#### INFLUENCE OF ATMOSPHERIC PROCESSES ON

### THE PHYSICO-CHEMICAL PROPERTIES OF PRIMARY PARTICLES AND THEIR IMPACT ON PUBLIC EXPOSURE

by

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Zhi Ning

### Dedication

To my parents

for their inseparable support without reserve and their lasting caring with gently love;

To my dear Jay

for her persistent love and confidence in me.

### Acknowledgements

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## **Table of Contents**

Dedication			ii
Acknowledge	ments		iii
List of Tables			ix
List of Figures	5		x
Abstract			xiii
Chapter 1	Introd	uction	1
1.1	Backgi	round	1
	1.1.1	Characteristics of atmospheric particulate matter	1
	1.1.2	Source of ambient particles and their atmospheric processes	3
	1.1.3	Health effects of particulate matter	4
1.2	Ration	ale of the current research	5
1.3	Thesis	overview	7
Chapter 2	Chara	cterization of atmospheric primary aerosols	10
<b>Chapter 2</b> 2.1	Chara Particle with he	cterization of atmospheric primary aerosols e concentration and characteristics near a major freeway eavy-duty diesel traffic	10 10
<b>Chapter 2</b> 2.1	Chara Particle with he 2.1.1	cterization of atmospheric primary aerosols e concentration and characteristics near a major freeway eavy-duty diesel traffic Abstract	10 10 10
Chapter 2 2.1	Chara Particle with he 2.1.1 2.1.2	cterization of atmospheric primary aerosols e concentration and characteristics near a major freeway eavy-duty diesel traffic Abstract Introduction	10 10 10 11
Chapter 2 2.1	<b>Chara</b> Particle with he 2.1.1 2.1.2 2.1.3	cterization of atmospheric primary aerosols e concentration and characteristics near a major freeway eavy-duty diesel traffic Abstract Introduction Materials and Methods	10 10 10 11 13
Chapter 2 2.1	<b>Chara</b> Particle with he 2.1.1 2.1.2 2.1.3 2.1.4	cterization of atmospheric primary aerosols e concentration and characteristics near a major freeway eavy-duty diesel traffic Abstract Introduction Materials and Methods Results	10 10 10 11 13 16
Chapter 2 2.1	Chara Particle with he 2.1.1 2.1.2 2.1.3 2.1.4	cterization of atmospheric primary aerosolse concentration and characteristics near a major freewayeavy-duty diesel trafficAbstractIntroductionMaterials and MethodsResults2.1.4.1Particle and co-pollutant concentrations nextto the freeway	10 10 11 13 16 16
Chapter 2 2.1	<b>Chara</b> Particle with he 2.1.1 2.1.2 2.1.3 2.1.4	cterization of atmospheric primary aerosolse concentration and characteristics near a major freewayeavy-duty diesel trafficAbstractIntroductionMaterials and MethodsResults2.1.4.1Particle and co-pollutant concentrations next to the freeway2.1.4.2Diurnal profiles	10 10 11 13 16 16 19
Chapter 2 2.1	Chara Particle with he 2.1.1 2.1.2 2.1.3 2.1.4	cterization of atmospheric primary aerosolse concentration and characteristics near a major freewayeavy-duty diesel trafficAbstractIntroductionMaterials and MethodsResults2.1.4.1Particle and co-pollutant concentrations next to the freeway2.1.4.2Diurnal profiles2.1.4.3Comparison with previous studies	10 10 10 11 13 16 16 19 23
Chapter 2 2.1	<b>Chara</b> Particle with he 2.1.1 2.1.2 2.1.3 2.1.4	cterization of atmospheric primary aerosolse concentration and characteristics near a major freewayeavy-duty diesel trafficAbstractIntroductionMaterials and MethodsResults2.1.4.1Particle and co-pollutant concentrations next to the freeway2.1.4.2Diurnal profiles2.1.4.3Comparison with previous studies2.1.4.4Particle size distributions	10 10 11 13 16 16 16 19 23 26
Chapter 2 2.1	<b>Chara</b> Particle with he 2.1.1 2.1.2 2.1.3 2.1.4	cterization of atmospheric primary aerosolse concentration and characteristics near a major freewayeavy-duty diesel trafficAbstractIntroductionMaterials and MethodsResults2.1.4.1Particle and co-pollutant concentrations next to the freeway2.1.4.2Diurnal profiles2.1.4.3Comparison with previous studies2.1.4.4Particle size distributions2.1.4.5Statistical processing of sampled variables	10 10 11 13 16 16 16 19 23 26 29
Chapter 2 2.1	<b>Chara</b> Particle with he 2.1.1 2.1.2 2.1.3 2.1.4	cterization of atmospheric primary aerosolse concentration and characteristics near a major freewayeavy-duty diesel trafficAbstractIntroductionMaterials and MethodsResults2.1.4.1Particle and co-pollutant concentrations next to the freeway2.1.4.2Diurnal profiles2.1.4.3Comparison with previous studies2.1.4.4Particle size distributions2.1.4.5Statistical processing of sampled variablesAcknowledgments	$ \begin{array}{c} 10\\ 10\\ 10\\ 11\\ 13\\ 16\\ 16\\ 19\\ 23\\ 26\\ 29\\ 32\\ \end{array} $
2.1 2.2	<b>Chara</b> Particle with he 2.1.1 2.1.2 2.1.3 2.1.4 2.1.5 Fine, u	cterization of atmospheric primary aerosolse concentration and characteristics near a major freewayeavy-duty diesel trafficAbstractIntroductionMaterials and MethodsResults2.1.4.1Particle and co-pollutant concentrations next to the freeway2.1.4.2Diurnal profiles2.1.4.3Comparison with previous studies2.1.4.4Particle size distributions2.1.4.5Statistical processing of sampled variables Acknowledgments	10 10 11 13 16 16 19 23 26 29 32 33
2.1 2.2	Chara Particle with he 2.1.1 2.1.2 2.1.3 2.1.4 2.1.5 Fine, u major f	cterization of atmospheric primary aerosolse concentration and characteristics near a major freewayeavy-duty diesel trafficAbstractIntroductionMaterials and MethodsResults2.1.4.1Particle and co-pollutant concentrations next to the freeway2.1.4.2Diurnal profiles2.1.4.3Comparison with previous studies2.1.4.4Particle size distributions2.1.4.5Statistical processing of sampled variablesAcknowledgmentsAltrafine and nanoparticle trace organic compositions near a freeway with a high heavy duty diesel fraction	10 10 11 13 16 16 16 19 23 26 29 32 33
<b>Chapter 2</b> 2.1 2.2	<b>Chara</b> Particle with he 2.1.1 2.1.2 2.1.3 2.1.4 2.1.5 Fine, u major f 2.2.1	cterization of atmospheric primary aerosolse concentration and characteristics near a major freeway eavy-duty diesel traffic AbstractAbstractIntroductionMaterials and MethodsResults2.1.4.1Particle and co-pollutant concentrations next to the freeway2.1.4.2Diurnal profiles2.1.4.3Comparison with previous studies2.1.4.4Particle size distributions2.1.4.5Statistical processing of sampled variables AcknowledgmentsAcknowledgmentsAcknowledgmentsAcknowledgmentsAbstract	10 10 10 11 13 16 16 16 19 23 26 29 32 33 33

	2.2.3	Methods		36
		2.2.3.1	Site description	36
		2.2.3.2	Sampling protocol	37
		2.2.3.3	Sample analysis	39
	2.2.4	Results an	nd discussion	41
		2.2.4.1	Accumulation and ultrafine chemical composition	41
		2.2.4.2	Size-segregated ultrafine particle chemical composition	43
		2.2.4.3	Particle acidity	46
		2.2.4.4	Normalized size distribution of PAHs, hopanes and steranes.	48
	2.2.5	Summary	and conclusions	53
	2.2.6	Acknowle	edgments	54
Chapter 3	Effect of fuel-ba	of dilution sed PM en	on primary particles by the investigation of nission factors	55
3.1	Abstra	ct		55
3.2	Introdu	uction		56
3.3	Experi	mental met	hods	58
	3.3.1	Sampling	locations	58
	3.3.2	Sampling	and analysis	60
	3.3.3	Emission	factors from roadway measurements	61
	3.3.4	Reconstru	cted emission factors	63
3.4	Results	s and Discu	ission	64
	3.4.1	Comparis factors fo	on of roadway and reconstructed tunnel emission r particle number and other chemical species	64
	3.4.2	Comparis factors fo	on of roadway and reconstructed tunnel emission r organic tracers	68
	3.4.3	Comparis elemental	on in emission factors for trace elements, metals, and organic carbon	74
	3.4.4	Comparis and sterar	ons in the emission factors of PAHs, hopanes	80
3.5	Summa	ary and Co	nclusions	84
3.6	Acknow	wledgment	S	85
Chapter 4	Photoc in the a	chemical re atmospher	eactions and formation of secondary aerosols re	86
4.1	Daily v aerosol	variation in	physical characterization of urban ultrafine	86
	4.1.1	Abstract		86
	4.1.2	Introducti	on	86

	4.1.3	Experime	ntal Methods	90
		4.1.3.1	Site Meteorology	91
		4.1.3.2	Gas composition measurements	91
		4.1.3.3	Aerosol measurements - Continuous measurements	91
		4.1.3.4	Aerosol measurements - Intermittent measurements	92
	4.1.4	Results an	nd Discussion	93
		4.1.4.1	Meteorology	93
		4.1.4.2	MOUDI/SMPS mass concentration comparison	94
		4.1.4.3	Hourly average gas- and aerosol-phase concentrations	95
	4.1.5	Conclusio	ons	100
	4.1.6	Acknowle	edgements	101
4.2	Daily	variation in	chemical characteristics of urban ultrafine	102
	aeroso	ls and infer	ence of their sources	
	4.2.1	Abstract		102
	4.2.2	Introduct	lon	103
	4.2.3	Experime	intal methods	105
		4.2.3.1	Sampling location	105
		4.2.3.2	Sampling protocol	106
		4.2.3.3	Sample analysis	107
	4.2.4	Results a	nd discussion	109
		4.2.4.1	Mass concentration and mass balance	109
		4.2.4.2	Inorganic Ions	113
		4.2.4.3	Carbonaceous compounds	117
		4.2.4.4	Organic speciation	119
	4.2.5	Acknowle	edgement	123
Chapter 5	Atmos their i	spheric pro mpact on 1	ocesses of primary particles and inference to public exposure	124
5.1	Abstra	ict	Γ	124
5.2	Introd	uction		125
5.3	Atmos	spheric proc	esses and combustion related aerosols	127
	5.3.1	Nucleatio	n and condensation	128
	5.3.2	Role of at	tmospheric dilution	131
		5.3.2.1	Dilution effects on non-labile PM components	132
		5.3.2.2	Dilution effects on semi-volatile PM Components	133

	5.3.3 Photochemical reactions of primary emissions and secondary aerosol formation	142
5.4	PM volatility and its impact on public exposure health	147
Chapter 6	Conclusions and future recommendation	152
6.1	Conclusions	152
6.2	Discussion and future recommendations	153
Bibliography		157
Appendix		176

## **List of Tables**

Table 2-1:	Instrumentation used and species measured during the study.	15
Table 2-2:	Summary of particle and copollutant levels next to the freeway for the three cases: campaign, a rainy day, and a day when the freeway was closed.	17
Table 2-3:	Comparison of concentrations in different studies involving heavy- duty diesel vehicle traffic. Underlined values have been corrected for the different dilution ratios, calculated on the basis of the $CO_2$ concentrations.	23
Table 2-4:	Multiplication coefficients for the standardized independent variables used to formulate the reconstructed concentrations.	30
Table 2-5:	Meteorological and traffic data in the sampling site.	37
Table 2-6:	Comparison of mass fraction of PAHs in segregated particles to the study by Riddle et al (Riddle et al., 2007)	50
Table 2-7:	Comparison of mass fraction of Hopanes in segregated particles to the study by Riddle et al (Riddle et al., 2007)	52
Table 3-1:	Emission factors (expressed in mg kg-1 of fuel burned, or particle kg-1 of fuel burned) of particle number (PN), $PM_{2.5}$ mass, organic and elemental carbon (OC and EC, respectively), sulfate and metals at the CA-110 and the I-710 sites	65
Table 3-2a:	Emission factors of PAHs, Hopanes and Steranes analyzed in $PM_{2.5}$ samples collected at the freeway (I-710)	69
Table 3-2b:	Emission factors of PAHs, Hopanes and Steranes analyzed in $PM_{2.5}$ samples collected at the freeway (CA-110)	70
Table 4-1:	Observations summary	90
Table 4-2:	Meteorological parameters and measured gases concentrations in the morning and afternoon periods during the study	110
Table 5-1:	Comparison of concentrations at different environments (Ntziachristos et al.,2007)	133

# **List of Figures**

Figure 1-1:	Typical particle size distributions by number, surface area, and mass	2
Figure 2-1:	Sampling site in the proximity of the I-710 freeway	13
Figure 2-2:	Diurnal profile of measured variables normalized over the maximum hourly value recorded (given in the legend within parentheses). (a) meteorological conditions, (b) traffic data, (c) particle physical parameters, (d) particle chemical parameters.	22
Figure 2-3:	Particle size distributions near freeway (a) Mean geometric hourly size distributions measured during the seven-week campaign; (b) Comparison of the grand average size distribution measured next to the freeway with typical exhaust size distributions of two heavy duty vehicles measured in the laboratory; (c): Effect of individual events on the particle size distributions.	27
Figure 2-4:	Fractions of chemical species in total mass of (a) accumulation particles (b) ultrafine particles at freeway and background site	42
Figure 2-5:	Size distribution of particle mass concentration (0.018 <dp<2.5 <math="">\mum)</dp<2.5>	44
Figure 2-6:	Chemical mass balance of segregated ultrafine particles	45
Figure 2-7:	Ratio of measured to required ammonium for neutralization at freeway and background sites. (BG: background; FW: freeway; A: accumulation; UF: ultrafine)	46
Figure 2-8:	Normalized size distribution of PAHs measured at near freeway site.	50
Figure 2-9:	Normalized size distribution of hopanes/steranes measured near freeway	52
Figure 3-1:	Comparison among measured and reconstructed emission factors of elemental carbon (EC), sulfate and particle number (PN) from the I-170 freeway (1a) and the CA-110 highway (1b). Particulate EC results are reported in both fine and ultrafine (UF) modes.	66
Figure 3-2:	Comparison among the emission factors of PAHs reconstructed from tunnel measurements and those estimated at the I-710 freeway (2a) and at the CA-110 highway (2b).	71
Figure 3-3:	Comparison among the $PM_{2.5}$ emission factors of hopanes and steranes reconstructed from tunnel measurements and those estimated at the I-710 freeway (a) and at the CA-110 highway (b).	73

Figure 3-4:	Comparison among $PM_{2.5}$ emission factors of organic and elemental carbon (OC and EC, respectively), metals and trace elements from roadway measurements and tunnel and dynamometer studies.	76
Figure 3-5:	Comparison among $PM_{2.5}$ emission factors of PAHs, hopanes and steranes for HDVs (a) and LDVs (b) from roadway measurements and tunnel and dynamometer studies. All values are expressed in mg kg <sup>-1</sup> of fuel burned.	83
Figure 4-1:	MOUDI- and SMPS-derived ultrafine mass concentrations by week (week 1: 28–30 June, 5–6 July; week 2: 7, 10–13 July; week 3: 14, 17–20 July; week 4: 21, 24–27 July 2007). The error bars show the standard error of the mean.	94
Figure 4-2:	Selected representative (CO, NOx, PM2.5, black carbon (BC)) hourly average gas and aerosol data. The error bars show the standard error of the mean.	95
Figure 4-3:	Hourly mean ultrafine aerosol number concentration contour plot (monthly average), dN/d(log dp).	97
Figure 4-4:	Hourly mean $O_3$ , NOx, temperature and ultrafine aerosol number concentrations (monthly average). The error bars show the standard error of the mean	98
Figure 4-5:	Hourly mean nucleation ( $V_{\text{UFN}}$ , <50 nm) and accumulation ( $V_{\text{UFA}}$ , 50–180 nm) mode ultrafine particle volume, accumulation mode ( $V_{\text{A}}$ , 180–2500 nm) particle volume and black carbon concentrations (monthly average). The error bars show the standard error of the mean.	99
Figure 4-6:	Weekly and average mass concentrations of ultrafine (U) particles and mass balance of measured species in the morning (AM) and afternoon (PM).	111
Figure 4-7:	Mass fractions of sulfate, nitrate and ammonium in total mass of ultrafine (U) particles in the morning (AM) and afternoon (PM) periods.	114
Figure 4-8:	Weekly and average ratios of measured ammonium to required ammonium concentration for complete neutralization of ultrafine (U) and accumulation (A) particles in the morning (AM) and afternoon (PM) periods.	116
Figure 4-9:	Average OC and EC concentrations of ultrafine (U) & accumulation (A) particles in the morning (AM) and afternoon (PM).	118

