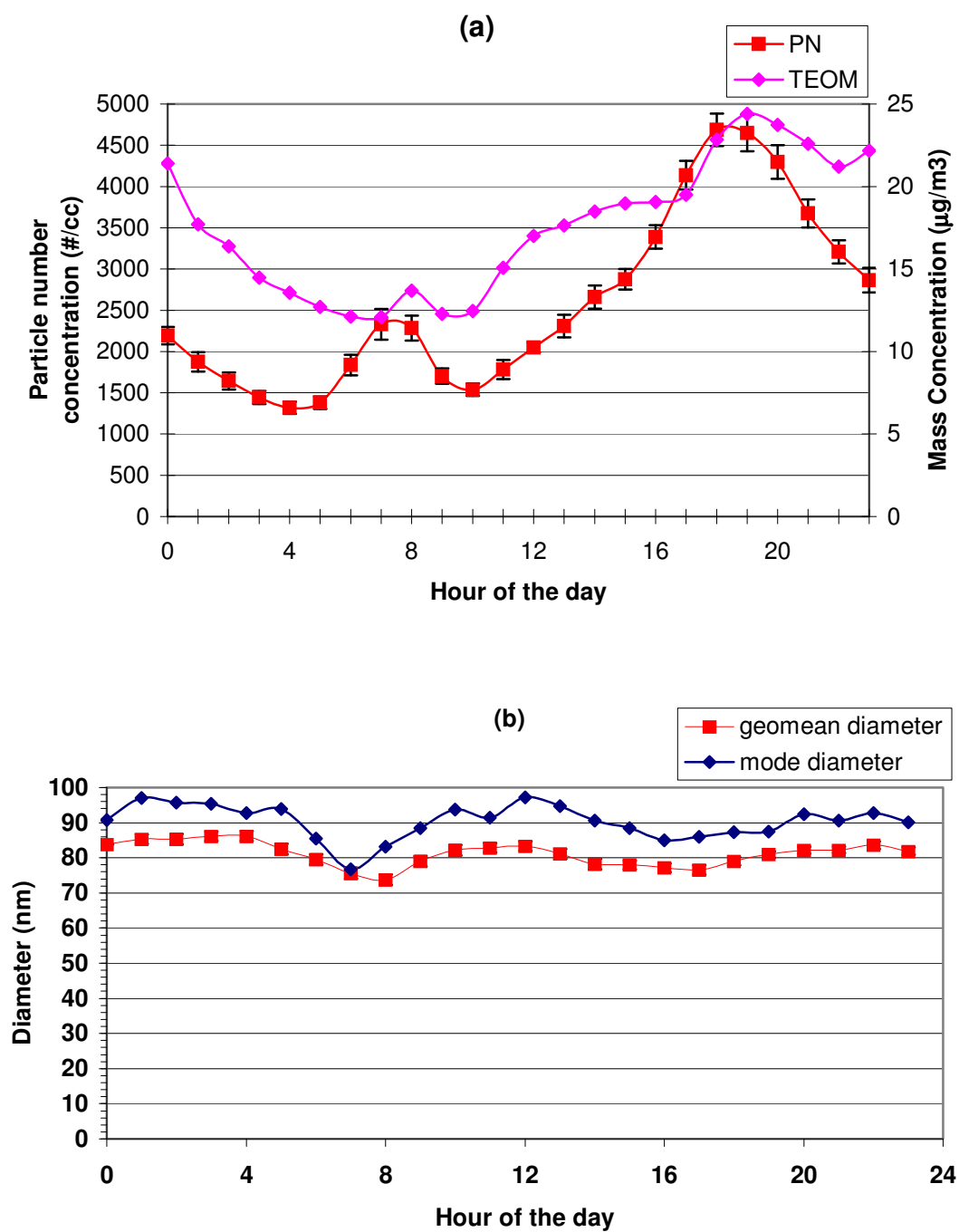
Figure 46.. Particulate characteristics in Alpine, CA. (Jan 2004).
(a). PN0.5 and PM$_{10}$ mass concentration as a function of hour of the day.
(b). Geomean diameter and mode diameters as a function of hour of the day

(a)

(b)
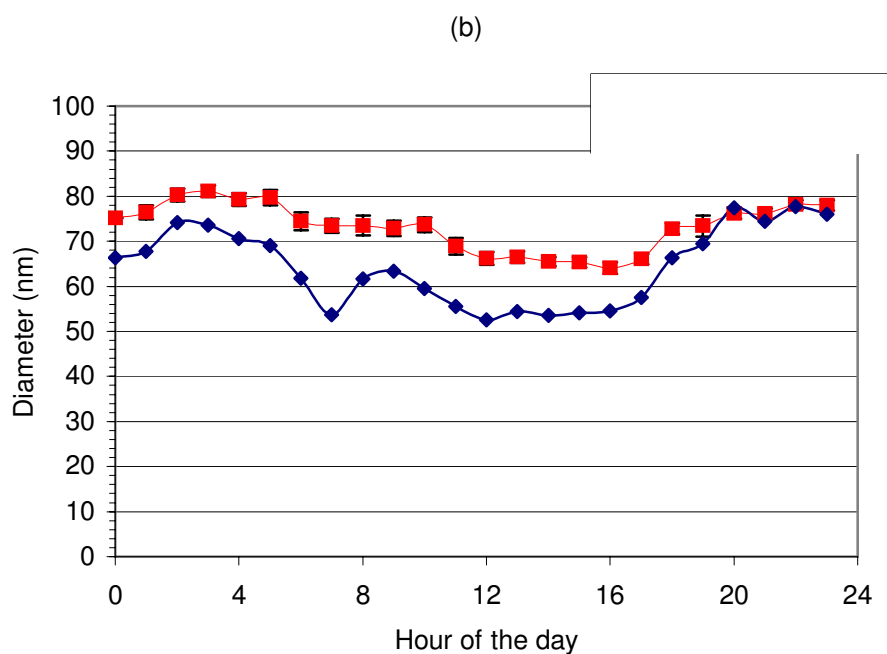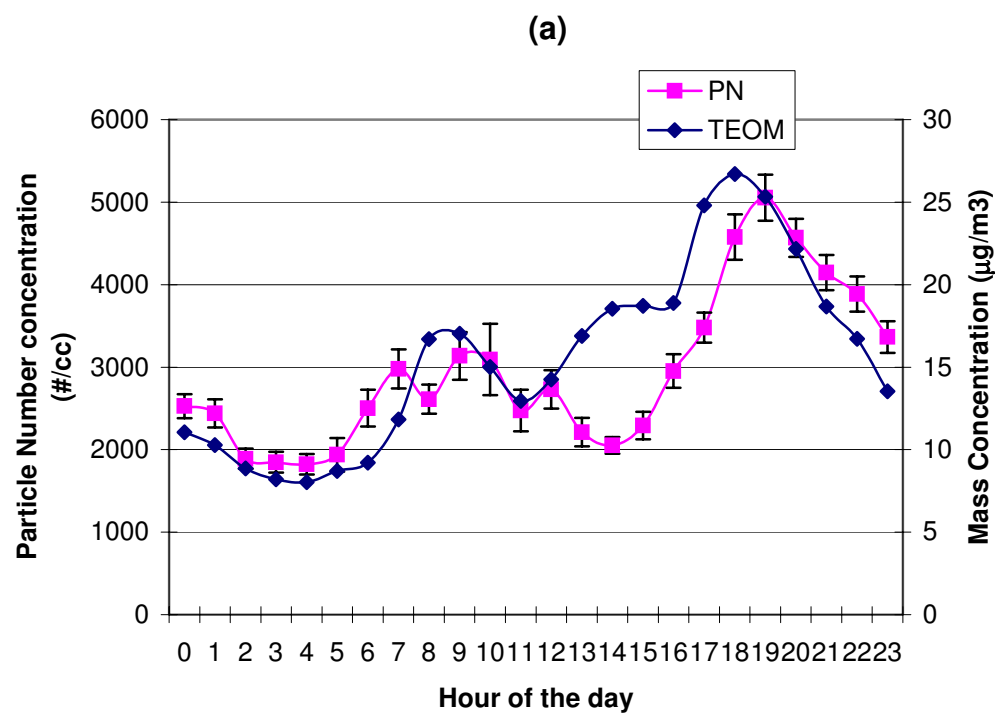
Figure 47. Particulate characteristics in Santa Maria, CA. (Feb, 2004).
(a). PN0.5 and PM_{10} mass concentration as a function of hour of the day.
(b). Geomean diameter and mode diameters as a function of hour of the day
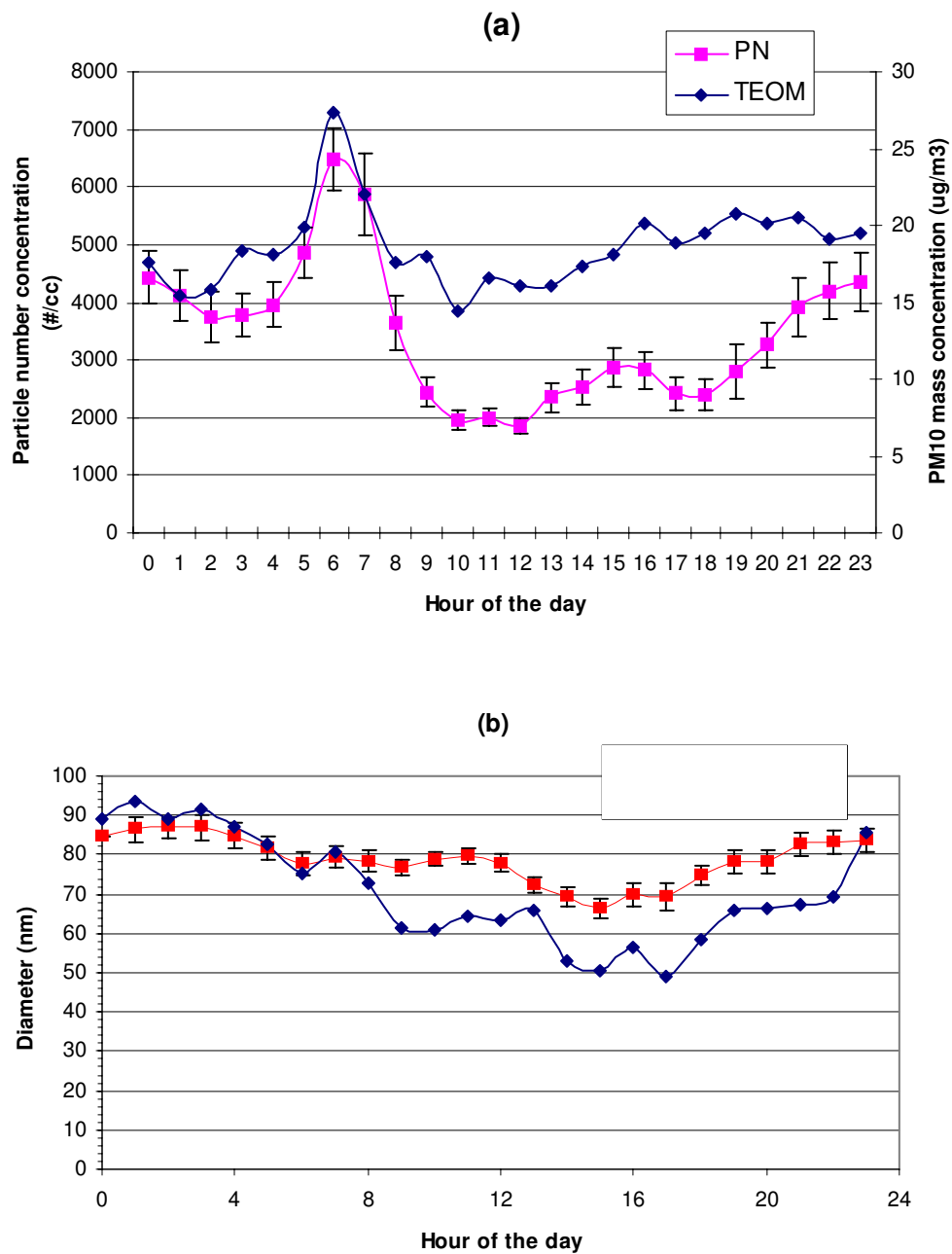
(a)

(b)
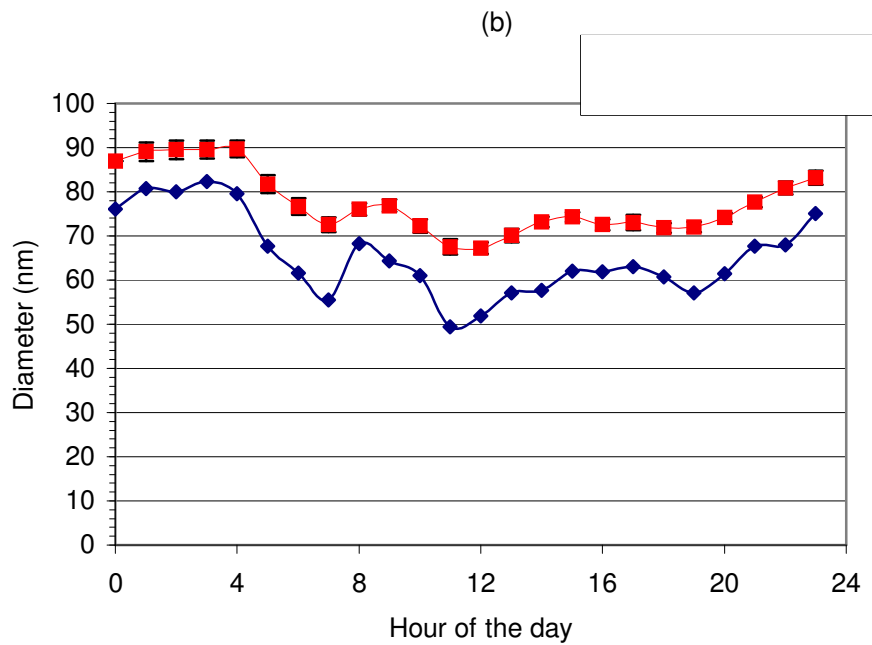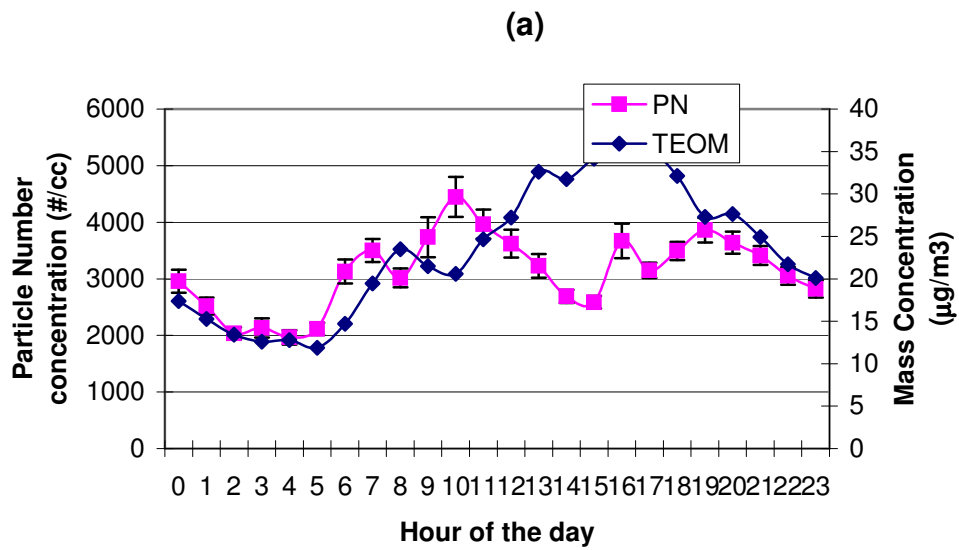
Figure 48. Particulate characteristics in Santa Maria , CA. (Mar 2004).
(a). PN0.5 and PM_{10} mass concentration as a function of hour of the day.
(b). Geomean diameter and mode diameters as a function of hour of the day

(a)

(b)
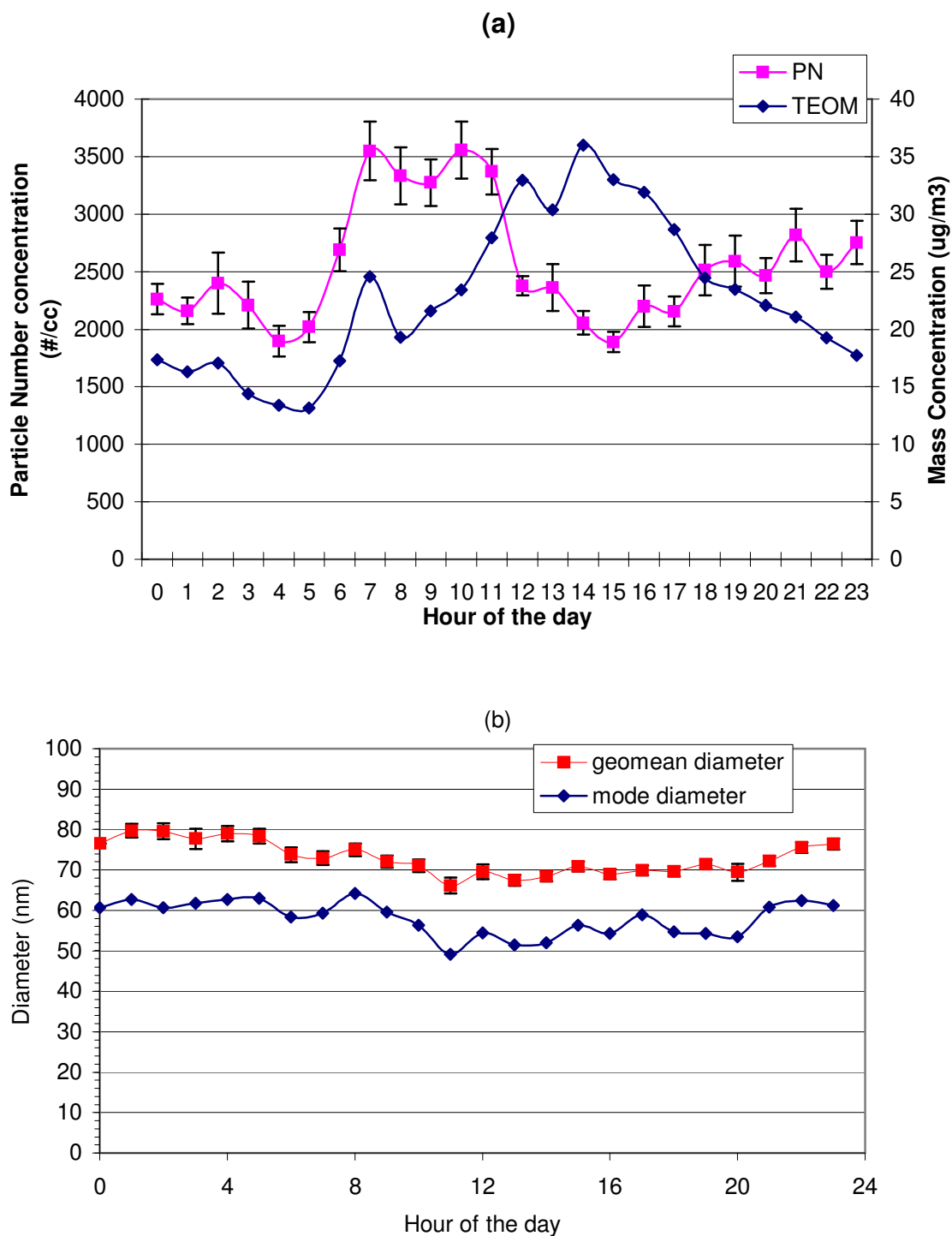
Figure 49. Particulate characteristics in Santa Maria, CA. (Apr 2004).
(a). PN0.5 and PM$_{10}$ mass concentration as a function of hour of the day.
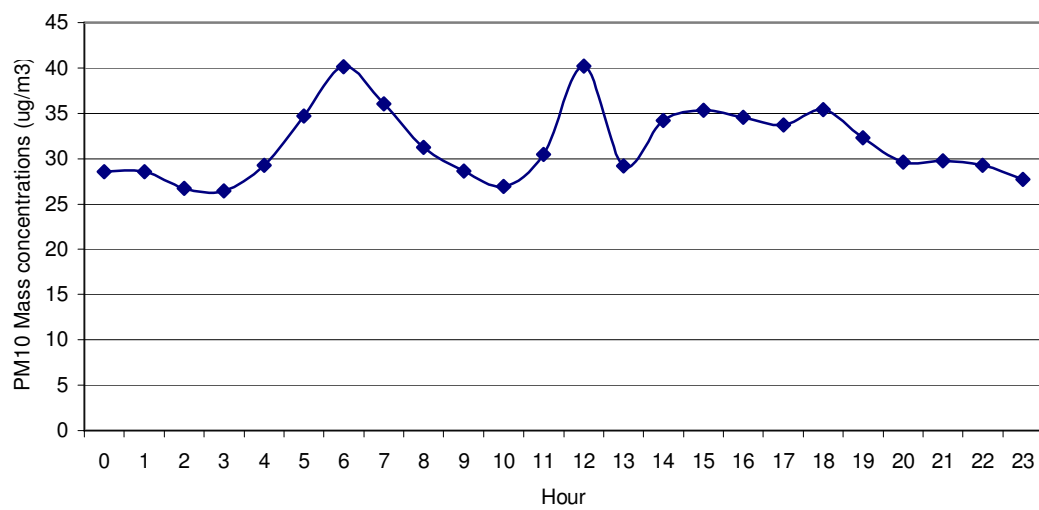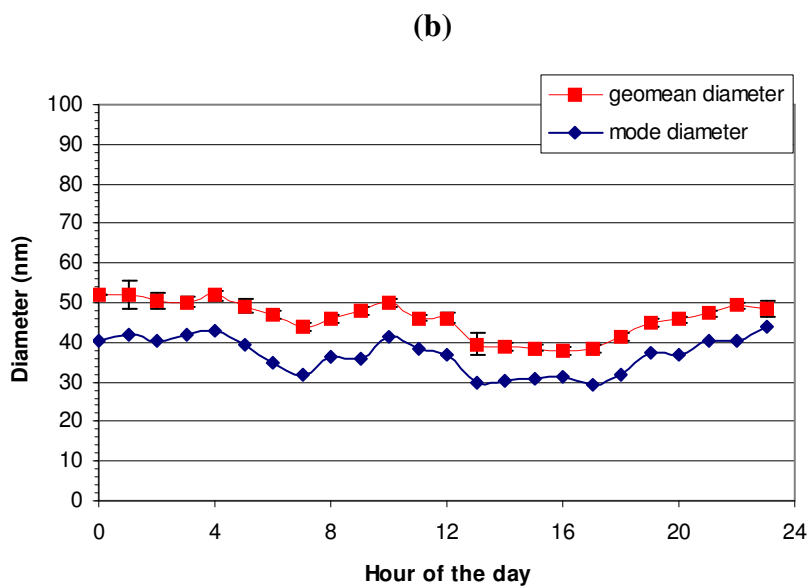(b). Geomean diameter and mode diameters as a function of hour of the day
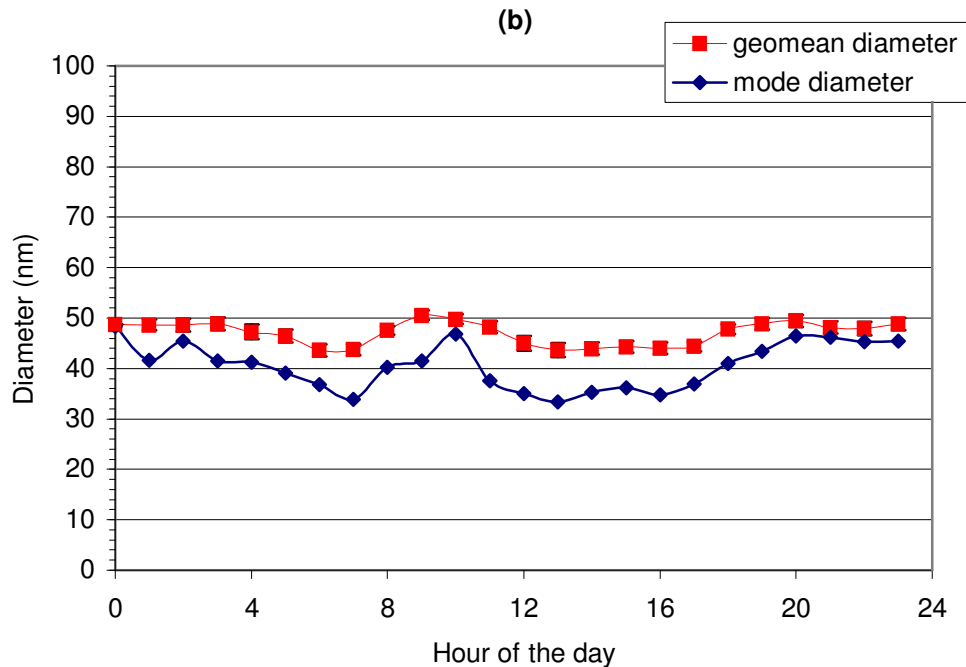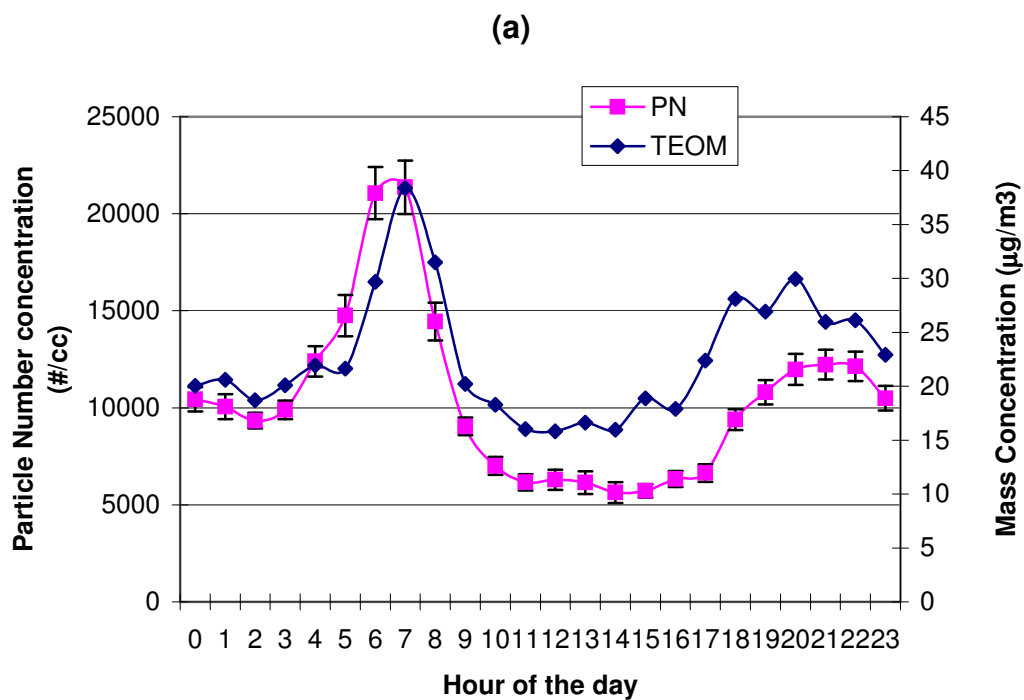
Figure 50. Particulate characteristics in Lancaster , CA. (Mar 2004).
(a). PN0.5 and PM_{10} mass concentration as a function of hour of the day.
(b). Geomean diameter and mode diameters as a function of hour of the day
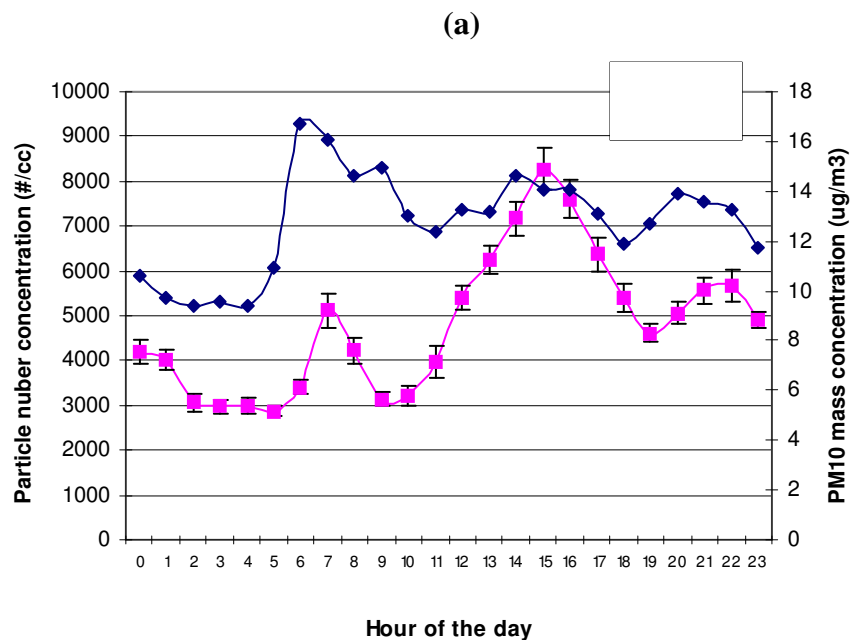
(a)

(b)
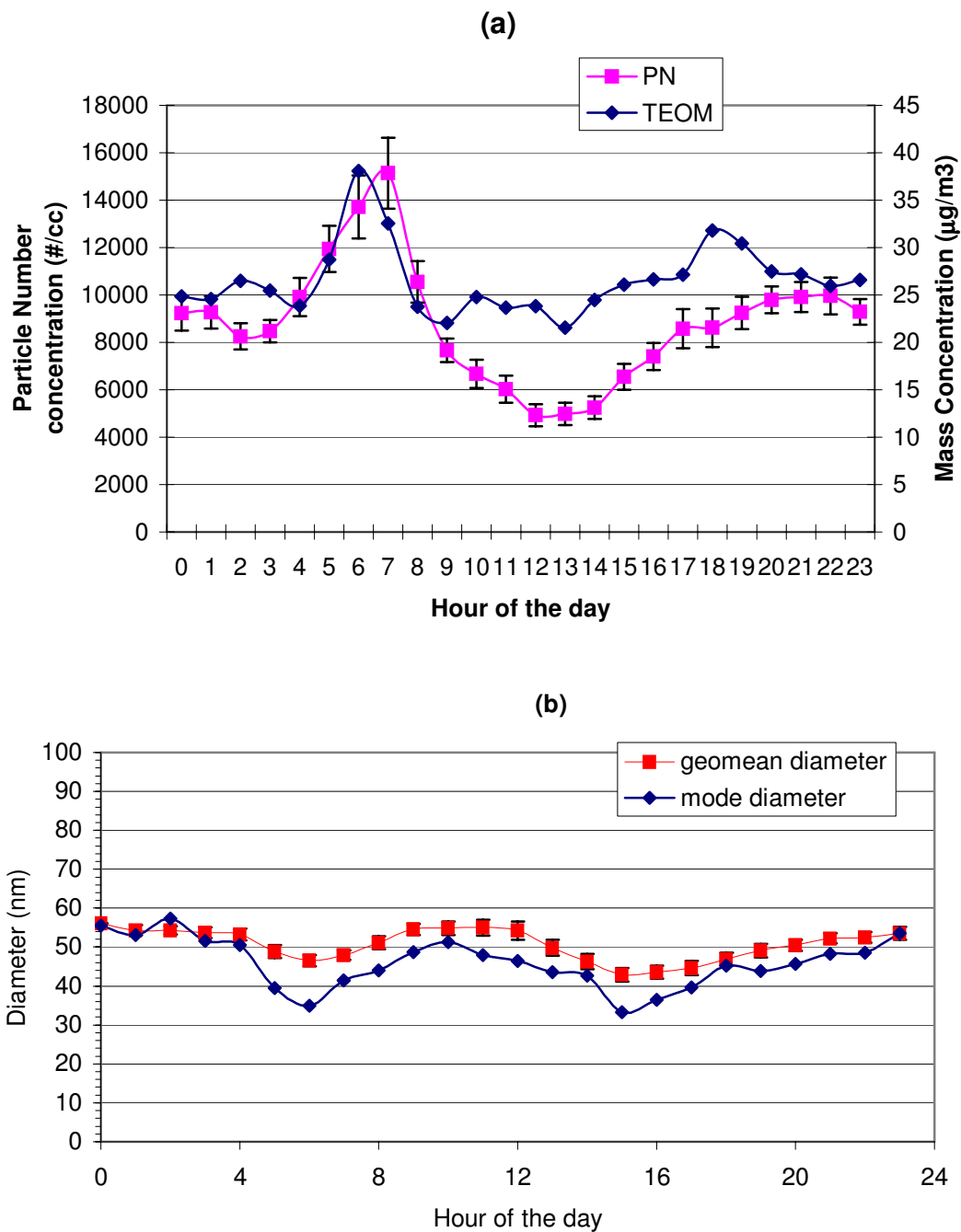
Figure 51. Particulate characteristics in Lancaster, CA. (Apr, 2004)
(a). PN0.5 and PM_{10} mass concentration as a function of hour of the day.
(b). Geomean diameter and mode diameters as a function of hour of the day

(a)

(b)
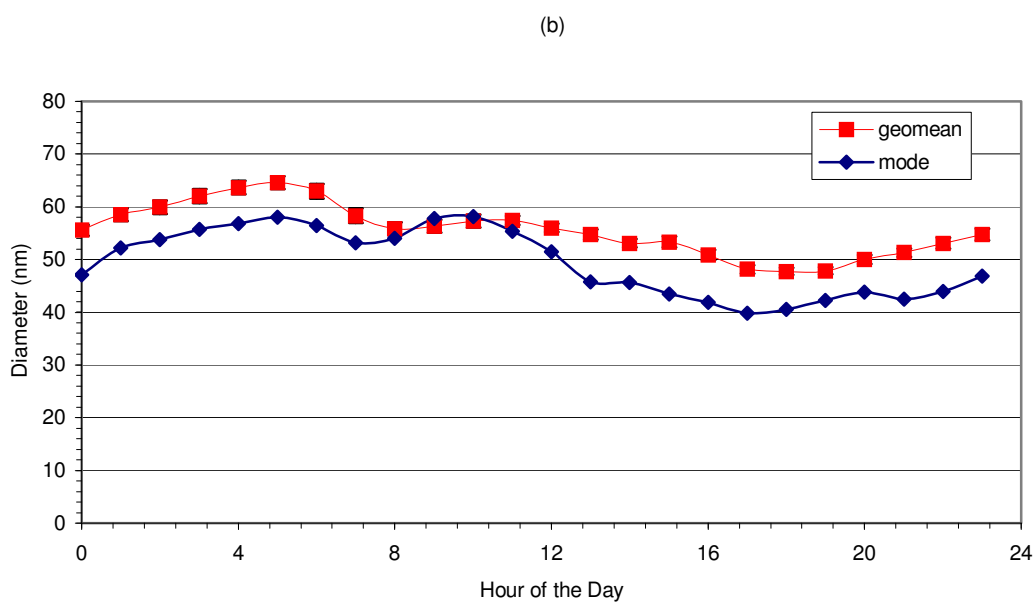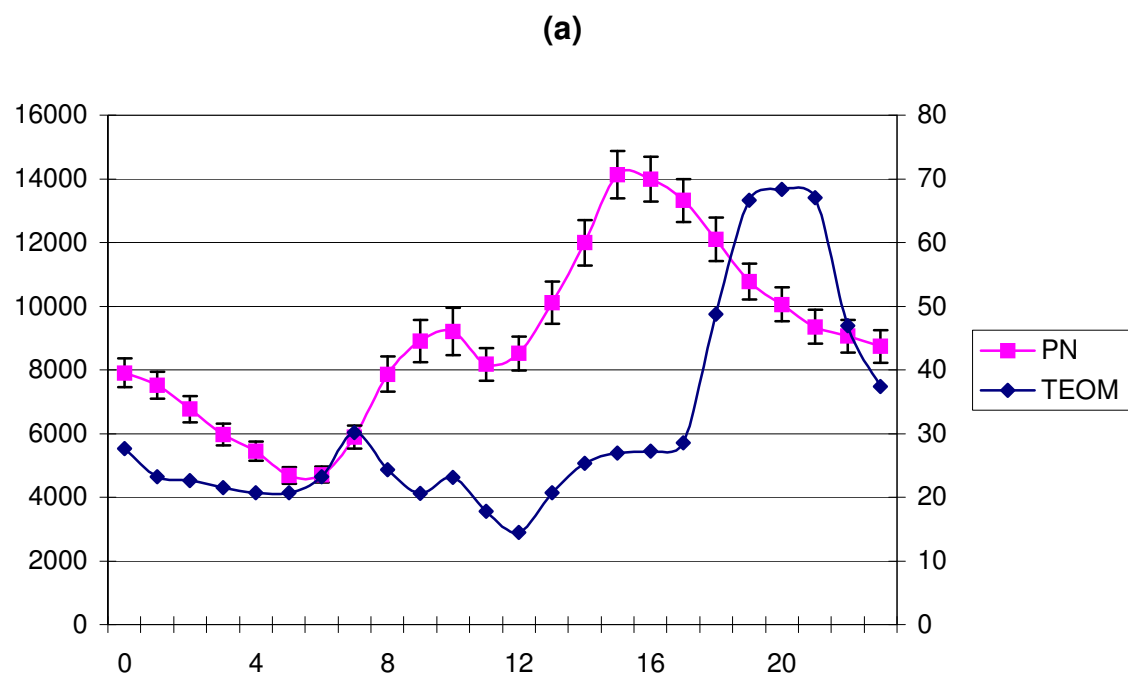
Figure 52. Particulate characteristics in Glendora, CA. (May, 2004).
(a). PN0.5 and PM$_{10}$ mass concentration as a function of hour of the day.
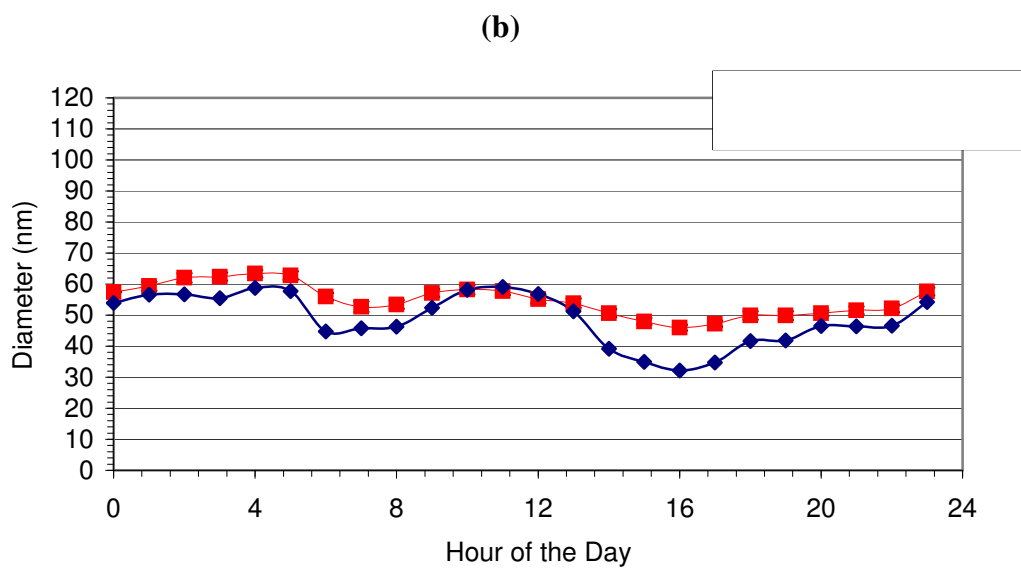(b). Geomean diameter and mode diameters as a function of hour of the day

