

INVESTIGATION OF PHYSICO-CHEMICAL CHARACTERISTICS OF
PARTICULATE MATTER FROM VEHICULAR SOURCES

by

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Subhasis Biswas

Dedication

To my father

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Abstract

Particles from vehicular sources have drawn public attention for their potential to cause health risks. Beside chemical composition of these particles, their physical attributes are considered to be critical in eliciting adverse health outcomes. This thesis provides valuable information on particle physico-chemical properties with special focus on physical parameters such as size distribution, volatility, effective density, fractal dimension, surface area etc. Particle effective density and fractal dimensions were measured near a gasoline and a mixed freeway with significant diesel fleet. Diesel vehicles emit higher fraction of low density chain agglomerates compared to gasoline vehicles. Particle density at a receptor site showed interesting diurnal trend with peaks during sunny afternoons. Overall, particles demonstrated an inverse relation between size and density. Particle volatility, an important parameter to infer exposure to commuters, was measured near a pure gasoline and diesel dominated mixed-traffic freeway. Diesel particulates were associated with higher content of non-volatiles than those generated from gasoline engines and correlated excellently with the refractory elemental carbon emissions. Particle mixing characteristics not only depend on the fleet composition but also on environmental factors. Thus, to investigate the effect of meteorological conditions on particle characteristics experimental campaigns were designed to capture seasonal and diurnal variability. Although the daytime seasonal influences on particle volatility were minimal, strong diurnal changes were observed during winter. Finally, the physical characteristics of particles from diesel vehicles retrofitted with advanced emission control technologies were determined by controlled studies with a dynamometer set-up. These

after treatment devices were efficient in removing solid particles, but were less effective in controlling volatile species which formed fresh nucleation mode particles. Particle volatility, density, surface diameter and extent of agglomeration were determined and compared with respect to a baseline vehicle. Our results indicate that vehicles with strong nucleation mode particles are associated with higher volatility and density and lower agglomeration.

Chapter 1: Introduction

1.1 BACKGROUND

1.1.1 Air pollutants and ambient particulate matter

Airborne substances that can cause harms to human beings or to the environment are considered to be air pollutants. Air pollutants may be natural or man-made and can take the form of solid particles, liquid droplets or gases. EPA has listed 188 toxic air pollutants under the 1990 Clean Air Act Amendment. These pollutants comprises of particulate matter (PM), volatile organic compounds (VOCs) and halogen compounds as well as more commonly-known pollutants such as lead, mercury and asbestos (source: US EPA).

Ambient particulate matter, also known as aerosols are suspension of solid and/or liquid droplets in the atmosphere. They are conglomerates of many pollutant subclasses, potentially comprising of different organic and inorganic species. Anthropogenic as well as natural sources contribute to the PM in the atmosphere. Natural sources include wood burning, volcanic eruptions, sea sprays etc. while automobiles, industries, construction activities are examples of man made sources. Besides primary sources, photochemical reaction produces freshly nucleated particles from gaseous pollutants, termed as secondary aerosol formation depending on their saturation ratio and environmental conditions (Seinfeld and Pandis, 1998).

Atmospheric particles are defined by their characteristics or equivalent diameter as most particles do not have perfectly spherical shape. As particles behave differently in different force field, concept of different size terms such as aerodynamic, mobility, or optical diameters have been introduced in aerosol science (Willeke and Baron, 1993). According to aerodynamic diameter PMs are classified into three major groups, i.e. ultrafine ($<0.1\mu\text{m}$), fine ($0.1\text{-}2.5\mu\text{m}$) and coarse ($2.5\text{-}10\mu\text{m}$) modes (Whitby and Sverdrup 1980). Ultrafine particles dominate the number distribution while fine particles, the surface area. The mass distribution has two distinct modes attributing to accumulation and coarse particles. These particles according to their sizes have different sources. While nucleation and automobiles emit most of the ultrafine particles, combustion, atmospheric reaction and coagulation of small particles contributes to the fine mode. Coarse particles are generated primarily by mechanical grinding process or from sea salt sprays. The removal of coarse particles is due to gravitation while ultrafine particles are removed primarily by diffusion. The fine particles are too large to be removed by diffusion and too small to settle down by gravity and generally stays in the atmosphere for the longest time. Also due to their size they interfere with the visible wavelength ($0.3\text{-}0.7\mu\text{m}$) reducing visibility (Hinds, 1999).

1.1.2 Health effects of particulate matter

For the last few decades there has been growing concerns over adverse health effects due to elevated level of particulate matter. These concerns were fuelled by historic air pollution episodes such as London smog in 1952, the first well documented case, where human mortality and hospital admission rates were directly linked to foul air quality.

Several epidemiological studies (Dockery et al., 1993; Pope et al., 1995; Gielen et al., 1997) have demonstrated positive correlations between PM mass and morbidity and/or mortality. The effects are more prominent in susceptible populations such as elderly or population with existing cardiovascular and pulmonary diseases (Saldiva et al., 2002). Few studies have shown that particles can retard fetal growth during pregnancy (Dejmek et al., 1999) or affect gene expressions (Dominici et al 2003).

Particle related regulation started in 1970s when US EPA as part of the Clean Air Act incorporated total suspended particulate (TSP) matter as one of the criteria pollutants. TSP is replaced subsequently, by PM₁₀ (particles <10µm aerodynamic size) standards, in 1987, as only these particles are considered to be the respirable fraction of suspended particles. Generally larger particle (2.5-10µm) of PM₁₀ can be removed easily by impaction or settling in the upper respiratory tract, while particles smaller than 2.5µm penetrate through the alveolar region due to their low scavenging properties (Hinds, 1999), posing potential health risk. Their physicochemical nature and growing evidence of higher toxicity in numerous studies, pave the way for a new legislation on PM_{2.5} standards in 1997.

With immense technological advancements in recent years to measure and concentrate ultrafine particles, scientific communities have shifted their focus to ultrafine particle related health effects. To date, limited, but significant toxicological and epidemiological studies have been carried out involving ultrafine particles. Li et al. (2003) have demonstrated that UFPs induce cellular hemeoxygenase-1 (HO-1) expression, a sensitive

marker for oxidative stress. UFPs were also found to penetrate deep into cellular organelles and damage mitochondria, the compartment for energy synthesis. Heyder et al (1996) and Peters et al. (1997) have also shown strong association between health effects and ultrafine exposure.

1.2 RATIONALE OF THE CURRENT RESEARCH

To account for the different type of health effects, several questions regarding the particle nature needs to be addressed scientifically. Moreover, whether the mass based NAAQS standard for PM_{10} and $PM_{2.5}$ are sufficient to deal with the growing concerns over ultrafine toxicity, make it a classical policy dilemma. Till date, our knowledge linking health outcomes and particle property is limited and little is known about the actual exposure to toxic components of particulate matter. Thus, not only the size of particulate matter but their chemical nature and morphological structure may be instrumental in determining their relative toxicity. Particles with high organic carbon and polycyclic aromatic hydrocarbons (PAHs) are supposed to pose more risk compared to inorganic components (Mauderly et al., 1993, 1994). Likewise, a combustion generated fractal particle with condensed organics, is hard to be removed from lungs than a spherical one and are potentially more toxic.

My endeavor in this thesis is to account for different properties of particles, physical as well as chemical from mobile sources. As the major source of particulate matter in Los Angeles basin is from vehicular emissions, significant amount of research efforts has been channeled to characterize emissions generated from major freeways of California.

Particles generated from a pure gasoline freeway and a freeway with significant diesel fleet, have been sampled and their volatility and effective density measured, besides size distribution and size resolved chemical speciation. The diurnal as well as seasonal effects were also taken into consideration to capture the dynamic nature of particle evolution with respect to changing environmental conditions.

The final work of this thesis involves dynamometer studies of particles generated from different heavy duty diesel vehicles. The primary objective of this work is to determine exactly how the volatile and non-volatile fractions are different in physico-chemical as well as toxicological behaviors. We have focused only on the physical characterization of particulates emitted downstream of heavy duty diesel vehicles retrofitted with various advanced emission control technologies. This would further compliment the findings from freeway experiments, in a way that this would be a controlled study with known parameters.

1.3 THESIS OVERVIEW

The major thrust of this thesis is to address the health concerns already described before (Section 1.2). It is important to know the physico-chemical characteristics of particles to link mechanistically with health effects and to understand the evolution process of freshly emitted aerosols with time (Jacobson and Seinfeld, 2004; Zhang et al, 2004). Thus, the major goal of the thesis is the determination of particle physical properties such as volatility, effective density, size distribution and their chemical speciation (Chapter 2, 3, 4, 5 and 6).

The thesis consists of seven chapters with first (Chapter 1) being the introduction. This section provides a general overview on air pollution, significance and characteristics of particles and particle related health effects. It also identifies the rationale of this thesis and outlines a brief layout.

Chapters 2, 3, 4, 5, 6 shift gear and deal with the measurement of particle characteristics. Chapter 2 is focused on determination of particle effective density in urban environments with an emphasis on mobile and secondary sources. Effective density is responsible for particle depositional and transport behaviors in different segments of lungs, which ultimately determine the level of toxicity (Park et al., 2004). It is also the link between mobility and aerodynamic size of particles and an indirect measure of fractal dimension. Lower the fractal dimension or effective density of particles more is their shape irregularities. This study used a DMA-APM (Aerosol particle mass analyzer) measurement technique (McMurry et al., 2002) to measure density of fine and ultrafine particles generated from diesel or gasoline freeway, secondary atmospheric processes or from marine or urban background. This broad database of effective density can be used in future studies as reference for determining actual particle mass.

Volatility plays an important role in the gas to particle phase partitioning of volatile and semi-volatile organics and determines the mixing characteristics (internal/external) and size distribution (Zhu et al. 2002; Jacobson and Seinfeld, 2004; Srivastava et al, 2006). It is also crucial in policy making on future emission control technologies. Although non-volatile particles or non-volatile cores can be easily filtered out from the tailpipe exhaust

stream, the semi-volatile or volatile species will penetrate through and may condense to form new particles. Chapter 3 describes volatility and chemical characteristics of particles generated from a light-duty pure gasoline vehicle freeway (CA-110 freeway) during summer of 2004. Two sites were chosen, i.e. one just 2.5m away from the freeway for freshly emitted aerosols and at 150m to capture downwind or background aerosol. Ultrafine particle (20, 40, 80 and 120nm) volatility was measured by tandem differential mobility analyzer (TDMA) (Sakurai et al., 2003; Orsini et al., 1999) at different temperatures and their volatility ratios were calculated at 60 and 110°C. Size resolved chemical speciation is also reported from filter-based analysis taken concurrently with MOUDI and high-volume sampler.

We replicated the volatility experiments at the same sites during our winter campaign at CA-110 freeway, which gave us a unique opportunity to compare the winter vs summertime volatility characteristics. Temperature and other meteorological parameters can have significant impact on the particle composition and volatility (Kittelson et al., 2004; Wei et al., 2001). Therefore, Chapter 4 will focus on the seasonal as well as diurnal variability of particle volatility and chemical composition. The volatility comparison was based on changes in mode diameter at different temperature and their volatility ratios.

As most urban freeway comprise of a fleet of diesel vehicles, our efforts at CA-110 are further complemented by winter study (2006) at interstate 710 freeway. This freeway is a major truck route in California and diesel vehicles contributes a significant fraction (20-25%) of its total traffic (Zhu et al., 2002). Diesel emissions have been proven to be

carcinogenic in nature and are generally dominated by chain agglomerates of elemental carbon with condensed volatiles and semi volatiles (Kittelson, 1998; Sakurai et al 2003; Park et al., 2004). We have reported and compared the wintertime particle volatility of I-710 and CA-110 freeway in Chapter 5. This work also includes carbon speciation carried out by EC-OC monitor and Aethalometer.

The final work is documented in Chapter 6. Particulate matter (PM) emitted from vehicular sources consists of both non-volatile and semi-volatile fractions. Emission control technologies used in compliance with US 2007 Emissions Standards remove effectively the non-volatile fraction, but are less effective at controlling the volatile fraction. Removal of the non-volatile PM can favor the formation of nano particles ($dp < 0.05 \mu\text{m}$) by enhancing nucleation of condensing vapors. Toxicological studies have associated ultrafine particles with adverse health outcomes. However, there are limited references about physicochemical and toxicological properties specific to the semi-volatile and non-volatile fraction. An extensive study has been initiated by University of Southern California in collaboration with California Air Resource Board (CARB) to bridge the knowledge gap. Although the primary objective of this extensive study is to determine particle toxicity, the focus of this chapter will be limited only to present the physical characteristics of particulate emissions from heavy duty diesel (HDD) vehicles operated with different emission control technologies. Physical properties such as size distribution and volatility both in terms of number and mass, surface diameter, particle agglomeration and density are reported. The sampling for this study was conducted at the CARB's Heavy-Duty Diesel Emissions Test Laboratory (HDETL). The sampling

train included heavy duty (HD) dynamometer chassis, constant volume sampling (CVS) dilution tunnel and aerosol samplers. A group of four vehicles in combination with six after treatment devices i.e. selective catalytic (vanadium or zeolite based catalyst) reduction systems, continuously regenerating technology (CRT), Catalyzed filter (DPX), electric particulate filter and catalyzed CRT (CCRT) were evaluated under three driving cycles: cruise, urban dynamometer driving schedule (UDDS) and idle. All the results were compared with respect to a Baseline vehicle (without any control).

The summary and major conclusions of these thesis extracted from individual chapters are elaborated in chapter 7. This chapter will also discuss about the potential research areas based on the findings of this work and few policy issues that need to be addressed.

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Chapter 2: Determination of Particle Effective Density in Urban Environments with a Differential Mobility Analyzer and Aerosol Particle Mass Analyzer

2.1 ABSTRACT

Effective densities of atmospheric aerosols in various locations of the Los Angeles Basin were determined by a DMA-APM technique. Effective density was calculated by comparing voltage distributions of sampled atmospheric aerosols with PSL particles of known density. The five sites chosen for field experiments were: (1) Interstate-710 Freeway, impacted by heavy-duty diesel vehicles; (2) State Route CA-110, open only to gasoline vehicles; (3) Riverside, a receptor site known for secondary particle formation; (4) University of Southern California, a typical urban and industrial environment; and (5) Coast for marine aerosol. The size range selected for this study was from 50 nm to 414 nm. While 50 nm particles exhibited a single effective density multiple effective densities were measured for each of the other particle sizes as significant fractions of these particles are transported from background sources. Regardless of location, 322–414 nm particle effective densities were considerably lower than unity. The lowest effective densities ($\sim 0.1 \text{ g cm}^{-3}$) were reported for I-710, confirming that diesel combustion aerosols are rich in chain agglomerates with large void spaces. Riverside exhibited high effective densities ($\sim 1.2\text{--}1.5 \text{ g cm}^{-3}$) for 50–202 nm particles, which we hypothesize is due to transformations that occur during advection from Los Angeles. Measurements of diurnal variation of effective density at Riverside support this hypothesis. Overall, our results suggest that effective density declines as the particle mobility diameter increases irrespective of location. Fractal dimensions calculated from average effective densities

were lowest for I-710 ($D_f = 2.41$) and CA-110 ($D_f = 2.54$) aerosols, presumably due to the influence of vehicular combustion emission on these sites. By contrast, average fractal dimensions at USC, Riverside and Coast were found to be 2.79, 2.83, and 2.92, respectively. High fractal dimensions at these sites may be the effects of aging, moisture absorption and/or organic vapor condensation on the particles, which fills void space and makes particles more spherical.

2.2 INTRODUCTION

Recent toxicological and epidemiological research has found various adverse health effects related to fine and ultrafine particles (Dockery and Pope, 1994; Peters et al., 1997; Li et al., 2003, Oberdörster et al., 1996). However, the mechanisms by which these health effects are elicited have not been determined, creating speculation that chemistry, surface area, number of particles, or a combination of these properties may be responsible. Additionally, a current review of epidemiological studies has found a relationship between freeways and cancer rates (Mack, 2004). Ambient particles, unlike other gaseous co-pollutants, are unique in that their complete characterization would require knowledge of their size distribution, mass and number concentrations as well as their chemical composition. All of these important parameters determine the site of particle deposition in the respiratory track and the degree to which they may exert adverse health effects.

In addition to the above list, particle density is an important parameter, because it determines the transport and depositional properties of particles in lungs. In most cases, the “average” particle density of a given size range (which, in most studies, is restricted

to fine PM, or PM_{2.5}) is determined indirectly by knowing the bulk chemical composition of that range. Typically, this involves measurement of the relative mass fractions of key PM constituents, such as elemental and organic carbon (EC-OC), inorganic ions (sulfate, nitrate and ammonium) and selected trace elements and metals. Atmospheric aerosol particles are often assumed to be completely spherical in shape, but combustion-generated particles are ubiquitously found to grow from nearly spherical primary particles into fractal-like agglomerate structures with high carbon content. Combustion is a well-known source of fine and ultrafine particles and a source to which humans are frequently exposed, especially in relation to traffic and mobile sources. Diesel engines in particular emit large amounts of these agglomerate soot particles (Park et al., 2004; Burtscher, 2005).

Agglomerate particles are characterized by high surface area and low density, both of which have implications in toxicity and deposition in the lungs. To account for particle morphologies substantially different from spherical shapes, the term “effective density” has often been employed in the aerosol field. Effective density is proportional to the ratio of aerosol bulk density to its shape factor (Khlystov et al., 2004) and can be defined by the following equation:

$$\rho_e = \frac{1}{\chi} \frac{d_{ve}^2 C_{ve}}{d_{me}^2 C_{me}} \rho_{true} \quad (1)$$

Where ρ_e is the effective density, χ is dynamic shape factor, d_{ve} is the volume equivalent diameter, d_{me} is the mobility equivalent diameter, C is the Cunningham correction factor, and ρ_{true} is the bulk density of the material (McMurry et al., 2002).

Fractal dimension (D_f) is an indirect measure of the morphology of irregularly shaped agglomerate particles. Traditionally, light-scattering measurements as well as transmission electron microscopy (TEM) have been used to provide data on soot fractal dimension. However, these methods are very tedious, as they only measure few particles at a time, and they cannot be used “on-line” to provide this information near-continuously. These methods also contribute to the discrepancy of soot aggregate properties; light-scattering data are heavily weighted by particles at the large end of the size distribution. TEM derivations of the fractal dimension of 3D objects are limited to a two-dimensional field, and thus suffer from problems of primary particle overlap, screening effects, and cluster anisotropy (Wentzel et al., 2003). The various measurement techniques presume different definitions for particle size, including radius of gyration, maximum length and mobility diameter. Kutz and Schmidt-Ott (1990) coupled a differential mobility analyzer (DMA) with an impactor to collect particles for TEM analysis. Although this study incorporated mobility diameter measurements, it still suffered from the TEM limitations discussed above. Fractal dimension (D_f) can readily be measured if one knows the effective density of particles of difference sizes. The relationship is given by Park et al. (2003):

$$\rho_e = C d_{me}^{D_f-3} \quad (2)$$

Where D_f is fractal dimension and C is a constant.

Researchers have used different experimental approaches to determine particle effective density. Few studies have been carried out to determine its seasonal and diurnal characteristics for $PM_{2.5}$ (Morawska et al., 1999; Kuhlbusch et al., 2001; Pitz et al., 2003). Hanel and Thudium (1977) determined the bulk dry aerosol density by measuring the volume and mass of particles, independently. As part of the Pittsburgh Supersite efforts, Khlystov et al. (2004) developed an algorithm to merge SMPS and APS distributions and combined them with MOUDI mass concentrations to determine aerosol density for size fractionated PM_{10} . Recently, researchers have employed a tandem set-up of a DMA and electrical low-pressure impactor (ELPI) for diesel particles (Maricq et al., 2000; Ahlvik et al., 1998). Virtanen et al. (2004) calculated effective density by simultaneously measuring the mobility and aerodynamic size distributions with an SMPS and an ELPI, using a best-fit technique to match distributions. These studies eliminate the need to visually inspect particles in order to estimate their fractal dimension, which increases the number of particles that can be sampled. Recent studies, however, have indicated rapid overloading in ELPI impactor stages due to the “fluffy” structure of diesel particles, reducing their usefulness (Van Gulijk et al., 2001). McMurry et al. (2002) developed a novel and elegant technique to measure particle effective density via a tandem differential mobility analyzer (TDMA) and aerosol particle mass analyzer (APM). The number of particles that can be sampled greatly increases with this method.

The present study employs the same DMA-APM set-up used by McMurry et al. (2002) to determine the effective density of various types of atmospheric aerosols in the Los Angeles Basin. Building upon the findings of the McMurry et al. (2002) study, which

was conducted in one location and was restricted to two aerosol mobility diameters, our study's goal was to create a broader database of effective aerosol densities for different particle sizes in the range of 50 to 414 nm and at different locations in Southern California, each of which is impacted by distinct particle sources and formation mechanisms.

2.3 METHODS

2.3.1 Experimental design

This study is based on a methodology similar to one developed by McMurry et al. (2002), in which a differential mobility analyzer (DMA) precedes the APM. A schematic of the DMA-APM setup is shown in Figure 2.1. A near-monodisperse aerosol of a known particle mobility diameter is selected by the DMA of the Scanning Mobility Particle Sizer (SMPS Model 3081, TSI Inc., St. Paul, MN), which is connected upstream of the APM (Model 10, Kanomax USA inc, Andover, N.J.). The DMA is equipped with a Kr⁸⁵ neutralizer that brings the aerosols to the Boltzmann equilibrium. The inlet and sheath flow rates in the DMA were 0.5 liters per minute (LPM) and 5.0 LPM, respectively. This configuration enables the system to select particles between 15 nm and 500 nm, affording flexibility to select both ultrafine and accumulation mode particles.

Ehara et al. (1996) first proposed the APM to classify particles according to their mass to charge ratio. Classification occurs between the narrow annular space, also termed the operating space, available between two rotating coaxial cylindrical electrodes. The outer cylinder (inner radius = 63mm) is grounded while classifying voltage is applied to the

inner cylinder (outer radius = 60 mm). The angular velocity of inner and outer electrodes is the same. Therefore, when the aerosol is introduced into the operating space, it acquires the same angular velocity as that of the electrodes. Particles thus experience radial electrical and centrifugal forces, which act in opposite directions. When the forces balance each other, the particles will penetrate through the rotating cylinders to the downstream detector.

The principal equation describing the force balance is

$$m\omega^2r = \frac{\pi d_{ve}^3}{6} \rho_{true} \omega^2r = neE_{APM}, \quad (3)$$

where m is particle mass, ω is APM angular velocity, r is the radial distance to the annular gap from the axis of rotation, and E_{APM} is the electric field.

After selection by the DMA, particles mix with 0.5 LPM of particle-free air (HEPA capsule, Gelman laboratory) and then pass through the APM. A Condensation Particle Counter (CPC Model 3022A, TSI inc., St. Paul, MN) counts those particles that have the APM-selected mass. The CPC operated at 0.3 LPM, therefore a diaphragm pump pulled an additional 0.7 LPM in order to satisfy the 1.0 LPM minimum flow requirement of the APM. Three APM rotational velocities (1000 RPM, 2000 RPM, 3000 RPM) were chosen in order to adequately measure the desired size range of particles.

Higher rotational velocities make it possible to sample less massive particles. For each particle size, the voltage on the APM was scanned manually, and the particle concentrations corresponding to each voltage were recorded. The residence time of the

APM was considered when matching particle concentrations measured by the CPC with their corresponding voltage settings on the APM. Thus, APM voltage was fixed for a time period much longer than its residence time to account for transient particle penetration between voltage steps. In addition, concentrations at the beginning and end of measurements at each voltage step were discarded.

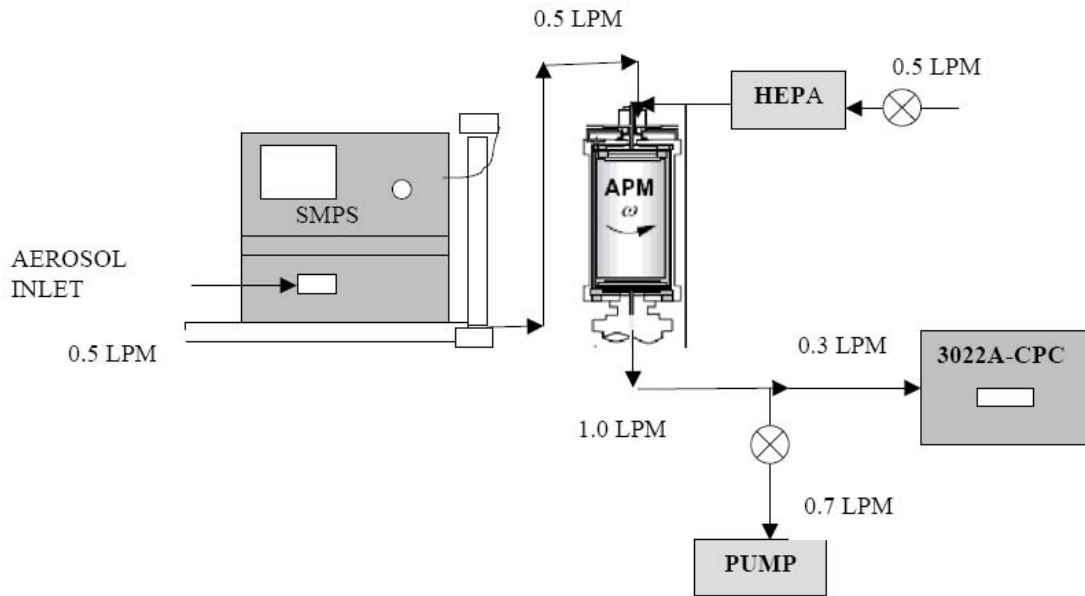


Figure 2.1 Schematic of DMA-APM set-up.

PSL particle sizes were selected keeping in mind the limitations of both the DMA and the APM. The APM voltage corresponding to the maximum number concentration for the selected PSL particle size was used as the reference voltage ($V_{\text{APM PSL}}$) in equations 4-6.

$$\frac{m_{test} \omega^2 r}{m_{PSL} \omega^2 r} = \frac{\rho_{true} \frac{\pi d_{ve}^3}{6}}{\rho_{PSL} \frac{\pi d_{PSL}^3}{6}} = \frac{neE_{APM-sample}}{neE_{APM-PSL}} = \frac{V_{APM-sample}}{V_{APM-PSL}}, \quad (4)$$

where, V_{APM} is the APM voltage for sample and PSL aerosols, and ρ_{PSL} is the material density of PSL particles.

For spherical particles $d_{ve} = d_{me} = d_{PSL}$, therefore

$$\rho_{true(sphere)} = \rho_{PSL} \frac{V_{APM-sample}}{V_{APM-PSL}}, \quad (5)$$

and the effective density of irregularly shaped particles can be given by

$$\rho_e = \rho_{PSL} \frac{V_{APM-sample}}{V_{APM-PSL}}. \quad (6)$$

2.3.2 Laboratory experiments

Before performing ambient sampling, PSL particles between 50-414 nm were measured by the DMA-APM tandem to construct each particle's reference voltage distribution. Monodisperse polystyrene latex (PSL, Polyscience Inc., Warrington, PA) particles were generated by atomizing their respective solutions with a constant output Nebulizer (HEART, VORTRAN Medical Technology, Inc., Sacramento, CA). Sufficient dilution of HEPA-filtered, particle free dry room air was supplied in a 2-liter glass container to remove moisture from the nebulized particles. Particles were neutralized by a series of Po-210 neutralizers (NDR Inc., Grand Island, NY) before entering the DMA-APM

tandem. The density of PSL particles is 1.054 gcm^{-3} , which has been used as the reference density for particle effective density calculations.

2.3.3 Atmospheric experiments

To determine the effective density of atmospheric particles with different characteristics, sampling was conducted at five locations in the Los Angeles Basin, each of which is influenced by varied emission sources and formation mechanisms (Figure 2.2).

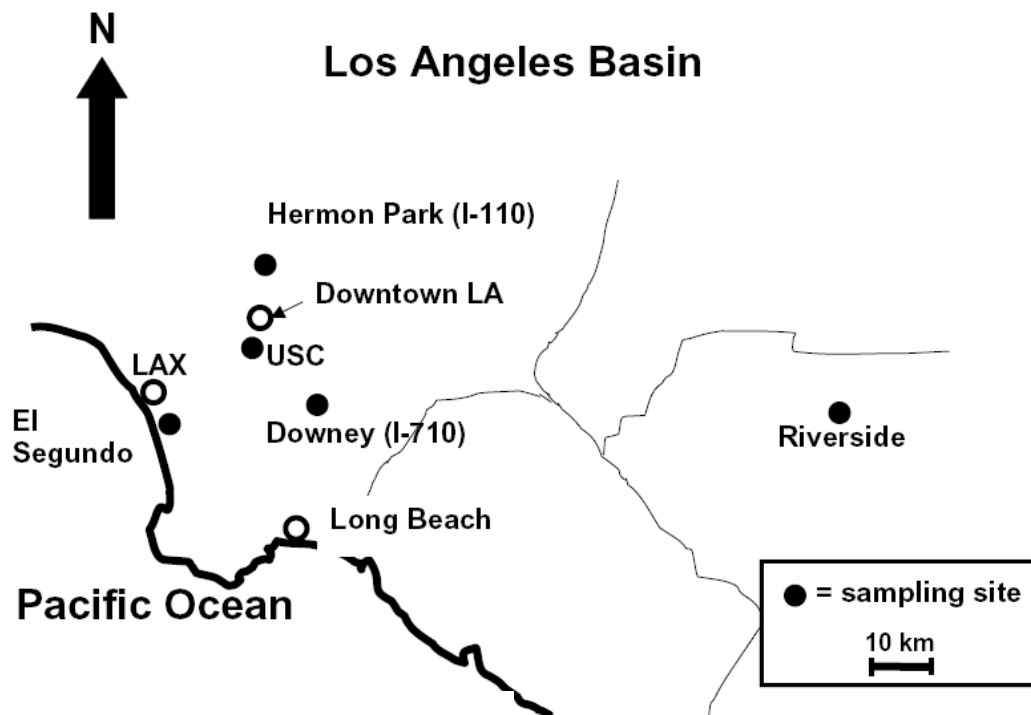


Figure 2.2 Sampling sites

The sampling period extended from early September to late October of 2005, with 5-7 days spent at each site. The University of Southern California's Particle Instrumentation

Unit of the Southern California Supersite (USC) represents a typical urban/traffic/industrial environment. It is about 100 m downwind of CA-110 freeway and 2 miles south of downtown Los Angeles. The next sampling location was a site 5 meters away from I-710 freeway in Downey, CA. This eight-lane freeway is a major heavy commercial truck route with approximately 25-30% diesel truck traffic (Zhu et al., 2002). Previous studies have shown that a relatively high elemental carbon content and low effective density characterizes particles generated due to diesel combustion (Sharma et al., 2005; Burtcher, 2005; Keskinen et al., 1998). State Route 110 (CA-110), between downtown Los Angeles and Pasadena, CA (USA) is the oldest freeway in the U.S. and thus cannot accommodate large trucks. It offers a unique opportunity to sample particles generated predominantly by light-duty gasoline vehicles. The sampling location is in the Hermon Park within 2-3 meters from the edge of the freeway. The Riverside site is situated within the facilities of the Citrus Research Center and the Agricultural Experiment Station of the University of California, Riverside. It is a receptor site as aged particles from Los Angeles are advected to the site by the westerly winds (Geller et al., 2002). It is also influenced by the upwind stationary ammonia sources that react with advected NO_x to form ammonium nitrate. In addition, Riverside is a typical location for photochemical organic aerosol formation due to high solar radiation that contributes to temperatures often in excess of 30°C during the afternoon. Coastal aerosols were measured at El Segundo beach on the Pacific coast. This site is impacted by marine aerosols comprised mainly of sea salt and organic compounds. The average number concentration in the afternoon is very low, typically in the range of 2,000-5,000 particles cm⁻³ (Biswas et al., 2005) because the onshore flow during the afternoon is stronger. The

concentrations at this site may be slightly higher in the morning when the offshore flow from overnight moves the more polluted urban mix towards the coast, where it stagnates (Hughes et al., 1999). Finally, we measured effective densities of particles generated by a brush fire, which flared up during the study period. Sampling occurred on one afternoon at a location within two miles downwind of the fire. The opportunistic nature of this event and the relative unpredictability of the fire and wind directions allowed for measurement of only two particle sizes.

2.4 RESULTS AND DISCUSSION

2.4.1 Laboratory experiments

The first phase of the laboratory evaluation was to determine the reference APM voltages for particles of known size and density. Before scanning the voltage with the APM, the DMA was connected directly to the CPC to confirm the mode particle diameter of the PSL number concentration and the degree to which each aerosol was monodisperse. The DMA was set to the voltage (or mobility diameter) corresponding to the maximum number concentration from the mobility scan. An iterative process of varying voltage and rotational velocity allowed us to select a set of APM operating parameters to scan voltages within the range of the instrument. Table 2.1 summarizes the APM operating characteristics, and Figure 2.3 illustrates particle number concentrations (N) penetrating the APM as a function of APM voltage for all sampled PSL particle sizes. Due to the large variation between number concentrations of different particle sizes, N for 50 nm PSL is plotted on the primary (left) y-axis, while all other PSL sizes are plotted on the secondary (right) y-axis. It is evident from this figure that small changes in particle

diameter equate to large variations in APM voltage. Because of constraints of the APM, 50 nm particles were the smallest reliably sampled in this study, and the greater width of the voltage distribution at this size is most likely the result of proximity to the limit of detection (LOD) of the APM. The APM operating characteristics for each particle size remained constant throughout all successive experiments.

Table 2.1 APM sampling parameters

Particle Diameter (nm)	Rotational Velocity (RPM)	PSL Peak Voltage (V)
50	3000	14
118	2000	75
146	2000	140
202	1000	130
322	1000	760
414	1000	1660

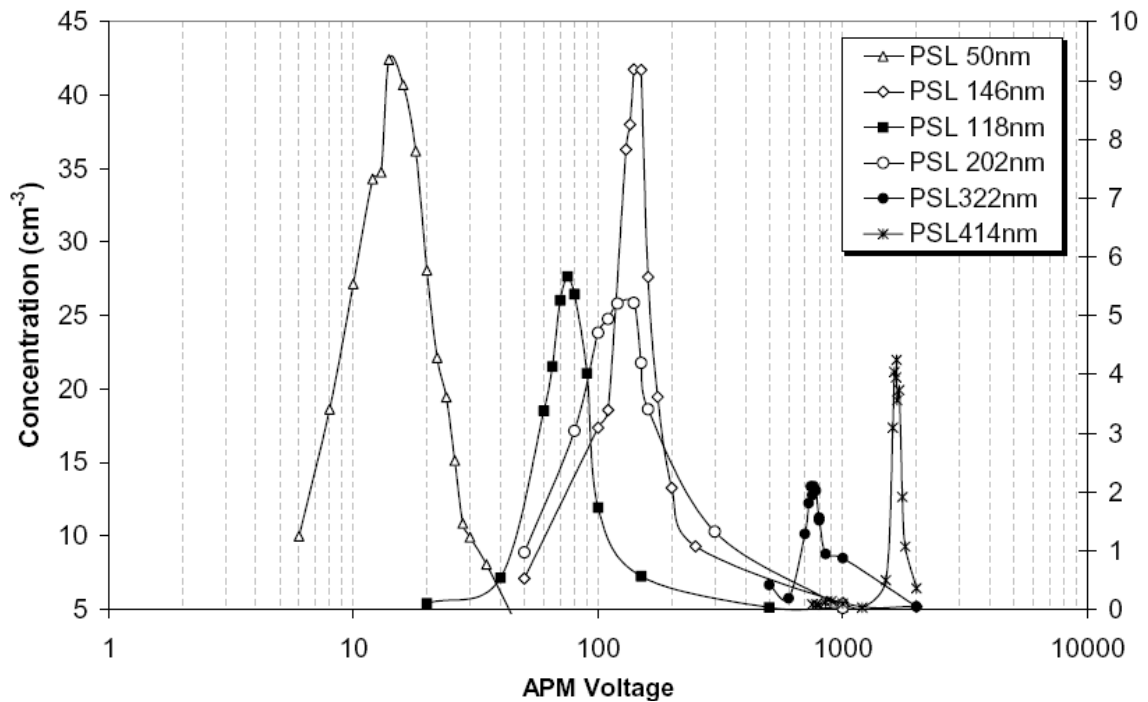


Figure 2.3 Number concentration downstream of APM versus APM classifying voltage for PSL spheres.

2.4.2 Spatial variability of density

The apparent particle density depends on many parameters, including temperature and humidity, radiation, wind conditions, and atmospheric mixing (Pitz et al., 2003). Thus, effective density is expected to be quite variable and uncorrelated to a single meteorological or particulate measurement parameter. Since this study focuses on the effective density variability based on size and site, care was taken to ensure that data were recorded during periods that are representative of the prevailing ambient conditions in the Los Angeles Basin. A case study presenting preliminary results on diurnal variation of effective density is presented later in this discussion, but further analysis is beyond the scope of this study.

Samples were usually taken during the afternoon hours (12:00-16:00) at each location in order to minimize the bias due to diurnal density changes. Because sampling at each site occurred during a defined short time interval, multiple scans for each particle size were similar. Approximately 2-4 scans lasting between 30-60 minutes each for every particle size were recorded, of which representative scans at each location are presented. In addition to sampling within the prescribed time interval, representative scans were selected such that the times of the scans nearly coincided at each location. Table 2.2 describes the local weather conditions at each site on the days sampled. With the exception of Riverside, temperatures and relative humidities are generally comparable between sites. Riverside's location about 100 km inland and in the vicinity of Southern California deserts accounts for its distinctive meteorology, which in general led to warmer and drier conditions compared to the rest of the sites.

Upon completion of the reference measurements, the system was deployed at all prescribed field locations. The following section discusses the associations between effective density and particle size at the different field locations. A figure showing a typical DMA-APM voltage scan is presented in Figure 2.3. The peaks of the voltage distribution were used to determine effective densities, and the data are summarized in Table 2.3. In some locations, data could not be collected for a particle size because ambient concentrations were below the detection limit of the instrument. As previously mentioned, 50 nm was the lowest particle size selected for effective density measurements. As noted earlier, 50 nm is near the LOD of the APM, which is likely to be a reason for broadening of the voltage distributions for these particles.

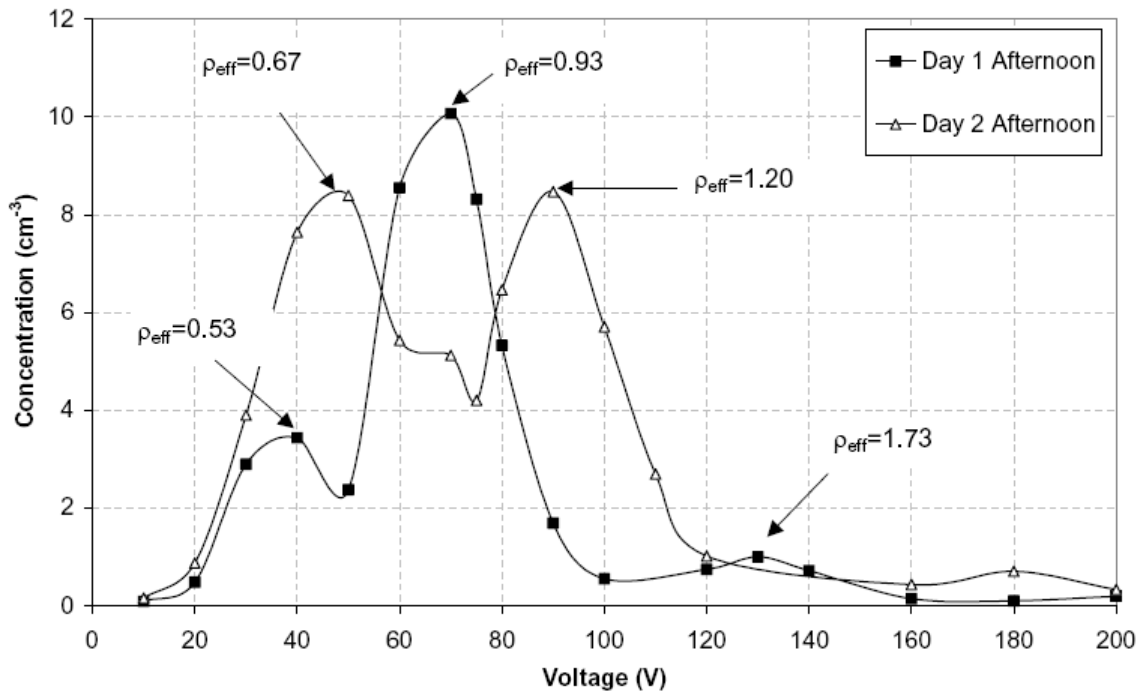


Figure 2.4 Number concentration through DMA-APM as a function of APM voltage for atmospheric particles at I-710 with $d_{me}=118\text{nm}$.

Table 2.2 Ambient temperature and relative humidity ranges for all sampling locations.

Sampling Location	Temp (°C)	RH(%)
USC	20.0 -22.2	55.0 - 63.0
Interstate-110 freeway	20.1 - 25.6	36.0 - 66.0
Riverside	23.3 - 31.7	11.0 - 56.0
Coast	16.7 - 21.1	71.0 - 93.0
Interstate-710 freeway	19.4 - 26.7	45.0 – 84.1

The effective densities at I-710, CA-110, and USC are around unity, which, along with the assumption that these particles are close to spherical, is likely explained by condensation of organic vapors onto a solid core particle. These three sites are most influenced by vehicular sources, which emit semivolatile particles, mostly found in the

sub-50nm range following nucleation and growth processes (Harris and Maricq, 2001; Sakurai et al., 2003). Maricq et al. (2004) reported $\rho_e = 1.2 \text{ g cm}^{-3}$ for 50 nm diesel soot by using an Electrical Low Pressure Impactor (ELPI) and SMPS while Park et al. (2003) stated a density of $\sim 1 \text{ g cm}^{-3}$ by comparing SMPS and filter mass measurements. Previous studies at CA-110 have demonstrated that these particles may be internally or externally mixed, depending on size, and are highly volatile in nature (Kuhn et al., 2005 a,b). USC and CA-110 had two measured effective densities, $0.98 \text{ g cm}^{-3}/1.51 \text{ g cm}^{-3}$ and $1.24 \pm 0.05 \text{ g cm}^{-3}/1.65 \text{ g cm}^{-3}$, respectively, suggesting externally mixed aerosol populations. This range of densities may be explained by particles being a mixture of chemical components, the majority of which is composed of elemental carbon, organic carbon, and water vapor.