- Figure 4-10: Average organic species concentration of ultrafine particles in the morning and afternoon: (a) n-alkanes; (b) PAHs; (c) Hopanes and Steranes; (d) Organic acids.
- Figure 5-1: Number and mass emission factors from different vehicles (Biswas et 128 al., 2008)
- Figure 5-2: Particle size distributions at different sampling locations near freeway 129 (Zhu et al., 2002)
- Figure 5-3: Fuel-based OC and EC emissions from low-load diesel (left column), 132 medium-load diesel (middle column), and wood smoke (right column) experiments (Lipsky and Robinson, 2006).
- Figure 5-4: Normalized particle number concentration from different size ranges 135 as a function of distance from the 710 freeway (Zhu et al., 2002)
- Figure 5-5: Distance and fuel-based particle number emission factors in Highway 137 405 summer (a) and winter (b) studies. The error bars only denote those of distanced-based emission factors (Zhang et al., 2005).
- Figure 5-6: Fuel-based organic aerosols emission factor as a function of their 139 concentrations and dilution ratios (Robinson et al., 2007)
- Figure 5-7: Fuel-based emission factors of PAHs, hopanes and steranes in various 141 environments with different dilution conditions (Ning et al., 2008).
- Figure 5-8: Average PAHs (a), n-alkanes (b), organic acids (b) concentrations of 145 ultrafine particles in the morning (AM) and afternoon (PM) (Ning et al., 2007).
- Figure 5-9: Predicted SOA fractions in OA from traditional and revised models, 147 and their comparison with ambient measurement data (Robinson et al., 2007)
- Figure 5-10: Relationship between redox activity and semi-volatile PM fraction 149 (Biswas et al., 2008)
- Figure 5-11: Redox activity from various studies with respect to atmospheric 150 dilution ratio (Biswas et al., 2008)

### Abstract

Primary sources, especially vehicle emissions, are the dominant contributors of ambient particulate matter (PM) in urban environments. Upon their emissions from primary sources, ambient PM undergoes various atmospheric processes which may alter their physic-chemical and toxicological properties before the exposure to the public. This thesis first investigates the physic-chemical properties of ambient ultrafine aerosols characterized as from primary source in the immediate vicinity of a major freeway in Los Angeles. Then the thesis examines the atmospheric processes (dilution and photochemical oxidation) that dominate the dynamics of primary aerosols following their emission. Atmospheric dilution affects the dynamic behavior of aerosols by affecting the ambient concentration levels of non-labile PM species and also shifting the gas-particle partitioning of the semivolatile PM component. This study discusses the roles of dilution in changing the physico-chemical properties of the ambient aerosols by comparing the normalized fuel-based emission factors of various PM species. This information is complemented with an investigation of secondary aerosol formation from atmospheric photochemical reactions that alters the PM volatility, solubility and chemical properties. Based on the experimental investigation, the thesis reviews the recent findings that link PM semi-volatile components and their redox activity, and also discusses the influence and importance of PM volatility on particle toxicity. Lastly, this thesis discusses possible metrics to regulate PM emissions and establish ambient air quality standards that are pertinent to public health, and suggests future investigations aimed to improve our current understanding of the adverse health effects of public exposure to ambient aerosols.

### **Chapter 1 Introduction**

#### 1.1 Background

#### **1.1.1** Characteristics of atmospheric particulate matter

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. Particles have different chemical composition, sizes and shapes (e.g. spheres, cylinders, plates, or combinations of these shapes).

The size of the particles is one of the most influential characteristic of particles in context of their behavior and health outcome, which is usually identified by aerodynamic diameter. Aerodynamic diameter is a diameter of a sphere that behaves aerodynamically like the actual particle. This aerosol particulate matter is divided into different groups based on their aerodynamic diameter. Particles with aerodynamic diameter larger than 10 microns are usually not the point of interest in environmental and health studies because of their short life time in the atmosphere and their deposition efficiency of about 100% in the nose (Hinds 1982).  $PM_{10}$ , generally defined as all particles equal to and less than 10 microns in aerodynamic diameter, are inhale-able and important to air pollution and exposure studies. These particles are grouped into two different size ranges,  $PM_{2.5}$ , i.e., particles with an aerodynamic diameter less than 2.5  $\mu$ m, and particles with aerodynamic diameter between 2.5 and 10  $\mu$ m, these particles are named "fine" and "coarse" PM respectively. Fine particles has a high residence time, of order of days to weeks, and can travel long distances, while most coarse particles typically deposit to the earth within minutes to hours and within tens of kilometers from the emission source (Hinds 1982). The fine particles are further grouped into two groups: particles with a diameter of less than about 180 nm are considered as the ultrafine particle fraction (UFP) whereas the range between 180 nm to 2.5  $\mu$ m is referred to as the accumulation mode (Ibald-Mulli et al. 2002). Typical particle size distribution is presented in Figure 1-1, which shows that ultrafine particles dominate the number distribution while accumulation mode particles dominate the mass distribution.



Figure 1-1 Typical particle size distributions by number, surface area, and mass

#### 1.1.2 Source of ambient particles and their atmospheric processes

Particles in the atmosphere can also be divided into two broad categories based on their sources: primary and secondary particles. Primary particles are directly emitted from combustion sources, such as light-duty and heavy-duty vehicles, wood smoke, off- road vehicles, oil combustion of refineries and marine vessels, and stationary sources, such as power plants. In urban areas, vehicular emissions constitute the majority of the primary particles in the atmosphere. These particles are mostly sub-micrometer agglomerates of solid carbonaceous materials residing mainly in accumulation mode (Morawska et al. 2008). Secondary particles are largely composed of sulfate, nitrate, ammonium and secondary organic aerosols (SOA). The inorganic secondary aerosols are formed in the atmosphere from the oxidation of gas-phase precursors such as sulfur dioxide  $(SO_2)$ (Seinfeld and Pandis 1998), nitric oxide (NO) and nitrogen oxides (NO<sub>x</sub>) (Pinder et al. 2004). By comparison, SOA formation mechanisms have not been fully understood. Generally, SOA may be formed by the oxidation of high molecular weight volatile organic compounds (VOCs) to produce low-volatility products, which subsequently condense onto the existing aerosols (Seinfeld and Pandis 1998). Particle phase heterogeneous reactions, including those occurring in clouds and fog, may also contribute the SOA formation in the atmosphere (Jang and Kamens 2001; Jang et al. 2003). Moreover, the gas-particle partitioning of semi-volatile organic aerosols may produce the gas-phase organic compounds in the atmosphere, which subsequently participate in the SOA formation (Robinson et al. 2007).

Atmospheric dynamic processes change the physical and chemical characteristics of combustion generated aerosols after their emission in the atmosphere. Particles from vehicle emissions often display a bi-modal size distribution with a large number fraction of the particles residing in nucleation mode ( $d_p < 30$  nm) (Kittelson 1998). Ambient measurements showed similar bimodal distributions in the proximity of freeways with diesel traffic (Zhu et al. 2002a; Ntziachristos et al. 2007c) or when following a diesel vehicle on the road (Vogt et al. 2003; Ronkko et al. 2006). The profile of ambient particle size distribution tends to change significantly with elevated numbers of nucleation mode particles during photochemical episodes due to the formation of secondary aerosols (Moore et al. 2007). Photochemical reactions in the atmosphere also lead to the alteration of particle chemical composition, thus creating seasonal and diurnal variations in the chemical characteristics of ambient aerosols. This review discusses the major atmospheric processes that dominate the dynamics of combustion related aerosols and synthesizes the current understanding of particles toxicity in the context of their adverse health effect of public exposure.

#### **1.1.3** Health effects of particulate matter

Ambient aerosol research has been motivated by many purposes and prominent among these are the impacts of atmospheric aerosols on human health. In the last decades, several epidemiological studies have linked adverse health effects of populations exposed to increased ambient fine ( $d_p$ <2.5 µm) and ultrafine particles (UFP) ( $d_p$  <180 nm) concentrations (Dockery et al. 1993; Laden et al. 2000; Peters and Pope 2002; Schulz et al. 2005). Particle size determines its deposition site and fraction in human lungs and its potential translocation to other target organs (Donaldson et al. 2000; Oberdorster 2003; Kreyling et al. 2006). Ultrafine particles dominate ambient particle number concentrations but contribute very little to the total mass. Several studies, however, suggest that UFP disproportionately induce oxidative stress in cells and are more toxic compared to larger particles of similar composition (Li et al. 2003; Nel 2005). For example, due to their small size, direct cellular uptake of UFP is possible as well as translocation to other sensitive target organs such as the heart and central nervous system (Oberdorster et al. 2005).

Particle composition, and surface area are also possible metrics affecting the health outcomes associated with UFP, although the dominant mechanisms for these outcomes remain largely unknown (Nel 2005). Particle toxicity studies have also linked individual particle chemical components with different adverse health effect. Organics and transition metal PM components have been identified as capable of inducing proinflammatory effects in the lung due to their ability to produce oxidative stress (Nel et al. 1998; Saldiva et al. 2002). Polar organic compounds such as quinones can act as catalysts to produce reactive oxygen species (ROS) directly (Monks et al. 1992) whereas polycyclic aromatic hydrocarbons (PAHs) can induce oxidative stress indirectly, through biotransformation to generate redox active quinones (Penning et al. 1999).

#### **1.2** Rationale of the current research

Epidemiological studies initially showed an association between exposure of particulate matter (PM) in the atmosphere and human mortality. Further investigation found

exposure to ultrafine particles is also associated with human adverse health (Nel 2005). Particle toxicity studies have also linked individual particle chemical components with different adverse health effect (Nel et al. 1998; Saldiva et al. 2002). These findings have raised considerable concern about human exposure to  $PM_{2.5}$  and ultrafine particles in urban area with vehicle emissions as the dominant primary particle sources. My endeavor in this thesis is to characterize the atmospheric ultrafine particles primarily emitted from vehicles including particle size distribution; mass concentrations and size resolved ultrafine particle chemical and organic compositions. The investigation was carried out near major freeways in Southern California which represent the typical source of primary particles in urban atmosphere.

Primary aerosols, especially vehicular PM emissions, are the dominant sources of ambient aerosols in the urban atmosphere. Upon emission from the vehicle tailpipes, the gas- particle mixture of exhaust undergoes various atmospheric dynamic processes, which change the physical and chemical characteristics of the ambient aerosols. These processes include dilution, evaporation and possible re-condensation of organic vapors onto pre-existing PM, and secondary aerosols formation, all of which control the dynamics of the exhaust mixtures shortly after their emissions from vehicles.

This research investigated the evolution of particle physicochemical properties with respect to changing environmental conditions, including dilution as well as photochemical reactions. For non-labile PM species, dilution changes their atmospheric concentrations in the ambient by dispersion. During dilution and cooling, gaseous precursors nucleate or condense onto pre-existing particles. For semi-volatile aerosols, dilution affects their gas-particle phase partitioning and alters the physical (size distribution, concentrations etc) and chemical properties (semi-volatile fraction) of the aerosol. With the presence of photo oxidants in the atmosphere, secondary inorganic aerosols, such as sulfate, nitrate and ammonium are formed, and secondary organic aerosols (SOA) are also produced by photo oxidation of gas phase volatile organic compounds (VOC) in the atmosphere.

Semi-volatile PM contains a wide variety of organic compounds and their fraction in the total PM determines their overall toxicological potency, thus their ability to induce adverse health effects. Recent toxicity studies have shown a direct correlation between the semi-volatile PM fraction and PM redox activity, indicating the significance of PM volatility in effecting public exposure to ambient aerosols. This research reviewed this relationship that is reflected in the correlation between ambient dilution ratio, which affects the fraction of semi-volatile species in total PM, and their redox activity.

#### **1.3** Thesis overview

This thesis summarizes of the research work during my Ph. D study in the past years aiming to consolidate the current understanding of the characterization of the atmospheric primary aerosols from vehicles emissions, to investigate the principle atmospheric transformation processes that affect the solid and semi-volatile components of the primary aerosols, and to discuss the inference of such atmospheric processes to the public exposure. Finally, the thesis discusses possible metrics to regulate PM emissions and establish ambient air quality standards that are pertinent to public health, and suggests future investigations aimed to improve our current understanding of the adverse health effects of population exposure to combustion -generated aerosols.

Chapter 1 provides a general overview on air pollution of atmospheric aerosols, the significance and characteristics of particles and particle related health effects. It also identifies the rationale of this thesis and outlines a brief layout.

Chapter 2 describes the physical and chemical characteristics of the primary aerosols in the atmosphere measured at an immediate adjacent location downwind of a major freeway in Southern California with a high fraction of diesel trucks. This chapter is constituted of two sections of: 1. the particle size distributions, number concentrations and chemical components concentrations; and 2. the size segregated fine, ultrafine and nanoparticles trace organic compositions of the measure aerosols characterized of the primary emissions from the freeway.

Chapter 3 proposes a methodology to quantify the fuel based PM species emission factors based on the freeway measurement by normalizing the fuel carbon content and the dilution conditions with the measured PM species concentrations. By investigating the fuel based emission factors of non-labile and semi-volatile components of the aerosols measure near freeway, and comparing the results with the different dilution conditions from chassis dynamometer and tunnel environment studies, this chapter attempts to depict the effect of dilution conditions on the characteristics of primary aerosols. Chapter 4 presents the observation of secondary in-organic and organic aerosols formation as the products of photochemical reactions in the atmosphere. This study was carried out by investigating the diurnal profiles of ultrafine particles physical and chemical characteristics during morning rush hour with vehicle emissions as dominant source and during afternoon periods with representative photo-oxidation episodes. Measured gases concentrations, particle size distributions, inorganic ions, and organic species concentrations showed different profiles during morning and afternoon periods indicating the effect of photochemical reactions on the alternation of properties of primary aerosols.

Chapter 5 summarizes the previous investigation of atmospheric processes that dominate the dynamics of primary aerosols following their emissions from mobile sources, and their effect on the characteristics of atmospheric aerosols with a particular focus on the PM semi-volatile components. Following this discussion, the chapter reviews the recent findings that link PM semi-volatile components and their redox activity, and the influence and importance of PM volatility on particle toxicity.

Chapter 6 discusses possible metrics to regulate PM emissions and establish ambient air quality standards that are pertinent to public health, and suggests future investigations aimed to improve our current understanding of the adverse health effects of population exposure to combustion -generated aerosols.

# Chapter 2 Characterization of atmospheric primary aerosols

#### 2.1 Particle concentration and characteristics near a major freeway with heavyduty diesel traffic

#### 2.1.1 Abstract

This study presents the number and surface concentration and size distribution of particles next to the I-710 freeway during February and April 2006. I-710 has the highest ratio (up to 25%) of heavy duty diesel vehicles in the Los Angeles freeway network. Particle concentration measurements were accompanied by measurements of black carbon, elemental and organic carbon and gaseous species (CO, CO<sub>2</sub>). Using the incremental increase of CO<sub>2</sub> over the background as an indication of the dilution ratio, the study makes possible to compare particle concentrations measured by the freeway to concentrations measured in road tunnels and in the laboratory. A principal component analysis on the measurements showed that the volume of the accumulation mode (40-640 nm) is positively correlated with the black carbon concentration, which is evident of the diesel truck operation, while the volume of nucleation mode (16-40 nm) mostly depends on ambient conditions and increases in the evening as the temperature and the ambient mixing layer decrease. In addition, multivariate regressions showed that light and heavy organic carbon concentrations are positively correlated with the particle volume in the nucleation and accumulation modes respectively. The results of this study may be used to predict the effect of vehicle technology and ambient condition variations on the particle size distribution and concentration next to major freeways.