(a)

(b)
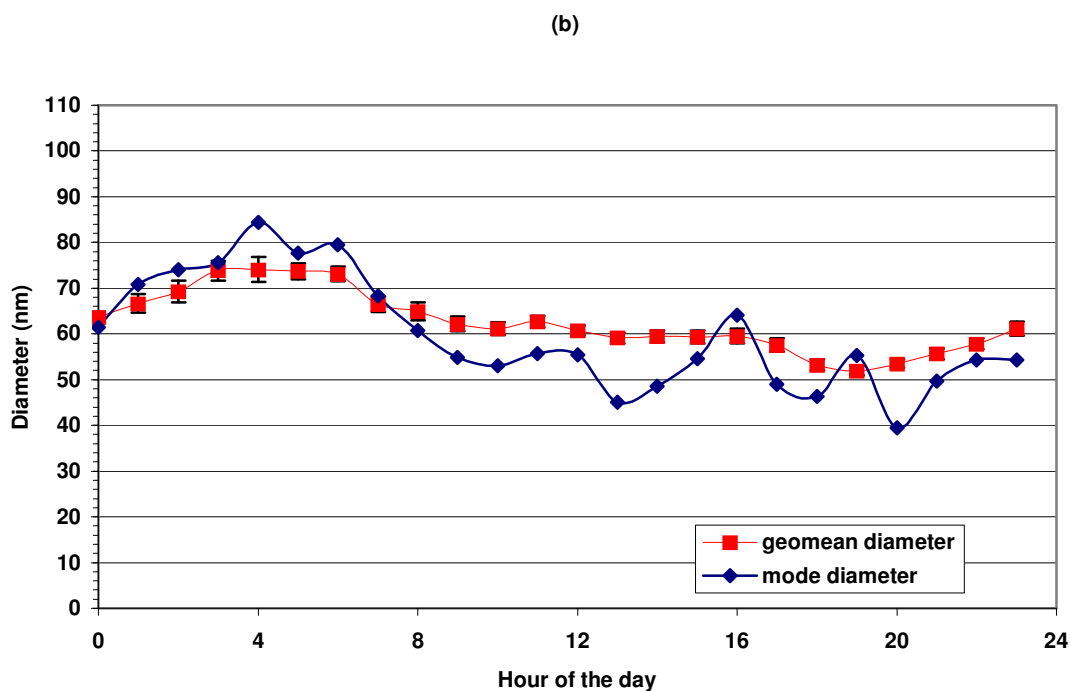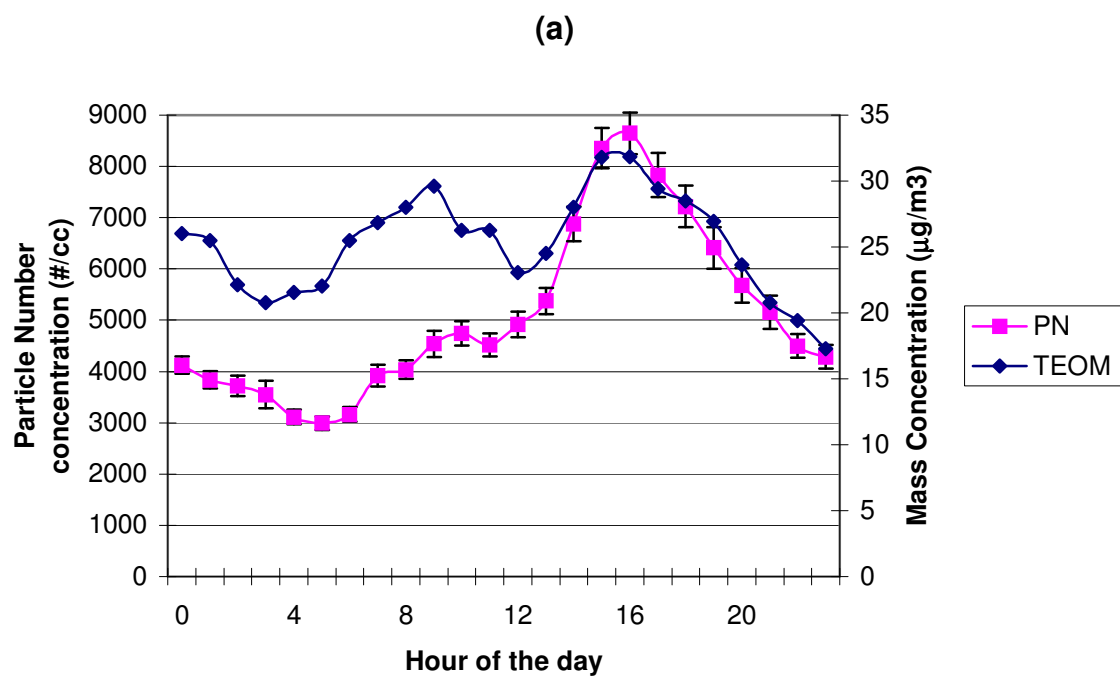
Figure 53. Particulate characteristics in Glendora, CA. (Jun, 2004).
(a). PN0.5 and PM_{10} mass concentration as a function of hour of the day.
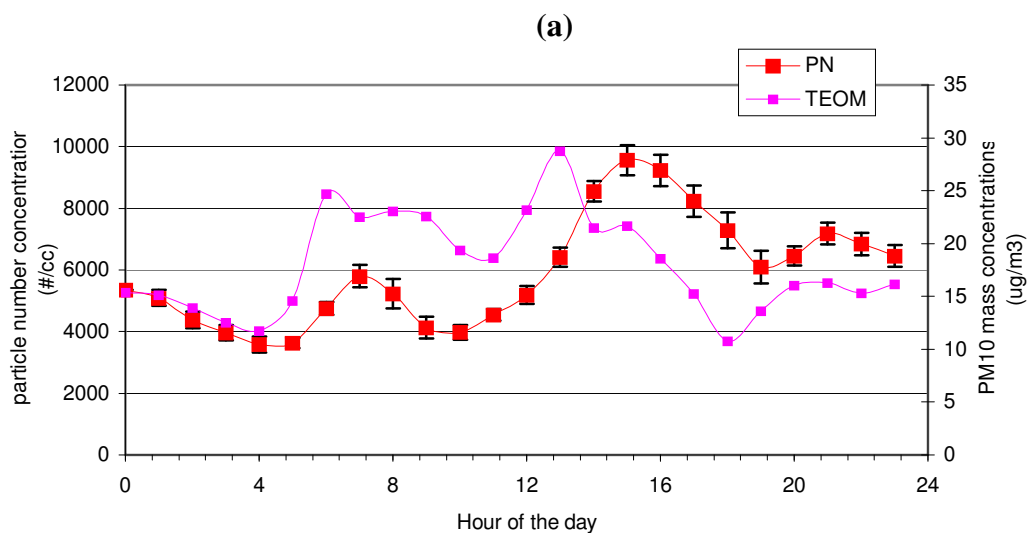(b). Geomean diameter and mode diameters as a function of hour of the day

(a)

(b)
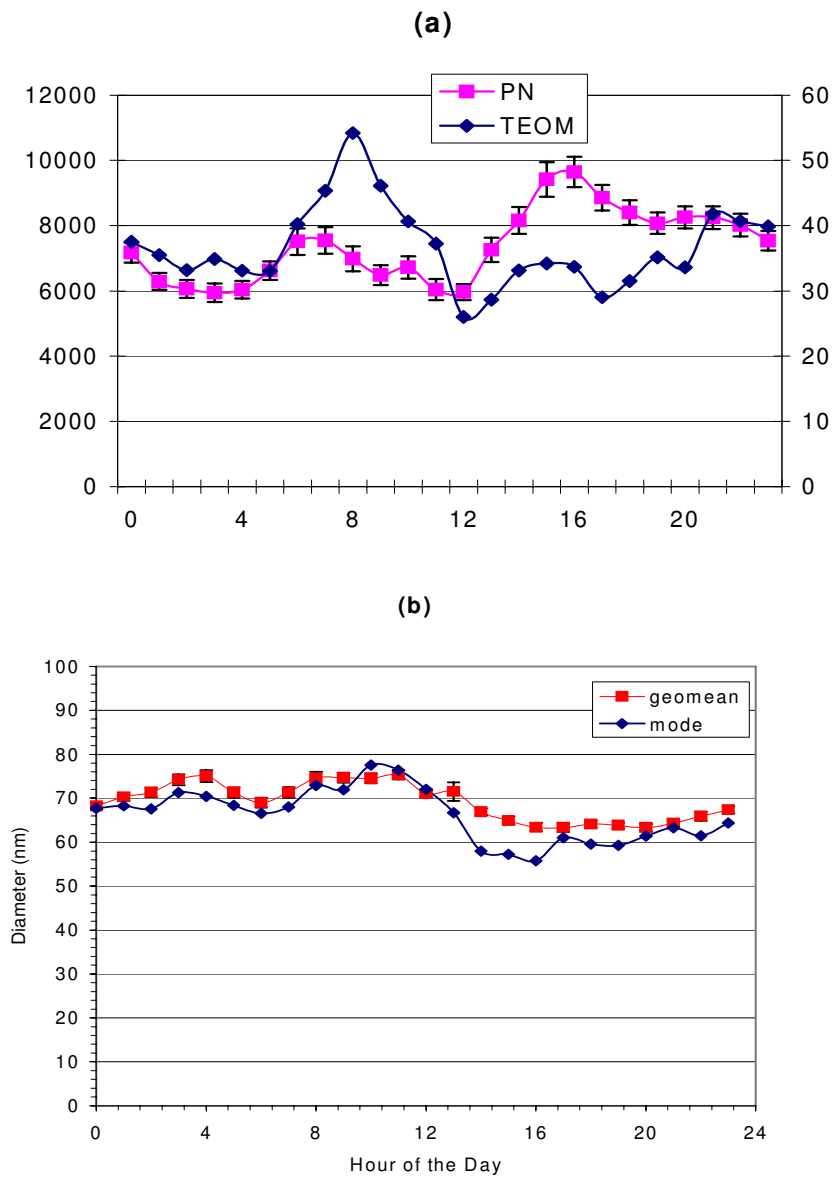
Figure 54. Particulate characteristics in Upland, CA. (May 2004).
(a). PN0.5 and PM_{10} mass concentration as a function of hour of the day.
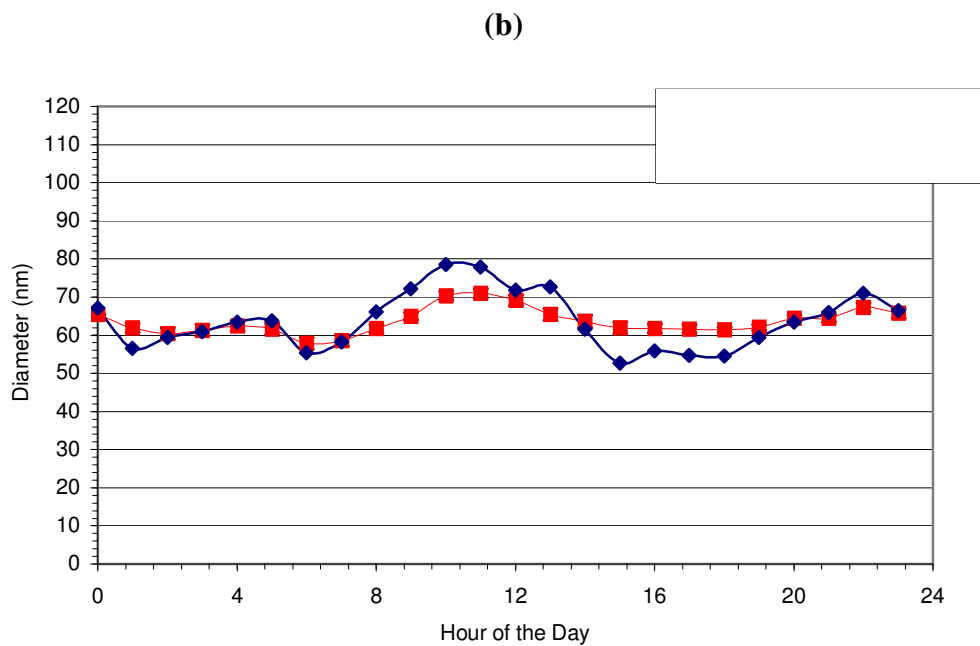(b) Geomean diameter and mode diameter as a function of hour of the day
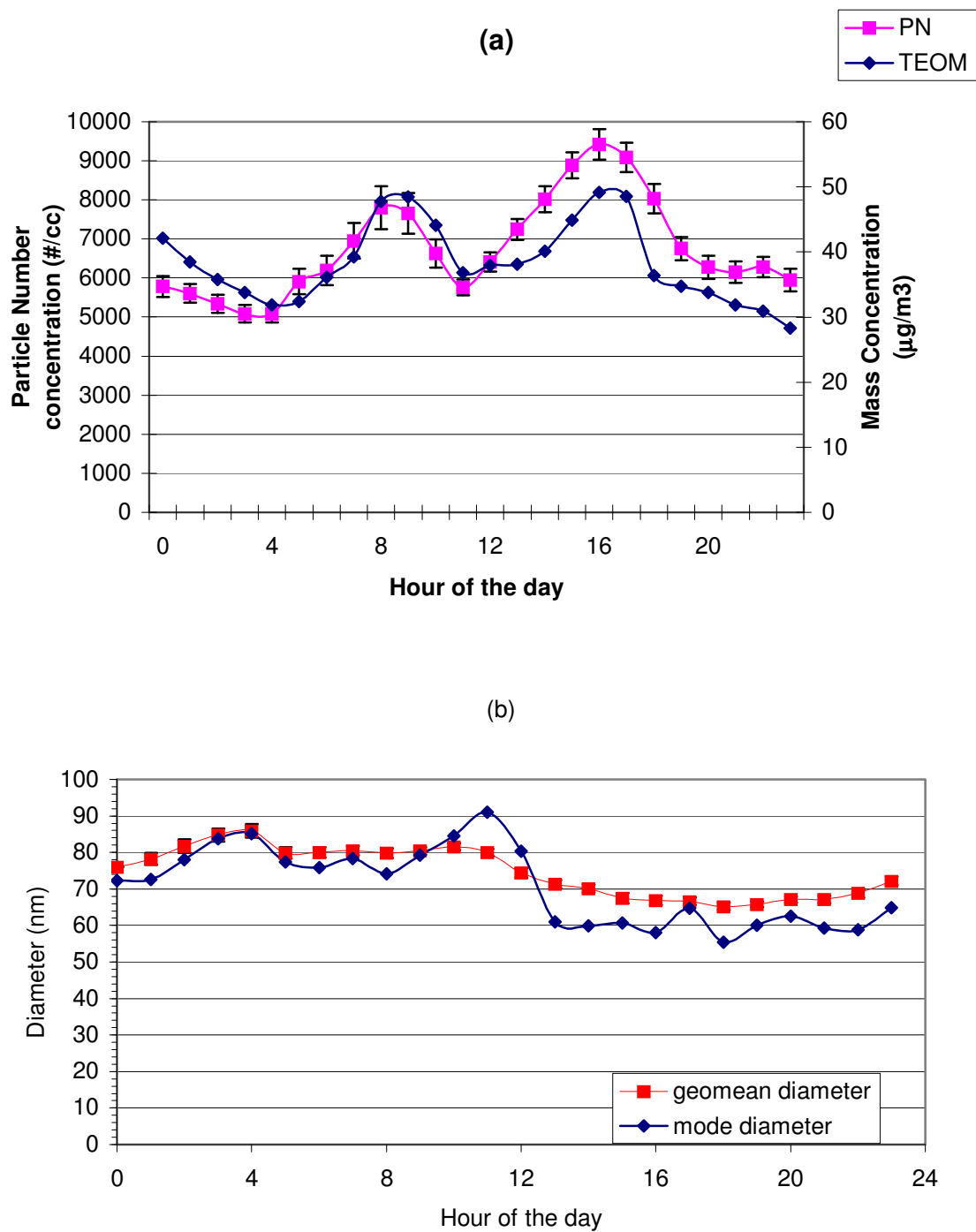
Figure 55. Particulate characteristics in Upland, CA. (Jun 2004).
(a). PN0.5 and PM$_{10}$ mass concentration as a function of hour of the day.
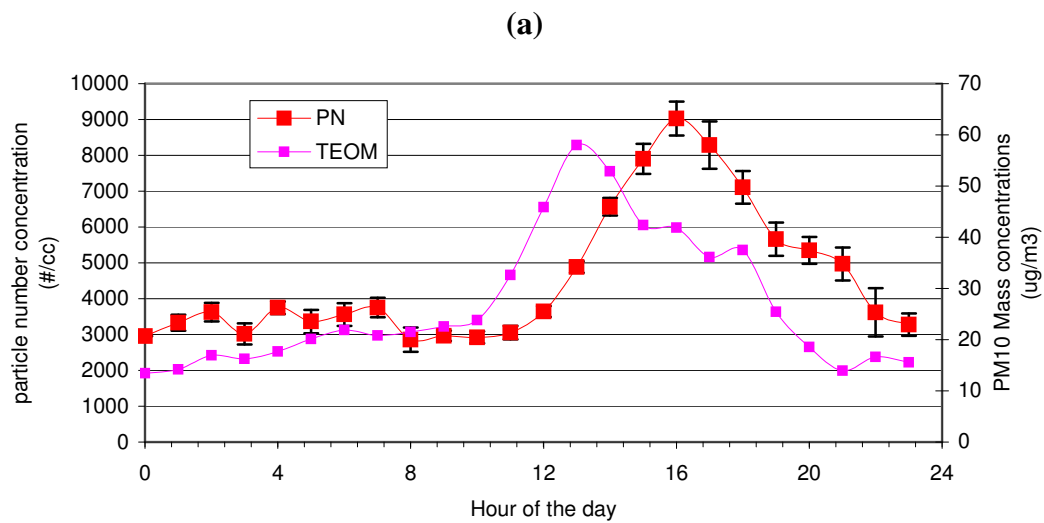(b). Geomean diameter and mode diameters as a function of hour of the day

(a)

(b)
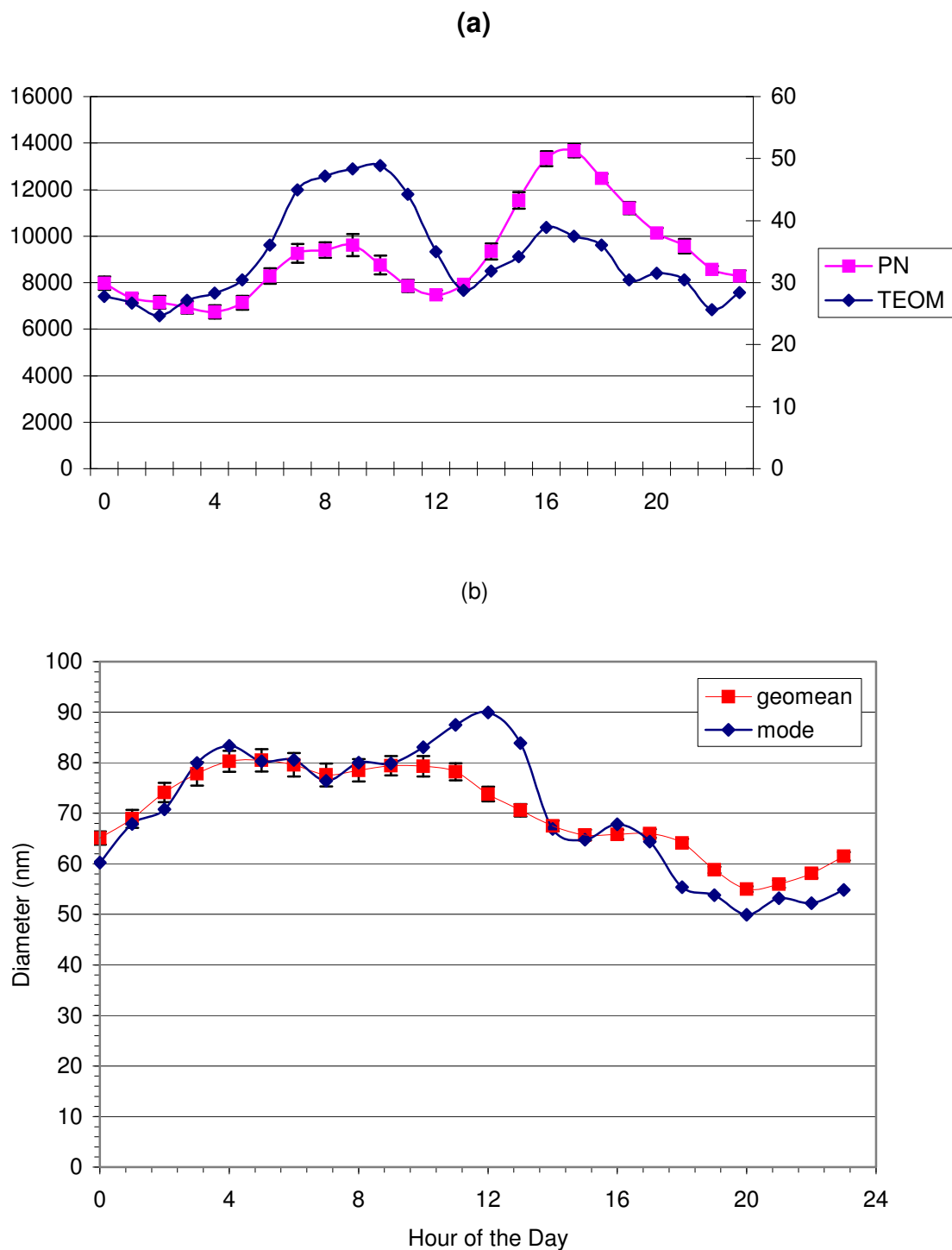
Figure 56. Particulate characteristics in Upland , CA. (Jul 2004).
(a). PN0.5 and PM$_{10}$ mass concentration as a function of hour of the day.
(b). Geomean diameter and mode diameters as a function of hour of the day

(a)

■ Freway 110 □ Freeway 710

(b)

□ Freeway 710 ■ Freeway 110
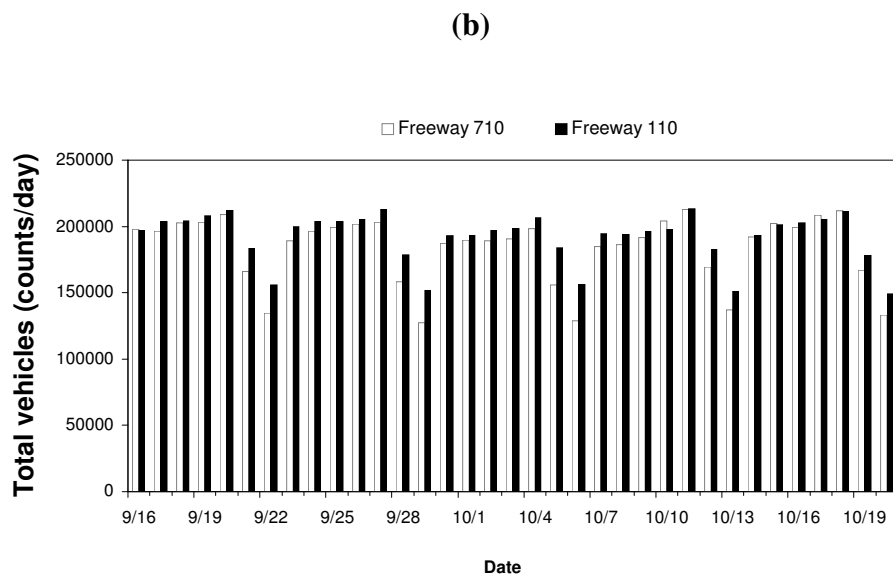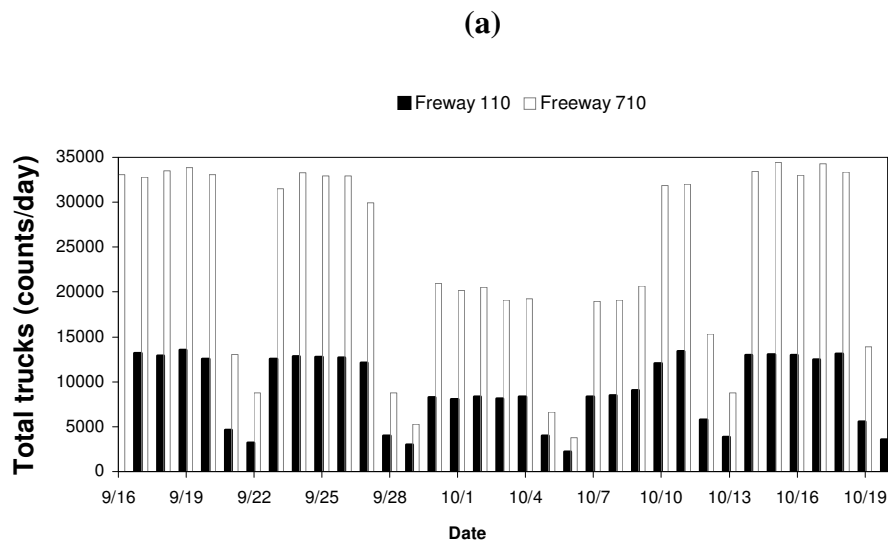
Figure 57 Daily traffic data for Freeways 710 and 410 before, during and after port strike at Long Beach in Sep-Oct 2002 a) total truck counts, and b) total vehicle counts

(a)

(b)

(c)
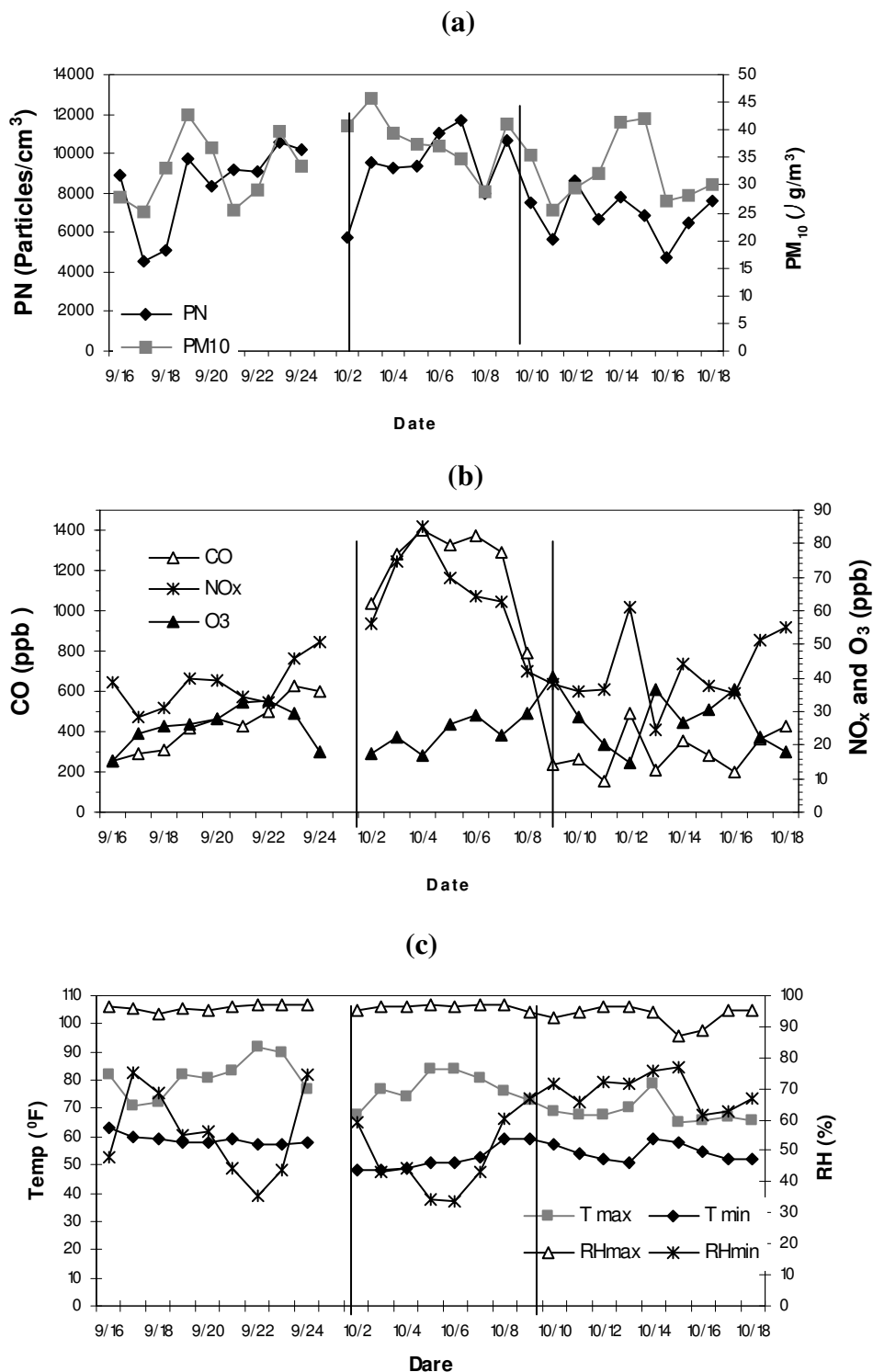
Figure 58. 24-hour averaged a) PN and PM$_{10}$, b) CO, NOx, and O3,c) temperature and RH - before, during and after the port strike at Long Beach in Sep-Oct 2002
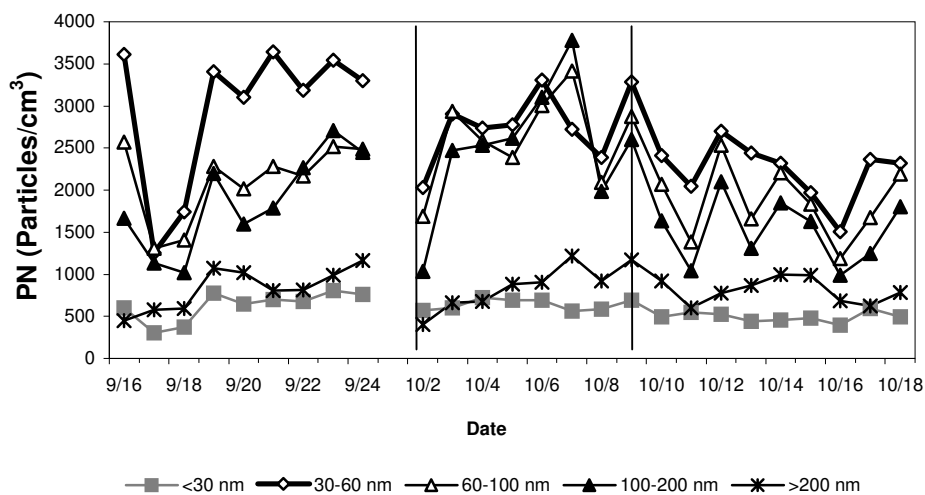
Figure 59. 24-hour averaged size-segregated PN before, during and after port strike at Long Beach in Sep-Oct 2002.
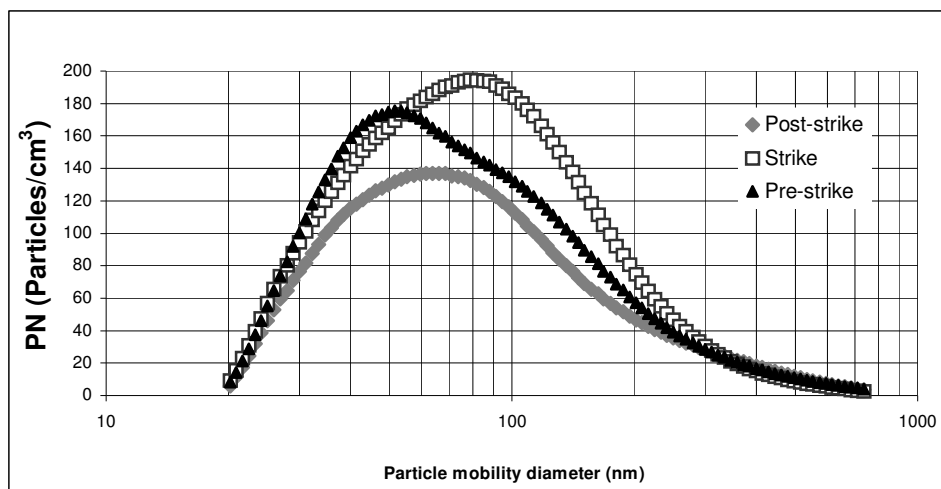
Figure 60. Average particle size distribution before, during and after the port strike at Long Beach in Sep-Oct 2002

Associations between Particle Number and Gaseous Co-Pollutant Concentrations in the Los Angeles Basin

Satya B. Sardar, Philip M. Fine, Heesong Yoon, and Constantinos Sioutas
Department of Civil and Environmental Engineering, University of Southern California, Los Angeles

ABSTRACT
Continuous measurements of particle number (PN), particle mass (PM_{10}), and gaseous pollutants [carbon monoxide (CO), nitric oxide (NO), oxides of nitrogen (NO_x), and ozone (O_3)] were performed at five urban sites in the Los Angeles Basin to support the University of Southern California Children's Health Study in 2002. The degree of correlation between hourly PN and concentrations of CO, NO, and nitrogen dioxide (NO_2) at each site over the entire year was generally low to moderate (*r* values in the range of 0.1–0.5), with a few notable exceptions. In general, associations between PN and O_3 were either negative or insignificant. Similar analyses of seasonal data resulted in levels of correlation with large variation, ranging from 0.0 to 0.94 depending on site and season. Summertime data showed a generally higher correlation between the 24-hr average PN concentrations and CO, NO, and NO_2 than corresponding hourly concentrations. Hourly correlations between PN and both CO and NO were strengthened during morning rush-hour periods, indicating a common vehicular source. Comparing hourly particle number concentrations between sites also showed low to moderate spatial correlations, with most correlation coefficients below 0.4. Given the low to moderate associations found in this study, gaseous co-pollutants should not be used as surrogates to assess human exposure to airborne particle number concentrations.

IMPLICATIONS
The overall lack of significant associations between hourly and 24-hr PN versus gaseous co-pollutant concentrations can be attributed to the differences in the sources and formation mechanisms that are responsible for generating these pollutants in the environment of the Los Angeles Basin. These associations may become stronger for specific pollutants and time periods, for example, between PN, CO, and NO during traffic rush hours. However, if examined on a yearly or even on a seasonal basis, the results from this study suggest that co-pollutants such as CO, O_3, or NO_x cannot be used as surrogates to assess human exposure to PN in epidemiologic studies. These findings also imply that potential confounding effects of co-pollutants will not affect epidemiologic analysis seeking to link ultrafine particles to health effects because of the general lack of associations between PN and co-pollutant concentrations.

INTRODUCTION
Recent research has demonstrated that numerous adverse health outcomes are associated with atmospheric particulate matter (PM). Epidemiologic studies have shown significant relationships between ambient PM and respiratory-related mortality and morbidity.[1,2] The observed effects are even more significant in susceptible populations, such as the elderly, with pre-existing respiratory and cardiovascular diseases.[3] Toxicological studies by Oberdorster[4] and Donaldson et al.[5] have concluded that ultrafine particles (particles with diameters less than ~100 nm) are comparatively more toxic than larger particles with identical chemical composition and mass. Because of their small size, ultrafine particles contribute very little to the overall PM mass but comprise a significant majority of the number of airborne particles in the atmosphere.[3,6]

It is still unknown whether the observed PM health effects are related to particle number (PN), particle surface area, particle mass, or particle chemical composition. Studies on rodents show that inflammatory response is more prominent when ultrafine particles are administered compared with larger particles,[3] suggesting either a particle number or surface area effect. Toxicological studies also have shown that ultrafine particles have higher oxidative stress potential and can penetrate and destroy mitochondria within epithelial cells.[7] Penttinen et al.[8] tested the hypothesis that high numbers of ultrafine particles in the atmosphere can induce alveolar inflammation and exacerbation of pre-existing cardiopulmonary diseases. They found that daily mean number concentration and peak expiratory flow (PEF) are negatively associated and that the effect is most prominent with particles in the ultrafine range. Another study by Peters et al.[9] found associations between number concentrations of ultrafine PM and lowered PEF among asthmatic adults.