Organic speciation of ultrafine particles from dynamometer and tunnel studies has yielded a component known as the unresolved complex mixture (UCM), which resembles motor oil ($\rho \sim 0.87 \text{ g cm}^{-3}$) in gas chromatograph traces (Phuleria et al., 2005a; Schauer et al., 1999). Black carbon has a density between $1.8 - 2.1 \text{ g cm}^{-3}$ (Lide, 1992), and organic compounds can have densities between 0.77 and 1.90 g cm^{-3} (Turpin and Lim, 2001). Thus, a particle containing some amount of each will likely exhibit a density that is an average of its component densities.

Coastal 50 nm particles demonstrated an effective density of 0.90 g cm^{-3} . Interestingly, Turpin and Lim (2001) estimated nearly the same aerosol density for San Nicolas Island, a background site for Los Angeles. Coastal marine aerosols predominantly consist of

organics with high moisture content, which may lead to such low effective density particles (Jaffe et al., 2005). It is also possible that particles emitted from ships anchored off the Southern California coast affect the coastal site at certain times, which would also justify the low measured density. It should be noted that USC and coastal measurements of 50 nm particles produced the widest voltage distributions, which may be due to low concentrations at these sites that may result in relatively poor APM separation efficiency.

It is evident from Table 2.3 that the average measured effective density of 50 nm particles at Riverside, $1.41 \pm 0.12 \text{ g cm}^{-3}$, is unique compared to the other locations. The number-based particle size distributions in that location during the photochemically active period (defined in Los Angeles as the period between April through October) are bimodal, with a distinct mode between 40-60 nm and another at 90-110 nm (Kim et al., 2002).

The smaller mode particles, which are likely organic in nature, are thought to be generated by photochemical reactions (Blando and Turpin, 2000; Jang et al., 2002), whereas the larger mode particles represent an aged aerosol advected eastward to that area of Riverside from central Los Angeles (Fine et al., 2004). Historically, the density of secondary organic aerosol (SOA) was estimated by elaborate chemical speciation and mathematical calculations (Bahreini et al., 2005). It is difficult, however, to identify the complete composition of SOA due to instrumental limitations that prevent us from identifying all species formed by these atmospheric reactions. An effective density of approximately 1.4 g cm^{-3} is expected for unseeded SOA aerosols as most of the organic precursors are of similar density (Bahareini et al., 2005).

Table 2.3 Summary of APM measurements conducted in the Los Angeles Basin in September/October 2004.

			APM Voltage, V			Number Concentration, cm ⁻³			Effective Density, g cm ⁻³			Aerodynamic diameter, nm		
Location	Date	Time	V ₁	V ₂	V ₃	N ₁	N ₂	N ₃	ρ _{e1}	ρ _{e2}	ρ _{e3}	d _{ae1}	d _{ae2}	d _{ae3}
d _{me} =50nm														
710	9/20/2005	16:45-18:00	13	-----	-----	10.5	-----	-----	0.98	-----	-----	50	-----	-----
	9/21/2005	14:15-15:00	16	-----	-----	10.0	-----	-----	1.20	-----	-----	53	-----	-----
110	9/26/2005	15:30-16:30	17	-----	-----	7.3	-----	-----	1.28	-----	-----	54	-----	-----
	9/28/2005	13:00-13:30	16	22	-----	6.5	4.2	-----	1.20	1.66	-----	53	59	-----
USC	9/8/2005	16:00-17:00	13	20	-----	1.0	0.7	-----	0.98	-----	-----	50	-----	-----
Coast	9/23/2005	16:15-17:00	12	-----	-----	1.0	-----	-----	0.90	-----	-----	48	-----	-----
	9/27/2005	14:45-15:15	17	-----	-----	2.5	-----	-----	1.28	-----	-----	54	-----	-----
Riverside	9/29/2005	14:30-15:00	20	-----	-----	2.8	-----	-----	1.51	-----	-----	57	-----	-----
	9/29/2005	16:00-16:30	19	-----	-----	3.0	-----	-----	1.43	-----	-----	56	-----	-----
d _{me} =118nm														
710	9/20/2005	8:30-10:00	40	60	-----	15.0	19.9	-----	0.56	0.84	-----	97	111	-----
	9/20/2005	13:00-14:00	40	70	-----	3.4	10.1	-----	0.56	0.98	-----	97	117	-----
	9/21/2005	8:45-9:45	-----	80	160	-----	20.8	3.7	-----	1.12	2.25	-----	123	155
	9/21/2005	13:15-14:15	50	90	-----	8.4	8.5	-----	0.70	1.26	-----	105	128	-----
110	9/26/2005	12:45-13:45	70	90	-----	5.3	7.7	-----	0.98	1.26	-----	117	128	-----
	9/26/2005	16:30-17:00	70	100	-----	1.7	3.5	-----	0.98	1.41	-----	117	132	-----
	9/28/2005	13:30-14:15	50	100	-----	1.1	2.5	-----	0.70	1.41	-----	105	132	-----
	9/8/2005	17:00-18:00	-----	75	-----	-----	3.8	-----	-----	1.05	-----	-----	120	-----
USC	9/23/2005	12:15-13:15	-----	90	165	-----	1.4	0.4	-----	1.26	2.32	-----	128	156
Coast	9/27/2005	10:30-11:15	-----	100	175	-----	2.0	0.3	-----	1.41	2.46	-----	132	159
	9/27/2005	12:30-13:15	-----	100	190	-----	2.3	0.2	-----	1.41	2.67	-----	132	164
	9/29/2005	12:30-13:00	-----	105	-----	-----	1.1	-----	-----	1.48	-----	-----	134	-----
	9/29/2005	15:30-16:00	-----	100	-----	-----	1.5	-----	-----	1.41	-----	-----	132	-----
Fire	9/30/2005	13:15-13:45	-----	100	-----	-----	11	-----	-----	1.41	-----	-----	132	-----
d _{me} =202nm														
710	9/20/2005	10:00-11:15	50	-----	180	8.8	-----	0.6	0.41	-----	1.46	149	-----	229
	9/20/2005	14:30-15:15	50	100	220	10.8	6.9	0.5	0.41	0.81	1.78	149	188	245
	9/21/2005	9:45-10:15	-----	115	250	-----	12.5	0.9	-----	0.93	2.03	-----	197	256
	9/21/2005	11:45-12:45	-----	130	-----	-----	6.3	-----	-----	1.05	-----	-----	206	-----
110	9/26/2005	13:45-14:30	40	130	-----	1.3	3.2	-----	0.32	1.05	-----	139	206	-----
	9/26/2005	17:00-17:30	40	140	-----	1.3	1.3	-----	0.32	1.14	-----	139	211	-----
	9/28/2005	14:15-15:00	40	140	200	1.3	1.5	0.5	0.32	1.14	1.62	139	211	237
	9/12/2005	11:00-12:00	-----	150	290	-----	2.9	0.4	-----	1.22	2.35	-----	216	269
USC	9/13/2005	15:00-16:00	-----	130	-----	-----	1.4	-----	-----	1.05	-----	-----	206	-----
	9/14/2005	11:00-12:00	40	130	300	0.9	1.8	0.5	0.32	1.05	2.43	139	206	272
Coast	9/14/2005	13:00-13:45	-----	130	260	-----	1.3	0.4	-----	1.05	2.11	-----	206	259
	9/23/2005	13:15-14:15	-----	120	260	-----	1.7	0.5	-----	0.97	2.11	-----	200	259
	9/27/2005	9:00-10:00	60	130	-----	1.9	3.8	-----	0.49	1.05	-----	159	206	-----
	9/27/2005	13:15-13:45	-----	140	-----	-----	1.4	-----	-----	1.14	-----	-----	211	-----
Riverside	9/27/2005	16:00-16:30	-----	135	-----	-----	2.1	-----	-----	1.09	-----	-----	208	-----
	10/11/2005	10:45-11:30	50	130	-----	1.4	2.0	-----	0.41	1.05	-----	149	206	-----
	10/11/2005	14:15-15:00	80	135	-----	1.0	2.4	-----	0.65	1.09	-----	175	208	-----
	9/30/2005	12:15-13:15	-----	120	260	-----	17.0	2.0	-----	0.97	2.11	-----	200	259
d _{me} =322nm														
710	9/20/2005	11:15-12:00	150	350	-----	0.6	1.1	-----	0.21	0.49	-----	191	253	-----
	9/20/2005	15:15-16:00	110	440	-----	1.1	0.8	-----	0.15	0.61	-----	172	273	-----
	9/21/2005	10:15-11:00	100	500	-----	1.2	1.4	-----	0.14	0.69	-----	167	285	-----
	9/21/2005	12:40-13:15	140	540	-----	1.0	0.6	-----	0.19	0.75	-----	186	292	-----
110	9/26/2005	14:30-15:30	200	570	-----	0.2	0.4	-----	0.28	0.79	-----	210	298	-----
	9/26/2005	17:45-18:15	150	-----	-----	0.2	-----	-----	0.21	-----	-----	191	-----	-----
	9/28/2005	12:30-13:00	200	-----	-----	0.2	-----	-----	0.28	-----	-----	210	-----	-----
	9/12/2005	12:00-13:00	-----	530	-----	-----	0.7	-----	-----	0.74	-----	-----	291	-----
USC	9/13/2005	11:00-12:00	-----	530	-----	-----	0.3	-----	-----	0.74	-----	-----	291	-----
	9/14/2005	12:00-13:00	-----	550	-----	-----	0.9	-----	-----	0.76	-----	-----	294	-----
	9/14/2005	14:30-15:15	-----	510	-----	-----	0.7	-----	-----	0.71	-----	-----	287	-----
d _{me} =414nm														
710	9/20/2005	12:00-13:00	200	700	-----	0.9	0.5	-----	0.12	0.42	-----	204	310	-----
	9/20/2005	16:00-16:45	170	900	1000	0.7	0.2	0.3	0.10	0.54	0.60	194	338	350
	9/21/2005	8:00-9:00	200	-----	1000	1.8	-----	0.7	0.12	-----	0.60	204	-----	350
	9/21/2005	11:00-11:45	-----	-----	1100	-----	-----	0.3	-----	-----	0.66	-----	-----	361
USC	9/14/2005	13:45-14:30	-----	-----	1100	-----	-----	0.2	-----	-----	0.66	-----	-----	361

All sites, with the exception of I-710 and CA-110, have 118 nm particles with effective densities greater than unity. CA-110 and I-710 emissions contained particles with effective densities as low as 0.70 gcm^{-3} and 0.56 gcm^{-3} , respectively, indicating the presence of chain agglomerates with fractal dimensions <3.0 . The 710 freeway is influenced by heavy-duty diesel vehicles, which commonly emit two distinct modes of particles. One mode consists of carbonaceous solid agglomerate particles, occurring between 100-200 nm in mobility diameter, while the more semivolatile particles exist in the sub-50 nm mode, as discussed earlier (Harris and Maricq, 2001; Sakurai et al., 2003; Kuhn et al., 2005a,b). The particles at I-710 appear to be externally mixed with the majority existing as organic droplets and a smaller population of low-density agglomerates. Fractal agglomerate particles of 118 nm mobility diameter were found only on one day and in much lower concentrations at CA-110 because only gasoline vehicle emissions impact the site, which in general tend to emit lower elemental carbon than heavy duty diesel (Schauer et al., 2002). Furthermore, the number distribution rapidly drops off after 50 nm at CA-110, which means that 118 nm particles sampled at this site may likely be more closely associated with the urban background (Kuhn et al., 2005a). Therefore, measured densities between 0.98 and 1.41 gcm^{-3} are probably indicative of complex particles, composed of ammonium nitrate, metals, organic compounds and water (Kuhn et al., 2005b). The majority of 118 nm particles in the coastal site also exhibited an effective density close to 1.26 gcm^{-3} , which is likely due to hydrated sulfate droplets. As argued by Kleeman et al. (1999), the similarity in sulfate concentrations throughout the Los Angeles basin confirms that the majority of the sub-micrometer sulfate aerosol in

that area in recent years is advected into the urban area from over the Pacific Ocean, with a minority of the sulfate aerosol formed by atmospheric reactions within the air basin itself. This situation is due to the strict controls on SO₂ emissions that have been adopted in the South Coast Air Basin.

The effective density measured for 118 nm particles at USC is similar to that at I-710, except without the second lower density corresponding to fractal-like agglomerates. The site is impacted by mostly light duty and some heavy duty vehicle emissions (although to a much lesser extent than the I-710), and is located sufficiently far downwind from the freeway for nuclei mode particles to grow to that range, as demonstrated by the experimental measurements of Zhu et al. (2002) and the modeling work of Zhang et al. (2005). Supersaturated organic vapors condensing onto the surface of these particles result in densities around 1.0 gcm⁻³.

An interesting observation is that the density of 118 nm particles was slightly higher than that of 50 nm particles at Riverside. This may be because 118 nm particles are likely an internal mixture of heavier components, such as ammonium nitrate and organic compounds, which form during advection and long range transport of air parcels from Los Angeles to the receptor site of Riverside, situated about 100 km downwind. Due to time and other experimental field constraints, field measurements of 146 nm particles were conducted at a few of the sampling locations. At USC, 146 nm particles had a higher effective density ($\rho_e=1.43 \text{ gcm}^{-3}$) than 118 nm particles ($\rho_e=1.05 \text{ gcm}^{-3}$), which may be due to the additional condensation of higher density species such as ammonium

nitrate on to primary particles. It should be noted that in this as well as other locations of our study, the influence of the nearby freeways decreases with increasing particle size, suggesting that a significant fraction of these larger particles are representative of the urban background aerosol. I-710 particles with 146 nm diameter also exhibited a bimodal distribution, with two significant differences from 118 nm. The higher density mode occurs at $\rho_e=1.43 \text{ gcm}^{-3}$, compared to $\rho_e=1.05 \text{ gcm}^{-3}$ for 118 nm particles. This difference may be explained by a higher contribution of urban background (than freeway) to this particle size or higher association of particle-bound metals and other high-density compounds from the freeway with this particle size. The second difference is that the low-density peak of 146 nm particles ($\rho_e=0.68 \text{ gcm}^{-3}$) had a higher number concentration than the high-density peak, which is indicative of a higher percentage of carbonaceous soot agglomerates, directly emitted by diesel vehicles on the freeway, at that mobility diameter. Similar to 118 nm particles, the majority of 146 nm particles at Riverside are part of an aged aerosol transported from Los Angeles, resulting in an effective density of $\rho_e=1.38 \pm 0.06 \text{ gcm}^{-3}$. Low densities were measured in the morning and will be discussed in the subsequent section.

Similar to other sizes, 202 nm particles at USC are mostly contained in one large mode with $\rho_e=1.09 \pm 0.08 \text{ gcm}^{-3}$, indicative of an internally mixed aerosol of mostly organic chemical composition. The coastal aerosol has a high content of 202 nm particles with effective densities near 1.0 gcm^{-3} , which is probably due to the large amount of condensed water vapor associated with hygroscopic (mostly sulfate) aerosols in that site. The majority of 202 nm particles at I-710 fit into a bimodal distribution with effective

densities of both modes having values less than unity. The lighter fraction ($\rho_e=0.41 \pm 0 \text{ g cm}^{-3}$) dominated the heavier one ($\rho_e=0.93 \pm 0.12 \text{ g cm}^{-3}$), which could include low-density agglomerates that have been coated with organic vapors, resulting in an increase in effective density. Density in Riverside is still well above unity for a majority of 202 nm particles ($\rho_e=1.09 \pm 0.03 \text{ g cm}^{-3}$), but there is a clear decrease when compared to smaller particle sizes. Although particles within the accumulation mode in Riverside are likely to be internally mixed with little dependence of chemical composition on particle diameter, there may be void space or particle bound water associated with the larger particles that reduces the effective density. Similar to 146 nm particles, significant concentrations of low density particles were measured in the morning.

Unlike other locations and particle sizes, effective densities greater than 2.0 g cm^{-3} were measured for 118 nm and 202 nm particles. The higher effective density particles may reflect complex urban background mixtures of ammonium sulfate, ammonium nitrate, and metals observed in previous field studies in the basin (Hughes et al., 2000). For the marine background aerosols, the larger peak is $0.97\text{-}1.26 \text{ g cm}^{-3}$, which is consistent with the density of a hygroscopic aerosol at high relative humidity conditions. The much smaller peak at around 2 g cm^{-3} , based solely on density values, would indicate that sea salt spray generated by breaking waves is most likely the source. Sea salt spray is composed of sodium chloride particles, which have a bulk density of 2.16 g cm^{-3} . Although previous studies showed that ocean spray generates super-micrometer particles (Kleeman et al., 1999), it is conceivable that the measured particles represent a “tail” in the size distribution of coarser sodium chloride PM. McMurry et al. (2002) also reported

particle densities close to 2.0 gcm^{-3} for 309 nm particles on multiple occasions. While no conclusions were drawn about the chemical composition of these particles, the authors of that study did rule out multiple charging as the source of this signal. It is unlikely that multiply charged particles are contributing to this secondary mode here because number concentration decreases rapidly with increasing particle diameter, and the number of multiply charged particles is a very minute fraction of total concentration.

During our sampling period, a brush fire occurred in Southern California, which provided a unique opportunity to determine effective densities of fire emission particles. Because of the relatively unstable nature of this event due to the changes in both fire and wind direction, only two sizes, i.e., 118 nm and 202 nm, could be measured. The particle density is roughly around unity for 202 nm and 1.4 gcm^{-3} for 118 nm particles. A previous study in Southern California reported size distributions with a mode diameter of 100-200 nm for particles emitted by forest fires (Phuleria et al., 2005b). The chemical composition of $\text{PM}_{2.5}$ emitted by wood burning and prescribed burns has been shown to be dominated by organic carbon (Kleeman et al., 1999; Robinson et al., 2004). The average of the bulk densities of the various organic species could result in the reported effective densities. Another study found wood combustion particles, although composed of small primary particles, to be compact in shape instead of fractal (Colbeck et al., 1997). This may explain fire-emitted particle effective densities greater than or equal to unity.

Because 322 nm particles are less abundant in the atmosphere, concentrations at all locations approached the noise level of the CPC. No data could be reported for Riverside and the coast. Regardless of the site, the effective density of 322 nm particles was almost invariably smaller than unity. The probability that particles are fractal agglomerates, which have associated void spaces, would likely increase with particle diameter because these particles are often altered by atmospheric transformations and have the potential to scavenge smaller particles. The two freeway locations both exhibit two distinct effective densities, at 0.14-0.28 gcm⁻³ and 0.49-0.79 gcm⁻³. The lower end of the range of each is found at I-710, which is likely influenced by the increased presence of carbon-rich fractal agglomerates from diesel emissions at this site. The existence of an effective density mode around 0.6-0.8 gcm⁻³ at each site may signify that a fraction of 322 nm particles is regional in nature. Similar detection limit problems occurred for 414 nm particles that were found for 322 nm particles. The very low concentrations, which were often less than one particle per cm³, increased sampling uncertainty so that conclusive data could only be recorded at USC and I-710. As with 322 nm, all 414 nm particles have effective densities below unity, and the reasons for this are likely similar to those presented for 322 nm particles above. A very low-density ($\rho_e \sim 0.1$ gcm⁻³) population of particles was measured at I-710.

2.4.3 Diurnal variability of particle density at Riverside

The relative consistency of the vehicle emissions that are the dominant aerosol source at the freeway sites (I-710 and CA-110) made it difficult to draw any meaningful conclusions concerning diurnal variation of effective density in these locations. Limited

data at the coast also prevented analysis of diurnal variability. Riverside was selected as the site at which to conduct multiple measurements in order to investigate diurnal variability of particle effective density because of its consistent daily meteorological variation (e.g. temperature, relativity and wind velocity vary similarly from day-to-day). The daily fluctuation in wind velocity at Riverside generally favors the impact of local sources in the mornings, whereas afternoons are dominated by photochemically produced aerosols as well as regional aerosols advected to that site from urban upwind locations (Kim et al., 2002; Fine et al., 2004).

As reported in an earlier section, photochemical byproducts were thought to attribute to the effective density of 50 nm particles at Riverside ($\rho_e \sim 1.4 \text{ gcm}^{-3}$). Figure 2.5 further illustrates the possible effect of photochemical formation on the effective density for 50 nm particles. Hourly data have been plotted from 11th October 2005, during which the temperature peaked at 28°C between 13:00-15:00. The effective particle density during this time period was 1.35-1.4 gcm^{-3} . As the sun angle rapidly decreased and temperature declined to 23°C after 16:00, the particle density dropped to a value of 1.2 gcm^{-3} .

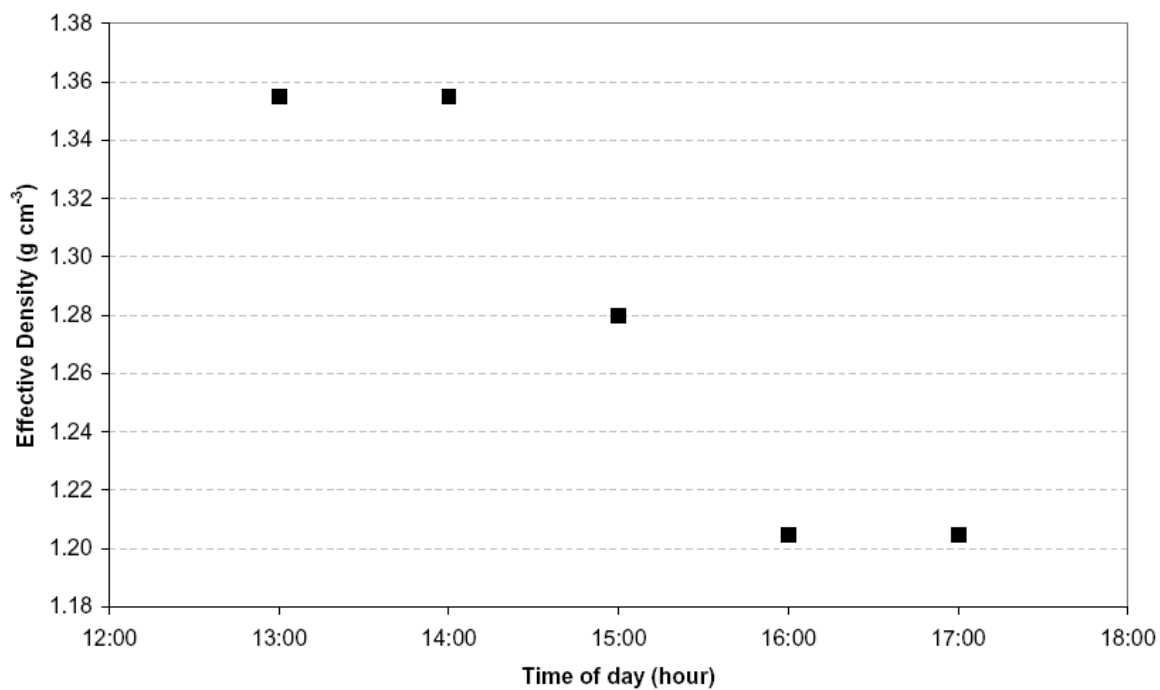


Figure 2.5 Diurnal variation of effective density for 50 nm atmospheric particles in Riverside, CA.

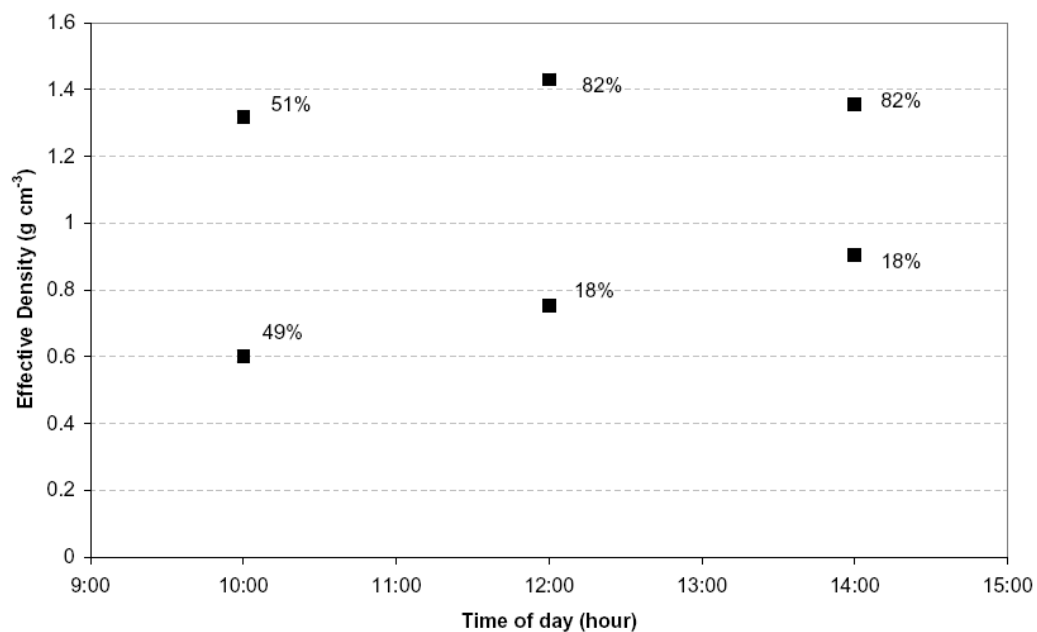


Figure 2.6 Diurnal variation of effective density for 146 nm atmospheric particles in Riverside, CA.

Particles between 118-202 nm have either a shoulder or second mode that occurs only in the morning. Figure 2.6 displays the diurnal variation in effective density for 146 nm particles. A significant number of morning particles exhibit densities less than unity, which is probably an effect of local morning traffic emissions that can affect the site due to stagnant conditions. In addition to visible morning traffic effects, effective density at Riverside varied slightly throughout the afternoon. The possible effect of photochemistry on 50 nm particles has been previously discussed, but particles between 118-202 nm also increase in effective density as the day progresses from morning to afternoon. It is likely that the stronger advection in the afternoon transports particles with higher proportions of SOA and ammonium salts, while particles lose water as temperatures rise.

2.4.4 Dependence of effective density on particle diameter

From the results of the five particle sizes studied, it is evident that effective density decreases with increasing particle mobility diameter. This phenomenon appears to occur regardless of starting density and location. Figures 2.7-2.9 show the relationship between particle effective density and mobility diameter at I-710, CA-110 and USC, respectively. At I-710 all particle sizes other than 50 nm have two effective densities associated with each.

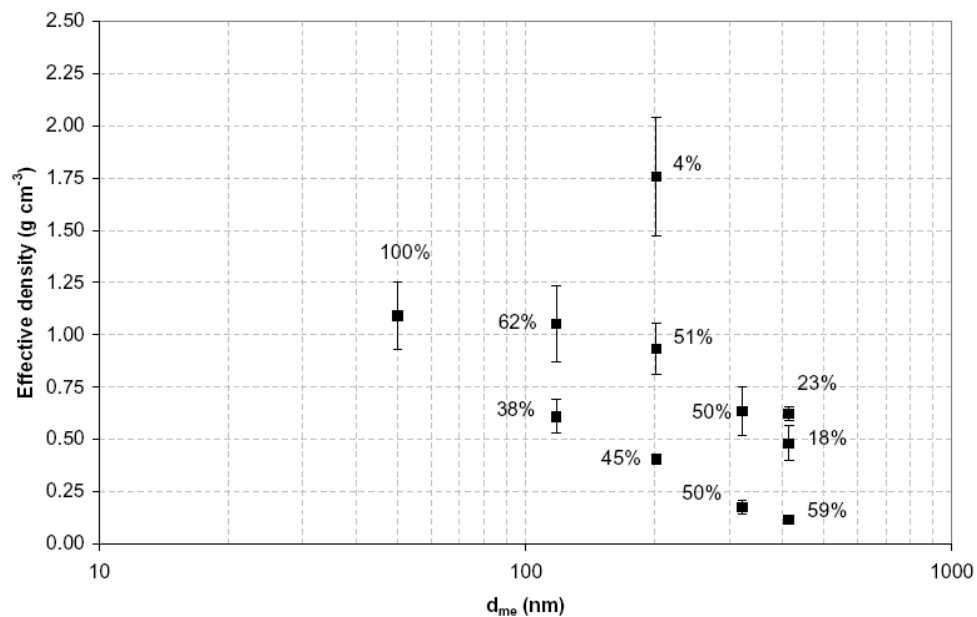


Figure 2.7 Effective density variations with respect to particle mobility diameter at I-710. Data labels indicate percentage of number concentration measured for each particle size with respective effective density.

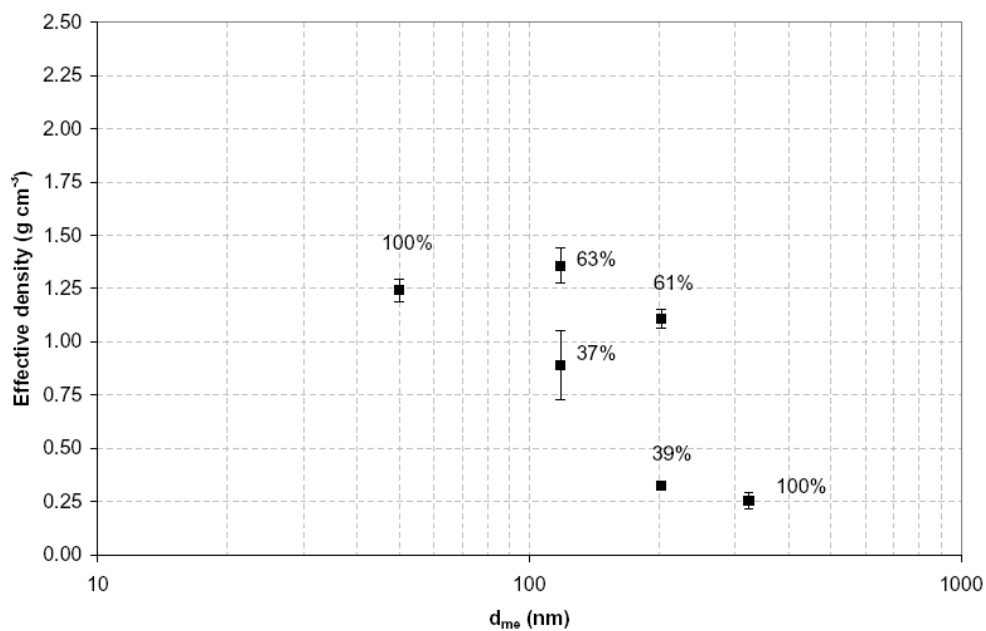


Figure 2.8 Effective density variations with respect to particle mobility diameter at CA-110. Data labels indicate percentage of number concentration measured for each particle size with respective effective density.

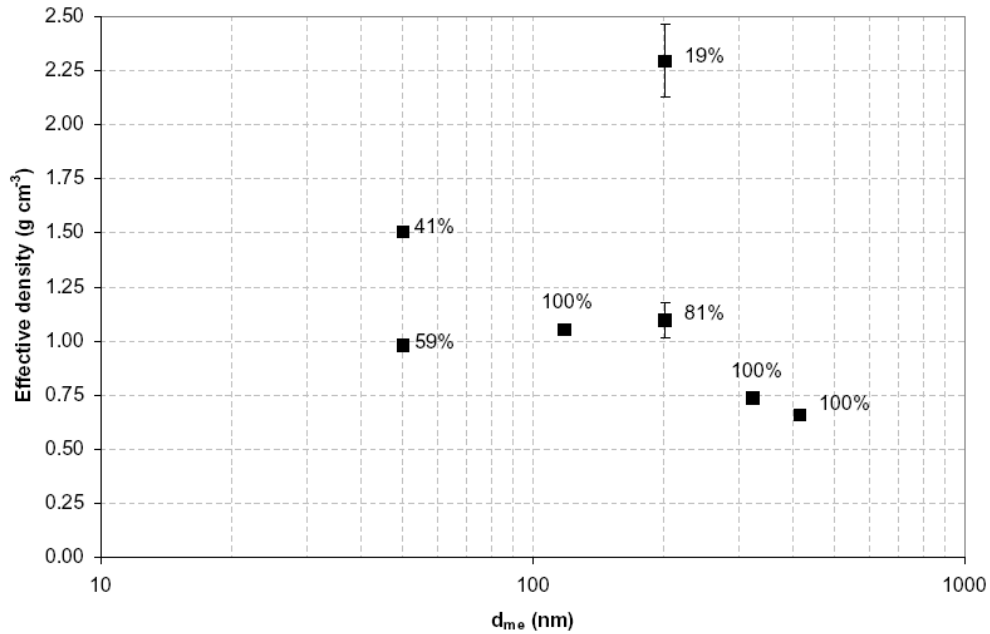


Figure 2.9 Effective density variation with respect to particle mobility diameter at USC. Data labels indicate percentage of number concentration measured for each particle size with respective effective density.

These densities appear to align themselves into two groups: a high effective density line, and a low effective density line. Both lines decrease with the same slope, which suggests particle mobility diameter is an important indicator of effective density. Although not as many data points are available, a similar trend is observed at CA-110, and effective density decreases with particle diameter at USC for $d_p > 200$ nm.

Interestingly, larger diameter agglomerates have lower effective densities than smaller ones, suggesting that void space increases with particle diameter. Fuchs (1964) opined that effective density might vary 0.1 to 0.7 times the primary particle density, while Pontikakis (2001) assumed effective densities as low as 0.05 g cm^{-3} for modeling of diesel

particle retention filters. The results of this study corroborate these arguments and imply the possible existence of density as low as 0.05 gcm^{-3} .

Table 2.4 summarizes the effective densities and fractal dimensions reported for all sites and particle sizes sampled. Effective densities are averaged by particle size and site without consideration of diurnal variation by calculating the centroid APM voltage from each scan. Laboratory experiments with spherical particles show particles of different masses penetrate the APM at a particular voltage, which broadens the distribution, but the centroid voltage and peak voltage are nearly equal due to the symmetry of this distribution. The shoulders seen in atmospheric voltage scans are due to particles with different shapes and/or densities. Thus, taking the centroid voltage of a scan with multiple voltage peaks will be minimally affected by APM separation efficiency while weighting the average effective density based on number concentration measured at each voltage. As previously mentioned, size-averaged effective density decreases with increasing particle mobility diameter for all effective densities. This effect is most prominent for I-710, where larger particles (414 nm) demonstrated average ρ_e as low as 0.31 gcm^{-3} . Ahlvik et al. (1998) and Park et al. (2003) also reported similar low effective densities for diluted diesel exhaust aerosols with a DMA followed by an ELPI and APM, respectively. The effective density of the marine aerosol did not show much variation, with $\rho_e \sim 1.0 \text{ gcm}^{-3}$ for all particle sizes. Salt particles may absorb a significant amount of moisture and dissolve into droplets, which mask any irregularities in shape. Riverside is characterized by high-density ($\rho_e > 1$) particles between 50-202 nm in diameter, mostly the result of photochemical processes and advection of the Los Angeles urban plume

upwind of that site. Irrespective of site, 322 nm and 414 nm particles have densities less than unity. Although vehicle sources are known to emit carbonaceous agglomerates, particles of these two sizes may also be agglomerates of other primary atmospheric particles formed during coagulation and atmospheric chemical reactions.

2.4.5 Estimates of aerosol fractal dimension

The fractal dimension for each location was calculated from Equation 2 by plotting the logarithm of mobility diameter versus the logarithm of average effective density values in Table 2.4. Fractal dimension can increase with the presence of water (Mikhailov et al., 1996), so it is not surprising that the highest fractal dimension was found at the coast ($D_f = 2.92 \pm 0.15$). The lack of combustion emissions at this site also validates this result. Conversely, the I-710 fractal dimension was the lowest of all sites ($D_f = 2.41 \pm 0.22$), presumably due to the much higher contribution of diesel trucks at that location. Previous dynamometer studies have reported a fractal dimension of 2.3 ± 0.1 for vehicle exhaust with DMA-ELPI and DMA-APM systems, which is in good agreement with the current I-710 results (Maricq et al., 2004; Van Gujik et al., 2004; Park et al., 2003). Diesel freeway aerosols may have higher fractal dimensions than pure diesel exhaust due to changes in particles between the tailpipe and the sample inlet.

CA-110 freeway aerosols had a fractal dimension slightly higher than I-710 ($D_f = 2.54 \pm 0.28$), indicating that gasoline vehicles generate chain agglomerates, especially in the higher range of particles (>200 nm). Particles at USC did not have a particularly low fractal dimension ($D_f = 2.79 \pm 0.15$), although these particles may contain significant

amounts of EC (Sardar et al., 2005). The USC location is much farther from vehicle sources than the two freeway sites. Because fractal agglomerates have a very high surface area, it is conceivable that they are altered by vapor condensation, adsorption and/or scavenging between the time of emission and the time of sampling at USC. This will lead to morphological changes of the original aggregate particle to become more compact. Finally, the fractal dimension in Riverside was calculated as 2.83 ± 0.06 . Because Riverside is significantly downwind of the freshly emitted particles from Los Angeles, these particles undergo many changes due to temperature, relative humidity, and chemical reactions before reaching Riverside. All of these will have an effect on particle morphology. It is unknown, however, if fractal agglomerates retain their structure within a droplet or if they become more compact due to alterations in the primary particle arrangement.

Table 2.4 Summary of average effective densities of different field locations and their fractal dimensions

Mobility diameter (d_m , nm)	Average Effective density (ρ_e), g cm ⁻³				
	USC	710-freeway	110-freeway	Riverside	Coast
50	1.14 ± 0.1	1.13 ± 0.10	1.45 ± 0.12	1.40 ± 0.10	1.19 ± 0.10
118	1.12 ± 0.14	1.00 ± 0.12	1.17 ± 0.02	1.40 ± 0.06	1.14 ± 0.23
146	1.21 ± 0.08	0.94 ± 0.16	NA	1.29 ± 0.06	0.99 ± 0.10
202	1.14 ± 0.24	0.78 ± 0.26	0.99 ± 0.09	1.06 ± 0.09	1.06 ± 0.20
322	0.86 ± 0.11	0.49 ± 0.07	0.59 ± 0.27	NA	NA
414	0.73 ± 0.10	0.31 ± 0.02	0.58 ± 0.06	NA	NA
Fractal Dimension	2.79 ± 0.15	2.41 ± 0.22	2.54 ± 0.28	2.83 ± 0.06	2.92 ± 0.15

2.5 SUMMARY AND CONCLUSIONS

This study employed a previously developed tandem of the APM and SMPS to determine in-situ effective density of atmospheric particles over a mobility size range of 50-414 nm. Field-testing of ambient particles revealed effective density of unity or more for 50nm particles, indicative of their spherical nature. The lower density of marine aerosols may be due to the presence of a significant amount of organics. Riverside aerosols, with an effective density as high as 1.4-1.5 gcm^{-3} for this particle size, are thought to be predominantly generated from photochemical reactions.

A significant number of particles at I-710 may be chain agglomerates, which is demonstrated by the bimodal density distribution measured there. The majority of 118nm and 146nm particles, however, are internally mixed, originating from background urban sources. Morning traffic can produce a bimodal density distribution for these particles similar to that of I-710, as shown by the diurnal variation at Riverside. CA-110 freeway exhibited low-density 202 nm particles, generated from gasoline-powered vehicles. The urban and marine background sources have a higher density fraction at 202 nm mobility size, which most likely is comprised of ammonium sulfate, ammonium nitrate, and metals.

Low concentrations of 322 nm and 414 nm particles increased sampling uncertainty at some locations. The effective density for these particles is very low, ranging from 0.1 to 0.7 gcm^{-3} . Densities this low is explained by the high probability that these particles have void space associated with them. It is evident from the results that with the increase in

particle size, effective density decreased irrespective of location. Thus, it can be concluded that particle morphology varied from nearly solid spheres in the small sizes to agglomerate chains at higher sizes.

Although not the focus of this study, diurnal density variation was revealed at Riverside, CA. Low effective density particles are present in the morning, due to the influence of local traffic, but these particles disappear in the afternoon. In addition, the effective density of both smaller and larger particles increases in the afternoon, presumably due to increased photochemistry and higher proportion of secondary organic aerosols. A more comprehensive examination of diurnal effects at various sites merits future consideration. Calculated fractal dimensions yielded predictable results, with $D_f = 2.41$ for Interstate 710, a freeway with a high heavy duty diesel vehicle traffic. Similarly, a low average particle fractal dimension (2.54) was found at the gasoline vehicle dominated freeway (CA-110), which is also affected by the presence of chain agglomerates. The fractal dimensions at USC, Riverside and the coast were 2.79, 2.87 and 2.92, respectively, indicating that overall the average shape of particles in these locations approaches that of a sphere. As one would expect, fractal dimension increases with distance from traffic emissions across these sites. The higher fractal dimension at USC compared to the freeway sites demonstrates that fractals diminish quickly with distance away from freeway, which may be due to vapor condensation-adsorption on particles. Fractal dimensions approach 3.0 at Riverside and the coast due to the much lower impact of emissions from combustion processes at these sites.