#### 2.1.2 Introduction

Various epidemiological studies have concluded that a positive correlation exists between airborne particulate matter (PM) and adverse effects on human health (Dockery et al. 1993; Pope et al. 1995; Vedal 1997). Recent toxicological studies corroborate these findings both in vitro and in vivo (Becker et al. 2003; Li et al. 2003; Kleinman et al. 2005). With respect to specific PM sources, the California Air Resources Board has labeled diesel exhaust as a toxic air contaminant due to its carcinogenicity (CARB 1998). Although this compelling evidence exists, the causal mechanisms behind these toxic responses remain uncertain. Consequently, which metric of PM—mass, surface area, or number of particles—most responsible for toxicity is unknown. However, ultrafine particles ( $d_p$ <100 nm) elicit a higher adverse response per unit mass than fine ( $d_p < 2.5$ µm) and coarse particles (2.5 µm< $d_p$  <10 µm) (Donaldson et al. 2001; Oberdorster 2001).

Dynamometer experiments have shown motor vehicles to emit high concentrations of particles by number, and heavy-duty diesel vehicles without particle traps, in particular, emit high PM mass concentrations (Maricq et al. 1999b; Ntziachristos et al. 2006). Many such tests have determined that size distributions of particles from diesel and gasoline engines are typically between 20-130 nm and 20-60 nm, respectively. Recently, sampling conducted in freeway microenvironments also has confirmed high concentrations of PM due to motor vehicles (Zhu et al. 2004; Westerdahl et al. 2005). Zhu et al. (2004) found that particle number concentration was highly influenced by distance from the freeway, with a large spike in number next to the roadway that decays to background levels within 100 m.  $PM_{2.5}$  (particulate matter less than 2.5  $\mu$ m in

aerodynamic diameter) mass concentration was nearly unaffected over the same distances. The Westerdahl et al. study (2005) reported concentrations of PM and various copollutants while driving on various roads and highways. Concentrations on some of the freeways sampled in that study peaked as high as 240,000 particles/cm<sup>3</sup>. Thus, it has been suggested that exposure to motor vehicle exhaust emissions during commute constitutes a large fraction of one's daily personal PM exposure.

The vast freeway network in Los Angeles accommodates over six million registered vehicles. Therefore, it is reasonable that most PM<sub>2.5</sub> originates from vehicles, which has been proven in urban areas (Schauer et al. 1996; Hitchins et al. 2000). This PM is both directly emitted, via combustion and mechanical wear, and formed via secondary reactions of direct emissions, whereby organic and inorganic vapors undergo gas-toparticle conversion in the atmosphere (Shi and Harrison 1999; Cyrys et al. 2003). Roadways with high heavy-duty diesel traffic have been shown to have elevated particle number and mass concentrations, especially that of black carbon (Westerdahl et al. 2005). The goal of this study is to provide detailed information on the physical and chemical characteristics of particles originating from a major freeway during the winter season with a significant fraction of heavy duty diesel vehicles. This was accomplished by measuring semi-continuous and time-integrated particle number, surface area, mass and chemistry adjacent to I-710 from February to April 2006. Data at this location and season were then compared to recent data from an on-road study on the same freeway and a recent study performed at a roadway tunnel in northern California.

#### 2.1.3 Materials and Methods

The I-710 freeway is a 26 m wide eight-lane highway connecting the ports complex of Long Beach and San Pedro to the shipping yards in East Los Angeles. For this reason, as much as 25% diesel traffic has been reported on this freeway (http://traffic-counts.dot.ca.gov). Total traffic counts are also very high, with between 150,000 and 200,000 vehicles per day passing the sampling location. The sampling site was located in a paved property run by the Imperial Flood Control Yard in South Gate, CA. This location shown in Figure 2-1, is directly adjacent to the roadway with no other immediate sources either upwind or downwind. Just downwind of the site are a bike path and the Los Angeles River, a concrete lined drainage channel.



Figure 2-1 Sampling site in the proximity of the I-710 freeway

To ensure that sample probes were within the plume of the freeway, wind speed and direction were monitored with a portable weather station (Monitor II, Weather Systems Company, San Jose, CA). This instrument also recorded local temperature and relative

humidity. Data were logged over 5 min intervals during the entire study. The monitor was located 2 m above the ground, and direction was calibrated daily by aligning the weather vane with a compass.

Traffic data were collected by two methods that were used to create a comprehensive traffic profile. Total traffic volume (including all vehicle types) and average vehicle speed were obtained from the California Department of Transportation (Caltrans, www.dot.ca.gov), which has vehicle loop sensors positioned along the freeway at a location within a mile of the sampling site. Manual and videotaped counts were also taken for 1 min out of every 5 min during randomly selected sampling intervals. Estimates of traffic counts broken down by vehicle type were done by analyzing the videotapes and counting the number of axles per vehicle. Both gaseous and particulate pollutant concentrations were measured with various continuous and time-integrated instruments, approximately 10 m from the shoulder of the freeway. The prevailing southwesterly winds transported the fresh freeway emissions to the sampling location. Instruments were located in a retrofitted box truck that was driven to the site each day. Copper and antistatic tubes were extended approximately 1 m above the truck's roof to ensure representative sampling. Tubing diameter was chosen such that the approximate residence time was less than 1 s in the sampling lines.

Instrument	Model/Manufacturer	Species Sampled
Q-Trak Plus	8554, TSI Inc.	CO, CO <sub>2</sub> , Temperature, Relative Humidity
SMPS	3936L, consisting of DMA 3081L and CPC 3022A, TSI Inc.	Particle number/size distribution (16-638 nm mobility)
СРС	3022A, TSI Inc.	Number concentration (>6 nm mobility)
APS	3020A, TSI Inc.	Particle number/size distribution (0.7-2.5 µm aerodynamic)
NSAM	3550, TSI Inc.	Particle active surface concentration (<~1 μm aerodynamic)
OC/EC	3F/Sunset Labs Inc.	Organic and elemental carbon
Aethalometer	AE-20/Anderson Instruments Inc.	Black carbon

Table 2-1Instrumentation used and species measured during the study.

Table 2-1 lists the instruments used in this study and the species sampled. The continuously measured gas species included carbon monoxide (CO) and carbon dioxide (CO<sub>2</sub>). CO/CO<sub>2</sub> measurements were recorded with handheld air quality monitors (Q-Trak Plus). The Q-Traks were calibrated both before and during the study period by performing zero and span checks, with gas standards provided by the manufacturer. Additionally, the Q-Traks were frequently connected to zero and span gases to confirm that no drift was occurring over the course of the study. Particle size distributions in the range 16 to 638 nm (mobility diameter) were recorded every 120 s by a Scanning Mobility Particle Sizer (SMPS), using a sample flowrate of 0.3 L min<sup>-1</sup> and a sheath flow rate of 3.0 L min<sup>-1</sup>. A Condensation Particle Counter (CPC) recorded continuous total particle counts. Particle number and mass (by assuming an average density of 1.0 g cm<sup>-3</sup>) concentrations in the range of 0.7-2.5  $\mu$ m (aerodynamic diameter) were measured in 5

min intervals by means of the Aerodynamic Particle Sizer (APS). Particle number concentrations by both SMPS and APS were determined by integrating over the particle number size distribution. Continuous particle surface concentration was measured with the recently developed Nanoparticle Surface Area Monitor (NSAM). This measures the total particle surface area available for diffusion of ions. A dual beam aethalometer measured black carbon (BC) concentrations every 5 min. In addition, an organic carbon (OC)/elemental carbon (EC) field instrument (OC/EC) measured hourly PM<sub>2.5</sub> elemental and organic carbon concentrations. This instrument allows for the separation of particulate OC into four response peaks representing different volatility fractions of OC (15). For the purposes of this study, peaks 2-4 were summed and considered as the least volatile or heavy OC fraction (HOC), while peak 1 represented the lighter, most volatile OC fraction (LOC).

#### 2.1.4 Results

#### 2.1.4.1 Particle and co-pollutant concentrations next to the freeway

Meteorological and traffic parameters were measured during the course of sampling. The average wind direction was  $215\pm39$  degrees, which placed the sampling site directly downwind of freeway traffic emissions, and the mean wind speed was  $1.8 \pm 0.9$  ms<sup>-1</sup> (all ranges given as mean  $\pm$  standard deviation). The temperature and relative humidity were 19.6  $\pm 5.0$  degree C and 46.2  $\pm 16.3\%$ , respectively, with a diurnal profile shown later in the paper. Caltrans reported total volumes of north- and south-bound lanes in the range of  $5180 \pm 640$  h<sup>-1</sup> and  $5640 \pm 800$  h<sup>-1</sup>, respectively. The average traffic speeds of north and

south bound lanes were  $78 \pm 28$  km h<sup>-1</sup> and  $85 \pm 12$  km h<sup>-1</sup>, respectively. Video recordings revealed that 11-21% of vehicles on the freeway were HDVs. However, when expressed as an absolute hourly density on the freeway, the HDV number did not significantly differ during the sampling hours (1700-2160 h<sup>-1</sup>). This range is slightly lower than previously reported in studies conducted in 2001 (16) on the same freeway, possibly due to the opening of a railway line (Alameda Corridor) in 2002, which is used for the transport of goods from the Los Angeles port.

	campaign average			rainy day			freeway closed		
	average	range	SD <sup>a</sup>	average	range	SD <sup>a</sup>	average	range	SD <sup>a</sup>
$N_{\text{CPC}}$ (cm <sup>-3</sup> )	$8.6 imes10^4$	$1.1  imes 10^4 - 3.2  imes 10^5$	$5.4 imes10^4$	$3.4 imes10^4$	$1.3  imes 10^4 - 8.3  imes 10^4$	$2.2 \times 10^4$	$3.1  imes 10^4$	$2.5  imes 10^4 - 3.8  imes 10^4$	$6.8 imes10^3$
N <sub>SMPS</sub> (cm <sup>-3</sup> )	$1.9  imes 10^4$	$3.7  imes 10^3 - 5.4  imes 10^4$	$9.4  imes 10^3$	$5.5 imes10^3$	$2.3  imes 10^3 - 1.0  imes 10^4$	$3.0 \times 10^3$	$6.5 imes10^3$	$5.1  imes 10^3 - 8.0  imes 10^3$	$1.4 \times 10^3$
PM <sub>0.7-2.5</sub> (µg/m <sup>3</sup> )	6.4	1.7-30	3.6	8.2	6.7-8.8	0.85	2.1	1.7-2.3	0.27
surface (µm/cm <sup>3</sup> )	153	36-303	55	41	20-64	19	57	45-71	12
V <sub>NM</sub> (µm <sup>3</sup> /cm <sup>3</sup> )	0.094	0.011-0.22	0.047	0.031	0.011-0.061	0.02	0.049	0.035-0.058	0.13
V <sub>AM</sub> (µm <sup>3</sup> /cm <sup>3</sup> )	16.3	3.66-36.5	6.96	7.1	4.73-9.79	1.86	4.3	3.7-5.6	1.1
Geomean $d_{ m p}$ (nm)	50	28-96	11	53	40-60	7	46	42-52	4
EC (µg/m <sup>3</sup> )	3.2	0.3-11.2	2.2	0.7	0.3-1.15	0.3	0.40	0.3-0.5	0.2
BC $(\mu g/m^3)$	4.4	0.5-10.1	2.1	2.6	0.8-9.8	2.8	0.8	0.8	< 0.1
LOC (ug/m <sup>3</sup> )	2.4	0.9-5.3	0.8	1.3	1.1-1.7	0.2	3.0	2.8-3.2	0.3
HOC (ug/m <sup>3</sup> )	2.0	0.1-11.2	1.4	1.2	0.9-1.8	0.3	1.6	1.5-1.8	0.2
CO (ppmv)	0.23	0.10-3.6	0.35	0.01	< 0.09	0.02	0.29	<1.2	0.53
CO <sub>2</sub> (ppmv)	426	359-567	30	402	384-430	14	405	401-410	3.6
<sup>a</sup> Standard deviation	on.								

# Table 2-2Summary of particle and copollutant levels next to the freeway for the<br/>three cases: campaign, a rainy day, and a day when the freeway was closed.

Table 2-2 presents the mean particle and co-pollutant levels measured near the freeway over the 7-week sampling period (120-140 hour of data, depending on the magnitude considered). The average CPC particle number concentration was 86 000 cm<sup>-3</sup> during the course of the whole campaign whereas the average SMPS concentration was 19 000cm<sup>-3</sup>. The difference between the two instruments can be attributed to the different size ranges (CPC > 6 nm, SMPS 16-638 nm) and particle losses in the SMPS, and it is a strong indication that the particle concentration near the freeway is dominated by particles less

than 16 nm in diameter. The high particle number concentration below 16 nm is consistent with the results of Zhu et al. (2004), conducted in the winter of 2002 next to the same freeway. The particle surface concentration was  $153\pm55 \ \mu\text{m}^2\text{cm}^{-3}$ . With regard to carbon species, BC concentration measured  $4.4 \pm 2.1 \ \mu\text{gcm}^{-3}$ , which is at similar levels with EC ( $3.2 \pm 2.2 \ \mu\text{g cm}^{-3}$ ) and total OC ( $4.4 \pm 1.6 \ \mu\text{g cm}^{-3}$ ). The fraction of EC and BC to PM<sub>0.7-2.5</sub> was 50% and 68%, respectively. In a previous study at the Caldecott tunnel (Hering et al. 1984) with 3-6% diesel vehicles, EC accounted for 30-38% of PM<sub>2.5</sub>. It was also reported that, on average, BC accounted for 50% of PM<sub>3</sub> at the entrance and 30% at the exit in Gubrist tunnel with 16% diesel vehicles (Weingartner et al. 1997). EC is considered a marker for diesel exhaust aerosol emissions in tunnels (Funasaka et al. 1998), and the results presented in this study are consistent with earlier studies with similar diesel fractions.

Table 2-2 also shows the volumes of nucleation (16-40 nm) and accumulation (40-638 nm) mode particles, calculated from the SMPS distributions. By combining the volume of accumulation mode particles with the effective particle density, we obtain an estimation of the particle mass in this size range. Next to the 710 freeway, the effective density of particles in the 322-414 nm mobility range, where most of the accumulation mode volume resides, varies between 0.49 and 0.31 g cm<sup>-3</sup> g (Geller et al. 2006a). Using this density range, the particle mass in the accumulation mode is calculated to have been between 5.0 and 8.0  $\mu$ g cm<sup>-3</sup>, which is within the range of the sum of EC and TOC concentrations shown in Table 2-2. This suggests that these two species accounted for the

majority of particle mass in that location and for that size range. Particle and co-pollutant concentrations during two special events are also included in Table 2-2. During freeway closure, which occurred for a single day (March 8) due to police activity, the particle number, mass, and surface area concentrations significantly dropped due to the absence of the most dominant particle emission sources, given that there are no other significant ultrafine particle sources in that area (Zhu et al. 2004). Average EC and BC also declined to levels much lower than the whole campaign average, thus demonstrating that vehicle activity on the freeway is their main source. However, OC species did not decline as much, indicating that there are some significant sources of background organic carbon, including, for example, secondary organic aerosols (SOA) as well as existing background concentration due to "aged" OC produced in previous days that had yet to be transported out of the Los Angeles Basin. A second special occasion occurred for a rainy day (March 20), when sampling took place during light rain conditions. Rain led to particle scavenging from the atmosphere, resulting in a decrease in particle number and surface area concentrations.