As one of many sources contributing to urban air pollution in general, the combustion of fossil fuel in motor vehicles is one of the major primary emission sources

of ultrafine particles in urban atmospheres.[10,11] Recent studies have demonstrated how ultrafine number concentrations drop dramatically with increasing distance from busy freeways in the Los Angeles Basin, confirming that vehicular pollution is the major source of ultrafine particles near and on the freeways and that high particle number counts can be a very local phenomenon (on scales of 100–500 m).[12,13] Source tests also have demonstrated that vehicles emit significant numbers of particle in the size range of 40–100 nm.[14–16] Particles with diameters less than 30 nm emitted from vehicles consist primarily of condensed semi-volatile material such as hydrocarbons derived from lubricating oils.[17] Other combustion sources, such as food cooking and wood burning, also can be sources of ultrafine particles to the atmosphere.[18,19]

In addition to primary, or direct, ultrafine particle emissions, photochemical secondary formation in the atmosphere also is responsible for the formation of ultrafine particles in the atmosphere.[20–26] Kulmala et al.[20] investigated particle formation by secondary processes and showed that such particle formation events are more distinct in the summer. Evidence of summertime secondary particle formation also is given by the studies of Shi and Qian[22] and Birmili et al.,[23] where they observed enhanced particle growth rates during that season. Particle formation rates depend strongly on the intensity of solar radiation,[20] but the exact mechanism by which the process occurs is not fully understood.[27] Once formed, particles are transformed by coagulation and condensation in the atmosphere as they are advected downwind. This long-range transport, as well as photochemical particle formation in the atmosphere, can lead to increased particle number observations downwind of urban areas.[24,28]

Ultrafine particles and co-pollutants, such as nitrogen oxide (NO) and carbon monoxide (CO), are emitted by both diesel and gasoline engines.[11,24] A previous study found significant correlation at street level in central Copenhagen between CO, NO_x, and particle number.[29] Such results may lead epidemiologists to believe that these vehicular co-pollutants will serve as surrogates for particle number. However, co-pollutant associations measured at a roadside may not necessarily reflect potential associations further downwind, where most of the population is exposed.

Strong correlations between various co-pollutants and PM also can make it difficult to estimate the contribution of each pollutant to the observed health outcome because of confounding effects.[30] Additional health studies have shown that ultrafine particles in the presence of a gaseous co-pollutant, ozone (O_3), can have a significantly enhanced adverse health effect, greater than the sum of the effects from the co-pollutants alone.[3] For these reasons, it is essential to fully understand the relationships

among co-pollutants not just near vehicles or roadways but at all locations and times of human exposure.

Because of the different nature of sources, formation mechanisms, and atmospheric processes associated with each co-pollutant, one might expect the extent of correlation among co-pollutants to diminish as distance from the sources increases. For example, CO is largely unreactive on the time scales of urban transport and, thus, atmospheric concentrations are determined by emissions and dispersion alone.[31] NO, however, reacts to form nitrogen dioxide (NO_2), which can subsequently react to form nitric acid (HNO_3).[32] Particle number concentrations are influenced in the atmosphere by coagulation and by photochemical secondary processes.[20] Poor correlation among co-pollutants also might occur at or very near the source (i.e., tailpipe) because different combustion conditions will affect the emissions of different pollutants in different ways. Ultrafine particles from vehicles are formed in the engines, in the exhaust pipe, or immediately after exhaust to the atmosphere.[29] An appreciable portion of ultrafine particles from vehicular emissions may originate from uncombusted lubricating oil.[17] Thus, particle formation will depend strongly on the engine load, engine temperature, ambient temperature, and ambient relative humidity.[33,34] Hence, given the various combustion conditions at the sources and the different atmospheric behaviors, significant associations among co-pollutants may not be expected. The current study demonstrates these results by exploring the relationship between continuous and time-integrated particle number concentrations and those of various co-pollutants [i.e., NO, NO_2, O_3, particulate matter with aerodynamic diameter less than 10 μm (PM_{10}), and CO] at five sites in the Los Angeles Basin for the entire 2002 calendar year.

METHODS

Measurements of particle number, CO, O_3, PM_{10}, NO, and NO_x were conducted as part of the routine sampling protocol of the South Coast Air Quality Management District. Continuous data were collected concurrently over the calendar year 2002 at five different sites in the Los Angeles Basin (Figure 1) in support of the University of Southern California Children's Health Study (CHS). The data from this sampling campaign, which started in 1993, are currently being used by CHS epidemiologists to investigate the association between air pollution and the incidence, prevalence, and severity of childhood asthma and lung function.[35]

The five sites selected for the current analysis are Long Beach, Glendora, Mira Loma, Upland, and Riverside. The choice of sampling sites considered in this study is based on their location within the Los Angeles Basin as well as the adverse health outcomes observed at these
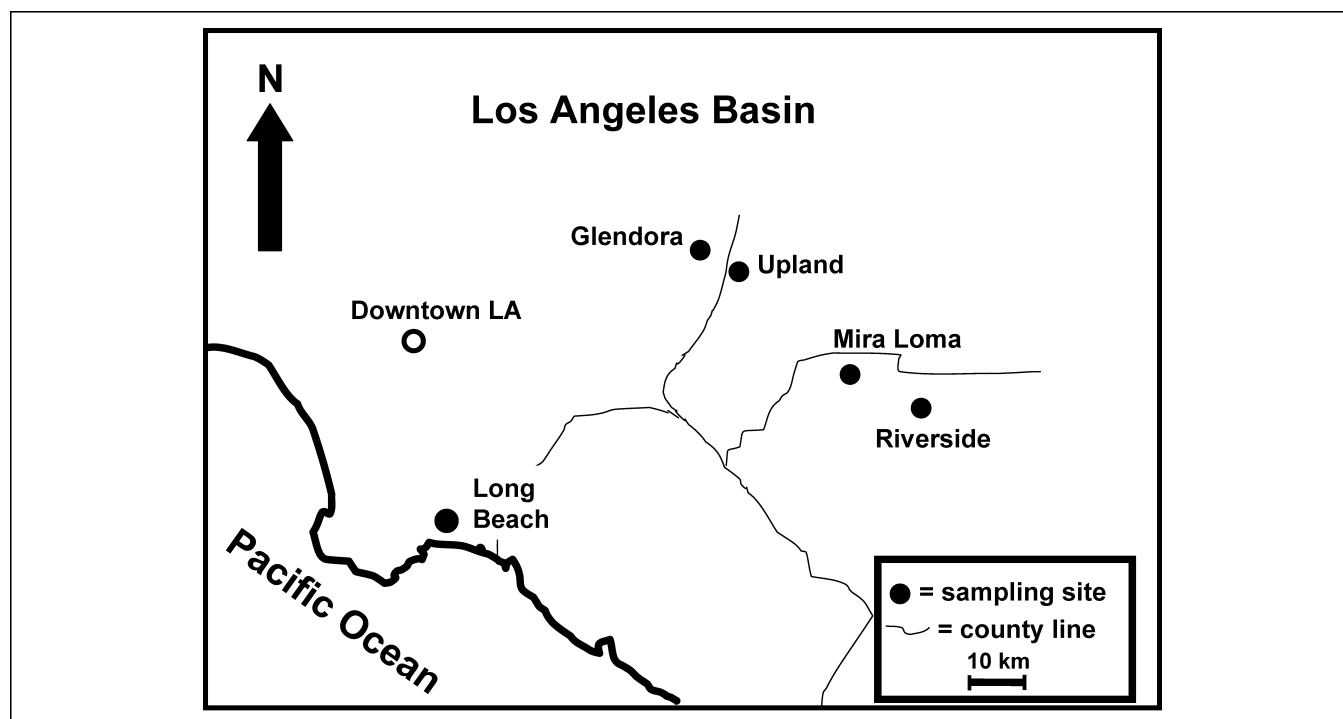
Figure 1. Locations of the source site (Long Beach) and the receptor sites (Mira Loma, Riverside, Upland, and Glendora) in the Los Angeles Basin.

sites[36] attributed to air pollution. Kunzli et al.[36] have studied these sites as part of the CHS investigating the long-term consequences of air pollution on the health of children. These sites generally are considered typical polluted urban areas of the Los Angeles Basin and have shown high prevalence of early childhood asthma among the residents. The high incidence of adverse effects of air pollution at these sites makes them appropriate locations to investigate the associations between PN and various co-pollutants.

The Long Beach station is located on one of the busiest streets in Long Beach and is ~0.8 km northeast of a major freeway. The Glendora station is located in a residential area, at least 3 km away from major roadways. The Upland site is less than 1 km north of a freeway and is located in a residential area ~6 km downwind of the Glendora site. The Mira Loma site is situated inside Jurupa Valley High School. It is directly east of a major freeway interchange (~3 km), is surrounded by several major warehouse facilities and residential communities, and is located ~80 km east of downtown Los Angeles. The sampling location at Riverside is at the Citrus Research Center and Agricultural Experiment Station (CRS–AES), a part of the University of California–Riverside. It is ~10 km southeast of the Mira Loma site and is situated upwind of surrounding freeways and major roads.

The five sites also are differentiated based on the characteristics of the air pollution in the Los Angeles Basin. Because of the relatively western location and the surrounding urban environment, Long Beach is considered a "source" site, where fresh particles are emitted primarily from vehicular and industrial sources, and thus represents well-mixed urban air. The other sites, Riverside, Upland, Glendora, and Mira Loma, are designated "receptor" sites, which have comparatively less traffic density and experience advected, aged, and photochemically processed air masses from the central Los Angeles area.[37] The transport time of air masses from source to receptor sites can vary from a few hours to more than a day. It is important to note that a receptor site may be close to a freeway, for example, the site at Upland. The proximity of Upland to a freeway alters some of the characteristics typical of a receptor site, adding the influence of local traffic to the regional effects. Glendora and Upland are on what has been termed the vehicular trajectory, while Mira Loma and Riverside are on the so-called nitrate (NO_3^-) trajectory, influenced by the Chino area dairy farms, a strong ammonia (NH_3) source leading to high concentrations of ammonium nitrate (NH_4NO_3).[32,38]

Particle number (particle diameter >15 nm) concentrations were measured continuously by a CPC (condensation particle counter, Model 3022/A, TSI Inc.). The CPC was set at a flow rate of 1.5 L/min. PM_{10} mass was measured using a tapered element oscillating microbalance (TEOM 1400A, R&P Inc.). The concentrations of CO were measured near-continuously by means of a Thermo Environmental Inc. Model 48C trace-level CO monitor. Concentrations of NO and NO_2 were measured by a continuous chemiluminescence analyzer (Monitor Labs Model 8840), and O_3 concentrations were measured using a UV photometer (Dasibi Model 1003 AH). Continuous particle

number and gaseous co-pollutant concentrations were averaged to form 1- and 24-hr average values for the subsequent analysis. All instruments were calibrated every 3 months by AQMD (Air Quality Management District) and ARB (Air Resource Board). The sampling, which is part of a compliance measurement network, was subjected to rigorous quality assurance procedures.

The analysis presented here is limited to assessing the associations among co-pollutants, presenting explanations for the presence or lack of associations, and discussing the implications for epidemiologic studies using such data. A thorough examination of the diurnal, geographical, and seasonal patterns of these six co-pollutants will be presented in a future publication.

RESULTS AND DISCUSSION

The Pearson correlation coefficient (r) between the hourly and 24-hr average PN concentration data and the co-pollutant concentrations (CO, NO, O_3, NO_2, and PM_{10}) are shown in Tables 1 and 2, respectively. Given the large number of data, even low values of r can indicate significance.[39] For example, hourly correlations in most cases were based on over 2000 data points, for which r values as low as 0.05 are significant at a $p = 0.05$ level. Nevertheless, these small values of r should be viewed cautiously in the context of exposure and epidemiology and as to whether one of these pollutants can be substituted as a predictive surrogate of another. The results shown in Tables 1 and 2 are based on the entire data set from the calendar year 2002. The r values for the hourly concentrations ranged from a high of 0.66 for PN versus CO in Upland down to practically 0.00. Interestingly, associations between PN and O_3 resulted in negative correlations in most cases, based on both hourly and 24-hr data. Similarly, the r for the 24-hr average concentrations ranged from 0.00 to 0.68 (PN vs. NO_2 in Long Beach). The values shown in Table 1 and Table 2 indicate generally low to moderate (i.e., $r < 0.5$) levels of association between PN and co-pollutants, and in only few cases, moderate to high (r between 0.5 and 0.68) levels of correlation on both an hourly and 24-hr basis. Based on these results, which were highly variable among sites, using any of these co-pollutants as a

Table 1. Hourly Pearson correlation coefficient, r, of PN vs. co-pollutant concentrations for the entire calendar year 2002, all sites.

	Glendora/TD	Long Beach	Mira Loma	Riverside	Upland
CO	0.13	0.46	0.47	0.52	0.66
NO	0.06	0.44	0.60	0.59	0.65
NO_2	0.21	0.50	0.24	0.32	0.17
PM_{10}	0.18	0.27	0.00	−0.16	0.14
O_3	0.30	−0.22	−0.34	−0.04	−0.26

Table 2. 24-hr average Pearson correlation coefficient, r, of PN vs. co-pollutant concentrations for the entire calendar year 2002, all sites.

	Glendora	Long Beach	Mira Loma	Riverside	Upland
CO	0.00	0.50	0.44	0.39	0.63
NO	0.30	0.48	0.34	0.32	0.66
NO_2	0.07	0.68	0.11	0.23	0.08
PM_{10}	−0.18	0.10	−0.17	−0.32	−0.19
O_3	−0.31	−0.63	−0.33	−0.26	−0.54

surrogate for ultrafine particles over a prolonged time period, such as an entire year, in Los Angeles is likely to introduce a high level of error in PN predictions.

Figures 2a-e display the scatter plots of the hourly concentrations of PN versus the five measured co-pollutants at the Upland site, where the highest correlations were observed. The relatively high correlations of PN with CO and NO are driven by the higher concentration values, indicating the occasional influence of vehicular sources emitting these three pollutants. The other four sites show even lower levels of correlation between PN and co-pollutants (as shown in Tables 1 and 2) and are not graphically represented.

It is possible that seasonal differences in source strengths, ambient temperatures, sunlight, and weather patterns, which might affect different pollutants differently, could account for the lack of correlation over an entire year. Thus, the data were separated by season to determine whether the associations among co-pollutants improved. The seasons were defined as winter (December–February); spring (March–May); summer (June–August); and fall (September–November). December 2002 was combined with January and February 2002 to form a winter period. Table 3 shows the Pearson correlation coefficients between PN and the other co-pollutant (both hourly and 24-hr average) concentrations for the five sites and the four seasons. The lowest levels of correlation ($r <$ 0.59) between PN and co-pollutants, for any season and for both averaging times, were observed in Glendora. The apparent lack of correlation with NO and CO may be caused by the minimal traffic influence at that site, which is located in a residential area and away from major roadways. However, at the Upland site, which is located only 6 km to the east, the hourly correlation between PN and the other primary vehicular emissions (CO and NO) showed higher correlations, particularly in the winter and fall. The PN correlations with CO and NO were almost always lower for the 24-hr average data than for the hourly averages. The high hourly correlations for vehicular pollutants suggest a local traffic source at Upland. Furthermore, the association is higher in the winter, when stagnant conditions and lower inversion layers trap

Figure 2. Hourly PN vs. co-pollutant concentrations at Upland for the entire year 2002. (a) CO, (b) NO, (c) NO_2, (d) PM_{10}, and (e) O_3.

Table 3. Hourly and 24-hr average Pearson correlation coefficient (*r*) of PN vs. co-pollutant concentrations on a seasonal basis.

Winter	Glendora		Long Beach		Mira Loma		Riverside		Upland	
	24-hr Avg.	Hourly	24-hr Avg.	Hourly	24-hr Avg.	Hourly	24-hr Avg.	Hourly	24-hr Avg.	Hourly
CO	0.20	0.19	0.33	0.47	0.17	0.43	0.33	0.43	0.55	0.74
NO	0.35	0.42	0.58	0.48	0.55	0.67	0.41	0.53	0.54	0.72
NO_2	0.37	0.33	0.64	0.58	0.34	0.29	0.38	0.33	0.20	0.35
PM_{10}	0.03	0.30	0.19	0.54	0.51	0.53	0.06	0.01	0.17	0.41
O_3	−0.64	−0.37	−0.42	−0.28	−0.48	−0.65	−0.02	−0.14	−0.38	−0.25

Spring	Glendora		Long Beach		Mira Loma		Riverside		Upland	
	24-hr Avg.	Hourly	24-hr Avg.	Hourly	24-hr Avg.	Hourly	24-hr Avg.	Hourly	24-hr Avg.	Hourly
CO	0.04	0.14	0.27	0.28	0.46	0.59	0.38	0.61	0.50	0.57
NO	0.49	0.00	0.39	0.41	0.36	0.70	0.38	0.66	0.63	0.59
NO_2	0.16	0.29	0.52	0.34	0.46	0.46	0.30	0.48	0.34	0.30
PM_{10}	0.13	0.37	0.10	0.18	0.14	0.25	−0.11	−0.05	0.06	0.26
O_3	−0.24	−0.40	−0.54	−0.15	−0.23	−0.03	−0.18	−0.04	−0.21	−0.16

Summer	Glendora		Long Beach		Mira Loma		Riverside		Upland	
	24-hr Avg.	Hourly	24-hr Avg.	Hourly	24-hr Avg.	Hourly	24-hr Avg.	Hourly	24-hr Avg.	Hourly
CO	0.27	0.14	0.46	0.40	0.56	0.49	0.71	0.54	0.52	0.48
NO	0.36	0.10	0.61	0.49	0.67	0.65	0.87	0.65	0.49	0.38
NO_2	0.37	0.28	0.68	0.53	0.78	0.50	0.79	0.70	0.55	0.33
PM_{10}	0.45	0.46	0.31	0.44	0.57	0.26	0.52	0.30	0.16	0.21
O_3	0.07	0.59	−0.17	0.23	0.30	0.11	0.56	0.17	0.05	0.19

Fall	Glendora		Long Beach		Mira Loma		Riverside		Upland	
	24-hr Avg.	Hourly	24-hr Avg.	Hourly	24-hr Avg.	Hourly	24-hr Avg.	Hourly	24-hr Avg.	Hourly
CO	0.25	0.31	0.88	0.56	0.32	0.47	0.41	0.41	0.53	0.64
NO	0.53	0.19	0.79	0.60	0.11	0.69	0.33	0.25	0.60	0.64
NO_2	0.38	0.35	0.94	0.66	0.20	0.45	0.49	0.33	0.29	0.32
PM_{10}	0.06	0.23	0.71	0.49	0.05	0.33	0.41	0.25	0.27	0.34
O_3	0.04	0.28	−0.10	−0.05	0.13	−0.23	0.52	0.10	−0.13	−0.25

pollutants near the ground and enhance the influence of local sources. Figures 3a and b display the scatter plots of the PN and CO data collected in Upland in the winter season. As mentioned before, the entire data set of 24-hr average values in Figure 3a shows a lower *r*, while the hourly data in Figure 3b are more correlated. The suggestion that traffic sources from the adjacent freeway heavily influence Upland is supported by the higher correlation for the morning rush-hour period between 5:00 and 8:00 a.m. Most of the higher levels of both pollutants were observed during this morning rush-hour period. As discussed earlier, Upland is situated close to a freeway and, even though it is a receptor site, pollutants generated on the adjacent freeway influence pollutant levels there. The strong diurnal patterns of traffic result in higher levels of hourly correlations compared with 24-hr average correlations.

The lower correlations between PN and both CO and NO in the spring and summer is most likely caused by the different meteorological conditions, which favor increased advection of pollutants from urban Los Angeles

areas located upwind of that site. The influence of an aged, transported air mass will act to reduce the modest associations among vehicular co-pollutants that one might expect from local emissions alone. Another factor may be photochemical secondary formation of particles in the atmosphere,[24,28] which would increase particle numbers while not affecting CO or NO levels. Other sites that showed moderate to relatively high levels of correlation among hourly measurements of vehicular pollutants and, thus, are thought to be influenced by local traffic, were Mira Loma and Riverside in the spring and summer.

Several previous studies have explored the relationship between PN and co-pollutants at locations that are heavily influenced by traffic.[8,29,40] Noble et al.[41] found high correlations between CO, NO, and hourly ultrafine particle number (UF) in winter in El Paso, TX, with Pearson correlation coefficients (*r*) ranging from 0.81 to 0.74 for UF versus CO and UF versus NO, respectively. Both sampling sites in this study were heavily influenced by traffic
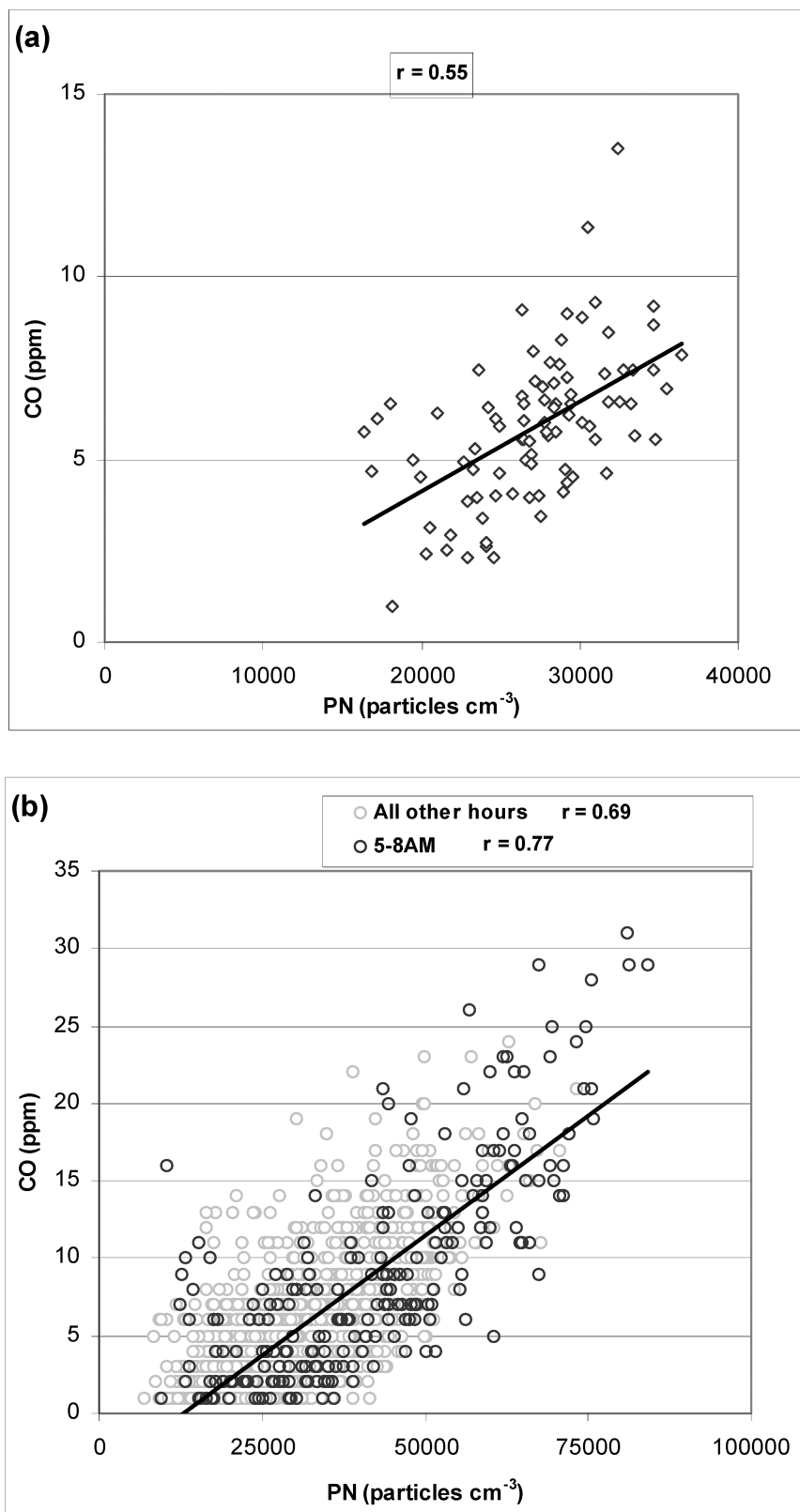
Figure 3. PN vs. CO in Upland during winter, 2002. (a) 24-hr average and (b) hourly.

sources. Cyrys et al.[11] found moderate Spearman correlation coefficients (*r*) between 0.57 and 0.55 for PN (0.01–2.5 μm) versus CO and NO_2, respectively, on an hourly

basis in Erfurt, Germany, for the entire calendar year of 1997. By comparison, the observed winter *r* in Upland for PN versus CO and NO of 0.74 and 0.72, respectively, are

similar to the El Paso study, and the CO versus PN correlation is actually higher than the Erfurt study.

Morawska et al.[42] also have found lower but significant correlations of PN with CO ($r = 0.45$) and NO_x ($r = 0.40$) over 10 months in Brisbane, Australia, at a site very near a freeway. While high correlations between hourly measurements of vehicular co-pollutants indicate a local traffic source, high correlations of 24-hr average co-pollutant concentrations may signify a different influence. Table 3 shows that the 24-hr correlation coefficients are often higher than their hourly counterparts, especially in the receptor sites, with the exception of Glendora. This trend is more pronounced in the summer season and applies to non-vehicular and secondary co-pollutants as well. The summer season showed high ($r > 0.70$) degrees of correlation of 24-hr PN with CO, NO, and NO_2 at Riverside, and moderately high correlations between PN and CO, NO, and NO_2 at Upland ($r = 0.49$–0.55) and Mira Loma ($r = 0.56$–0.78). In all these cases, the daily average data were more correlated than the hourly data. Thus, while the hourly levels of certain co-pollutants may not peak, dip, or vary in similar diurnal patterns, the 24-hr average levels of all pollutants might show higher correlations during a day of generally poor air quality.

The summer period in Los Angeles is characterized by increased on-shore flow and, thus, enhanced advection of air masses inland.[28,37] Pollutant concentrations, especially at inland sites, are, therefore, influenced by upwind sources and aged air parcels, as opposed to the influence of more local sources during the stagnant conditions in the winter. This may provide an explanation for the higher 24-hr correlations between PN and the more secondary (formed during transport and aging) co-pollutants during the warmer seasons. Interestingly, the highest associations between PN and PM_{10}, CO, NO, and NO_2 in the site of Long Beach, whether based on hourly or 24-hr data, were observed in the fall season. Also, 24-hr concentrations between PN versus CO, NO, and NO_2 were found to be in higher correlation than their corresponding hourly values in the summer period, similar to the rest of the sites.

The scatter plots for PN versus CO, NO, and NO_2 during the summer at Riverside are shown in Figures 4a-f. As already discussed, the correlation is higher in all cases for the 24-hr data than for the hourly data, reaching as high as $r = 0.87$ for NO. Although advection on generally polluted days is causing these high associations, the influence of local sources is not absent. The hourly data (Figures 4b, d, and f) demonstrate that the relatively high hourly correlations given in Table 3 are driven by the high levels during the morning commute hours.

In addition to traffic emissions, another source of ultrafine particles, and, thus, increased PN concentrations, is photochemical reactions in the atmosphere that form new particles by secondary processes.[24,28,43,44] The mechanisms of particle formation are still poorly understood, but it is expected that it is more likely to occur on days of high photochemical activity (an atmosphere with high concentrations of gaseous pollutants and a clear day with a high solar zenith angle). These conditions also will generally favor the production of O_3. Thus, one might expect increases in particle numbers from photochemical processes to accompany increases in O_3 concentrations.

To investigate this relationship further, the Glendora site was selected to minimize the effects of local traffic. As described, the low PN versus CO and NO correlations (Tables 1 and 2) at Glendora indicate that this site is influenced very little by local traffic sources. The summer season at Glendora was examined because this is when photochemistry is expected to be at its highest and it is when the highest hourly PN versus O_3 correlation was found ($r = 0.59$, Table 3). Studies by Shi and Qian, Stanier et al., and Kulmala et al. have observed that production of ultrafine particles by secondary processes are more pronounced in the summer period.[20–22] As shown in Figure 5, the r value of 0.59 increases to a maximum of 0.74 if PN is compared with O_3 levels ~2 hr before (i.e., a 2-hr lag time). Figure 6 shows how the r between PN and O_3 varies as the lag time is changed. The correlation starts increasing with a lag of 1 hr, and the peak correlation was found at 2 hr, as shown in Figure 5. This is followed by a decrease in the association as the lag time is increased to 3 hr or more. Thus, it seems that, while photochemistry is responsible for the increases in both pollutants, an increased association is found when PN levels are compared with O_3 concentrations 1–3 hr earlier. Previous investigations on secondary ultrafine particle formation showed that these particles are initially formed in the size range of 1–2 nm[45,46] and grow to larger sizes (such as those that can be detected by a CPC) either by condensation of low-volatility organics[44,47] on these nuclei or by heterogeneous organic reactions possibly catalyzed by the presence of acids.[27] Low-volatility organics are formed by the oxidation of organic vapors by hydroxyl radicals, and the photolysis of O_3 is one of the mechanisms by which hydroxyl radicals may be produced in the atmosphere.[48] It is hypothesized that the time period of ~1–3 hr for the strengthening of association between O_3 and PN is the time required for all of these processes to occur, starting from the production of hydroxyl radicals to the eventual growth of particles to a detectable size by the CPC, which in our case was larger than ~15 nm. The explanation also can be supported by the findings of Kulmala et al.,[20] where they observed a particle growth rate of 5 nm/hr during the summer. This is consistent with the observed lag time in that it would take ~1–3 hrs for the small particles to grow, by the condensation of
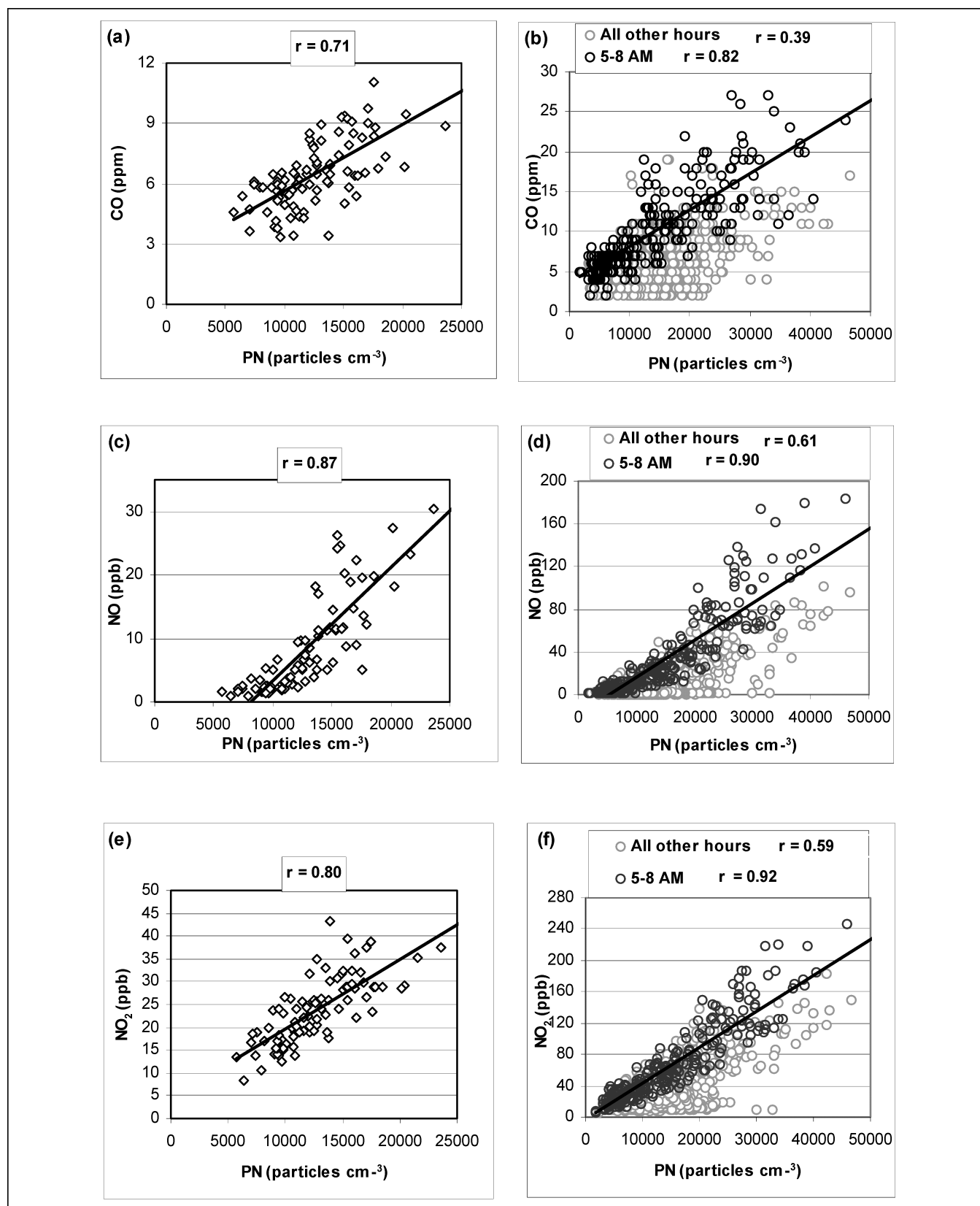
Figure 4. PN vs. CO, NO, and NO_2 in Riverside during summer, 2002. (a) 24-hr average PN vs. CO and (b) hourly PN vs. CO. (c) 24-hr average PN vs. NO. (d) Hourly PN vs. NO. (e) 24-hr average PN vs. NO_2. (f) Hourly PN vs. NO_2.
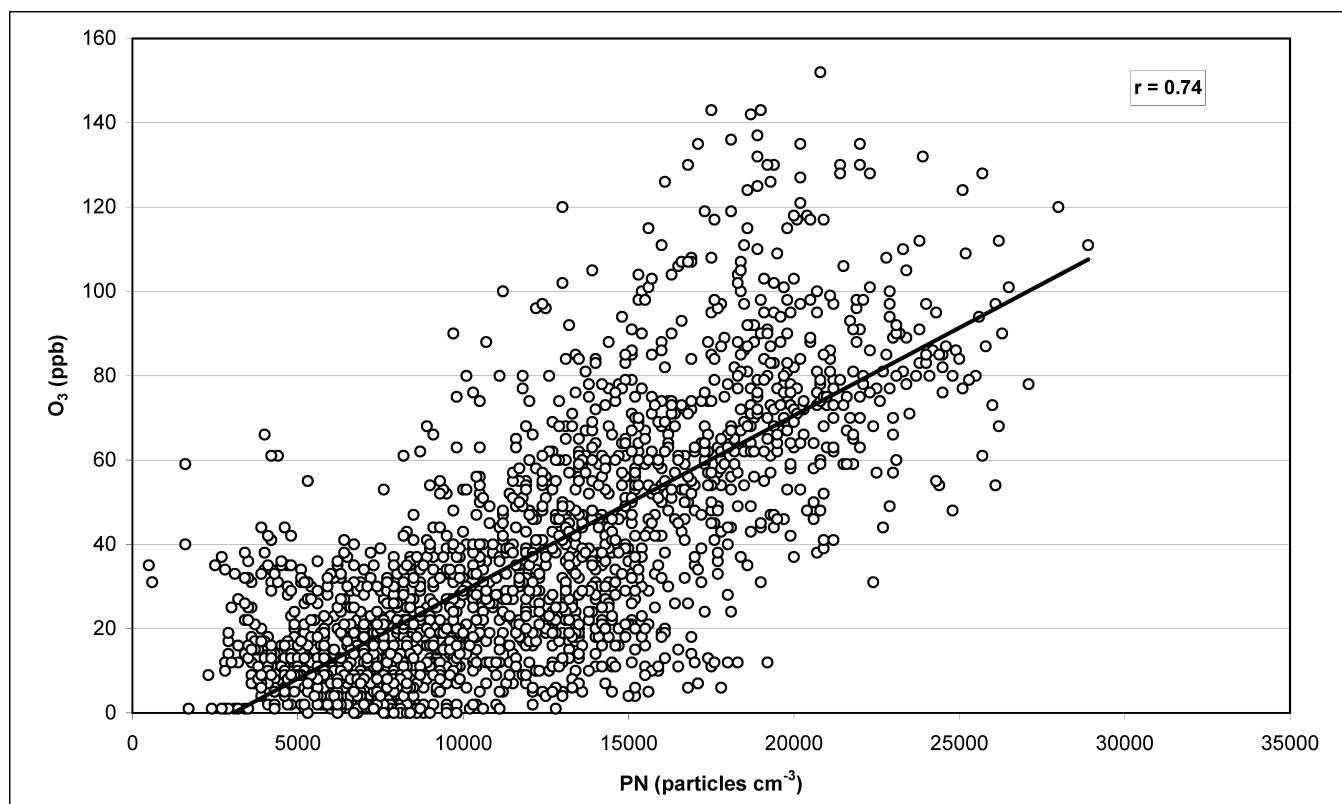
Figure 5. Hourly PN vs. O_3 concentrations in Glendora during summer 2002 with a lag time of 2 hr (PN vs. O_3 2 hr earlier).
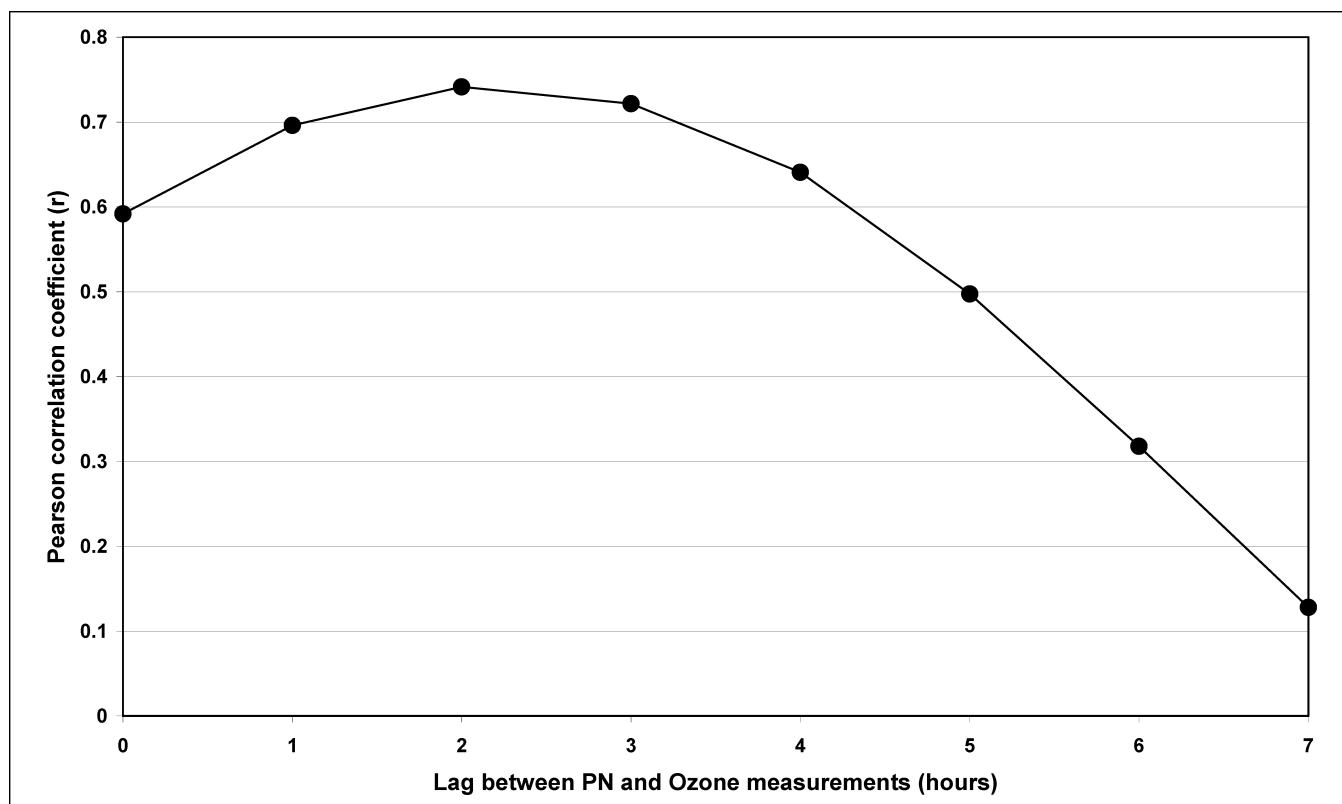
Figure 6. Pearson correlation coefficient, *r*, vs. lag time between measurements of O_3 and PN.

photochemically formed organics, to the size range of 15 nm, which then can be detected by the CPC.