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Chapter 3:

Physical and Chemical Characteristics and Volatility of PM in the Proximity of a Light-Duty Vehicle Freeway

3.1 ABSTRACT

Volatility properties of ultrafine particles were analyzed next to State Route 110 (Pasadena freeway CA), a light-duty vehicle freeway where heavy-duty traffic is prohibited. In addition, mass concentration and chemical composition of particulate matter (PM) were measured in coarse, accumulation, and ultrafine modes. On weekdays from 17 May to 4 June 2004, measurements were performed in two locations, one very close to the freeway (within 2.5m from the curb) and one at a distance of about 50m from the freeway. For measurement of mass and chemical composition, the study employed in each location a micro-orifice uniform deposit impactor (MOUDI) and a modified high-volume sampler. Both instruments sampled with the same size cutpoints: a coarse mode from 2.5 to 10 μm , an accumulation mode from 0.18 to 2.5 μm , and an ultra-fine mode of particles less than 0.18 μm in aerodynamic diameter. Alternately, a tandem differential mobility analyzer (TDMA) was used at the two sites. A heater between the two DMAs evaporated volatile material from the monodisperse aerosol, size selected by the first DMA. The second DMA analyzed the losses of volatile components. The ultrafine number concentrations next to the freeway were 46,000 cm^{-3} on average during the sampling period. The MOUDI ultrafine mass concentration, nitrate, and EC were higher next to the freeway than at the background site farther from the freeway. The other components analyzed in the ultrafine mode had similar concentrations next to the freeway and at the background site. Volatility ranged from about 65% volume losses of 120 nm

particles heated to 110°C to 95% of 20 nm particles. The 20 nm aerosol was only internally mixed, whereas increasing nonvolatile fractions were found for 40 nm (6% next to the freeway), 80 nm (20%), and 120 nm (28%) aerosols.

3.2 INTRODUCTION

Epidemiological and toxicological studies have demonstrated strong links between ambient particulate matter mass exposure and adverse health outcomes (National Research Council 2004). However, it is not clear which physical or chemical properties of particulate matter (PM) pose the greatest health risk. Recent results have shown that ultrafine particles are more toxic than larger particles (Donaldson et al. 2002; Li et al. 2003; Oberdorster 2000; Pietropaoli et al. 2004). Furthermore, individual particles have been shown to be capable of inducing mitochondrial damage (Li et al. 2003), suggesting that particle number concentrations, which are dominated by ultrafine particles, may be more indicative of some potential health impacts than particle mass concentrations. In urban environments the dominant sources of ultrafine particles are direct emissions from motor vehicles and secondary PM formed by photochemical or physical processes in the atmosphere (Fine et al. 2004b; Zhang et al. 2004b). Measurements of particle emissions from motor vehicles have been accomplished via dynamometer source testing (Chase et al. 2000; Kwon et al. 2003; Sakurai et al. 2003a, 2003b; Schauer et al. 1999, 2002; Suess and Prather 2002), roadway tunnel sampling (Allen et al. 2001; Fraser et al. 1998; Laschober et al. 2004; McGaughey et al. 2004), on-road chase experiments (Shah et al. 2004; Vogt et al. 2003), and roadside measurements (Harrison et al. 2003; Sturm et al. 2003; Zhu et al. 2002a, 2002b, 2004).

In general, particles directly emitted from motor vehicles are in the size range from 20 to 130 nm in aerodynamic diameter for diesel engines (Morawska et al. 1998) and from 20 to 60 nm for gasoline engines (Ristovski et al. 1998). It is known that many of the organic chemical constituents of PM emitted from vehicles are semivolatile, existing simultaneously in the gas and particle phases at equilibrium (Schauer et al. 1999, 2002). Thus, changes in ambient temperature and gas-phase concentrations of these components can affect the measured particle size distributions due to evaporation or condensation.

For this reason, it has been shown that the particle size distributions determined by dynamometer testing are dependent on the dilution ratios and dilution air conditions of the sampling apparatus (Holmen and Qu, 2004; Lyyranen et al. 2004; Vaaraslahti et al. 2002). Road tunnel sampling is also subject to the unusual dilution and temperature conditions found in the tunnel. Roadside measurements, as opposed to chase studies, offer the opportunity to measure particle size distributions averaged over the emissions from thousands of vehicles under “real-world” conditions (Hitchins et al. 2000). Zhu et al. (2002b) measured the size distributions of PM and the concentrations of gaseous copollutants in the proximity of a freeway mostly impacted by gasoline vehicles in West Los Angeles. Particle number concentrations (in the range from 6 to 220 nm) decreased more quickly with downwind distance from the freeway than CO and black carbon. Zhu et al. (2002a) obtained similar data in the vicinity of a freeway impacted heavily by heavy-duty diesel traffic. When these experiments were repeated in winter with cooler ambient temperatures and less atmospheric mixing (Zhu et al. 2004), particle number concentrations in the smallest size ranges were significantly higher. Zhang et al. (2004b)

demonstrated that condensation, evaporation, and dilution were the major factors affecting aerosol size distributions in the first 250 m downwind from freeways. The high concentrations of particle numbers in the proximity of freeways raises concerns for population exposure during commute. The particle volatility, which causes the dynamically shifting size distributions of these freshly emitted particles, needs to be better characterized to assess accurately population exposure to the physical and chemical properties of PM. A few previous studies have measured the volatility of PM in dynamometer tests using tandem differential mobility analyzer (TDMA) systems (e.g., Sakurai et al. 2003a). However, given the dependence of dynamometer tests on dilution conditions, assessment of the volatility of vehicular PM emissions under real-world conditions is needed. A previous roadside study measured the volatility of ultrafine PM downwind of a mixed heavy- and light-duty traffic freeway at two different distances both indoors and outdoors (Kuhn et al. 2005). The current study measured PM volatility properties next to a pure gasoline freeway where heavy-duty diesel vehicles are prohibited. Additional measurements were made of coarse, accumulation, and ultrafine PM mode mass and chemistry. Results will help to determine the properties of particles to which people are exposed in the vicinity of freeways.

3.3 METHODS

3.3.1 Sampling location and schedule

Measurements were conducted at the State Route 110 (SR 110), between downtown Los Angeles and Pasadena, CA (USA), where the freeway runs generally north–south. On this stretch of the freeway—historic Arroyo Seco Parkway, the first freeway in the

Western U.S.—only light-duty vehicles are allowed. This offers the unique opportunity of studying emissions from light-duty traffic under ambient conditions. The relatively short stretch of freeway offered a limited choice of sampling sites and, after evaluating the possibilities, Hermon Park in the Arroyo Seco on the east side, directly adjacent to the freeway (Figure 3.1) was chosen. This site was selected mainly for easy access to the freeway and available space close to the freeway not directly influenced by local street traffic. At Hermon Park, the freeway runs in southwest–northeast direction and has three north- and three southbound lanes, a crash barrier in the center, and no emergency lanes. The park is at the same level as the freeway, only slightly raised by less than 0.5 m.

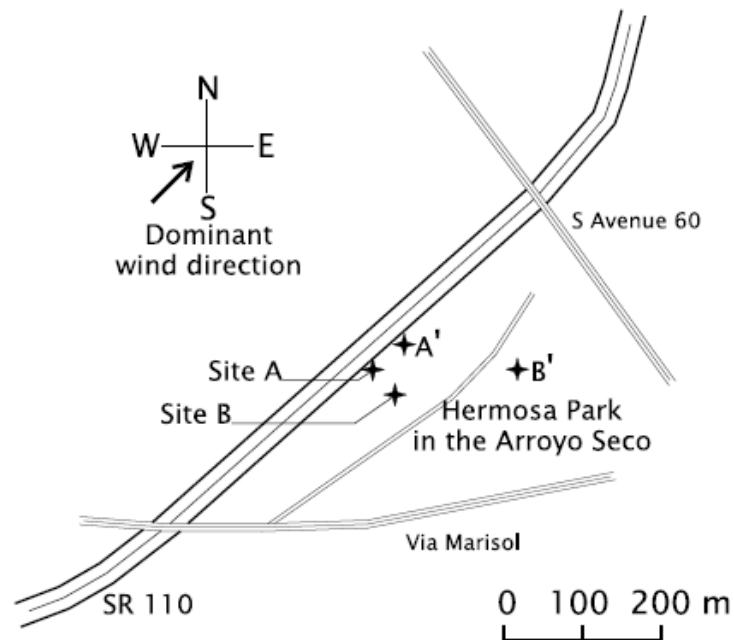


Figure 3.1 Sampling sites at SR 110.

The study took place from 17 May to 4 June 2004. Sampling was conducted on weekdays from about 12 pm to 7 pm, which captured the evening rush-hour traffic. This sampling

period represented typical summertime conditions in Los Angeles. The meteorological conditions are expected to influence particle volatility properties, as conditions for condensation of fresh ultrafine particles and evaporation of volatile material from these particles depend, among other parameters, on ambient temperature and humidity. It is therefore planned to repeat this study in the winter season so that seasonal variability can be addressed as well.

Measurements of particle volatility were carried out at two different locations. One was next to the edge of the northbound lanes of SR 110 (Site A: see Figure 1). The aerosol at this sampling site is heavily influenced by the freeway traffic. The sampling inlet was approximately 2.5 m away from the curb of the freeway. Site A and the freeway were separated only by a wide-meshed fence. The other location was about 50 m away from the freeway in southeast direction (Site B). This site is still influenced by the presence of the freeway and, to a lesser extent, by urban background and possibly some local street traffic. The vehicle-generated particles have some time to age before being sampled at Site B.

Particle chemical composition was measured at two sites concurrently. The first site (Site A') was on same side and at same distance (2.5 m) to the freeway as Site A, located at about 50 m northeast from Site A. The second site (Site B') was chosen to represent local background, which is not or only weakly influenced by the freeway. The site was about 150 m east from Site A', still in Hermon Park.

Traffic on SR 110 was free flowing during the whole sampling period. The traffic volume varied throughout the day, having a peak in the morning and one in the early evening corresponding to the rush hours. The morning rush hour is predominantly on the southbound lanes, while the evening rush hour is on the northbound lanes. The hourly averages of the total traffic density are shown in Figure 3.2. During the sampling period the average traffic density was about 5700 h^{-1} . Traffic speed was fairly constant during the day, and even during the rush hours the traffic did not slow down significantly. The average of the diurnal hourly averages was 108 km h^{-1} on the southbound lanes, with a standard deviation of only 2.8 km h^{-1} ; the average speed on the northbound lanes was 115 km h^{-1} with a standard deviation of only 2.6 km h^{-1} .

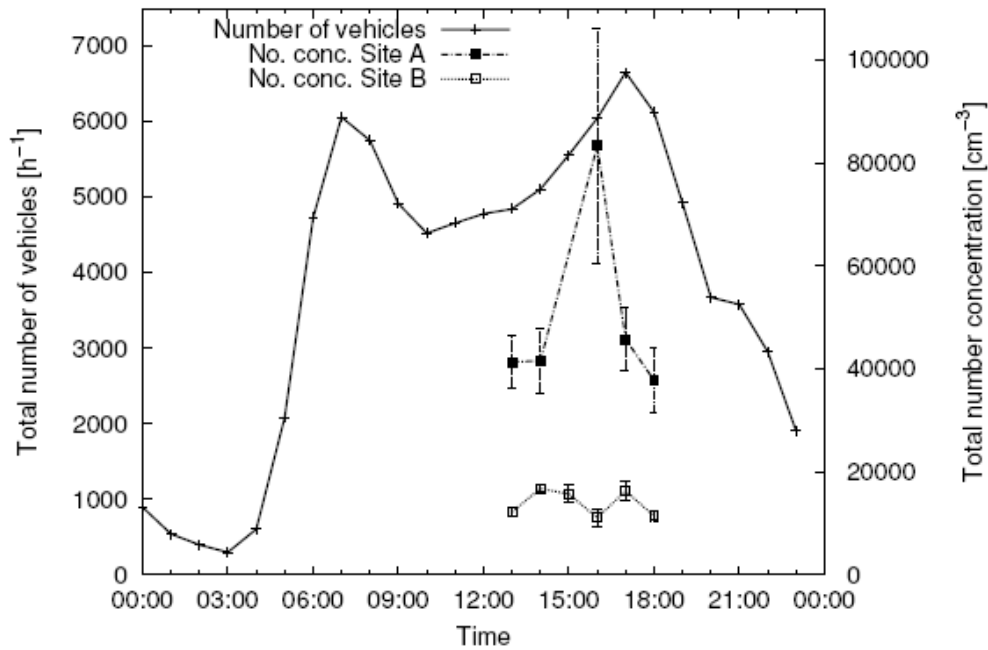


Figure 3.2 Total traffic density and total number concentrations at Site A and Site B (SMPS integrals with standard errors). Hourly averages over the whole sampling period are shown. The values are shown at the beginning of the averaged hour.

The wind direction, wind speed, and temperature were monitored with a weather station (Wizard III, Weather Systems Company, San Jose, CA, USA) connected to a computer for data logging. Data were averaged over 5 min intervals. The wind direction was recorded as predominantly coming from one of 16 directions (22.5° intervals: namely north (N), north-northeast (NNE), northeast (NE), etc.) during the 5 min averaging period. The wind vane was 2m above ground level about 20m southeast of SR 110 (close to Site A'). The average temperature during the sampling period was 25°C (standard deviation of 5°C). The relative humidity was monitored using a Q-Trak Plus (TSI Inc., St. Paul, MN, USA) and it was 51% on average (standard deviation of all 1 min averages of 10%). The predominant wind direction during the sampling period was SW (29%), and 66% of the 5 min averages had predominant wind directions SSW, SW, or WSW. The average wind speed during the sampling period was 1.6 m s⁻¹ (standard deviation of 0.5 m s⁻¹). For Site A the wind direction is not very important, as here the sampling takes place close to the freeway where the air is mixed by turbulences created by the flowing traffic. Hence, the majority of the particles at this site originate from fresh vehicular emissions. At Site B, on the other hand, wind direction is likely to influence the aerosol mixture sampled. Differently aged aerosol from different stretches of the freeway upstream of the site mixed with background aerosol arrives at the site. On average, it is expected that results from this site will show effects caused by aging of freeway-generated aerosol.

3.3.2 Measurements of particle chemical composition

A micro-orifice uniform deposit impactor (MOUDI; Model 110, MSP Corporation, Shoreview, MN, USA) sampled at 30 l min^{-1} to collect particles on Teflon substrates for determination of mass concentrations. Collocated with the MOUDI, a modified high-volume sampler (Fine et al. 2004a) concurrently collected PM_{10} in three size ranges on quartz fiber substrates. The stages in the MOUDI were chosen to correspond to the same size cut-points as the high-volume sampler: a coarse mode from 2.5 to $10 \mu\text{m}$, an accumulation mode from 0.18 to $2.5 \mu\text{m}$, and an ultrafine mode of particles less than $0.18 \mu\text{m}$ in aerodynamic diameter. The 47 mm Teflon filters from the MOUDI were pre and post-weighed after 24 h of equilibration at 45 to 50% relative humidity and a temperature range of 20–24°C. After weighing to determine particle mass concentration, filters were analyzed by X-ray fluorescence analysis (XRF) for metals and other trace elements (Dzubay 1977). Portions of the quartz fiber filters from the high-volume sampler were analyzed for elemental carbon and organic carbon (EC/OC) by thermal desorption/optical transmission analysis (Birch and Cary 1996). Additional portions of the quartz fiber filters were used to determine sulfate and nitrate concentrations by ion chromatography (Mueller et al. 1978). Two 4.5 kW gasoline-powered portable generators provided the electric power for the pumps of MOUDI and high-volume samplers. The generators were placed approximately 20 m downwind of Site A' and Site B', so that no measurement could be biased by the generator's exhaust. During the sampling period the MOUDI and high-volume sampler operated from 12 pm to 7 pm every day. The filters were deployed for several days. At both sites five periods were sampled: 17–21 May, 24–26 May, 27–28 May, 1–2 June, and 3–4 June 2004.

3.3.3 Particle volatility measurements

The TDMA system used to measure the volatility of particles is shown in Figure 3. The two scanning mobility particle sizers (SMPS; TSI model 3936) consisted of a bipolar charger (with an ^{85}Kr source), a long DMA (model 3081), and a condensation particle counter (CPC; TSI model 3022A). The first SMPS (SMPS1) sampled selected particles of a certain narrow size range from ambient aerosol. It operated with an aerosol flow rate of 1.5 l min^{-1} and a sheath air flow rate of 15 l min^{-1} . Clean filtered air was introduced into the aerosol flow after size selection to increase its flow rate to 1.8 l min^{-1} . This monodisperse aerosol flow was split into two streams. One stream went into the CPC of SMPS1 (control CPC, sample flow rate of 0.3 l min^{-1}), which measured the concentration of this monodisperse aerosol. The other stream traveled through a heater unit, where the aerosol was conditioned to a certain fixed temperature. After passing through the heater, the aerosol went through DMA2 (DMA of the second SMPS, SMPS2) without passing through the bipolar charger. SMPS2 (in scanning mode) measured the size distribution of the conditioned aerosol and was operated with a CPC aerosol flow rate of 1.5 l min^{-1} and a sheath air flow rate of 15 l min^{-1} . Two computers were used for data logging from control CPC and SMPS2.

The heater used to condition the aerosol is described in Kuhn et al. (2005). The Aerosol Instrument Manager software (version 5.2, TSI Inc., St. Paul, MN, USA) was used for inversion of the measured number concentrations (CPC of SMPS2) to the size distribution. It was assumed that particles did not lose their charge during heating and evaporation of the volatile fraction; therefore, all particles were still charged (as by

electrostatic size selection by SMPS1) when they entered DMA2. This assumption was justified by looking at the ratio of particles remaining after heating, which was close to 1 when all particles had sizes above the detection limit of SMPS2 (see Section “Volatility Comparisons” below). The electric power for the instruments was provided by four lead batteries and an inverter (ProSine 2.0, 2 kW inverter and charger).

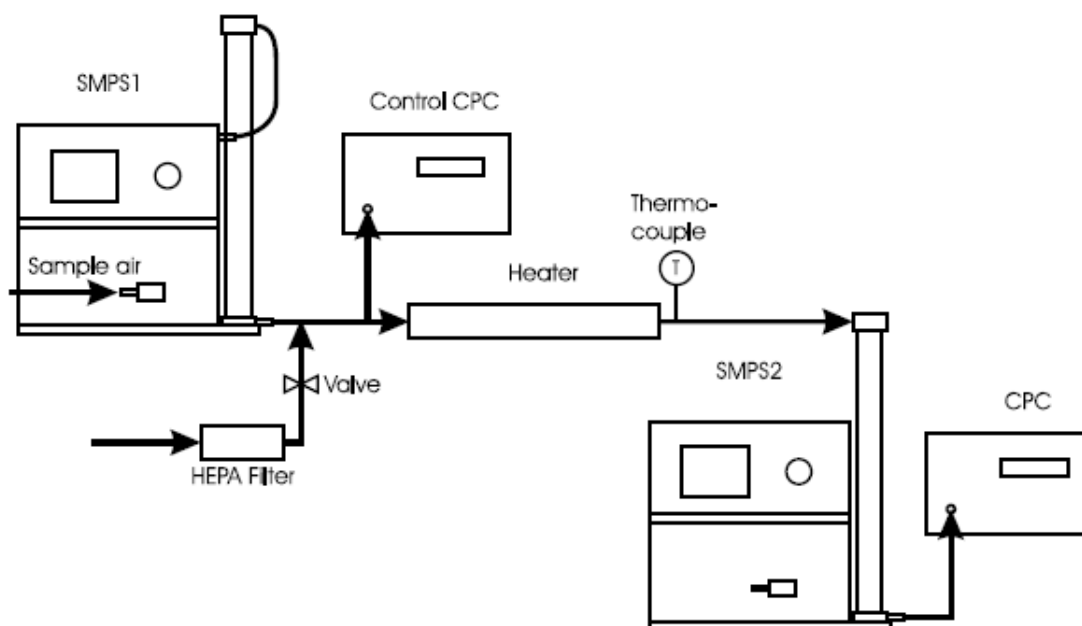


Figure 3.3 Set-up used for volatility measurements.

Measurements of volatility were conducted at both Site A and Site B. During a typical measurement cycle at one site, a certain particle size was fixed and the size distribution measured at ambient temperature and after conditioning at two different heated temperatures. A measurement cycle was concluded by measuring the full size distribution of the ambient aerosol directly (DMA of SMPS1 bypassed and heater turned off). Up to three measurement cycles were carried out each day, of which the last was started after 4

pm, to capture the evening rush-hour condition. For each selected particle size two or three measurement cycles were carried out on different days, of which one was during the evening rush hour.

Four particle diameters were chosen within the ultrafine size range: 20, 40, 80, and 120 nm. For heating, aerosol flow temperatures of 60°C and 110°C were chosen to determine ultrafine particle volatility. We expected most of the volatile material to evaporate at 110°C (Philippin et al. 2004), and we selected this temperature so that we could compare results with our previous study (Kuhn et al. 2005) close to a mixed heavy- and light-duty traffic freeway. The temperature of 60°C was selected to represent an intermediate state of volatilization.

Measurements of size distributions were repeated three to six times while the aerosol temperature was kept constant. Each size distribution was measured with 81 SMPS channels from 8.2 to 146 nm (midpoint diameters). The size distribution was measured in scanning mode by SMPS2 in 162 s; consequently, each SMPS channel was sampled for 2s. The control CPC was used with an averaging time of 2 s. The control CPC data could therefore be used to normalize the SMPS data by dividing the value of each channel by the control CPC concentration at the same time that the channel was scanned. The repeated measurements of distributions at same conditions showed variations caused, at Site A, by the extreme vicinity to the source (freeway traffic) and its temporal variations. At Site B, the source is more distant and variations here are caused by temporal changes of the source as well as by local wind conditions changing the aerosol mixture sampled at

the site. However, the average of these repeated measurements are similar to averages of measurements taken at different times of the day or on a different day. Therefore, the average of all measurements at a given site, sampled particle size, and conditioning temperature was used for comparison with averages at different site, size, or temperature.

3.4 RESULTS AND DISCUSSION

3.4.1 Particle chemical composition

Table 3.1 shows the results from the chemical analysis of the MOUDI and high-volume sampler filters and substrates from the two sites. At Site A', directly next to the freeway, mass concentrations in the coarse and accumulation size ranges were similar to Site B', whereas ultrafine mass concentration was higher at Site A'. Nitrate was found in similar concentrations in the accumulation mode but showed higher concentrations in the coarse and ultrafine modes next to the freeway (Site A'). Sulfate, on the other hand, was similar in the coarse and accumulation modes, while the ultrafine mode concentration was somewhat higher away from the freeway (Site B'). Interestingly, the elemental mass concentrations in the coarse size range were either similar or higher at Site B' (higher for Na, Mg, Al, Si, S, Cl, K, Ca, Ni, Zn, and Ba). Exceptions, where coarse concentrations were higher at Site A', were nitrate and copper. This trend in the coarse PM concentrations between the two sites suggests that light-duty vehicles may not be a significant source of coarse particles. This is consistent with the findings of Sternbeck et al. (2002) and Charron and Harrison (2003), who showed that heavy-duty vehicles generate higher amounts of coarse PM due to stronger abrasion processes, including tire wear and brake linings. Sternbeck et al. (2002) showed that a higher correlation exists

between particle barium, a common element in brake linings, and heavy-duty traffic than light-duty traffic. In addition, contributions from brake wear are likely to be very small at SR 110 because of the steady speed conditions, with very little braking happening during the sampling period.

Table 3.1 PM₁₀ size fractionated, chemically speciated data. All mass concentrations given in µg.m⁻³

	Coarse		Accum.		Ultrafine			Coarse		Accum.		Ultrafine	
	A'	B'	A'	B'	A'	B'		A'	B'	A'	B'	A'	B'
Mass							K						
Mean	23.000	21.457	18.995	19.194	5.113	3.268	Mean	0.360	0.711	0.024	0.023	0.023	0.038
SD	7.912	7.569	9.492	6.082	1.729	1.490	SD	0.099	0.216	0.004	0.007	0.005	0.036
Nitrate							Ca						
Mean	1.855	1.387	1.889	2.069	1.090	0.737	Mean	0.847	1.663	0.033	0.031	0.041	0.083
SD	0.837	0.357	1.407	1.253	0.204	0.246	SD	0.222	0.628	0.005	0.011	0.009	0.092
Sulfate							Ti						
Mean	0.570	0.547	2.727	3.560	1.748	2.352	Mean	0.136	0.197	0.008	0.005	0.011	0.012
SD	0.202	0.144	1.569	2.251	0.579	0.659	SD	0.043	0.084	0.001	0.001	0.003	0.012
OC							V						
Mean	0.638	0.807	2.529	2.167	7.387	6.080	Mean	0.009	0.008	0.005	0.005	0.002	0.001
SD	0.117	0.267	1.142	0.831	1.912	2.061	SD	0.003	0.007	0.001	0.002	0.001	0.001
EC							Fe						
Mean	0.031	0.038	0.198	0.118	1.109	0.663	Mean	1.971	2.447	0.123	0.061	0.124	0.120
SD	0.007	0.017	0.216	0.104	0.558	0.235	SD	0.648	0.916	0.009	0.023	0.032	0.115
Na							Ni						
Mean	0.734	1.148	0.034	0.039	0.002	0.016	Mean	0.001	0.003	0.002	0.002	0.000	0.000
SD	0.123	0.264	0.008	0.013	0.002	0.015	SD	0.000	0.001	0.001	0.001	0.000	0.000
Mg							Cu						
Mean	0.124	0.239	0.003	0.003	0.003	0.006	Mean	0.081	0.054	0.007	0.002	0.006	0.002
SD	0.027	0.055	0.002	0.003	0.003	0.006	SD	0.027	0.021	0.001	0.001	0.002	0.002
Al							Zn						
Mean	0.325	0.775	0.008	0.011	0.033	0.065	Mean	0.039	0.059	0.009	0.008	0.006	0.007
SD	0.121	0.267	0.004	0.008	0.005	0.064	SD	0.013	0.029	0.004	0.004	0.003	0.006
Si							Ba						
Mean	1.039	2.449	0.032	0.087	0.104	0.209	Mean	0.105	0.159	0.014	0.004	0.011	0.006
SD	0.384	0.853	0.010	0.117	0.014	0.204	SD	0.057	0.043	0.003	0.003	0.006	0.008
S							Sb						
Mean	0.640	1.021	0.533	0.593	0.260	0.299	Mean	0.011	0.012	0.001	0.001	0.001	0.001
SD	0.306	0.358	0.164	0.161	0.229	0.259	SD	0.008	0.008	0.001	0.001	0.001	0.001
Cl							Pb						
Mean	1.154	1.676	0.046	0.042	0.004	0.019	Mean	0.008	0.021	0.002	0.001	0.001	0.002
SD	0.501	0.755	0.033	0.033	0.002	0.028	SD	0.007	0.011	0.001	0.001	0.001	0.001

With only a few exceptions (Fe being the most prominent), the accumulation mode concentrations were similar at both sites, thereby confirming that this size range represents for the most part a background urban aerosol, unaffected by local traffic. In the ultrafine size range, the most noticeable difference was observed for mass, nitrate, and EC concentrations, which were higher at Site A', possibly reflecting the effect of light-duty emissions. Most other species occurred in similar concentrations in the ultrafine mode. Vanadium and copper were also higher at Site A' but were present in concentrations close to the uncertainty level at Site B'. Sulfate, sodium, and titanium were higher at Site B'. In the case of OC in the ultrafine mode, n reasonably high concentrations were measured, often exceeding the total ultrafine mass concentration. This is caused by adsorption of organic vapors, which in the ultrafine size range become large in relation to the relatively low amount of particulate matter collected on the filter (Mader and Pankow, 2001).

This phenomenon is not expected to affect the coarse and accumulation modes as drastically since these particle size ranges were collected by impaction onto substrates and not by filtration. Therefore, the actual ultrafine particle OC content remains unknown, although other studies have shown that ultrafine gasoline vehicle emissions are primarily composed of OC (Kleeman et al. 2000).

3.4.2 Number, surface and mass concentrations

Integrating the SMPS size distributions of ambient aerosol of the two sites yields number, surface, and volume concentrations. Mass concentration can be estimated from volume concentration assuming a certain density. Mass concentration measured in the ultrafine mode of the MOUDI can be compared to the SMPS volume concentration. Table 3.2 shows the values found in this study. Differences between the calculated SMPS and the measured ultrafine MOUDI mass concentrations may result from losses of volatile and semivolatile materials from the MOUDI filters before analysis, which would result in reduced MOUDI mass. Deviations of the shape of the particles from spherical may also result in differences in mass concentrations due to the different sizing techniques (McMurry et al. 2002; Park et al. 2003; Shen et al. 2002). In addition, the particle bounce problem, which causes larger particles to be collected in lower stages of the MOUDI, might result in overestimated MOUDI ultrafine mass. Shen et al. (2002) observed in the ultrafine range a higher MOUDI than SMPS mass.

Table 3.2 SMPS total number, surface, and volume concentrations are shown. Surface and volume concentrations were calculated assuming spherical particles.

Site	Number	St. dev.	Surface	Volume	Mass	MOUDI
	cm^{-3}	cm^{-3}	$\mu\text{m}^2 \cdot \text{cm}^{-3}$	$\mu\text{m}^3 \cdot \text{cm}^{-3}$	$\mu\text{g} \cdot \text{m}^{-3}$	$\mu\text{g} \cdot \text{m}^{-3}$
Site A	46 000	29 800	65.0	3.57	5.71	6.32
Site B	13 600	4 680	18.6	0.995	1.59	2.49

3.4.3 Size distribution of ambient aerosol

All measured size distributions of ambient aerosol from each site were averaged, as shown in Figure 3.4. The size distribution next to the freeway (Site A) shows two modes at about 10 and 20 nm. Two modes below 30 nm were also found at the Interstates 710 (I-710) and 405 (I-405), with 25 and 7% heavy-duty vehicles, respectively, in Los Angeles, CA during studies conducted under similar meteorological conditions in the summer season (Zhu et al. 2002a, 2002b). These modes might arise from nucleation of semivolatiles very near the vehicle tailpipe. There is also a less pronounced mode at 50 nm in the size distribution at Site A. At 60 and 90 m distance from I-405, Zhu et al. (2002b) found a dominant mode at about 40 nm. This, as well as the 50 nm mode in this study might be explained by condensational growth (Zhang et al. 2004a). With the wind direction predominantly parallel to the freeway, such growth could occur while the aging particles remain close to the freeway. At Site B no modes can be seen, indicating that the modes at Site A are characteristic of the freeway-generated aerosol. Dilution and mixing with urban background yield the lower concentrations at Site B. Despite these similarities of distributions at Site A to freeways with up to 25% heavy-duty vehicles, the number concentrations are significantly lower at SR 110. This difference cannot be accounted for only by the difference in traffic volume between the two freeways, which suggests that heavy-duty vehicles emit higher particle number concentrations than light-duty vehicles (Kittelson et al. 2004).

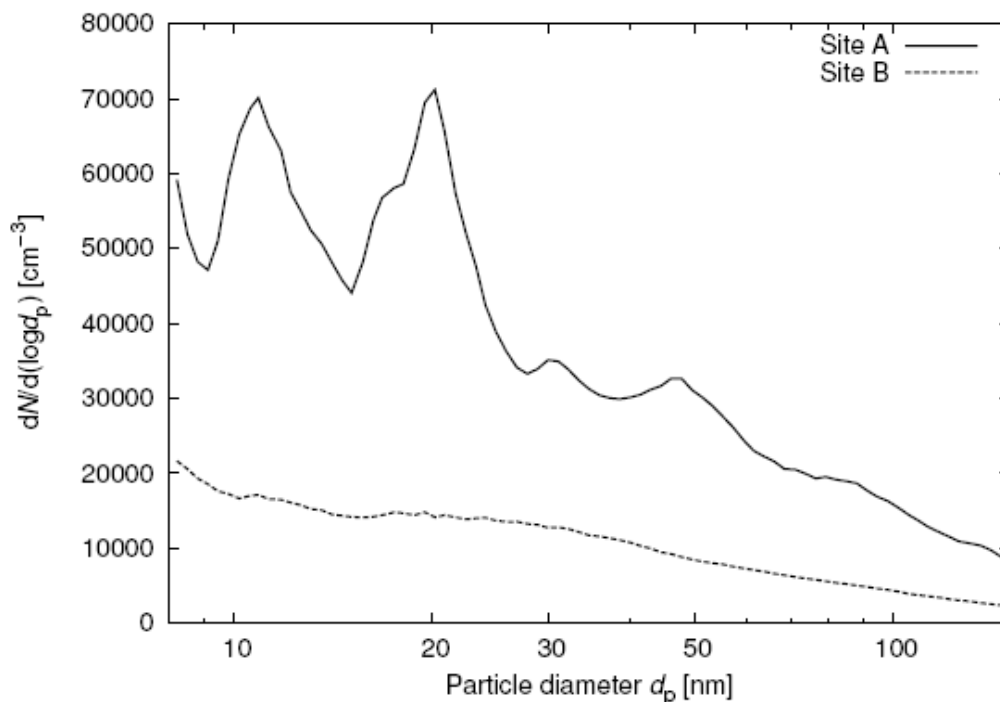


Figure 3.4 Average size distributions of ambient aerosol. At Site A results from eight measurement cycles (each containing six size distributions) were averaged. At Site B eleven measurement cycles were averaged.

3.4.4 Volatility properties

3.4.4.1 Size distribution changes

Figure 3.5 shows averaged results from volatility measurements. For each selected particle size at both sites, three normalized number size distributions are shown: the first represents the selected monodisperse aerosol at ambient temperature without conditioning (no heating); the second shows the size distribution after heating to 60°C; the third after heating to 110°C. The presented size distributions are averaged over all measurements.

The diameter of each measured particle size shrank when heated. This resulted in a decrease of the mode diameter d_m (mode decrease Δd_m) from the original size of the monodisperse aerosol towards much smaller diameters. The distribution also broadened when the aerosol was heated. This broadening effect is stronger at Site B, because the aerosol originating from freeway traffic is diluted and mixed with particles from multiple other sources with a wider range of volatility characteristics. At Site A (next to the freeway) the aerosol originates mainly from freeway traffic and hence most particles of a given size have similar characteristics.

For the 80 and 120 nm aerosols the unimodal distributions split into bimodal distributions upon heating to 110°C. In each case a mode exists at the original (before heating) particle diameter, and a new mode with a wider range forms at a smaller diameter. This indicates that these aerosols are externally mixed, that is, each aerosol consists of two groups of particles having very different volatilities.

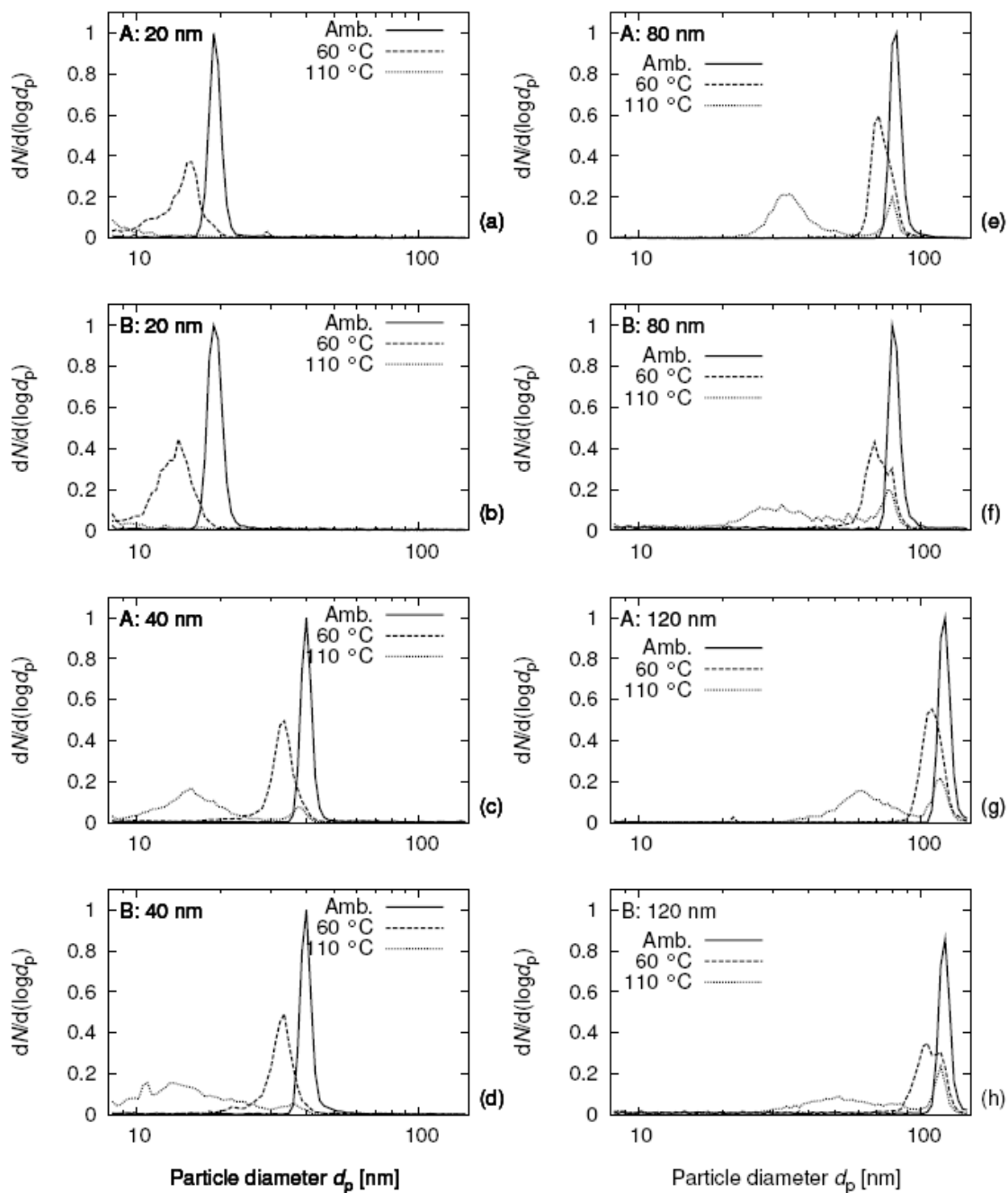


Figure 3.5 Average number size distribution (normalized to maximum at 1) at ambient temperature (≈25°C) and after conditioning (heating) at 60°C and 110°C. (a) 20 nm aerosol at Site A, (b) 20 nm at Site B, (c) 40 nm at Site A, (d) 40 nm at Site B, (e) 80 nm at Site A, (f) 80 nm at Site B, (g) 120 nm at Site A, (h) 120 nm at Site B.

Highly volatile particles lose a significant fraction of volume to the vapor phase, as is demonstrated by the mode that decreased significantly in diameter. These particles are designated mostly volatile because volatile material dominates their compositions. Particles that, on the other hand, do not shrink significantly contribute to the mode that remains near the original diameter. Those particles will be referred to as nonvolatile.

Figure 3.5 shows that 40 nm aerosol, at both Site A and Site B, had only a very small nonvolatile mode at 110°C. This indicates that it is externally mixed, but the fraction of nonvolatile particles is very small compared to the 80 and 120 nm aerosols. The 20 nm aerosol does not show external mixing on the size distributions at 110°C. This suggests that the vast majority of the 20 nm particles are semivolatile. Hence, the 20 nm aerosol is only internally mixed, and the particles are composed mainly of volatile material and may or may not contain some material that is not volatile (such as a solid core, the size of which may be smaller than the lower sizing limit of the SMPS, which in our experiments was 8 nm). This is essentially the same at both sites and was also found by Kuhn et al. (2005). For diesel exhaust, Sakurai et al. (2003b) found a solid core below about 8 nm for 30 nm particles and below 4 nm for 12 nm particles.

Table 3.3 summarizes mathematical formulations of various volatility ratios based on the evaporation profiles described above. These ratios will be used extensively in this chapter as well as in subsequent chapters to quantify level of mixing. As described by Kuhn et al. (2005), the ratios Φ_N and Φ_V can be used to describe the relative amount of number and volume that remains after heating the aerosol. Φ_N and Φ_V ratio at 110°C are further

segregated into mostly volatile (Φ_{Nm} , Φ_{Vm}) and non-volatile fractions (Φ_{Nn} , Φ_{Vn}). The extent of external mixing can be described by the ratio (Φ_{Nn}) of the integral of the nonvolatile mode of the normalized number size distribution at 110°C to the integral of the normalized distribution at ambient temperature.

Table 3.3 Mathematical formulations of the various volatility terms

Equation	Symbol	Description
$A = \int_L^U n_{amb} d(\log d_p)$	A	:Total number concentration at ambient temperature
$B = \int_L^U \pi/6 d_p^3 n_{amb} d(\log d_p)$	B	:Total volume of the ambient size distribution
$\Phi_N(60^\circ\text{C}) = A^{-1} \int_L^U n_{60^\circ\text{C}} d(\log d_p)$	N	:Number concentration, $dN/d(\log d_p)$
$\Phi_V(60^\circ\text{C}) = B^{-1} \int_L^U \pi/6 d_p^3 n_{60^\circ\text{C}} d(\log d_p)$	L	:Lower size distribution endpoint
	U	:Upper size distribution endpoint
	C	:Diameter of minimum local concentration between the non-volatile and volatile modes in thermally treated samples at 110°C
$\Phi_N(110^\circ\text{C}) = A^{-1} \int_L^U n_{110^\circ\text{C}} d(\log d_p)$		
$\Phi_V(110^\circ\text{C}) = B^{-1} \int_L^U \pi/6 d_p^3 n_{110^\circ\text{C}} d(\log d_p)$	$\Phi_N(60^\circ\text{C})$	:Total number or volume remaining at 60°C
$\Phi_{Nm} = A^{-1} \int_L^C n_{110^\circ\text{C}} d(\log d_p)$	$\Phi_V(60^\circ\text{C})$	
$\Phi_{Nn} = A^{-1} \int_C^U n_{110^\circ\text{C}} d(\log d_p)$	$\Phi_N(110^\circ\text{C})$, $\Phi_V(110^\circ\text{C})$	:Total number or volume remaining at 110°C
$\Phi_{Vm} = B^{-1} \int_C^U \pi/6 d_p^3 n_{110^\circ\text{C}} d(\log d_p)$	$\Phi_{Nm}(110^\circ\text{C})$, $\Phi_{Vm}(110^\circ\text{C})$	:Mostly-volatile number or volume fraction at 110°C
$\Psi_{Nm} = \Phi_{Nm} / (1 - \Phi_{Nn})$	$\Phi_{Nn}(110^\circ\text{C})$, $\Phi_{Vn}(110^\circ\text{C})$	:Non-volatile number or volume fraction at 110°C
$\Psi_{Vm} = \Phi_{Vm} / (1 - \Phi_{Nn})$	$\Psi_{Nm}(110^\circ\text{C})$, $\Psi_{Vm}(110^\circ\text{C})$	:Relative ratio of mostly-volatile number or volume fraction at 110°C

In addition, the new ratios Ψ_{Nm} for number and Ψ_{Vm} for volume concentrations are introduced to characterize the relative amount of the mostly volatile component that remains after heating of the aerosol. Assuming that there are no number losses of nonvolatile particles, the fraction of mostly volatile particles (before losses) can be calculated as $1 - \Phi_{Nn}$. The ratio Ψ_{Nm} is then $\Psi_{Nm} = \Phi_{Nm} / (1 - \Phi_{Nn})$, where Φ_{Nm} is the ratio of the integral of the mostly volatile mode at 110°C to the integral of the distribution at ambient temperature (defined like Φ_{Nn} , but for the mostly volatile mode). The ratio Ψ_{Vm} is calculated as $\Psi_{Vm} = \Phi_{Vm} / (1 - \Phi_{Nn})$, where Φ_{Vm} is the ratio of the integral of the mostly volatile volume mode at 110°C to the integral of the volume distribution at ambient temperature (like Φ_{Nm} , but calculated using volume size distribution).