#### 2.1.4.2 Diurnal Profiles

Figure 2-2 shows the averaged diurnal trends of the various parameters categorized as (a) meteorologicaland (b) traffic conditions, and (c) particle chemical and (d) physical properties. The y-axis is the normalized value of the different parameters with y of 100 equal to the values listed in brackets for each parameter. The x-axis in the figures shows the sampling hour, which ranges from 11:00 to 19:00. As the day progressed, relative humidity increased while the temperature and solar radiation decreased. Wind speed was

consistent throughout the day with a small peak in the early afternoon while total traffic volume on the freeway was consistent during the sampling period, with slight increases during morning and afternoon rush hours. The average speed in the north-bound lane dropped during congestion, between 15:00 and 17:00. In Figure 2-2b, the "CO<sub>2</sub> Production" profile corresponds to the total CO<sub>2</sub> production rate (tons/h) per km due to the vehicle activity. This has been calculated on the basis of activity data provided by Caltrans for driving speeds and traffic volume, the split in diesel HDV and gasoline cars, and appropriate  $CO_2$  emission functions for each vehicle category. The total  $CO_2$ production changed very little during the study, due to the relatively constant speeds and traffic volumes during the day. During congestion, the CO<sub>2</sub> production rate increased mildly due to the acceleration deceleration driving pattern. However, the increase is not substantial due to the relative reduction of the total traffic volume. Both EC and BC average concentrations display a bimodal pattern and agree with each other very well, indicating identical sources of EC and BC (Figure 2-2c). Two peaks were observed at 11:00 and later in the afternoon (15:00-16:00) corresponding to the diurnal pattern of the traffic rush hours. The diurnal patterns of OC species do not follow traffic as closely and this is a further indication that these may come from both direct traffic emissions as well as secondary formation mechanisms through photochemical reactions.

With regard to particle concentrations, SMPS total number concentration, surface concentration, and volume of nucleation and accumulation modes all peaked at 16:00 when traffic was congested. These associations strongly indicate the link between particle concentrations and traffic emission on the freeway. Harrison et al. (1999) have also

reported that roadside particle number and surface concentrations have the same general pattern of behavior as the vehicle emission source. On the other hand, the CPC number concentration showed a monotonically increasing trend from 50,000 cm<sup>-3</sup> to 110,000 cm<sup>-3</sup> as the day progressed. This can be explained by the nucleation process of small particles with decreasing temperature in the evening. Similar results have also been observed by Kuhn et al. (2005b). These results indicate that the particle concentration and characteristics next to the freeway are influenced by a combination of the traffic activity and the meteorological conditions. The statistical analysis presented in a following section will help to further identify the underlying associations.



Figure 2-2 Diurnal profile of measured variables normalized over the maximum hourly value recorded (given in the legend within parentheses). (a) meteorological conditions, (b) traffic data, (c) particle physical parameters, (d) particle chemical parameters.

#### 2.1.4.3 Comparison with Previous Studies

Particle characterization studies in the vicinity of freeways or tunnels with diesel HDV traffic have been conducted in the past. Westerdahl et al. (2005) measured particle characteristics by driving a mobile lab on fixed routes in the Los Angeles road network, including a stretch of the I-710 freeway where they chased different vehicle plumes. In another study, Geller et al. (2005) measured size distributions in the Caldecott tunnel (Bore 1), located in Orinda, CA.

	2006 study			Westerdahl et al. ( <i>10</i> )	Geller et al. (24)		
location	I-710		I-710 I-710		Caldecott Tunnel (Bore 1)		
period	20 m from freeway median strip		i strip	Feb-Apr 2003		Aug 2004	
sampling hours	12 pm-4 pm	5 pm-	7 pm	1 eb Api 2003		12 pm-6 pm	
passenger cars (h <sup>-1</sup> )	8359	102	50	7580ª		4041	
light-duty trucks (h <sup>-1</sup> )	600	36	0			91	
heavy-duty trucks (h <sup>-1</sup> )	1630	122	25	1040 <sup>a</sup>		64	
temperature (°C)	21.4	14.	4	21		23.3	
RH (%)	42	60	)			59	
wind speed (m/s)	2.2	1.2	2	2.0			
	measured	measured	measure	d corrected for DR <sup>b</sup>	measured	corrected for DR <sup>b</sup>	
CPC (cm <sup>-3</sup> )	75000	98500	190000	36600 (5400)	637500	92600 (10100)	
CO (ppm)	0.27	0.11	1.9	0.28 (0.05)	8.78	2.18 (0.21)	
BC ( $\mu$ g/m <sup>3</sup> )	4.6	2.8	12	3.4 (0.6)	27.5 <sup>c</sup>	6.8 (1.4)	
relative dilution ratio	1:1			1:10.2 (1.22)		1:7.3 (0.82)	

<sup>a</sup> Daily averages from CalTrans. <sup>b</sup> Values in parentheses correspond to calculation uncertainty (see Supporting Information). <sup>c</sup> Elemental carbon.

# Table 2-3 Comparison of concentrations in different studies involving heavy-duty diesel vehicle traffic. Underlined values have been corrected for the different dilution ratios, calculated on the basis of the CO<sub>2</sub> concentrations.

Table 2-3 compares measured particle number and copollutant concentrations from these two studies to the current one. All studies were conducted under similar temperature and relative humidity conditions and the wind-speed was also very similar in the two non-tunnel studies. The diesel truck fraction was 3.7% in the Caldecott tunnel, and the road had a positive gradient of +4.2%. It is important to correct for the dilution ratio (DR) in the various sampling locations before comparing pollutant concentrations between these
studies. This correction enables us to decouple the effects of fleet operation and ambient conditions on pollutant levels from the influence of the exact position of the monitoring station. The DR calculation is based on the ratio of the fleet-average exhaust CO<sub>2</sub> concentration over the incremental ambient CO<sub>2</sub> increase, and it is given as Supporting Information. Carbon dioxide has been used in several studies as a tracer to derive fuelspecific emissions from ambient pollutants concentrations or to deduce emission factors in tunnel measurements. While the fundamentals of those approaches are similar to our study, we use the incremental increase in ambient  $CO_2$  to deduce dilution conditions in different environments. The calculations show that the DR by the freeway (present study) is  $10.2 \pm 1.22$  times higher than in-freeway, and  $7.3 \pm 0.83$  times higher than in the tunnel. These ratios are consistent with the conceptual model of Zhang and Wexler (2004), who estimated that the road-to-ambient process is associated with an additional DR of 10. Concentrations varied in the range 75 to 637.5 thousand particles per cm<sup>3</sup> in the different studies before correcting for the DR. After correction (italicized values in Table 2-3), concentrations reached rather similar levels, which can lead to interesting conclusions. The in-freeway concentrations of particle number and BC measured by Westerdahl et al. (2005) are lower than the values of this study while CO is at the same levels. This may be attributed to the different mixing of the exhaust when sampling in the freeway as opposed to next to the freeway. When following traffic, there is a larger probability to follow a car than a truck, due to the larger density of passenger cars. The different mixing would have a limited effect on the DR calculated, since the CO<sub>2</sub> concentration in the exhaust of the two vehicle types is different (gasoline 12.5%; diesel 7.1%). However, it is not possible

to calculate a more precise DR than the one corresponding to mean fleet operation, unless the probabilities of following a car VS a truck plume are known. Nevertheless, the effect of different mixing on DR is negligible compared to the orders of magnitude difference expected for the concentration of BC and particle number in the exhaust of the two vehicle types. Therefore, the higher CO/BC ratio of the Westerdahl et al. (2005) study, compared to the present results, is suggestive of the larger CO/BC ratio from gasoline vehicles. This is consistent with the much higher ratio of CO over light extinction by the exhaust plume of gasoline compared to diesel vehicles (Kuhns et al. 2004). For the same reason, the DR-corrected particle number concentration is lower than that measured next to the freeway, which is due to the lower on-road particle number emission factors of gasoline cars vs diesel trucks (Kittelson et al. 2004; Geller et al. 2005). On the other hand, the particle number and BC concentration in the Caldecott tunnel are at the same or slightly higher levels than next to the freeway after DR correction, despite the much lower fraction of diesel vehicles in the tunnel. This is most probably due to the uphill driving in the tunnel, which has a significant effect on the engine load. Using typical values for road resistance and solving the equation of motion for LGVs and HDDVs, 4.2% positive road gradient corresponds to 1.6 times increase in engine load for a light duty gasoline engine and a 2.9 increase for a diesel truck engine. The high particle number concentrations in this case are consistent with the findings of Kittelson et al. (2004) and Maricq et al. (1999b), who show a large increase in particle number from gasoline vehicles as the engine load increases. The effect of engine load on particle number concentration is not as significant in diesel engines (Ntziachristos et al. 2006) but

does increase BC emissions (Zielinska et al. 2004a), which leads to the relatively high ambient concentration of BC, despite the small fraction of diesel vehicles.

#### **2.1.4.4 Particle Size Distributions**

Figure 2-3 shows particle size distributions obtained next to the freeway during different hours of the day (panel a), over different special events (panel b), and, finally, in comparison to HDV particle exhaust distributions measured in the laboratory (panel c). The ambient particle distributions (campaign grand average and hourly averages) are the geometric mean of the corresponding size distributions recorded over the 7-week sampling period. Figure 2-3a shows that the particle size distribution next to the diesel freeway was bimodal, with a nucleation mode in the size range below 40-50 nm and an accumulation mode peaking at 70-80 nm during all sampling hours. This bimodal distribution has been typically encountered in the proximity of freeways with diesel traffic (Zhu et al. 2004) or when following a diesel vehicle on the road (Giechaskiel et al. 2005) but has not been present when sampling in the proximity of a gasoline freeway (Kuhn et al. 2005b). During freeway closure (Figure 2-3b), there was no trafficemission source and the particle dropped significantly compared to the induced average. In addition, the size distribution became monomodal within the range 16-638 nm studied, with a peak concentration of  $12,000 \text{ cm}^{-3}$  at 30 nm.



Figure 2-3 Particle size distributions near freeway (a) Mean geometric hourly size distributions measured during the seven-week campaign; (b) Comparison of the grand average size distribution measured next to the freeway with typical exhaust size distributions of two heavy duty vehicles measured in the laboratory; (c): Effect of individual events on the particle size distributions.

attempts to explain the bimodal size distribution by comparing the average size distribution recorded next to the 710 freeway to typical size distributions obtained by older technology (Euro I) and more recent technology (Euro III) HDVs (Thompson et al. 2004). These distributions correspond to mode 5 of the European heavy-duty Stationary Cycle (ESC 5), which stands for moderate speed (60% of maximum speed) and 50% load, both typical of freeway driving. The exhaust concentrations have been corrected for the DR considered at the sampling location and the contribution of HDV exhaust flow rate to the mean fleet exhaust flow rate. The comparison shows excellent agreement in the size range of both particle modes, between freeway and laboratory sampling. In addition, the concentration of particles larger than 40-50 nm (accumulation mode) measured in the laboratory is very close to the levels measured next to the freeway. However, the accumulation mode distribution is wider next to the freeway than in the laboratory studies, which may be due to the averaging effect on the size distributions of several vehicles, and/or to the contribution of other particle sources (secondary particles and non exhaust vehicle particles). With regard to the nucleation mode particles, the size range determined in the laboratory from the Euro I engine (employing a primary DR of 12.5:1, a dilution temperature of 32 degree C, and a residence time of 2.5 s) is similar to the size distribution measured next to the freeway. However, the actual number concentration depends on the vehicle technology and the sampling conditions. In addition, the nucleation mode formed next to the freeway also depends on species emitted by gasoline vehicles. The comparison of the tunnel, on-road, dynamometer, and present studies demonstrates that the measurement of the incremental increase in ambient CO<sub>2</sub> due to

traffic is a good indicator of the DR at the sampling location and can be used to infer concentrations at other locations with similar conditions. This can be used to decouple the effect of sampling position from the difference in the measured pollutant levels.

#### 2.1.4.5 Statistical Processing of the Sampled Variables

A multivariate linear regression analysis was performed on a dataset of 86 hourly average values of traffic, ambient, and pollutant concentration data, in order to associate particle concentrations next to the freeway with traffic and ambient conditions as well as copollutant concentrations. The dataset size was limited to 86 h because it was necessary to have a complete set of values for all 22 variables recorded during sampling. The variables included all magnitudes shown in Figure 2-2, with the addition of thePM<sub>0.7-2.5</sub> mass and the time of sampling. "CO<sub>2</sub> Production" was excluded because it was not possible to have a precise estimate for each hour of the sampling period. The dependent variables considered in the regressions were the  $CO_2$  concentration, the CPC particle number, the surface concentration, and the volumes of particles in the nucleation (16-40 nm) and accumulation (40-638 nm) modes. All other recorded variables were considered independent. For the CO<sub>2</sub> regression in particular, only traffic data and ambient conditions were considered as independent variables. All regressions were carried out with SPSS 12.0 and only final linear combinations at a confidence level of 99.5% were considered. The results of the multivariate linear regression analysis are shown in Table 2-4. The values in the table correspond to the multiplication factors for the standardized independent variables (input).

	reconstructed variables				
independent variables	CO <sub>2</sub> (24 ppmv)	surface (61.4 μm/cm³)	V <sub>AM</sub> (7.2 μm³/cm³)	ν <sub>NM</sub> (0.049 μm³/cm³)	
wind speed (0.90 m/s)	-0.24			-0.18	
wind direction (32°)	+0.53				
solar radiation (209 W/m <sup>2</sup> )	-0.38	+0.21	+0.35		
BC (2.0 $\mu$ g/m <sup>3</sup> )		+0.23	+0.46	+0.33	
LOC (0.79 $\mu q/m^3$ )		+0.36		+0.22	
HOC $(0.96 \mu g/m^3)$			+0.24		
CO <sub>2</sub> (24 ppmv)		+0.68	+0.49	+0.51	

# Table 2-4Multiplication coefficients for the standardized independent variablesused to formulate the reconstructed concentrations. Values in parenthesescorrespond to one standard deviation for the corresponding variable.

The linear combination of the multiplication factor and the standardized input variable leads to a reconstructed value of the dependent variable. The correlation of the dependent (measured) variables and the reconstructed variables is satisfactory with regression slopes on the order of 0.91-1.0 and  $R^2$  above 0.6. However, it was not possible to derive a reconstructed variable that would satisfactorily correlate with the CPC particle number. This is probably because the nucleation of new particles is a highly sensitive, nonlinear function of the input variables, and it is therefore not possible to linearly associate it with the independent variables considered.

Given the satisfactory correlations between the reconstructed and the dependent variables, the values in Table 2-4 may be used to establish the associations of the dependent with the independent variables. The multiplication coefficients in this table correspond to standardized variables. For example, a decrease in the wind speed by one standard deviation (which corresponds to a variation of 0.9 m/s) would increase the  $CO_2$  concentration by 0.24 standard deviations. Based on these values, it is evident that  $CO_2$  concentration increases as wind speed decreases, as wind direction changes toward the west (moving the sampling point closer to the freeway), and in the afternoon and evening

hours as the sun sets and the mixing height decreases. These relationships confirm that  $CO_2$  is a very good indicator of the DR. Interestingly,  $CO_2$  concentration does not depend on the traffic volume and conditions because there was little variation of the  $CO_2$  emitted per hour on the highway, as shown in Figure 2-2b (standard deviation over mean was 13% for the whole measurement campaign). Presumably, this variation is not high enough to cause a measurable difference in the  $CO_2$  concentration levels.

The CO<sub>2</sub> concentration was then used as an independent variable to reconstruct the concentration of the particle surface and volume concentrations. Table 2-4 shows that all three particle concentration expressions are positively affected by the CO<sub>2</sub> concentration, which is consistent with an increase in the concentration of these variables with decreasing DR. All concentrations are also positively associated with BC. Interestingly, LOC is positively associated with the nucleation mode volume, while HOC is associated with the accumulation mode. There is evidence (Phuleria et al. 2006) that the gasoline OC profile is shifted to heavier species than the diesel one. This would imply that the nucleation mode volume in the size range 16-40 nm is mainly associated with the diesel activity on the freeway. This is consistent both with the laboratory measurements (Figure 2-3c) and with the findings of Zhu et al. (2004) who found that next to the diesel freeway (I-710) a distinct particle mode appears in the 20-30 nm range. This mode is clearly separated by a higher nucleation mode forming below 10 nm and was not evident when sampling next to a (mainly) gasoline freeway (I-405).

It needs to be noted that a high particle concentration below 16 nm is also evident in our study when comparing the CPC and SMPS recordings. Unfortunately, due to the lack of linear correlation of the CPC recordings with any of the other measured variables, it was not possible to link the origin of this nanoparticle (6-16 nm) mode to either diesel or gasoline vehicles.