Concurrent measurements at different sites allow the investigation of the geographical homogeneity of PN concentrations across the Los Angeles Basin. This is important for epidemiologic studies that require predictions of human exposure based on a limited number of sampling locations. Table 4 shows the Pearson correlation coefficient, *r*, from intersite correlations of concurrently measured PN concentrations. For all four seasons, correlations of hourly data across sites results in relatively low *r* values, mostly below 0.3. In almost all cases, the 24-hr average PN concentrations were more correlated across sites than were the hourly data. The spatial correlations between the 24-hr PN concentrations increase in the spring and summer periods, especially among the receptor sites of Upland, Mira Loma, Riverside, and Glendora. As was previously mentioned, meteorological conditions that favor a poor air quality day will lead to high particle number and other pollutant levels across the basin, even if the timing of the daily peaks varies enough to cause minimal hourly associations among sites. Examined on a yearly basis, however, the *r* values are low enough to indicate that particle number concentrations are spatially inhomogeneous

and that using central site monitoring to predict population exposure to PN on an hourly or even daily basis would not be accurate. Although this finding was somewhat anticipated, the analysis presented here is the first of its kind in the Los Angeles Basin and has serious implications in regulatory and compliance monitoring. For instance, Glendora and Upland, which are only 6 km apart, show moderate to relatively high levels of correlation in the range of 0.63–0.71 of 24-hr average PN for three seasons (spring, summer, and fall), but have an *r* of only 0.23 in the winter, when stagnate weather conditions limit transport. Similarly, the correlation coefficients based on hourly concentrations range from 0.33 in the winter to 0.55 in the summer.

Figure 7a demonstrates why the Glendora/Upland association is moderate ($r = 0.55$) on an hourly basis in the summer, despite the proximity of the two sites. The scatter plot shows that, during the morning traffic hours from 5:00 to 8:00 a.m., Upland experiences an excess of particle numbers relative to Glendora because of the local vehicular sources. When this time period is excluded from the analysis, the *r* increases to 0.70. The clustering of the non-morning data about the 1:1 line shows that the general PN levels at these sites are comparable. Because these two sites are separated by ~6 km east to west, it will take time for an air mass at Glendora to be transported to Upland downwind. Figure 7b shows the same data as Figure 7a, but the Upland data are now compared with Glendora data measured 1 hr previously. The *r* of the non-morning traffic data increases to 0.74, and it is clear that the amount of scatter around the 1:1 line decreases. Figures 7c and d show lag times of 2 and 3 hr between the sites, and the *r* are observed to decrease while the scatter visibly increases. A 1-hr lag suggests an approximate wind speed of 6 km/hr, which is typical at those sites at that time of year.[24] Thus, the Upland site is influenced by both local traffic sources (especially in the morning) and the advection of air masses from upwind. Similar to Upland, the measured PN concentrations in any other location, for any season and time of day, are a combination of the contributions of three major sources, that is, traffic, long-range transport via advection, and photochemistry (in the summer). The regional nature of the latter two source/formation mechanisms (i.e., long-range transport and photochemistry), would tend to create a spatially homogeneous ultrafine aerosol, but the varying degrees to which vehicular sources influence a specific sampling site disrupt this homogeneity.

Again, an attempt was made to find correlations among individual co-pollutants at proximal sites, for example, Glendora versus Upland and Mira Loma versus Riverside, by taking the hourly concentrations for the entire year 2002. At Glendora and Upland, the intra-species

Table 4. 24-hr average and hourly (*italic*) Pearson correlation coefficient (*r*) of PN vs. PN across sites on a seasonal basis.

Winter	Glendora	Long Beach	Mira Loma	Riverside	Upland
Glendora	—	0.17	0.23	−0.63	0.23
Long Beach	*0.25*	—	−0.20	0.58	0.38
Mira Loma	*0.11*	*0.13*	—	0.32	0.33
Riverside	*−0.41*	*0.13*	*0.22*	—	0.62
Upland	*0.33*	*0.44*	*0.42*	*0.12*	—

Spring	Glendora	Long Beach	Mira Loma	Riverside	Upland
Glendora	—	0.50	0.13	0.33	0.71
Long Beach	*0.27*	—	0.54	0.21	0.70
Mira Loma	*0.12*	*0.13*	—	0.75	0.63
Riverside	*−0.15*	*0.07*	*0.27*	—	0.60
Upland	*0.37*	*0.29*	*0.49*	*0.45*	—

Summer	Glendora	Long Beach	Mira Loma	Riverside	Upland
Glendora	—	0.32	0.46	0.52	0.63
Long Beach	*0.40*	—	0.41	0.54	0.31
Mira Loma	*0.22*	*0.01*	—	0.70	0.51
Riverside	*0.13*	*0.01*	*0.13*	—	0.78
Upland	*0.55*	*0.04*	*0.08*	*0.25*	—

Fall	Glendora	Long Beach	Mira Loma	Riverside	Upland
Glendora	—	−0.18	0.27	0.43	0.66
Long Beach	*0.25*	—	0.30	0.19	0.09
Mira Loma	*0.09*	*0.12*	—	0.08	0.47
Riverside	*0.03*	*0.05*	*0.22*	—	0.21
Upland	*0.44*	*0.23*	*0.45*	*0.14*	—

Figure 7. Comparison of PN concentrations in Upland and Glendora during summer 2002. (a) No lag time, (b) 1-hr lag time, (c) 2-hr lag time, and (d) 3-hr lag time. Dashed lines indicate the ideal 1:1 relationship and therefore, does not fit the data.

associations for CO, NO, NO_2, and O_3 are found to be 0.12, 0.48, 0.73, and 0.92, respectively. For Riverside and Mira Loma, the correlations for CO, NO, NO_2, and O_3 were found to be 0.65, 0.79, 0.83, and 0.95, respectively. It is important to note that even pollutants like CO and NO with typically local character are found to be correlated. The high association between O_3 obviously signifies regional nature of the pollutant. The most important conclusion from this analysis is that the spatial inhomogeneity of PN at Riverside and Mira Loma is higher than that for CO or NO, which makes the analysis of PN associations at proximal sites extremely informative. The 24-hr average yearly data also were analyzed to determine the inter-correlations between PN, PM_{10}, and gaseous co-pollutants at all five sites. The 24-hr average Pearson correlation coefficients for all species are shown in Table 5. The associations between PN and the other pollutants already were

discussed and presented in Table 2. The varying degree of correlations among CO, NO, and NO_2 in each site (r values ranging from 0.29 to 0.84), probably reflects differences in the mix of traffic sources (i.e., gasoline vs. diesel engines) impacting each location. It is interesting to point out that in almost every site, the 24-hr concentrations of O_3 are negatively correlated with those of CO and NO when examined over an entire year. O_3 reaches its highest concentrations in the summer time, during the peak of the photochemical period, whereas the concentrations of CO and NO are maximum in the winter, when inversions and the depressed mixing depth of the atmosphere tend to increase the contribution of local vehicular emissions to air pollution. Riverside and Mira Loma show similar r values for PN versus the co-pollutants as well as among CO, NO, and NO_2. This similarity may be explained by the close proximity of the two sites.

Table 5. 24-hr average Pearson correlation coefficient, *r*, between all species sampled for the entire calendar year 2002, all sites.

Long Beach	PN	CO	NO	NO$_2$	PM$_{10}$	O$_3$
PN	1.00	—	—	—	—	—
CO	0.50	1.00	—	—	—	—
NO	0.48	0.58	1.00	—	—	—
NO$_2$	0.68	0.66	0.68	1.00	—	—
PM$_{10}$	0.10	0.08	0.10	0.34	1.00	—
O$_3$	−0.63	−0.59	−0.63	−0.77	−0.02	1.00
Riverside	**PN**	**CO**	**NO**	**NO$_2$**	**PM$_{10}$**	**O$_3$**
PN	1.00	—	—	—	—	—
CO	0.39	1.00	—	—	—	—
NO	0.32	0.76	1.00	—	—	—
NO$_2$	0.23	0.68	0.63	1.00	—	—
PM$_{10}$	−0.32	0.32	−0.55	−0.14	1.00	—
O$_3$	−0.26	0.07	−0.05	0.37	0.50	1.00
Mira Loma	**PN**	**CO**	**NO**	**NO$_2$**	**PM$_{10}$**	**O$_3$**
PN	1.00	—	—	—	—	—
CO	0.44	1.00	—	—	—	—
NO	0.34	0.69	1.00	—	—	—
NO$_2$	0.11	0.53	0.55	1.00	—	—
PM$_{10}$	−0.17	0.21	0.14	0.59	1.00	—
O$_3$	−0.33	−0.48	−0.56	−0.31	0.29	1.00
Upland	**PN**	**CO**	**NO**	**NO$_2$**	**PM$_{10}$**	**O$_3$**
PN	1.00	—	—	—	—	—
CO	0.63	1.00	—	—	—	—
NO	0.66	0.84	1.00	—	—	—
NO$_2$	0.08	0.52	0.51	1.00	—	—
PM$_{10}$	−0.19	0.19	0.19	0.68	1.00	—
O$_3$	−0.54	−0.26	−0.35	0.26	0.41	1.00
Glendora	**PN**	**CO**	**NO**	**NO$_2$**	**PM$_{10}$**	**O$_3$**
PN	1.00	—	—	—	—	—
CO	0.00	1.00	—	—	—	—
NO	0.30	0.29	1.00	—	—	—
NO$_2$	0.07	0.50	0.47	1.00	—	—
PM$_{10}$	−0.18	0.33	0.04	0.56	1.00	—
O$_3$	−0.31	0.17	−0.24	0.18	0.56	1.00

The degree of correlation between 24-hr concentrations of PM$_{10}$ and gaseous co-pollutants also is variable between sites. While PM$_{10}$ is moderately (*r* = 0.34) associated only with NO$_2$ at the source site of Long Beach, its degree of correlation with O$_3$ increases substantially at the receptor sites, with *r* varying from 0.29 in Mira Loma to 0.56 in Glendora, thus reflecting the impact of secondary processes in PM formation. The impact of traffic sources on PM$_{10}$ concentrations in every site also is indicated by the moderate to high correlations between PM$_{10}$ and either CO or NO$_2$, with *r* values ranging from 0.32 between PM$_{10}$ and CO in Riverside to 0.68 between PM$_{10}$ and NO$_2$ in Upland.

SUMMARY AND CONCLUSIONS

Ultrafine particles, which dominate the particle number concentration of ambient aerosols, recently have been the focus of several health studies. It has been hypothesized traditionally that these particles originate from vehicular emissions; thus, the concentrations of gases such as CO, NO, or NO$_2$ that also originate from traffic sources can be used as a surrogate measures of ultrafine PM. The advantage of this approach is that concentrations of these gases are monitored routinely in compliance networks and on personal levels by means of relatively simple and easy-to-use monitors. The validity of the assumption using gases as surrogates of ultrafine PM was tested in this study in five sites of the Los Angeles Basin over the course of one calendar year.

The results presented in this paper indicate that there are overall weak to moderate associations for both hourly and 24-hr average concentrations between PN and other co-pollutants when considered for the whole calendar year of 2002. Results suggest that, at least in Los Angeles, gaseous co-pollutants cannot be used as surrogates of PN to assess human exposure. Comparing particle number concentrations between sites also showed low to modest spatial correlations, a result that further complicates monitoring for ultrafine particles either for regulatory purposes or in support of epidemiologic studies.

REFERENCES
1. Adler, K.B.; Fischer, B.M.; Wright, D.T.; Cohn, L.A.; Becker, S. Interactions between Respiratory Epithelial-Cells and Cytokines—Relationships to Lung Inflammation; *Cells Cyt. Lung Inflam.* **1994**, *725*, 128-145.
2. Dockery, D.W.; Pope, C.A.; Xu, X.P.; Spengler, J.D.; Ware, J.H.; Fay, M.E.; Ferris, B.G.; Speizer, F.E. An Association between Air-Pollution and Mortality in 6 United States Cities; *N. Engl. J. Med.* **1993**, *329*, 1753-1759.
3. Oberdorster, G. Pulmonary Effects of Inhaled Ultrafine Particles; *Int. Arch. Occup. Environ. Health* **2001**, *74*, 1-8.
4. Oberdorster, G. Significance of Particle Parameters in the Evaluation of Exposure-Dose-Response Relationships of Inhaled Particles; *Partic. Sci. Technol.* **1996**, *14*, 135-151.

5. Donaldson, K.; Li, X.Y.; MacNee, W. Ultrafine (Nanometer) Particle Mediated Lung Injury; *J. Aerosol Sci.* **1998**, *29*, 553-560.

6. Morawska, L.; Bofinger, N.D.; Kocis, L.; Nwankwoala, A. Submicrometer and Supermicrometer Particles from Diesel Vehicle Emissions; *Environ. Sci. Technol.* **1998**, *32*, 2033-2042.

7. Li, N.; Sioutas, C.; Cho, A.; Schmitz, D.; Misra, C.; Sempf, J.; Wang, M.Y.; Oberley, T.; Froines, J.; Nel, A. Ultrafine Particulate Pollutants Induce Oxidative Stress and Mitochondrial Damage; *Environ. Health Perspect.* **2003**, *111*, 455-460.

8. Penttinen, P.; Timonen, K.L.; Tiittanen, P.; Mirme, A.; Ruuskanen, J.; Pekkanen, J. Ultrafine Particles in Urban Air and Respiratory Health among Adult Asthmatics; *Eur. Respir. J.* **2001**, *17*, 428-435.

9. Peters, A.; Wichmann, H.E.; Tuch, T.; Heinrich, J.; Heyder, J. Respiratory Effects Are Associated with the Number of Ultrafine Particles; *Am. J Respir. Crit. Care Med.* **1997**, *155*, 1376-1383.

10. Shi, J.P.; Khan, A.A.; Harrison, R.M. Measurements of Ultrafine Particle Concentration and Size Distribution in the Urban Atmosphere; *Sci. Total Environ.* **1999**, *235*, 51-64.

11. Cyrys, J.; Stolzel, M.; Heinrich, J.; Kreyling, W.G.; Menzel, N.; Wittmaack, K.; Tuch, T.; Wichmann, H.E. Elemental Composition and Sources of Fine and Ultrafine Ambient Particles in Erfurt, Germany; *Sci. Total Environ.* **2003**, *305*, 143-156.

12. Zhu, Y.F.; Hinds, W.C.; Kim, S.; Shen, S.; Sioutas, C. Study of Ultrafine Particles near a Major Highway with Heavy-Duty Diesel Traffic; *Atmos. Environ.* **2002**, *36*, 4323-4335.

13. Zhu, Y.F.; Hinds, W.C.; Kim, S.; Sioutas, C. Concentration and Size Distribution of Ultrafine Particles near a Major Highway; *J. Air & Waste Manage. Assoc.* **2002**, *52*, 1032-1042.

14. Harris, S.J.; Maricq, M.M. Signature Size Distributions for Diesel and Gasoline Engine Exhaust Particulate Matter; *J. Aerosol Sci.* **2001**, *32*, 749-764.

15. Tobias, H.J.; Beving, D.E.; Ziemann, P.J.; Sakurai, H.; Zuk, M.; McMurry, P.H.; Zarling, D.; Waytulonis, R.; Kittelson, D.B. Chemical Analysis of Diesel Engine Nanoparticles Using a Nano-DMA/Thermal Desorption Particle Beam Mass Spectrometer; *Environ. Sci. Technol.* **2001**, *35*, 2233-2243.

16. Kleeman, M.J.; Schauer, J.J.; Cass, G.R. Size and Composition Distribution of Fine Particulate Matter Emitted from Motor Vehicles; *Environ. Sci. Technol.* **2000**, *34*, 1132-1142.

17. Kittelson, D.B. Engines and Nanoparticles: A Review. *J. Aerosol Sci.* **1998**, *29(5-6)*, 575-588.

18. Schauer, J.J.; Kleeman, M.J.; Cass, G.R.; Simoneit, B.R.T. Measurement of Emissions from Air Pollution Sources. 3. C-1-C-29 Organic Compounds from Fireplace Combustion of Wood; *Environ. Sci. Technol.* **2001**, *35*, 1716-1728.

19. Kleeman, M.J.; Hughes, L.S.; Allen, J.O.; Cass, G.R. Source Contributions to the Size and Composition Distribution of Atmospheric Particles: Southern California in September 1996; *Environ. Sci. Technol.* **1999**, *33*, 4331-4341.

20. Kulmala, M.; Vehkamäki, H.; Petäjä, T.; Dal Maso, M.; Lauri, A.; Kerminen, V.M.; Birmili, W.; McMurry, P.H. Formation and Growth Rates of Ultrafine Atmospheric Particles; A Review of Observations; *J. Aerosol Sci.* **2004**, *35*, 143-176.

21. Stanier, C.O.; Khlystov, A.Y.; Pandis, S.N. Investigation of Nucleation Bursts during the Pittsburgh Air Quality Study. In *Abstracts of the Sixth Aerosol Conference,* 2002; pp 1291-1292.

22. Shi, J.P.; Qian, Y. Continuous Measurements of 3 nm to 10 nm Aerosol Size Distributions in St. Louis. M.S. Thesis, Department of Mechanical Engineering, University of Minnesota, Minneapolis, MN, 2003.

23. Birmili, W.; Berresheim, H.; Plass-Dulmer, C.; Elste, T.; Gilge, S.; Wiedensohler, A.; Uhrner, U. The Hohenpeissenberg Aerosol Formation Experiment (HAFEX): A Long-Term Study Including Size-Resolved Aerosol, H2SO4, OH, and Monoterpenes Measurements; *Atmos. Chem. Phys.* **2003**, *3*, 361-376.

24. Kim, S.; Shen, S.; Sioutas, C.; Zhu, Y.F.; Hinds, W.C. Size Distribution and Diurnal and Seasonal Trends of Ultrafine Particles in Source and Receptor Sites of the Los Angeles Basin; *J. Air & Waste Manage. Assoc.* **2002**, *52*, 297-307.

25. Baumgardner, D.; Raga, G.B.; Muhlia, A. Evidence for the Formation of CCN by Photochemical Processes in Mexico City; *Atmos. Environ.* **2004**, *38*, 357-367.

26. Fine, P.M.; Shen, S.; Sioutas, C. Inferring the Sources of Fine and Ultrafine Particulate Matter at Downwind Receptor Sites in the Los Angeles Basin Using Multiple Continuous Measurements; *Aerosol Sci. and Technol.* **2004**, *38*, 182-195.

27. Zhang, K.M.; Wexler, A.S. A Hypothesis for Growth of Fresh Atmospheric Nuclei; *J. Geophys. Res.–Atmos.* **2002**, *107*(D21), Art. No. 4577.

28. Fine, P.M.; Jaques, P.A.; Hering, S.V.; Sioutas, C. Performance Evaluation and Use of a Continuous Monitor for Measuring Size-Fractionated $PM_{2.5}$ Nitrate; *Aerosol Sci. Technol.* **2003**, *37*, 342-354.

29. Wahlin, P.; Palmgren, F.; Van Dingenen, R. Experimental Studies of Ultrafine Particles in Streets and the Relationship to Traffic; *Atmos. Environ.* **2001**, *35*, S63-S69.

30. Sarnat, J.A.; Schwartz, J.; Catalano, P.J.; Suh, H.H. Gaseous Pollutants in Particulate Matter Epidemiology: Confounders or Surrogates?; *Environ. Health Perspect.* **2001**, *109*, 1053-1061.

31. Holloway, T.; Levy, H.; Kasibhatla, P. Global Distribution of Carbon Monoxide; *J. Geophys. Res.–Atmos.* **2000**, *105*, 12123-12147.

32. Hughes, L.S.; Allen, J.O.; Salmon, L.G.; Mayo, P.R.; Johnson, R.J.; Cass, G.R. Evolution of Nitrogen Species Air Pollutants along Trajectories Crossing the Los Angeles Area; *Environ. Sci. Technol.* **2002**, *36*, 3928-3935.

33. Kreisberg, N.M.; Stolzenburg, M.R.; Hering, S.V.; Dick, W.D.; McMurry, P.H.A. New Method for Measuring the Dependence of Particle Size Distributions on Relative Humidity, With Application to the Southeastern Aerosol and Visibility Study; *J. Geophys. Res.—Atmos.* **2001**, *106*, 14935-14949.

34. Park, K.; Cao, F.; Kittelson, D.B.; McMurry, P.H. Relationship between Particle Mass and Mobility for Diesel Exhaust Particles; *Environ. Sci. Technol.* **2003**, *37*, 577-583.

35. Peters, J.M.; McConnell, R.; Berhane, K.; Millstein, J.; Lurmann, F.; Gauderman, J.; Avol, E.; Gilliland, F.; Thomas, D. Air Pollution and the Incidence, Prevalence and Severity of Childhood Asthma: Results from the Southern California Children's Health Study; *Epidemiology* **2002**, *13*, S132-S132.

36. Kunzli, N.; McConnell, R.; Bates, D.; Bastain, T.; Hricko, A.; Lurmann, F.; Avol, E.; Gilliland, F.; Peters, J. Breathless in Los Angeles: The Exhausting Search for Clean Air; *Am. J. Public Health* **2003**, *93*, 1494-1499.

37. Allen, J.O.; Hughes, L.S.; Salmon, L.G.; Mayo, P.R.; Johnson, R.J.; Cass, G.R. *Characterization and Evolution of Primary and Secondary Aerosols during $PM_{2.5}$ and PM_{10} Episodes in the South Coast Air Basin*; Report A-22 to the Coordinating Research Council: Alpharetta, GA, 2000.

38. Hughes, L.S.; Allen, J.O.; Bhave, P.; Kleeman, M.J.; Cass, G.R.; Liu, D.Y.; Fergenson, D.F.; Morrical, B.D.; Prather, K.A. Evolution of Atmospheric Particles along Trajectories Crossing the Los Angeles Basin; *Environ. Sci. Technol* **2000**, *34*, 3058-3068.

39. Moore, D.S.; Mccabe, G.P. Introduction to the Practise of Statistics; W.H. Freeman: New York, NY, 1998; p 696.

40. Ketzel, M.; Wahlin, P.; Berkowicz, R.; Palmgren, F. Particle and Trace Gas Emission Factors under Urban Driving Conditions in Copenhagen Based on Street and Roof-Level Observations; *Atmos. Environ.* **2003**, *37*, 2735-2749.

41. Noble, C.A.; Mukerjee, S.; Gonzales, M.; Rodes, C.E.; Lawless, P.A.; Natarajan, S.; Myers, E.A.; Norris, G.A.; Smith, L.; Ozkaynak, H.; Neas, L.M. Continuous Measurement of Fine and Ultrafine Particulate Matter, Criteria Pollutants and Meteorological Conditions in Urban El Paso, Texas; *Atmos. Environ.* **2003**, *37*, 827-840.

42. Morawska, L.; Thomas, S.; Bofinger, N.; Wainwright, D.; Neale, D. Comprehensive Characterization of Aerosols in a Subtropical Urban Atmosphere: Particle Size Distribution and Correlation with Gaseous Pollutants; *Atmos. Environ.* **1998**, *32*, 2467-2478.

43. Wehner, B.; Wiedensohler, A. Long Term Measurements of Submicrometer Urban Aerosols: Statistical Analysis for Correlations with Meteorological Conditions and Trace Gases; *Atmos. Chem. Phys.* **2003**, *3*, 867-879.

44. Pandis, S.N.; Harley, R.A.; Cass, G.R.; Seinfeld, J.H. Secondary Organic Aerosol Formation and Transport; *Atmos. Environ. Part A—General Topics* **1992**, *26*, 2269-2282.

45. Weber, R.J.; Marti, J.J.; McMurry, P.H.; Eisele, F.L.; Tanner, D.J.; Jefferson, A. Measurements of New Particle Formation and Ultrafine Particle Growth Rates at a Clean Continental Site; *J. Geophys. Res.—Atmos.* **1997**, *102*, 4375-4385.

46. Harrison, R.M.; Jones, M.; Collins, G. Measurements of the Physical Properties of Particles in the Urban Atmosphere; *Atmos. Environ.* **1999**, *33*, 309-321.

47. Shi, J.P.; Harrison, R.M. Investigation of Ultrafine Particle Formation during Diesel Exhaust Dilution; *Environ. Sci. Technol.* **1999**, *33*, 3730-3736.

48. Harrison, R.M.; Shi, J.P.; Xi, S.H.; Khan, A.; Mark, D.; Kinnersley, R.; Yin, J.X. Measurement of Number, Mass and Size Distribution of Particles in the Atmosphere; *Phil. Trans. Royal Soc. London Series A—Math. Phys. Eng. Sci.* **2000**, *358*, 2567-2579.

About the Authors

Dr. Constantinos Sioutas is a professor, Dr. Philip M. Fine is a research assistant professor, and Satya B. Sardar and Heesong Yoon are Ph.D. students of environmental engineering at the University of Southern California. Address correspondence to: Dr. Constantinos Sioutas, Department of Civil and Environmental Engineering, University of Southern California KAP-210, 3620 S. Vermont Ave., Los Angeles, CA 90089; e-mail: sioutas@usc.edu.

Air Quality Impacts of the October 2003 Southern California Wildfires

Harish C. Phuleria[1], Philip M. Fine[1], Yifang Zhu[2], and Constantinos Sioutas[1,*]

[1]Department of Civil and Environmental Engineering, University of Southern California, 3620 S. Vermont Avenue, Los Angeles, CA 90089

[2]University of California, Los Angeles, Department of Environmental Health Sciences, 650 Charles E. Young Drive South, Los Angeles, CA 90095

[*] **Author to whom correspondence should be addressed (E-mail: sioutas@usc.edu)**

Abstract

In Southern California, dry summers followed by hot and dry westerly wind conditions contribute to the region's autumn fire season. In late October of 2003, 13 large Southern California wildfires burned more than 750,000 acres of land, destroyed over 3,500 structures, and displaced approximately 100,000 people. The fire episode was declared the deadliest and most devastating in more than a decade, and local media advised individuals to stay indoors to avoid exposure to excessive levels of PM, CO, VOCs, and ozone caused by the wildfires. This study examines the actual impact of these wildfires on air quality in urban Los Angeles using "opportunistic" data from other air pollution studies being conducted at the time of the fires. Measurements of pollutant gases (CO, NO_x, and ozone), particulate matter (PM), particle number concentrations (PN) and particle size distributions at several sampling locations in the LA basin before, during, and after the fire episode are presented. In general, the wildfires caused the greatest increases in PM_{10} levels (a factor of 3-4) and lesser increases in CO, NO, and PN (a factor of up to 2). NO_2 levels remained essentially unchanged and ozone concentrations dropped during the fire episode. Particle size distributions of air sampled downwind of the fires showed number modes at diameters between 100 and 200 nm, significantly larger than that of typical urban air. The particles in this size range were shown to effectively penetrate indoors, raising questions about the effectiveness of staying indoors to avoid exposure to wildfire emissions.

Introduction

Wildfires can produce substantial increases in the concentration of gaseous pollutants such as carbon monoxide (CO), nitrogen oxides (NO$_x$), ozone (O$_3$), and volatile organic compounds (VOCs) [*Cheng et al.*, 1998; *Crutzen and Andreae*, 1990] as well as particulate matter (PM) [*Dennis et al.*, 2002; *Lighty et al.*, 2000]. In recent years, there has been much interest in studying the impact of wildfires in elevating the concentrations of pollutants in the atmosphere. For instance, high CO concentrations that occurred episodically in the Southeastern United States during the summer of 1995 have been attributed to large forest fires in Canada [*Wotawa and Trainer*, 2000]. In addition to regional and local impacts [*Bravo et al.*, 2002] wildfires contribute significantly to global emissions of atmospheric trace gases including NO$_x$, CO, and CO$_2$ [*Crutzen et al.*, 1979]. Concerns arising from PM emissions from wildfires include acute health effects, direct and indirect climate forcing, and regional visibility [*Bravo et al.*, 2002; *LeCanut et al.*, 1996].

Emission inventories by the United States Environmental Protection Agency (US EPA) estimate that, for the calendar year 2001, wildfires in the U.S. emitted 7.1 million tons of CO, 0.98 million tons of VOCs, 0.60 million tons of PM$_{2.5}$, and 0.66 million tons of PM$_{10}$ to the atmosphere (National Emissions Inventory – Air Pollutant Emissions Trends, Current Emission Trends Summaries, August 2003, U.S. Environmental Protection Agency (USEPA), http://www.epa.gov/ttn/chief/trends/index.html). These amounts are significant, contributing 6%, 5%, 8% and 3% of the total CO, VOC, PM$_{2.5}$, and PM$_{10}$ emissions to the atmosphere in the United States in 2001, respectively. These figures obviously vary from year-to-year with the degree of wildfire activity, and in the

severe fire season of 2000, 18% of the total $PM_{2.5}$ emissions in the U.S. were estimated to originate from wildfires. Other emission inventories in specific areas have calculated significant NO_x emissions from wildfires as well [*Dennis et al.*, 2002]. Some systematic studies and source testing have been carried out for prescribed burns and controlled fires in North America [*Einfeld et al.*, 1991; *Radke et al.*, 1991; *Woods et al.*, 1991]. Other studies on wildfire emissions have taken advantage of existing pollution monitoring networks and other focused air pollution studies which happen to be sampling when a wildfire event occurs [*Bravo et al.*, 2002; *Brunke et al.*, 2001; *Cheng et al.*, 1998; *Goode et al.*, 2000; *Nance et al.*, 1993]. Such "opportunistic" studies can provide valuable information on wildfire pollutant emission rates and the impacts on air quality levels.

Dry summers, followed by conditions of hot and dry westerly winds (known as Santa Ana winds) contribute to Southern California's fire season in the autumn months. While the fire season usually starts around the middle of May, the exact date varies from year to year based on weather patterns and the moisture content, distribution, and amount of wild vegetation present. The fire season usually ends when cooler weather and precipitation conditions prevail. This usually occurs towards the end of October, but the fire season is occasionally extended well into January in some Southern California areas (California Department of Forestry and Fire Protection, Fire Statistics, http://www.fire.ca.gov/MiscDocuments/FAQs.asp#13). The presence of thick and dry foliage and bushy chaparral adds to the fire danger in the fire season in Southern California. In general, pollution levels are observed to be high during fire events [*Bravo et al.*, 2002]. The Los Angeles basin is surrounded by high mountains on three sides, opening to the Pacific Ocean to the west and southwest. The topography and frequent

temperature inversions lead to the accumulation of airborne pollutants, particularly in the eastern portion of the basin, due to the prevailing westerly sea breeze [*Lu and Turco*, 1996].

In late October of 2003, 13 large Southern California wildfires, ranging from Simi Valley in the North to San Diego 150 miles to the south, burned more than 750,000 acres of land, destroyed over 3,500 structures, including 2,700 homes, and displaced 100,000 people. Twenty human deaths were attributed to the wildfires. The cost of the damage has been estimated to be US$ 2 billion. The fires having the greatest effect on the air quality of the Los Angeles (LA) Basin included the Grand Prix and Old fires in San Bernardino County and the adjacent Padua fire in Los Angeles County. These fires were located to the northeast of central Los Angeles, with Santa Ana wind conditions, blowing towards the southwest, transporting emissions to the western portions of the Basin. The fuel was predominantly mixed chaparral, California sagebrush, annual grass and canyon live oak. Pine, perennial grass and other urban vegetation were also burned. The fires started around 23 October and had significant impacts on the air quality of the LA basin until 29 October, when the winds reversed direction and resumed their normal on-shore pattern (National Interagency Coordination Centre, 2003, Statistics and Summary, http://www.nifc.gov/news/2003_statssumm/intro_summary.pdf). This fire episode was declared the deadliest and most devastating in more than a decade, and there was a significant level of worldwide press coverage. Local media advised individuals to stay indoors to avoid exposure to excessive levels of PM, CO, VOCs, and ozone caused by the wildfires. This motivated the following analysis that examines the actual impact of these wildfires on air quality and measured pollutant concentrations in urban Los Angeles.

This paper presents measurements of pollutant gases (CO, NO_x, and ozone) as well as PM concentrations and characteristics at different sampling locations in the LA basin before, during, and after the October 2003 fire episode. In addition, the effect of fire on indoor particle concentrations and size distributions was also investigated. Since the fire episode could not be predicted, the current study took advantage of several pre-existing air pollution studies that were being conducted at the time of the wildfires. Given the "opportunistic" nature of these samples, the measurement techniques were not necessarily targeted for fire emissions, and not all of the data is complete in all sampling sites.

Methods

As part of the routine sampling of an ongoing study associated with the University of Southern California (USC) Children's Health Study (CHS), supported by the South Coast Air Quality Management District and the California Air Resources Board, concentrations of carbon monoxide (CO), ozone (O_3), nitrogen oxide (NO), nitrogen dioxide ($NO_{2,}$), particulate matter with aerodynamic diameters less than 10 μm (PM_{10}) and particle number (PN) are continuously measured in several locations in Southern California. Continuous data were collected concurrently throughout the calendar year 2003, and five sites within the LA Basin impacted by the wildfires were examined in this study: Long Beach, Glendora, Mira Loma, Upland and Riverside (see Figure 1). The choice of these sampling sites was based on their location within the Los Angeles Basin, the availability of the data for the desired period, and the observed impacts of the Grand Prix, Old and Padua fires. Generally, these urban sites are the most polluted among the monitoring sites of the CHS.

Located near a busy surface street, the Long Beach station is about 1 km northeast of a major freeway. The Glendora station is located in a residential area nestled in the foothills of the San Gabriel Mountains. It is at least 1 km away from major roadways and 3 km from the nearest freeway. The Upland site is also located in a residential area about 6 km downwind of the Glendora site, but is located within 1 km of the I-210 freeway. The Mira Loma site is located in a building on the Jurupa Valley High School campus. It is directly east of a major freeway interchange, is surrounded by several major warehouse facilities, and is located about 80 km east of downtown Los Angeles. The sampling location at Riverside is within the Citrus Research Center and Agricultural Experiment Station (CRCAES), a part of the University of California, Riverside. It is about 10 km southeast of the Mira Loma site and is situated upwind of surrounding freeways and major roads.

The concentrations of CO were measured near-continuously by means of a Thermo Environmental Inc. Model 48C trace level CO monitor. Concentrations of NO and NO_2 were measured with a Continuous Chemiluminescence Analyzer (Monitor Labs Model 8840), and O_3 concentrations were monitored using a UV photometer (Dasibi Model 1003 AH). Total particle number concentrations (greater than about 10 nm in diameter) were measured continuously by a Condensation Particle Counter (CPC, Model 3022/A, TSI Incorporated, St. Paul, MN) set at a flow rate of 1.5 L min^{-1}. At the Upland site, the CPC was connected to a Scanning Mobility Particle Sizer (SMPS, Model 3936, TSI Incorporated, St. Paul, MN), to measure the size distribution of submicrometer aerosols (15 - 750 nm) using an electrical mobility detection technique. In this configuration, the CPC flow rate was maintained at 0.3 L min^{-1} (with the sheath flow of

the SMPS set at 3 L min^{-1}), and particle number counts were calculated from the SMPS size distributions. Unfortunately, due to a brief power outage and limited site access resulting from the nearby fires, SMPS data was lost from the morning of 24 October to noon of the 29 October (the peak of the fire impact). However, the other monitors at this site continued to function properly in this time window. Continuous particle number and gaseous co-pollutant concentrations were averaged to form 1-hr and 24-hr average values for the subsequent analysis.

Hourly PM_{10} mass concentrations in each site were measured by a low temperature Differential Tapered Element Oscillating Microbalance monitor (low temperature TEOM 1400A, R&P Inc., Albany, NY). The design and performance evaluation of this monitor is described in greater detail by *Jaques et al.* [2004]. Briefly, the system consists of a size-selective PM_{10} inlet, followed by a Nafion$^{®}$ dryer that reduces the relative humidity of the sample aerosol to 50% or less. Downstream from the Nafion dryer and ahead of the TEOM sensor is an electrostatic precipitator (ESP) allowing for the removal of particles from the sample stream. The ESP is alternately switched on and off, for equal time periods of about 10 minutes. This dual sampling channel design makes it possible to account for effects such as volatilization of labile species, adsorption of organic vapors and changes in relative humidity and temperature, all of which affect the TEOM signal. The study by *Jaques et al.* [2004] showed that the time averaged TEOM PM_{10} mass concentrations agreed within ± 10% with those of collocated Federal Reference Methods (FRM).