3.4.4.2 Temperature dependence

The temperature dependence of the mode decrease Δdm at Site A is shown as a thermal desorption profile in Figure 3.6. This study shows larger decreases in mode diameters than a similar study that took place at I-405 in winter 2003/2004 at 15m distance to the freeway (Kuhn et al. 2005). The difference would probably be even larger if one considered seasonal effects on volatility (volatile fraction of PM would increase in winter due to colder temperatures). Hence, aerosols originating from gasoline traffic seem to be substantially more volatile in comparison to aerosols dominated by a mixture of heavy- and light-duty vehicles. The mode decrease was similar at both sites of this study, with the mode diameters decreasing slightly more at Site B than at Site A. This suggests that particle volatility properties do not change significantly from Site A to Site B.

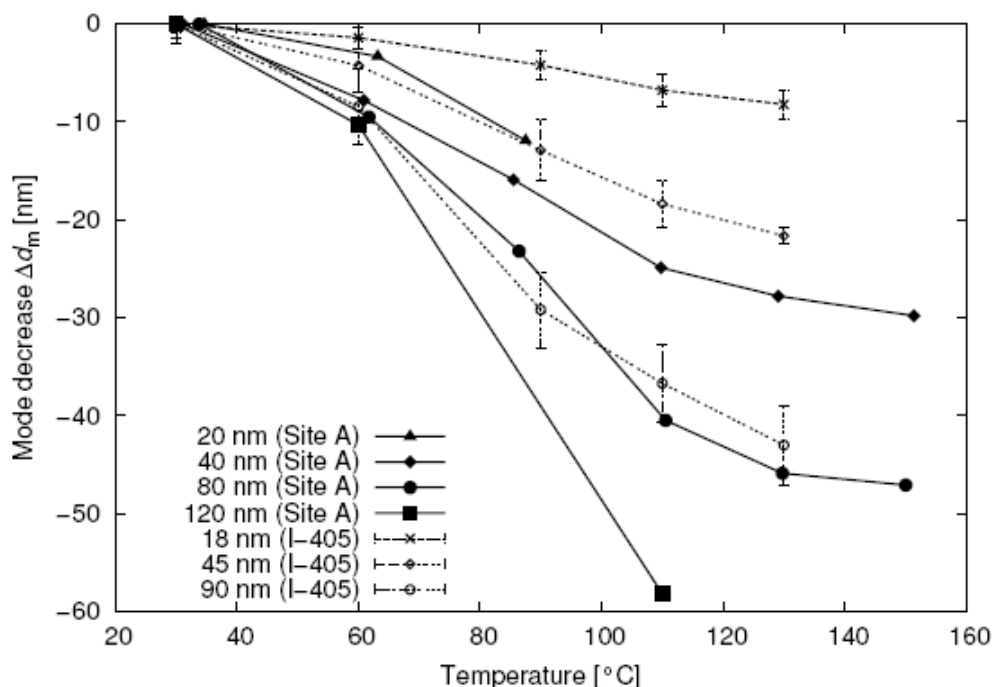


Figure 3.6 The temperature dependence of the mode decrease Δd_m is shown for 20 nm, 40 nm, 80 nm, and 120 nm aerosols at Site A (next to SR 110).

Note: For comparison, the mode decrease for 18 nm, 45 nm, and 90 nm aerosols at the I-405 (Kuhn et al., 2005), measured in winter 2003/2004 at 15 m distance to the freeway is shown.

3.4.4.3 Volatility comparisons

To examine particle volatility further, the ratios Φ_N , Φ_V , Ψ_{Nm} and Ψ_{Vm} have been calculated (Refer Table 3.3) from the integrals of the size distributions at ambient temperature, 60°C, and 110°C. and Φ_V at Site A and Site B are reported in Figure 3.7, and Ψ_{Nm} and Ψ_{Vm} in Figure 3.8. As Figures 3.7 and 3.8 show, in most cases heating did not result in significant particle number losses. Only 20nm particles heated to 110°C were lower in number concentrations than those at ambient temperature.

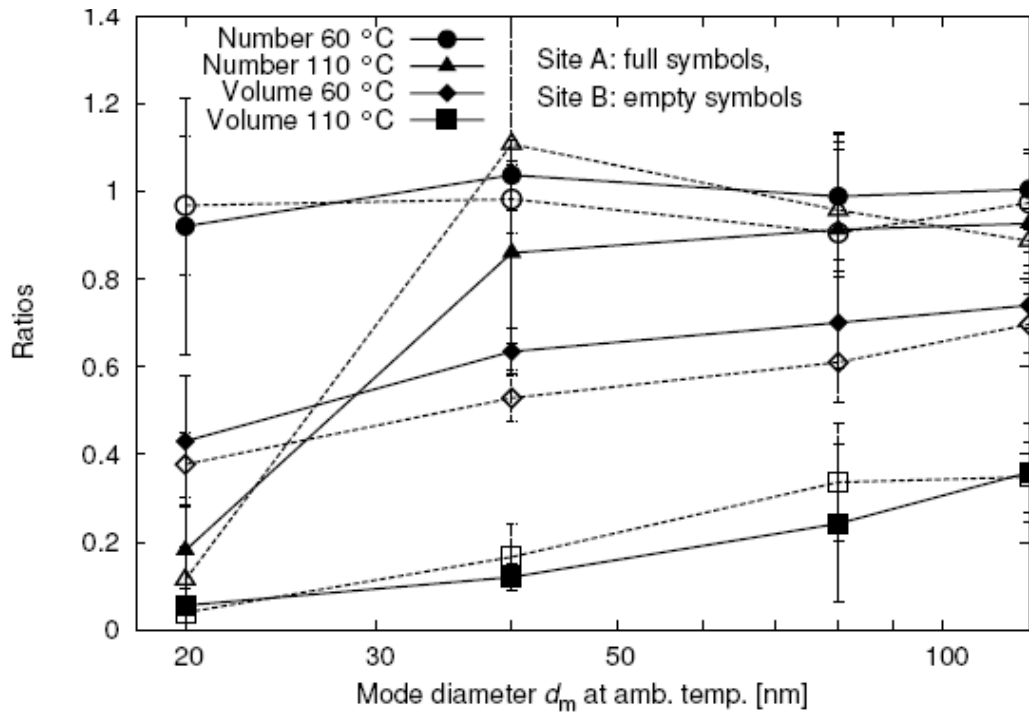


Figure 3.7 Number and volume concentration ratios Φ_N and Φ_V at Site A and Site B at 60°C and 110°C.

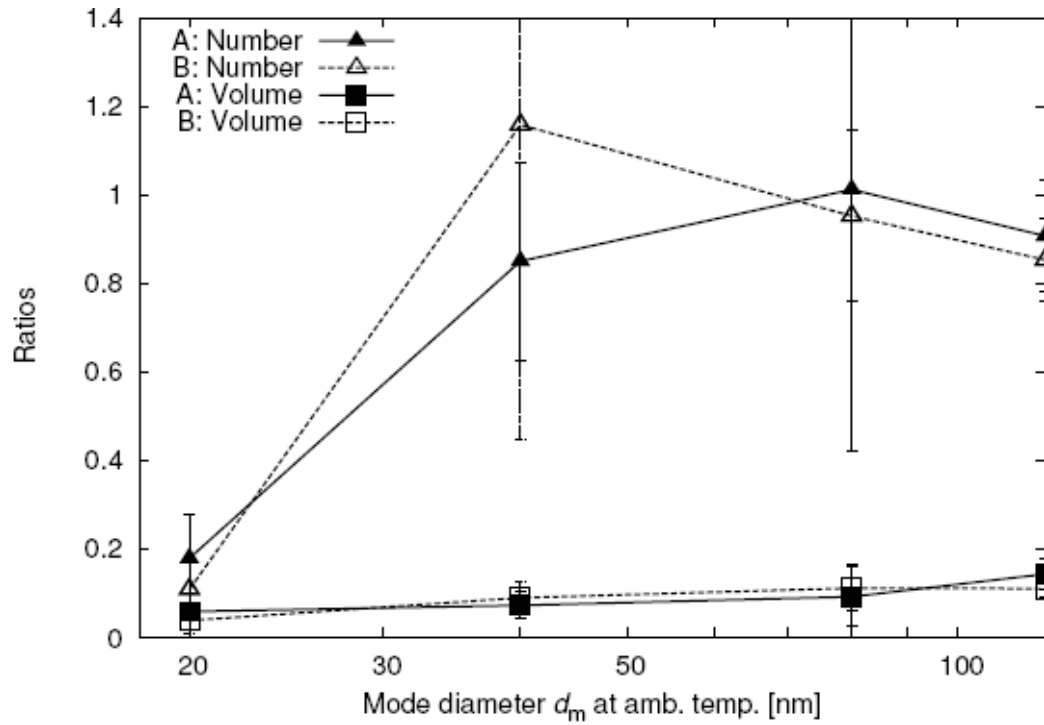


Figure 3.8 Number and volume concentration ratios Ψ_{Nm} and Ψ_{Vm} at Site A and Site B.

This may be due to shrinkage to sizes below the CPC's detection limit of 8 nm. All ratios at Site B are similar to those at Site A. Also the fractions Φ_{Nn} are similar, indicating that at the two sites the same fraction of the aerosol is nonvolatile. From Site A to Site B only the concentrations (number and volume, see Table 3.2) change significantly, while the average volatility remains relatively similar for any given particle size studied. However, particles that grow to larger sizes by condensation of volatile material might increase volatility as compared to particles that already have a larger size shortly after emission. This could be the reason for a slightly larger mode decrease observed for 120 nm particles at Site B ($\Delta dm = -67$ nm) compared to Site A (-58 nm) and higher volume losses at Site B ($\Psi_{Vm} = 0.11 \pm 0.02$) compared to Site A (0.14 ± 0.03). The volatility data from SR 110 was compared to data at the I-405 collected in winter 2003/2004 (Kuhn et al. 2005). The fractions Φ_{Nn} for data at I-405 were 17% for both 45 nm and 90 nm. This indicates that at SR 110 a lower fraction of particles in the range from 40 to 45 nm and a similar fraction of particles in the range from 80 to 90 nm are nonvolatile. The higher fraction of nonvolatile particles at the I-405 might originate, in part, from the diesel vehicles on that freeway (Sakurai et al. 2003a).

3.5 SUMMARY AND CONCLUSIONS

The volatile material content of ultrafine particles, as well as mass concentration and chemical composition of ultrafine, accumulation, and coarse PM were measured at the edge of a freeway with only gasoline vehicles. The number concentrations were relatively low at SR 110 as compared to freeways with mixed diesel and gasoline traffic. This may be due to lower emissions, in terms of ultrafine number concentration, of gasoline

vehicles. The MOUDI ultrafine mass concentration, nitrate, and EC were higher at Site A', which may result from the freeway emissions. The other components analyzed in the ultrafine mode had similar concentrations next to the freeway and at the background site (Site B'). In the coarse size range, on the other hand, mass concentration was similar at both sites, and most other components were either higher at Site B' (e.g., Na, Si, and Ba) or similar in concentration, which might suggest that light-duty vehicles may not be a significant source of coarse particles. The volatility properties at the two sites were similar on average. Relatively high volatility was found, with about 65% of volume of 120 nm particles lost when heated to 110°C, and about 95% of volume of 20 nm particles. Compared to particles from a mixed heavy- and light-duty freeway, aerosol originating from gasoline traffic in this study had a stronger mode decrease. After heating to 110°C particles shrank on average to about half their original size. Heating the particles more resulted in further decrease of their size or loss of particles as they shrank below the lower detection limit of the DMA, which was 8 nm in this study. For aerosols of 40nm particles and above external mixing was observed, with a nonvolatile fraction of up to 28% for 120 nm aerosol. This fraction increases with increasing mode diameter of the aerosol.

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Chapter 4:

Diurnal and Seasonal Characteristics of Particle Volatility and Chemical Composition in the Vicinity of a Light-duty Vehicle Freeway

4.1 ABSTRACT

During the winter of 2005, physicochemical properties of size-fractionated PM₁₀ particles were analyzed next to State Route 110 (Pasadena freeway in Los Angeles, CA, USA), a light-duty vehicle freeway, closed to heavy-duty traffic. We report volatility of ultrafine particles and chemical characteristics in the coarse, accumulation, and ultrafine modes very close to the freeway and at an urban background site. For measurement of mass and chemical composition, the study employed in each location a Micro-Orifice Uniform Deposit Impactor (MOUDI) and a modified high-volume sampler. Both instruments sampled with the same size cut-points. A tandem differential mobility analyzer (TDMA) was used at the two sampling sites to analyze the semivolatile fraction of the aerosols. Size distributions of the ambient aerosol were measured using a DMA and total number concentration using a condensation particle counter (CPC). In this study, which was a continuation of a campaign during summer 2004, we compared the seasonal, i.e. winter versus summer, and diurnal, i.e. daytime versus evening, variation in PM characteristics in the vicinity of this freeway. Conditions in winter differed most from those in summer during the evening rush-hour traffic, with much lower temperatures in the winter campaign. Diurnal variations in particle volatility were observed, with higher content of volatile material in aerosols sampled in the evenings. Particle number concentrations were also much higher during the evening hours, increasing from 67,000 to 110,000 cm⁻³. The average total number concentration next to the freeway was 80,000 cm⁻³ during the

sampling period, which was higher than in summer, when the average was 46,000 cm⁻³. External mixing was observed with increasing nonvolatile fractions for 40, 80, and 120nm particles (39% of particles). In general the volatility increased in the evenings, while the nonvolatile fraction decreased.

4.2 INTRODUCTION

Numerous epidemiological and toxicological studies have found associations between measured PM mass and adverse health outcomes (Dockery et al., 1993; Linn et al., 2000; Lippmann et al., 2003; Peters et al., 2001; Pope et al., 2002, 1995; Ritz et al., 2002; Samet et al., 2000). However, prevailing scientific opinion asserts that, when considering plausible biological mechanisms of injury, PM mass is probably only a surrogate measure of other physical or chemical properties of PM that are the actual cause of the observed health outcomes (NRC, 2004). Several studies have since attempted to link health effects or toxicity measurements with particle characteristics such as particle size, number concentration and chemical composition. For instance, ultrafine particles (with diameters less than about 100 nm) have been demonstrated to be more toxic and biologically active than larger particles (Li et al., 2002; Oberdorster, 2000). Other studies have found associations with PM chemical constituents such as sulfate (Batalha et al., 2002; Clarke et al., 2000), trace elements, and metals such as silicon (Wellenius et al., 2003), vanadium (Saldiva et al., 2002), iron, nickel, and zinc (Burnett et al., 2000), as well as elemental carbon (EC) (Mar et al., 2000; Metzger et al., 2004), and polycyclic aromatic hydrocarbons (PAH) (Dejmek et al., 2000).

In urban environment, vehicular emissions are one of the major sources of ultrafine and fine particles. Significant amount of the particles are generated from tailpipes, wear and tear of break linings (Sternbeck et al., 2002) and secondary formation from several organic gaseous precursors also originating from tailpipe emissions. Formation of atmospheric ultrafine particles is dependent on the dilution condition of the engine exhaust (Wei et al., 2001a, b; Khalek et al., 1999). Following emission, particle number concentration decreases exponentially with the distance from the freeway (Zhu et al., 2002). Several researchers have reported strong seasonal variation for the concentration and size distribution of ultrafine particles (Zhu et al., 2004; He et al. 2001; Kim et al. 2002; Kittelson, 1998). Winter months have been characterized with higher particulate matter due to atmospheric inversion. Colder ambient temperatures contribute to significantly increased nuclei mode particle formation in the vicinity of freeways (Kittelson et al., 2004a; Wei et al., 2001b).

Recent emission tests in either dynamometer or on road testing facilities have shown that particles emitted from diesel vehicles in general are externally mixed, i.e. different particles of the same size can have different chemical compositions. These tests have demonstrated that, depending on vehicle type, age and ambient conditions, between 70% and 90% of the particles by number and 10% and 30% by mass may consist of more volatile material than others (known as semivolatile), and upon heating, will partially or completely evaporate (Sakurai et al., 2003a, b; Kittelson et al., 2004b). Thus, particles from vehicles can be thought of having two components: a semivolatile fraction arising

from vapor to particle condensation upon cooling in or near the tailpipe, and a nonvolatile fraction created in the engine in particle form. In diesel engines, the nonvolatile portion is known to primarily consist of EC, which is often coated with more volatile organic species (Sakurai et al., 2003a). Using single particle mass spectroscopy it has been shown that EC particles dominate gasoline emissions in the ultrafine size range by number for newer light-duty vehicles, whereas organic carbon (OC) dominates gasoline emissions of some older vehicles (Sodeman et al, 2005). Determination of organic compounds has shown that many of the organic chemical constituents of PM emitted from both diesel and gasoline vehicles are semivolatile, existing simultaneously in the gas and particle phases at equilibrium (Schauer et al., 1999, 2002).

In a recent study, Zhang et al. (2004) have shown that in near freeway exposure situations, a dynamic exchange of semi volatile organics between the particle and gas phase occurs, which has significant effects on particle size and chemistry. For example, the volatility of these particles explains the more rapid decay in their concentration with respect to distance from a roadway, compared to that of non-labile PM species (such as EC) or gaseous copollutants such as carbon monoxide (CO) and nitrogen oxides (NO_x), the concentration decrease of which would be affected mostly by atmospheric dilution. The increased dilution with distance to roadway decreases the concentration of vapors in equilibrium with these particles, which enhances evaporation of these vapors from the particle phase to re-establish equilibrium (Zhang et al., 2004).

The exposure and health implications of these findings have not yet been investigated. Exposure and dose of some of these potentially toxic semivolatile species may differ according to whether they are in the gas or particle phases. The volatile component of these particles may likely be present in its gaseous phase in indoor environments as the aerosol becomes heated and or vapor concentration decreases by adsorption to indoor surfaces when infiltrating indoors in the wintertime. Finally, given that the majority of people's exposure during commute will be dominated (at least based on particle numbers) to these particles, it would be useful to know whether the nonvolatile or semivolatile material is more toxic. This would not only narrow down the search for the most toxic PM components, thereby aiding mechanistic investigations, but would also suggest new emission control technologies that better protect the public health.

Several studies have been performed to determine the chemical nature and volatility of the aerosol (e.g. Sakurai et al., 2003a; Orsini et al., 1999). These studies made use of a tandem differential mobility analyzer (TDMA) configuration, in which particle volatility is measured for a given size by selecting a fairly monodisperse aerosol by the first DMA, heating it to a selected temperature and measuring the resulting size distribution of the heated aerosol by means of the second DMA. In a previous study, Kuhn et al. (2005a) measured physicochemical characteristics (including volatility) of particles in the proximity of a pure gasoline freeway (CA 110 freeway) during the summer time, using a tandem DMA set-up. They found that the volatile component ranged from about 65% volume of 120 nm particles, to 95% volume of 20 nm particles. Particles with a diameter of 40 nm or larger were externally mixed, with a fraction of the aerosol, which increased

with increasing diameter, being nonvolatile. In the present study, which is a continuation of the Kuhn et al. (2005a) work, we compare the seasonal, i.e. winter versus summer, and diurnal, here limited to daytime versus evening, variations in PM characteristics in the vicinity of this freeway. In addition to particle volatility properties, we also report detailed chemical characteristics of these particles close to the freeway and compare them to a close urban background site.

It should be noted that the present study was part of a larger, continuing effort by investigators of the Southern California Particle Center and Supersite to determine and compare the toxicity of PM emitted from heavy-duty and light-duty vehicles. In addition to and concurrently with our measurements, PM samples were collected for in vitro toxicity tests, the results of which will be described in future publications.

4.3 EXPERIMENTAL METHODS

4.3.1 Sampling location and schedule (traffic, weather)

Sampling location and schedule were chosen identical to those used by Kuhn et al. (2005a) in volatility measurements in summer and described in section 3.3.1. During the whole sampling period, vehicle speed was fairly constant on SR 110 and traffic was free flowing. The traffic volume varied throughout the day with a peak during morning and one during evening rush hours, when traffic was predominantly on the northbound lanes. The hourly averages of the total traffic density (vehicles on north- and southbound lanes) are shown in Figure 4.1.

During the sampling period the average traffic density was about 5100 h^{-1} . Figure 4.1 also shows diurnal hourly averages of total number concentrations at the two sampling sites, which are discussed later in the Results and discussion section.

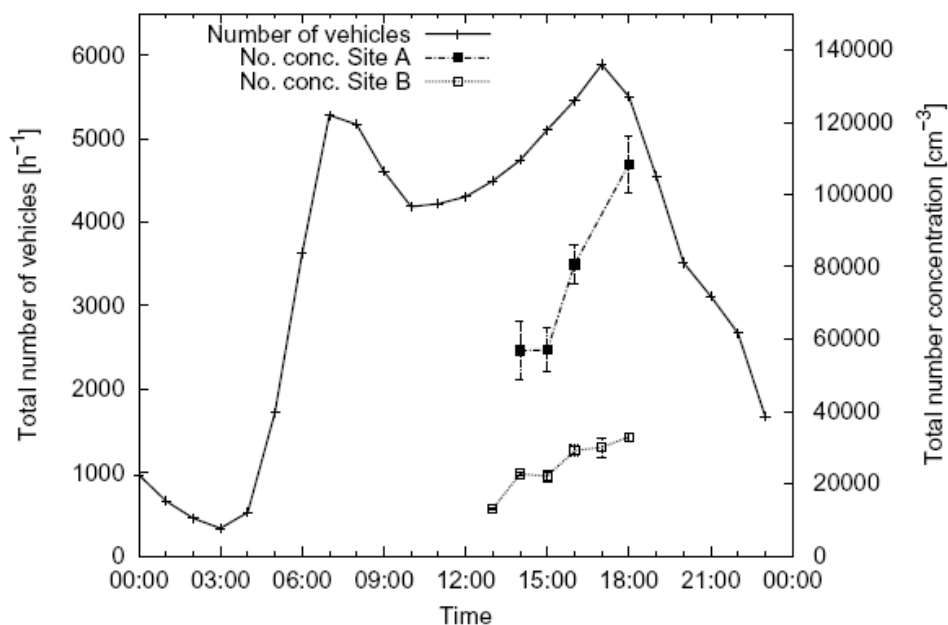


Figure 4.1 Total number of vehicles shown as averaged diurnal trend during all days of the sampling period. Total ambient number concentrations increased during afternoon and evening. In the cooler evening hours the concentration increased significantly at Site A, even when traffic volume declined.

Wind direction, speed, and temperature were recorded with a weather station (Wizard III, Weather Systems Company, San Jose, CA, USA). Data were averaged over 1 min intervals. The average temperature during the sampling period was 21.7°C with a standard deviation (S.D.) of 5.8°C . The temperatures decreased rapidly in the late afternoon and after sunset (around 5 p.m.). The average temperature before 5 p.m. was 23.5°C (S.D.: 4.9°C) and after 5 p.m. 14.3°C (S.D.: 2.8°C). The relative humidity was measured by a Q-Trak Plus (TSI Inc., St. Paul, MN, USA) and was on average 39%

(S.D.: 22%), but changed drastically during the day, with an average of 32% (S.D.: 16%) before 5 p.m. and 72% (S.D.: 8%) after 5 p.m. The conditions before 5 p.m. (during daytime) were quite similar to the conditions during the summer study (25 °C; RH of 51%), whereas only the conditions after 5 p.m. (in the evenings) were different. For comparison with the summer study, the data were therefore in most cases separately averaged for daytime and evenings. The average wind speed was 0.5 ms^{-1} (S.D.: 0.5 ms^{-1}), substantially lower than in the summer (1.6 ms^{-1}). Many times the recorded wind speed was zero (33% of all 1 min intervals), but even when these data were excluded from the average, the wind speed was only 0.8 ms^{-1} . The wind speed decreased in the evenings, frequently being zero (78% of recorded wind speeds were zero against 20% during daytime). The predominant wind directions were southwest and south–southwest (about 25–35% of the time each), very similar to wind directions in summer. The meteorological conditions were similar during sampling at the two sites. In general they were stable and consistent during this and our summer study, which is typical for Southern California’s stable climate. The outlined differences in the conditions allow therefore for a seasonal comparison of our results, even though it remains limited to several weeks per season.

4.3.2 Measurements of particle chemical composition

Described in section 3.3.2

4.3.3 Particle volatility measurements

Same as described in section 3.3.3

4.4 RESULTS AND DISCUSSION

4.4.1 Particle chemical composition

The averaged results from MOUDI and high volume sampler are shown in Table 4.1. Only elements with concentrations higher than $0.01 \mu\text{g m}^{-3}$ in all modes are reported. At Site A, the mass concentrations were higher than at Site B in all three size modes, reflecting the influence of the freeway. Contrary to our summer study, the mass concentrations in the accumulation mode were higher than the coarse mode. In the summer study the coarse mass concentrations were the highest (23 and $21.5 \mu\text{g m}^{-3}$ for Site A and B, respectively), compared to 19.0 and $19.2 \mu\text{g m}^{-3}$ in accumulation mode and 5.1 and $3.3 \mu\text{g m}^{-3}$ in ultrafine mode for Sites A and B, respectively. Higher wind speeds and drier conditions in summer might have caused more re-suspension of road dust and consequently a predominant coarse mode. Concentrations of the species Na, Si, Cl, K, Ca, Ti, Fe, Cu, and Ba were dominated by the coarse mode concentrations. They result mostly from road dust, but also from break and tire wear and sea salt. All these species were much higher in summer (e.g. Fe here 0.7 was $2.0 \mu\text{g m}^{-3}$) caused by the higher wind speed. Most of sulfate and nitrate were found in accumulation and ultrafine modes.

As in summer, the concentrations in the accumulation modes were very similar at both sites for most species, confirming again that this size range represents for the most part a background urban aerosol, unaffected by local traffic. The mass concentration in the coarse mode was higher at Site A compared to Site B. Most species concentrations in the coarse mode, however, were similar and did not have a statistically significant difference. Only OC, EC, Cu, and Ba concentrations were significantly higher at Site A. EC was

found predominantly in the ultrafine mode and concentration was higher at Site A, because most EC originates from vehicular emissions in that size range. Concentrations of EC were also higher at Site A in the accumulation and coarse modes. OC concentrations were higher in accumulation than in coarse mode. The high values for OC in the ultrafine mode are biased by a positive sampling artifact, caused by adsorption of OC in the gas phase passing through the filter (Mader and Pankow, 2001). The actual values of ultrafine OC are therefore not known. Accumulation and coarse mode OC concentrations are much less affected by a positive artifact, considering that particles in these size ranges are collected by impaction on substrates, which are bypassed by the deflected air flow due to the stagnation zone created around the substrate. In addition to EC, also the ultrafine sulfate concentrations were slightly higher at Site A. Concentrations for other species were similar or slightly higher at Site B (Na, Si, S, K, Ca, and Fe). Most of these species are, however, dominated by the coarse mode concentrations, where most of them were similar at both sites.

In the summer study, coarse PM concentrations were generally higher, as mentioned earlier. Accumulation and ultrafine mode concentrations, on the other hand, were generally more similar in the two seasons, with the exception of sulfate and sulfur concentrations, which were considerably higher in summer (in summer sulfate was about four times higher in accumulation mode, sulfur twice in accumulation and nine times in ultrafine mode), possibly due to increased photochemical formation of these species during that period. Ultrafine mass concentrations were slightly higher in winter, possibly due to the lower temperatures enhancing more nucleation of ultrafine particles, as well as

by less mixing in the atmosphere. In particular EC, OC, and nitrate concentrations were higher in winter.

Table 4.1 Chemical speciation, $\mu\text{g m}^{-3}$

	Coarse		Accumulation		Ultrafine			Coarse		Accumulation		Ultrafine	
	A'	B'	A'	B'	A'	B'		A'	B'	A'	B'	A'	B'
Mass							Cr						
Mean	7.60	4.92	13.98	10.62	6.00	5.04	Mean	0.00	0.00	0.00	0.00	0.00	0.00
SD	0.66	0.58	11.13	5.48	1.54	1.17	SD	0.00	0.00	0.00	0.00	0.00	0.00
OC							Mn						
Mean	1.37	0.77	2.17	2.17	14.55	10.66	Mean	0.01	0.01	0.00	0.00	0.00	0.00
SD	0.67	0.46	0.93	1.02	5.76	7.41	SD	0.00	0.00	0.00	0.00	0.00	0.00
EC							Fe						
Mean	0.21	0.05	0.14	0.12	1.90	1.50	Mean	0.66	0.56	0.342	0.301	0.095	0.161
SD	0.21	0.04	0.07	0.03	1.30	1.04	SD	0.16	0.17	0.096	0.148	0.053	0.084
Sulfate							Cu						
Mean	0.27	0.17	0.77	0.82	1.58	1.23	Mean	0.03	0.02	0.020	0.015	0.006	0.007
SD	0.20	0.10	0.71	0.90	0.79	0.36	SD	0.01	0.01	0.007	0.009	0.002	0.004
Nitrate							Zn						
Mean	0.67	0.49	2.38	2.49	2.82	3.01	Mean	0.01	0.01	0.021	0.019	0.005	0.007
SD	0.55	0.48	3.20	3.79	1.62	1.42	SD	0.01	0.00	0.006	0.006	0.002	0.003
Al							Sr						
Mean	0.15	0.15	0.04	0.06	0.39	0.47	Mean	0.00	0.00	0.001	0.002	0.001	0.001
SD	0.08	0.02	0.01	0.02	0.61	0.40	SD	0.00	0.00	0.000	0.001	0.000	0.000
Si							Zr						
Mean	0.56	0.54	0.17	0.21	0.11	0.20	Mean	0.01	0.00	0.004	0.003	0.001	0.001
SD	0.22	0.13	0.06	0.08	0.06	0.08	SD	0.00	0.00	0.002	0.001	0.000	0.001
S							Ba						
Mean	0.08	0.06	0.34	0.27	0.03	0.06	Mean	0.04	0.03	0.026	0.022	0.004	0.009
SD	0.05	0.02	0.34	0.22	0.01	0.03	SD	0.01	0.01	0.011	0.015	0.003	0.007
Cl							Pb						
Mean	0.10	0.11	0.02	0.01	0.00	0.01	Mean	0.01	0.00	0.004	0.004	0.002	0.003
SD	0.07	0.09	0.03	0.01	0.00	0.01	SD	0.00	0.00	0.003	0.003	0.001	0.001
K							Ca						
Mean	0.08	0.08	0.04	0.05	0.02	0.04	Mean	0.27	0.26	0.086	0.100	0.044	0.095
SD	0.04	0.02	0.01	0.01	0.01	0.01	SD	0.10	0.04	0.033	0.036	0.024	0.039
Ti							Ti						
Mean	0.03	0.03	0.02	0.02	0.01	0.01	Mean	0.03	0.03	0.019	0.015	0.007	0.013
SD	0.01	0.01	0.01	0.01	0.00	0.01	SD	0.01	0.01	0.007	0.007	0.004	0.007

Interestingly, while all other species concentrations in the coarse mode were much higher in summer, EC and OC concentrations were higher in winter at Site A and similar at Site B. This indicates that these, in contrast to the other coarse species, originate mostly from traffic emissions, which are higher in winter due to the colder temperatures and associated inversions. Increased OC in the coarse PM mode in the winter may also be a

result of condensed vapor phase on pre-existing particles in that size range. This phenomenon is expected to also affect OC in the accumulation mode, but the generally higher background OC levels in that mode make it less evident, as shown in Table 4.1.

4.4.2 Size distribution and concentrations of ambient

Ambient size distributions measured at Sites A and B are shown in Figure 4.2, which also includes a comparison with distributions measured in the summer study. At Site A, there is a dominant mode at around 20 nm, originating from nucleation of tailpipe emissions from the freeway, which is more pronounced in evenings. At Site B there is no freeway mode but, for this study (winter), the size distribution has a broad mode around 50nm during daytime and a bimodal shape with modes at 30 and 100nm in the evening. These mode diameters are higher than those found in the summer study, where a mode at 30 nm was observed (see Figure 4.2b). Zhang et al. (2004) showed that, depending on ambient dilution conditions, particles could either continue to grow by condensation or shrink again due to evaporation. Therefore, the greater mode diameter could be caused by enhanced condensational growth due to less dilution in winter (i.e., less mixing as well as lower wind speeds). Such growth could affect both freeway generated particles and urban background aerosol. The daytime size distribution at Site A in winter was almost identical to that measured in summer. Both distributions had a mode at 20nm, and between 10 and 20 nm the distributions remained at a similar concentration level as at the 20 nm mode. This was different in the evening in winter, where below the 20 nm mode the concentration decreased steeply. Zhu et al. (2004) observed a mode between 10 and 20nm in addition to a mode at around 30 nm in summer at I 405 freeway in Los

Angeles, whereas in the winter only one mode was evident in that size range. In measurements at various distances downwind from I 405 in summer (Zhu et al., 2004, 2002) the mode below 20nm was dominant only at the closest distance to the freeway and disappeared at increased distance. The most remarkable difference between the distributions during daytime and evenings is the increased number concentration in the evenings, as it will be discussed later, due to the decreased temperatures. This is especially true for Site A. However, also at Site B a significant increase in the evenings was observed, in part caused by the increased concentration at the freeway but possibly also by increased ambient background concentrations. Average number, surface, volume, and mass concentrations determined from the size distributions of ambient aerosol are listed in Table 4.2. The number concentrations are taken from the control CPC measurements. Figure 4.1 also shows the number concentrations from the control CPC as diurnal hourly averages in comparison with traffic volume. A sharp increase could be observed at Site A after 4 p.m. The relative increase is higher than that observed for traffic volume: from 2 p.m. to 6 p.m. the particle number concentration increased by 91%, while at the same time traffic increased only by 16% (37% from noon to maximum at 5 p.m.). Traffic volume is therefore not the only cause for increased number concentrations but also the continuously decreasing ambient temperature, which enhances particle formation by condensation of super-saturated organic vapors originating from vehicles. This phenomenon is discussed more extensively in a subsequent section (see Volatility Properties). In summer, with warmer temperatures in the evening, the number concentration reached a maximum in late afternoon associated with rush hour traffic and then declined again in the evening.

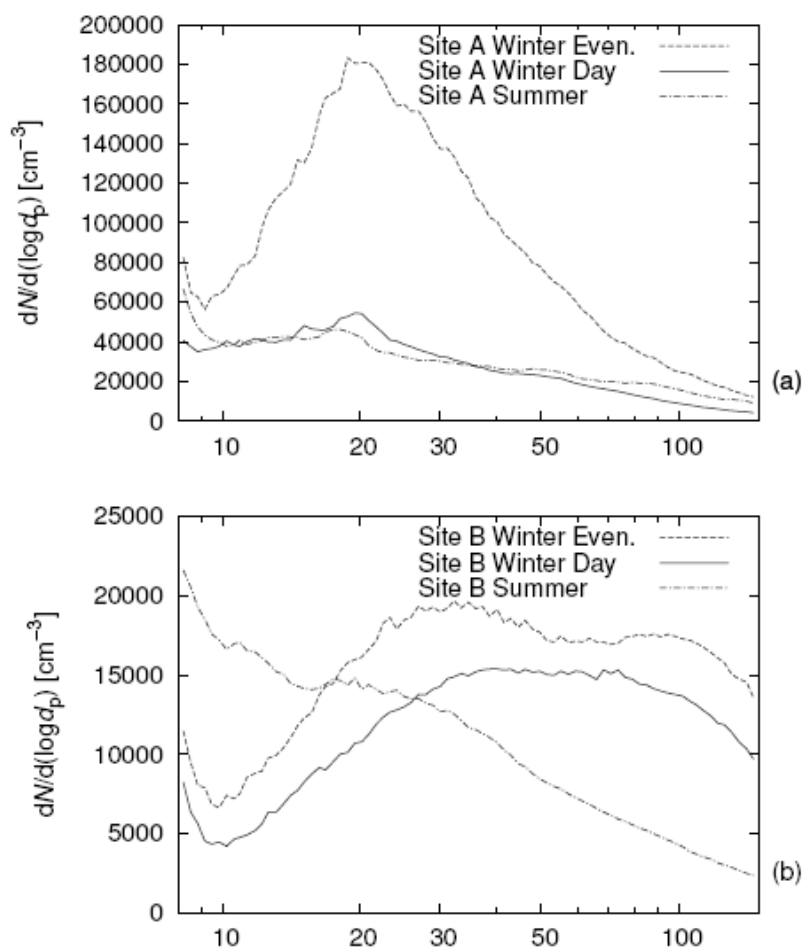


Figure 4.2 Size distributions at a) Site A and b) Site B. Size distributions from winter (this study) are shown daytime and evenings (after 5 p.m.). Size distributions from the summer study are also shown for comparison

Table 4. 2 Number, surface, volume, and mass concentrations

Site	Number cm-3	St. dev. cm-3	Surface um2 cm-3	Volume um3 cm-3	Mass ug m-3	MOUDI ug m-3
Site A	80 052	33 855	73.1	3.54	5.67	6.74
Site A Day	66 682	25 872	43.2	2.15	3.45	
Site A Evening	108 461	31 711	136.5	6.5	10.4	
Site B	25 713	7 410	53.5	3.44	5.5	4.70
Site B Day	21 805	6 122	48.4	3.09	4.94	
Site B Evening	31 966	4 406	61.6	3.99	6.39	

The measured number size distributions were converted to surface and volume size distributions assuming spherical particles. These distributions were integrated to yield surface and volume concentrations. The mass concentration was calculated from the volume concentration using a constant particle density of 1600 kgm^{-3} . The difference observed in number concentration between daytime and evenings results also in a difference for surface and volume concentrations. Gravimetrically determined mass concentrations from the MOUDI sampled during the same sampling periods are reported for comparison (see Table 4.2).

4.4.3. Volatility properties

4.4.3.1 Size distribution changes

Fig. 4.3 shows averaged results from volatility measurements for 40 and 120nm particles. For every case three normalized number size distributions are shown: the first represents the selected monodisperse aerosol at ambient temperature without conditioning; the second shows the size distribution after heating to 60°C ; and the third after heating to 110°C . The presented size distributions were averaged over all measurements during either daytime or evenings. The diameter of each measured particle size shrank when heated resulting in a particle mode decrease Δd_m . The distribution also broadened when the aerosol was heated, since not all particles have the same composition and volatility. As in summer, for the 80 nm (not shown in Figure 4.3) and 120nm aerosols the unimodal distributions split into bimodal distributions (mostly volatile and nonvolatile modes) when heated to 110°C . This indicates that these aerosols were externally mixed and consisted of particles containing volatile material and particles containing only

nonvolatile material. To a lesser extent the 40nm particles were externally mixed, and a smaller fraction Φ_{Nn} of nonvolatile particles was detected, on average more in the evenings.

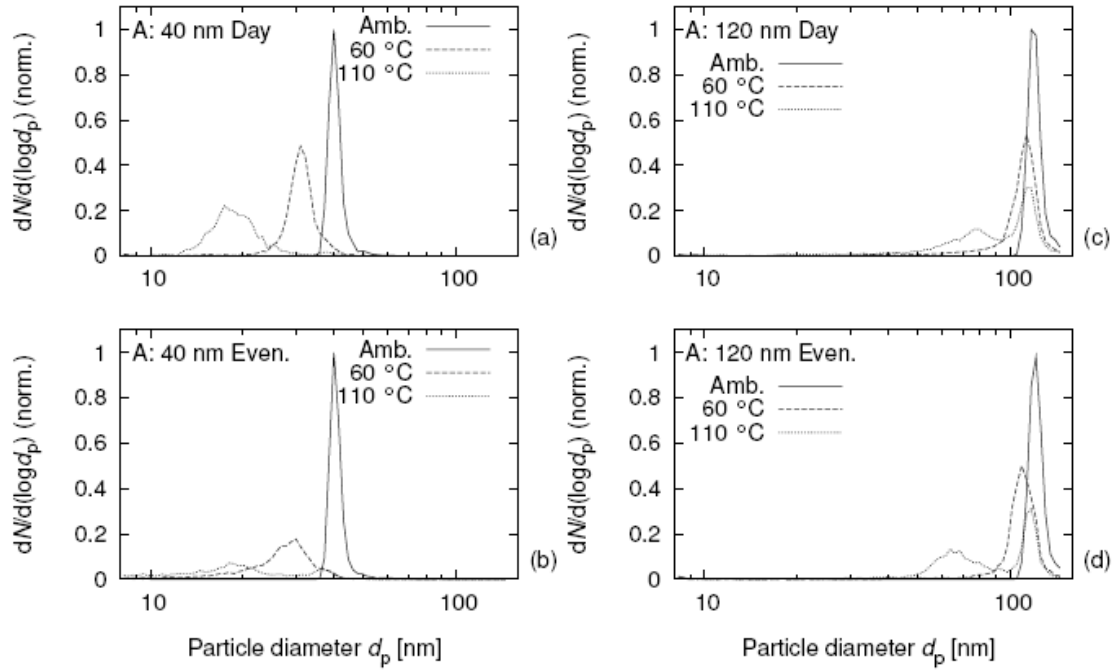


Figure 4.3 Normalized volatility size distributions at Site A. Averaged size distributions of monodisperse aerosol at ambient temperature and after heating to 60 and 110°C are shown for a) 40 nm aerosol during daytime, b) 40 nm in the evening, c) 120 nm during daytime, and d) 120 nm in the evening.