The regression analysis also shows that the NM volume concentration is negatively correlated to the wind-speed. This is in addition to the effect of wind on dilution, expressed by the  $CO_2$  correlation, and can be an indication of NM evaporation as the wind-speed increases. Finally, the volume of accumulation mode is positively correlated with the solar radiation. This indicates that there may be other processes, unrelated to traffic, that contribute to a significant portion of the aerosol in that size range, such as secondary formation by photochemical activity.

#### 2.1.5 Acknowledgments

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## 2.2 Fine, ultrafine and nanoparticle trace organic compositions near a major freeway with a high heavy duty diesel fraction

#### 2.2.1 Abstract

Individual organic compounds such as hopanes and steranes (originating in lube oil) and selected polycyclic aromatic compounds (PAHs) (generated via combustion) found in particulate emissions from vehicles have proven useful in source apportionment of ambient particulate matter. Currently, little ambient data exists for a majority of these species. Trace organic species in the size-segregated ultrafine (<0.18 µm) and accumulation (0.18-2.5 µm) particulate matter (PM) modes were measured during the winter season next to a busy Southern California freeway with significant (~20%) diesel traffic. The ultrafine mode was further segregated into 4 size ranges (18-32 nm, 32-56 nm, 56-100 nm, and 100-180nm) with a NanoMOUDI low-pressure cascade impactor sampler. Both ambient and concentrated size-segregated impactor samples were taken in order to collect enough mass for chemical analysis. Accumulation and size segregated ultrafine mode particles were analyzed by various methods to investigate their chemical composition. Particle acidity and its relationship with size were also investigated by the ratio of measured and required ammonium for neutralization with nitrate and sulfate. All the measured organic species exhibited decreasing concentrations with size in the ultrafine mode. The most abundant PAHs in the ultrafine and accumulation modes were pyrene and benzo(ghi)perylene, whereas norhopane dominated the hopanes and steranes concentrations. This study is the first to present size-segregated organics species in the ultrafine range of PM in an ambient environment.

#### 2.2.2 Introduction

Several epidemiological studies have linked adverse health outcomes to measured particulate matter (PM) mass (Samet et al. 2000; Peters et al. 2001; Pope et al. 2002). Toxicological studies have found similar associations, which are particularly strong between adverse health effects and ultrafine particle (UFP) mass, defined here as particles with aerodynamic diameters less than 0.18  $\mu$ m (Donaldson et al. 2002; Cyrys et al. 2003; Nel 2005). Because the biological mechanisms responsible for PM toxicity remain uncertain, recent studies have attempted to link toxicity with specific PM characteristics, such as particle size, number concentration and chemical composition. These relationships have been explored for sulfate (Clarke et al. 2000; Batalha et al. 2002), trace elements and metals, including Si (Wellenius et al. 2003), V (Saldiva et al. 2002), Fe, Ni, and Zn (Burnett et al. 2000), as well as elemental carbon (Mar et al. 2000; Metzger et al. 2004), and polycyclic aromatic hydrocarbons (PAH) (Dejmek et al. 2000). One current theory supposes that organic compounds present either within the volume or on the surface of a particle may catalyze generation of reactive oxygen species (ROS) (Li et al. 2002).

PM consists of a variety of organic compounds, some of which are better tracers of sources (Schauer and Cass 2000), due to their conservative, non-labile nature, while others are semi-volatile and/or participate in chemical reactions that are a principal component in secondary aerosol formation (Robinson et al. 2007). The size distribution of atmospheric particle-bound trace organic species is an important piece of information that is often used for source apportionment, particle formation and evolution, and

calculation of atmospheric lifetimes. The development of low-pressure cascade impactors has made it possible to explore size distributions of particles and their chemical characteristics within the UFP range. Such data are particularly important for ambient UFP because the respiratory deposition fraction of these particles increases sharply and monotonically with decreasing size (Montoya et al. 2004; Kreyling et al. 2006).

A previous study conducted by our group at the same location (Ntziachristos et al. 2007b) focused on the size distribution of trace elements and metals. While trace elements and metals compose only a small fraction of UFP mass, these species were investigated due to their potential impact on health. Organic matter, however, constitutes the vast majority of UFP mass (Hughes et al. 1998), although most of the individual compounds have yet to be quantified (Phuleria et al. 2007). While dynamometer testing has been employed to measure the size-segregated UFP organic species for specific vehicles, ambient data have not been available for realistic time scales due to low concentrations.

In this study, we report size-fractionated concentrations of organic species in the  $PM_{0.18}$  and accumulation mode ( $PM_{0.18-2.5}$ ) ranges of  $PM_{2.5}$  in a site adjacent to a major freeway with a significant fraction of heavy-duty diesel vehicles, as part of our continuing efforts to characterize PM in the vicinity of freeways with different share of heavy-duty and light-duty vehicles in the Los Angeles Basin (LAB). A low-pressure cascade impactor was coupled with a particle concentrator in order to significantly decrease the sampling time required for sample collection. Data at this location are then compared to those from specific vehicles tested at a dynamometer facility (Riddle et al. 2007). This type of data

analysis attempts to resolve the differences between tailpipe emissions sampling and actual concentrations found in ambient environments by isolating tracer compounds and their size distributions. It can be readily applied to toxicological endpoints related to PM as well.

#### 2.2.3 Methods

#### 2.2.3.1 Site description

The present study was carried out next to the I-710 freeway in Los Angeles, California. The 26-m wide, eight-lane freeway connects the Port of Long Beach and Port of Los Angeles to the shipping yards in East Los Angeles, making it the primary throughway for heavy-duty diesel truck traffic between the two industrial locations. Previous studies have reported between 15-25% heavy-duty diesel traffic on I-710 (Zhu et al. 2002a; Ntziachristos et al. 2007c). Including gasoline vehicles, between 150,000-250,000 vehicles passed the sampling site each day. Sampling was located downwind of the freeway in a paved property maintained by the Imperial Flood Control Yard in South Gate, CA. This location is directly adjacent to the roadway with no other immediate sources either upwind or downwind. A second sampling site was located about 1.6 km east (downwind) of the I-710 freeway at Rancho Los Amigos National Rehabilitation Center in order to collect a representative urban background sample.

A portable weather station (Monitor II, Weather Systems Company, San Jose, CA, USA) recorded the meteorological data at the freeway sampling site at 5-minute intervals throughout the study. The monitor was located 2 m above the ground, and wind direction

was calibrated daily by aligning the weather vane with a compass. Table 2-5 lists the average meteorological data and the average traffic volume and speed in both freeway directions, which was obtained from California Department of Transportation (http://www.dot.ca.gov/). Vehicle class was determined by watching video footage of the traffic passing the sampling site at selected times during the study. Light duty gasoline-powered vehicles were most commonly found while 11-21% vehicles were observed to be heavy-duty diesel trucks.

Parameter	Average	Standard Deviation
Wind direction (degree)	215	39
Wind speed (m/s)	1.83	0.85
Temperature (°C)	19.6	5.0
Relative humidity (%)	46.2	16.3
CO (ppmv)	0.23	0.35
CO <sub>2</sub> (ppmv)	426	30
Southbound traffic volume (veh/h)	5639	801
Southbound traffic speed (km/h)	84.5	12.1
Northbound traffic volume (veh/h)	5177	637
Northbound traffic speed (km/h)	77.6	27.7

#### Table 2-5Meteorological and traffic data in the sampling site.

#### 2.2.3.2 Sampling protocol

The campaign took place during seven weeks in the period of February to April 2006. Two micro-orifice uniform deposit impactors (MOUDI, MSP Inc., Minneapolis MN) sampled concurrently at 30 l min<sup>-1</sup> at the freeway and urban sites. Forty-seven millimeter Teflon (PTFE, 2  $\mu$ m pore) filters were used as impaction substrates for coarse (PM<sub>2.5-10</sub>) and PM<sub>0.18-2.5</sub> sampling, and 37 mm PTFE filters were used to collect PM<sub>0.18</sub>. In addition to the MOUDI, two tri-mode high-volume impactor samplers (Geller et al. 2002) sampling at 450 l min<sup>-1</sup> collected the same three MOUDI size fractions of PM at both sites for the purpose of analyzing elemental and organic carbon (EC-OC) as well as organic speciation measurements of size fractionated PM<sub>10</sub>. Coarse PM was collected on a 47 mm quartz impaction substrate.  $PM_{0.18-2.5}$  was collected on ten quartz impaction strips, and  $PM_{0.18}$  was collected on a 203 mm × 254 mm quartz filter. The seven-week sampling period yielded a total of four samples, each of which was a composite of seven hours (10:00 AM to 5:00 PM) per day and five days (Monday-Friday) per week.

In order to collect sufficient PM loadings for organic species analysis over the 35-hr sampling week, a NanoMOUDI/MOUDI (Nano-Micro Orifice Uniform Deposit Impactor, Model 115, MSP Inc., Minneapolis MN) was connected downstream of a Versatile Aerosol Concentration Enrichment System (VACES) to collect enriched ambient aerosols at the freeway site only. This methodology is described in detail by Geller et al. (Geller et al. 2002). The VACES enriches ambient particles by a factor of 20-40, depending on the required output flow rate (Sioutas et al. 1999b; Kim et al. 2001b; Kim et al. 2001a; Geller et al. 2002). In the present study, the VACES operated at 2001 min<sup>-1</sup> and concentrated PM into a flow of 11.5 l min<sup>-1</sup>. Of that flow, 10 l min<sup>-1</sup> was drawn through the NanoMOUDI/MOUDI and 1.5 l min<sup>-1</sup> through a scanning mobility particle sizer (SMPS, Model 3936L, TSI Inc., St. Paul MN). Thus, the ideal concentration enrichment was by a factor of 17. Ntziachristos et al. (2007b) provides comprehensive results of the performance of the VACES during the experiments.

The NanoMOUDI/MOUDI tandem classified PM in the following size ranges: 2.5  $\mu$ m-0.18  $\mu$ m, 0.18  $\mu$ m-0.10  $\mu$ m, 0.10  $\mu$ m-0.056  $\mu$ m, 0.056  $\mu$ m-0.032  $\mu$ m and 0.032  $\mu$ m-0.018  $\mu$ m. The acceleration nozzle plates of the MOUDI were masked to block twothirds of the nozzles so that the designated size cuts can be maintained at the working flow rate of 101 min<sup>-1</sup> through the NanoMOUDI (Sardar et al. 2005). Impaction substrates were alternated weekly between aluminum, to analyze organic species, and PTFE filters, to analyze metals and inorganic ions, which are presented in a separate paper (Ntziachristos et al. 2007b). A total of three sets (one per week) of each substrate type were collected at the freeway site.

#### 2.2.3.3 Sample analysis

Gravimetric and chemical analyses are described at length by Ntziachristos et al. (2007b) and summarized below. The PTFE filters/substrates were weighed three times before and after sampling using a microbalance (Model MT-5, Mettler Toledo Inc., Highstown NJ) after allowing at least 24 hrs of equilibration at a temperature of 22-24°C and a relative humidity of 40-45%. Aluminum substrates were subsequently analyzed for trace element and metal content and inorganic ions, including sulfate, nitrate, ammonium, potassium and sodium by means of inductively coupled plasma mass spectroscopy (ICPMS) and ion chromatography, respectively. The quartz substrates and filters of the tri-mode high volume impactor were analyzed for elemental and organic carbon (EC and OC) by means of Thermal Evolution/Optical Transmittance (TOT) analysis (Schauer et al. 2003a).

Methods for the quantification of individual organic compounds in ambient particulate matter were based on earlier established solvent extraction methods (Schauer et al. 1999; Schauer et al. 2002a; Sheesley et al. 2003). Procedures for sample extraction and molecular quantification for the organic tracers is described in detail elsewhere (Phuleria et al. 2007) and only a brief summary is presented here. The aluminum substrates from the NanoMOUDI samples were spiked with known amounts of isotope labeled internal standard compounds, including three deuterated PAHs, two deuterated alkanoic acids, deuterated cholestane, deuterated cholesterol, and C13 labeled levoglucosan. Samples were extracted in dichloromethane and methanol and were combined and reduced in volume to approximately 1 mL by rotary evaporation followed by pure nitrogen evaporation. One fraction of the extracts was derivatized for organic acid analysis, the results of which are not presented here. The other fraction was further reduced to a specified volume ranging from 50 to 200 µL by evaporation under pure nitrogen. The final target volume was determined based on the amount of organic carbon mass in each sample (Phuleria et al. 2007).

The underivatized samples were analyzed by auto-injection into a GC/MSD system (GC model 5890, MSD model 5973, Agilent). A 30 m  $\times$  0.25 mm DB-5MS capillary column (Agilent) was used with a splitless injection. Along with the samples, a set of authentic quantification standard solutions were also injected and used to determine response factors for the compounds of interest. While some compounds are quantified based on the response of a matching compound in the standard mixtures, others for which matching standards were not available are quantified using the response factors of compounds with

similar structures and retention times. Analytical errors for these methods have been reported to be no more than 25% (Sheesley et al. 2003; Fine et al. 2004).

#### 2.2.4 Results and discussion

#### 2.2.4.1 Accumulation and ultrafine chemical composition

Figure 2-4a shows the average fractions of chemical species in the total mass of accumulation mode particles at the freeway and urban sites. Accumulation mode PM mass concentrations were 14.6 and 7.8  $\mu$ g/m<sup>3</sup> at freeway site and urban sites, respectively. The most abundant species in accumulation mode PM next to the freeway are nitrate (35%), OC (29%) and sulfate (10%). This result is consistent with previous studies by Kuhn et al. (Kuhn et al. 2005b) in freeway environments and by Sardar et al. (2005) at other locations in Southern California.

Figure 2-4b shows the average fractions of chemical composition of ultrafine particles at the freeway and urban sites. Similar to the accumulation mode, UFP mass concentrations next to the freeway  $(3.4 \ \mu g/m^3)$  were slightly higher than those measured at the urban site  $(2.5 \ \mu g/m^3)$ , which is consistent with the study of Zhu et al. (2004), who found that vehicles on the freeway contributed substantially to the number concentration within 150 m of the freeway but little to the mass concentration. OC and EC are the most abundant of all UFP species at the freeway due to their predominance in vehicular exhaust emissions (Kuhn et al. 2005b).



Figure 2-4 Fractions of chemical species in total mass of (a) accumulation particles (b) ultrafine particles at freeway and background site

Average composition of UFP next to the freeway (49% OC, 27% EC, 12% nitrate, 8% sulfate) was also comparable to previous studies by Sardar et al. (2005) (32-69% OC, 1-

34% EC, 0-24% sulfate, and 0-4% nitrate) and by Cass et al. (Cass et al. 2000) (32-67% OC, 3.5-17.5% EC, 0-19% nitrate and 1-18% sulfate) at other locations in Southern California. Both accumulation and ultrafine EC concentrations at the freeway are statistically significantly higher than their respective background concentrations due to the influence of the diesel vehicle traffic on the freeway.

#### 2.2.4.2 Size-segregated ultrafine particle chemical composition

In addition to the chemical composition analysis of the accumulation and ultrafine particles from the MOUDI, UFP were further segregated into the following four size ranges using the NanoMOUDI: 180-100 nm, 100-56nm, 56-32 nm, and 32-18 nm. Figure 2-5 shows the fraction of UFP mass in each NanoMOUDI size range. Data correspond to the average of three weeks of NanoMOUDI samples, except for the 18-32 nm size range, which is a composite of all three weeks due to low mass loadings. Error bars correspond to standard deviations of the weekly samples. Segregated particle mass fractions were 61%, 29%, 7.2% and 2.6% in the size ranges of 180-100 nm, 100-56nm, 56-32 nm, and 32-18 nm, respectively. Previous studies have reported size-segregated ultrafine PM concentrations at other locations in the Los Angeles Basin (Geller et al. 2002; Sardar et al. 2005). The UFP mass distribution at the freeway site is similar to that reported by Sardar et al. (2005) at an urban Los Angeles location, but the absolute mass concentrations were higher near the freeway.