In addition to the data collected at the CHS sites, semi-continuous $PM_{2.5}$ (fine) and ultrafine PM mass concentrations were measured at the Southern California Supersite

located near downtown Los Angeles at the University of Southern California (USC). Two-hour PM mass concentration data was collected with a Beta Attenuation Monitor (BAM, Model 1020, Met One instruments, Inc., OR) [*Chung et al.,* 2001]. The BAM consisted of a size-selective inlet (2.5 µm for fine and 0.15 µm for ultrafine) [*Chakrabarti et al.,* 2004], a filter tape, a beta radiation source, and a beta radiation detector. The difference in the transmission of beta radiation through the filter tape before and after a particulate sample has been collected, is measured and used to determine the mass of collected particulate matter. Continuous operation is achieved by automatic advancement of the filter tape between sampling periods.

Finally, in a concurrent but unrelated study, particle size distributions were measured indoors and outdoors of a two-bedroom apartment in the Westwood Village area near the University of California, Los Angeles. The residence is located about 100 m mostly downwind (east) of the I-405 freeway, a very busy traffic source. A Scanning Mobility Particle Sizer (SMPS 3936, TSI Inc., St. Paul., MN) was set up in a bedroom and sampled alternating indoor and outdoor size distributions on a 24-hr basis. The aerosol sampling flow rate of the SMPS was set to 1.5 L min^{-1} in order to measure particles as low as 6 nm as well as to minimize the diffusion losses of ultrafine particles during sampling. The maximum size detectable at these settings was 220 nm, and a scan time of 180 s was used. The sampling lines were kept the same length and as short as possible (1.5 m) for both indoor and outdoors samples. Measurements were made through a switching manifold that alternately sampled indoor and outdoor air, each for 9-minute periods, in which three size distributions were taken in sequence. There were no known major indoor sources of aerosols in the residence for the period from 10 am to 7 pm,

when the residents were at work and from 11 pm to 7 am when the residents were asleep in the other bedroom. The door of the sampling bedroom was always kept closed to minimize the influence of any other possible indoor activity. The residence was under natural ventilation with windows closed at all times during the sampling period. This study provided a unique opportunity to monitor infiltration of PM of outdoor origin into the indoor environment, and to estimate indoor exposures to PM from the wildfires.

Results and Discussion

Figures 2a-e present the 24-hour average concentrations of CO, NO, NO_2, O_3, PM_{10} and particle number (PN) before, during and after the October fire period in Southern California at the five CHS sampling sites examined in this study. A summary of the average concentrations of the pollutants before, during and after the fire is given in Table1. As surmised from the news reports and the data, the period of fire influence was from the 23–29 October. Figure 2 clearly shows that the concentrations of all the pollutants drastically decreased on 30 October and then increased back to more typical levels by 4 or 5 November. The rapid decline is associated with the wind reversal on the afternoon of 29 October when an on-shore wind pattern replaced the Santa Ana conditions, followed by rainfall on 30 and 31 October. Figure 3a displays a satellite photo from NASA Earth Observatory on 28 October 2003 showing the extent of the fires and the prevailing wind direction during the peak of the fire episode. On 29 October, the winds shifted to an on-shore pattern (Figure 3b) blowing fresh fire emissions towards the east away from the LA Basin. The fires continued to burn for many days after, but the cooler and wetter weather helped the firefighting effort and the fires were under control within another week.

The data summary in Table 1 indicates that with the exceptions of NO_2 and O_3, the concentrations of CO, NO, PM_{10} and PN during the fire event were significantly higher (at the p=0.05 level) than their respective values preceding the fire event. Statistical comparisons between during and post-fire concentrations was not conducted, because, as evident from the data in Table 1 and Figure 2, the unstable and wet weather conditions during the week of 30 October to 5 November resulted in lower than average air pollutant concentrations. It is of particular note, however, that the most dramatic increase in the concentrations of any pollutant during the fire events was observed for the PM_{10} concentrations, which, with the exception of one site (Glendora), rose by almost three to four-fold in all sites during this period. While typical PM_{10} concentrations in Los Angeles are on the order of 50 μg m^{-3} or less [*Christoforou et al.*, 2000], levels rose to near or above 200 μg m^{-3} at some sites during the fires. PM_{10} levels at Glendora did not rise to the same degree, possibly due to the site's location at the base of a canyon in the San Gabriel Mountains. The Santa Ana winds tend to blow down the mountain canyons, and there was little or no fire activity in or upwind of this particular canyon. Upland, on the other hand, was within 2-3 kilometers and directly downwind of extreme wildfire activity. The other three sites were all further downwind from the wildfires, but all sites experienced atypical PM_{10} levels. It is possible that the higher wind speeds during Santa Ana conditions increased re-suspended dust emissions that contributed to the elevated PM_{10} levels. This effect, if dominant, should be observed at all sites. However, the fact that Glendora PM_{10} levels remained within the "typical" range indicates that the impact of fire smoke plumes is the main cause of the elevated PM_{10} levels. Previously reported

data during Santa Ana events without fires also demonstrate that such high levels of PM_{10} are not typically observed on a 24-hour basis [*Geller et al., 2003*, in press].

By contrast, the total particle number concentrations, also shown in Figure 2, did not exhibit the same extreme concentration increases during the fires. PN levels increased significantly only in Mira Loma and perhaps Riverside, and only by an approximate factor of two. Even these higher levels of PN have been observed on occasion under typical, non-fire influenced, conditions in the LA Basin [*Kim et al.*, 2002]. No significant increase in PN was observed at Long Beach, and Glendora, the latter being minimally affected by the fires as discussed above. Due to the aforementioned power outage, PN data was not available at the closest site to the fires, Upland, during the wildfire period. Emissions testing of foliar fuels demonstrate that high particle number levels are emitted from these sources. However, given the observed high PM mass levels, and thus the increased PM surface area in the fire smoke plumes, it is conceivable that emitted smaller particles are scavenged by coagulation with larger particles in the smoke plume [*Formenti et al.*, 2003]. This process may occur over the few hours that it takes for the fire particles to reach our sampling sites. Many of the smaller particles, which make up the majority of particle number concentrations, may no longer exist as individual particles. Thus, PM mass levels remain high while PN levels are diminished. This hypothesis may explain why the largest PN increase was seen at Mira Loma and Riverside, both of which are much closer to the fire areas than the sites further downwind such as Long Beach.

Similar to particle number, CO concentrations at these sites were only modestly affected by the fires. With the exception of Glendora, the observed increases were

statistically significant at the p=0.05 level, but the degree of increase was much less than that observed for PM_{10}. Mira Loma, Upland and Long Beach experienced CO around twice normal levels during the fire. As in the case of PN, CO concentrations in the area of Glendora appear to be unaffected by the fire events. The relatively low increase in CO due to the fires can be explained by other, more significant sources of CO in Los Angeles. Emission factors from the USEPA (AP-42, Fifth Edition, Volume I – Chapter 13.1: Wildfires and Prescribed Burning, USEPA, October 1996) and other studies [*Barbosa et al.*, 1999; *Pereira et al.*, 1999; *Scholes et al.*, 1996] show that the ratio of CO mass to PM_{10} mass in wildfire emissions lies typically between 8-16. The same ratio for various motor vehicles under varying driving conditions is much higher, ranging from about 200 to over 2000 [*Cadle et al.*, 2001; *Chase et al.*, 2000]. In urban areas dominated by vehicular sources, wildfires will thus affect ambient levels of CO to a lesser degree than the ambient levels of PM_{10}. A review of historical pollutant data during Santa Ana conditions without fire activity (9 February 2002 and 6 January 2003) shows that CO levels can diminish due to fewer CO sources upwind and increased basin ventilation. However, this effect is inconsistent, and varies greatly with sampling site and from event to event. Thus, no true "Santa Ana baseline" can be established for comparison purposes. For this reason, comparisons are limited to the "typical" conditions before the fire episode.

NO concentrations follow similar trends with those for CO and PN (i.e. they increase significantly in every location during the fire) but this increase is on the order of two-fold or less, hence smaller than the increase observed for PM_{10}. While the increase in NO concentrations during the fire event seems to be minor at the Riverside location, the

12

nearby Mira Loma site shows more than double the NO levels relative to levels before the fire events. It is possible that Mira Loma may have been more directly downwind of fire areas than Riverside, which would explain this discrepancy. This is supported by the observed PM_{10} levels at these two sites, which also increased more dramatically in Mira Loma than in Riverside. Relative to NO, PN, and PM_{10}, the effect of fires was negligible for NO_2 as the concentrations did not change significantly in any of the five sampling sites during the fire events. While some NO_2 is emitted directly from combustion processes, most of the NO_2 in urban air is formed in the atmosphere by the reaction of NO with ozone. Under normal conditions in Los Angeles, NO, and thus NO_2 levels are dominated by diesel vehicle emissions [*Fujita et al.*, 2003]. However, the NO increases observed during the fires were not accompanied by corresponding increases in NO_2 concentrations. Although no conclusive explanation can be determined from the current data, it is possible that the PM in the fire smoke blanketing the LA basin blocked incoming solar radiation and thus reduced photochemical activity in the atmosphere. This would result in lower ozone levels and thus, lower observed levels of NO_2. Increased concentrations of organic gases (VOCs) emitted by the fires may also play a role in the complex atmospheric chemistry of NO, NO_2, and ozone [*Cheng et al.*, 1998]. Interestingly, with the exception of Glendora, which experienced marginally (but not significant) increased O_3 concentrations during the fire episode, the concentrations of O_3 decreased by about 25-50% at all the other sites during the fire period. As mentioned above, the fire smoke covering the basin and the corresponding reduction in photochemical activity may be a possible explanation for this decrease in concentration.

The effect of the wind direction change can also be seen in the hourly concentrations of the measured pollutants in Upland as shown in Figures 4a and b. The high concentrations of PM_{10} at Upland can be clearly seen during the entire fire period, with the highest hourly concentration measured at 769 µg m^{-3}. On October 29th, at 12:00 P.M., the PM_{10} level was 153 µg m^{-3} and within one hour it dropped to 65 µg m^{-3}. Within four hours, PM_{10} concentrations dropped to below 20 µg m^{-3}. This marks the time of the wind reversal mentioned above. Unfortunately, hourly data of particle number concentrations in this time frame are not available due to the power outage. Similar to the 24-hr data, the hourly gaseous pollutant levels did not increase as much as the PM_{10} levels during the period of wildfire influence. However, with the exception of ozone, concentrations of all the gaseous pollutants dropped precipitously when the wind reversal occurred.

Semi-continuous ultrafine and fine ($PM_{2.5}$) particle mass concentration data support the argument that the atmospheric concentrations of smaller particles (measured above as PN), increased to a lesser extent than the larger particles. Figure 5 displays the 2-hour ultrafine and fine PM mass obtained from the BAM measurements at the USC site. The average ultrafine particle mass concentrations increased from an average value of 5.4 ($\pm$ 2.3) to 6.9 ($\pm$ 2.7) µg m^{-3}. While this increase is statistically significant ($p<0.01$), it is still less dramatic than the obvious increase in $PM_{2.5}$ during the fire events. The average concentration of $PM_{2.5}$ more than doubled, from 19.1 ($\pm$ 5.2) to 51.3 ($\pm$ 26.1) µg m^{-3}. The highest fine particle mass measured during the fire episode at USC was 115 µg m^{-3}. The wind reversal was marked by a steep reduction in fine particle mass midday

on 29 October when the fine PM dropped from 105 µg m^{-3} in the morning to 25 µg m^{-3} by 2:00 P.M.

Figures 6a and b show the one-hour averaged particle size distribution at Upland corresponding to the times marked by vertical lines in Figure 4(a). Because of the loss of SMPS data for almost entire fire period, we have selected times just before (Figure 6a) and just after (Figure 6b) the power outage. The particle size distribution at a given hour (10 A.M and 12 P.M.) was averaged for different days before and after the fire, and compared to the same hour during the influence of the fires. It can be seen that the size distribution corresponding to the periods of fire influence significantly differs from those without the fire influence. The mode in the number-based particle size distribution spans from 100 to 300 nm and is indicative of the wildfire smoke. Previous emissions testing have shown similarly large number modes in the particle size distributions from the burning of foliar fuels [*Hays et al.*, 2002]. Such large diameter number modes are not normally seen in urban locations (Kim et al. 2002) where particle number concentrations are dominated either by primary vehicular emissions or by nucleation processes [*Woo et al.*, 2001]. Since particle volume is proportional to the cube of the diameter, a modest increase in particle number concentrations in these larger size modes is sufficient to account for the larger increases observed for PM mass.

Indoor and outdoor particle number size distributions were also available from a concurrent study near UCLA in the western portion of the Los Angeles Basin. Figures 7a and b display ambient and corresponding indoor particle size distributions from 11 pm-midnight for different days during and after the fire events. This period was selected to minimize the influence of any possible indoor sources (i.e., cooking, cleaning) and

outdoor traffic from the nearby freeway. The effect of the fires on indoor concentration is evident, with an aerosol mode diameter at about 200 nm on 26 and 28 October, and then a shift to a lower size range (between 50 to 70 nm) on 30 October and 1 November, respectively. Number concentrations both indoors and outdoors also decrease as we move away from the fire period. It is of interest to note that on 26 October (i.e., in the middle of the wildfire period), the indoor and outdoor size distributions are virtually identical in both number concentration and mode, which suggests that the majority of the outdoor aerosol infiltrated indoors with a penetration value close to 1. This is not a surprising result, considering that based on our measurements, the majority of the particles emitted from the fire are in the 100 – 300 nm range. This is also the range of maximum indoor penetration of outdoor aerosols and minimum indoor deposition rate [*Allen et al.*, 2003; *Long et al.*, 2001]. As the mode in aerosol size distributions shifts to smaller sizes, the indoor concentrations are approximately 50 – 75% lower than outdoors, which is also consistent with the penetration values determined by *Long et al.*, [2001] and *Wallace and Howard-Reed*, [2002] for the particles in the 40 – 80 nm range.

To put the above results in perspective, Figures 8a and b show the measured indoor and outdoor particle size distributions during the morning traffic commute period, from 6 A.M. to 7 A.M., while the wildfires were still active (27 October) and after the fire event (November 4). The outdoor size distribution on 27 October is characterized by one dominant mode at about 25 nm, which is associated with vehicular emissions [*Zhu et al.*, 2002a; *Zhu et al.*, 2002b], followed by a second mode at about 200 nm, which reflects the influence of the wildfires. The indoor size distribution for that date (Figure 8a) shows that the super-100 nm particles are virtually at identical concentrations with their

corresponding outdoor levels, whereas the concentrations of smaller particles indoors are substantially lower than those outdoors. Similar trends are also shown in Figure 8b, with the exception that the second mode in the 200 nm range observed during the fire period no longer exists in either the indoor or outdoor environment.

The data plotted in Figures 8a and b indicates an average outdoor-to-indoor penetration ratio of about 0.15 to 0.20 for particles in the 20-50 nm range, which, as stated above, originate from nearby traffic sources. This value is somewhat lower than the indoor penetration ratios reported by *Long et al.*, [2001] and *Wallace and Howard-Reed*, [2002] for that size range, which normally range between 0.3 – 0.7, depending on home characteristics and air exchange rates. One possible explanation for the lower values observed in our study may be that, as shown in recent reports in the literature [*Sakurai et al.*, 2003; *Tobias et al.*, 2001], sub-50 nm particles from vehicular emissions consist of semi-volatile material, compared to the mostly non-volatile particles in the 50-100 nm range. Thus, after penetrating indoors, they may have completely evaporated or shrunk to sizes below about 6 nm, the lower size detection limit of the SMPS. It is unknown what source, size or composition of ambient PM is responsible for the observed health effects. But our results show that the prevailing advice during the fire episode for people to stay indoors may not be effective in reducing exposure to most of the particles emitted from wildfires.

Summary and Conclusions

Coincidental air pollution sampling campaigns proved valuable in determining the impacts of the October, 2003 wildfire episode on pollutant levels in the Los Angeles

Basin. The greatest impact was observed on PM_{10} concentrations which increased by factors of three or four depending on location. CO and NO levels increased to a lesser extent (a factor of approximately two), most likely due to the different relative emission rates of these pollutants from wildfires compared to typical urban sources such as traffic. Particle number concentrations and NO_2 were essentially unchanged, except at the sites nearest the fires where PN levels almost doubled. Ozone levels during the fires were observed to be lower during the fires at some sites, a possible result of light scattering by the smoke plume reducing photochemical activity levels. Particle number distributions downwind of the fires displayed number modes with diameters between 100 and 200 nm, larger than typical urban aerosol and explaining the larger increases in PM_{10} and $PM_{2.5}$ mass concentrations than that for ultrafine particle mass and particle number. These particles were also shown to penetrate effectively indoors, calling into question the prevailing advice to the public to remain inside to avoid exposure to harmful wildfire emissions.

Acknowledgments

References

Allen, R., T. Larson, L. Sheppard, L. Wallace, and L.J.S. Liu (2003), Use of real-time light scattering data to estimate the contribution of infiltrated and indoor-generated particles to indoor air, *Environmental Science & Technology*, *37* (16), 3484-3492.

Barbosa, P.M., D. Stroppiana, J.M. Gregoire, and J.M.C. Pereira (1999), An assessment of vegetation fire in Africa (1981-1991): Burned areas, burned biomass, and atmospheric emissions, *Global Biogeochemical Cycles*, *13* (4), 933-950.

Bravo, A.H., E.R. Sosa, A.P. Sanchez, P.M. Jaimes, and R.M.I. Saavedra (2002), Impact of wildfires on the air quality of Mexico City, 1992-1999, *Environmental Pollution*, *117* (2), 243-253.

Brunke, E.G., C. Labuschagne, and H.E. Scheel (2001), Trace gas variations at Cape Point, South Africa, during May 1997 following a regional biomass burning episode, *Atmospheric Environment*, *35* (4), 777-786.

Cadle, S.H., P. Mulawa, P. Groblicki, C. Laroo, R.A. Ragazzi, K. Nelson, G. Gallagher, and B. Zielinska (2001), In-use light-duty gasoline vehicle particulate matter emissions on three driving cycles, *Environmental Science & Technology*, *35* (1), 26-32.

Chakrabarti, B., M. Singh, and C. Sioutas (2004), Development of a continuous monitor for measuring the mass concentration of ultrafine PM, *Aerosol Science & Technology*, in press.

Chase, R.E., G.J. Duszkiewicz, T.E. Jensen, D. Lewis, E.J. Schlaps, A.T. Weibel, S. Cadle, and P. Mulawa (2000), Particle mass emission rates from current-technology, light-duty gasoline vehicles, *Journal of the Air & Waste Management Association*, *50* (6), 930-935.

Cheng, L., K.M. McDonald, R.P. Angle, and H.S. Sandhu (1998), Forest fire enhanced photochemical air pollution. A case study, *Atmospheric Environment*, *32* (4), 673-681.

Christoforou, C.S., L.G. Salmon, M.P. Hannigan, P.A. Solomon, and G.R. Cass (2000), Trends in fine particle concentration and chemical composition in Southern California, *Journal of the Air & Waste Management Association*, *50* (1), 43-53.

Chung, A., D. P. Y. Chang, M. J. Kleeman, K. D. Perry, T. A. Cahill, D. Dutcher, E. M. McDougall and K. Stroud (2001), Comparison of real time instruments used to monitor airborne particulate matter, *Journal of the Air & Waste Management Association*, *51* (1), 109-120.

Crutzen, P.J., and M.O. Andreae (1990), Biomass Burning in the Tropics - Impact on Atmospheric Chemistry and Biogeochemical Cycles, *Science*, *250* (4988), 1669-1678.

Crutzen, P.J., L.E. Heidt, J.P. Krasnec, W.H. Pollock, and W. Seiler (1979), Biomass Burning as a Source of Atmospheric Gases CO, H_2, N_2O, NO, CH_3Cl and COS, *Nature*, *282* (5736), 253-256.

Dennis, A., M. Fraser, S. Anderson, and D. Allen (2002), Air pollutant emissions associated with forest, grassland, and agricultural burning in Texas, *Atmospheric Environment*, *36* (23), 3779-3792.

Einfeld, W., D.E. Ward, and C.C. Hardy (1991), Effects of Fire Behaviour on Prescribed Fire Smoke Characteristics: A Case Study, *Global Biomass Burning: Atmospheric, Climatic, and Biospheric Implications*, edited by J. S. Levine, pp. 412-419, MIT Press, Cambridge, Mass.

Formenti, P., W. Elbert, W. Maenhaut, J. Haywood, S. Osborne, and M.O. Andreae (2003), Inorganic and carbonaceous aerosols during the Southern African Regional Science Initiative (SAFARI 2000) experiment: Chemical characteristics, physical properties, and emission data for smoke from African biomass burning, *Journal of Geophysical Research-Atmospheres*, *108* (D13), 8576.

Fujita, E.M., D.E. Campbell, B. Zielinska, J.C. Sagebiel, J.L. Bowen, W.S. Goliff, W.R. Stockwell, and D.R. Lawson (2003), Diurnal and weekday variations in the source contributions of ozone precursors in California's South Coast Air Basin, *Journal of the Air & Waste Management Association*, *53* (7), 844-863.

Geller M.D., P.M. Fine, and C. Sioutas (2003), The relationship between real-time and time-integrated coarse (2.5-10 mm) intermodal (1.0-2.5 mm) and fine particulate matter (<2.5 mm) in the Los Angeles basin, *Journal of the Air & Waste Management Association*, in press.

Goode, J.G., R.J. Yokelson, D.E. Ward, R.A. Susott, R.E. Babbitt, M.A. Davies, and W.M. Hao (2000), Measurements of excess O_3, CO_2, CO, CH_4, C_2H_4, C_2H_2, HCN, NO, NH_3, HCOOH, CH_3COOH, HCHO, and CH_3OH in 1997 Alaskan biomass burning plumes by airborne fourier transform infrared spectroscopy (AFTIR), *Journal of Geophysical Research-Atmospheres*, *105* (D17), 22147-22166.

Hays, M.D., C.D. Geron, K.J. Linna, N.D. Smith, and J.J. Schauer (2002), Speciation of gas-phase and fine particle emissions from burning of foliar fuels, *Environmental Science & Technology*, *36* (11), 2281-2295.

Jaques, P. A., J. L. Ambs, and C. Sioutas (2004), Field evaluation of the differential TEOM monitor for continuous $PM_{2.5}$ mass concentrations, *Aerosol Science & Technology*, in press.

Kim, S., S. Shen, C. Sioutas, Y.F. Zhu, and W.C. Hinds (2002), Size distribution and diurnal and seasonal trends of ultrafine particles in source and receptor sites of the Los Angeles basin, *Journal of the Air & Waste Management Association*, *52* (3), 297-307.

LeCanut, P., M.O. Andreae, G.W. Harris, F.G. Wienhold, and T. Zenker (1996), Airborne studies of emissions from savanna fires in southern Africa .1. Aerosol emissions measured with a laser optical particle counter, *Journal of Geophysical Research-Atmospheres*, *101* (D19), 23615-23630.

Lighty, J.S., M.V. John, and F.S. Adel (2000), Combustion aerosols: Factors governing their size and composition and implications to human health, *Journal of the Air & Waste Management Association*, *50*, 1565-1618.

Long, C.M., H.H. Suh, L. Kobzik, P.J. Catalano, Y.Y. Ning, and P. Koutrakis (2001), A pilot investigation of the relative toxicity of indoor and outdoor fine particles: In

vitro effects of endotoxin and other particulate properties, *Environmental Health Perspectives*, *109* (10), 1019-1026.

Lu, R., and R.P. Turco (1996), Ozone distributions over the Los Angeles basin: Three-dimensional simulations with the SMOG model, *Atmospheric Environment*, *30* (24), 4155-4176.

Nance, J.D., P.V. Hobbs, and L.F. Radke (1993), Airborne measurements of gases and particles from an Alaskan wildfire, *Journal of Geophysical Research-Atmospheres*, *98* (D8), 14873-14882.

Pereira, J.M.C., B.S. Pereira, P. Barbosa, D. Stroppiana, M.J.P. Vasconcelos, and J.M. Gregoire (1999), Satellite monitoring of fire in the EXPRESSO study area during the 1996 dry season experiment: Active fires, burnt area, and atmospheric emissions, *Journal of Geophysical Research-Atmospheres*, *104* (D23), 30701-30712.

Radke, L.F., D.A. Hegg, P.V. Hobbs, J.D. Nance, J.H. Lyons, K.K. Laursen, R.E. Weiss, P.J. Riggan, and D.E. Ward (1991), Particulate and Trace gas emissions from Large Biomass Fires in North America, *Global Biomass Burning: Atmospheric, Climatic, and Biospheric Implications*, edited by J. S Levine, pp. 209-224, MIT Press, Cambridge, Mass.

Sakurai, H., K. Park, P.H. McMurry, D.D. Zarling, D.B. Kittelson, and P.J. Ziemann (2003), Size-dependent mixing characteristics of volatile and nonvolatile components in diesel exhaust aerosols, *Environmental Science & Technology*, *37* (24), 5487-5495.

Scholes, R.J., D.E. Ward, and C.O. Justice (1996), Emissions of trace gases and aerosol particles due to vegetation burning in southern hemisphere Africa, *Journal of Geophysical Research-Atmospheres*, *101* (D19), 23677-23682.

Tobias, H.J., D.E. Beving, P.J. Ziemann, H. Sakurai, M. Zuk, P.H. McMurry, D. Zarling, R. Waytulonis, and D.B. Kittelson (2001), Chemical analysis of diesel engine nanoparticles using a nano-DMA/thermal desorption particle beam mass spectrometer, *Environmental Science & Technology*, *35* (11), 2233-2243.

Wallace, L., and C. Howard-Reed (2002), Continuous monitoring of ultrafine, fine, and coarse particles in a residence for 18 months in 1999-2000, *Journal of the Air & Waste Management Association*, *52* (7), 828-844.

Woo, K.S., D.R. Chen, D.Y.H. Pui, and P.H. McMurry (2001), Measurement of Atlanta aerosol size distributions: Observations of ultrafine particle events, *Aerosol Science and Technology*, *34* (1), 75-87.

Woods, D.C., R.L. Chaun, W.R. Cofer III, and J.S. Levine (1991), Aerosol Characterization in Smoke Plumes from a Wetland fire, *Global Biomass Burning: Atmospheric, Climatic, and Biospheric Implications*, *edited by J. S. Levine*, pp. 240-244, MIT Press, Cambridge, Mass.

Wotawa, G., and M. Trainer (2000), The influence of Canadian forest fires on pollutant concentrations in the United States, *Science*, *288* (5464), 324-328.

Zhu, Y.F., W.C. Hinds, S. Kim, S. Shen, and C. Sioutas (2002a), Study of ultrafine particles near a major highway with heavy-duty diesel traffic, *Atmospheric Environment*, *36* (27), 4323-4335.

Zhu, Y.F., W.C. Hinds, S. Kim, and C. Sioutas (2002b), Concentration and size distribution of ultrafine particles near a major highway, *Journal of the Air & Waste Management Association*, *52* (9), 1032-1042.

Table 1: Average hourly concentrations of pollutants with the standard deviation at the five CHS sites before, during and after the fire

	Average Concentration ($\pm$ SD)					
	CO (ppm)	NO (ppb)	NO_2 (ppb)	O_3 (ppb)	PM_{10} (μg m^{-3})	PN (particles cm^{-3})
Pre Fire						
Glendora	9 $\pm$ 3	11 $\pm$ 16	37 $\pm$ 16	37 $\pm$ 21	12 $\pm$ 14	10400 $\pm$ 5500
Long Beach	6 $\pm$ 6	23 $\pm$ 49	47 $\pm$ 19	29 $\pm$ 18	33 $\pm$ 16	19300 $\pm$ 12400
Mira Loma	6 $\pm$ 4	45 $\pm$ 54	29 $\pm$ 14	25 $\pm$ 26	61 $\pm$ 35	16200 $\pm$ 8200
UC Riverside	8 $\pm$ 6	40 $\pm$ 29	33 $\pm$ 19	29 $\pm$ 29	47 $\pm$ 23	16200 $\pm$ 12100
Upland	10 $\pm$ 4	24 $\pm$ 28	44 $\pm$ 16	21 $\pm$ 23	39 $\pm$ 18	9000 $\pm$ 3700
During Fire						
Glendora	11 $\pm$ 5	**25 $\pm$ 30**	39 $\pm$ 28	44 $\pm$ 23	**27 $\pm$ 25**	12200 $\pm$ 6200
Long Beach	**14 $\pm$ 9**	**55 $\pm$ 68**	56 $\pm$ 24	**15 $\pm$ 16**	**93 $\pm$ 92**	18000 $\pm$ 8500
Mira Loma	**12 $\pm$ 8**	**105 $\pm$ 85**	39 $\pm$ 26	**17 $\pm$ 18**	**215 $\pm$ 171**	**28500$\pm$ 14600**
UC Riverside	**12 $\pm$ 7**	**46 $\pm$ 36**	42 $\pm$ 22	**18 $\pm$ 21**	**121 $\pm$ 112**	**28800 $\pm$ 16100**
Upland	**15 $\pm$ 7**	**43 $\pm$ 34**	47 $\pm$ 24	**15 $\pm$ 16**	**165 $\pm$ 138**	Data not available
Post Fire						
Glendora	5 $\pm$ 2	5 $\pm$ 5	17 $\pm$ 11	31 $\pm$ 11	18 $\pm$ 29	11000 $\pm$ 6300
Long Beach	8 $\pm$ 6	39 $\pm$ 49	32 $\pm$ 11	16 $\pm$ 12	21 $\pm$ 10	8600 $\pm$ 9700
Mira Loma	4 $\pm$ 3	57 $\pm$ 45	20 $\pm$ 11	19 $\pm$ 15	28 $\pm$ 16	23900 $\pm$ 10700
UC Riverside	6 $\pm$ 4	14 $\pm$ 25	20 $\pm$ 10	23 $\pm$ 15	18 $\pm$ 10	17400$\pm$ 11000
Upland	6 $\pm$ 4	21 $\pm$ 25	23 $\pm$ 12	17 $\pm$ 13	19 $\pm$ 10	16700 $\pm$ 8600

Data in bold indicate statistically significant differences between the pre- and during fire concentrations at $p=0.05$

List of Figures

Figure 1   Map showing the fire area and the sampling sites in the Los Angeles basin.

Figure 2   24-hour averaged PM and gaseous pollutant concentrations during the study at a) Glendora, b) Long Beach, c) Mira Loma, d) UC Riverside and e) Upland. For comparison purposes, CO concentrations (in ppb) have been divided by 20, and PN concentrations (in # cm^{-3}) have been divided by 100, as indicated in the legend.

Figure 3   Satellite images from NASA earth observatory showing a) Southern California during the peak of the fire episode on 28 October 2003, with the smoke plumes blowing west, and b) the same area after the wind reversal with a visible marine layer and blowing the smoke plumes towards the northeast on the afternoon of 29 October 2003.

Figure 4   Hourly a) PM and b) gaseous pollutant concentrations at Upland.

Figure 5   Two-hour averaged fine (FP) and ultrafine (UFP) particle mass concentrations at USC.

Figure 6   Particle size distributions at Upland a) at 10AM: before, 24 October 2003, and after the fires; and b) at 12PM: before, 29 October 2003, and after the fires.

Figure 7   Particle size distributions on different days at 11PM in Westwood Village: a) Outdoor; and b) Indoor.

Figure 8   Indoor/Outdoor particle size distributions at 6AM in Westwood Village on a) 27 October 2003; and b) 4 November 2003
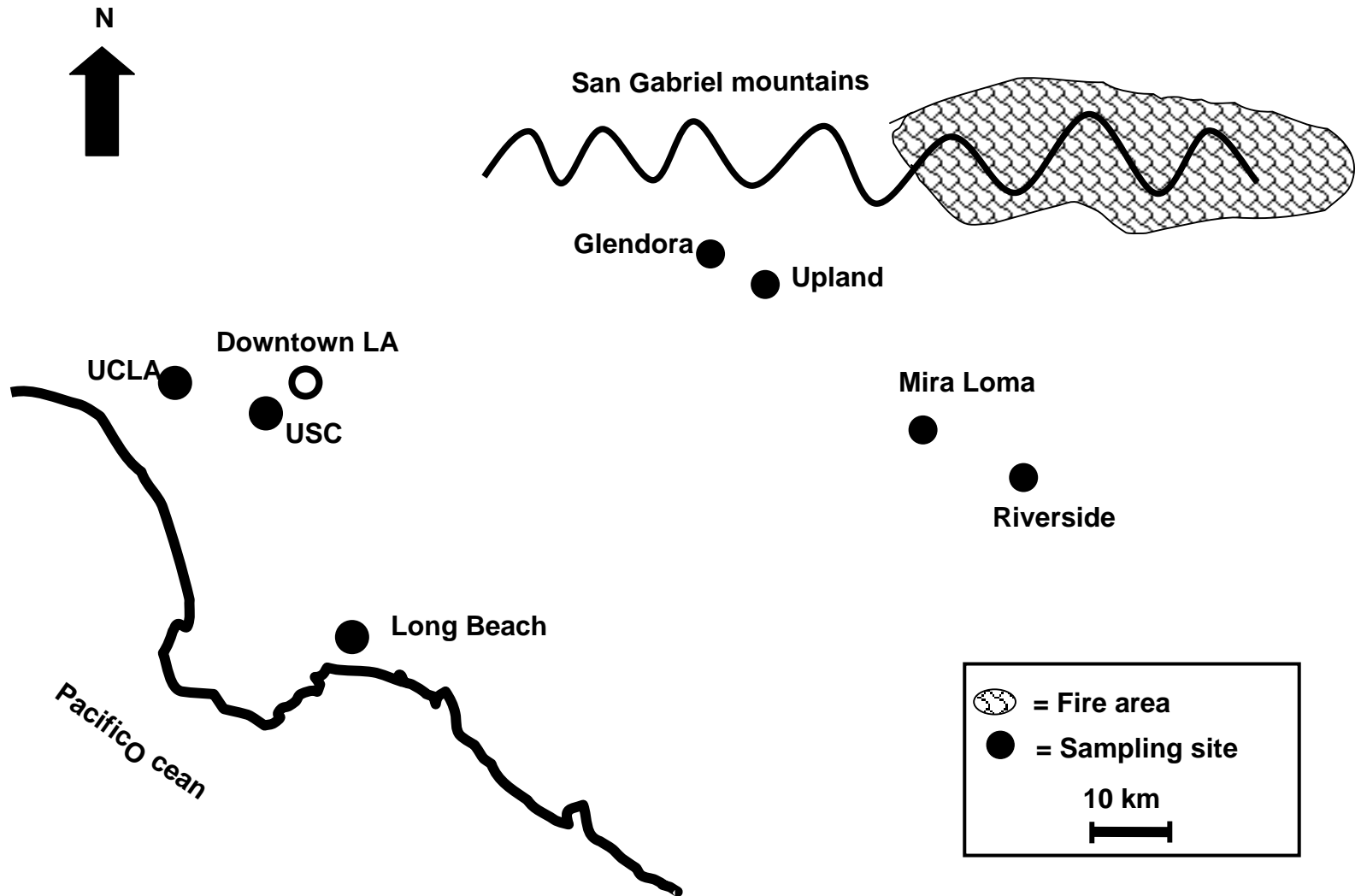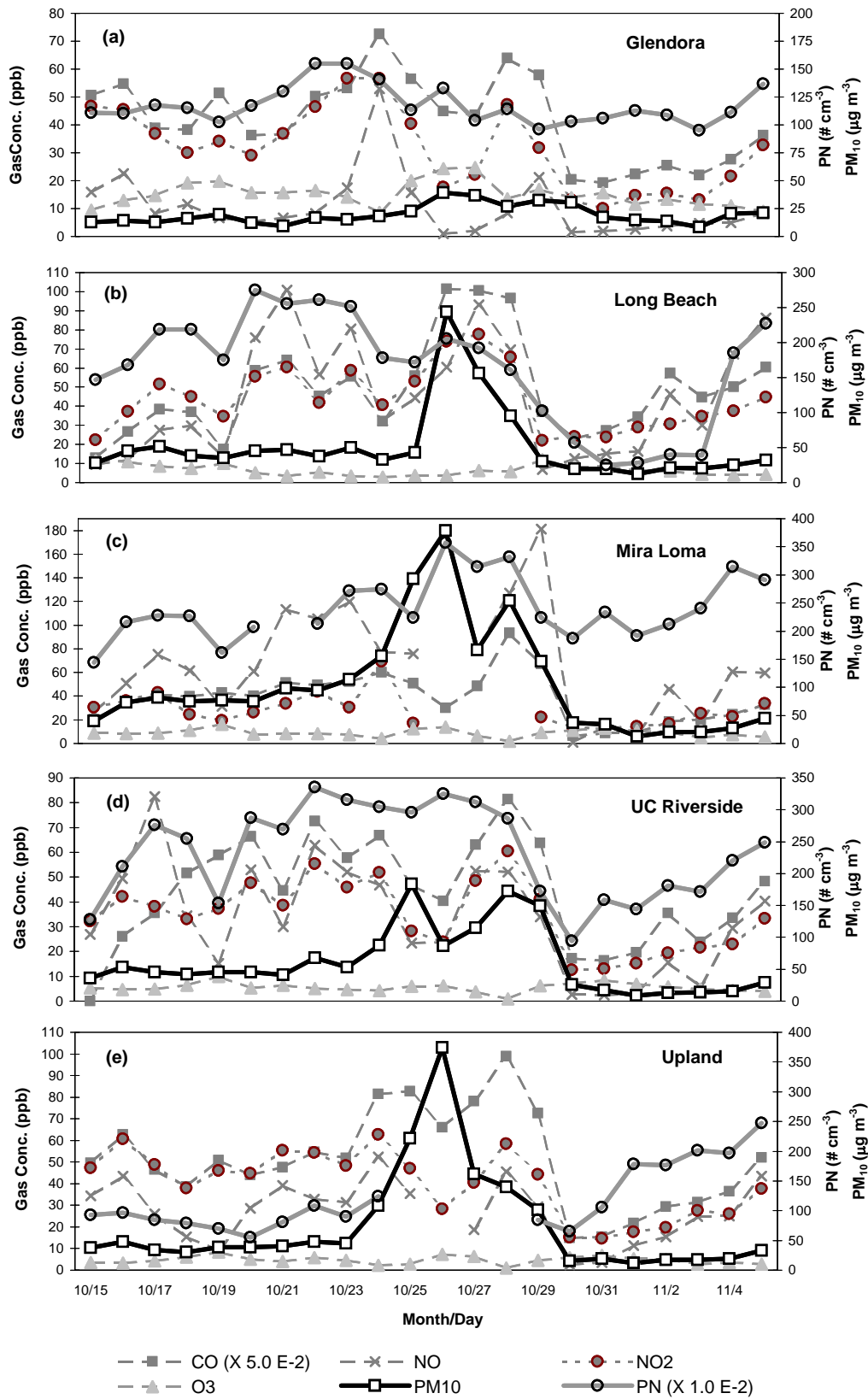
Figure 1