The volatile content of PM increased in the evenings, as shown in Fig.4.3, which resulted in a stronger mode decrease for 120nm ($\Delta d_m = -55\text{nm}$ in evening versus -42 nm at daytime) and, in case of 40 nm aerosol, in a similar mode decrease, but a lower relative mode height. The latter case implies that some particles were highly volatile so that at 110 °C, and to some extent even at 60 °C, they shrank to a size that could not be detected

by our instruments. On 18 January, 2005, while sampling at Site A, the volatility appeared to be reduced. For 40nm during daytime, a mode decrease of -18 nm was observed, whereas the average decrease of the other days was -22 nm. For 80nm particles, the volatility in the evening was measured on 18 January and showed very similar characteristics to that measured during daytime on other days, whereas for other aerosol sizes measured in the other evenings, the volatility appeared to increase compared to daytime, as shown above (see Figure 4.3). This was presumably caused by meteorological conditions that were distinctively different on 18 January. The wind was coming from northeast, the opposite direction of the southwesterly winds on the other days. The wind speed was lower than average on that day (0.4 ms^{-1} when speed was greater than zero, 29% of the recorded wind speed values were greater than zero). These conditions lasted for only a short period of time. On 19 January the wind directions reversed again to the normal southwest origin. Conditions on 18 January brought different air masses to the sampling. On normal days with southwesterly winds, air masses from the Los Angeles downtown area affected the sampling site, whereas for this episode, cleaner air masses from the area of San Gabriel Mountains came to the site. In the following analysis all data from this day were therefore excluded.

4.4.3.2 Temperature dependence

For 80 and 120 nm aerosols, volatility size distributions were measured at several different heater temperatures up to aerosol temperatures of 160°C during daytime. The mode decrease was determined for each measured size distribution and averages are presented in Figure 4.4

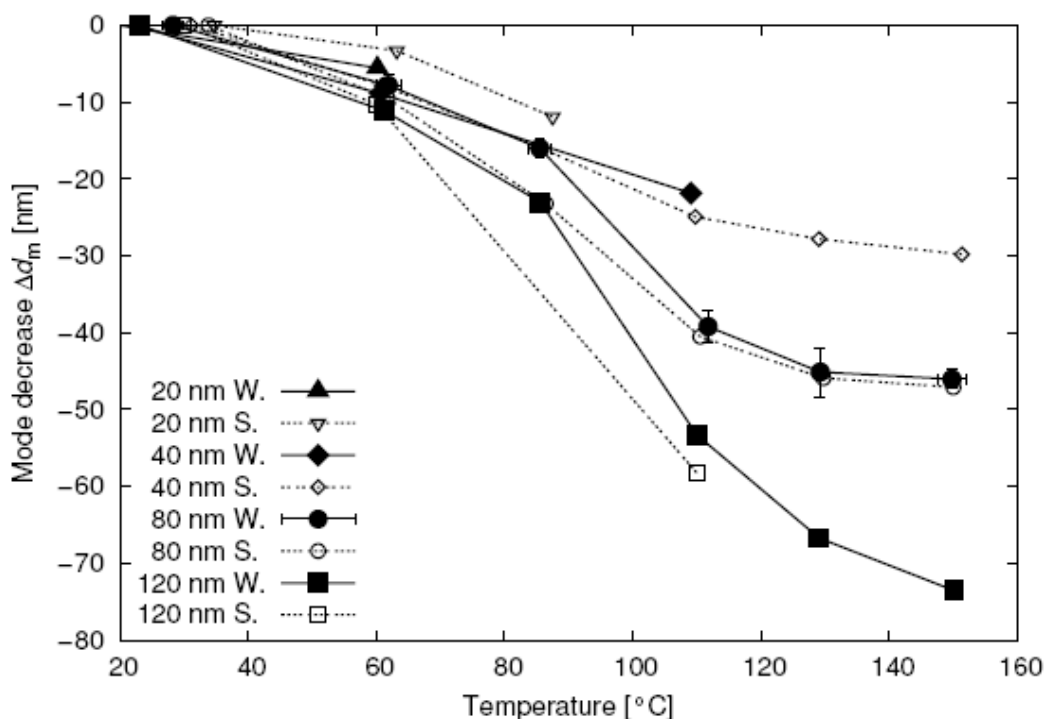


Figure 4.4 Mode decrease Δd_m as function of temperature.

Note: For this study (winter, denoted W.) the mode decreases for temperatures up to 160°C were determined from each measured size distribution and averages are presented for the average temperatures of the respective distributions. The values for 80 nm are shown with the standard deviations of the aerosol temperature and mode decrease. For comparison the data from the summer study (S.) is shown as mode decreases from averaged size distributions.

For 20 and 40nm results for temperatures up to 80 and 110 °C, respectively, are also shown. The mode decreases measured here are similar to results from the summer study. As in summer, for 80 nm particles, the mode decrease seems to level off above 130 °C, indicating the presence of a nonvolatile core for these particles. Average particle mode decreases for measurements at 60 and 110 °C are shown in Table 3. In general, the mode decrease is stronger in the evening than during daytime, consistent with the increased semivolatile particle content of the aerosols during that time. In case of the 40nm

particles at Site A, however, the higher volatility in the evening was, as mentioned before, not indicated as much by a decrease in mode diameter, but by increased particle number losses as well as increased aerosol volume losses, as it will be discussed in the following section. Furthermore, no sizable differences in mode decreases between Sites A and B were observed.

Table 4.3 Average particle mode decrease Δd_m (in nm)

Site A daytime					Site B daytime				
Temp.	20 nm	40 nm	80 nm	120 nm	Temp.	20 nm	40 nm	80 nm	120 nm
60	-2.3	-8.9	-11	-6.3	60	-2.7	-4.7	-10	-28
110	-9.3	-21	-39	-43	110	-10	-16	-34	-49
Site A evening					Site B evening				
Temp.	20 nm	40 nm	80 nm	120 nm	Temp.	20 nm	40 nm	80 nm	120 nm
60	-5.4	-12	-12	-10	60		-6.6	-12	-10
110		-21	-36	-54	110		-19	-39	-51

4.4.3.3 Volatility comparison

At 60 °C the number-based fraction of the remaining aerosol after heating, Φ_N , is close to unity for aerosols of 40nm in diameter or larger at Site A, and for all aerosols studied at Site B. At 110 °C the ratio is close to one for aerosols of 80 and 120nm in diameter. This indicates that in these cases no particles are lost, only volatile material is lost from the particles, resulting in a particle volume loss, but not in a number decrease. In the remaining cases Φ_N is less than one because part of the particles shrinks to sizes below the detection limit of the second SMPS (in our case equal to 8.2 nm) or completely evaporated. This causes the lowest ratios at the lowest aerosol size of 20, 0.26 and 0.60nm on average for Site A and Site B, respectively. Such losses seem to be higher at Site A, indicating higher aerosol volatility close to the freeway, a result that is also

consistent with the modeling work of Zhang et al. (2004). The remaining volume fractions, Φ_V , after heating the aerosols range from about 0.4 to 0.8 for to 60 °C and 0.03 to about 0.4 for 110 °C. In general the ratio increased with increasing aerosol diameter. The ratios at 110 °C are slightly lower in the evenings, indicating somewhat higher particle volatility at that time. Higher content of volatile material might be caused by enhanced condensational growth favored in the colder evening temperatures resulting in a lowered saturation vapor pressure of organic species. The ratios from our summer study were similar to ratios here.

The nonvolatile fractions Φ_{Nn} , which are given in Table 4.4, show that around 30% or more of the particles with diameters of 80 and 120nm are nonvolatile at Site A. The fractions were slightly higher during daytime for these particles. This may be indirectly caused by higher particle formation through nucleation in the cooler evening period, which would increase the fraction of volatile particles and thereby decrease the nonvolatile fraction. At Site A, higher fractions of nonvolatile particles were found than at Site B. In our summer study, the nonvolatile fractions were lower, i.e., 0.20 and 0.28, for 80 and 120 nm, respectively. As opposed to observations for 80 and 120 nm particles, the nonvolatile fraction at 40nm is higher in the evenings at Site A (9% in evening against 3% during day). These particles were the smallest for which external mixing was observed. For the 20nm particles, no nonvolatile fraction was observed here or in summer, a result that suggests that these smaller particles are only internally mixed.

Table 4.4 Nonvolatile fractions Φ_{Nn} . Fraction of particles that are nonvolatile and form nonvolatile mode at 110°C.

Particle diameter	Site A (daytime)		Site B (daytime)		Site A (evening)		Site B (evening)	
	110 °C	SD	110 °C	SD	110 °C	SD	110 °C	SD
40 nm	0.03	0.01	0.10	0.03	0.09	0.03	0.10	0.03
80 nm	0.34	0.18	0.26	0.03	0.28	0.06	0.13	0.01
120 nm	0.40	0.15	0.23	0.01	0.35	0.03	0.27	0.03

The remaining volume of the mostly volatile fraction, Ψ_{Vm} , is shown in Figure 4.5. In general, particle volatility increased during the evenings at both sites. The colder temperatures in the evening are likely to enhance condensation of semivolatile material on the ultrafine particles, and hence increase the volatile material found on the particles. The fractions in summer appear to fall between daytime and evening values found in this study. At Site B the values of the remaining volume of the mostly volatile fraction were slightly higher than at Site A, indicating a modest decrease in volatility when moving away from the freeway.

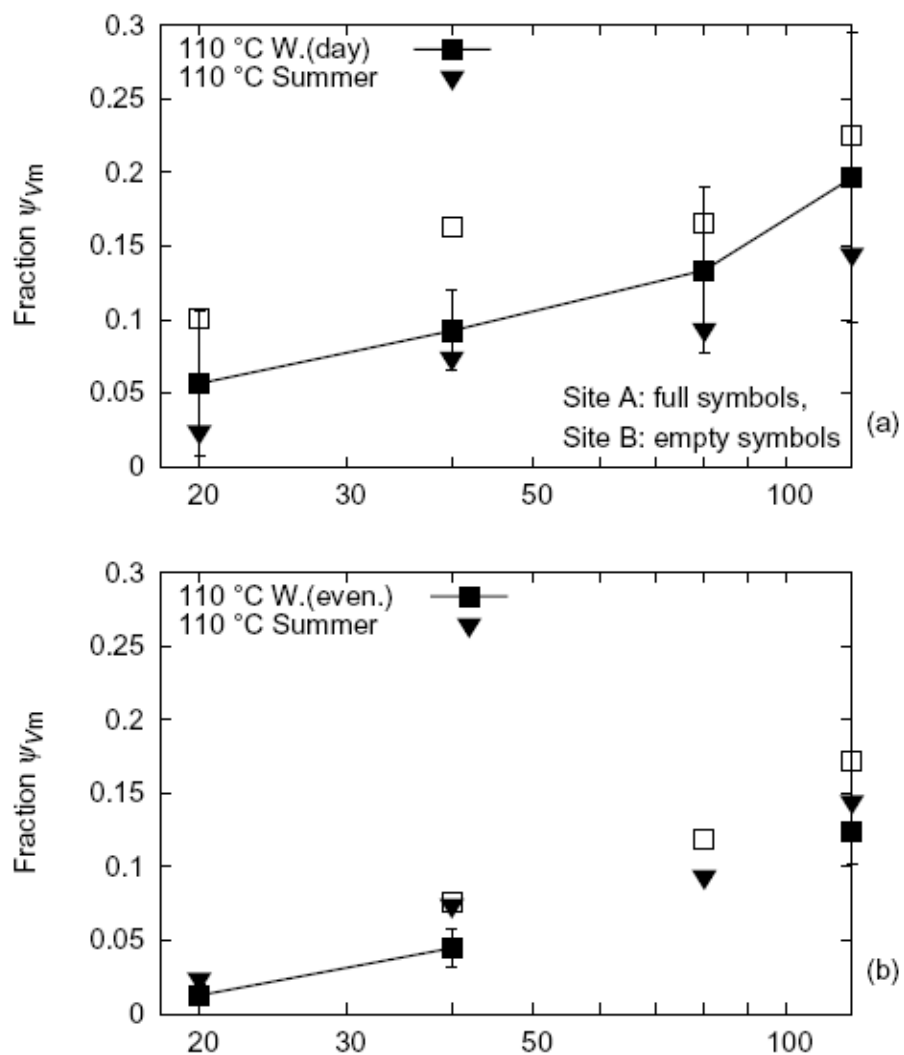


Figure 4.5 Fraction ψ_{vm} , remaining volume of mostly volatile particles

4.5 CONCLUSIONS

In this study we compared the seasonal, i.e. winter versus summer, and diurnal, i.e. daytime versus evening, variations in PM characteristics in the vicinity of a light-duty vehicles freeway. While daytime meteorological conditions in winter differed only slightly from conditions in our summer study, the winter evenings were considerably

cooler and had a higher relative humidity. PM mass concentrations in coarse, accumulation, and ultrafine modes were higher at the proximal site to the freeway. Lower wind speeds in winter are responsible for relatively low coarse PM mass concentrations. Accumulation mode concentrations were in general similar in the two seasons, with the exception of sulfur and sulfate, which were higher in summer due to increased photochemistry. By contrast, the ultrafine mass concentrations were higher in winter, in particular for EC and OC. This suggests that cooler winter temperatures may favor particle formation by enhancing nucleation of vehicular exhaust, which caused also the number concentration to increase to $110,000 \text{ cm}^{-3}$ in the evenings. Concentration and size distribution during daytime, on the other hand, were similar to results from our summer study in this location. Generally larger aerosol mode diameters were observed in the urban background site, possibly due to the lower dilution and increased condensational growth of freeway and urban background aerosols. Similarly to our summer study, 40, 80, and 120nm aerosols were externally mixed, with increasing nonvolatile fractions for increasing aerosol sizes. Nonvolatile aerosol fractions were higher during daytime and decreased in the evening, when an increased volatility was observed. While the sampling site of the present study offered a unique opportunity to characterize freeway emissions from predominantly gasoline vehicles, most urban freeways include a fleet of diesel vehicles that contributes significantly to emissions. Future research at diesel-dominated freeways will complement this work. This is important to assess the exposure of people commuting or living close to freeways.

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Chapter 5:

Particle Volatility in the Vicinity of a Freeway with Heavy-Duty Diesel Traffic

5.1 ABSTRACT

During February-March 2006, a major field sampling campaign was conducted adjacently to the Interstate 710 (I-710) freeway in Los Angeles, CA. I-710 has high traffic volumes (ca. 11,000 vehicles h⁻¹) and a high percentage (17-18%) of heavy-duty diesel vehicle (HDDV) traffic. The volatility of ambient particles of 20, 40, 80 and 120 nm in diameter was investigated using a Tandem Differential Mobility Analyzer (TDMA) at two locations – close to the freeway (10 m) and approximately 150 m downwind. The smallest particles (20 nm) are mostly volatile at both locations. Larger particles (e.g. ≥ 40 nm) showed evidence of external mixing, with the nonvolatile fraction increasing with particle size. Particle volatility increased with decreasing ambient temperature. The HDDVs contribute to relatively larger nonvolatile particle number and volume fractions and greater external mixing than earlier observations at a pure light-duty gasoline vehicle freeway (Kuhn et al., 2005, *Atmospheric Environment*, 39, 7154). Finally, the fraction of externally mixed soot particles decreased with distance to the I-710, a result of atmospheric processes such as vapor adsorption and condensation as well as particle coagulation as the aerosols move away from the freeway.

5.2 INTRODUCTION

Numerous epidemiological and toxicological studies have found associations between particulate matter (PM) mass and adverse health outcomes, including increased morbidity, mortality, asthma, lung cancer, and other impairments in susceptible populations (Dockery et al., 1993; Pope et al., 1995; Peters et al., 1997; NRC, 2004). Prevailing scientific opinion asserts that PM mass may be only a surrogate measure of other physical or chemical properties of PM that are the actual cause of the observed health outcomes (NRC, 2004). Because of their increased number and surface area as well as high pulmonary deposition efficiency, ultrafine particles (defined as those with physical diameters smaller than 100-150 nm) are particularly important in atmospheric chemistry and environmental health. These particles can carry large amounts of adsorbed or condensed toxic air pollutants (oxidant gases, organic compounds, and transition metals) many of which have been identified as having pro-inflammatory effects (Xia et al., 2004; Li et al., 2003). Experimental data show that, compared to larger particles, ultrafine particles are capable of avoiding phagocytosis by alveolar macrophages and gain entry to pulmonary interstitial sites, including vascular endothelium (Oberdörster 2001). These particles may thus induce pulmonary inflammation and enter circulation to reach other target organs, including the cardiovascular system (Nemmar et al. 2002, 2004; Oberdörster 2001; Oberdörster et al. 2002; Nel, 2005).

In Los Angeles, the principal source of ultrafine particulate matter near roadways is vehicular traffic (Schauer et al., 1996). Numerous studies have been conducted to characterize the properties of exhaust particulate emissions from light-duty gasoline

vehicles (LGV) and heavy-duty diesel vehicles (HDDV) (e.g. Morawska et al. 2005; Geller et al., 2005; Tobias et al., 2001; Sakurai et al., 2003a; b; Wehner et al., 2004). HDDV particulate exhaust number and mass emission rates are higher per vehicle mile than from LGVs. Typical LGVs have one to two orders of magnitude lower PM emission rates than HDDVs (Schauer et al., 2002; Kittelson et al., 2001), although differences in traffic volume can mitigate the impact of HDDVs on ambient aerosol concentrations. Studies conducted in dynamometer facilities have shown that particles emitted from diesel vehicles are externally mixed, i.e. different particles of the same size can have different chemical compositions. Depending on vehicle type, age and ambient conditions, a substantial fraction of ultrafine particles emitted by vehicles may consist of semi-volatile material (Sakurai et al., 2003a; b; Kittelson et al., 2004b). These particles are formed from vapor-to-particle condensation processes of super-saturated organic vapors and sulfates, which result from exhaust cooling in or near the tailpipe. These particles typically fall within the sub-50 nm in mobility diameter range, and are known as the “nucleation” mode of the vehicle exhaust. Both LGV and HDDV emit nuclei mode PM (Ristovski et al., 1998; Charron and Harrison, 2003; Kittelson et al., 2004a; Morawska et al., 1998a; b; Tobias et al., 2001). In addition, HDDVs produce larger soot agglomerates (in the 50-200 nm mobility diameter range), which constitute the bulk of PM mass and consist typically of particles with an elemental carbon core and low vapor pressure hydrocarbons and sulfur compounds adsorbed on their surface (Burtcher, 2005).

Particle volatility is an important property of PM emitted from vehicles. For example, their volatility may explain the more rapid decay in their concentration with respect to distance from a roadway, compared to that of non-labile PM species (such as elemental carbon) or gaseous co-pollutants such as CO and NO_x, the concentration decrease of which is affected mostly by atmospheric dilution (Zhu et al., 2002a; b). The increased dilution with distance to roadway decreases the concentration of vapors in equilibrium with these particles, thereby enhancing evaporation of these labile species from the particle surface to re-establish equilibrium (Zhang et al, 2004). Semivolatile organics may also undergo rapid evaporation from smaller particles and re-condensation onto larger particles within the ultrafine range as they move away from the roadway, thus causing substantial changes in particle size and chemical composition with distance to the freeway (Zhang et al., 2004). Moreover, recent studies report increases in the emission rates of semi-volatile particles due to unintended enhanced nucleation occurring downstream of after treatment devices, which remove more effectively the accumulation PM mode of the exhaust (Sakurai et al., 2003; Vaaraslahti et al., 2004). Higher concentrations of the accumulation PM offer a large surface area for adsorption of condensable volatile compounds, a process that counteracts the formation of smaller particles by nucleation. The reduction of the available PM surface for adsorption of the semivolatile material thus favors formation of the semi-volatile nucleation mode particles.

Particle volatility may also be important in the context of exposure and health effects attributable to PM. As shown in recent studies in Southern California (Zhu et al., 2005),

semi-volatile PM decrease in size or completely evaporate as outdoor aerosols penetrate indoors. The decrease in size and-or partition between the aerosol-gas phases of these particles affect their respiratory deposition rate as well as the area in which they deposit in the lung. Since particle volatility is an indication of particle composition and/or solubility, it is important to study the volatility of ultrafine particles next to freeways affected mostly by LGVs or HDDVs.

Several groups have studied particle volatility by making use of a tandem differential mobility analyzer (TDMA) configuration, in which particle volatility is measured by selecting a fairly monodisperse aerosol by the first DMA, heating it to a selected temperature and measuring the resulting size distribution of the heated aerosol by means of the second DMA (e.g. Sakurai et al., 2003a; Orsini et al., 1999). Aerosol size distributions and volatility were also measured in previous studies undertaken by the Southern California Particle Center (Kuhn et al, 2005a and 2005b) in the proximity of a pure gasoline freeway (CA 110 freeway). In the present study, which is a continuation of our previous work on PM volatility, we report PM characteristics and volatility in the vicinity of the I-710, the largest HDDV freeway (both in total number as well as percent of diesel vehicles) in the state of California, and compare them to those measured in the vicinity of the pure LGV freeway. The differences between wintertime observations at I-710 and CA-110 are emphasized to explore the impact of HDDV traffic, which is expected to increase in the future, on aerosol behavior and evolution adjacent to freeways.

5.3 EXPERIMENTAL METHODS

5.3.1 Sampling site

The experiments were carried out adjacent to the I-710 freeway, approximately 400 m north of the Imperial Highway (Figure 5.1) in South Gate, CA. The I-710 has four north and four south bound lanes separated by a median and runs parallel or over the Los Angeles River in this area.

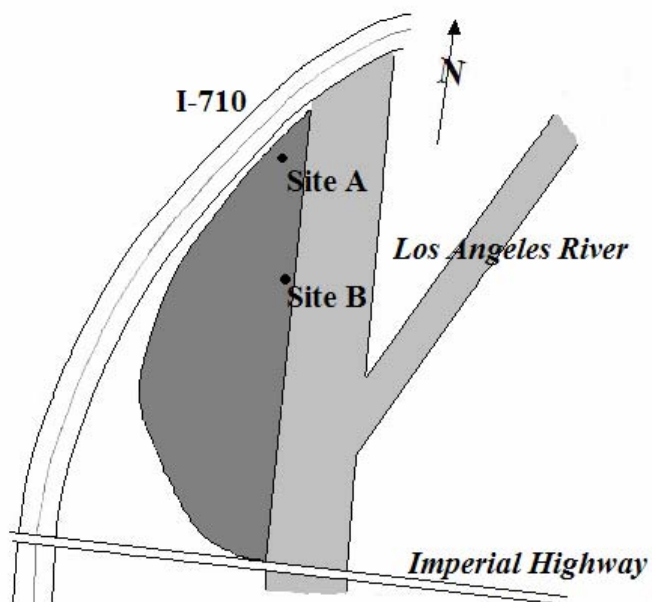


Figure 5.1 Sampling sites in the proximity of the I-710 freeway

The volatility study was conducted from February 6 through March 7, 2006. Each day a maximum of three sets of particle volatility measurements (described below) were performed between 12:00 to 19:00 to match the sampling periods used in the earlier CA-110 gasoline freeway studies (Kuhn et al., 2005b,c). Sampling was carried out at two

sites – A and B (Figure 1). Site (A) was within 10 m of the freeway shoulder. The proximity of I-710 and the prevailing wind direction over the freeway (SSW/SW, details below) suggest that I-710-associated vehicular emissions should dominate aerosol sampling at site A. After observing freshly emitted aerosols at site A, the sampling equipment was transferred to site B, approximately 150 m downwind of the freeway on a bike path parallel to the Los Angeles River, to sample a more atmospherically “aged” aerosol. This site was thus considered representative of the urban background, and its location-distance with respect to the freeway was based on the work of Zhu et al (2002b). They showed that at roughly 100-150 m downwind a freeway the aerosol characteristics become virtually indistinguishable from those of the urban background.

5.3.2 Ambient conditions

A weather station was located at site A throughout this study (Monitor II weather station, Davis Instrument Corporation, Hayward, CA). Data were primarily logged at one-minute intervals, and hourly average data are reported here (Table 1). Following sunset (17:30 at the start of the study), ambient temperatures dropped rapidly to 14 – 16°C. At site A, the relative humidity (RH) was reasonably constant (33–43%). A higher mean (35-50% in daylight) and more variable RH values were observed at site B. Following sunset a sharp increase in RH to more than 60% on average was observed. Wind speed and direction were both very consistent (Table 5.1) during the study. The average wind speeds were 1.3 m s⁻¹ (site A) and 2.4 m s⁻¹ (site B) which decreased following sunset. At the I-710, the wind during the sampling periods was predominantly from the SSW direction and shifted towards SW as the day progressed. Site B was directly downwind from the I-710.

Table 5.1 Meteorological information at the I-710 freeway^a

Time (PST)	Temperature (°C)		Relative Humidity (%)		Wind speed (m s⁻¹)		Wind direction (deg)	
	Site A	Site B	Site A	Site B	Site A	Site B	Site A	Site B
Day – early afternoon (12:00–16:00)	23.7±5.0	21.4±1.6	32±13	39±14	2.1±0.9	2.9±0.9	212±35	208±23
Day – late afternoon (16:00–18:00)	18.4±4.0	17.4±2.7	42±20	49±17	1.2±0.8	2.7±0.4	242±36	231±9
Evening (18:00–19:00)	16.2±3.4	13.7±1.3	36±20	69±12	0.6±0.3	1.7±0.7	237±49	229±2

^amean value ± one standard deviation

5.3.3 Traffic data

Traffic data, including volume and mean speed, for both the north and south lanes of the I-710 at South Gate, CA were provided in 15 minute intervals by the California Department of Transportation and were converted to hourly intervals (Table 5.2). On average the vehicle volume was approximately 10,000 – 11,000 vehicles hour⁻¹ with a slight increase observed during the late afternoon commute (16:00 – 18:00). Zhu et al. (2004) reported a similar traffic density during their study at the I-710 freeway. To distinguish between LGVs and HDDVs, we used a video recorder to monitor traffic for a total of 15 hours over multiple days during the field campaign.

The mean HDDV traffic fraction derived from the video record was 17 – 18% on average, which is ~ 25 – 30% lower than that previously reported for the I-710 (23 – 25%, Zhu et al., 2004).

Vehicle mean speed varied from 61 – 72 km h⁻¹. Typically speeds were maintained at ca. 69 km h⁻¹ until the onset of the afternoon commute when they decreased to ca. 61 km h⁻¹ on average. The average speed usually recovered by 18:00, although rapid fluctuations in vehicle speed were observed.

Table 5.2 Traffic data^a for the volatility study

Time (PST)	Vehicle speed ^b (km h ⁻¹)	Traffic flowrate ^b (vehicles h ⁻¹)
Day – early afternoon (12:00 – 16:00)	69±9	10361±3086
Day – late afternoon (16:00 – 18:00)	61±7	11224±2930
Evening (18:00 – 19:00)	72±11	10983±2848

^a combining I-710 N and S data for the 12 study days

^b mean value ± 95% confidence level

5.3.4 Volatility measurement setup and sampling

We used a same Tandem Differential Mobility Analyzer (TDMA) to measure particle volatility (schematic shown in Figure 3.3). The method was first developed by Rader and McMurry (1986). An extensive discussion of the physical design and sampling technique has been previously provided (Kuhn et al., 2005a,b,c). Experiments were performed in our mobile laboratory using copper tubing (0.64 cm in diameter, 3 m long) as the aerosol inlet. Elaborate set-up for TDMA is reported in section 3.3.3.

5.3.5 Aerosol carbon measurements

Two on-line instruments were used to measure the carbon content of the aerosol at site A. “Black” carbon (BC) – a surrogate for elemental carbon (EC) – was measured

continuously at a flow rate of 2 lpm using 3 minute sampling periods by a two-channel Aethalometer (model AE-21, Thermo-Andersen, Smyrna, GA) and averaged hourly for the study sampling period. Organic carbon (OC) in four volatility fractions and EC data were measured on hourly basis using a semi-continuous OC/EC monitor (model 3F, Sunset Laboratory, Inc, Portland, OR) following the method presented by Arhami et al. (2006).

The four OC fractions provided by the instrument were combined and reported as light organic carbon (LOC), which is distinguished by heating the sample at 310°C and as heavy organic carbon (HOC), which is equivalent to the sum of organic carbon above 310°C.

5.4. RESULTS AND DISCUSSION

5.4.1 Ambient size distributions

Typical daily-average early and late afternoon, and evening ambient size distributions, measured at both sites, are shown in Figure 5.2. The late afternoon distribution peaks at ca. 19 nm (Figure 5.2a) adjacent to the freeway. The total measured CPC particle concentration is approximately 55,000 cm⁻³ on average during the afternoon and concentrations increase as the afternoon progresses. In the evening, the total concentration increased on average by 75% compared to the overall afternoon value to 96,000 cm⁻³, and the mean size decreased with the highest values observed in the sub-20nm particle range. Particle concentrations in the accumulation mode (i.e. 450nm) increase somewhat throughout the day, but the large change in mean concentration is

driven by nucleation mode particles. By contrast, the shape of the size distributions at site B (Figure 5.2b) does not significantly change between the afternoon and evening profiles and the main number concentration mode is always found for particle sizes >10 nm. The afternoon profiles are essentially the same given the variability in the data. However, the total particle concentration increased into the evening ($82,000 \text{ cm}^{-3}$) from the average for the afternoon ($48,000 \text{ cm}^{-3}$).

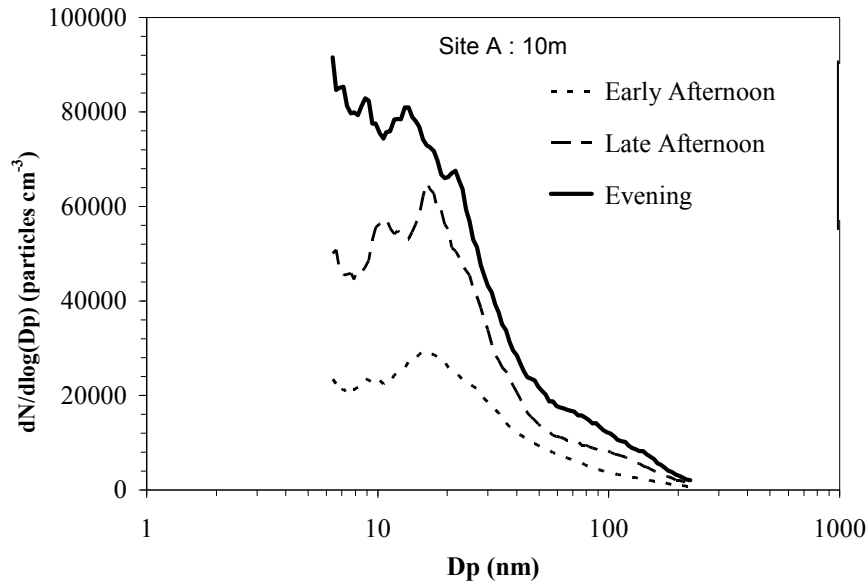


Figure 5.2

Figure 5.2 (continued)

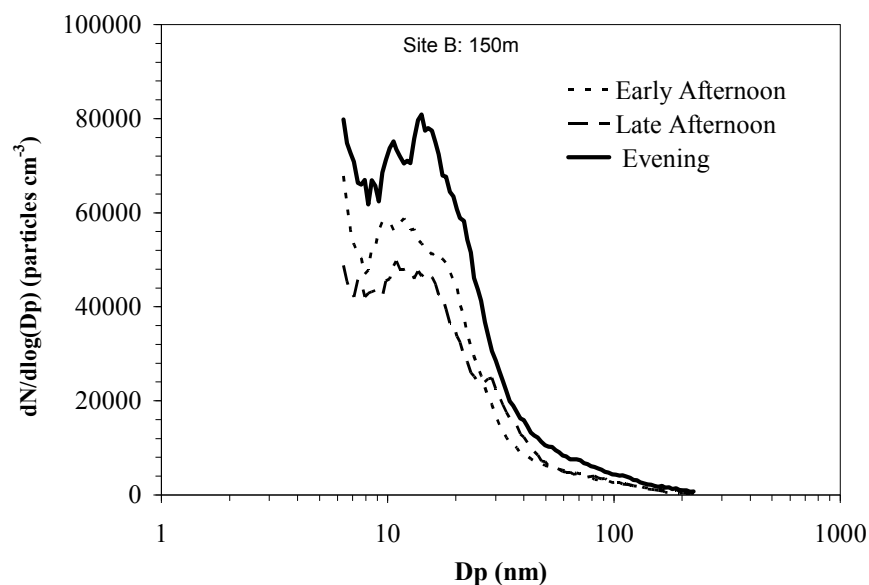


Figure 5.2 Typical ambient size distributions at each site for afternoon (dashed) and evening (solid line) (a) site A, and (b) site B.

These results suggest the influence of enhanced condensation of mostly organic vapors, also generated by vehicles, at decreased temperatures in the evening hours and with increasing distance from the freeway, causing particle growth across the observed range. During our earlier study at the CA-110 freeway, a decrease of 9 °C on average between day and evening observations resulted in sharply higher total number concentrations (66,000 and 108,000 cm^{-3} , respectively, 2.5m from the freeway). (Kuhn et al., 2005c). High particle concentrations >20 nm in diameter were observed both before and after sunset, but the near-freeway site was closer to vehicular traffic at the CA-110 than during this study (~ 10 m away). The influence of the increased proximity to the freeway and the lower wind speeds ($0.5 \pm 0.5 \text{ ms}^{-1}$) for the CA-110 study appear to offset the contribution

of particle emissions from HDDV next to I-710, probably due to different dilution ratios at the two sites (Ntziachristos et al., 2006). However, it is important to mention that in both winter freeway studies, the particle size distribution shifts to larger particle sizes as we move downwind of the freeway, most likely due to the effects of particle growth by means of condensation and/or adsorption of organic vapors onto the particle surface, as well as possible loss of smaller particles due to coagulation and curvature enhanced evaporation of volatile species.

5.4.2 Particle volatility

5.4.2.1 Evaporation profiles

Representative particle number distributions showing ambient and thermally treated particles at 60°C and 110°C are shown in Figure 5.3 for both afternoon and evening sampling periods at site A and initial particle sizes of 40 and 120 nm. All size distributions are normalized over the peak concentration of the monodisperse ambient aerosol. In general, the size distribution changes from a narrow, quasi-monodisperse distribution at ambient temperature to a broader distribution with one or more modes as the temperature increases. In the afternoon samples, the initial mode diameter does not shrink considerably at 60°C, but two distinct particle modes become evident at 110°C – the “non volatile” or refractory mode, with little diameter change over the ambient, and the “mostly volatile” mode with the larger diameter difference (Figures 5.3a, 5.3c). The bimodal distributions at the higher temperature suggest that ambient aerosols next to the I-710 freeway are externally mixed, that is both volatile and non volatile particles may exist at the same size range. In the evening samples, heating to 60°C considerably

changes the mean size of most of the aerosol and heating to 110°C leaves only a small portion of nonvolatile particles (Figure 5.3b). Particles in the size range 40-120 nm thus become more volatile and more internally mixed in the evening than in the afternoon. This is an indication of stronger particle growth due to enhanced vapor-to-particle condensation in the evening, which can be explained by the lower temperature coupled with the higher humidity and stagnant conditions discussed earlier. This is consistent with the growth of mean particle size discussed in Figure 5.2.

Twenty nanometer particles (not shown in Figure 5.3) did not demonstrate any bimodal distribution when heated. In principle, most of the 20 nm particles shrunk below the lower cut-off size of the SMPS (ca. 7 nm) while the remaining ones exhibited a single mode with a peak at ~10 nm. This shows that few nonvolatile species are present in this size range, and that these particles are almost exclusively internally mixed.

During the winter CA-110 freeway volatility study (Kuhn et al., 2005c), investigations of 20 and 40 nm particles discerned no/little evidence for external mixing, although a small nonvolatile fraction was detected for some initially 40 nm particles. The presence of HDDVs at the I-710 freeway thus increases the non-volatile fraction and the degree of external mixing at smaller sizes (e.g. 40 nm) than at the CA-110. The evening/afternoon volatility pattern at the I-710 and CA-110 freeways are similar with a larger volatile fraction after sunset compared to the afternoon (Figures 5.3a, 5.3c).

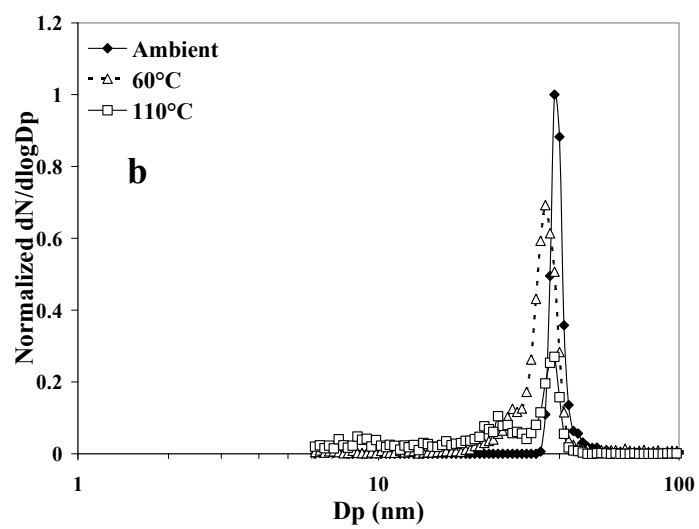
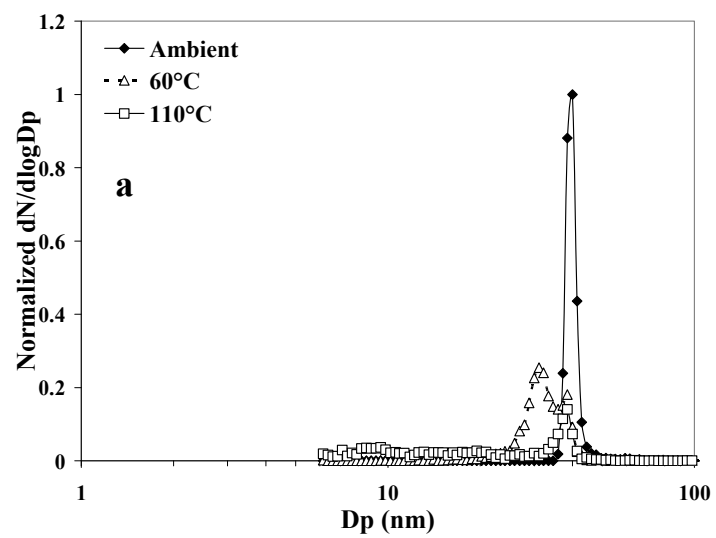


Figure 5.3

Figure 5.3 (Continued)

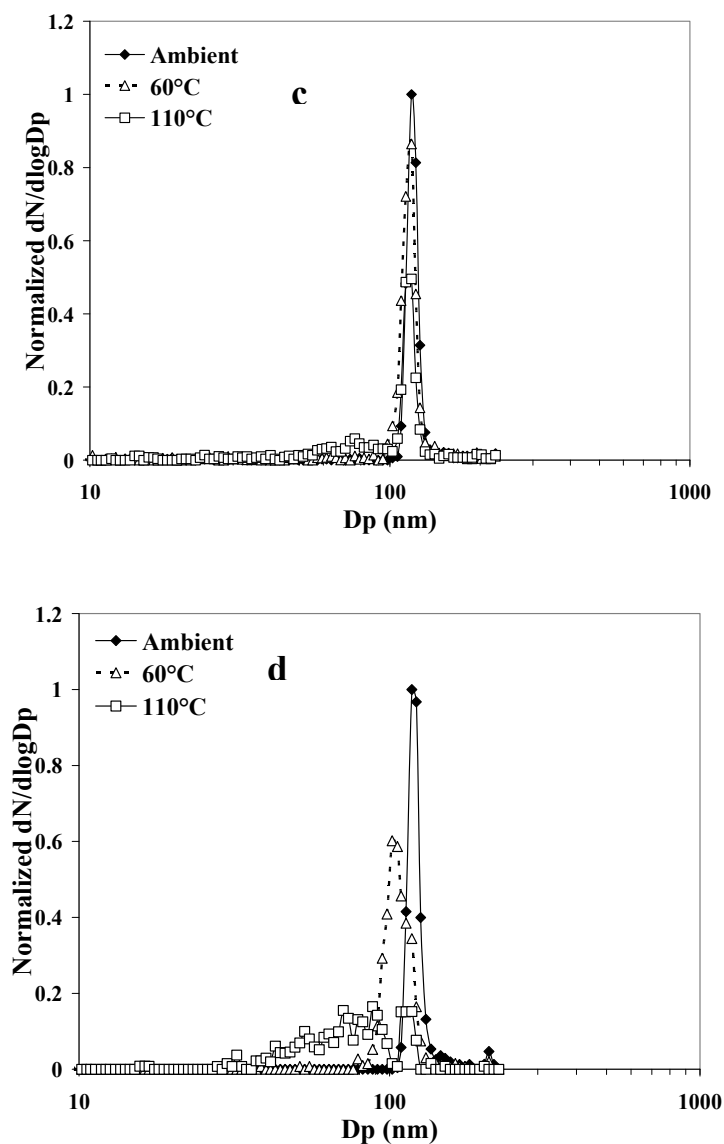


Figure 5.3 Aerosol size distribution change in response to heating at site A (a) 40 nm, afternoon, (b) 40 nm, evening, (c) 120 nm, afternoon, and (d) 120 nm, evening

5.4.2.2 Mode changes

Changes in the mode diameter (Δd_m) as a function of temperature and time of day are also useful for interpreting the diurnal changes in volatility. These values are shown in

Table 5.3 and correspond to the average mode change obtained from all evaporation profiles, such as those shown in Figure 5.3. For comparison, mean Δd_m values from the CA-110 freeway (Kuhn et al., 2005c) for both the afternoon and evening samples are also shown in Table 5.3. Data from the extended temperature range (60 to 150°C) experiments are included only for 80 and 120 nm particles as most of the smaller particles completely volatilize above 110°C. In general, the mode decrease is larger in the evening than the daytime for the I-710 freeway, similar to the winter results at the CA-110 freeway. For example, 120 nm particles exhibit a change in diameter of 30 nm at 110 °C in the evening compared to a non-detectable change during the day. The daytime 120nm particles are almost entirely non-volatile, with only a slight change in size ($\Delta d_m = 5$ nm) at 150 °C.