Figure 2-5 Size distribution of particle mass concentration (0.018 $\mu$ m < $d_p$ < 2.5  $\mu$ m)

Figure 2-6 shows the chemical mass balance of the four size ranges of ultrafine particles. Measured chemical species include nitrate, sulfate, ammonium and total elements. Because of increased uncertainty associated with the determination of the EC/OC split-point when aluminum is the collection substrate (Schauer and Cass 2000), our data are reported as total carbon (TC) in the NanoMOUDI ranges. Extensive studies have shown that more than 85% of the particle mass can be explained by the major chemical species (Hughes et al. 1998; Cass et al. 2000; Chow et al. 2006). As shown in Figure 2-6, the contributions of nitrate and sulfate to total mass show the same bimodal distribution pattern in the ultrafine mode with peaks at 32-56 nm and 100-180 nm, respectively. These results are consistent with observations of Geller et al. (2002) at other locations in Southern California. For sulfate, the 32–56 nm mode probably originates from sulfur

contained in diesel vehicular emissions, whereas the 100–180 nm mode is mostly generated by photochemical oxidation of sulfur dioxide (SO<sub>2</sub>) to sulfate (Shi and Harrison 1999). The fraction of ammonium is mostly low for all size ranges (1.4 to 2.8%) due to the lack of major sources (Viets 1971; Denmead et al. 1976) at the freeway site. The contribution of elements to the total mass is lower than 5.5% for nearly each respective size range. Total carbon is the major component of particulate mass, accounting for 75% to 86% of the total in all four size ranges. Cass et al. (2000) reported 51.2% of UFP attributed to total carbon in Pasadena, CA and 69% in central Los Angeles near a site with high traffic density. The higher TC fraction for all ultrafine size ranges reported in the present study reflects the dominant influence of vehicular emissions from freeway traffic at the sampling site.



Figure 2-6 Chemical mass balance of segregated ultrafine particles.

#### 2.2.4.3 Particle acidity

Particle acidity can be examined by means of the ratio of measured ammonium concentrations to the concentrations needed to fully neutralize the measured sulfate and nitrate (Zhang et al. 2004). A value of one suggests that sulfate and nitrate might be fully neutralized by ammonium in the form of  $(NH_4)_2SO_4$  and  $NH_4NO_3$ . A value close to zero suggests that the particles are predominately  $H_2SO_4$ . The ammonium ratios in accumulation and ultrafine mode particles can be used to determine the degree of neutralization of particles in the respective size ranges.



Figure 2-7 Ratio of measured to required ammonium for neutralization at freeway and background sites (BG: background; FW: freeway; A: accumulation; UF: ultrafine)

Figure 2-7 shows the ammonium ratio plots for the accumulation and ultrafine particles at the freeway and background sites, as well as the size segregated ultrafine particles at the

freeway site only, for which NanoMOUDI data were available. Error bars reflect the standard deviation of the average of weekly samples. Accumulation mode particles are almost neutralized at both freeway and background sites, with the ratio of measured to the required ammonium for neutralization being 0.75 and 0.76, respectively. However, UFP appear to be more acidic, with ammonium ratio of 0.47 at freeway site, and a slightly higher ratio of 0.53 at the background site. Similarly, Grose et al. (2006) found that UFP sulfate in vehicle exhaust is mostly in the form of sulfuric acid or ammonium bisulfate instead of ammonium sulfate. It has been argued that UFPs may be acidic in the immediate vicinity of the roadway and become neutralized a short distance downwind (Mcmurry et al. 1983). The higher UFP acidity at freeway and background sites is similar to a recent study by Ning et al. (2007), who reasoned that ammonia preferentially reacts on the surface of larger particles mostly in the accumulation mode, considering that this range dominates the surface area of the ambient PM size distribution.

In addition to the comparison with accumulation mode particles, UFP near the freeway were further segregated into four size ranges to investigate the relationship between UFP acidity and their size. Uncertainty is shown by error bars representing the standard deviation of the average of weekly samples, except for the last stage of 18 to 32 nm, which was the composite of the three weeks sample. As shown in Figure 2-7, the ammonium ratio tends to decrease with particle size, indicating increasing acidity with decreasing particle size. These results support the findings of Ning et al. (Ning et al. 2007) for an urban site in Los Angeles, CA. Our observations are consistent with those by Zhang et al. (Zhang et al. 2004), who demonstrated a multi-modal size distribution for

PM-bound ammonium, having an intermediate mode at 150-180 nm and a nucleation mode 30-70 nm. Furthermore, our results support the notion that sulfur in the ultrafine mode is mostly associated with sulfuric acid that serves as the stable nanoparticle core on whose surface supersaturated organic vapors in the vehicle exhaust condense. This pathway is proposed as the major formation mechanism of these ultrafine particles in the exhaust (Schauer et al. 2003b; Zielinska et al. 2004b). By contrast, particles in the accumulation mode range are mostly in the form of partially or fully neutralized ammonium sulfate salts. This is a result of their longer residence time in the atmosphere (i.e., their "aging") combined with their larger surface area, both of which favor the preferential condensation of ammonia that neutralizes their acidity.

#### **2.2.4.4** Normalized size distribution of PAHs, hopanes and steranes.

Thirteen PAHs and ten hopanes/steranes have been quantified in the present study. The size distributions and the average  $PM_{2.5}$  concentration (± standard deviation) of the measured PAHs and hopanes/steranes are presented in Figures 2-8 and 2-9, respectively. The solid lines represent the ratio of measured mass in each size fraction to the total analyte mass, and the uncertainties are shown by the standard deviation of the average of the weekly samples. Pyrene, benzo(ghi)fluoranthene and fluoranthene are the predominant PAHs near the freeway. Although dynamometer studies have shown high concentrations of low molecular weight PAHs (i.e., naphthalene, methylnaphthalnees, and dimethylnaphthalenes) in spark-ignition and diesel vehicle exhaust (Zielinska et al. 2004a), concentrations of these species were under detection limits in the present study. Low molecular weight PAHs have higher vapor pressures than heavier PAHs, hopanes

and steranes (Schauer et al. 2003b), and gas-particle partitioning of these PAHs is strongly influenced by ambient temperature (Mader and Pankow 2002). Four ring PAHs display a monomodal distribution with highest ratio in the accumulation mode. Miguel et al. (1998) reported that diesel vehicles predominantly emit the lighter PAHs, such as fluoranthene and pyrene. Dynamometer studies on diesel vehicles have presented similar distribution patterns (Zielinska et al. 2004b; Riddle et al. 2007). Riddle et al. (2007) measured the size distribution of PAHs from four heavy-duty diesel vehicles under various driving modes in a dynamometer study and found that the fraction of PAHs in different size ranges is dependent on the vehicle age, driving mode and load. Table 2-6 compares normalized mass fractions of selected PAHs from I-710 with other studies. Riddle et al. (2007) reported the mass fraction of analyte in each size range to the total mass of analyte measured from 0.056 to 1.8 µm while particles between 0.018 and 2.5 um were sampled in the present study. Considering only the overlapping size ranges, the mass fractions of fluoranthene and pyrene at I-710 are well within the range given by various vehicles and driving cycles tested on a dynamometer (Riddle et al. 2007). This indicates that it may be possible to estimate the concentration of organic tracers next to the freeway by averaging emission profiles of different vehicles and driving cycles measured on a dynamometer. Compared to lighter-MW PAHs, five- and six-ring nonvolatile PAHs, including benzo(a)pyrene, benzo(e)pyrene, perylene, indeno(123cd)pyrene, benzo(ghi)perylene and coronene, showed elevated ratios in the 32-56 nm size range. For benzo(a)pyrene, indeno(123-cd)pyrene and coronene, the distributions were bimodal with a peak at 32-56 nm.



Figure 2-8 Normalized size distribution of PAHs measured at near freeway site.

	Fluoranthene				Pyrene		
Size range (µm)	0.056-0.100	0.100-0.180	0.180-1.8	0.056-0.100	0.100-0.180	0.180-1.8	
99 Idle/Creep	0.1	0.31	0.59	0.09	0.38	0.53	
99 56K load	0.18	0.48	0.34	0.19	0.48	0.33	
98 56K load	0.07	0.19	0.74	0.09	0.29	0.62	
98 66K load	0.12	0.39	0.49	0.15	0.4	0.45	
92 56K load	0.22	0.48	0.3	0.22	0.52	0.26	
85 56K load	0.18	0.39	0.43	0.18	0.38	0.43	
this study	$0.15\pm0.04$	$0.34 \pm 0.07$	0.44 ±	0.16 ± 0.04	$0.36 \pm 0.08$	$0.42 \pm 0.05^{*}$	

\* Reported size range is 0.180-2.5 µm.

Table 2-6Comparison of mass fraction of PAHs in segregated particles to the<br/>study by Riddle et al (2007)

Unfortunately, these patterns have not been observed by Riddle et al. (2007) since their minimum size cut was only 56 nm. Figure 2-8 shows the normalized size distributions of hopanes and steranes. All of these species have highly elevated ratios in the size range of 56-100nm, and the majority of them have bimodal size distributions peaking at 56-100 nm and 0.18-2.5 µm. Although hopanes and steranes come from both light-duty gasoline and heavy-duty diesel vehicles, the high fraction of diesel vehicles on I-710 freeway (16% to 20%) likely dominates hopanes and steranes emissions. Dynamometer studies have also observed the 56-100 nm mode for hopanes emitted from diesel vehicles under a high simulated inertial load (Riddle et al. 2007).

For other driving conditions, the mode tends to shift to larger size ranges. These observations are consistent with the results in the present study as shown in Figure 2-9. In addition, measured fractions of hopanes and steranes in different size ranges have also shown great consistency with other studies. Table 2-7 shows the comparison of the mass fractions of 17a(h)-21b(h)-norhopane and 17a(h)-21b(h)-hopane in the size range of 56-100 nm, 100-180 nm and 0.18-1.8 µm, respectively. Similar to the PAHs species, reported ratios in the present study are well within the ranges given by the Riddle et al. (2007) dynamometer study.



Figure 2-9 Normalized size distribution of hopanes/steranes measured near freeway

	17a(h)-21b(h)-Norhopane			17a(h)-21b(h)-hopane		
Size range (µm)	0.056-0.100	0.100-0.180	0.180-1.8	0.056-0.100	0.100-0.180	0.180-1.8
99 Idle/Creep	0.13	0.3	0.58	0.2	0.27	0.53
99 56K load	0.22	0.35	0.42	0.26	0.42	0.32
98 56K load	0.18	0.43	0.39	0.18	0.42	0.4
98 66K load	0.39	0.32	0.29	0.38	0.28	0.34
92 56K load	0.27	0.32	0.41	0.2	0.29	0.51
85 56K load	0.13	0.3	0.57	0.14	0.27	0.59
this study	$0.23 \pm 0.03$	$0.23 \pm 0.06$	0.46 ±0.05*	0.26 ±0.03	$0.22 \pm 0.06$	0.41 ± 0.04*

\* Reported size range is 0.180-2.5 µm.

Table 2-7Comparison of mass fraction of Hopanes in segregated particles to the<br/>study by Riddle et al (2007).

#### 2.2.5 Summary and conclusions

This study presents the chemical composition of size-segregated fine, ultrafine and nanoparticle PM collected at an urban site and beside a heavily trafficked freeway with high diesel vehicle fraction in Los Angeles. It is the first study to present size-segregated ambient organic species concentrations within the ultrafine mode. Nitrate and organic carbon were found to be the most abundant species in accumulation mode, while organic carbon dominates the ultrafine mode. Particle acidity and its relationship with particle size were also investigated by the ratio of measured and required ammonium concentration to neutralize sulfate and nitrate. UFP were much more acidic compared to the fully neutralized accumulation mode particles. Within the ultrafine mode, an increasing trend of acidity was observed with decreasing particle size, which may have implications for atmospheric chemistry and health effects. Trace organics composition of size-segregated PM<sub>2.5</sub>, including size-segregated UFP, was measured directly adjacent to the freeway. Good agreement exists between the distributions of PAHs and hopanes/steranes presented herein and those from a dynamometer study. Thus, it may be plausible to estimate the concentration of organic tracers next to the freeway by averaging emission profiles of different vehicles and driving cycles measured on a dynamometer if the dilution factor (typically calculated based on CO<sub>2</sub> concentrations) between dynamometer and the freeway is known or can be determined .

#### 2.2.6 Acknowledgments

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### Chapter 3 Effect of dilution on primary particles by the investigation of fuel-based PM emission factors

#### 3.1 Abstract

Emission factors of various particle species from light and heavy duty vehicles (LDVs and HDVs, respectively), including organic and elemental carbon (OC and EC,), sulfate, polycyclic aromatic hydrocarbons (PAHs), hopanes, steranes, trace metals, elements, and particle number (PN), were estimated based on roadway measurements. Sampling campaigns were conducted at two different roadways: the CA-110 highway (where only gasoline-powered vehicles are allowed), and the I-710 freeway (where about 20% of the total number of vehicles are diesel-powered trucks). The PM emission factors determined in these roadways were compared to those reconstructed from recent source emission data from the Caldecott tunnel (Phuleria et al., 2006), and those from previous tunnel and chassis dynamometer studies. Very good agreement between estimated and reconstructed emission factors was found for PN, EC, sulfate, high molecular weight (MW) PAHs, hopanes and steranes. This suggests that PM speciated chemical data collected at roadsides can be used to calculate reliable emission factors for several important particulate species at other locations, characterized by a similar mix of on-road motor vehicles. The agreement between our results and other studies in the emission factors of trace elements and metals varied from very good (for species such as Cu, Mo, Ba, Pb) to poor (for species such as Mg, Fe, Ca) probably because the atmospheric concentrations of the latter elements are associated with both traffic and non-traffic sources, and the relative abundances of Mg, Ca, and Fe in road dust varies considerably across locations. The emission factors of OC and EC were clearly highest for HDVs, and those of PAHs, hopanes, and steranes from our roadway measurements were well within the range of values reported in the literature from tunnel and dynamometer studies. The approach presented in this paper allows for a straight-forward estimation of PM emission factors from ambient, near-freeway measurements. Although the uncertainties inherent in the method proposed here must be acknowledged (e.g. assumptions were made to estimate the average fleet composition and the total carbon content in the vehicles' exhaust) our results are generally in very good agreement with those in the available literature for most non-labile PM species.

#### 3.2 Introduction

Numerous epidemiological studies have found positive associations between adverse respiratory and cardiovascular effects and exposure to atmospheric particulate matter (PM) (Samet et al. 2000; Pope et al. 2002; USEPA 2004). In addition, toxicological experiments on human volunteers, laboratory animals, and tissues have provided some evidence of adverse effects for ultra-fine particles (aerodynamic diameter <  $0.1-0.2 \mu m$ ) and outdoor fine PM (PM<sub>2.5</sub>; aerodynamic diameter <  $2.5 \mu m$ ) (Oberdorster et al. 2004; Nel 2005). Although the biological mechanisms responsible for the toxicity of PM are still uncertain, researchers have recently attempted to link the toxicity of PM with several of its chemical components, including organic and elemental carbon (OC and EC,

respectively) (Mar et al. 2000; Metzger et al. 2004), trace metals (Saldiva et al. 2002; Wellenius et al. 2003) and polycyclic aromatic hydrocarbons (PAH) (Dejmek et al. 2000). In urban environments, light- and heavy-duty vehicles have become the major source of ultrafine, fine and in some cases coarse PM (Gertler et al. 2000) via fuel combustion, mechanical and tire wear, and secondary aerosol formation from both organic and inorganic gaseous precursors (Schauer et al. 1996; Mysliwiec and Kleeman 2002). It is therefore essential to characterize and quantify vehicle emissions in order to evaluate the impact on human health and the environment, and also to assess the overall effectiveness of exhaust control technologies.

Different approaches have been used to characterize vehicular emissions, including chassis dynamometer tests (Schauer et al. 1999; Schauer et al. 2002b; Zielinska et al. 2004b), roadway tunnels studies (Geller et al. 2005; Phuleria et al. 2006) and roadside measurements (Kuhn et al. 2005b; Ntziachristos et al. 2007c). Chassis dynamometer experiments have the ability to examine vehicle emissions under different driving/loading settings and to effectively evaluate exhaust control technologies. However, a controlled laboratory environment may not necessarily be representative of real-world driving conditions (Zhang and Morawska 2002), and non-tailpipe emissions such as those from tire wear, the wear of brake linings and re-suspended road dust (Allen et al. 2001) are not accounted for by these types of studies. Roadway tunnel experiments characterize a large portion of all on-road vehicles, providing a detailed analysis of the overall vehicle fleet emissions (Phuleria et al. 2006). However, a limitation of these studies is that they provide information that is specific to a particular tunnel under restricted driving

conditions. Thus, these results may not be broadly applicable to open roadways. Finally, although roadside pollutant concentration measurements characterize well freeways emissions under actual ambient and driving conditions, they may be influenced by changes in the local meteorological and environmental conditions (Ntziachristos et al. 2007c), which could make it difficult to directly compare the pollutant levels at different locations.