Figure 2
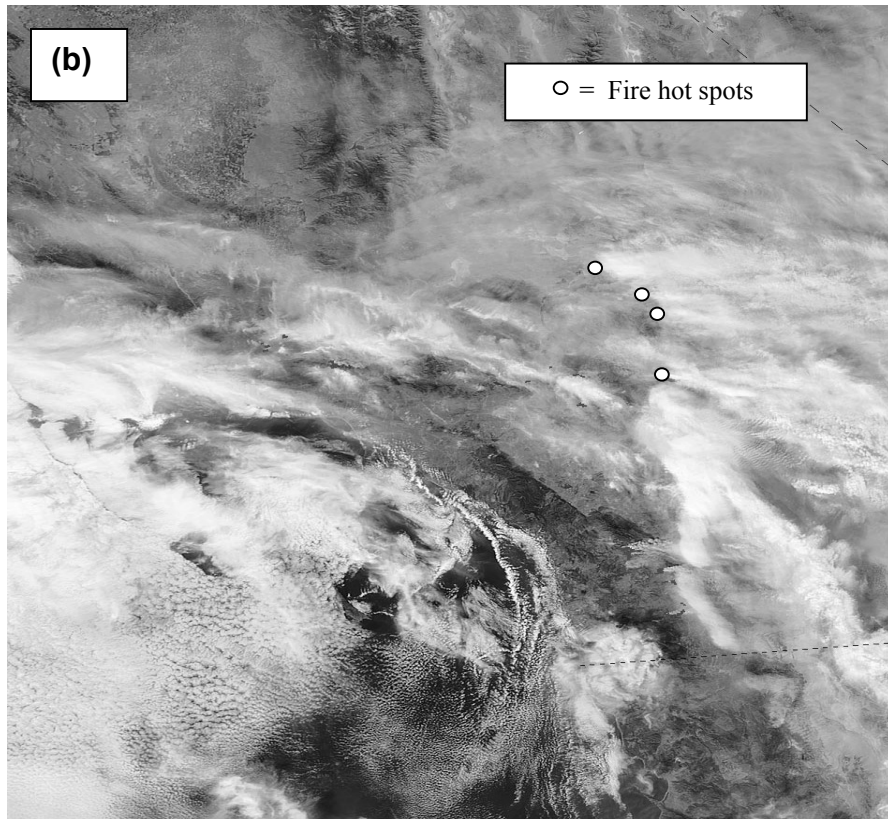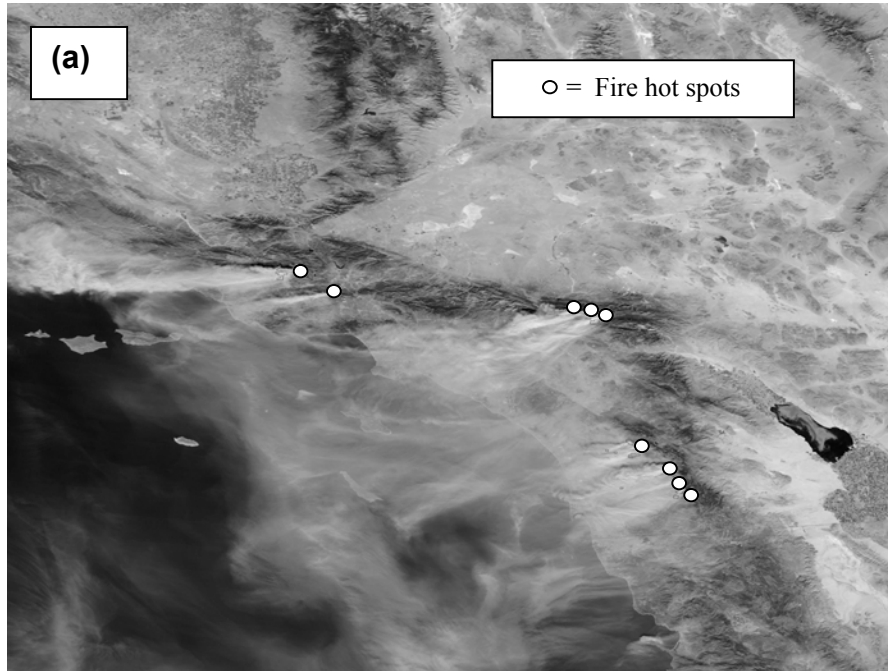
Figure 3

(a)

O = Fire hot spots

(b)

O = Fire hot spots
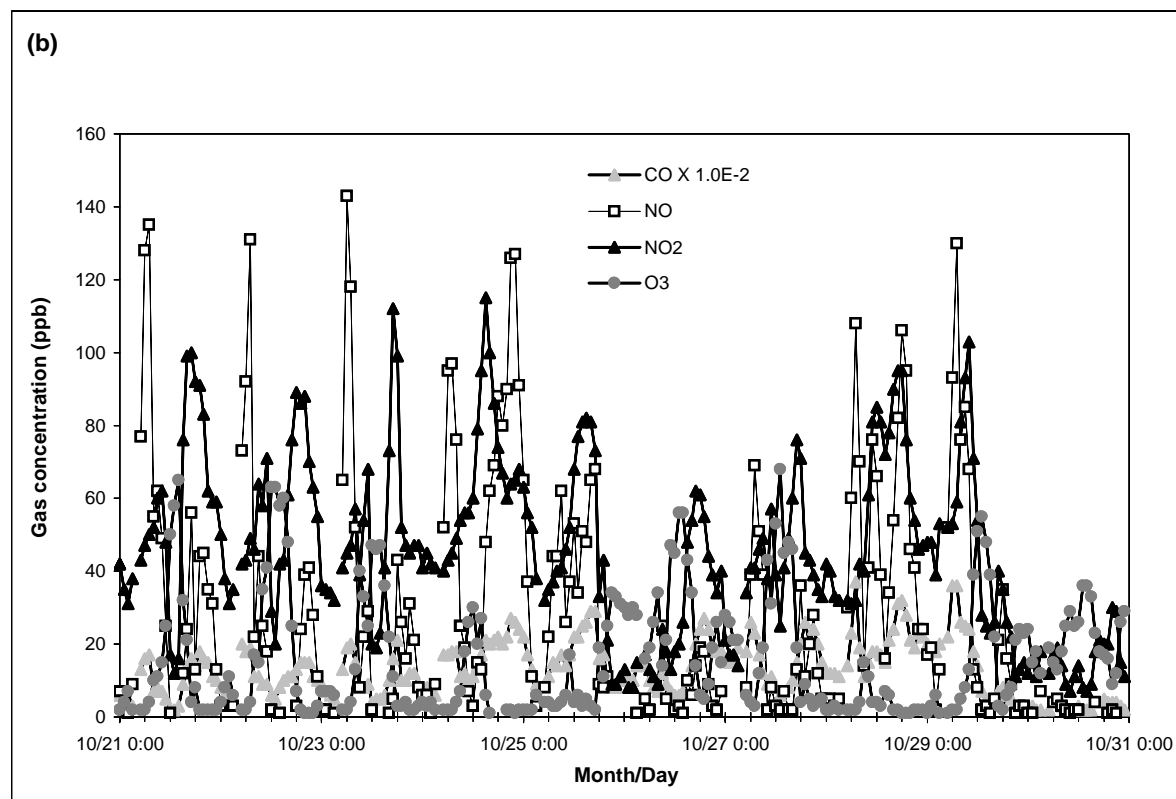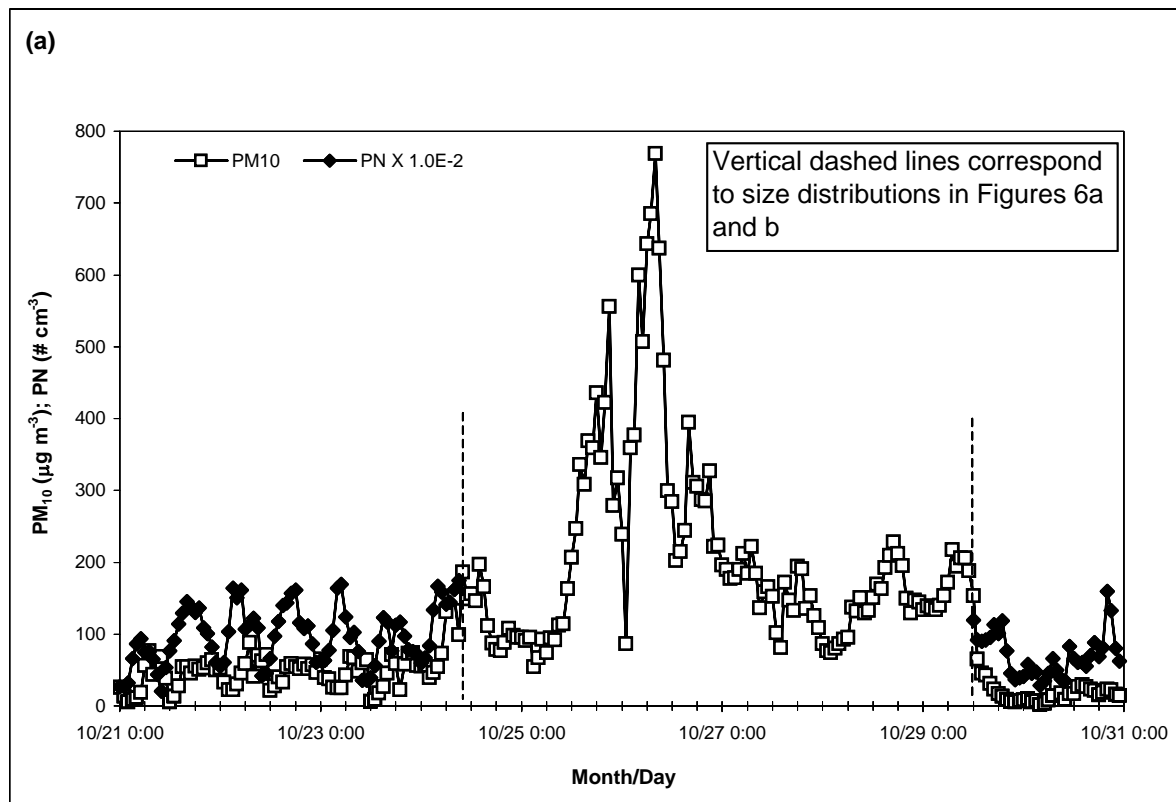
Figure 4

Figure 5

Figure 6

Figure 7

(a)

(b)
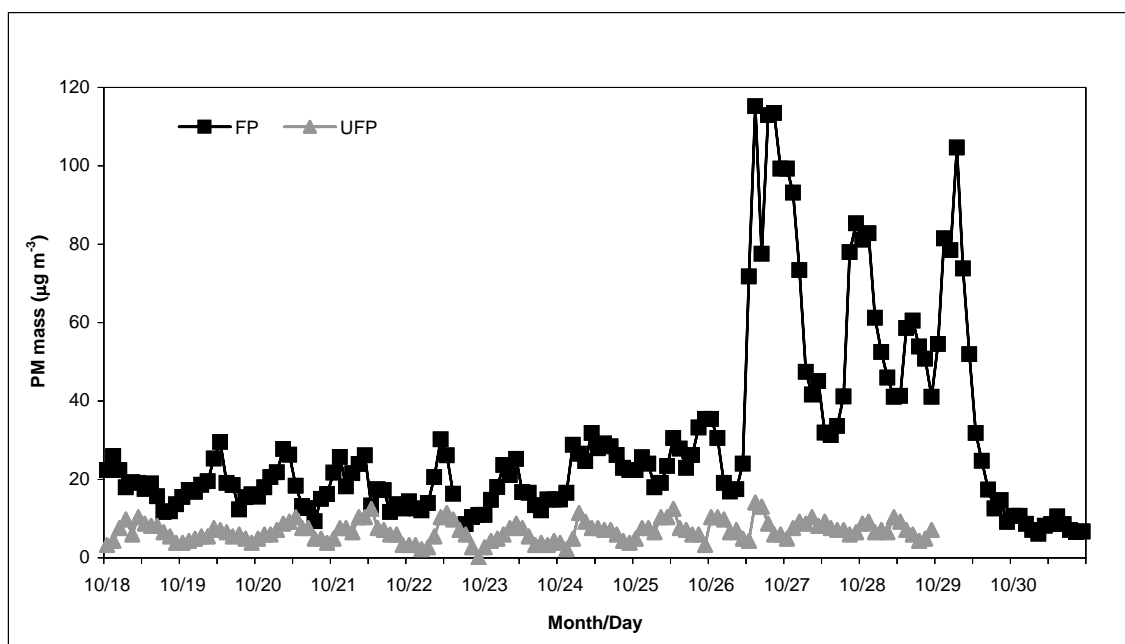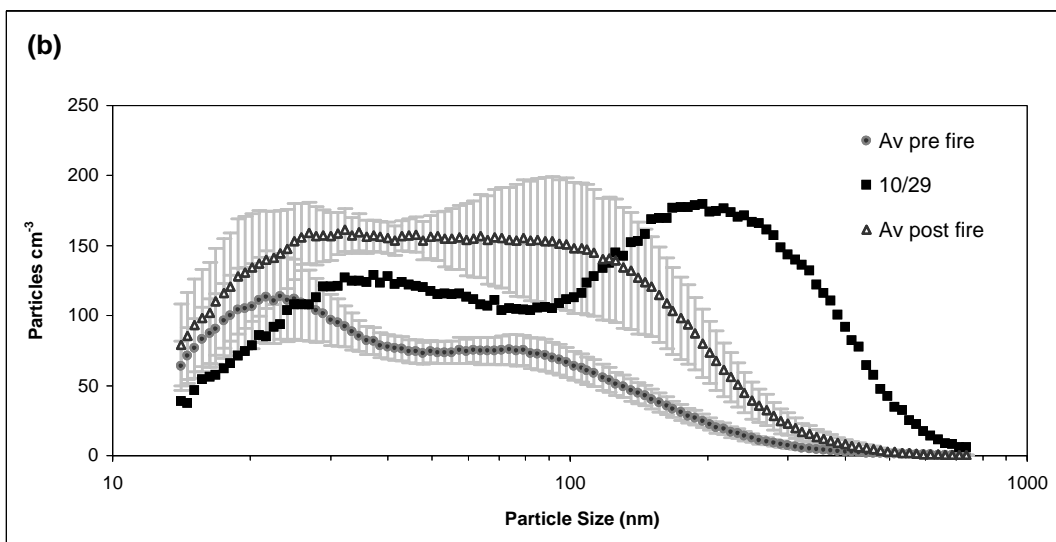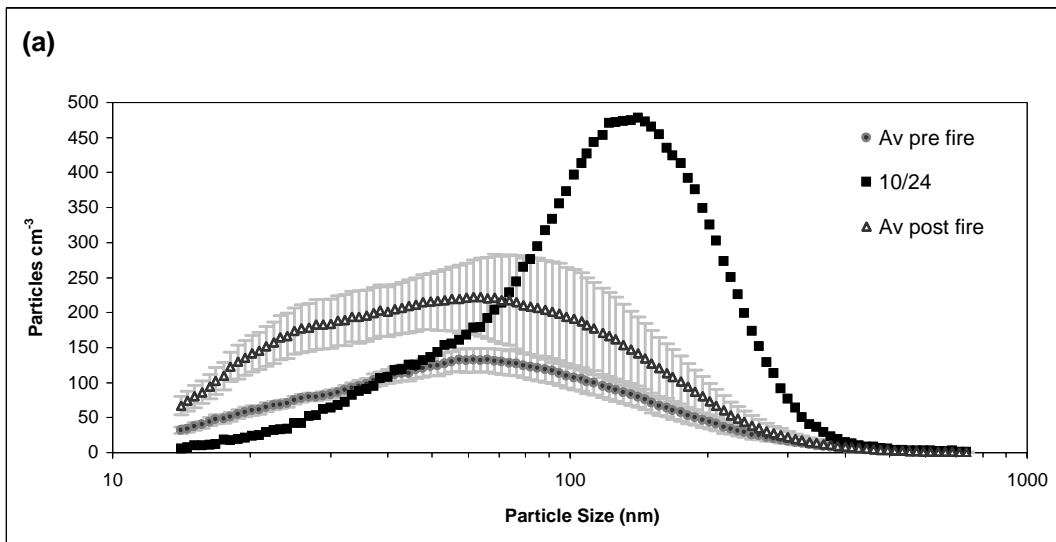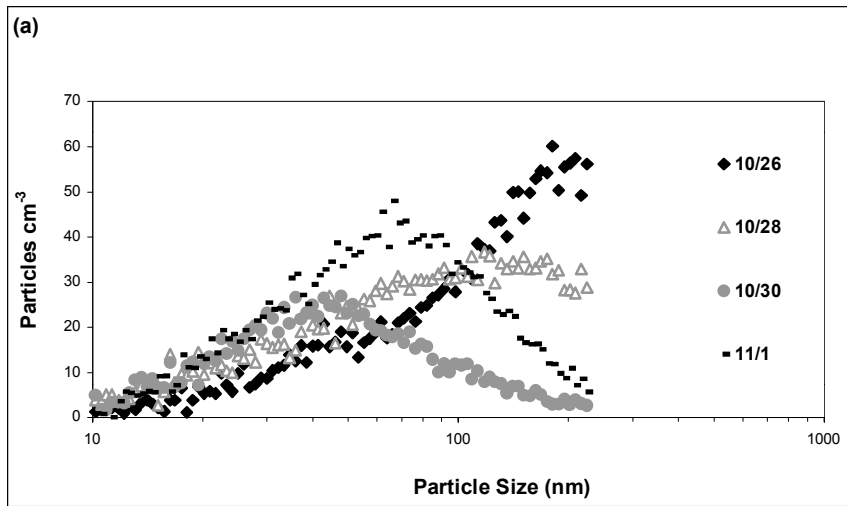
Figure 8
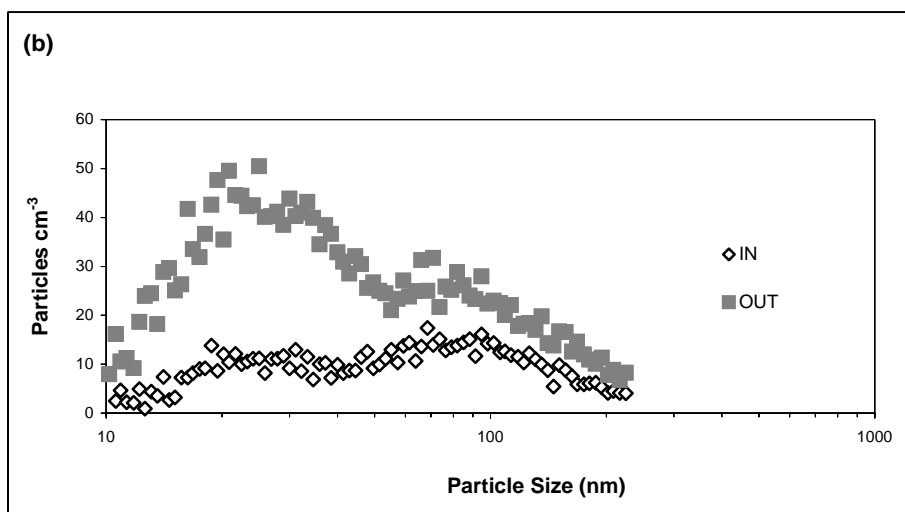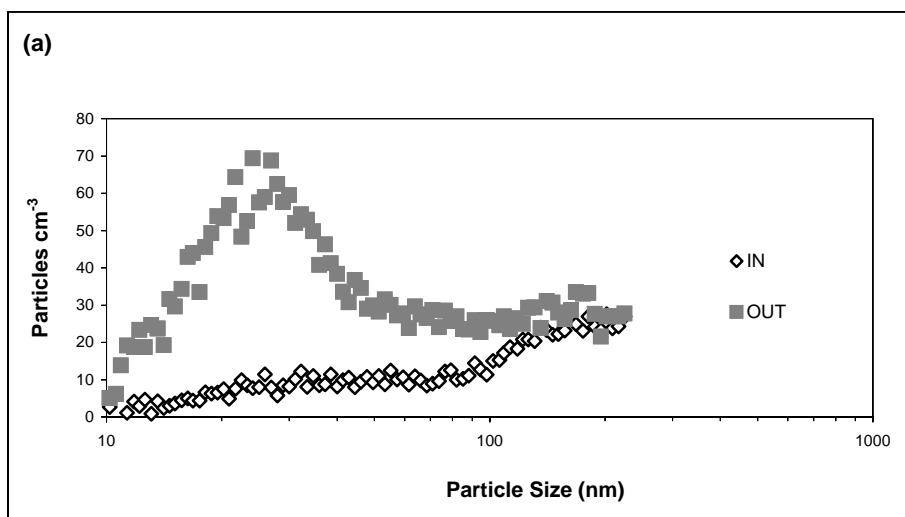
Seasonal and Spatial Trends in Particle Number Concentrations and Size Distributions at the Children's Health Study Sites in Southern California

Manisha Singh*, Harish C. Phuleria*, Kenneth Bowers¶ and Constantinos Sioutas*‡

*Department of Civil and Environmental Engineering, University of Southern California, 3620 South Vermont Avenue, Los Angeles, CA 90089
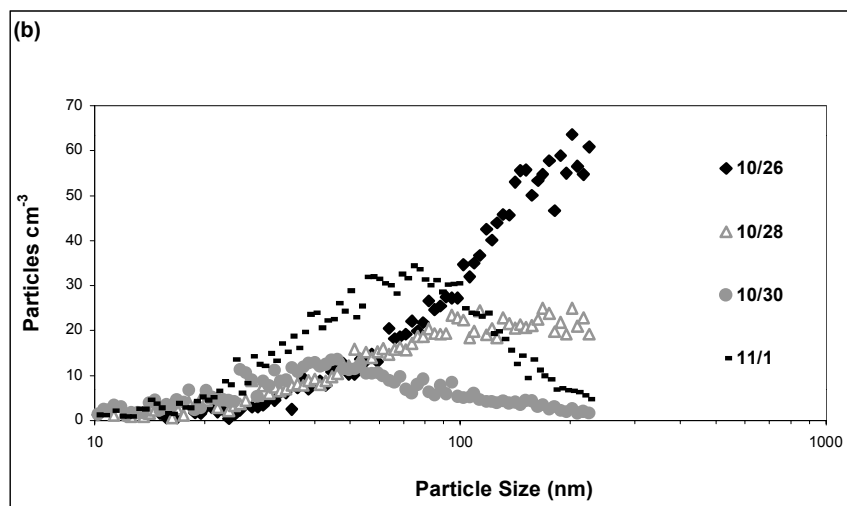
¶California Air Resources Board, 1001 I Street, Sacramento, CA 96812

‡ Author to whom correspondence should be addressed, email: sioutas@usc.edu, Tel: +1-213-740-6134, Fax: +1-213-744-1426

Abstract

Continuous measurements of particle number, particle mass (PM_{10}) and gaseous co-pollutants (NO_x, CO and O_3) were obtained at eight sites (urban, suburban and remote) in Southern California during years 2002 and 2003 in support of University of Southern California Children's Health Study. We report the spatial and temporal variation of particle numbers and size distributions within these sites. Higher average total particle number concentrations are found in winter (November to February), compared to summer (July to September) and spring (March to June) in all urban sites. Contribution of local vehicular emissions is most evident in cooler months, whereas effects of long-range transport of particles are enhanced during warmer periods. The particle size profile is most represented by a combination of the spatial effects, e.g. sources, atmospheric processes and meteorological conditions prevalent at each location. Afternoon periods in the warmer months are characterized by elevated number concentrations that either coincide or follow a peak in ozone concentrations, suggesting the formation of new particles by photochemistry. Results show no meaningful correlation between particle number and mass, indicating that mass based standards may not be effective in controlling ultrafine particles. The study of the impact of the Union worker's strike at port of Long Beach in October 2002 revealed statistically significant increase in particle number concentrations in the 60-200 nm range ($p<0.001$), which are indicative of contributions of emissions from the idling ships at the port.

Introduction

A number of observational studies have demonstrated acute and chronic effects of ambient particles on human health (Dockery and Pope 1994; Zanobetti et al. 2000; Pope, 2000). To this date, however, there appears to be heterogeneity in particulate matter (PM) concentrations and PM-associated health effects between locations within an urban setting, which raises considerable uncertainties as to whether PM mass, number, size, bulk or surface chemistry are the appropriate metrics associated with PM toxicity. For example, recent studies have shown that atmospheric ultrafine particles (with physical diameter < 100 nm) have the potential for eliciting adverse health effect (Oberdörster and Utell, 2002; Li et al., 2003; Li et al., 2004; Xia et al., 2004). Recent epidemiological studies by Peters et al. (1997), have demonstrated association between health effects and exposures to ultrafine particles compared to accumulation mode or coarse particles.

In the complex environment of an urban atmosphere, there is great variability in the number and type of sources of particles as well as in the diurnal and seasonal patterns of their emission strengths, all of which affect human exposure. Traffic is without doubt one of the most dominate sources of particles in urban areas (Shi et al., 1999; Cyrys et al., 2003). Recent studies have shown a dramatic decrease of ultrafine number concentrations with increasing distance from busy freeways in Los Angeles, thereby demonstrating that vehicular pollution is a major source of ultrafine particles and that high number concentrations can be a localized phenomenon, on scales of 100-300 meters (Zhu et al., 2002a,b). In addition to their direct emission in the atmosphere, particles may be formed as a result of photochemical reactions from gaseous precursors, including particulate sulfate formed from precursor sulfur dioxide, and secondary organic aerosols, formed

from oxidation of aromatic hydrocarbons (Derwent et al., 2000). The secondary aerosol formation is largely governed by meteorological factors (Mäkelä et al., 1997, Kim et al., 2002). The high degree of temporal variability of the meteorological parameters such as degree of solar radiation, atmospheric mixing depth, humidity, and temperature - all contribute to the temporal variation in particulate number concentrations at a location.

Understanding how the number concentrations of particles change as a function of particle size, time of the day, location and season may help characterize the sources of these emissions as well as refine human exposure parameters used in epidemiological studies that attempt to link particulate levels and health effects they induce.

Due to recent health concerns, particle size distributions and number concentrations in several cities have been measured. Some recent continental sampling campaigns that measured size distributions include the Pittsburgh Air Quality Study (Stanier et al., 2004), the Atlanta PM Supersite program (Woo et al., 2001), and sampling campaigns in Los Angeles (Kim et al., 2002; Fine et al., 2004), Northern Europe (Ruuskanen et al., 2001), Tennessee (Cheng and Tanner, 2002), Brisbane, Australia (Morawska et al., 2002), the UK (Harrison et al., 2000), Estonia and Finland (Kikas et al., 1996) and Central Europe (Birmili et al., 2001). Most of these studies were conducted in urban areas in which the vast majority of ultrafine PM originate from primary sources (Morawska et al., 1998; Harrison et al., 2000; Woo et al., 2001), thus their diurnal profiles match those of local vehicular sources. The majority of these studies were also intensive in nature, conducted for a period ranging from a few weeks to a few months.

Shi et al. (2001) measured temporally resolved number concentrations to examine periods of nucleation events. Lawless et al. (2001) used the near continuous data obtained

from an SMPS and an optical particle counter to distinguish between primary and secondary contributions to $PM_{2.5}$ in Fresno, CA. These studies were intensive in nature, focusing on one specific location and for a limited time period. The spatial aerosol characteristics at different locations of a city have also been examined. Kim et al. (2002) identified periods of photochemistry and long range advection as sources of ultrafine PM at two sites in Los Angeles Basin in addition to local vehicular emissions. Fine et al. (2004) inferred sources of ultrafine particles at two different locations in the eastern portion of Los Angeles Basin. Buzorius et al. (1999) measured aerosol characteristics at a series of sites in Helsinki, Finland in order to investigate the transport of aerosol traveling from source sites to receptor sites. Ruuskanen et al. (2001) conducted monitoring in three different European cities using continuous monitors to describe differences among the sites as well as diurnal variations of particle mass and number concentrations. Little information has been reported on the seasonal patterns of size distributions due to the lack of long-term monitoring. Stanier et al. (2004) measured aerosol size distributions at one location in Pittsburgh for an entire year, providing one of the first data sets in Northern United States from which seasonal patterns can be described.

The work presented in this paper is intended to provide more comprehensive information about spatial, seasonal as well as diurnal variations of atmospheric particle numbers and size distributions (14-700 nm) within Southern California. This paper utilizes the data set generated in support of the University of Southern California (USC) Children's Health Study (CHS). The CHS, which began in 1993, is one of the largest investigations of the long-term consequences of air pollution on the respiratory health of children. The main goal of CHS is to identify chronic effects of ambient pollutants in

Southern California by performing cross-sectional and longitudinal studies in school children in several communities with varying exposures to particulate matter,ozone, and acid vapors. In this paper we present ambient particle number characteristics measured at eight sites classified as urban (source and receptor) and remote (suburban/ mountainous) sites in Southern California during the years 2002 and 2003. The particle number concentration data is supported by gaseous copollutants data to help differentiate (mostly) ultrafine particle sources and formation mechanisms at each site as well as their prevalence over different times of day and different seasons.

Methods

Concentrations of carbon monoxide (CO), ozone (O_3), total nitrogen oxide species (NO_x), mass of particulate matter with aerodynamic diameters less than 10 μm (PM_{10}) and total particle numbers (PN) were continuously measured in several locations in Southern California as a part of the University of Southern California Children's Health Study, supported by the South Coast Air Quality Management District (SCAQMD) and the California Air Resources Board (CARB). Size resolved sub-micrometer particle numbers (14-700 nm) were measured under an additional contract from the CARB and SCAQMD. Continuous data were collected concurrently throughout the calendar years 2002 and 2003. Eight sites were examined in this study, six within the Los Angeles Basin (LAB): Long Beach, Mira Loma, Upland, Riverside, Lake Arrowhead and USC; and two sites at other areas of Southern California: Alpine and Lancaster (as shown in Figure 1). Selection of the sampling sites, discussed in greater detail by Künzli et al. (2003), was made on the basis of their location within the LAB and the presumed contrasting air

quality (hence exposure) regimes in terms of PM and gaseous co-pollutants, which have differentially affected children's health. Located near a busy surface street, the Long Beach station is about 0.5 km northeast of freeway I-405 and approximately 1.5 km east of freeway I-710. The Long Beach station is mostly downwind of these two freeways as well as the Long Beach port which is situated approximately 7 km south of the sampling station. The Upland site is located in a residential area inside a community trailer park about 100 m from San Bernardino road, and is within 2 km (mostly downwind i.e., north-east) of the freeway 210. The Mira Loma site (about 80 km east of downtown Los Angeles) is located in a building on the Jurupa Valley High School campus, directly southeast of the intersection of freeways 60 and 15. It is surrounded by several major warehouse facilities with frequent heavy-duty diesel truck traffic (Sardar et al., 2004; Na et al., 2004) and near several major cattle feeding operations. The sampling location at Riverside is within the Citrus Research Center and Agricultural Experiment Station (CRCAES), a part of the University of California, Riverside. It is about 20 km southeast of the Mira Loma site and is situated upwind of surrounding freeways and major roads (Phuleria et al., 2004). The desert site of Lancaster is located in the office of Mojave desert AQMD and is approximately 2 km away from the nearest freeway 14. The Lake Arrowhead monitoring station is located in the rim of World High School near highway 18, at an elevation of about 1700 m. It is a purely serene mountainous site with very few local emission sources, but heavily impacted by transported, aged air pollutants. The sampling site at USC is located near downtown Los Angeles, just 100 m downwind of freeway 110. The Alpine station is a remote suburban to rural site located approximately

50 km east of downtown San Diego (approximately 200 km southeast of downtown Los Angeles).

Fresh emissions from vehicular and industrial sources primarily make Long Beach a "source" site, which is at a relatively western location in the LAB and has an urban surrounding. USC, also, has an urban surrounding and is considered a "source" site. It represents an urban mix of industrial, vehicular and construction sources. Riverside, Upland and Mira Loma and Lake Arrowhead are designated "receptor" sites where the aerosol is composed of advected, aged and photochemically processed air mass from the central Los Angeles Area. The time for air masses to transport from source to receptor sites can vary from a few hours to more than a day (Sardar et al, 2004). It should be noted here that the designation of these sites as "receptors" by no means precludes the impact of local traffic sources, as it will be discussed later in this paper.

The concentrations of CO were measured near-continuously by means of a Thermo Environmental Inc. Model 48C trace level CO monitor. A continuous Chemiluminescence Analyzer (Monitor Labs Model 8840) was used for the measurement of concentrations of NO_x, while O_3 concentrations were monitored using a UV photometer (Dasibi Model 1003 AH). Total particle number concentrations (greater than about 10 nm in diameter) were measured continuously by a Condensation Particle Counter (CPC, Model 3022/A, TSI Incorporated, St. Paul, MN) set at a flow rate of 1.5 L min^{-1}. In addition to the continuous data described above, efforts were made to monitor the number-based particle size distributions in each site for 1-3 months duration during a warmer and a cooler period. Accordingly, three Scanning Mobility Particle Sizers (SMPS, Model 3936, TSI Incorporated, St. Paul, MN) were deployed by rotation at each

site during selected time periods, as shown in Table 1, to measure the size distribution of sub-micrometer aerosols (14-700 nm) using an electrical mobility detection technique. In this configuration, the CPC flow rate was maintained at 0.3 L min^{-1} (with the sheath flow of the SMPS set at 3 L min^{-1}), and size- segregated particle number concentrations were recorded. The CPC total count data were excluded for the months when the CPC was in the SMPS configuration (Table 1; Figure 2). Continuous particle number and gaseous co-pollutant concentrations were averaged over 1-hour and 24-hour intervals for the subsequent analysis.

Hourly PM_{10} mass concentrations in each site were measured by low temperature Differential Tapered Element Oscillating Microbalance monitors (low temperature TEOM 1400A, R&P Inc., Albany, NY). Jacques et al. (2004) have described the design and performance evaluation of this monitor in greater detail. Briefly, the system consists of a size-selective PM_{10} inlet, followed by a Nafion$^{®}$ dryer that reduces the relative humidity of the sample aerosol to 50% or less. Downstream from the Nafion dryer and ahead of the TEOM sensor is an electrostatic precipitator (ESP) to alternately remove particles from the sample stream or allow the particle laden sample stream to continue to the sensor. The ESP is alternately switched on and off, for equal time periods of about 10 minutes. This dual sampling channel design makes it possible to account for effects such as volatilization of labile species, adsorption of organic vapors and changes in relative humidity and temperature, all of which affect the TEOM signal. The study by Jacques et al. (2004) showed that the time averaged TEOM PM_{10} mass concentrations agreed within ± 10% with those of collocated Federal Reference Methods (FRM).

Results

The section describing our results is divided into the following parts: Seasonal and spatial trends; Diurnal trends; Relation between PM mass, PM surface area and PM numbers; and Long Beach October 2002 strike analysis. The latter part is an "opportunistic" study focusing on the impact of the union workers strike at the port of Long Beach on air quality.

Seasonal and Spatial Trends

Descriptive statistics (surface area and number median diameter) of the measured particle size distributions are included in Table 2. Figure 2 shows monthly averaged total particle number concentrations measured using the CPC along with the monthly averaged minimum and maximum ambient temperatures, in the eight sites sampled during the calendar year 2003. The error bars indicate the standard error calculated based on the sampling size. A key observation in Figure 2 is the higher average particle number concentrations in winter (November to February), compared to summer (July to September) and spring (March to June) in all of the urban sites, e.g., USC, Long Beach, Riverside, Upland, Mira Loma and Lancaster. The total particle number concentrations at these sites were quite similar and ranged from 25,000-30,000 particles/cm^3 in winter months to 12,000-15,000 particles/cm^3 in summer/spring months. High number concentrations at the urban sites during winter are likely due to lower temperatures favoring particle formation by condensable organics freshly emitted from vehicles. Additionally, relative to summer, the decreased atmospheric mixing height, combined

9

with more stagnant conditions, restrict the aerosol dispersal, and would thus lead to increase in contribution of local and primary sources to measured number concentrations.

The lowest levels of particle number concentrations were observed at Lake Arrowhead, which is a remote mountainous site. The averaged particle concentrations at this site ranged from 6,000-8,000 particles/cm^3 in summer months and 3,000-5,000 particles/cm^3 in winter months (Figure 2g). The Lake Arrowhead sampling site is located at an elevation of 1700 m. The inversion layer is generally below the station location during morning and evening periods. As the day progresses, the warmer temperature cause the inversion layer to rise and subsequently the inversion layer passes the station elevation and the station is under the inversion layer. During summer months, as a consequence of the elevated mixing height the site is under the inversion layer for longer periods leading to higher number concentrations. Additionally, low atmospheric pressure and higher mid-day wind speed during summer favor long-range transport of the aerosol from the much more polluted upwind areas.

Particle counts at Alpine, although higher than those observed at Lake Arrowhead, are much lower than those observed in the urban sites, discussed earlier. This site is impacted by very few local traffic emissions and is largely a receptor site of the San Diego metropolitan area. On most summer days, an afternoon peak of particles of possibly secondary origin occurs several hours after the change of wind direction from easterly to westerly. Monthly averaged particle counts range between 9,000 - 13,000 particles/cm^3. A detailed discussion about the seasonal variations in particulate characteristics at Alpine is presented in a later section, where size distributions in two separate seasons are discussed.