In absolute levels, particle mode changes are greater for the pure gasoline vehicle freeway, compared to the I-710 freeway for most particle sizes. Only the 20 nm particles exhibit identical size changes during the day at both freeways. In a study at the I-405 freeway, 12.8, 17 and 27.7 nm smaller diameters were reported for initial particle diameters of 27, 45 and 90 nm, respectively (Kuhn et al., 2005a). These results suggest that ultrafine particles at that freeway displayed intermediate volatility between this I-710 and the CA-110 freeway studies, which is consistent with the intermediate HDDV fraction at the I-405 (5–7%) compared to the CA-110 (0%) and the I-710 (17-18%). These results suggest that an inverse relationship may exist between ultrafine particle

volatility and the HDDV fraction of vehicular traffic. Our observations are also consistent with HDDV dynamometer studies, showing that the diesel exhaust aerosol is less volatile than that observed at the I-710 (Kwon et al., 2003; Shi et al., 2000).

Table 5.3 Particle diameter mode decrease as a function of temperature and time of day adjacent to the I-710 and CA-110^a freeways

		Particle diameter	Temperature				
Site A			60°C	85°C	110°C	130°C	150°C
I-710	Afternoon	20 nm	-2.9	-10.3	-9.7	-	-
	Evening		-2.0	-	-12.9	-	-
CA-110	Afternoon		-2.3	-	-9.3	-	-
	Evening		-5.4	-	-	-	-
I-710	Afternoon	40 nm	-5.5	-8.5	-13.1	-	-
	Evening		-8.9	-	-	-	-
CA-110	Afternoon		-8.9	-	-21.0	-	-
	Evening		-12.0	-	-21.0	-	-
I-710	Afternoon	80 nm	-3.6	-2.7	-12.2	-40.6	-41.9
	Evening		-	-	-	-	-
CA-110	Afternoon		-11.0	-	-39.0	-	-
	Evening		-	-	-	-	-
I-710	Afternoon	120 nm	0.0	0.0	0.0	0.0	-5.0
	Evening		-16.0	-	-29.8	-	-
CA-110	Afternoon		-6.3	-	-43.0	-65.0	-72.0
	Evening		-10.0	-	-54.0	-	-

^a CA-110 data from Kuhn et al. (2005c)

5.4.2.3 Volatility ratios of different particle sizes

To quantify these observations further and to facilitate comparison to earlier studies, a series of dimensionless ratios, previously developed and defined by Kuhn et al. (2005a; b; c), were calculated. These ratios express different aspects of the particle volatility as a function of changes in the observed particle number and volume. The notation used and the mathematical formulas defining these terms are explained in Table 3.3. The ratios Φ_N and Φ_V correspond to the fraction of the particles, by number and volume, respectively, remaining after heating to a defined temperature (110°C). These ratios consist of two

sub-components: the non-volatile (Φ_{Nn} , Φ_{Vn}) fraction which corresponds to particles not appreciably changing size upon heating, and the mostly volatile (Φ_{Nm} , Φ_{Vm}) fraction which represents particles not completely vaporized but decreased in size after heating. The volatility ratios for the I-710 winter study are shown by sampling location in Table 5. In order to explore the diurnal variability in volatility, the data for site A are separated into three time periods: early afternoon (12:00 – 16:00); late afternoon (16:00 – 18:00) and evening (18:00 – 19:00). The late afternoon time period also includes the afternoon rush hour.

The number concentration ratios (Φ_N) indicate that while most (>85% at Site A) of the 80-120 nm particles are conserved at 110°C, the smaller 20 and 40 nm particles experienced significant number loss (58 and 23% respectively at site A) due to complete volatilization. The 20 nm particles yielded the lowest values for Φ_N (0.08 – 0.57) and Φ_V (0.02-0.17), consistent with their higher observed volatility compared to the larger particles. Particles measured in the late afternoon exhibit lower volatility and higher nonvolatile fraction ratios (Φ_{Nn} , Φ_{Vn}) than during all other time periods. The mostly volatile fractions (Φ_{Nm} , Φ_{Vm}) are, however, variable throughout the day. While the 20 and 40 nm particles lost a significant fraction (57-80% by number, 75-80% by volume) of their mostly volatile component during the evening period, the 120 nm particles, by contrast, showed an increase after sunset.

Freshly emitted (site A) and downwind (site B) particle ratios exhibit key similarities and differences as a function of particle size (Figure 5.4). 20 nm particles consist of almost

entirely volatile material at both sites. Larger particles are substantially less volatile closer to the freeway than at the downwind site. The aerosol in site A is enhanced in externally mixed soot particles, as a result of the emissions of the nearby HDDV.

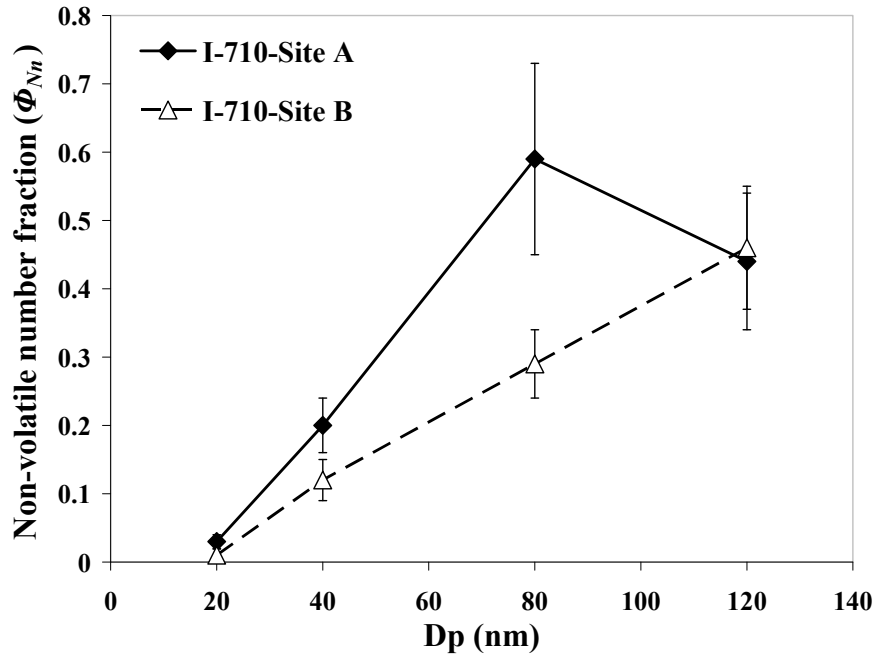


Figure 5.4 Non-volatile number fraction at site A and site B.

The non-volatile fraction peaks around 80 nm particles, which is in good agreement with the recent findings of Rose et al. (2006) who also showed a peak of the non volatile aerosol fraction in an urban street canyon, affected by HDDV traffic, at 80 nm in mobility diameter. Although results in Figure 4 do not include evening measurements of 80 nm particles, which might increase the mean volatility (see Table 5), this size range also exhibited the highest non-volatile fraction of all particle sizes in late afternoon measurements. Additionally, dynamometer studies (Harris and Maricq, 2001; Thompson et al., 2004) have shown that soot aerosol emissions peak at ~80 nm. This is an indication that aerosols in this size range consist of a high diesel soot fraction. By comparison, the

particle size distribution of the non volatile fraction at Site B increases monotonically with increasing size, following the profile of previously published results in urban background areas (Kuhn et al., 2005a; Orsini et al., 1999; Philippin et al., 2004), or at sites in the vicinity of exclusively LGV traffic (Kuhn et al., 2005b), which are discussed in the following paragraph. As the mostly externally mixed particles emitted by HDDV move away from the freeway, they are subjected to transformation processes in the atmosphere, such as condensation-adsorption of organic vapors and heterogeneous coagulation with other particles, and as result they become internally mixed with semi-volatile material.

A series of volume ratio comparisons further illustrates the overall volatility differences between the I-710 and CA-110 winter studies (Figure 5.5). Particles in the size range 40–120 nm experience smaller volume loss next to the I-710 freeway (Φ_V range = 0.27–0.56), compared to the CA-110, Φ_V range = 0.11–0.43), when heated at 110 °C. In addition, the refractory non-volatile volume fraction (Φ_{Vn}) exhibits similar behavior to that of Φ_V . To emphasize the importance of overall particle volatility, $1-\Phi_{Vn}$ is shown in Figure 5.5b. The consistent offset in non-volatile fraction ratio between the two freeways for particles >40nm is most likely due to the influence of HDDV exhaust soot particles, as previously discussed. The non-volatile fraction increased with size and the highest value is at 80nm particles ($\Phi_{Vn} = 56\%$) at the I-710 freeway. The mostly-volatile fraction (Φ_{Vm}) data (Figure 5.5c) shows that although the HDDV and LGV freeway particles exhibit similar trends, HDDVs seem to have more mostly-volatile material present in all size ranges (except 80nm). Differences in chemical composition of the exhaust between the two

freeways and, critically, the gas-to-particle phase partitioning behavior of the more volatile species may contribute to these observations (Phuleria et al., 2006; Miguel et al., 1998; Shrivastava et al., 2006; Tobias et al., 2001). A slight, but still important difference appears even for 20nm particles between the two freeways. The volume of 20nm particles not evaporating at 110 °C next to the I-710 is only 10% but still almost twice as much as that next to the CA-110 freeway (Figure 5.5a). This difference mainly comes from mostly-volatile particles because the non-volatile fraction at 20nm is negligible in both cases (Figure 5.5b). This would mean that a small, but still measurable, fraction of nanometer scale particles next to a HDDV freeway may persist even at high temperatures. Dynamometer studies of diesel exhaust aerosol (e.g. Ntziachristos et al., 2004) have also shown that small but non-zero concentrations of sub-20nm particles can be measured downstream of a thermodenuder operating at 250 °C, a result that supports the findings of our study.

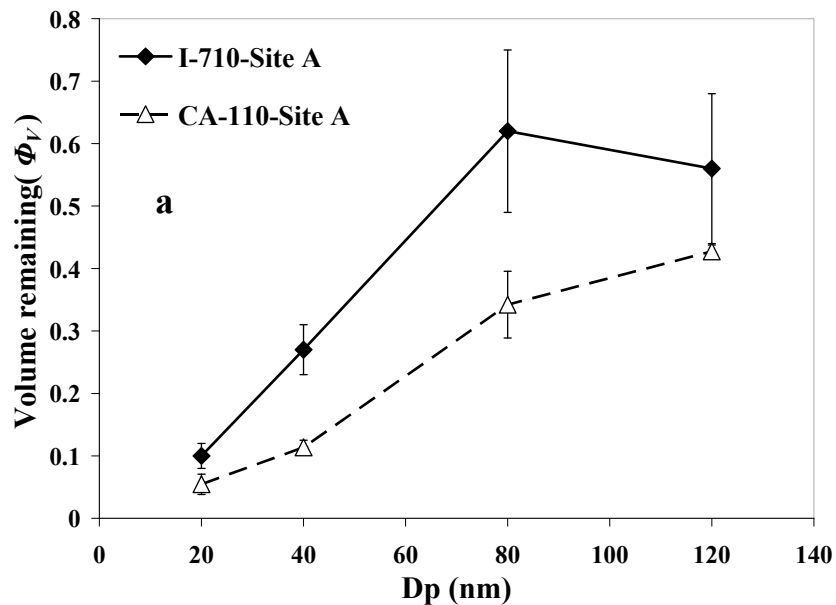


Figure 5.5

Figure 5.5 (Continued)

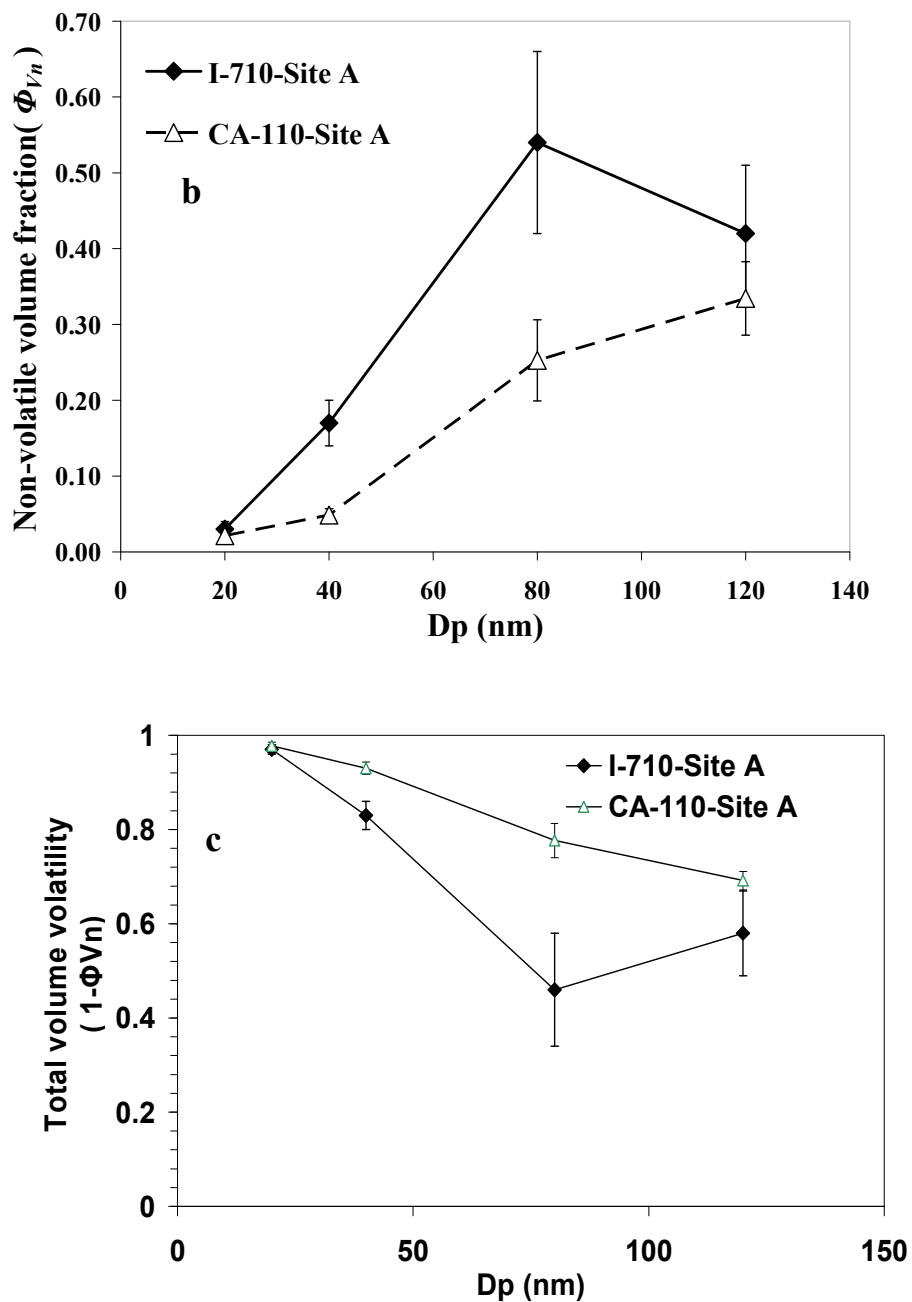


Figure 5.5 Particle volatility ratios next to the I-710 and CA-110 freeways: (a) volume ratio of particles remaining at 110 1C, Φ_V , (b) total volatile volume fraction, $1 - \Phi_{Vn}$, and (c) mostly-volatile volume fraction, Φ_{Vm} .

5.4.2.4 Dependence of volatility ratios on carbon speciation

Some useful insight into explaining the diurnal variance of volatility is gained by comparing the observed changes in particle properties with concurrent measurements of particulate-phase carbon species. Selected PM_{2.5} aerosol carbon – EC, BC, LOC, HOC concentrations and the particle non-volatile (Φ_{Vn} : 20, 40, 80, 120 nm) and mostly volatile volume fraction (Φ_{Vn} : 120 nm only) are shown in Figure 5.6 by time period. The EC and BC concentrations are very similar to each other and start at ca. 4 $\mu\text{gC m}^{-3}$ in the early afternoon, increasing to about 5.5 $\mu\text{gC m}^{-3}$ and decreasing to 3.5 $\mu\text{gC m}^{-3}$ in the evening. The increase in EC and BC in the late afternoon is probably due to the decrease in mean traffic speed during the rush hour and the increase in the frequency of transient vehicle operation under these conditions (Geller et al., 2006).

The non-volatile fractions, especially for 80 and 120nm particles, follow the same trends to the EC and BC concentrations and peak in the late afternoon samples. This can be interpreted as primary EC/BC exhaust particles being the most significant source of PM in that size range. Rose et al. (2006) found a similar diurnal profile for 80 nm particles near a busy street with soot particles (non-volatiles) increasing by 60% at the start of rush hour (17:00) and decreasing later on during the evening. LOC slightly decreased (14%) over the course of the day, while HOC gradually (38%) after sunset. Although the TDMA observations cannot distinguish specifically between HOC and EC/BC, the mostly volatile fraction of 120 nm particles and HOC are both found to peak in the evening. Ntziachristos et al. (2006) also found that the volume of the accumulation mode (>40 nm) next to the I-710 freeway is correlated with the HOC species concentration. Both these

observations are good indications that the mostly volatile fraction in this size range largely consists of HOC. The increase in volatility after sunset may be more an effect of ambient conditions, as discussed earlier, rather than changes in the EC, BC and/or HOC concentrations.

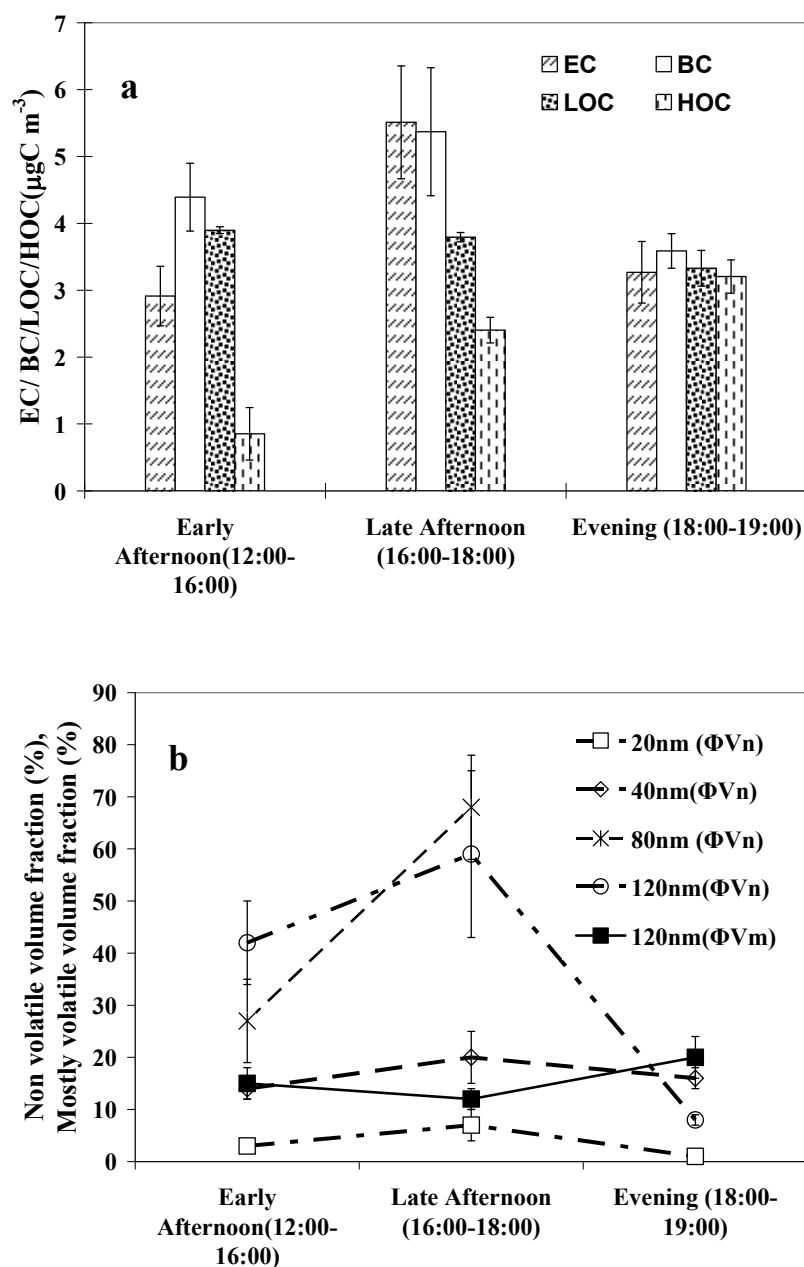


Figure 5.6 (a) Concentration of elemental carbon, black carbon and organic carbon species, and (b) particle volatility ratios at site A, for different hours during day

Although the TDMA observations cannot distinguish specifically between HOC and EC/BC, the mostly volatile fraction of 120 nm particles and HOC are both found to peak in the evening. Ntziachristos et al. (2006) also found that the volume of the accumulation mode (>40 nm) next to the I-710 freeway is correlated with the HOC species concentration. Both these observations are good indications that the mostly volatile fraction in this size range largely consists of HOC. The increase in volatility after sunset may be more an effect of ambient conditions, as discussed earlier, rather than changes in the EC, BC and/or HOC concentrations.

5.5. SUMMARY AND CONCLUSIONS

Particle volatility was studied next to a freeway with 17-18% heavy duty diesel traffic. The campaign took place in February-March 2006 between 12:00 – 19:00. Measurements were conducted using a TDMA with intermediate heating, sampling particles next to the freeway and 150 m downwind of the freeway. The volatility of four different particle sizes was determined (20, 40, 80, 120 nm) by heating the particles at 110°C downstream of the first DMA, before they are sampled by the downstream SMPS. In addition to the total number and volume fractions which remained after heating, particle volatility was expressed with two other ratios: the “non-volatile” particle ratio, which corresponds to particles that did not significantly change size after heating and the “mostly-volatile” ratio, which corresponds to particles that changed size after heating. An externally mixed aerosol, i.e consisting of particles with different composition, will result in high non-volatile and mostly-volatile ratios upon heating, as opposed to an internally mixed

aerosol which consists of particles with the same composition. Particles next to the diesel freeway were mostly externally mixed. The non-volatile fraction generally increased with particle size, while the mostly-volatile fraction did not significantly vary as a function of particle size, but peaked at 14% by volume for 120 nm particles. Total volatility decreased with increasing particle size, starting from 58% by number at 20 nm down to 11% at 120 nm. The decrease of particle volatility and increase in the non-volatile fraction as particle size increases is an effect of diesel soot emissions, which are mainly emitted in the range above 40 nm.

Particle volatility measured next to the diesel freeway was lower in all particle sizes than next to a pure gasoline freeway (Kuhn et al., 2005b; c) under similar meteorological conditions. Both the non-volatile and the mostly-volatile fractions were up to 50% higher in the diesel freeway, indicating that a more externally mixed aerosol in that environment. The difference was also evident for particles as small as 20 nm, with the diesel freeway particles exhibiting twice as much mostly-volatile content, compared to the gasoline freeway.

Particle volatility changed during the day, with the highest non-volatile content of PM observed during the afternoon rush hour (16:00 – 18:00). The non-volatile content peaked at 80 nm particles, which coincide with the peak soot mode concentration, as measured in dynamometer studies. In addition, the non-volatile content was found to correlate with the black and elemental carbon concentrations, which also peaked during the rush hour due to the transient vehicle operation. In the evening, particles became more volatile in

all size ranges, probably due to enhanced condensational growth by absorption of organics as the temperature drops. In particular, the mostly-volatile content of 120 nm particles peaked in the evening when the concentration of heavy organic carbon peaked as well. This shows that a significant fraction of the particle mass at this size range may be associated with condensed heavy organic species.

Finally, the comparison of volatility next to the freeway and 150 m downwind of the freeway showed that particles become more internally mixed as they move away from the freeway, as an effect of coagulation and organic vapor condensation. This effect is more important as particle size decreases.

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Chapter 6:

Physical Properties of Particulate Matter (PM) from Newer Heavy Duty Diesel Vehicles Operating with Advanced PM and NO_x Emission Control Technologies

6.1 ABSTRACT

Emission control technologies designed to meet the 2007 and 2010 emission standards for heavy-duty diesel vehicles (HDDV) remove effectively the non-volatile fraction of particles, but are comparatively less efficient at controlling the semi-volatile components. A collaborative study between the California Air Resources Board (CARB) and the University of Southern California was initiated to investigate the physicochemical and toxicological characteristic of the semi-volatile and non-volatile PM fractions from HDDV emissions. This paper reports the physical properties, including size distribution, volatility (in terms of number and mass), surface, agglomeration and density of particles emitted from HDDV retrofitted with advanced emission control devices. Four vehicles in combination with six aftertreatment devices (V-SCRT[®], Z-SCRT[®], CRT[®], DPX, Hybrid-CCRT[®], EPF) were tested under three driving cycles: steady state (cruise), transient (urban dynamometer driving schedule, UDDS) and idle. A HDDV without any control device served as the baseline vehicle. Substantial reduction of PM mass emissions (>90%) was accomplished for the HDDV operating with advanced emission control technologies. This reduction was not observed for particle number concentrations under cruise conditions, with the exceptions of the Hybrid-CCRT[®] and EPF vehicles, which were efficient in controlling both - mass and number emissions. In general, significant nucleation mode particles (<50nm) were formed during cruise cycles in comparison with the UDDS cycles, which emit higher PM mass in the accumulation mode. The nucleation

mode particles (<50nm) were mainly internally mixed, and evaporated considerably between 150 to 230°C. Compared to the baseline vehicle, particles from vehicles with some control technology (except of the Hybrid-CCRT®) had a higher mass specific surface area and were compact in nature (density > 1 g cm⁻³). The baseline vehicle produced lower density (0.34-0.44 g cm⁻³) particles.

6.2 INTRODUCTION

Recent *in vitro* and *in vivo* animal studies suggest that ultrafine particles may be more toxic than both PM_{2.5} and PM₁₀ (Li et al., 2003; Oberdörster, 2000). The most prominent sources of ultrafine particles in an urban metropolis like Los Angeles are vehicular emissions and secondary photochemical reactions (Fine et al., 2004; Zhang et al., 2004). Heavy-duty diesel trucks constitute only a small fraction of the total fleet in California but have an important contribution to the emissions of fine and ultrafine particles. Diesel exhaust particles (DEP) are normally agglomerates of hundreds of volatile/semivolatile species adsorbed onto its refractory carbonaceous core (Bayona et al., 1988). Some of these constituents are known carcinogens (Stayner et al., 1998; Solomon and Balmes, 2003). Also DEP are capable of inducing systemic inflammation by imparting oxidative stress in susceptible cells (Koike et al., 2002; Shima et al., 2006) and are instrumental in causing asthma symptoms and may contribute to cardiopulmonary diseases (McClellan, 1987; Dockery et al., 1993, Nel et al., 2001).

As general perception has emerged towards the potential risks of diesel particulate matter (PM), policy makers are promulgating stricter emission control rules and regulations. The

US EPA 2007 emissions standard reduces the diesel PM mass emission from heavy duty engines ten fold from the old 0.1g/bhp-hr PM limit to 0.01g/bhp-hr (Merrion, 2003). To effectively meet such stringent emission standards, various advanced engine design and control technologies are being considered and rigorously evaluated for the newer fleet of heavy duty trucks. While these aftertreatment devices (such as diesel particulate filters [DPF]) have been highly efficient in removing refractory solid particles (>50nm), some of the potentially harmful volatile and semi volatile species (such as PAHs), originally emitted in the vapor phase at high plume temperature, may penetrate through (Kittelson et al., 2006; Matter et al., 1999a). As the exhaust temperature decreases drastically at the tail pipe exit, these vapor phase species condense and form fresh nucleation mode particles (Kittelson, 1998).

Various on-road as well as dynamometer experiments have shown that these particles are predominantly externally mixed (except particles <20nm). The volatile fraction roughly contributes 10-30% of the total mass and 70-90% of particles by number (Sakurai et al., 2003). Particle volatility is strongly dependent on gas to particle phase partitioning and is extremely sensitive to dilution and temperature conditions (Liu et al., 2007a; Abdul-Khalek et al., 1999; Wei et al., 2001a,b; Kuhn et al., 2005; Biswas et al., 2007). Zhang and Wexler (2004) showed that condensation, evaporation and dilution are the three major factors affecting the evolution of size distribution near a freeway. Thus, particle volatility plays key roles in shaping the particle size spectrum and eventually determining the level of human exposure to different aerosol components (volatile or non-volatile) originating from traffic emissions.

In addition to volatility, particle surface characteristics and morphology are two potentially important physical parameters in determining PM toxicity. Some researchers have argued that particle surface area is a better metric to predict health endpoints than particle mass or number and should be included as an essential element while considering new regulatory tools (Maynard 2006; Oberdörster et al., 2005; Nygaard et al., 2004). This is because the availability of reaction sites to cause cell damage is more likely to be directly proportional to surface area available to lungs (Maynard, 2006). Surface properties will also be relevant in future mobile emission scenarios, as the current control technologies are reported to generate considerable number of small particles (Bagley et al., 1998; Geller et al., 2005) leading to a net increase in surface area per unit mass of PM. Particle density is another important PM property, from which particle morphology or structure can be indirectly inferred (Maricq and Xu; 2004; McMurry et al., 2002). It is also vital in determining particle transport and deposition in human lungs, which eventually lead to differential health effect outcomes. A number of researchers have measured the effective density of diesel particles and quantified their fractal dimensions (Maricq and Xu; 2004; Geller et al. 2006; Park et al., 2004). Typically, DEP effective density decreases with the increase in size and has values ranging from as low as $\sim 0.10 \text{ g/cm}^3$ for agglomerate fractal structures to $\sim 2.0 \text{ g/cm}^3$ for primary elemental carbon spherules (Geller et al., 2006). The primary objective of this collaborative study between the California Air Resources Board (CARB) and the University of Southern California is to estimate physicochemical and toxicological characteristics of the volatile and non-volatile fractions of particles emitted from a variety of different engines, fuels and emissions control, each operating under different driving conditions using a

dynamometer set-up. In this paper we will focus only on the physical PM properties, i.e. size distribution, volatility, surface characteristics and density for diesel vehicles retrofitted with state-of-the-art aftertreatment devices. Comparisons within HD vehicle types and driving cycles and also with respect to a baseline vehicle (without any control technology) will be discussed. Details of PM chemical and toxicological characteristics from these vehicles will follow in subsequent publications.

6.3 METHODS

Experiments were carried out at the California Air Resources Board's (CARB) heavy-duty diesel emission testing laboratory (HDETL) in downtown Los Angeles. Ayala et al (2002) described the dynamometer specifications in details. Figure 1 shows the schematic of the experimental setup. The sampling train includes heavy-duty chassis dynamometer, constant volume sampling (CVS) dilution tunnel and aerosol samplers. Diesel vehicle exhausts were transported by a stainless steel hose pipe and diluted with filtered air through the CVS. Measurements were taken 18 diameter lengths downstream of the exhaust introduction in the CVS. Three driving cycles, i.e. steady state cruise (50mph), transient [EPA urban dynamometer driving schedule (UDDS)] and idle were tested to simulate various real-world driving conditions. The fuel used to run the engines was CARB ultra-low sulfur diesel (ULSD) with sulfur content less than 15 ppm. QA/QC were performed one day per week before the sampling. Tunnel blank levels were measured and vehicles were conditioned (warmed up) everyday before the start of official runs. The CVS was cleaned prior to starting the project.

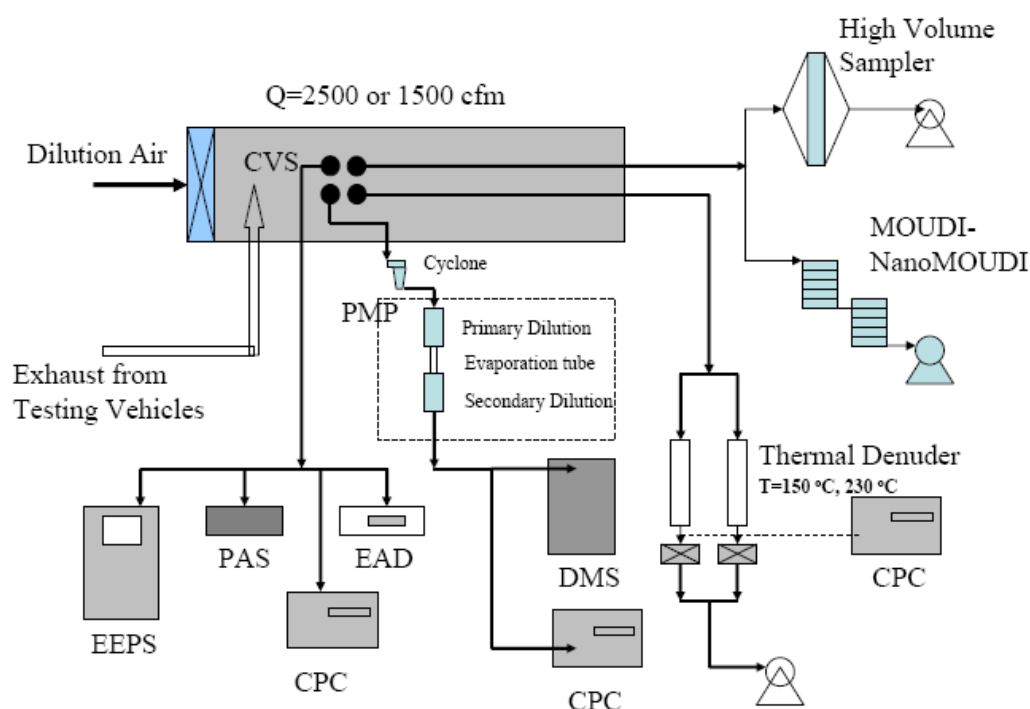


Figure 6.1 Experimental set-up

6.3.1 Vehicles

The test fleet comprised of four heavy-duty diesel vehicles in seven configurations (Table 1). A 1998 Kenworth truck served as a baseline vehicle, without any emission control technology. The same Kenworth truck was also tested with three different control technologies: a Continuously Regenerating Technology [CRT®], consisting of a diesel oxidation catalyst (DOC) followed by an uncatalyzed trap; CRT® in combination with a selective catalytic reduction system [Zeolite or vanadium based SCRT®s].

Table 6.1 Details of test fleet

Vehicle					Engine		After treatment (AT)		Dilution
Make	Nomenclature	Year	Miles	Tested Wt (lb)	Model	Size [L]	Type	Miles on AT	Approximate Dilution Ratio in CVS
Kenworth	V-SCRT®	1998	360000	53,320	Cummins M11, reflashed	11	Vanadium based SCRT®	50,000	9.2 Cruise 6-30 UDDS 14 Idle
Kenworth	Z-SCRT®	1998	360000	53,320	Cummins M11, reflashed	11	Zeolite based SCRT®	0 on SCR, 50,000 on CRT	9.2 Cruise 6-30 UDDS 14 Idle
International	DPX®	1999	40,000	20,920	International DT466E	7.6	Engelhard DPX	30,000	6.2 Cruise 5-25 UDDS 22 Idle
Gillig (35ft) with Allison Hybrid	Hybrid-CCRT®	2007	1000	NA	Cummins	5.9	CCRT®	1000	5-50 UDDS
Thompson-School Bus	EPF	1988	325000	NA	Cummins	5.9	Cleaire - Horizon	32,000	8.3 Cruise 8-80 UDDS 25 Idle
Kenworth	CRT®	1998	NA	53,320	Cummins M11, reflashed	11	Continuously Regenerating Technology	64,000	9.2 Cruise 6-30 UDDS 14 Idle
Kenworth	Baseline	1998	374000	53,320	Cummins M11, reflashed	11	None	NA.	9.2 Cruise 6-30 UDDS 14 Idle

The SCRT systems used for this study were prototype systems and not yet ready for full scale production. The other three test vehicles were a diesel hybrid electric bus, a school bus, and a Caltrans truck. The two SCRT® technologies consist of a wall-flow particulate trap (CRT) followed by a SCR section. The CRT® was the same in each configuration. The difference between them lies in the choice of catalysts (vanadium or Zeolite) for the SCR to control oxides of nitrogen (NO_x). The Caltrans truck, with a smaller engine (7.8 L) than the Kenworth truck (11 L, Table 1), is retrofitted with an Engelhard DPX® filter.

The DPX® filter is comprised of a diesel particulate trap with a catalytic wash-coat. The diesel hybrid electric bus (San Joaquin Valley RTD) is equipped with a catalyzed continuously regenerative trap, or CCRT®, consisting of a DOC followed by a catalyzed trap, which was virtually brand-new, with only 1000 miles on the odometer.

The last test vehicle was an Elk Grove school bus, equipped with an electric particle filter (EPF). The EPF consists of a non-catalyzed silicon carbide substrate for PM control, coupled with an electric heating element and a small blower. The trap is regenerated periodically using electricity from the grid (plug in configuration) during non-operational periods—mostly at night. Hereafter, the test fleet is referred as baseline, CRT®, V-SCRT®, Z-SCRT®, DPX®, hybrid-CCRT® and EPF. The dilution air flow rate at CVS was 2600 cfm ($74 \text{ m}^3 \text{ min}^{-1}$) for cruise and UDDS cycles, and 1600 cfm ($45.4 \text{ m}^3 \text{ min}^{-1}$) for the idle cycle. For EPF and Hybrid-CCRT®, the flow rates were maintained at 1600 cfm for all cycles. These flowrates result in approximate dilution ratios of 6-9 for cruise, 5-80 for UDDS, and 15-25 for idle.

6.3.2 Equipment and instruments

Specific descriptions of some of the instruments and equipment used for this study are provided in this section.

Nano-MOUDI : Size-resolved samples were collected using a micro-orifice uniform deposited impactor (MOUDI) upstream of a nano-MOUDI (MSP Corporation, Minneapolis, MN) loaded with pre-cleaned aluminum foil substrates. Particles were

classified in the following aerodynamic size ranges: 10-18nm, 18-32nm, 32-56nm, 56-100nm, 100-180nm, 180nm-2.5µm and >2.5µm. The MOUDI-Nano MOUDI tandem was operated for multiple runs in order to accumulate sufficient mass for chemical analysis for each vehicle and driving cycle.

DMS/ EEPS : Size distribution of engine exhausts from the CVS was monitored every second by two multiple channel differential mobility spectrometers: a DMS500 (Cambustion) and an engine exhaust particle sizer (EEPS 3090, TSI Inc.). Both DMS and EEPS classify particles on the basis of their mobility diameter. The cut-off size ranges of EEPS and DMS are 5.6-523 nm and 4.5-1000 nm, respectively. With high time resolutions, they are both capable of tracking transient particle behavior, especially during UDDS cycles. With few exceptions (V-SCRT, Z-SCRT only), in which the DMS was placed downstream of the particle measurement program (PMP) sampler, both instruments were connected directly to CVS.

PMP: A particle measurement program (PMP) protocol was developed in Europe to measure the solid particle emissions from light duty vehicles. The sampling train of PMP contains a volatile particle remover (VPR) and a particle counter. The VPR provides two stage dilution connected by an evaporation tube (ET). The temperature for the primary dilution, ET and secondary dilution is 150, 300 and ~35 °C, respectively. Detailed information for the PMP can be seen in Herner et al. (2007).

Thermodenuder: Particle volatility was determined by two thermodenuders (Model ELA-230, Dekati Ltd) sampling in parallel, each heating the entering aerosol to 150 and 230 °C, respectively. The thermodenuder consists of a heating section, followed by an adsorption/cooling unit. As aerosol stream was drawn from the CVS and passed through the heating tube, part of its volatile/semi-volatile components was sheared off. These labile species adsorb onto a layer of activated charcoal placed on the walls of the thermodenuder, leaving the non-volatile PM fraction to be collected on Teflon filters (47mm, PTFE, Gelman) placed downstream of the thermodenuders. Multiple runs were integrated to achieve desired sample mass loadings on these filters to perform various chemical and toxicological analyses. Solid particle number concentrations and size distributions were monitored intermittently by a condensation particle counter (CPC 3022 A, TSI Inc., MN) and a scanning mobility particle sizer (SMPS, TSI 3085).

Electrical Aerosol Detector (EAD): Several instruments are currently in use to assess PM surface related properties. In this study, a diffusion charger, the TSI EAD 3070A, was used to characterize the transient as well as steady state behavior of aerosols. The EAD consists of a unipolar diffusion charger and an electrometer. Particles are charged by diffusion and then drawn through the electrometer which records total current (I) carried by the aerosol stream. Studies have shown that the response of EAD is a function of $D_p^{1.13-1.16}$ (Woo et al., 2001; Jung and Kittelson, 2005; Wilson et al., 2006). This response is particularly an useful PM metric because it corresponds to the actual particle surface area exposed to the environment and can be used to quantify, for example, the area available for adsorption of gaseous species or for interaction with the epithelial

tissue in the lungs (Wilson et al., 2006). Because the EAD signal is closely related to aerosol diameter (Jung and Kittelson et al., 2005) the manufacturer has marketed this instrument to indicate total aerosol length in mm/cm³.