In the present study, the concentrations of several gas- and particle-phase species were measured near two major roadways in the Los Angeles Basin and at selected background sites to determine fuel-based roadway emission factors for specific PM components (i.e. OC, EC and sulfur), organic constituents (Polycyclic Aromatic Hydrocarbons or PAHs, hopanes and steranes), trace metals and elements, and particle number (PN). The calculated factors were compared to those reported in previous works as well as those reconstructed from size-segregated emission profiles obtained at the Caldecott tunnel, California, by Geller et al. (Geller et al. 2005) and Phuleria et al. (2006). Our study thus provides a convenient methodology to derive particle emission factors that can be used to assess PM exposure from roadway emissions.

#### **3.3** Experimental methods

#### 3.3.1 Sampling locations

The present study was carried out near two major freeways in the Los Angeles basin, the California State Highway (CA-110) and the Long Beach Freeway (I-710). The former connects Pasadena to downtown Los Angeles, where it merges into the I-110, which runs

southbound towards San Pedro and represents one of the main freeways in the Los Angeles County. Only light-duty gasoline-powered vehicles are allowed on the CA-110. Here, the sampling site was located downwind of the highway at 3 m from the edge of the northbound lanes on the east (downwind)-side. A background site was also set-up about 150 m downwind of the highway, in an area less influenced by the motor vehicles' emissions. Samples near the CA-110 were collected during two different campaigns that took place in the summer of 2004 (May–June 2004) and in winter (January) of 2005. During the sampling period, the average traffic density was estimated to be 5700 h–1 in the summer and 5100 h-1 in the winter. The average vehicle speed was about 112 kmh–1 in both seasons.

The I-710 is a 26m wide, eight-lane freeway connecting the ports complex of Long Beach and San Pedro to the shipping yards in East Los Angeles. The sampling site was located in a paved property, 3 m downwind of the edge of the freeway and away from the influence of any other immediate PM sources, while the background site was set-up about 1.6 Km downwind of the freeway. Samples were collected during 8 weeks between February and April, 2006. The average traffic volume and vehicle speed at the I-710 were about 5400 h<sup>-1</sup> and 81 kmh<sup>-1</sup>, respectively. The majority of the freeway traffic is comprised of light duty gasoline-powered cars and, typically, about 20% of the total number of vehicles is represented by heavy duty diesel powered trucks (Ntziachristos et al. 2007b; Ntziachristos et al. 2007c). Detailed information about the average traffic conditions at the CA-110 and at the I-710 have been presented by Kuhn et al. (2005a).
#### 3.3.2 Sampling and analysis

Similar sampling sites were set-up at both the CA-110 and the I-710, and at the corresponding background locations to monitor the same species concentrations and weather information concurrently. Ambient carbon dioxide (CO<sub>2</sub>) was measured continuously (1-min) using handheld air monitors (Q-Trak Plus Model 8554, TSI Inc., St. Paul, Minnesota). Continuous (1-min) ambient PN concentrations were measured using condensation particle counters (CPC, model 3022A, TSI Inc., St. Paul, MN). Two Micro-Orifice Uniform Deposit Impactors (MOUDI, MSP, Inc., Minneapolis, MN) (30 lmin<sup>-1</sup>) and two tri-mode High-Volume impactor samplers (450 lmin<sup>-1</sup>) were also deployed to collect size-segregated ambient aerosol filter samples. For the MOUDI, 47mm PTFE Teflon filters (2 µm pore, Gelman Science, Ann Arbor, MI), were used as impaction substrates for coarse (PM<sub>10</sub>-PM<sub>2.5</sub>) and accumulation (PM<sub>2.5</sub>-PM<sub>0.18</sub>) mode PM, and a 37mm PTFE Teflon filter (2 µm pore, Gelman Science, Ann Arbor, MI) was used to collect quasi-ultrafine PM ( $PM_{0.18}$ ). For the Hi-Volume samplers, coarse, accumulation and ultrafine PM were collected on a 47mm guartz fiber impaction substrate (Whatman Grade QM-A 1851-047, Whatman Inc, Florham Park, NJ), quartz fiber impaction strips, and a 203mm ×254mm quartz fiber filter (Pallflex Tissuquartz 2500QAT-UP-8 10, Pall Corp, East Hills, NY), respectively. All quartz substrates and filters were pre-baked at 550 °C for 12 hrs and stored in baked aluminum foil prior to deployment. A more detailed description of the sampling protocols adopted in this study can be found in Kuhn et al. (2005a; 2005b) and Ntziachristos et al. (2007c).

Gravimetric concentrations were determined by weighing the Teflon filters from the MOUDI before and after sampling using a microbalance (Model MT-5, Mettler Toledo Inc., Highstown NJ) after allowing 24 hrs for equilibration at a temperature of 22-24°C and a relative humidity of 40-45%. The filter-samples collected at the CA-110 were further analyzed by means of X-ray fluorescence analysis (XRF) for metals and other trace elements (Teflon filters), and by ion chromatography to determine the concentrations of sulfate and nitrate (Quartz filters). Similarly, the MOUDI filter-samples collected at the I-710 were analyzed by inductively coupled plasma-mass spectroscopy (ICP-MS) (Lough et al. 2005; Sheesley et al. 2005) and ion chromatography to determine the element and trace metal content, and the inorganic sulfate and nitrate concentrations, respectively. Portions of all Hi-Volume quartz filters/substrates collected at both roadway-sites were analyzed for OC and EC by thermal desorption/optical transmission analysis (Sunset Laboratory Inc., Tigard, OR) (Birch and Cary 1996), and for individual organic compounds/tracers concentrations by following a well established solventextraction/molecular quantification analysis protocol (Phuleria et al. 2006). At all locations wind direction/speed, temperature and humidity were recorded with a weather station (Wizard III, Weather Systems Company, San Jose, CA, USA).

#### **3.3.3** Emission factors from roadway measurements

A fuel-based emission factor for pollutants is defined as the mass or number of pollutant emitted per mass of fuel consumed (Miguel et al. 1998; Kirchstetter et al. 1999). Since gasoline engine combustion efficiencies in normal driving conditions are higher than 90% (this value is even higher for diesel engines), it is reasonable to assume that the carbon mass in the vehicle's exhaust is mostly in the form of  $CO_2$  and that the contribution of CO and other carbon-containing compounds to the total emitted carbon mass is negligible (Yli-Tuomi et al. 2005). Thus, the emission factor of a generic pollutant can be written as:

$$E_{p} = 10^{3} \left( \frac{[P]_{fw} - [P]_{bg}}{[CO_{2}]_{fw} - [CO_{2}]_{bg}} \right) W_{c}, \qquad (1)$$

where,  $E_p$  is the emission factor for the pollutant P (g/kg of fuel burned, or number count/kg of fuel burned). [P] is the mass or number concentration of the pollutant of interest (g/m<sup>3</sup>, or number count/m<sup>3</sup>).  $[CO_2]$  is the concentration of CO<sub>2</sub> in µg of carbon/m<sup>3</sup>. The subscripts fw and bg indicate freeway and background sites, respectively.  $w_c$  is the weight fraction of carbon in the considered fuel and it has been reported to be 0.87 for diesel and 0.85 for gasoline (Geller et al. 2005; Phuleria et al. 2006). Similar emission factor equations have also been used by Kirchstetter et al. (Kirchstetter et al. 1999), Phuleria et al. (Phuleria et al. 2006) and Yli-Tuomi et al. (Yli-Tuomi et al. 2005) to estimate  $E_p$  in tunnel environments and freeways. In our study, emission factors were calculated directly from pollutant concentrations measured in the proximity of the roadways and at background locations. For the CA-110, a value of 0.85 was used as the carbon weight fraction for gasoline since all vehicles on the highway are gasoline fuelled. For the I-710, the carbon weight fraction was adjusted for the fraction of operating diesel vehicles (around 20% of the total on-road fleet), yielding a value of 0.854 (Ntziachristos et al, 2007b).

#### 3.3.4 Reconstructed emission factors

Based on information about heavy-duty-diesel and light-duty-gasoline vehicles (HDV and LDV, respectively), reconstructed roadway emission factors for the pollutants of interest can be obtained according to the following equation:

$$E_{p,rec} = f_{HDV} \cdot E_{p,HDV} + f_{LDV} \cdot E_{p,LDV}, \qquad (2)$$

where,  $E_{p,rec}$  represents the expected mixed-fleet emission factor for the pollutant P (g of PM species/kg of fuel burned, or particle number/kg of fuel burned);  $f_{HDV}$  and  $f_{LDV}$  are the on-road fractions of HDV and LDV, respectively. For the I-710 freeway,  $f_{HDV} = 20\%$  and  $f_{LDV} = 80\%$ . For the CA-110 highway, we assumed that 100% of the on-road fleet was represented by LDV ( $f_{LDV} = 100\%$ ).  $E_{p,HDV}$  and  $E_{p,LDV}$  are the emission factors of pollutant P for HDV and LDV, respectively, and were obtained from data collected during a study conducted at the Caldecott tunnel in 2004 (Geller et al. 2005; Phuleria et al. 2006). The large population of mixed vehicles under real-world driving conditions in the tunnel has provided the most representative and up to date source emission profiles data available in California.

In addition, the emission factors from roadway measurements were used to reconstruct the HDV fleet emission factors ( $E_{HDV,rec}$ ) using the following equation:

$$E_{HDV,rec} = \frac{E_{710} - f_{LDV} \cdot E_{LDV}}{f_{HDV}}$$
(3)

where,  $E_{710}$  is the emission factor at the I-710 freeway,  $E_{LDV}$  is the LDV fleet emission factor and was assumed to be equal to that obtained at the CA-110 highway because the

fraction of LDVs there is virtually 100%.  $f_{LDV}$  and  $f_{HDV}$  are the fractions of LDVs and HDVs at the I-710 freeway (0.8 and 0.2, respectively).

#### 3.4 **Results and Discussion**

## 3.4.1 Comparison of roadway and reconstructed tunnel emission factors for particle number and other chemical species

Table 3-1 presents average emission factors (Ep) for PN, OC, EC and sulfate estimated at the CA-110 and the I-710, as well as those for HDV and LDV obtained from the study conducted at the Caldecott tunnel by Geller et al. (2005). The  $E_p$  values for all of the considered PM species are reported for both the ultrafine ( $d_p < 0.18 \ \mu m$ ) and fine ( $d_p < 2.5$  $\mu$ m) ranges. Although the traffic volumes at both roadways were similar during the study period, the E(PN) at the I-710 freeway was about 1.8 times higher than that at the CA-110 highway. Similarly, fine and ultrafine E(EC) estimates were about 5.5 times higher at the I-710 than at the CA-110. These results highlight the dominant contribution of diesel vehicles to ambient PN and EC concentrations and are supported by the emission factors data for HDV and LDV from previous studies referenced earlier. Furthermore, the E(OC)/E(EC) ratio for the fine fraction of PM was 5.2 and 1.9 at the CA-110 and I-710, respectively, which confirms the important contribution of diesel vehicles emissions to ambient EC. The relatively high emission factors for OC may be due, at least in part, to the effect of positive artifacts caused by adsorption of organic vapors in the sampling quartz fiber filter (Mader and Pankow 2002). E(sulfate) was higher at the I-710 than at the CA-110, probably because of the greater fraction of HDVs, which are known to emit higher amounts of sulfate due to the elevated sulfur content of their fuels (Phuleria et al. 2006).

	CA-110		I-710	
	Average	SD	Average	SD
Particle number (#kg <sup>-1</sup> )	$1.8 \times 10^{15}$	$2.5 \times 10^{14}$	$3.3 \times 10^{15}$	$1.1 \times 10^{15}$
$PM_{2.5}$ mass (mg kg <sup>-1</sup> )	113.6	25.9	219.0	39.1
$PM_{2.5}$ species (mg kg <sup>-1</sup> )				
OC	105.5	22.1	205.9	48.8
EC	20.5	4.9	110.1	13.7
Sulfate	5.4	1.8	8.3	4.9
$PM_{2.5}$ metals (mg kg <sup>-1</sup> )				
Mg	0.08	0.04	0.23	0.09
Р	_		0.13	0.04
S	_	_	2.83	0.99
K	0.09	0.07	0.19	0.05
Ca	0.17	0.09	0.56	0.24
V	_	_	0.02	0.01
Mn	0.03	0.01	0.01	0.01
Fe	2.41	0.17	1.68	0.61
Ni	_	_	0.01	0.01
Cu	0.18	0.01	0.08	0.03
Zn	_	_	0.07	0.03
Мо	0.01	0.01	0.01	0.01
Ba	0.4	0.06	0.28	0.1
Pb	-	_	0.02	0.01

# Table 3-1Emission factors (expressed in mg kg<sup>-1</sup> of fuel burned, or particle kg<sup>-1</sup>of fuel burned) of particle number (PN), PM2.5 mass, organic and elemental carbon(OC and EC, respectively), sulfate and metals at the CA-110 and the I-710 sites.

Figure 3-1 shows a comparison between the average emission factors for fine and ultrafine EC, sulfate and PN, estimated (*Ep*) and reconstructed (*Ep<sub>rec</sub>*) from data collected at the I-710 (Figure 3-1a), and at the CA-110 (Figure 3-1b). Error bars represent the standard deviation of the emission factors based on individual samples collected during this study. Although roadway environments tend to be substantially more affected by ambient conditions such as rapid air dilution and atmospheric dispersion than tunnels, the emission factors obtained at both the CA-110 and the I-710 show reasonable agreement with those reconstructed from tunnel measurements. The E(PN)/Erec(PN) ratios were 0.91



Figure 3-1 Comparison among measured and reconstructed emission factors of elemental carbon (EC), sulfate and particle number (PN) from the I-170 freeway (1a) and the CA-110 highway (1b). Particulate EC results are reported in both fine and ultrafine (UF) modes.

and 0.72 for the I-710 and the CA-110, respectively. The somewhat higher  $Erec(_{PN})$  estimates may be the result of coagulation of ultrafine particles emitted by vehicles inside the more confined tunnel environment (Zhu et al. 2002b). This is less likely to occur at

ambient conditions, when particle dispersion is maximized. Similar results were also found for fine EC, which E(EC)/Erec(EC) ratios were 0.70 and 0.67 at the CA-110 and the I-710, respectively. It is important to note that the higher levels at the latter location may also be due to the uphill driving, which has a significant effect on the engine load (Maricq et al. 1999a; Kittelson et al. 2004). Using typical values for road resistance and solving the equation of motion for LDVs and HDVs, Ntziachristos et al. (2007b) calculated that a positive road gradient of 4.2% in the Caldecott tunnel corresponds to 1.6 and 2.9 times increase in engine load for LDVs and HDVs, respectively. The same study showed that PN and BC concentrations in the tunnel are at the same, or slightly higher levels than next to the I-710 freeway, despite the much lower fraction of diesel vehicles in the former environment. The effect of engine load on PN emissions is more significant in gasoline engines, but does increase BC emissions in both LDVs and HDVs (Zielinska et al. 2004b). The small difference between Ep and  $Ep_{rec}$  data observed in Figures 1a and 1b may also reflect a reduction in PN and EC motor-vehicle emissions from 2004 to 2005 (i.e., the years separating the present study and the referenced tunnel experiments) as a result of improved emission reduction technologies and/or the introduction of cleaner diesel vehicles (http://www.epa.gov/otaq/regs/fuels/diesel/diesel.htm).