Figure 3 depicts the particle size distributions measured by the SMPS during different seasons at our sampling sites. Average number size distributions at USC in summer as well as winter are very similar and corroborate the hypothesis that this site is heavily influenced by fresh vehicular emissions. Particles in the 20 - 50 nm range, which could be attributed to traffic, are the most abundant at this site. Also, number concentrations of this size range increase during the winter period. USC has similar number median diameter during both seasons, an indication of the consistency of the sources (i.e., the traffic emissions from the nearby freeway I-110) affecting PM characteristics in that location. During the summer period, although total particle counts are lower due to more vertical mixing, particles < 20 nm diameter appear to be more abundant than in winter months. These particles could be due to contribution of enhanced photochemical particle formation in the summer months. Such new particle formation depends strongly on the intensity of solar radiation (O'Dowd et al.1999; Wehner and Wiedensohler, 2003), but the exact mechanism by which nucleation occurs is yet to be understood (Zhang and Wexler, 2002; Kulmala et al., 2004).

Similar to USC, at Long Beach which is also a site highly impacted by vehicular emissions, the average particle number concentrations are higher in winter than summer for the particles > 40 nm. However, summer months witness an increase in particles <40 nm diameters. The size distribution in summer supports the hypothesis that this site may be influenced markedly by photochemically generated particles. Given that this site is situated close to the ocean, with the only major upwind sources being the port and the nearby freeway 710, both of which are quite proximal (i.e., within 5 miles or less) to the site, the contribution of long range transport to particle numbers can be ruled out. The

number median diameter (NMD) of the aerosol is also lower in summer than in winter. Larger NMD in winter (79.9 nm) compared to summer (59.8 nm) may be due to high relative humidity in the winter months, which would contribute to growth of particles by condensation of water vapor in the air. It should be noted that the proximity of that site to the ocean results in unusually higher relative humidity levels compared to the rest of the urban sites, with prolonged periods of nighttime and morning fog. The smaller summertime NMD could be due to the increased photochemical production of smaller particles, as observed by Kim et al. (2002) and Wehner and Wiedensohler (2003). During the first week of October, union workers at the port of Long Beach went on strike. A detailed analysis of the effect of this strike on particulate characteristics of Long Beach is discussed in later section of this paper.

Riverside, Mira Loma and Upland are receptor sites downwind of the high concentration of sources in the western part of LAB. In addition to the effect of few local emission sources, particle number concentration at these receptor areas is also influenced by aged, advected aerosol from the west, especially in summer season. The Upland station was directly impacted by Southern California wildfires during late October 2003 because of its location some 3.5 km downwind of one of the 13 fires during that period. The impact of this fire on aerosol characteristics is discussed in detail by Phuleria et al. (2004) and thus we do not present the analysis here. However, for our seasonal characteristics analysis, we have excluded the data from that period.

At Riverside, the particle number concentrations are higher in winter compared to spring for particles <100nm. It is interesting to observe that the particles >100 nm are slightly higher in the spring period. The increase in the peak median size in springtime

may be due to the contribution of advected, thus aged aerosols, which are generally larger in diameter (Zhang and Wexler, 2002), from the western polluted regions of the Los Angeles Basin.

The size distribution of aerosols also shows some seasonal variation at Mira Loma. In addition to a decrease in particle number concentrations, the number size distribution shifted towards larger sizes in summer compared to winter. Decrease in particle counts of all size ranges in summer reflects the effect of more dilution with elevated mixing height in warmer months. As in Riverside, the NMD of the aerosol in Mira Loma is larger in warmer season (Table 2). This may be the result of the increased wind speeds and onshore flow in the warmer months, leading to increased advection of pollutant air parcels from the western LAB. This advected aerosol is generally larger in diameter as noted earlier and would lead to larger NMD of the summer/spring aerosols.

At the suburban remote site Alpine, in contrast to all the receptor sites discussed above, the particle numbers <100 nm are markedly higher in spring than in winter (Figure 3g). The NMD also shifts from 79 nm in winter to 43 nm in spring (Table 2). This may be due to increased summertime advection and photochemical particle formation. The influence of summer advection and photochemical particle formation is supported by wind data, which indicates a change in wind direction from easterly (offshore) to westerly (onshore). The westerly winds would bring the aging air-mass from the San Diego metropolitan area to the station. The afternoon peak of aged and photochemically-derived particles occurs several hours after the wind direction change, allowing time for the air mass to reach the station from San Diego.

Particle size distribution data is available for only summer months at Lancaster and Lake Arrowhead. Both sites display generally much lower number concentrations than the urban sites, as one would expect. The relatively large aerosol NMD of 82 and 78 nm at Lancaster and Lake Arrowhead, respectively, corroborate the absence of any major local sources, which would emit fresh hence smaller in size emitted PM.

Diurnal Trends

This section describes our observations of diurnal trends in particle numbers and gaseous copollutants, which, combined with the size distribution and number concentrations data, may provide insights into sources and possible formation mechanisms of particulate matter in each of these sites. Figures 4 through 9 display the diurnal variations of particle number (PN) and gaseous pollutants (O_3 and NO_x) concentrations averaged by time of day over the period that SMPS sampled at each of the sites. In these figures, particle sizes have been segregated into three ultrafine size ranges: 15-30nm, 30-60 nm and 60-100 nm.

The diurnal trends of PN in different size ranges and gaseous pollutants at USC and Long Beach during the winter sampling periods are shown in Figures 4a and 5a, respectively. As mentioned before, USC and Long Beach are close to vehicular sources and traffic is expected to be primary source of these particles at these sites. The number concentrations have also been observed to be higher during winter months. The diurnal pattern of NO_x is very similar to diurnal patterns of particle number concentrations. The morning and evening peaks of these pollutants correspond to morning and evening

commutes, which suggests that local traffic is the major contributor to ultrafine PM at both these sites during winter.

During summer months, secondary aerosol formation is favored and new ultrafine particles may form as a result of the condensation of low-volatility products of photochemical reactions (largely organic compounds) onto stable, nanometer-size particles (O'Dowd et al 1999; Kim et al., 2002; Sardar et al., 2004). Secondary aerosol formation is the most likely explanation for the diurnal trends in PN during the summer period at USC and Long Beach (Figures 4b and 5b, respectively) in which the peak particle concentrations during the afternoon period either coincide or slightly lag behind the peak in O_3 concentrations.

Figures 6a and 7a show the diurnal trends of particle numbers as well as gaseous copollutants during winter period at Riverside and Mira Loma, respectively. Similar to the winter diurnal trends of the source sites, we notice a peak in number concentrations in the morning and another smaller peak in the evening across all particle size ranges. The diurnal pattern of NO_x is very similar to diurnal profile of number concentrations at both these sites, indicating once again a traffic origin for these particles during winter. Since particle number counts are high and wind speeds are generally low in the morning, the traffic sources are local and specific to the sampling locations. The higher number concentrations in morning, relative to evening rush hour levels, may be a result of the low mixing height during morning hours, and the higher relative humidity, which may be affecting gas-to-particle conversion by condensation of organic vapors originating from vehicles. As the day progresses the temperature increases, causing the inversion height to rise. The lower NMD of aerosol during winter may also be explained by contribution

from fresh emissions in winter. The diurnal patterns of particle number concentrations show an additional peak during the afternoon in spring and summer months at Riverside and Mira Loma, respectively (Figures 6b, 7b), similar to those observed during the summer in Long Beach and USC. This peak is either concurrent or slightly lagging the O_3 peak, as in the previous sites. We attribute this increase to secondary aerosol production by photochemical reactions, as discussed earlier, with the lag between the PN and O_3 peaks possibly being due to the time that is required for the newly formed particles to grow to a size that can be detected by the SMPS (i.e., >15 nm).

Similar diurnal patterns of particle counts for winter and summer to the LAB sites are observed at Alpine, depicted in Figure 8. During winter, higher numbers are observed in the morning, when the mixing height of the atmosphere is low. As the day progresses, the temperature increases and mixing height rises, correspondingly the particle number concentrations drop due to dilution and dispersion, and they increase again in evening and night when the mixing height depresses. The diurnal trends of particle concentrations also track well those of NO_x. During the warmer period (April and May 2002), the diurnal profile of particulates displays a different trend. There is a surge in particle numbers in the afternoon, especially for particles below 60 nm, following a very similar pattern to the diurnal profile of O_3, which implies photochemical formation of these particles and air mass advection, as seen at the urban sites discussed earlier.

The diurnal profile of number concentrations and gaseous pollutant concentrations averaged by time of the day over two months (July-August 2002) of SMPS sampling in Lake Arrowhead is shown in Figure 9. The diurnal patterns of O_3 and NO_x are very similar to the diurnal patterns of particle number concentrations. All pollutant

concentrations increase during later part of the day. As discussed earlier, Lake Arrowhead is located at an elevation of approximately 1700 m with negligible local pollution sources. During early morning and night, the inversion layer is generally below the station location. As the day progresses, the warmer temperature cause the inversion layer to rise. Eventually, the station is under the inversion layer. In addition to the contribution of photochemical activity to the total particle numbers, the rise in particle numbers during that period is also a result of the increased vertical mixing and advection, which brings to the site aged and more polluted air parcels originating in the western parts of LAB. This is also supported by the unusual rise in NO_x concentrations in the middle of the day, also seen in Figure 9, which cannot be attributed to an increase in traffic or any other factors.

Correlations between PM Numbers, PM Surface Area and PM mass

Table 3 presents the Pearson correlation coefficient (R) between total particle number concentrations and total surface area concentrations calculated from the SMPS data assuming spherical particles. A moderate to high correlation (i.e., R=0.55-0.90) was observed between particle number and surface area concentrations for all sites in both sampling periods. This correlation was somewhat lower in the warmer period for all the sites in this study except Riverside and Long Beach. Strom et al. (2003) also found higher correlations between particle number and surface area in winter compared to summer. This finding is consistent with the hypothesis that the increased aerosol surface area acts as a deposition site for gaseous precursors to condense, thereby preventing new

particle formation, as one would expect. The increased surface area may also act as a sink of ultrafine particles via heterogeneous coagulation.

The correlation of hourly and 24-hour averaged PM_{10} and particle number (PN) concentrations is shown in Table 4 for the different CHS sites. In general, the correlations were found to be weak-to-moderate (i.e., $R < 0.5$), except of the site in Alpine, where relatively strong correlations were observed in the springtime between both the hourly as well as 24-hour averaged concentrations. No particular trend in the hourly or 24-hour data between different seasons was observed that could be applied to all sites, as the relationship between the hourly and 24-hour PN and PM_{10} varied differentially from site-to-site and within seasons, as evident in the data shown in Table 4.

Long Beach October 2002 strike analysis

During the period of September 30 to October 9, 2002, union workers at the port of Long Beach, CA went on strike. The port which is located upwind to the sampling site is considered a major contributor to PM at Long Beach as a result of emissions from ships (Isakson et al., 2003), but perhaps more so because of the heavy-duty truck traffic associated with the port (Chow et al., 1994). It was interesting to determine whether significant changes in particle and co-pollutant characteristics were observed due to this strike. In order to understand the effects of this strike, we present the PM as well as co pollutant characteristics from pre-, during and post-strike periods in this section. Unfortunately, we do not have the SMPS data from September 25 to October 1, 2002, due to calibration and maintenance performed on the instruments at that time, therefore PM characteristics for the pre-strike period are studied from September 16-24, 2002 and

for the strike period from October 2-9, 2002. Gaseous co-pollutant data are available throughout the pre-, during- and post-strike periods.

During the strike period, the following three major changes occurred that might have influenced air pollution in that area. First, there was a significant decrease in diesel truck traffic both on the nearby freeways 710 and 110 as well as local surface streets (Figure 10a). Second, about 200 ships were idling off the coast, immediately upwind of the Long Beach throughout the strike period (CNN, 2002). Third, there were significant changes in weather conditions during that period. While in September the weather in Long Beach was warm with the exception of the morning hours, it changed in early October (coincidentally with the strike) to cooler with mostly overcast days (Figure 11c). These weather conditions continued after the strike period. This change may be expected to increase particle concentration by enhancing formation by condensation, but to also particle size condensational growth of the formed particles.

Figure 11a shows the 24-hour averaged concentrations of particle number and PM_{10} during the strike and non-strike period. It should be noted here that since the CPC was used in conjunction with the SMPS, the total particle numbers shown in Figure 11a reflect the sum of the particle counts in each size bin of the SMPS and not those measured by the CPC alone. As other studies have indicated, this may underestimate quite substantially the total particle concentrations (Liu and Deshler, 2003).

The results of Figure 11a as well as our statistical analysis did not reveal any statistically significant impact of the strike on PN as well as PM_{10} concentrations ($p > 0.05$). The corresponding concentrations of gaseous co pollutants during the strike/non-strike period are presented in Figure 11b. There is a statistically significant increase in

NO$_x$ and CO concentrations during the strike compared to pre- as well as post-strike period (p < 0.001). High amounts of NO$_x$ and CO emissions from ships have been observed in previous studies (Corbett and Fishback, 1997; Sinha et al., 2003; Cooper, 2003; Saxe and Larsen, 2004). These emissions have been reported to be more pronounced when the ships are at berth and idling (Cooper, 2003). An additional explanation for the elevated CO levels during the strike may be related to the increase in light duty traffic, shown in Figure 10. It can be seen that the total volume of traffic on both the freeways 110 and 710 was approximately the same during the strike and non-strike periods (Figure 11b), while the diesel traffic was substantially reduced by more than 40% on 710 and about 25% on 110 freeways (Figure 10a), which implies that the gasoline vehicle traffic may have increased by 10-20%, leading to some elevation in CO concentrations. We believe, however, that the majority of the increase in CO levels must be attributed to emissions from the idling ships.

Emissions from diesel engines operating in ships contribute significantly to sub-micrometer range particles and typically have bimodal size distributions, with a dominant mode in the sub-40 nm and a weaker mode in the range of 70-100 nm (Isakson et al., 2003). Figure 12 shows the particle number concentrations in different size ranges through the strike/non-strike period. Particle concentrations below 30 nm seem unaffected by the strike. Even if a large number of these particles were emitted by ships, it is conceivable that a substantial fraction of them did not reach the sampling station due to coagulation, possible hygroscopic growth and-or volatilization processes that may have occurred during their transport. Particle numbers concentrations in the 60 to 100 nm as well as 100-200 nm ranges were, however, significantly elevated during the strike

(p <0.001), which may be indicative of the contributions of emissions from the idling ships.

The average size distributions of the particle number concentrations before, during and after the strike are shown in Figure 13. It can be seen that particle concentrations in the size range 60-300 nm were higher during the strike, as discussed above ($p < 0.001$). Also, the mode before and after the strike is smaller compared to the strike period, further supporting the argument for the larger-sized particles originating from ship emissions compared to those from heavy and light duty vehicles.

Discussion

Particle number concentrations and size distributions in complex urban environments can be seen to be highly variable on temporal scales, from diurnal to seasonal, and spatially, from local scale influences, such as distances from highways, to regional scale influences, such as long range transport across air basins. Seasonal difference in solar intensity, temperature, and relative humidity can also strongly influence the diurnal size profile.

This work presents novel data, generated over a 2-year period, related to atmospheric particle numbers and size distributions (14-700 nm) at eight sites within Southern California generated in support of the University of Southern California Children's Health Study (CHS). The urban site (classified as source and receptor) and remote site (classified as suburban and mountainous) PM size distributions measured during CHS form an excellent data set for research on particle sources and aerosol processes.

In this study we see enhanced contribution of local emission sources during cooler months with stagnant meteorological conditions at all sites. During warmer months, effects of long-range dispersal of aerosol are observed most clearly at the easterly receptor sites of Riverside, Mira Loma and Lake Arrowhead. The increased wind speeds and onshore flow in the warmer months, lead to increased advection of pollutant parcels from the polluted western areas of the LAB (Fine et al., 2004). Additionally, dry and hot summer conditions would limit ultrafine particle growth to accumulation mode during transport (Kim et al., 2002).

In addition to the contribution of vehicular emissions to particle concentrations in Los Angeles, photochemical formation by secondary reactions in the atmosphere appears to be a major source of PM during the afternoon periods in the warmer months at all sites. Current studies by a number of groups have investigated and confirmed the photochemical formation of ultrafine particles in urban atmosphere. In addition to our observations in Los Angeles, secondary particle formation events have been observed in urban areas, including Pittsburgh (Stanier et al., 2004), St. Louis (Shi and Qian, 2003), and Mexico City (Baumgardner et al., 2004). An excellent review of this topic is given by Kulmala et al. (2004). The actual formation mechanism of nanoparticles in the range of 1-3 nm remains largely unknown and has recently become the subject of intensive research in the field of atmospheric science. Current hypotheses on the composition of these fresh nuclei include the binary nucleation of water and sulfuric acid (Kulmala, 2002), ternary nucleation of ammonia-sulfuric acid-water (Weber et al., 1997), and ion-induced nucleation (Yu and Turco, 2001). There is also general consensus that the species responsible for further growth of these nanoparticles to the > 10 nm range are

different than the nucleating species (Stanier et al., 2004). Our current understanding of atmospheric nanoparticle processes suggests that growth of these particles to larger sizes within the ultrafine PM mode occurs by condensation of low volatility organic species. These species are products of photochemical oxidation of volatile organic precursors on these pre-existing nuclei (O'Dowd et al., 1999; Kulmala et al., 2004). In fact, recent studies by Zhang et al. (2004) showed that nucleation rates of sulfuric acid are greatly increased in the presence of organic acids (including products of atmospheric photochemical reactions), by forming unusually stable organic-sulfuric acid complexes, thereby reducing the nucleation barrier of sulfuric acid.

It is interesting to note in our field measurements that summertime levels of ultrafine particles at source sites, such as long Beach and USC peaked in midday (i.e., noon to 1 pm), whereas ultrafine PM numbers peak slightly later (i.e., between 3-4 pm) in the inland receptor sites. A time delay in the peak concentrations observed at the receptor sites is possibly due to the transport time for polluted air masses to reach those sites.

The correlation between particle number concentrations and PM_{10} has been widely studied and weak-to-moderate correlations have been generally observed between the two (Morawska et al., 1998; Woo et al., 2001; Noble et al., 2003; Fine et al., 2004; Sardar et al, 2004). Since the fine to ultrafine particle counts are dominated by very small particles and the PM_{10} mass is dominated by fewer, much larger particles, low correlation should be expected, especially in air masses dominated by fresher particles (either primary emission particles or freshly formed secondary particles). In our study, we also found weak-to-moderate correlations between PM_{10} and number concentrations with no particular seasonal trend. These findings are very important from a regulatory

perspective because they imply that controlling ambient PM_{10} mass via national air quality standards may not necessarily reduce human exposure to ultrafine particles that dominate the particle counts and have recently been shown to have toxic effects (as discussed in the introductory part of the paper).

In conclusion, the results presented in this paper indicate that location and season significantly influence particle number and size distributions in locations within Southern California. Strong diurnal and seasonal patterns in number concentrations are evident as a direct effect of the sources, formation mechanisms, as well as meteorological conditions prevalent at each location during different times of the day and year. These results will be used in the CHS as a first order indicator of not only human exposure, but also inhaled dose to ultrafine PM. They will also be used for the development and validation of predictive models for population exposure assessment to ultrafine PM in complex urban environemnts, such as that of the Los Angels Basin.

References

Baumgardner D., Raga G.B., and Muhlia A. Evidence for the formation of CCN by photochemical processes in Mexico City. *Atmos Environ* 2004: 38(3): 357-367.

Birmili W., Wiedensolher A., Heintzenber J. and Lehmann K. Atmospheric particle number size distribution in central Europe: statistical relations to air masses and meteorology. *J Geophys Res* 2001:106 (D23): 32005-32018.

Buzorius G., Hameri K., Pekkanen J. and Kulmala M. Spatial variation of Aerosol Number Concentration in Helinski City. *Atmos Environ* 1999: 33: 553-565.

Cheng M.D. and Tanner R.L. Characterization of ultrafine and fine particles at a site near the Great Smoky Mountains. *Atmos Environ* 2002: 36: 5795-5806.

Chow J.C., Watson J.G., Fujita E.M., Lu Z., Lawson D.R. and Ashbaugh L.L. Temporal and spatial variations of $PM_{2.5}$ and PM_{10} aerosol in the Southern California air quality study. *Atmos Environ* 1994: 28 (12): 2061-2080.

CNN, Long Beach harbor strike, Internet, accessed August 24, 2004, http://money.cnn.com/2002/10/08/news/ports_longshoremen

Cooper D.A. Exhaust emissions from ships at berth. *Atmos Environ* 2003: 37: 3817-3830.

Corbett J.J. and Fischbeck P. Emissions from ships. *Science* 1997: 278 (5339): 823-824.

Cyrys J., Stolzel M., Heinrich J., Kreyling W.G., Menzel N., Wittmaack K., Tuch T. and Wichmann H.E. Elemental composition and sources of fine and ultrafine ambient particles in Erfurt, Germany. *Sc Total Env* 2003: 305: 143-156.

Derwent R.G., Davies T.J., Delaney M., Dollard G.J., Field R.A., Dumitrean P., Nason P.D., Jones B.M.R. and Pepler S.A. Analysis and interpretation of the continuous hourly monitoring data for 26 C_2–C_8 hydrocarbons at 12 United Kingdom sites during 1996. *Atmos Environ* 2000: 34 (2): 297-312.

Dockery D.W. and Pope C.A. Acute respiratory effects of particulate air pollution. *Ann Rev of Pub Hlth* 1994: 15: 107-132.

Fine P.M., Shen S. and Sioutas C. Inferring the sources of fine and ultrafine particulate matter at downwind receptor sites in the Los Angeles Basin using multiple continuous measurements. *Aerosol Sci Technol* 2004: 18: 182-195.

Harrison R.M., Shi J.P., Xi S., Khan A., Mark D., Kinnersley R. and Yin J. Measurement of number mass and size distribution of particles in the atmosphere. *Phil Tran. R Soc Lond* 2000: 358: 2567-2580.

Isakson J., Persson T.A. and Lindgren E.S. Identification and assessment of ship emissions and their effects in the harbour of Goteborg Sweden. *Atmos Environ* 2003: 35: 3659-3666.

Jacques P.A., Ambs J.L., Grant W.L. and Sioutas C. Field evaluation of the differential TEOM monitor for continuous $PM_{2.5}$ mass concentrations. *Aerosol Sci Technol* 2004 (Suppl. 1): 38: 49-59.

Kikas U., Mirma A., Tamm E. and Raunemaa T. Statistical characteristics of aerosol in Baltic sea region. *J Geophys Res* 1996: 101 (D14): 19319-19327.

Kim S., Shen S., Sioutas C., Zhu Y. F. and Hinds W. C. Size distribution and diurnal and seasonal trends of ultrafine particles in source and receptor sites of the Los Angeles Basin. *J Air Waste Manage Assoc* 2002: 52: 297-307.

Kulmala M. How particles nucleate and grow. *Science.* 2002: 302: 1000-1001

Kulmala M., Vehkamäki H., Petäjä T., Dal Maso M., Lauri A., Kerminen V.M., Birmili W. and McMurry P.H. Formation and growth rates of ultrafine atmospheric particles: a review of observations. *J Aerosol Sci* 2004: 35: 143-176.

Künzli N., McConnell R., Bates D., Bastain T., Hricko A., Lurmann F., Avol E., Gilliland F. and Peters J. Breathless in Los Angeles: The exhausting search for clean air. *Am J Pub Hlth* 2003: 93(9): 1494-1499.

Lawless P.A., Rodes C.E. and Evans G. Aerosol concentration during the 1999 Fresno exposure studies as functions of size season and meteorology. *Aerosol Sci Technol* 2001: 34: 66-74.

Li N., Alam J., Eiguren A., Slaughter N., Wang X., Huang A., Wang M., Sioutas C. and Nel, A.E. Nrf2 is a Key Transcription Factor in Antioxidant Defense in Macrophages and Epithelial Cells: Protecting Against the Injurious Effects of Pro-oxidative Air Pollutants. *J Immunol* 2004: 173 (5): 3467-3481.

Li N., Sioutas C., Froines J.R., Cho A., Misra C and Nel A., Ultrafine Particulate Pollutants Induce Oxidative Stress and Mitochondrial Damage. *Environ Health Persp* 2003: 111 (4): 455-460.

Liu P.S.K. and Deshler T. Causes of concentration differences between a Scanning Mobility Particle Sizer and a Condensation Particle Counter. *Aerosol Sci Technol* 2003: 37: 917-923.

Mäkelä J.M., Aalto P., Jokinen P., Pohja T., Nissinen A., Palmroth S., Markkanen T., Seitsonen K., Lihavainen H. and Kulmala M. Observations of ultrafine aerosol particle formation and growth in boreal forest. *Geophys Res Lett* 1997: 24: 1219-1222.

Morawska L., Jayarantne E.R., Mengersen K. and Thomas S. Differences in airborne particle and gaseous concentrations in urban air between weekdays and weekends. *Atmos Environ* 2002: 36: 4375-4383.

Morawska L., Bofinger N.D., Kocis L. and Nwankwoala A. Comprehensive characterization of aerosols in a subtropical urban atmosphere: particle size distribution and correlation with gaseous pollutants. *Atmos Environ* 1998: 32 (14-15): 2467-2478.

Na K.S., Sawant A.A., Song C. and Cocker D.R. Primary and secondary carbonaceous species in the atmosphere of Western Riverside County, California. *Atmos Environ* 2004: 38 (9): 1345-1355.

Noble C.A., Mukerjee S., Gonzales M., Rodes C.E., Lawless P.A., Natarajan S., Myers E.A., Norris G.A., Smith L., Ozkaynak H. and Neas L.M. Continuous measurement of fine and ultrafine particulate matter criteria pollutants and meteorological conditions in urban El Paso, Texas. *Atmos Environ* 2003: 37: 827-840.

Oberdörster G. and Utell M.J. Ultrafine particles in the urban air: To the respiratory tract-and beyond? *Environ Health Persp* 2002: 110 (8): A440-A441.

O'Dowd C., McFiggans G., Creasey D.J., Pirjola L., Hoell C., Smith M.H., Allan B.J., Plane J.M.C., Heard D.E., Lee J.D., Pilling M.J. and Kulmala M. On the photochemical production of new particles in the coastal boundary layer. *Geophys Res Lett* 1999: 26 (12): 1707-1710.

Peters A., Wichmann H.E., Tuch T. and Heinrich J. Respiratory effects are associated with the number of ultrafine particles. *Amer J Resp Crit Care Med* 1997: 155: 1376-1383.

Phuleria H.C., Fine P.M., Zhu Y. and Sioutas C. Characterization of Particulate Matter and co-pollutants during the fall 2003 Southern California fires. *J Geophy Res-Atmos* 2004 *(in press)*

Pope C.A. Review: epidemiological basis for particulate air pollution health standards. *Aerosol Sci Technol* 2000: 32 (1): 4-14.

Ruuskanen J., Tuch. Th., Ten Brink H., Peters A., Khystov A., Mirme A., Kos G.P.A., Brunekreef B., Wichmann H.E., Buzorius G., Vallius M., Kreyling W.G. and Pekkanen J. Concentrations of ultrafine, fine and PM$_{2.5}$ particles in three European cities. *Atmos Environ* 2001: 35: 3729-3738.

Sardar S.B., Fine P.M., Hoon A. and Sioutas C. Associations between particle number and gaseous copollutants concentrations in the Los Angeles Basin. *J Air Waste Manage Assoc* 2004 (*in press*).

Saxe H. and Larsen T. Air pollution from ships in three Danish ports. *Atmos Environ* 2004: 38: 4057-4067.

Shi J.P. and Qian Y. Aerosol size distributions (3 nm to 3 um) measured at St. Louis Supersite (4/1/01-4/30/02) *M. S. Thesis Department of Mechanical Engineering University of Minnesota Minneapolis MN, 55455.* 2003.

Shi J.P., Evans D.E., Khan A.A. and Harrison R.M. Sources and concentration of nanoparticles (<10 nm diameter) in the urban atmosphere. *Atmos Environ* 2001: 35:1193-1202.

Shi J.P.; Khan A.A. and Harrison R.M. Measurements of ultrafine particle concentration and size distribution in the urban atmosphere. *Sci Total Environ* 1999: 235: 51-64

Sinha P., Hobbs P.V., Yokelson R.J., Christian T.J., Kirchstetter T.W. and Bruintjes R. Emissions of trace gases and particles from two ships in the southern Atlantic Ocean. *Atmos Environ.* 2003: 37: 2139-2148.

Stanier C.O., Khlystov A.Y. and Pandis S.N. Ambient aerosol size distributions and number concentrations measured during the Pittsburgh Air Quality Study (PAQS). *Atmos Environ.* 2004: 38: 3275-3284.

Strom J., Umegard J., Torseth K., Tunved P., Hansson H.-C., Holmen K., Wismann V., Herber A. and Langlo G.K. One-year particle size distribution and aerosol chemical composition measurements at the Zeppelin Station, Svalbard, March 2000-March 2001. *Atmos Environ.* 2003: 28: 1181-1190.

Weber R.J., Marti J.J., McMurry P.H., Eisle, F.L., Tanner D.J. and Jefferson A. Measurement of new particle formation and ultrafine particle growth rates at a clean continental site. *J Geophy Res* 1997: 102 (D4): 4375-4385.

Wehner B., Wiedensohler A. A long-term measurement of submicrometer urban aerosols: statistical analysis for correlations with meteorological conditions and trace gases. *Atmos Chem Phys* 2003: 3: 867-879.

Woo K.S., Chen D.R., Pui D.Y.H. and McMurry P.H. Measurement of Atlanta aerosol size distributions: observations of ultrafine particle events. *Aerosol Sci Technol* 2001: 34: 75-87.

Xia T., Korge P., Weiss J.N., Li N., Venkatesen M.I., Sioutas C., and Nel A. Quinones and Aromatic Chemical Compounds in Particulate Matter (PM) Induce Mitochondrial Dysfunction: Implications for Ultrafine Particle Toxicity. *Environ. Health Persp.* 2004: 112 (14): 1347-1359.

Yu F. and Turco R.P. From molecular clusters to nanoparticles: Role of ambient ionization in tropospheric aerosol formation. *J Geophy Res* 2001: 106 (D5): 4797-4814.

Zanobetti A., Schwartz J. and Dockery D.W. Airborne particles are a risk factor for hospital admissions for heart and lung disease. *Environ. Health Persp.* 2000: 108(11): 1071-1077.

Zhang R., Suh I., Zhao J., Fortner E.C., Tie X., Molina L.T., and Molina M.J. Atmospheric new particle formation enhanced by organic acids. *Science* 2004: 304: 1487-1490.

Zhang K.M. and Wexler A.S. A hypothesis for growth of fresh atmospheric nuclei. *J Geophy Res-Atmos* 2002:107 (D21): 4577.

Zhu Y.F., Hinds W.C., Kim S., Shen S. and Sioutas C. Study of ultrafine particles near a major highway with heavy-duty diesel traffic. *Atmos Environ* 2002a: 36: 4323-4335.

Zhu Y.F., Hinds W.C., Kim S. and Sioutas C. Concentration and size distribution of ultrafine particles near a major highway. *J. Air Waste Manage. Assoc.* 2002b: 52: 1032-1042.

Table 1: Sampling periods during which SMPS-CPC configuration was employed at various sampling sites

Site no	Site name	Sampling periods
1	Long Beach	Nov '02; Aug-Sep '03
2	Mira Loma	Jan-Feb '02; Jun '02
3	UC Riverside	Nov '02; Mar-Apr '02
4	USC	Dec '02 - Jan '03; Sep '03
5	Upland	Aug to Oct '03; Nov, '03 - Jan '04
6	Alpine	Apr-May '03; Dec '03 - Jan '04
7	Lancaster	Jun-Jul '03
8	Lake Arrowhead	Jul-Aug '02

Table 2: Summary statistics showing average total particle surface area (SA) and number median diameter (NMD)

Site no	Site Name	Season	Period	Particle SA ($\mu m^2/cm^3$)		NMD (nm)	
				Grand avg.	SD	Grand avg.	SD
1	Long Beach	Winter	Nov '02	609.5	320.1	79.9	18.8
	Long beach	Summer	Aug-Sep '03	330.0	166.0	59.8	18.3
2	Mira Loma	Winter	Jan-Feb '02	674.5	418.5	65.2	19.4
	Mira Loma	Spring	Jun '02	542.9	231.9	81.6	20.5
3	Riverside	Winter	Nov '02	290.3	255.2	47.7	16.6
	Riverside	Spring	Mar-Apr '02	334.0	273.0	62.6	21.3
4	USC	Summer	Sep '03	437.4	331.7	45.9	11.2
	USC	Winter	Dec '02 - Jan '03	329.4	210.4	45.4	14.2
5	Upland	Summer[1]	Aug-Sep-Oct '03	371.7	161.9	61.5	14.1
	Upland	Winter	Nov-Dec '03 - Jan '04	473.7	300.6	56.6	13.6
6	Alpine	Spring	Apr-May '03	122.4	101.7	42.9	14.4
	Alpine	Winter	Dec '03 - Jan '04	135.1	116.5	79.3	18.5
7	Lancaster	Spring	Jun-Jul '03	164.9	136.0	81.9	18.0
8	Lake Arrowhead	Summer	Jul-Aug '02	154.9	117.4	77.9	16.7

----
[1] The data corresponding to the October Fire in Southern California is excluded

Table 3: Pearson correlation coefficient (R) between total particle number concentration and total particle surface area concentration

Site no	Site name	Season	Period	Pearson correl. coeff.
1	Long Beach	Winter	Nov '02	0.76
	Long beach	Summer	Aug-Sep '03	0.80
2	Mira Loma	Winter	Jan-Feb '02	0.76
	Mira Loma	Spring	Jun '02	0.53
3	Riverside	Winter	Nov '02	0.69
	Riverside	Spring	Mar-Apr '02	0.69
4	USC	Winter	Dec '02 - Jan '03	0.65
	USC	Summer	Sep '03	0.58
5	Upland	Winter	Nov-Dec '03 - Jan '04	0.74
	Upland	Summer	Aug-Sep-Oct '03	0.68
6	Alpine	Winter	Dec '03 - Jan '04	0.90
	Alpine	Spring	Apr-May '03	0.68
7	Lancaster	Spring	Jun-Jul '03	0.57
8	Lake Arrowhead	Summer	Jul-Aug '02	0.84

Table 4: Correlation coefficient (R) between total particle number concentration and PM_{10}

Site no	Site	Season	Period	Pearson correl. coeff.	
				Hourly average	Daily average
1	Long Beach	Winter	Nov '02	NA	NA
	Long beach	Summer	Aug-Sep '03	0.28	0.29
2	Mira Loma	Winter	Feb '02	0.38	0.31
	Mira Loma	Spring	Jun '02	0.29	0.43
3	UC Riverside	Winter	Nov '02	-0.13	0.29
	UC Riverside	Spring	Mar-Apr '02	0.46	0.53
4	USC	Winter	Dec '02 - Jan '03	0.14	0.49
	USC	Summer	Sep '03	0.26	0.35
5	Upland	Winter	Nov-Dec '03 - Jan '04	0.47	0.20
	Upland	Summer	Aug-Sep-Oct '03	0.19	-0.03
6	Alpine	Winter	Dec '03 - Jan '04	0.16	-0.02
	Alpine	Spring	May '03	0.51	0.71
7	Lancaster	Spring	Jun-Jul '03	0.48	0.59
8	Lake Arrowhead	Summer	Jul-Aug '02	0.36	0.26

List of Figures

Figure 11   24-hour averaged a) PN and PM_{10}, b) CO, NO_x, and O_3, and c) temperature

and RH - before, during and after the port strike at Long Beach in Sep-Oct

2002

Figure 12   24-hour averaged size segregated PN before, during and after port strike at

Long Beach in Sep-Oct 2002

Figure 13   Average particle number size distribution before, during and after the port

strike at Long Beach in Sep-Oct 2002

Figure 1

Figure 2 a

Figure 2 b
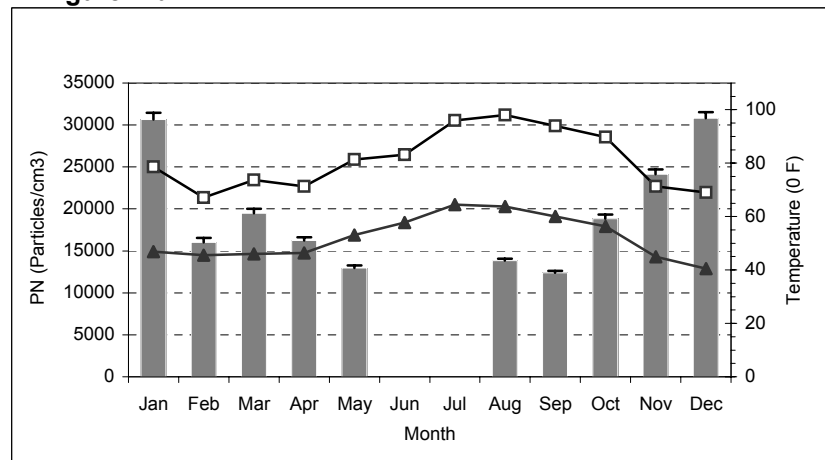
Figure 2 c[1]
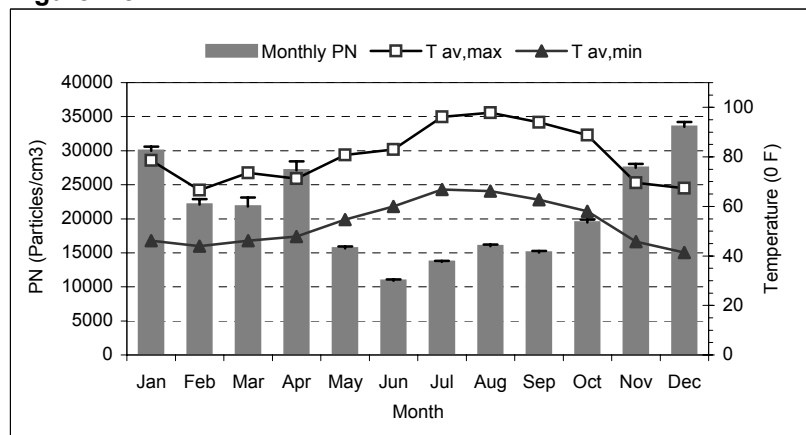
Figure 2 d
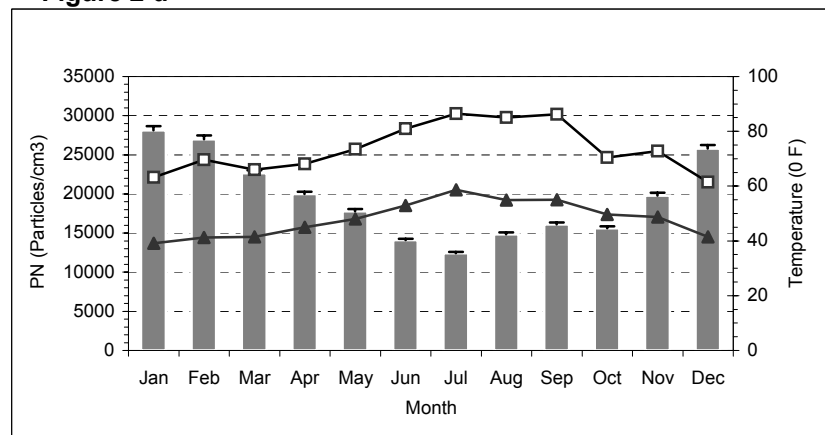
[1]The temperature data for Mira Loma was not available. The data plotted above
was taken from the nearest available site Riverside firestation (around 10 kms east of Mira Loma)