6.3.3 Data Reduction

The physical properties of aerosols from the various vehicles and driving cycles were reduced to four variables, originally introduced by Ntziachristos and Samaras (2006) intended to serve as a means to discriminate the effects of fuel, driving condition and vehicle control technology on particle emissions in dynamometer studies. These variables are:

Reduced Variable 1: Volatility ratio

$$R = \frac{N_{Exhaust}}{N_{TD}} \quad (1)$$

Where,

$N_{Exhaust}$ = Total DMS or EEPS number concentration at the CVS ($D_p \geq 7\text{nm}$)

N_{TD} = Number concentration measured by CPC after the thermodenuders ($D_p \geq 7\text{nm}$).

This is a measure of particle volatility in terms of number concentration.

Reduced Variable 2: Surface rated diameter

The EAD electrometer current is given by

$$I = N_p N_t e Q \quad (2) \quad (\text{Woo et al., 2001})$$

Where,

I = Total current measured by EAD (fA)

N_p = Charge (charge/particle) attachment = $0.0181 D_s^{1.13}$ (Jung and Kittelson, 2005)

D_s = Surface rated diameter, nm

e = elementary charge, 1.6×10^{-19} coulomb

Q = Aerosol flow rate through EAD, 1.5 lpm (1.5 lpm aerosol, 1 lpm sheath flow)

N_t = total exhaust particle number, 10-1000nm from DMS; 10-523nm for EEPS.

Note: Particle number in the 523-1000nm is insignificant

Now substituting in equation 2

$$D_s = \left(\frac{I}{0.0181 N_t e Q} \right)^{1/1.13} \quad (3)$$

Reduced Variable 3: Mass specific Surface area

$$A = \frac{S}{PM} \quad (4)$$

A = Mass specific surface area ($\text{m}^2 \text{g}^{-1}$)

S = Surface concentration, in $\text{m}^2 \text{km}^{-1}$

For the calculation of A , the EAD current was converted to particle surface area using the conversion factor of $65 \mu\text{m}^2/\text{pA}$ ($R^2 = 0.9$, Alveolar deposition) reported by Wilson et al (2006).

PM = Total particle mass between 10nm-2.5 μm nano MOUDI stage, in mg km^{-1} .

The nano-MOUDI substrate mass ($\leq 2.5\mu\text{m}$) measurements were in excellent agreement with parallel CARB reference filter measurements ($R^2=0.99$; Slope =0.95, Intercept: 2.4 mg km^{-1}) and used to calculate mass based parameters. Filter mass was used only for V-SCRT-Cruise (nano-Moudi data not available)

It is a measure of particle agglomeration. Particle agglomeration increases with decreasing A .

Reduced Variable 4: Particle Density

$$\rho = \frac{PM_{\text{NanoMOUDI}}}{V_{\text{EEPS/DMS}}} \quad (5)$$

Where,

ρ = Density, g cm^{-3}

$PM_{\text{NanoMOUDI}}$ = Composite mass from 10nm to 2.5 μm size ranges on the impaction plates (except V-SCRT Cruise)

$V_{\text{EEPS/DMS}}$ = Total volume measured from DMS-EEPS or DMS size distribution assuming all the particles to be spherical

6.4 RESULTS AND DISCUSSION

6.4.1 Size distribution

Figure 6.2 presents tunnel blank- subtracted mean size distributions for vehicles at different operating conditions. These distributions derived from DMS/EEPS measurements are grand averages of multiple runs for each driving cycle. The data are reported in terms of number per vehicle kilometer traveled for cruise and UDDS cycles, and number per hour for idle cycle. The primary focus here is to give a brief overview in order to provide meaningful insights and support to some of the findings described in subsequent sections.

While performing preliminary quality assurance – quality control (QA/QC) of real time data for SCRT®s (V-cruise, UDDS, Z-Cruise), we noticed that few EEPS sizes channels (10-20nm) were almost always saturated due to particle over-loadings. These size bins were subsequently replaced with corresponding secondary dilution-corrected DMS data (the DMS was placed downstream of the PMP secondary dilution with the ET off) to obtain more accurate size distributions. For rest of the test fleet [except CRT®], we used data from the DMS, which was directly connected to the CVS. We have added a tunnel blank distribution in Figure 6.2 f (Baseline vehicle). Size distribution patterns for both SCRT®s are quite similar with sharp modes (Figure 6.2 a,b) at ~ 10nm. The distinguishable feature is the less prominent nucleation mode for UDDS runs especially for the Z-SCRT-UDDS cycle. This may be due to the fact that the Zeolite-SCRT requires much higher temperature to trigger and sustain nucleation than the vanadium based SCRT catalysts (Herner et al., 2007b). Moreover, in general the zeolite catalysts have lot

more catalytic surface area than vanadium catalysts and the Z-SCRT system used for this study is completely new (Table 6.1). These provide higher storage sites for sulfate generated by the upstream DOC and DPF during transient and low temperature testing. Although the main purpose of SCR® technologies is to reduce NO_x by ammonia, at elevated temperatures, their in-built catalysts may encourage the formation of sulfate, an important component acting potentially as seed aerosol for particle formation by condensation of semi-volatile organic vapors, as explained earlier. Chemical data collected will be used to determine composition and will be reported in future publications. For a brief sampling period, we bypassed the SCR portion from exhaust aftertreatment system (SCRT®) just to investigate the impact of the SCR catalysts. Although, this modification did not result in visible alteration of the shape (on log scale) of the distributions (CRT®, Figure 6.2e), number concentration decreased by a factor of 2-3 from the V-SCRT and Z-SCRT cruise cycles—suggesting SCR catalysts’s role on nucleation. Unlike cruise or UDDS runs, idle cycles are characterized with remarkably low particulate number emission rates, coupled with broad size distributions (Figure 6.2a, b). The second test engine, Engelherd-DPX® (Figure 6.2c) displays a dominant nucleation mode, almost identically to the SCRTs/CRT. It has been hypothesized that the catalyst wash-coat on DPF (if saturated) may be enhancing the conversion of SO₂ to SO₃/sulfate and partially stimulates the nucleation process (Hansen et al., 2001).

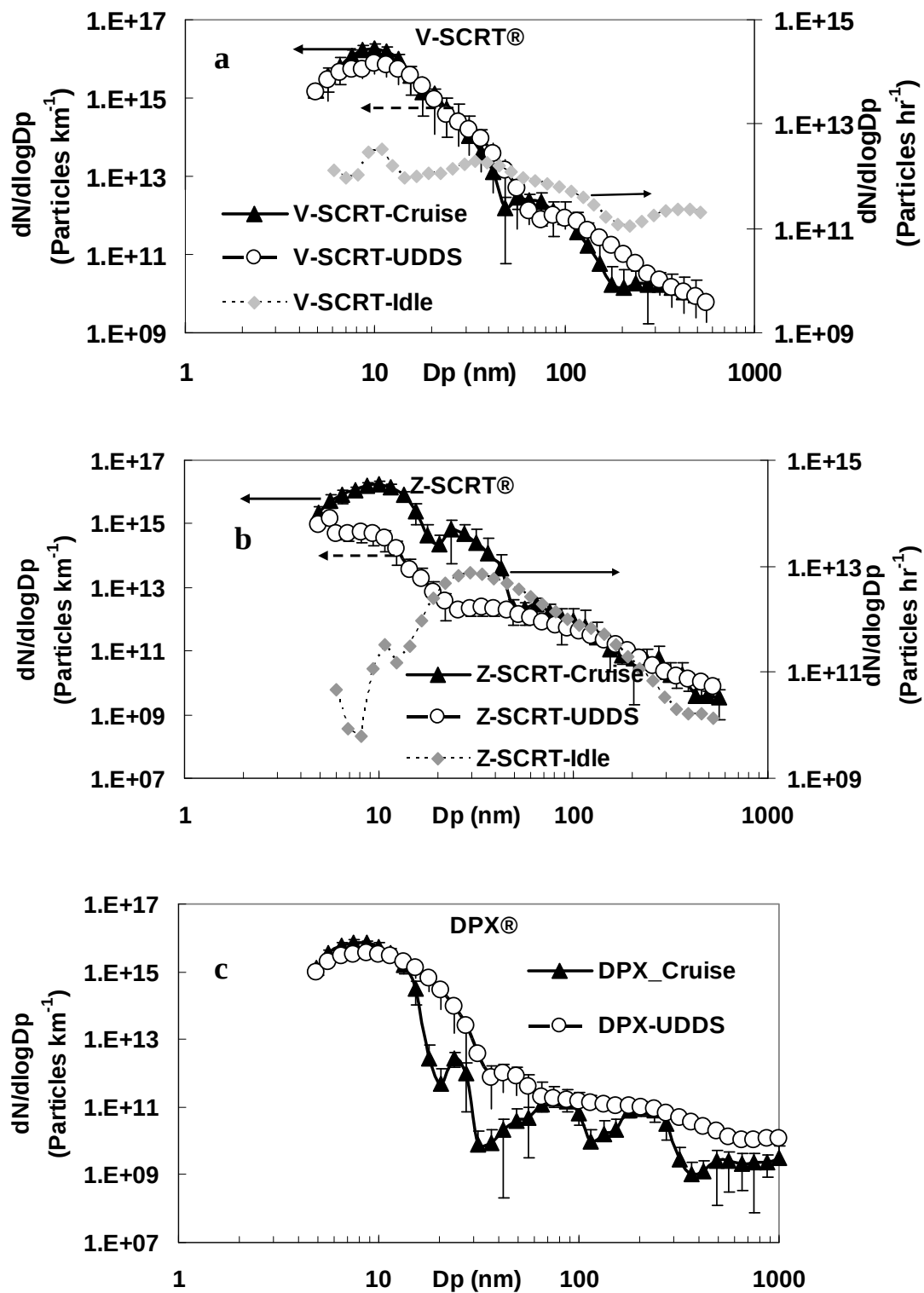


Figure 6.2

Figure 6.2 (continued)

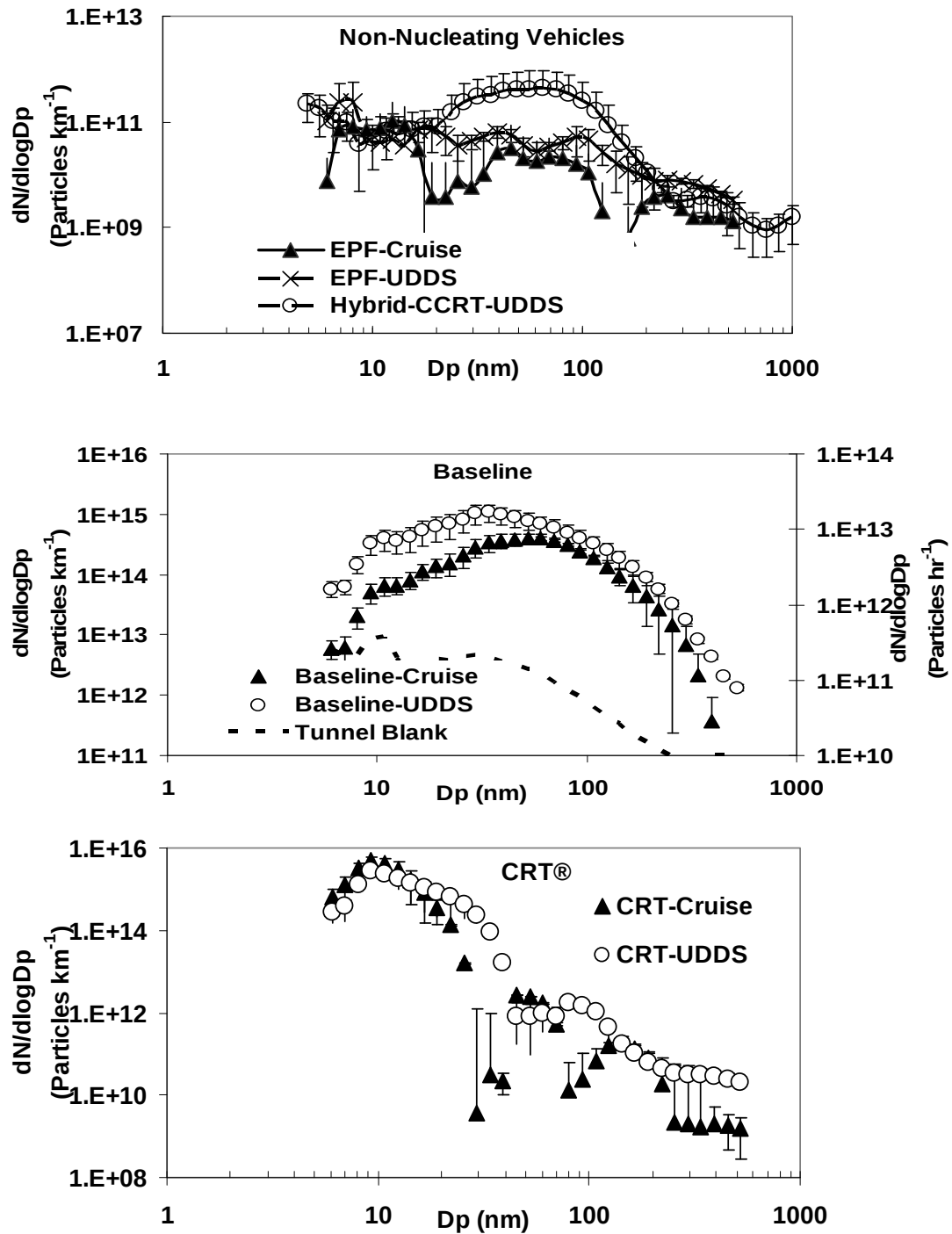


Figure 6.2 a, b, c, d, e, f Particle number size distribution

Contrary to the general notion that particulate filters augment nucleation, the hybrid vehicles [with a CCRT®] and the school bus [with an EPF] were found to be highly efficient in suppressing if not eliminating this PM mode. The Hybrid-CCRT® vehicle (Figure 6.2d) resulted in concentrations (CVS) in the range of $\sim 10^4$ particles cm^{-3} , thus a 1,000-fold improvement over the previously tested vehicles ($>10^7$ particles cm^{-3}). We hypothesize that the initial capacity of its relatively new trap (with only 1000 miles on it) to store sulfur has significantly suppressed the formation of nuclei mode particles. Once all the storage sites are saturated, nucleated sulfate particles are expected (Kittelson et al., 2006). For this vehicle only a few odd large particles are left downstream (Figure 6.2d). The school bus (Figure 6.2d), however, was the cleanest amongst the entire test fleet with number emissions less than 1500 particles cm^{-3} measured in the CVS. Thus, nucleation is not only control device specific but also a function of age and operating conditions e.g. temperature of the catalysts.

The baseline truck, on the other hand, represents the older genre of vehicles and was found to emit substantial amounts of larger particles (Figure 6.2f) with modes in the 60-100 nm range. Because of their large surface area, these accumulation mode particles act as adsorption sites and thus perfect sinks for organic vapors, leading to suppression of nucleation mode (Liu et al. 2007b).

6.4.2 Size segregated mass emission factors

Size fractionated mass emissions factors (in mg km^{-1} or mg hr^{-1}) are calculated based on the loadings on the MOUDI-nano-MOUDI impaction plates. The mass loadings on the

individual substrates are generally low for retrofitted vehicles and depending on size ranges variation in the order of 20-40% (*Standard Deviation/Mean*; from few duplicate measurements) are observed. Although a direct correspondence of mobility and aerodynamic diameters is not accurate without establishing some conversion factors, we can utilize the information from Figure 6.3 a,b,c,d,e,f,g to complement the mobility size distributions (Figure 6.2) described before. Number and mass based size distributions are found to be in reasonable agreement with each other in terms of their trends. The emission factors are remarkably low ($\sim 1\text{-}12\text{mg km}^{-1}$) for the fleet operated with control technologies compared to the baseline vehicle ($\sim 80\text{-}280\text{mg km}^{-1}$). While the majority (>95%) of PM mass is concentrated between 100nm-2.5 μm for the baseline truck, nuclei modes are clearly visible for vehicles retrofitted with control devices. Significant reduction (>90%) of the mass is achieved for vehicles retrofitted with control devices.

Some general trends and inferences can be drawn from Figure 2 and 3. Consistent with previous studies (Kittelson, 2006; Vaaraslahthi et al., 2004) the majority of the control technologies evaluated here have promoted bulk production of nano-size (nucleation) particles during steady state and high speed segment of transient running cycles. The cruise cycles on average generate higher nucleation and lesser accumulation mode particles than the UDDS cycles.

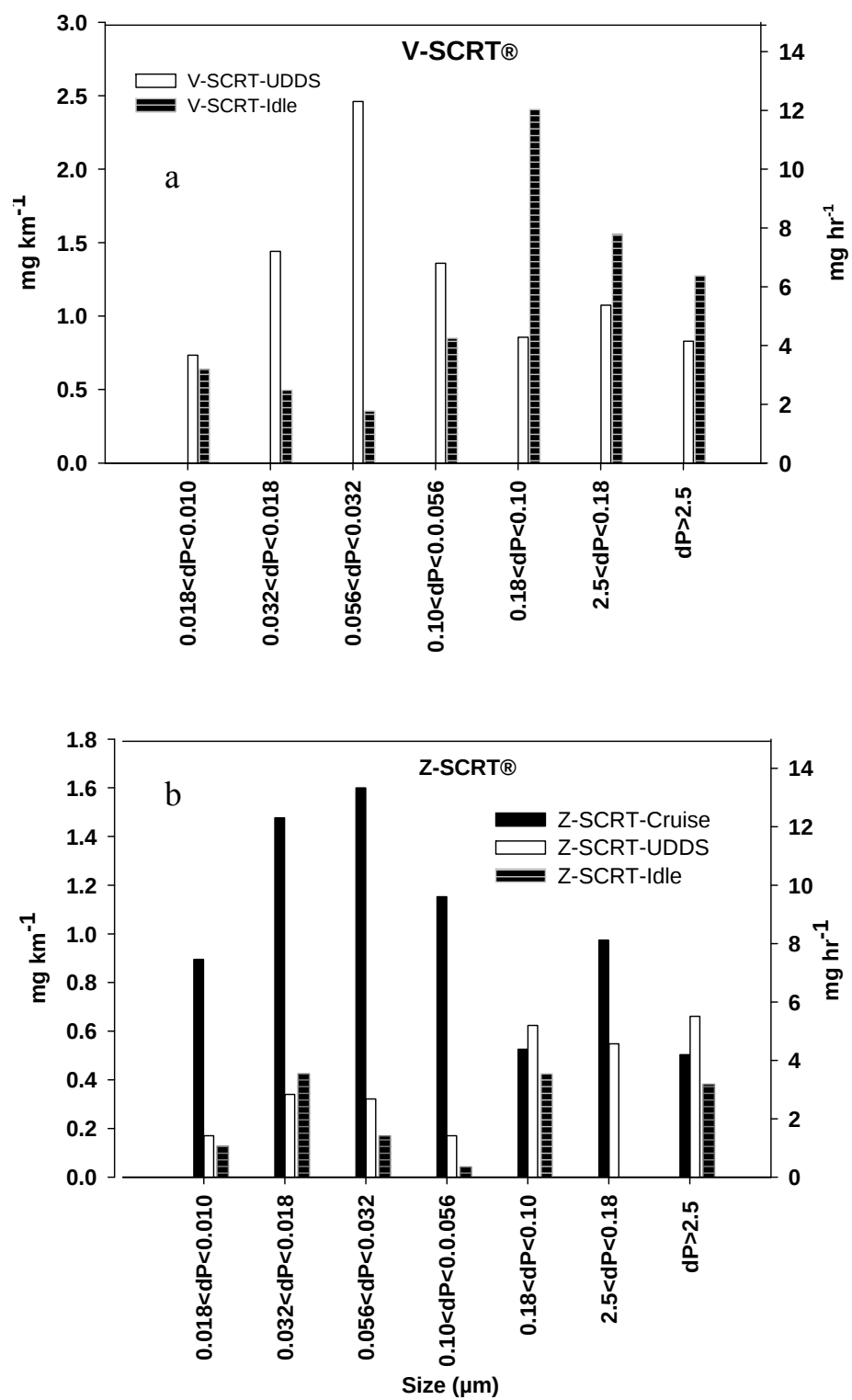


Figure 6.3

Figure 6.3 (continued)

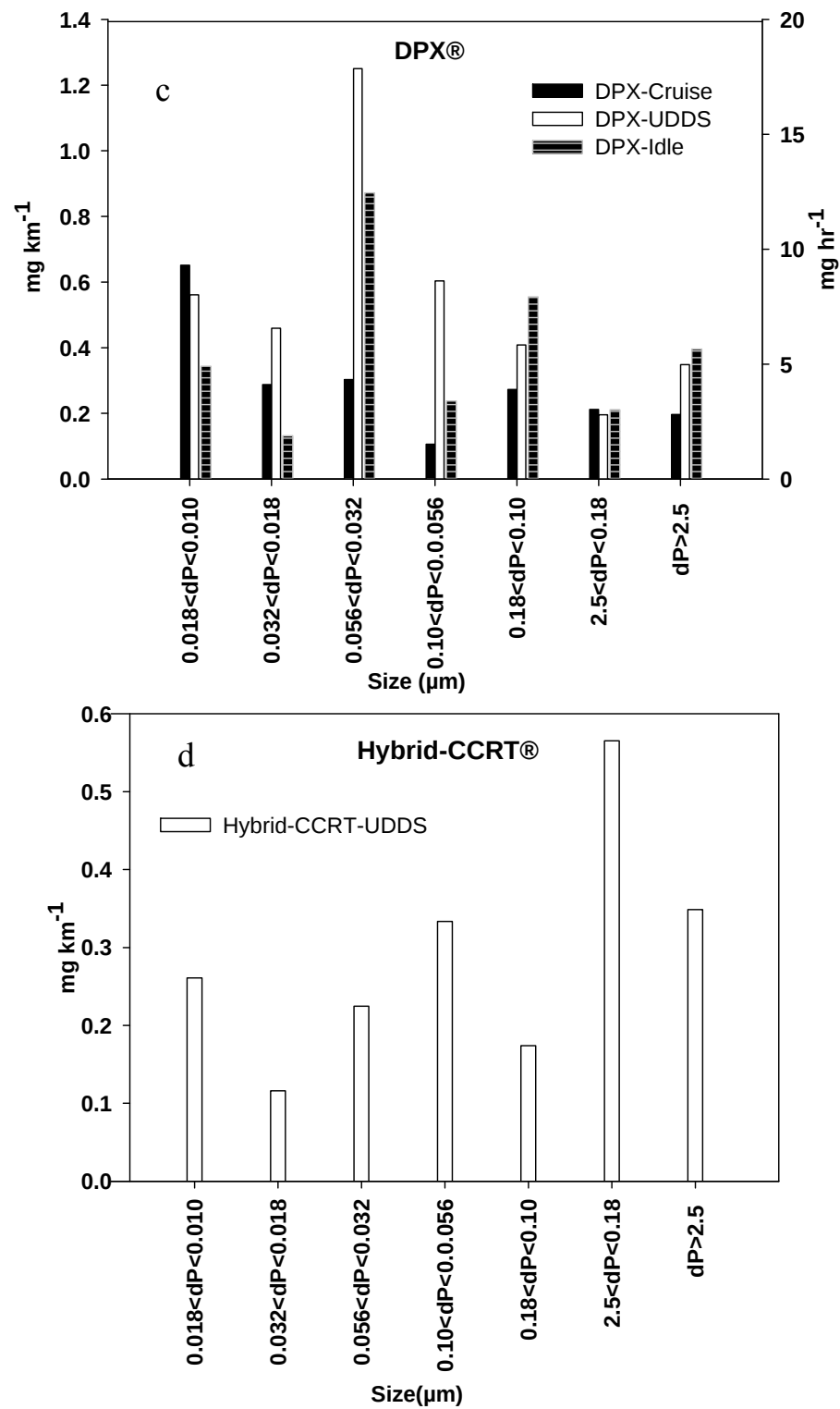


Figure 6.3 (continued)

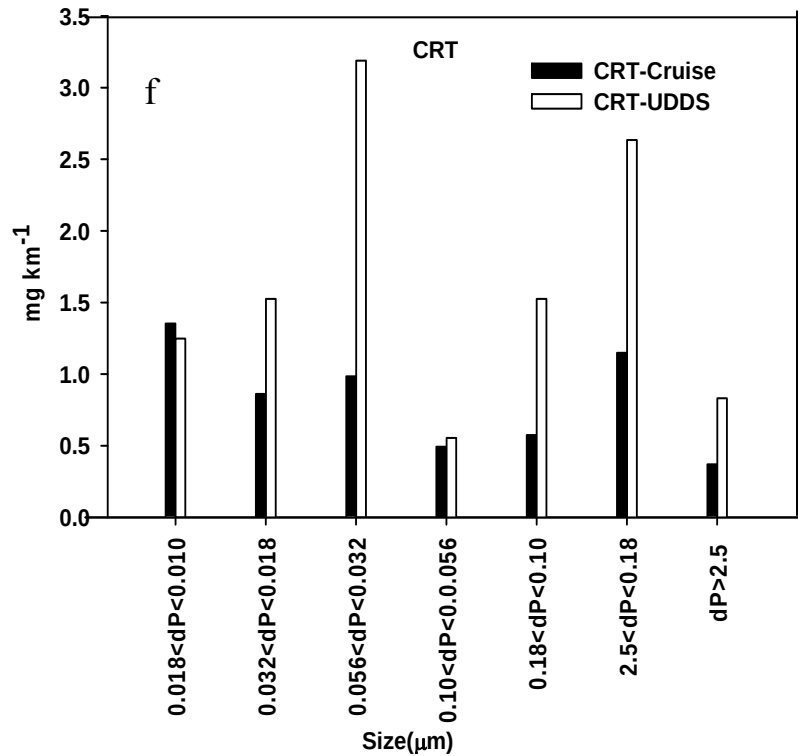
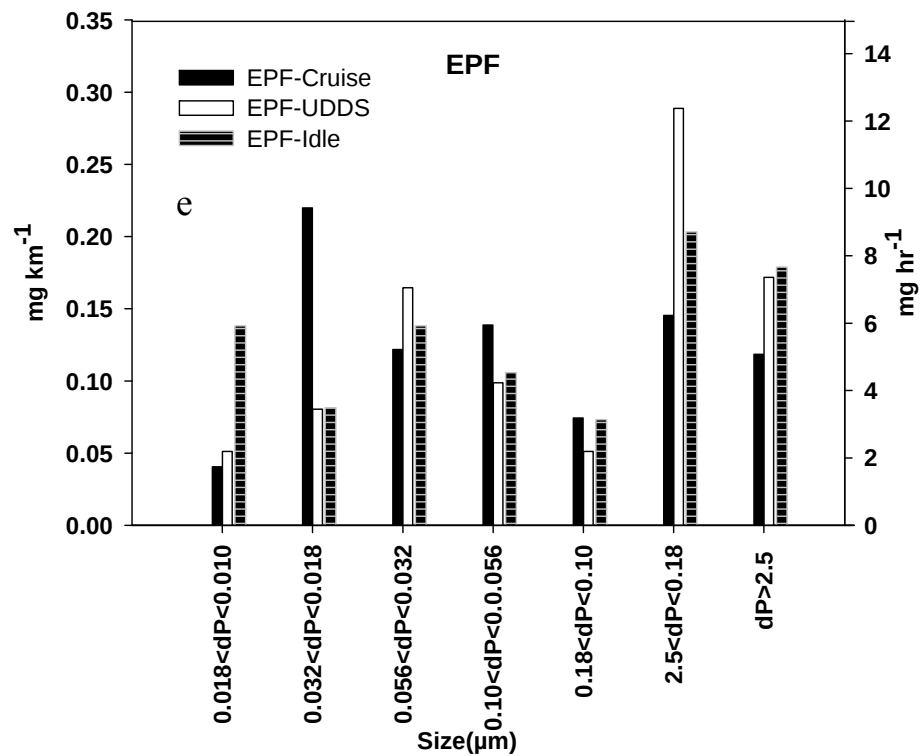


Figure 6.3 (continued)

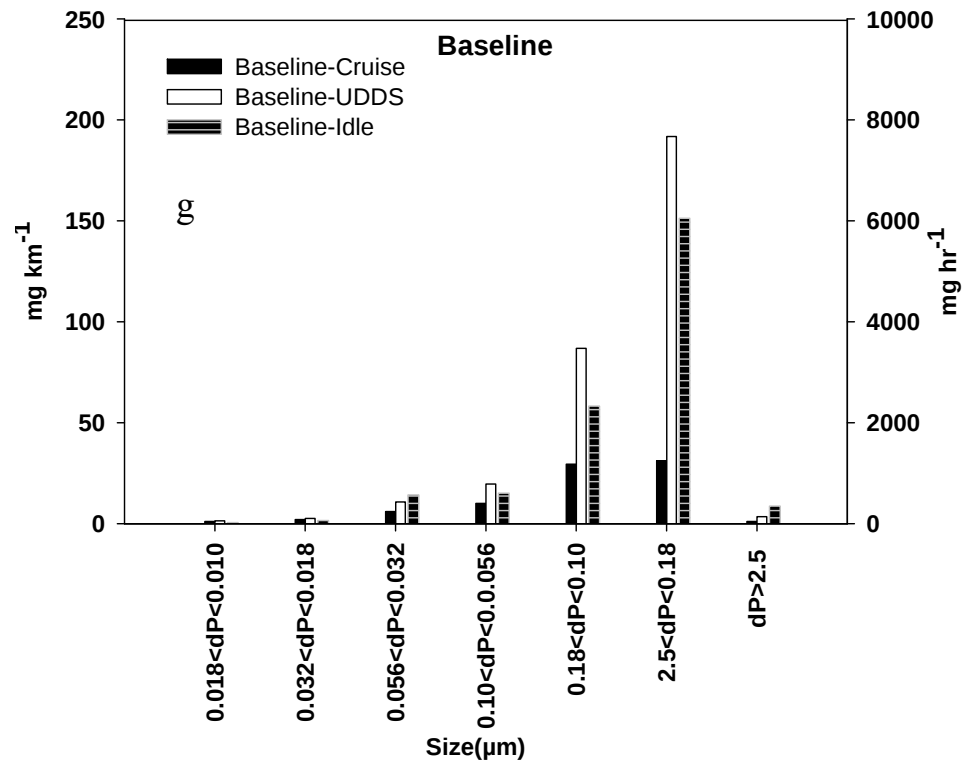


Figure 6.3 a, b, c, d, e, f, g Size fractionated mass emission factors

Note: V-SCRT-Cruise Nano Moudi data not available

The differences between these driving cycles are even more pronounced in mass distributions (Figure 6.3): significant shifts towards larger sizes are apparent in UDDS runs due to increased emission of accumulation mode particles during the acceleration processes (Polidori et al 2007). Aerosol formation mechanism, poorly understood till date, seems to be a function of vehicle type and driving conditions and retrofit design.

Figure 6.4 is an informative graph showing a plot of number EFs vs. Mass EFs (nano-MOUDI, except V-SCRT-Cruise) for each vehicle and driving cycle. Each data point corresponds to a cruise or an UDDS cycle for a given vehicle. The graph shows that for

several of the aftertreatment devices tested, particle number emissions increase with reduced mass emissions. There are some outliers or exceptions observed for Z-SCRT at UDDS cycle, Hybrid-CCRT®, EPF and Idle cycles (not shown) for which both number and mass EFs are relatively low. Thus, most of the new aftertreatment devices appear to be highly efficient in reducing mass emissions but some are not effective in controlling number concentrations due to the formation of nuclei mode particles. These findings are potentially very important if number based standards are considered in the future.

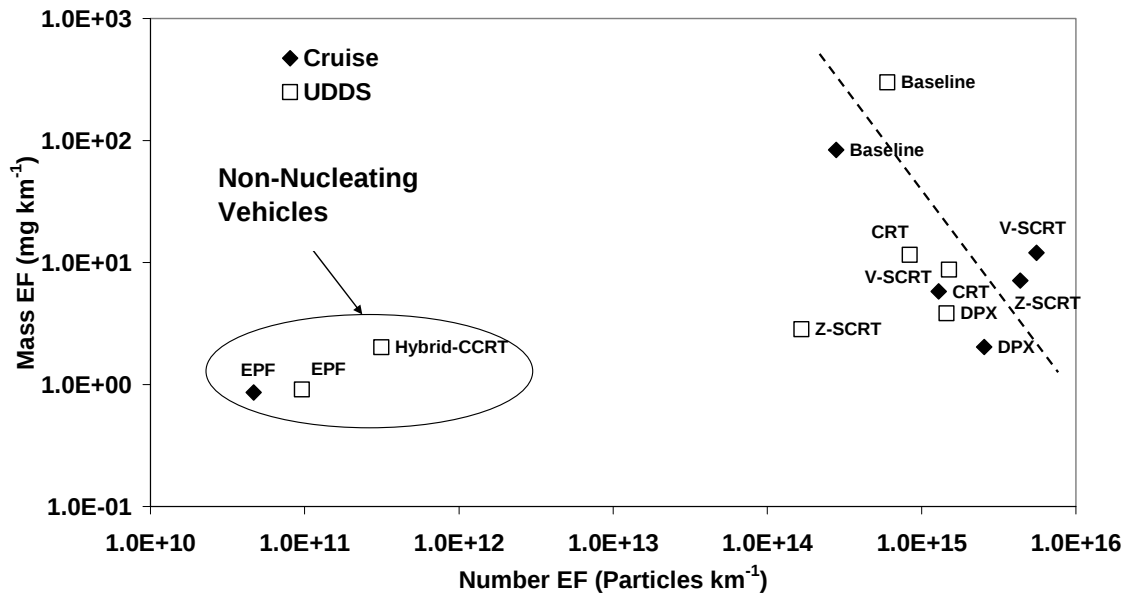


Figure 6.4 Number (DMS) and mass emission factors (nano-MOUDI).

6.4.3 Particle volatility

The extent of particle volatility in terms of total count is illustrated quantitatively by the reduced variable 1 (R) plotted in Figure 6.5 for various vehicles and cycles. R was calculated at 150 and 230°C except in few occasions (Hybrid-CCRT®, EPF) when both the thermodenuders were operated at 150°C to maximize our capability to collect mass of

non-volatile particles. Theoretically, this ratio (R) should be greater or equal to unity and its increase corresponds to higher particle volatility. For the majority of the cases, R at 230°C is at least an order of magnitude higher than their counterparts at 150°C, indicating complete disappearance of large fraction of particles within this temperature window.

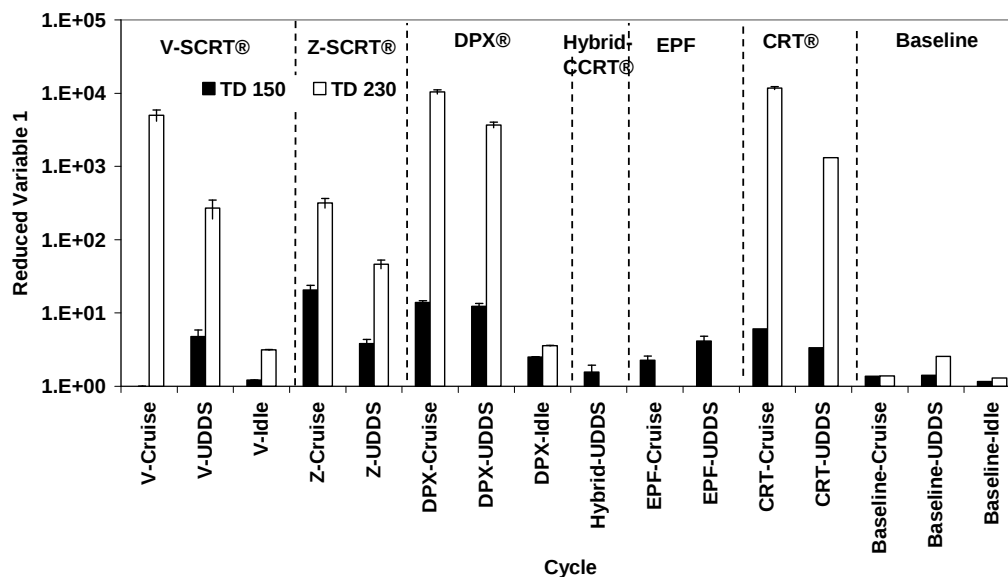


Figure 6.5 Reduced Variable 1 (R): Ratio of total particle to solid or thermo-denuded particle count.

Particle volatility was also observed to be somewhat sensitive to driving conditions and type of control technology used. For instance, cruise mode particles are extremely volatile with maximum R values (~ 4000-10000) at 230 °C for V-SCRT®, DPX® and CRT®. The fact that less than ~0.1% of particles persisted at 230°C for most of the fleet with control technologies can logically be explained by the presence of highly unstable (volatile) fresh nano particles. Although the same Kenworth truck is used to evaluate various aftertreatment devices (V-SCRT®, Z-SCRT®, CRT®), the Zeolite catalysts, especially during UDDS runs, seem to emit particles with a slightly higher heat

resilience, which is consistent with the fact that that nucleation mode particle were in lower concentrations for that vehicle and cycle (Figure 6.2b). As expected, the baseline vehicle had the highest fraction of non-volatile particles in all cycles. Lower volatility is also observed during all idle cycles, EPF and Hybrid-CCRT® vehicles. While we expect the baseline truck to emit large amounts of refractory elemental carbon, lower number loss for other vehicles/cycles should be attributed to their insignificant particle emission rate and/or absence of the nucleation mode particle formation.

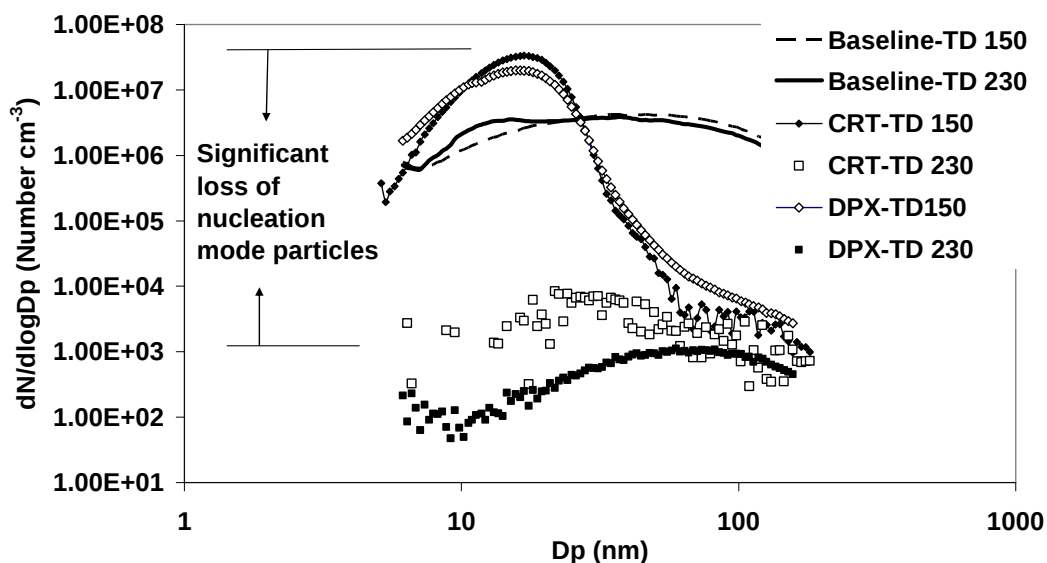


Figure 6.6 Size distribution of thermo denuded aerosols for cruise mode

Note: Available only for DPX®, CRT® and Baseline

The significant particle number loss between 150 to 230°C, especially for cruise cycles, may be better elucidated by the evaporation profiles shown in Figure 6. The majority of particles in the 7-20nm size range for DPX® and CRT ® have disappeared as the aerosol stream is heated from 150°C to 230°C. This is in total contrast to the baseline vehicle, where no noticeable shift in size spectrum is observed. Matter et al (1999a,b) reported

very similar thermal desorption trends between 172 and 204°C for particles sampled downstream of a DPF. These results further justify our temperature choices for the two thermodenuders, which will hopefully enable us to discern differences in the toxicological responses associated with the nucleation mode on particles of these different vehicles.

Figure 6.7 presents the amount of mass fraction retained (non-volatiles) at 150 and 230°C. We obtained these ratios from gravimetric filter measurement of denuded and undenuded samples. Particle number is not a good surrogate of its mass. Thus, except in the case of baseline vehicle, number loss (Figure 6.5, 6.6) has not linearly translated into equivalent particle mass reduction. While more than 99% of the particles completely disappear at 230°C for SCRTs, CRT and DPX at cruise and UDDS runs, an appreciable fraction of mass (20-40%) remains intact. Quite a reverse trend is observed for idling, EPF and Hybrid-CCRT® (low number emission scenarios with insignificant nucleation mode)—relatively low number volatility is accompanied with significant mass loss. A study (Biswas et al., 2007) conducted in close proximity of a freeway with the highest percentage of diesel fleet (~18%) in the US demonstrated that a substantial amount of particle mass could be lost from larger ultrafine particles (>40nm) due to heating without losing a significant amount of their total counts. The mode of the size distribution shifted to lower size ranges, as a result of the depletion of the aerosol mass, but overall these particles simply decreased in size but did not disappear during heating, unlike the much smaller nucleation mode PM.