Figure 2 e
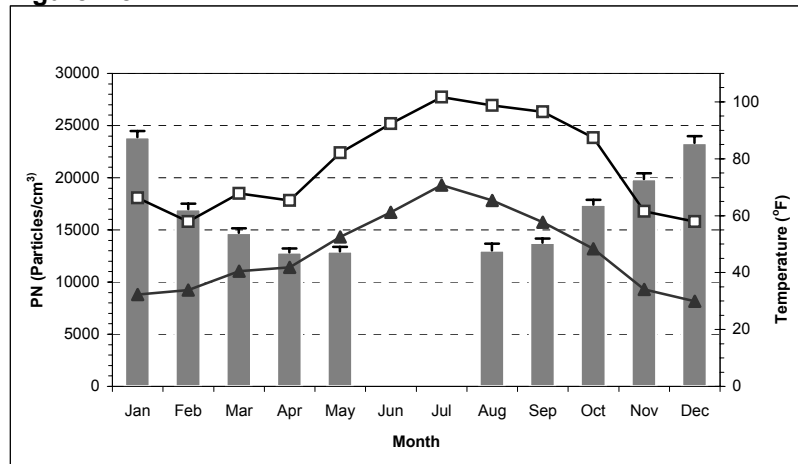
Figure 2 f
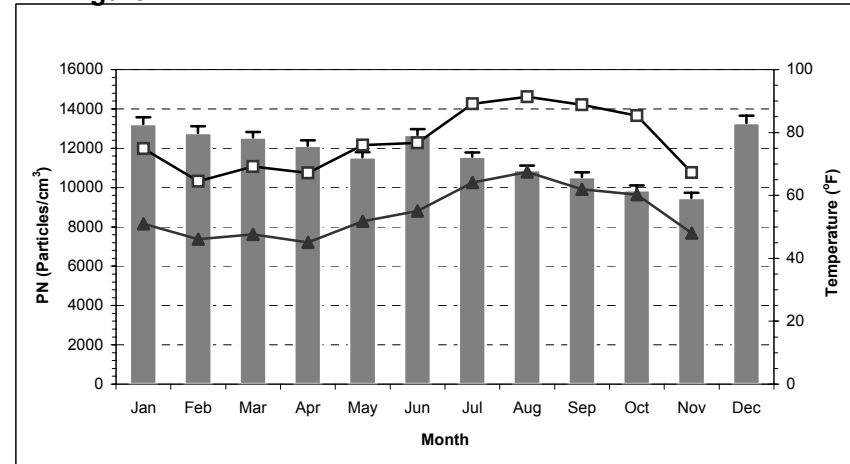
Figure 2 g
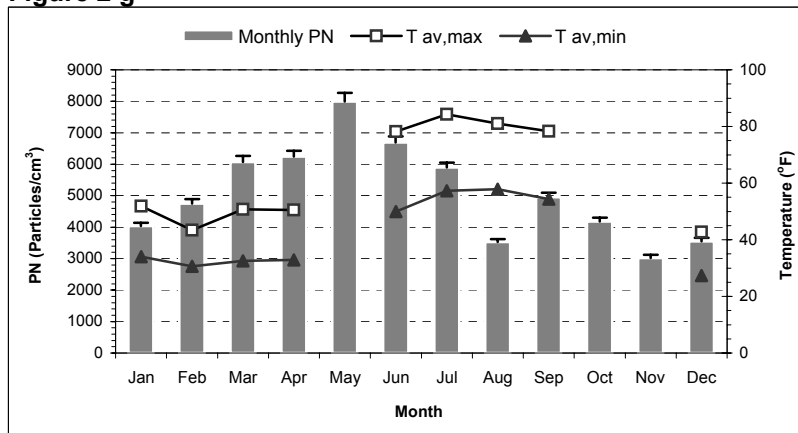
Figure 3 a
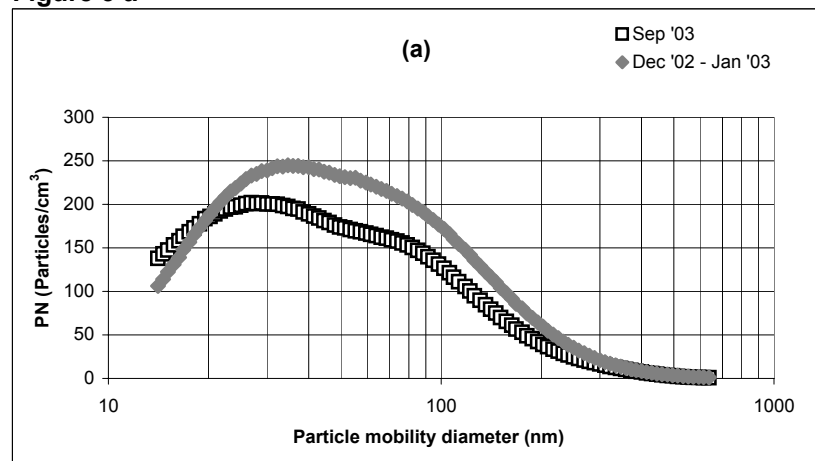
Figure 3 b
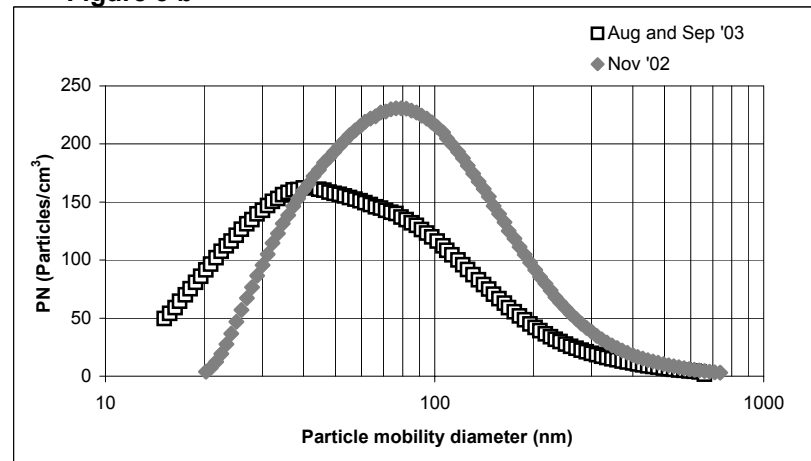
Figure 3 c
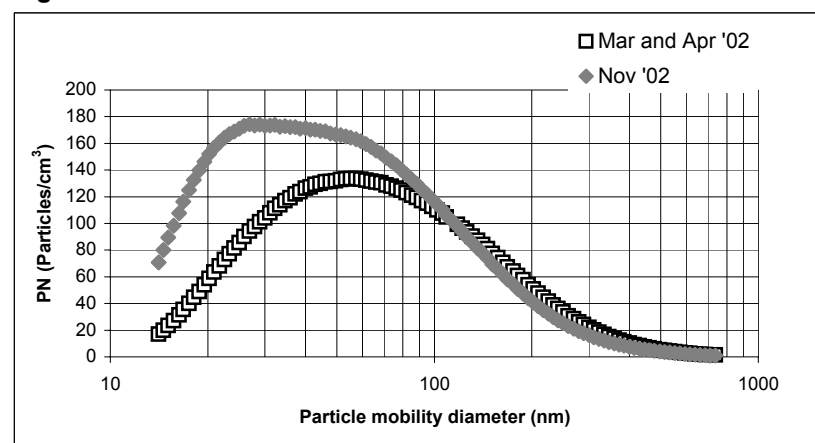
Figure 3 d
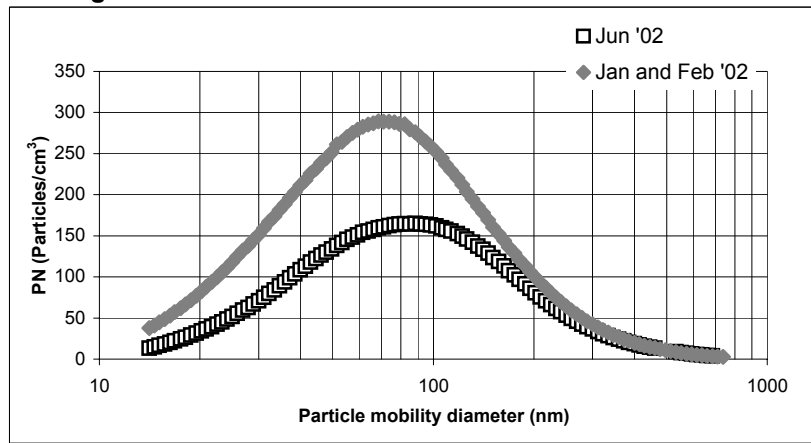
Figure 3 e
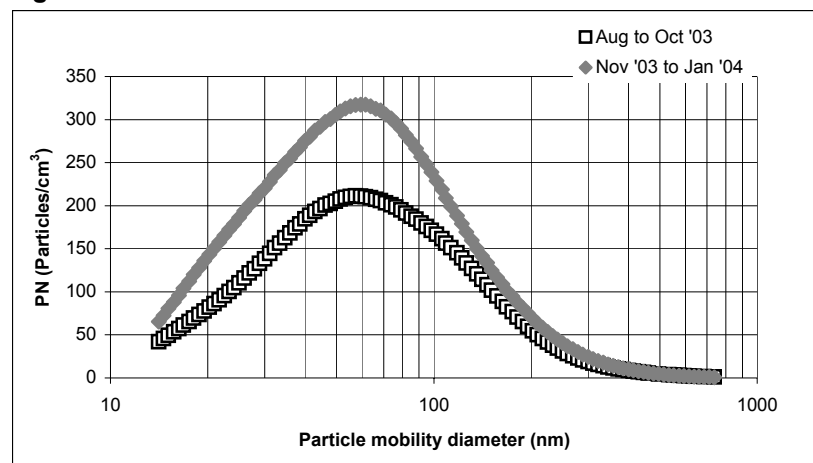
Figure 3 f
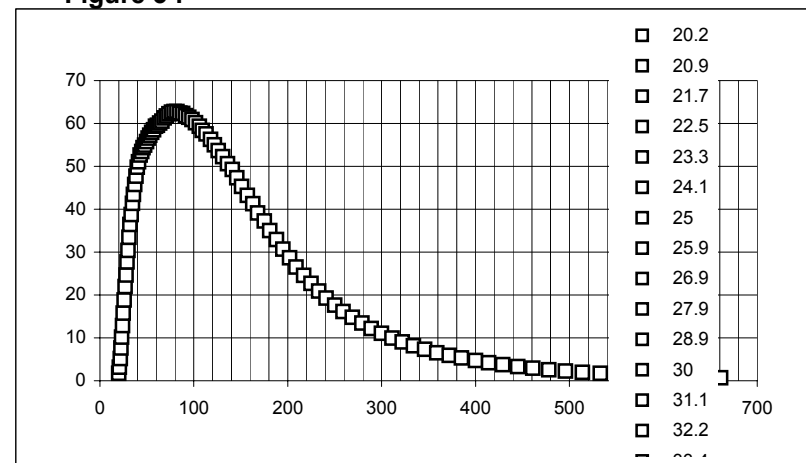
Figure 3 g
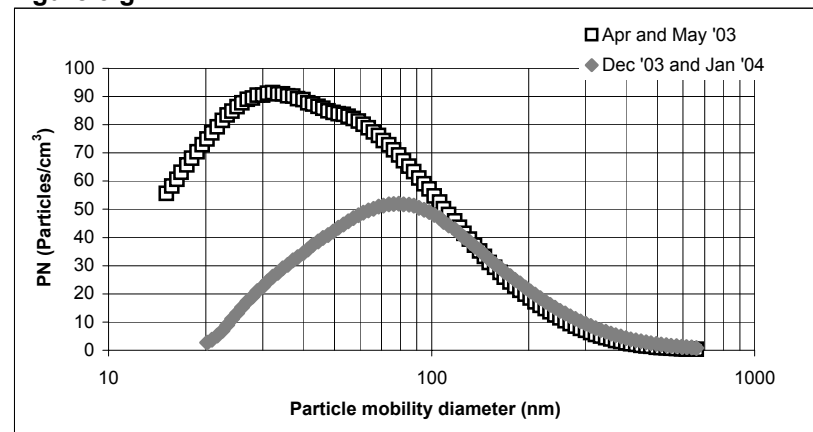
Figure 3 h
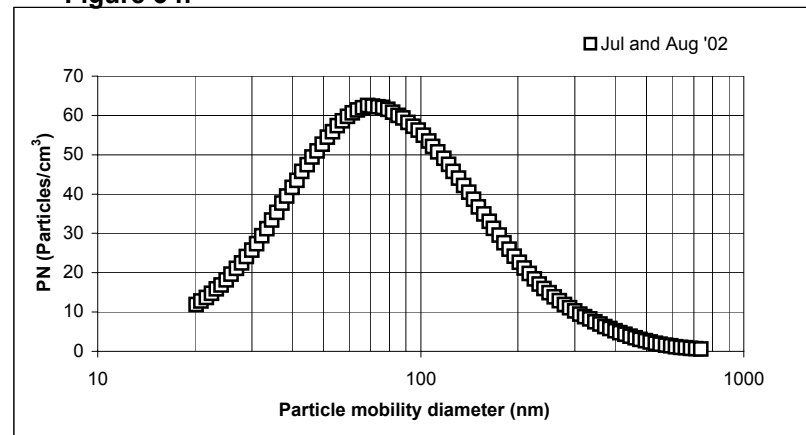
Figure 4a
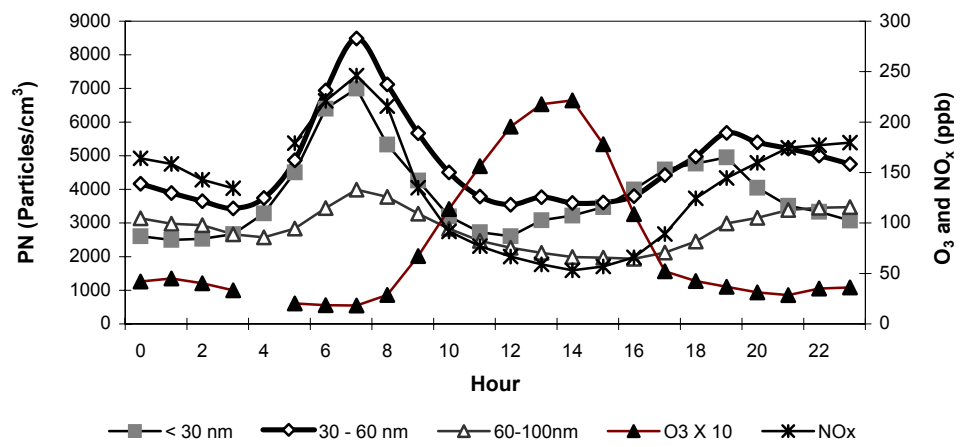
Figure 4b
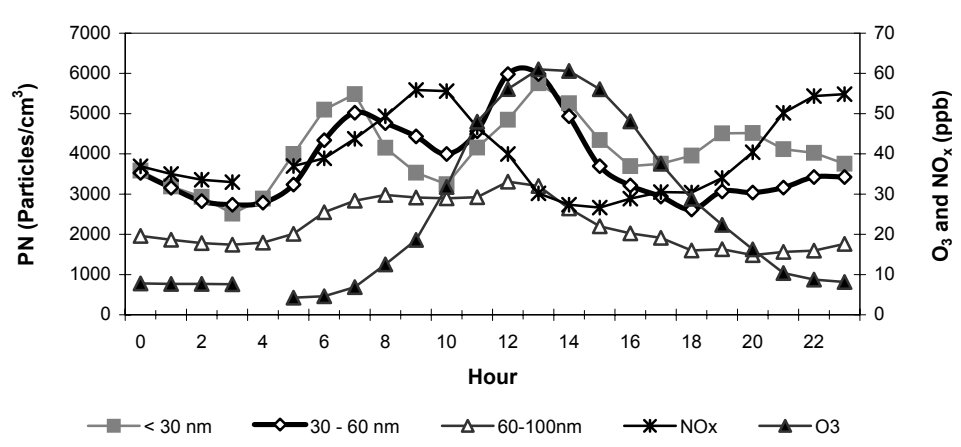
Figure 5 a
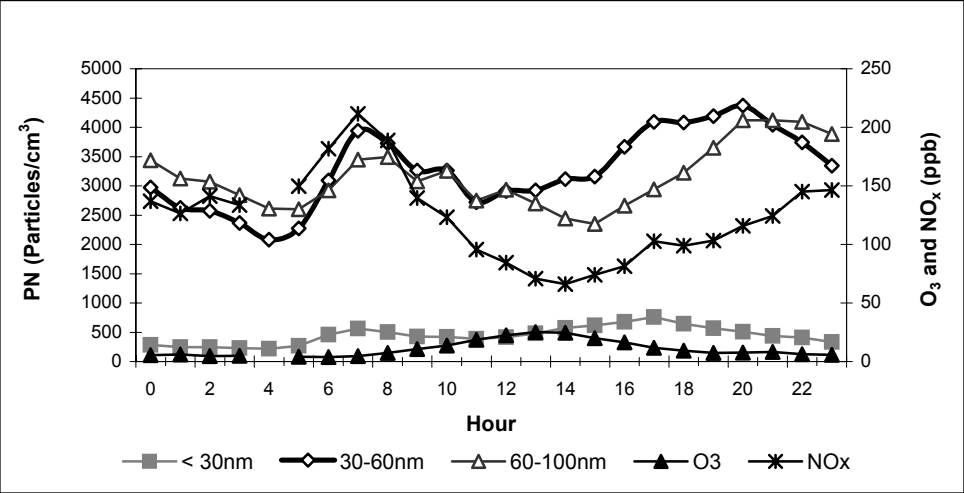
Figure 5 b
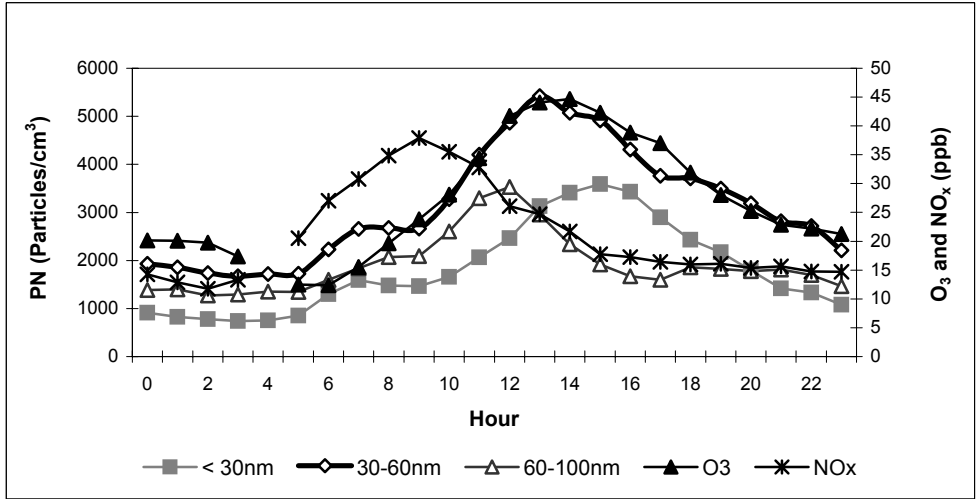
Figure 6 a
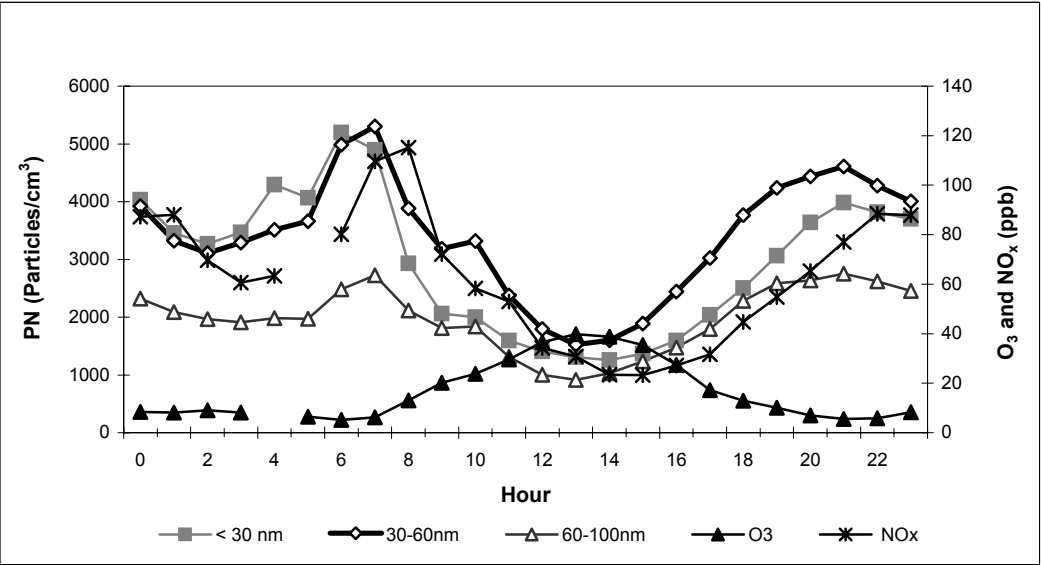
Figure 6 b
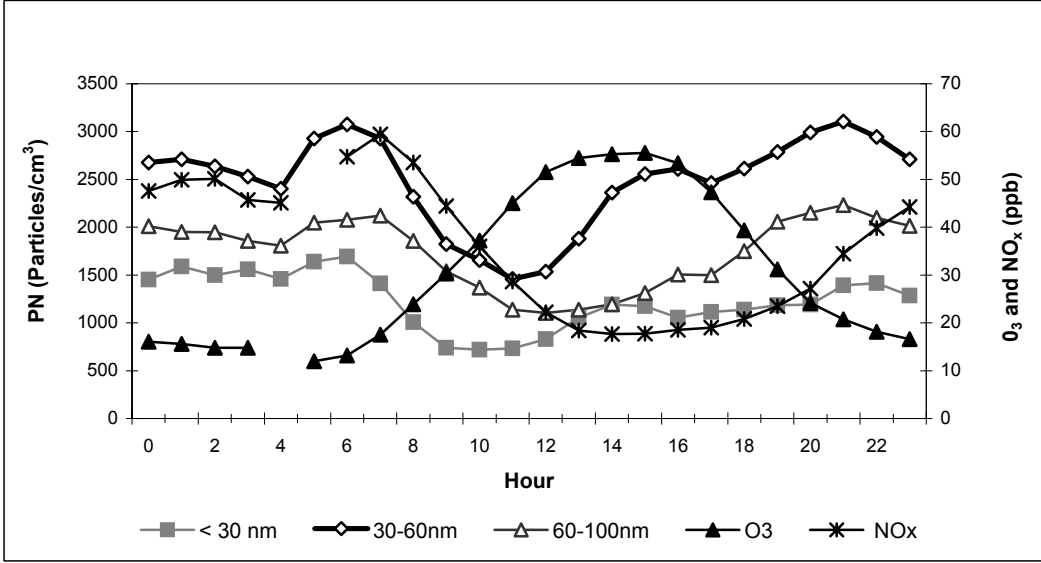
Figure 7 a
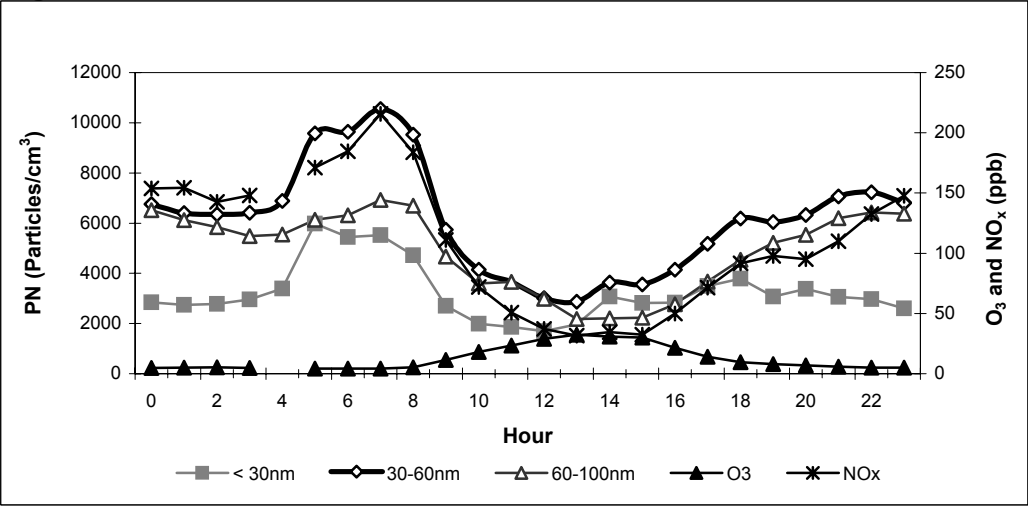
Figure 7 b
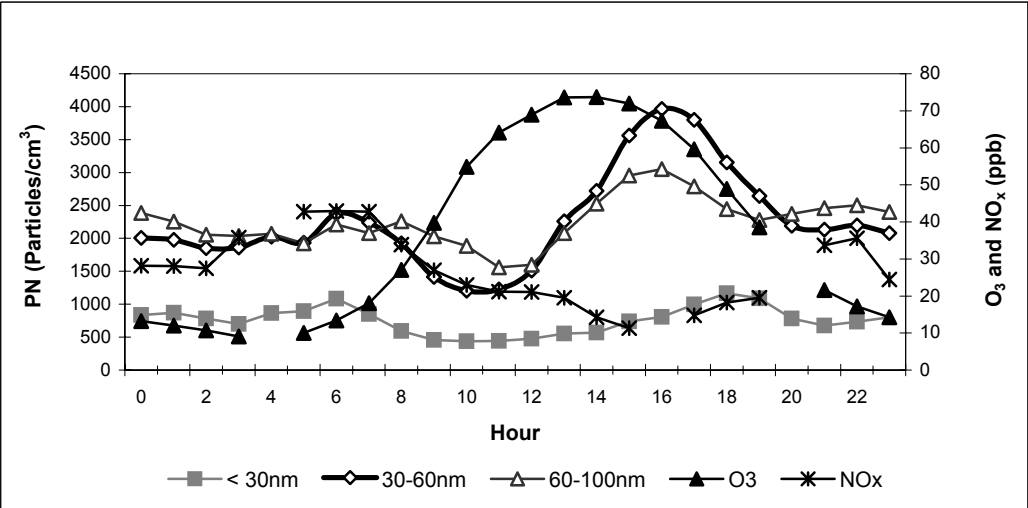
Figure 8 a
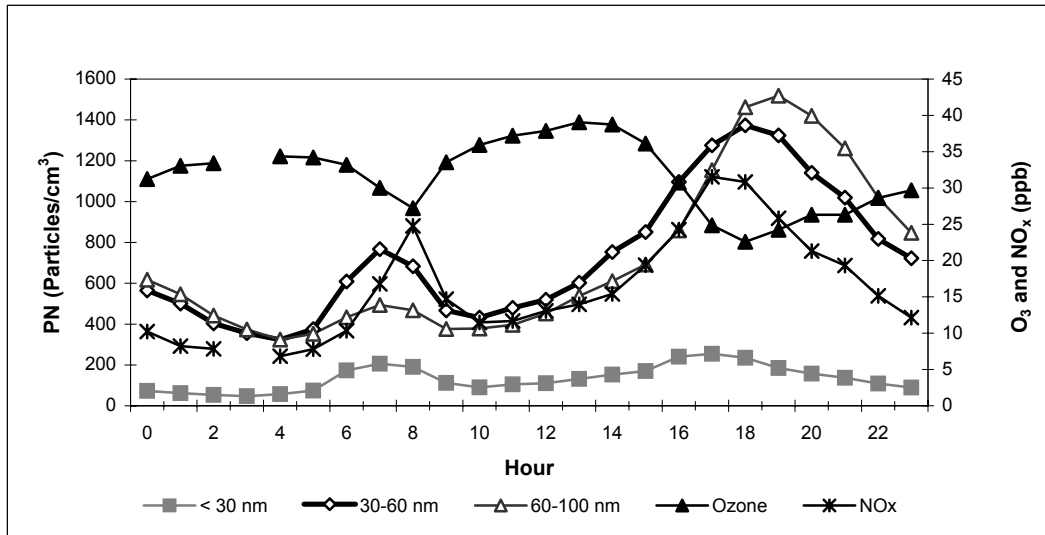
Figure 8 b
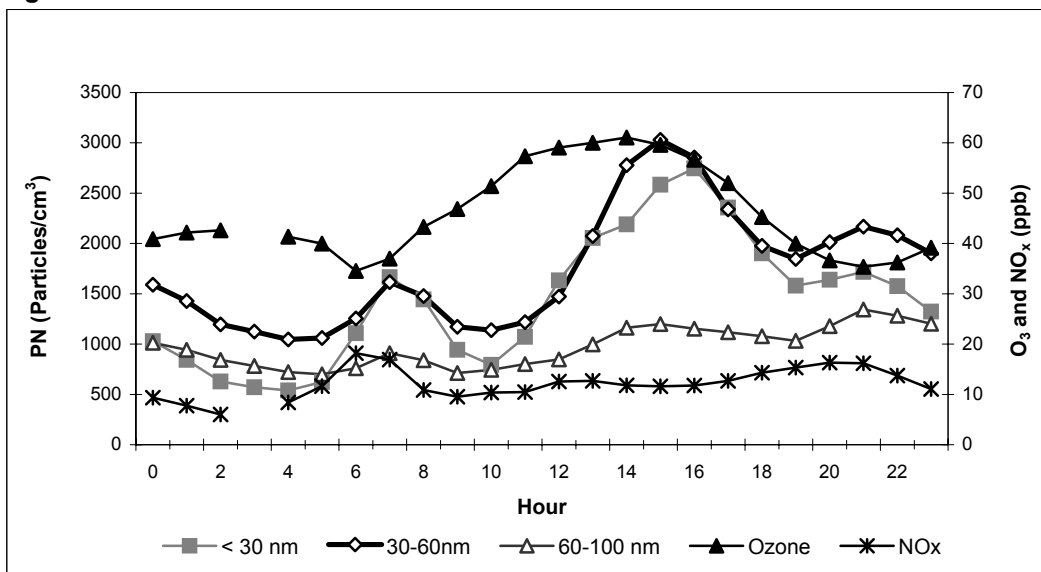
Figure 9
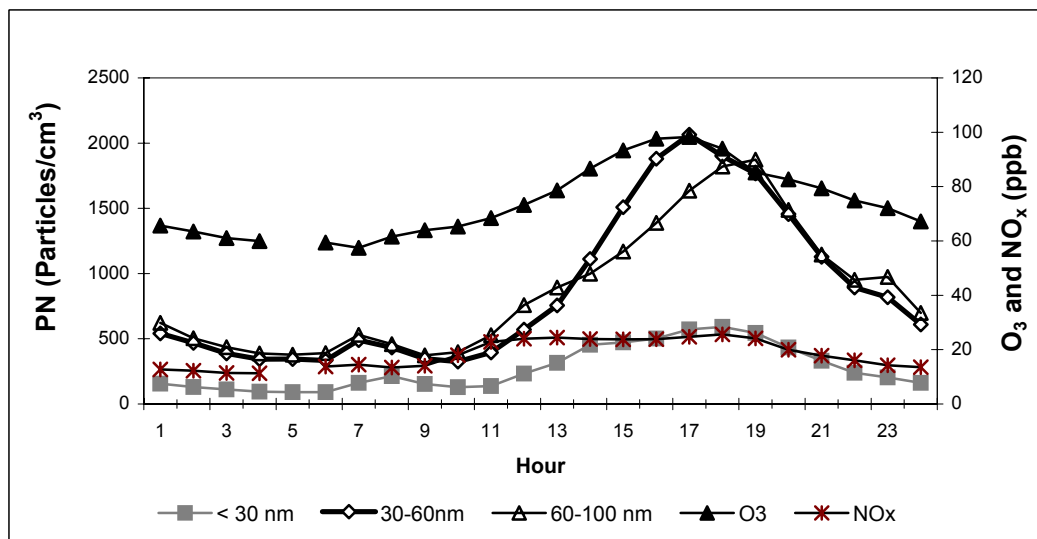
Figure 10 a
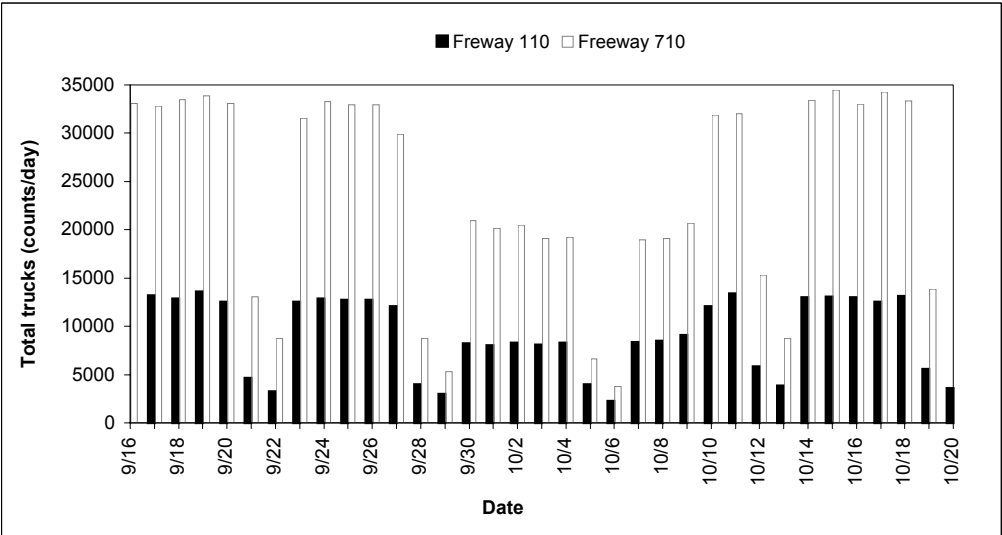
Figure 10 b
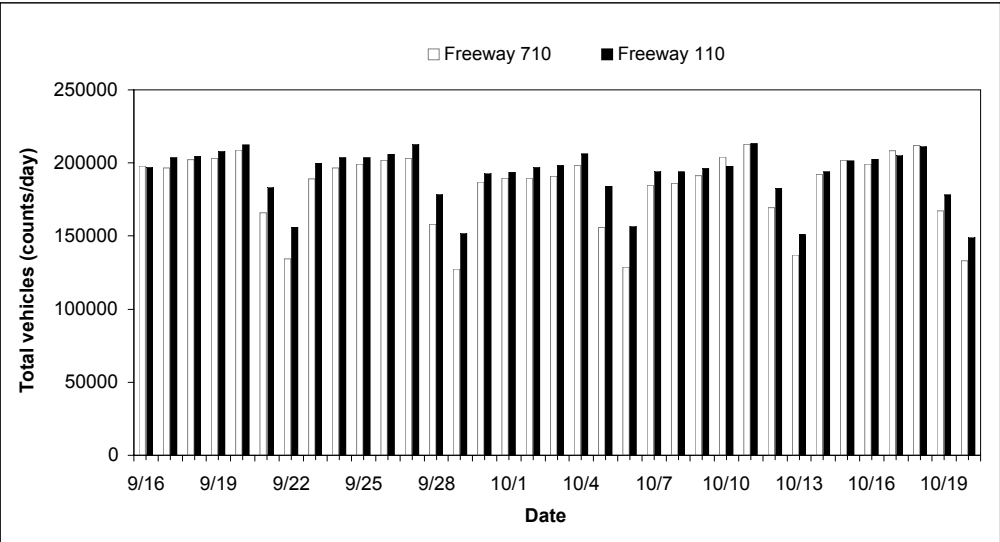
Figure 11 a
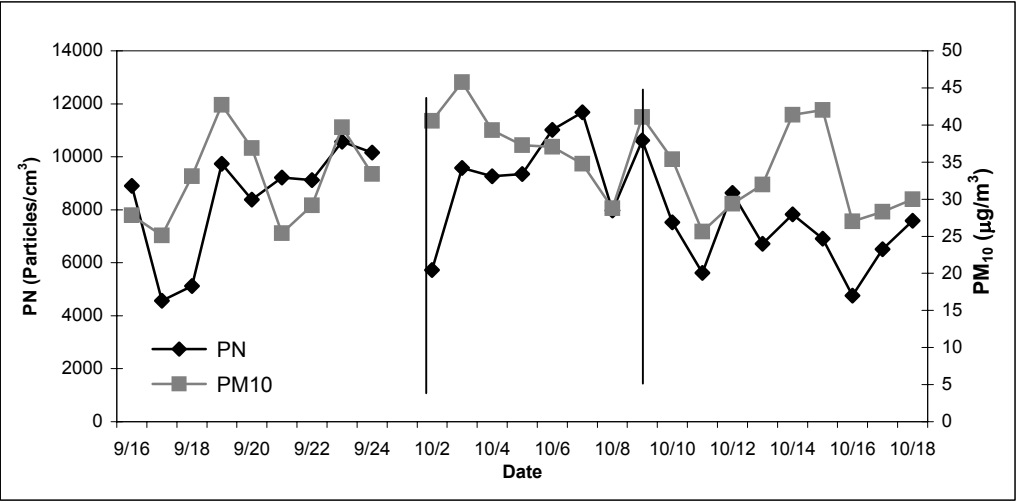
Figure 11 b

Figure 11 c

Figure 12

Figure 13