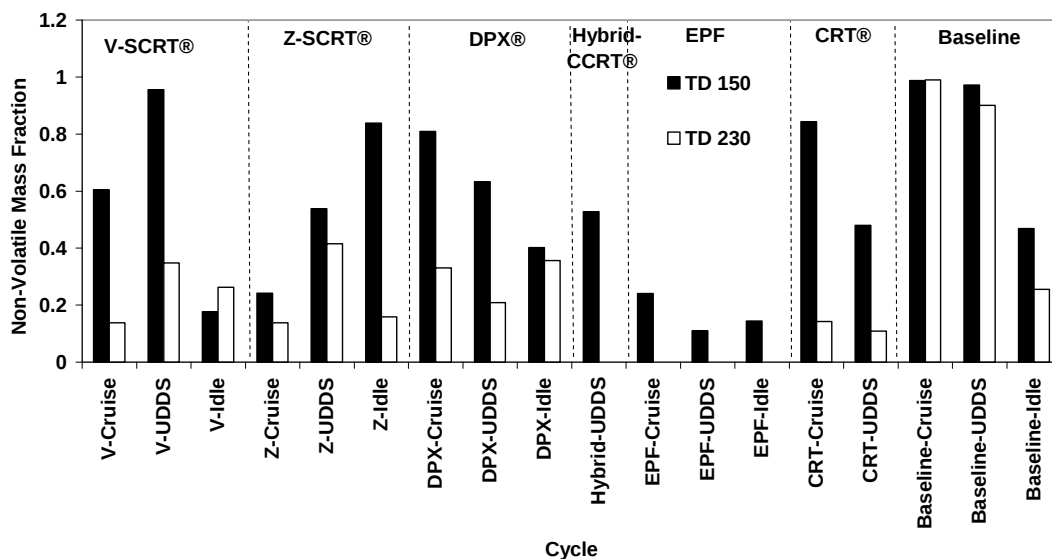


Figure 6.7 Mass fraction remaining at different thermodenuder temperature settings.

Particle volatility analysis could be used to at least in part infer particle chemical composition. Researchers have shown that diesel nuclei mode particles are dynamic mixtures of sulfate and organics (Groose et al., 2006; Scheer et al., 2005). Sulfates can either be in the form of pure sulfuric acid (classical binary nucleation theory of $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$) or neutralized salts (NH_4SO_4 , NH_4HSO_4 etc.). The neutralized species are refractory even at 200°C , however, H_2SO_4 evaporates completely at a much lower temperature ($\sim 125\text{-}150^\circ\text{C}$) due to its high vapor pressure (Orsini et al., 1999; Schmidt et al., 2002). The organic fraction is comprised not only of volatile unburned lube oil constituents, but also residual low vapor pressure organics (Tobias et al., 2001). From TEM analysis of particles captured downstream of a DPF, Mathis et al (2004) further inferred that these nano-particles are likely to be composites of various species possessing diverse volatility characteristics. Although, from the above discussion, the bulk loss of nucleation mode particles in Figures 6.5 and 6.6 appears to be due to evaporation of sulfates and

volatile/semi-volatile organics between 150 and 230°C, complete chemical speciation is essential to reach any educated conclusion. This will be the topic of a subsequent publication of our group.

6.4.4 Particle surface properties

6.4.4.1 Reduced variable 2: Surface rated diameter

The surface rated diameters (D_s) calculated from EAD surface concentrations are illustrated in Figure 6.8. Ideally, D_s should be very close, if not higher than the arithmetic mean particle diameter. Average surface rated diameters are calculated for all the vehicles except for school bus (EPF) where EAD signals are below the instruments detection limit. It is evident from the plot that cruise mode D_s , irrespective of types of control technologies, are smaller (~25-40nm) compared to the transient driving cycles (~75-100nm). This is consistent with the increased formation of elevated level of nuclei mode particles (< 50nm) during the steady state and larger amount of accumulation mode particles in UDDS cycles. Considering negligible variations in the accumulation modes (Haris and Maricq, 2001), also shown in our figures 6.2, 6.3, we can thus use D_s as a good indicator for the presence or absence of freshly nucleated particles.

During a typical transient run (i.e. UDDS cycles), an engine experiences acceleration, deceleration, steady state and idling phases, which result in frequent changes in exhaust particle characteristics in terms of their size distribution, total count and surface concentration. Acceleration and high speed cruise modes produce significant number of

small particles, followed by their absence during deceleration and idling. Thus, rapid variation in Ds coupled with higher accumulation modes (Figure 6.2, 6.3) eventually translates into higher mean surface diameter for UDDS runs.

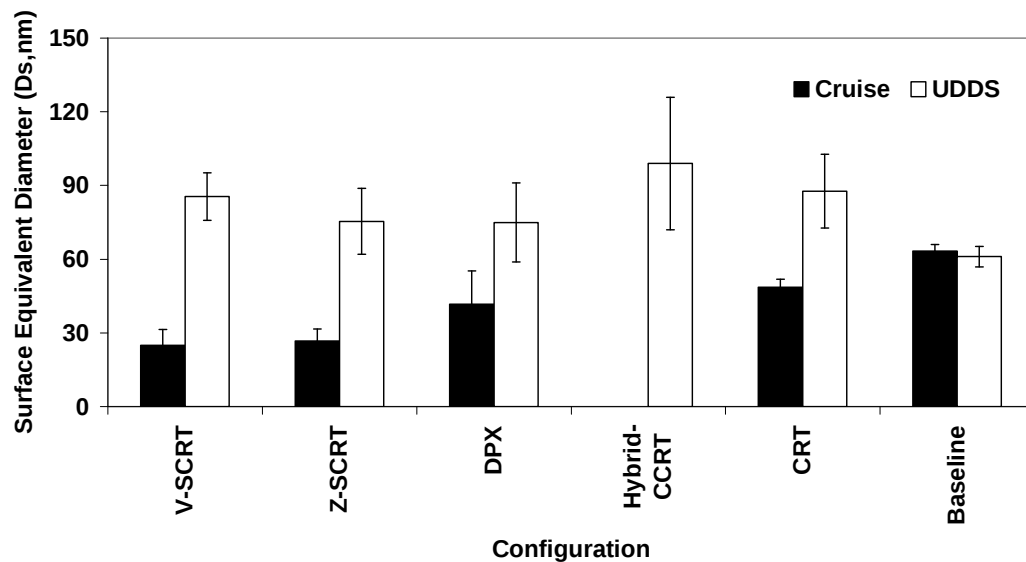


Figure 6.8 Reduced Variable 2: Surface rated diameter

This phenomenon can be elucidated succinctly by time series plots (Figure 6.9a,b) of particle number, EAD response (fA) and corresponding mean surface diameter (Ds) for a selected DPX® UDDS run (Figure 9a). EAD signals and total counts track each other well; however, the Ds plot follows a reverse trend. Surface diameter goes up and down (50-500nm) at the initiation of acceleration or deceleration when the total count is still low, or drops down drastically. The lowest surface diameter (~20-30nm) was recorded during the later stages of acceleration, or at high load conditions (steady state) as small particles predominate the size distribution.

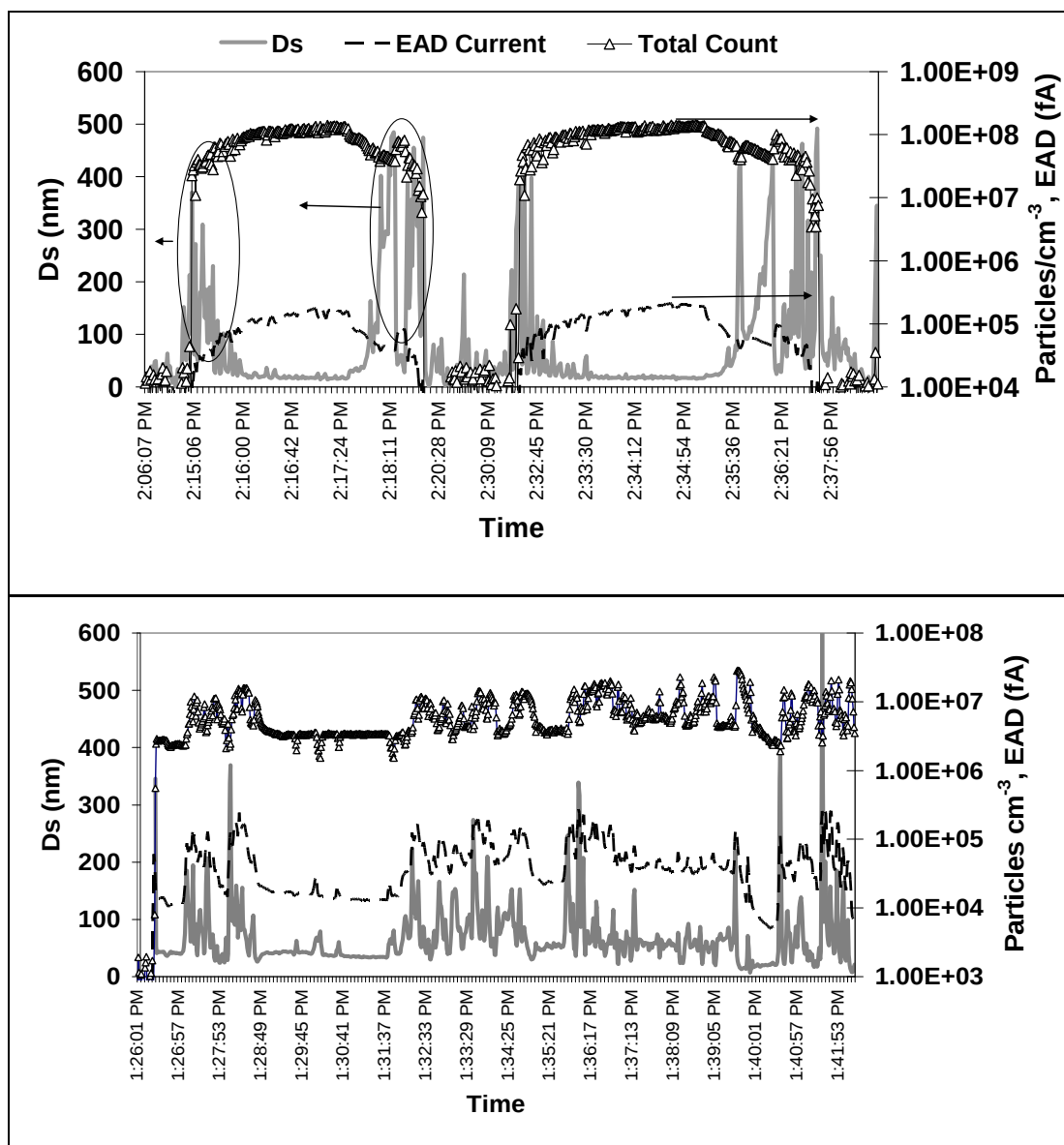


Figure 6.9 a, b Time series of surface diameter (Ds), surface concentration (EAD signal and total particle concentration (DMS count) for a) DPX® b) Baseline- UDDS run

Unlike the other vehicles (where similar behavior observed as that of Figure 6.9a), the baseline truck maintains a high particle number concentration ($>10^6$ particle cm⁻³) over the entire span of the UDDS runs, which greatly dampens the fluctuation in Ds (Figure 6.9b). This explains its resultant lower mean surface diameter (~ 60 nm) (Figure 6.8)

despite the significant contribution of accumulation mode particles. Also, the lower difference in D_s for the cruise and UDDS can be attributed to the relatively higher number of nucleation mode particles in UDDS than cruise unlike other vehicles.

6.4.4.2 Reduced variable 3: Mass specific surface concentration

Figure 6.10 shows mass specific surface concentrations for the various vehicles and driving cycles tested. This PM property is inversely proportional to the mean particle size of DEPs, thereby providing an indirect measure of the extent of particle agglomeration.

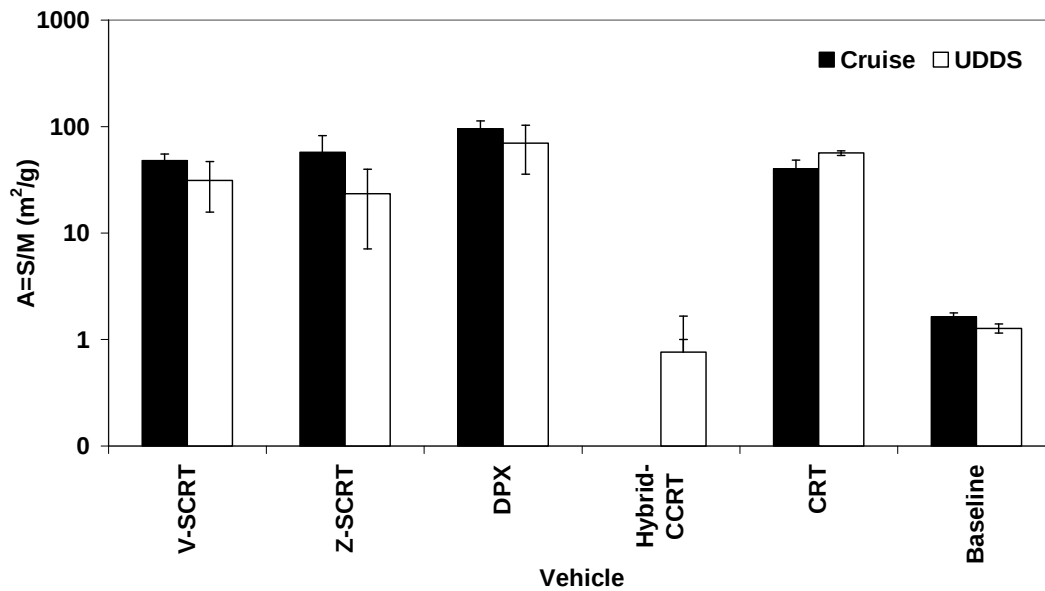


Figure 6.10 Reduced variable 3: Mass specific surface concentration

Therefore, the decrease of 'A' implies an increased contribution of coagulated or accumulation mode particles. The accumulation mode particles scavenge nucleation precursor species (Liu et al., 2007) as mentioned before. Thus, particle agglomeration is an important parameter to indicate suppression of nuclei mode particles.

The mass specific surface area, based on EAD surface concentration, have values in the range of $1\text{-}100\text{ m}^2\text{g}^{-1}$, which are consistent with those measured by Brunauer – Emmett – Teller (BET) technique ($26\text{-}72\text{ m}^2\text{g}^{-1}$, Duran et al., 2002). A study by Ntziachristos and Samaras (2006) reported somewhat higher values of the mass specific surface area from heavy-duty passenger vehicles ($300\text{-}500\text{ m}^2\text{g}^{-1}$).

Cruise cycles on average have slightly higher values (5-10%) of ‘A’ compared to their respective UDDS cycles of a given vehicle, indicating their less agglomerated particle structures. Although the shape and size of accumulation modes are quite similar, if not identical, for both cycles (Figure 6.2), steady state operations are associated with higher nucleation mode. As EAD signal is weighed towards smaller particles (Jung and Kittelson, 2005), cruise cycles are likely to trigger more EAD response than transient cycles. On the other hand, accumulation modes prevail over nucleation modes (Figure 6.2) for Hybrid-CCRT® at UDDS runs and the baseline vehicle, resulting in lower mass specific surface concentrations ($\sim 1\text{ m}^2\text{g}^{-1}$). Higher fractal agglomerates emitted by the Baseline vehicle may result in a lower value of A. The effect of nucleation is also observed for Z-SCRT-UDDS runs, which exhibited slightly lower (though statistically insignificant) “A” compared to other SCRTs configurations.

6.4.5 Particle specific density

Particle specific densities are calculated using equation 5 and shown in figure 11. This is a relatively simplistic approach towards estimating density—a more rigorous

experimental protocol involving sophisticated instruments such as Aerosol particle mass (APM) analyzer, Electrical low pressure impactor (ELPI) or Transmission electron microscopy (TEM) (McMurry et al, 2002; Mathis et al., 2004; Van Gulijk et al., 2004) therefore, is warranted for a comprehensive characterization. Total number concentration for the Hybrid-CCRT®, EPF and all idle cycles are below 10,000 particles cm^{-3} (CVS). At such low concentrations, the fast response instruments (EEPS or DMS) are not suited in determining actual volume distributions (Herner et al., 2007a). Therefore, density calculation was limited to cruise and UDDS runs for rest of the vehicles.

Untreated diesel exhausts are rich in loosely packed fractal chain agglomerates (Maricq et al., 2000; Park et al., 2004). This explains the low densities ($\sim 0.34\text{-}0.44 \text{ gcm}^{-3}$) observed for the baseline truck (Figure 6.11), which is also consistent with the results of the previous section (mass specific surface concentration). With the introduction of particle traps, however, most of these fractal-agglomerates are physically removed, leading to substantial alterations in particle morphology. Figure 6.11 reveals that density is higher than unity for the fleet with aftertreatment devices, implying that particles generated downstream of traps are structurally compact, in total contrast to those emitted from baseline vehicle. TEM image analysis conducted by Mathis et al. (2004) further provides evidence to the spherical shape of these particles.

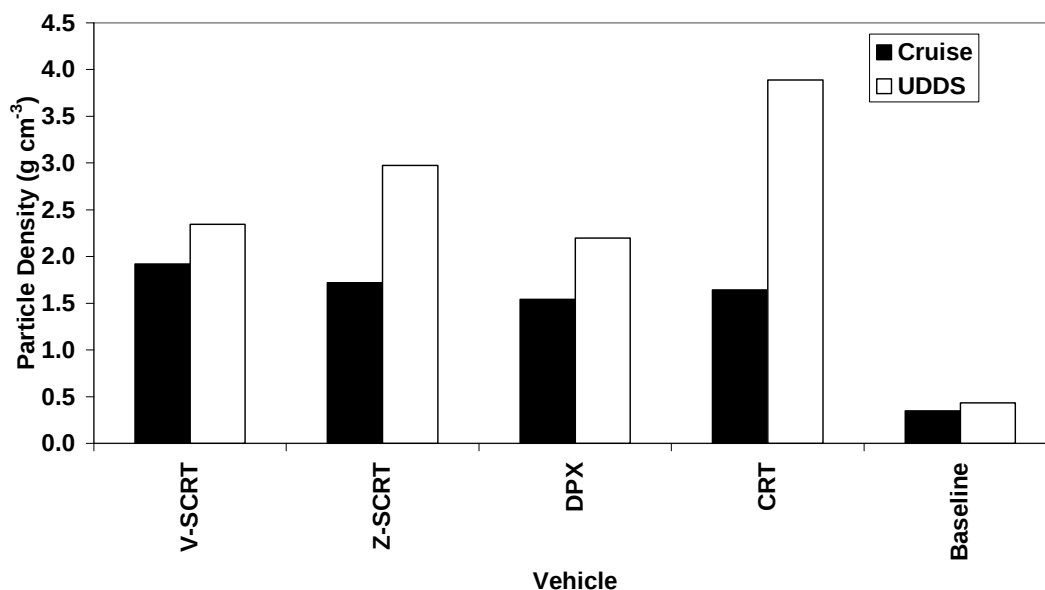


Figure 6.11 Reduced variable 4: Particle density

Densities for cruise cycles span from ~ 1.5 to 1.9 g cm^{-3} . It is evident from size distributions (Figure 6.2) that nucleation mode particles predominate during steady state driving conditions. These small nanoparticles are likely to be internal mixtures of fully or partially neutralized sulfates ($\rho = 1.7\text{--}1.84 \text{ g cm}^{-3}$), and organic species ($\rho \sim 0.9\text{--}1.8 \text{ g cm}^{-3}$) (Grose et al. 2006, McMurry et al. 2002). Our estimation of densities are thus in very good agreement with those of above mentioned chemical constituents.

UDDS cycle densities ($\sim 2.2\text{--}3.8 \text{ g cm}^{-3}$) are systematically higher than the cruise cycles. The higher range of these density values is quite unlikely, unless there is significant contribution from heavy metals. The values closer to 2 are consistent with the higher content of solid particles especially elemental carbon (though not necessarily in the form of fractal agglomerates) emitted in these cycles. The consistently lower densities ($\sim 0.5 \text{ g cm}^{-3}$) of the baseline vehicle are of particular note (Figure 6.10), and are consistent with

the higher fraction of agglomerated soot particles of that vehicle. The effective density values for the baseline are within the density range of agglomerate particles emitted by diesel vehicles, reported in earlier studies (Maricq et al., 2000; Maricq and Xu, 2004).

The density values obtained for the UDDS cycles may also be subjected to some artifacts introduced due to limitations in the instrument sensitivity. As concentration varies rapidly from few hundred particles to several millions in a typical UDDS run, real time instruments (EEPS or DMS) are prone to underestimate some of the size channels at low emission rate. This may cause some uncertainty in the overall aerosol volume measurements, thus leading to an overestimation of particle density. From a more qualitative than quantitative view point, these results suggest that the UDDS cycles appear to be emitting higher concentrations of non-volatile refractory particles and lower concentrations nucleation mode organics, which is also consistent with the results discussed in earlier section of this paper.

6.5 SUMMARY AND CONCLUSIONS

This investigation presents some of the first detailed particle characterization for advanced NO_x and PM retrofits for heavy duty diesel vehicles. The test fleet includes a diesel hybrid electric with a DPF (Hybrid-CCRT®), a continuously regenerating technology (CRT®), a vanadium-based SCR catalyst with a CRT® (V-SCRT®), a Zeolite-based SCR catalyst with a CRT® (Z-SCRT®), a DPX, and an EPF. A HDDV vehicle without emission controls served as the baseline vehicle. The fleet was tested under three driving cycles: cruise at 50 mph. UDDS and idle.

Remarkable reductions in PM mass emissions (>90%) were found for the test fleet compared to the baseline vehicle. However, enhanced nucleation mode particles were observed for some of the vehicles especially during cruise cycles. Comparing to cruise cycles, the UDDS cycles emit higher particle mass in the accumulation mode. Idle cycles are characterized with remarkably low particle number emission rates, coupled with fairly broad size distributions. The Hybrid-CCRT® and EPF vehicles were efficient in controlling both mass and number emissions.

The majority of particles by number evaporated by heating the aerosol to 150 - 230 °C, suggesting the nucleation mode particles are predominantly internally mixed and consist of semi-volatile compounds. Particles from the test fleet (except Hybrid-CCRT®) have shown about 100-fold higher active surface area per unit mass than the baseline vehicle. Particle densities during cruise cycles span from ~1.5 to 1.9 g cm⁻³, implying that particles from the test fleet are structurally compact, in contrast to those emitted from baseline vehicle. Higher particle densities (~2.2 to 3.8 g cm⁻³) were measured in the UDDS cycles, a result that may be due to the higher concentration of non-volatile refractory particles and lower concentrations nucleation mode organics emitted during these cycles. Chemical and toxicological analysis of the volatile and non-volatile fractions of PM emissions from the test fleet are under way and will be reported in future publications.

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Chapter 7: Conclusions and Future Research Directions

7.1 SUMMARY AND CONCLUSIONS

Numerous epidemiological and toxicological studies emphasized the need for robust experimental data on particle characteristics to establish mechanistic links between health effects and particulate matter. Unlike other pollutants, particle behavior is highly complex due to its heterogeneous nature. Any health outcome depends on the exposure of these particulates and the cellular level interaction of its numerous chemical constituents. Besides chemical characteristics of constituent species, particle size, morphology, volatility and exposed surface area are some of the essential physical properties to infer the extent of toxicity.

On road vehicles are responsible for majority of the particulate emission in a growing metropolis like Los Angeles. Due to their potential health risks, significant amount of our research efforts are dedicated solely on mobile source characterization. The main objective of this dissertation, therefore, is to create an invaluable database for the physico-chemical metrics of particulates, predominantly from vehicular exhausts. The following paragraphs will revisit individual topics described before and provide a brief recap of the major findings.

Effective density is an excellent measure to indicate particle depositional behavior in lungs and a reasonable estimate for particle morphology or fractal dimension. Realtime particle density over a wide mobility size range (50-414nm) was measured at different

locations of Los Angeles basin using a DMA-APM tandem set-up (Chapter 2). Although the primary focus of that study was to determine effective density at sources impacted heavily by vehicular emissions, a receptor site (Riverside, CA), a marine (El-Segundo beach) and an urban background (USC, also in proximity of a freeway) site were also monitored. Particles irrespective of their origin have exhibited structural irregularities with increasing size as effective density decreases reversely with particle diameter. Densities higher than unity for nucleation mode particles ($\sim 50\text{nm}$) indicate their likely spherical nature. On quantitative terms, however, this PM metric is source specific: particles from mobile sources (both gasoline and diesel freeways) have demonstrated highest fractal behavior, while particles from marine layer are almost spherical. The diesel dominated freeway produced particles having densities normally associated with chain agglomerates ($\text{density} < 1\text{ g cm}^{-3}$). Majority of the larger aerosols ($> 100\text{nm}$) were externally mixed as evidenced by their bimodal or tri-modal density distribution. Particles at Riverside had an interesting diurnal trend—density increased during the afternoon ($\sim 1.4\text{-}1.5\text{ g cm}^{-3}$) before subsiding eventually after sunset. The densities mentioned above correspond excellently to those of the secondary organic aerosols, formed due to high temperature photochemical reactions.

Considerable efforts in this thesis have been put to characterize particle volatility. Volatility is a key parameter which influences the dynamically evolving size distributions near freeways and is a vital tool in assessing exposure level to daily commuters. During summer of 2004, a month long field campaign was carried out to study ultrafine PM volatility properties next to a pure gasoline vehicle freeway with a tandem differential

mobility analyzer (TDMA) (Chapter 3). In addition, size fractionated particle chemical composition was measured for ultrafine, fine and coarse mode. Two sites were chosen: one close to the freeway shoulder and another 150m downwind. The nearby site was associated with higher concentration of ultrafine mass, nitrate, organics and elemental carbon than the downwind site. Particles volatility, however, have similar trend over the whole size ranges irrespective of location—volatility decreases as size increases. Thus as we move from nucleation (<40nm) to quasi accumulation (80-120nm) mode particles, mixing characteristics varies drastically from that of highly internal mixture of small particles to externally mixed large particles.

As environmental conditions such as dilution and temperature significantly influences particle volatility, identical set of experiments were carried out at the same sites during winter of 2005 (Chapter 4). This provided an opportunity to compare the seasonal (winter versus summer) and diurnal (daytime versus evening) variability of PM characteristics. While meteorological conditions during daytime hardly varied during these seasons, winter evenings were much cooler ($\sim 10^{\circ}\text{C}$). This trend in ambient conditions was also reflected in the particle mixing characteristics. Volatility was similar during daytime over the seasons, while winter evenings were associated with higher volatility due to formation of fresh nucleation mode particles at lower temperature and condensational growth of seed aerosols by semi-volatile species. Conforming general seasonal attributes, ultrafine particulate mass concentration, EC and OC were higher during winter and coarse mass and sulfate concentration were higher during summer season.

To complement and compare the impact of heavy duty diesel vehicles on particle volatility, the TDMA experiments were performed near a mixed fleet freeway (I-710) (Chapter 5) during winter of 2006. This freeway has huge traffic volume (~ 11000 vehicles hr^{-1}) and the highest percentage of diesel fleet (17-18%) in US. We observed similar diurnal pattern of lower volatility during daytime compared to evening. However, the striking distinction between the pure gasoline and the diesel vehicle dominated freeway was the extent of external mixing—non volatile particles from the diesel freeway were at least 20-40% higher. These non-volatile fractions have tracked the variation of elemental carbon excellently indicating refractory soot particles to be the dominant source of non-volatiles.

Chapter 6 discusses the physical characteristics of particulate matter from heavy duty diesel vehicles equipped with advanced particulate and NO_x emission control technologies. The primary objective of the project is to determine the relative toxicity of volatile and non-volatile species as majority of these emission control technologies selectively remove the refractory fractions of PM. Physical properties described here include particle size distributions (mass and number), volatility, surface diameter, mass specific surface area and density. Experiments were carried out at the dynamometer facility of California Air Resources Board (CARB). A total of six after treatment devices (V-SCRT®, Z-SCRT®, CRT®, DPX, Hybrid-CCRT®, EPF) were tested in three driving conditions, i.e. cruise, UDDS and Idle. The results were compared with a baseline vehicle. Although all these technologies have been efficient in reducing particle mass

some of them increased particle number concentration. The extent of nucleation is found to be a function of operating conditions, control technology, catalyst storage capacity etc. Cruise cycles were accompanied by higher nucleation and less accumulation mode particle in comparison with the transient cycle (UDDS). Particle volatility in terms of number is few orders of magnitude higher for particles downstream of the treatment devices compared to untreated aerosol. Most of the nucleation mode disappeared between 150 and 230°C, indicating significant contribution of sulfate in particle composition. Vehicles with strong nucleation mode (especially during Cruise cycle) demonstrated lower surface diameter and higher mass specific surface area or less agglomeration. Most of the particles except from baseline vehicle are compact in nature with density always above unity.

7.2 FUTURE RESEARCH DIRECTION AND POLICY ISSUES

This thesis has put an effort to improve our scientific understanding of particulates emitted from vehicular sources and provide valuable data sets on their physico-chemical properties. Considering the complexity of PM metrics, several questions remained unanswered and should be areas of active research in future. We will also discuss in this section a few policy issues which need to be addressed with care while formulating or implementing new regulations.

Volatility and upcoming studies

Particle volatility characterization constitutes bulk of this research work and is elaborated over several chapters of this dissertation (Chapters 3, 4, 5, 6). So far we have

differentiated successfully the impact of gasoline and diesel vehicles on particle volatility under field conditions and the effect of meteorological parameters by quantifying seasonal and diurnal variations. Particle mixing characteristics have also been studied in details for the newer heavy duty diesel fleet by controlled experiments with a dynamometer set-up. While all these research works have supported highly volatile nature of nucleation mode particles compared to accumulation mode, the magnitude of evaporation varied under different conditions. Based on our understanding so far we believe that volatility is not only size specific but also a function of other equally important factors such as type and age of vehicles, aftertreatment devices, engine exhaust temperature, driving cycles, ambient temperature, dilution conditions, penetrability and most importantly the chemical species present. Therefore, further efforts are warranted to develop a universal model which will predict the evolution of size distribution near roadways or congested traffic intersections and estimate human exposure by incorporating the probable factors listed above. Stringent emission regulations (US 2007, Euro V and Japan 2005) are being incorporated in developed countries in response to the growing evidences linking detrimental health effects and particulate matter exposure (Merrion, 2003). As these standards require at least 90% reduction in PM mass, several emission mitigation strategies are being considered and implemented. As mentioned before (Chapter 6), advanced control devices such as particulate traps are capable of removing solid refractory particles efficiently from vehicular emissions. However, they are not as effective in controlling volatile and semi volatile fractions, which forms fresh nucleation mode particles at lower tailpipe exit temperature (Chapter 6). As the current approach is to control only the refractory fraction of PM, major part of the potentially

harmful species remains unregulated. USC in collaboration with CARB has already started evaluating the toxicity of particles emitted downstream of advanced after treatment devices. These results will be reported in future publications. Besides these *in vitro* experiments, our research group is planning to move to the next level i.e. to perform *in vivo* chamber animal exposure experiments, designed to test the hypothesis that toxicity is mainly due to volatile nano-particles. Recently, USC is awarded a grant on a 3.5 years project to determine cardiopulmonary health effects of semi-volatile and non-volatile components of ultrafine PM. This project will examine in details the potential of these different PM fractions to induce oxidative stress and cause acute or chronic pulmonary and cardiovascular inflammation in mice. In addition, an interesting field campaign on measurement and modeling of in-vehicle air pollution exposure to commuters will be initiated soon. This study will further complement the freeway and dynamometer studies carried out so far. The in cabin number concentration is expected to be at elevated level with majority of the particles being composed of volatile and semi-volatile species. Although the air exchange rate is higher in vehicles under normal driving conditions, particle volatility will play key roles in determining exposure to the commuters. Depending on the age of the vehicles and driving conditions, it will be interesting to measure penetrability of volatile nano-particles and their toxicity.

Changes in particle characteristics

With the promulgation of new regulations, one can expect sea changes in particle characteristics in imminent future, as more and more old vehicles will be either phased out or retrofitted with control devices. Some of the freeway studies therefore, should be

repeated in the coming years to capture the progressively changing particle properties and investigate the fate of these new aerosols under atmospheric condition. A potent area of research will be to see whether these particles being volatile and insignificant in size are scavenged easily or grow to form larger accumulation mode particles.

Acidity

As most of the nuclei mode particles are predicted to be composed of sulfate in the form of pure sulfuric acid (Scheer et al., 2005), few experiments are necessary to determine the rate at which these acids get neutralized in freeway conditions and the extent of health hazard they pose to daily commuters. These experiments can be best accommodated with the in cabin on road exposure study described before.

Storage capacity of catalysts

Although majority of the advanced control devices enhanced nucleation, several of them on the contrary suppress this PM formation mechanism (Chapter 6). This phenomenon was attributed to the catalyst's initial storage capacity for sulfate. However, the hypothesis needs to be validated and complemented with further research in determining the point of saturation (mileage with respect to driving cycle) and identifying any detrimental effect on the catalysts performances. If these adsorbed sulfates can be periodically removed by regeneration techniques, there will be a significant achievement in reducing number emission.

Secondary aerosol formation

A study by Robinson et al. (2007) has shown that volatile species from diesel emissions are far more potent precursors for secondary aerosols than the widely published biogenic compounds. Thus, with respect to the future emission scenarios a study may be proposed to assess the effect of control devices on secondary organic aerosols formations and their toxicity after experiencing atmospheric reactions.

Emission inventory

Accurate emission factors (EF) are integral part of sound models for predicting future air pollution burden on atmosphere. With these emission control devices being used extensively in future, the existing models need to be upgraded and updated with new EFs. Also the relative contribution of molecular markers, used extensively in source apportionment techniques, is likely to change and should be part of the analysis process.

Global warming

The contribution of aerosols to global warming is still a “Puzzle” to scientists (Kiehl, 1999). Existing literatures and our preliminary findings suggest that sulfate will be the predominant chemical species (Grose et al., 2006) of diesel exhaust particles as most of the black carbons (BC) will be removed by traps. Black or elemental carbon is known to absorb sun light (Chameides and Bergin, 2002) where as sulfates scatter or reflect it. Few studies may be designed to predict the effect of changes in vehicular emission composition on the radiation balance.

Number EF: Particle measurement program (PMP)

Toxicity is likely to depend on the surface chemistry of particles (Maynard, 2006). In general, we observed higher nucleation mode particles for vehicles retrofitted with traps (Chapter 6) which will result in net surface area increase in future. Policy makers need to resolve whether surface area or particle number is a better metric than mass to indicate health hazards. Using the particle number as a regulatory tool has already been under consideration in some selected countries. For example, United Nations Economic Commission for Europe (UNECE) has taken an initiative to regulate solid particle number concentration through particle measurement program (PMP). However, there are serious drawbacks associated with this standard as most of the potentially harmful volatile particles remain unregulated. On the same line, California ARB is also evaluating the PMP for DPF equipped vehicles as an alternative measure to particle mass. In this approach, refractory particles are measured by heating and diluting exhaust particles through a secondary dilution system. PMP only considers particle larger than 20nm of size. The rationale to choose this size cut is to account for the accumulation mode particles assuming all particles below 20nm size are volatile. This is partially true as larger size particles (>20nm) may shrink below 20nm size during heating and dilution process without evaporating completely. Herner et al. (2007) estimated that particles <20nm contribute 25-75% of the total solid particle count determined after the PMP system. Thus, PMP should be modified to accommodate the larger particles which has solid cores coated with volatile substances and shrinks below 20nm size range during thermal treatment.

Air pollution in Asian mega cities

Majority of studies on particulate matter so far has been targeted to fulfill the need of developed countries. However, to accommodate the growing initiatives among policy makers and international organizations to curb air pollution related health risks, we envision considerable amount of research been diverted to characterize particulates in mega cities of developing nations. Some of the fast growing mega cities in Asia are among the most polluted in terms of airborne particulates. Although a number of studies has focused on PM as a whole (HEI, 2004), hardly any literature available on size fractionated particle characterization. Older buses and trucks, run by diesel fuel still constitute major fraction of the total traffic. As most of these vehicles are not fitted with any control devices, they emit significant amount of particulates, both in fine and ultrafine size ranges. The problem is compounded by frequent traffic congestions and mass use of “Auto rickshaw” (Gurjar et al., 2004). These auto-rickshaws are two stroke engines run by gasoline or on a mixture of petrol and kerosene.

Chapter 7 References

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Appendices: Additional Research Works

Appendix 1: A New Compact Aerosol Concentrator for Use in Conjunction with Low Flow-Rate Continuous Aerosol Instrumentation

Geller, M.D., **Biswas, S.**, Fine, P.M., Geller, M.D and Sioutas, C., *Journal of Aerosol Science*, 36(8):1006–1022, 2005.

Abstract: Currently available versatile aerosol concentration enrichment systems (VACES) have proven useful for providing elevated levels of ambient particulate matter to human and animal exposures, as well as for the collection of particles in aqueous solutions for in vitro studies. Previous studies have demonstrated that such systems do not significantly alter the physical or chemical properties of the particles. The current VACES configuration consumes significant electrical power for pumping and cooling, and requires attended operation by expert operators. A recent application of the VACES has been to provide a concentrated aerosol stream to continuous particle mass spectrometers in order to increase the spectrometer's hit rate or sensitivity. These instruments usually require low intake flow rates (< 1 l/ min) and often sample unattended, 24 h per day.

In order to better meet the requirements of these instruments, a new “mini-VACES” (m-VACES) system with a lower intake flow rate (30 l/min), a lower minor flow rate (1–1.5 l/min) and allowing for more automated operation was designed, built, and tested. The system is a scaled down version of the current VACES design, with many important

design improvements. Humidification of the air stream is achieved with a re-designed saturator consisting of a heated, moist absorbent material surrounding the intake flow. Cooling to achieve super saturation, and thus particle growth, is accomplished using a commercially available, solid-state, thermo-electric chiller. Once grown, the aerosol is concentrated using a new, smaller virtual impactor. Particles are then dried to their original size using a diffusion dryer filled with silica gel.

Results of the laboratory evaluation include close to predicted enrichment factors for laboratory-generated particles of different composition (ammonium nitrate, ammonium sulfate, adipic acid) as well as ambient aerosols. Particle size distributions measured by an SMPS before and after enrichment and drying show that particle size distributions are not altered. An APS provided data on the size distribution of particles after growth and concentration, but before drying. Filter based and continuous field experiments in which concentrated aerosol was compared to ambient outdoor levels also showed close to predicted enrichment factors for PM_{2.5} mass and black carbon, with no significant alteration of the particle size distribution.

Appendix 2:

Performance Evaluation of a Recently Developed Water Based Condensation Particles Counter

Biswas, S., Fine, P.M., Geller, M.D., Hering, S.V. and Sioutas, C. *Aerosol Science and Technology*, 39(5):419 – 427, 2005

Abstract: This study provides an inter comparison of the performance of a newly developed water-based condensation particle counter (WCPC) and a more widely used butanol-based CPC (TSI 3022A). Four test aerosols (ammonium nitrate, ammonium sulfate, adipic acid, and glutaric acid) were generated and tested in the laboratory before the instruments were deployed at four field locations (USC/downtown LA, I-710 Freeway, Pacific coast, and Los Angeles International Airport). Both instruments sampled the same incoming aerosol. Selected experiments utilized a differential mobility analyzer to select a particle size upstream of the CPCs. Evaluation of performance was based on the response of the instruments to varying particle composition, concentrations, and size. The results indicated good correlation between the two CPCs, with R^2 values ranging from 0.74–0.99. Good agreement was found between the two instruments for particle concentrations between 0 and 40,000 particles/cm³, with W-CPC/TSI 3022A ratios between 0.8 and 1.2. Due to differences in the photometric mode calibration of these instruments, the ratio drops to 0.6–0.8 between 40,000–100,000 particles/cm³. However, the ratio rises again for lab aerosols above 100,000 particles/cm³ to 1.0–1.1. Results of this evaluation show that the W-CPC is a reliable particle counting technology for particle concentrations encountered downstream of a DMA as well as in some ambient environments (<40,000 particles/cm³).

Appendix 3:

Real-time Characterization of Particle – Bound PAHs in Ambient Aerosols and from Motor – Vehicle Exhausts

Polidori, A., Hu, S., **Biswas, S.**, Delfino, R.J., Sioutas, C. Submitted to *Atmospheric Chemistry and Physics*, 2007.

Abstract: A photo-electric aerosol sensor, a diffusion charger, an Aethalometer, and a continuous particle counter were used along with other real-time instruments to characterize the particle-bound polycyclic aromatic hydrocarbon (p-PAH) content, and the physical/chemical characteristics of aerosols collected a) in Wilmington (CA) near the Los Angeles port and close to 2 major freeways, and b) at a dynamometer testing facility in downtown Los Angeles (CA), where 3 diesel trucks were tested. In Wilmington, the p-PAH, surface area, particle number, and “black” carbon concentrations were 4–8 times higher at 09:00–11:00 a.m. than between 17:00 and 18:00 p.m., suggesting that during rush hour traffic people living in that area are exposed to a higher number of diesel combustion particles enriched in p-PAH coatings. Dynamometer tests revealed that the p-PAH emissions from the “baseline” truck (no catalytic converted) were up to 200 times higher than those from the 2 vehicles equipped with advanced emission control technologies, and increased when the truck was accelerating. In Wilmington, integrated filter samples were collected and analyzed to determine the concentrations of the most abundant p-PAHs. A correlation between the total p-PAH concentration ($\mu\text{g}/\text{m}^3$) and the measured photo-electric aerosol sensor signal (fA) was also established. Estimated ambient p-PAH concentrations (Average = $0.64 \text{ ng}/\text{m}^3$; Standard deviation = $0.46 \text{ ng}/\text{m}^3$) were in good agreement with those reported in previous studies conducted in Los Angeles during a similar time period.

Finally, we calculated the approximate theoretical lifetime (70 years per 24-h/day) lung-cancer risk in the Wilmington area due to inhalation of multi-component p-PAHs and “black” carbon. Our results indicate that the lung-cancer risk is highest during rush hour traffic and lowest in the afternoon, and that the genotoxic risk of the considered p-PAHs does not seem to contribute to a significant part of the total lung-cancer risk attributable to “black” carbon.