Finally, the E(sulfate)/Erec(sulfate) ratio was higher at the CA-110 (1.41) than at the I-710 (0.66). The reasons for this discrepancy remain unclear, but estimated and reconstructed emission factors may be affected by inaccurate information about the onroad fleet composition, and driving conditions different from those considered here. Overall, these results demonstrate that the above equations can be used to derive roadway-based emission factors for several PM species that are at a minimum within reasonable agreement with those obtained in roadway tunnel measurements.

### 3.4.2 Comparison of roadway and reconstructed tunnel emission factors for organic tracers

Table 3-2a and 3-2b show average emission factors of PAHs, hopanes and steranes quantified from the analyses of the PM samples collected at the I-710 highway (2a) and the CA-110 freeway (2b). The emission factors of light molecular weight (MW) PAHs such as fluoranthene, pyrene and benzo-(ghi)-fluoranthene, estimated at the I-710 were significantly higher than those at the CA-110. Emission factors for heavier MW PAHs, such as benzo-(ghi)-perylene and coronene, however, were comparable at the two roadways, despite of the much higher diesel truck fractions at the I-710. The substantial PAH emission observed at the CA-110 can be attributed to the fact that the lube oil in gasoline vehicles absorbs and concentrates heavy molecular weight PAHs that are formed during combustion and, as a result, the PAHs associated with this class of vehicles were at least in part released in the atmosphere as a component of unburned lubrication oil. In contrast, the PAH profile of diesel vehicles is similar to the PAH content of their fuel (Zielinska et al., 2004).

The emission factor profiles for hopanes and steranes, considered to be reliable organic tracers for diesel and gasoline combustion and mostly found in engine lubricating oils (Rogge et al. 1993; Cass 1998), at the two roadways was quite similar with the values at the I-710 being higher by approximately 3-4 fold compared to those at the CA-110. Our results are consistent with those obtained by Phuleria et al. (2006) and Schauer et al.

(2002b), which indicated that light MW PAHs are predominantly emitted by diesel vehicles, while heavy MW PAHs are released by both gasoline and diesel cars/trucks. Furthermore, Phuleria et al. (2006) demonstrated that the emission factors of hopanes and steranes from LDVs are an order of magnitude lower than those from HDV, which further validates the findings of this study, considering the average 20% fraction of HDV on the I-710.

Species	Average	SD
PAHs	μg/kg of fuel burned	
Fluoranthene	16.29	2.81
Pyrene	23.21	4.17
Benzo(ghi)Fluoranthene	16.45	3.83
$Benz(\alpha)Anthracene$	12.24	2.85
Chrysene	9.13	2.63
Benzo ( $\beta$ +k)Fluoranthene	9.05	1.81
Benzo(j)Fluoranthene	2.53	0.51
Benzo(e)Pyrene	7.46	2.31
Benzo( $\alpha$ )Pyrene	3.52	1.84
Perylene	1.82	0.55
Indeno(cd)Pyrene	5.99	2.08
Benzo(ghi)Perylene	13.61	4.29
Coronene	7.09	1.42
Hopanes and Steranes		
22,29,30-Trisnorhopane	7.71	2.09
$17\alpha(H)-21\beta(H)-29$ -Norhopane	20.14	5.26
$17\alpha(H)-21\beta(H)$ -Hopane	14.14	4.53
22S-Homohopane	6.36	2.17
22R-Homohopane	4.92	2.06
22S-Bishomohopane	3.53	1.81
22R-Bishomohopane	2.60	0.78
20R, ααα-Cholestane	6.58	2.70
$20(R+S)$ , $\alpha\beta\beta$ -Sitostane	11.60	5.07

Table 3-2aEmission factors of PAHs, Hopanes and Steranes analyzed in  $PM_{2.5}$ samples collected at the freeway (I-710).

Species	Average	SD
PAHs	μg/kg of fuel burned	
Fluoranthene	2.86	0.46
Pyrene	3.3	0.54
Benzo(ghi)Fluoranthene	0.68	0.16
Benz( $\alpha$ )Anthracene	0.43	0.17
Chrysene/Triphenylene	2.73	0.41
Benzo(e)Pyrene	0.76	0.25
Benzo( $\alpha$ )Pyrene	0.4	0.18
Benzo ( $\beta$ +k)fluoranthene	1.29	0.35
Perylene	0.07	0.03
Indeno(cd)Pyrene	2.93	0.45
Benzo(ghi)Perylene	12.30	2.34
Coronene	6.21	1.22
Hopanes and Steranes		
22,29,30-Trisnorhopane	1.5	0.48
22,29,30-Trisnorneohopane	2.42	0.74
$17\alpha(H)-21\beta(H)-29$ -Norhopane	4.85	1.87
18α(H)-29-Norneohopane	1.78	0.76
$17\alpha(H)-21\beta(H)$ -Hopane	4.52	2.05
22S, $17\alpha(H)$ , $21\beta(H)$ -Homohopane	2.66	1.08
22R, $17\alpha(H)$ , $21\beta(H)$ -Homohopane	2.14	0.92
22S, $17\alpha(H)$ , $21\beta(H)$ -Bishomohopane	1.15	0.39
22R, $17\alpha(H)$ , $21\beta(H)$ -Bishomohopane	1.17	0.5
22S, $17\alpha(H)$ , $21\beta(H)$ -Trishomohopane	0.99	0.3
22R, $17\alpha(H)$ , $21\beta(H)$ -Trishomohopane	0.69	0.27
20R+S, $\alpha\beta\beta$ -Cholestane	0.33	0.09
20R,ααα-Cholestane	1.76	0.52
20R+S,αββ-Ergostane	0.02	0.01
20R+S, αββ-Sitostane	2.72	0.78

Table 3-2b Emission factors of PAHs, Hopanes and Steranes analyzed in  $PM_{2.5}$  samples collected at the freeway (CA-110).



Figure 3-2 Comparison among the emission factors of PAHs reconstructed from tunnel measurements and those estimated at the I-710 freeway (2a) and at the CA-110 highway (2b).

Figure 3-2 presents a comparison between the PAHs emission factors estimated  $(E(_{PAH}))$ at the I-710 freeway (2a) and at the CA-110 highway (2b), and the correspondent reconstructed values ( $E_{PAH, rec}$ ) obtained from Caldecott tunnel data (Phuleria et al. 2006) using equation 2 (error bars represent the standard deviation). E(PAH) and  $E_{PAH, rec}$  for high MW PAHs, such as indeno-(cd)-pyrene and coronene, are in very good agreement, with an estimated/reconstructed emission factor ratio (*Ep/Ep,rec*) of 0.90 at the I-710 and 1.08 at the CA-110, for the sum of PAHs with  $MW \ge 276$ . This agreement suggests that: a) speciated chemical data collected near roadways can be used to predict reliable emission factors of high MW PAHs at other locations characterized by a similar mix of on-road motor vehicles and engine operating conditions; and, b) roadway emission factors for high MW PAHs can be predicted with a reasonable accuracy by knowing the vehicle fleet composition and the vehicle source emission profiles. As for lighter MW PAHs, the estimated roadway emission factors were consistently lower than those reconstructed from tunnel data, with an average Ep/Ep, rec ratio of 0.49 at the I-710 and 0.40 at the CA-110, for the sum of PAHs with a MW≤ 228 and MW=252. This is probably because this class of organic compounds has relatively high vapor pressures (Schauer et al. 2003b) and, thus, can partition between the gas and the particle phase depending on ambient temperature (Mader and Pankow 2002). The relatively low and constant temperatures and decreased dilution conditions in the enclosed confines of the tunnel bore are likely to favor the partitioning of light MW PAH into the particle phase. By contrast, the higher temperature and dilution conditions observed near roadways tend to shift the gas-particle partitioning towards the gaseous phase, thus lowering the particle phase emission factors

of these species. The higher PAH ratios in the tunnel may also reflect the higher engine load conditions due to the 4% upward grade, as discussed earlier.



Figure 3-3 Comparison among the PM2.5 emission factors of hopanes and steranes reconstructed from tunnel measurements and those estimated at the I-710 freeway (a) and at the CA-110 highway (b). All values are expressed in mg per kg of fuel burned.

Figure 3-3 shows a comparison between the emission factors for hopanes and steranes estimated at the I-710 (3a) and at the CA-110 (3b), and those reconstructed from the correspondent tunnel measurements. Estimated and reconstructed values for most hopanes and steranes were in very good agreement (i.e., within 30% or less) which corroborates the use of these two classes of organic compounds as reliable tracers for vehicle emissions in different environments (Schauer et al. 1996; Cass 1998). The small differences observed between the *Ep* and *Ep*,*rec* values might be attributed, at least in part, to uncertainties related to the fleet composition and driving conditions. In addition, while in the present work emission factors were calculated considering that the total carbon mass in the vehicle exhausts is equal to the amount of measured  $CO_2$  (Equation 1), Phuleria et al. (Phuleria et al. 2006) assumed that the total emitted carbon is equal to the sum of measured  $CO_2$  and CO.

### **3.4.3** Comparison in emission factors for trace elements, metals, elemental and organic carbon (EC-OC).

Figure 3-4 presents a comparison among the emission factors for trace metals (*E(metals)*), elements (*E(elements)*), and organic and elemental carbon (*E(oc)* and *E(ec)*, respectively) obtained in this work at the I-710 and the CA-110 and those reported in recent roadway tunnel and dynamometer studies by Grieshop et al. (2006), Lough et al. (2005), Fujita et al. (2007) and Schauer et al. (1999; 2002). Grieshop et al. (Grieshop et al. 2006) determined fuel based emission factors at the Squirrel Hill Tunnel in Pittsburgh, PA, where the HDV fraction ranged from  $3.4 \pm 0.5\%$  during rush hours to  $14.5 \pm 4\%$  early in the morning (to favor a more direct comparison with our data only emission factors

corresponding to early morning traffic conditions were considered). Lough et al. (2005) obtained emission rates at two Tunnels in Milwaukee, WI, characterized by an HDV fraction between 1.5 and 10% (only data corresponding to the highest HDV fraction were taken into account in Figure 3-4). Emission rates were converted to fuel based emission factors using the following equation:

$$E_p = ER \times C_f \times D_f \tag{4}$$

where,  $E_p$  is the fuel based emission factor in PM mass of element/trace metal per kg of fuel burned (mg/kg of fuel burned); ER is the reported emission rate in PM mass of element/trace metal per km driven and per vehicle (mgkm<sup>-1</sup>veh<sup>-1</sup>);  $C_f$  and  $D_f$  are the average fuel consumption (lkm<sup>-1</sup>) and the fuel density (kgl<sup>-1</sup>), respectively, reported by Kirchstetter et al. (1999) and weighed by the fraction of gasoline/diesel fuelled vehicles. In a series of chassis dynamometer experiments conducted in the mid-1990s Schauer et al. determined emission rates for two medium duty diesel trucks (1999) and eleven gasolinepowered motor vehicles (2002). To facilitate the comparison with our CA-110 and I-710 data, the reported emission rates were converted to fuel-based emission factors (equation 4), and only reconstructed values (equation 2) were then considered in Figure 3-4. In that figure,  $E_{p, HDV}$  = emission factor of HDVs as reported by the author, and  $E_{p, LDV}$  = emission factor of LDVs equipped with catalytic converter. Finally, Fujita et al. (2007) ran a set of dynamometer tests on 30 diesel trucks, 57 light-duty gasoline vehicles and 2 light-duty diesel vehicles (grouped by vehicle weight, model year and mileage category) to assess the sources of uncertainties in quantifying the relative contributions of gasoline and diesel engines emissions to ambient PM2.5. Similarly, we converted their reported



Note: <sup>a</sup> 2000-2001 study in Howell tunnel (Milwaukee, WI) with 6-10% HDV fraction; <sup>b</sup> 2002 study in Squirrel Hill Tunnel (Pittsburgh, PA) with 14.5% HDV fraction; <sup>c</sup> Run on unified warm test cycle, 4 LDVs (Model year 1995-1997); <sup>d</sup> Rec (Reconstructed) emission factors based on 2 HDVs (Model year 1995) and 9 LDVs (Model year 1981-1994) tested on FTP cycle; Rec=0.2HDV+0.8LDV; <sup>c</sup> Rec (Reconstructed) emission factors based on unified warm test cycle of 4 LDVs (Model year 1995-1997) and highway test cycle of 15 HDVs (Model year 1985-2001). Rec=0.2HDV+0.8LDV;

## Figure 3-4 Comparison among $PM_{2.5}$ emission factors of organic and elemental carbon (OC and EC, respectively), metals and trace elements from roadway measurements and tunnel and dynamometer studies.

emission rates to fuel-based emission factors, and considered only: a) the results for low emitting LDVs in warm starting conditions (i.e., conditions comparable to our field measurements, and b) the emission factors reconstructed according to equation 2 (where,  $E_p$ , HDV = reported values for HDVs operating on highway driving cycles, and Ep, LDV = data for low emitting LDVs in warm starting conditions).

Very good agreement among studies was obtained for the species characterized by the lowest emission factors [i.e. Phosphorous (P), Potassium (K), Manganese (Mn), Copper (Cu), Molybdenum (Mo), Lead (Pb) and, Barium (Ba)], while the largest differences were observed for Magnesium (Mg), Sulfur (S), Calcium (Ca) and, especially, Iron (Fe) (Figure 3-4). Although the sum of the emissions of P, V, Ni, Cu, Mo, Ba and Pb does not represent a substantial fraction of the PM mass, most of these species are considered to be important in terms of health effects. For example, Pb was classified by the U.S. EPA as an air toxic, along with Mn, Ni and a few others elements/trace metals. Geller et al. (2006b) and Ntziachristos et al. (2007b) have shown that Ba and Cu are found in similar (Ba) or higher (Cu) amounts in gasoline vehicle exhausts, a result that is also corroborated by our own findings shown Table 3-1, indicating higher emission factor at the CA-110 than the I-710 for these two elements. Lead (Pb) is emitted from several sources, including fuel and motor oil combustion, brake wear, resuspension of enriched road dust and, in particular, wheel weights which are dropped from vehicle wheels and pulverized by traffic (Lough et al., 2005). Mo is used as a component of automotive catalysts and as an anti-friction additive in lubricating oils (Grieshop et al 2006) and its emission rates were not significantly elevated relative to background levels. Overall, the considerable contributions of LDV to the airborne PM concentrations of these species may explain the closer agreement in the emission factors among the various studies, as it reduces the relevance of the HDV fraction on their overall emissions.

As illustrated in Figure 3-4, the highest emission factors were found for Fe, Ca and S, the sum of which typically represents the most substantial portion of the element/trace metals contribution to atmospheric PM (Lough et al., 2005). Along with Mg, Fe and Ca are major components of crustal materials and soil, and their presence in the particulate phase

is predominantly attributed to road resuspension (Grieshop et al., 2006). This may explain why the emission factors of Fe, Ca, and Mg obtained during the considered tunnel studies were higher than those reported or reconstructed from the cited dynamometer experiments (Figure 3-4). Additional important roadway sources for these elements include combustion of motor oil additives for Ca, Mg, and S, and the wearing of engines, tires and brakes, and tailpipe emissions (for Fe). S is also produced in great amounts from emissions of sulfur containing fuel (Swietlicki et al. 1996; Kittelson 1998), the consumption of lubricant oil motor (Geller et al. 2006b), and additives such as zinc dithiophosphate (also a significant source of Zn along with brake- and tire-wear, and tailpipe emissions of motor oil) (Lough et al., 2005). As expected, the emission factor of S at the I-710 was among the highest because of the higher levels of sulfur in diesel fuel compared to gasoline fuel. The fact that the atmospheric concentrations of Fe, Ca, S, and Mg are associated with both traffic and non-traffic sources (e.g., road and soil dust), and that the relative abundances of Mg, Ca, and Fe in road dust varies considerably across locations complicates the direct comparison and interpretation of their emission factors and justify the discrepancies among studies observed in Figure 3-4. It is also interesting to note that the lowest emission factors for each of the considered element/trace metals were found in the two dynamometer studies, probably because they only include the contribution of motor-vehicles and not the additional effect of resuspension of road dust to the airborne concentrations of these PM species.

The highest emission factors for OC and EC ( $E_{OC}$  and  $E_{EC}$ , respectively) were observed at the I-710 and in the tunnel experiments by Grieshop et al. (2006) (Figure 3-4), and

78

were probably associated with the increased EC emissions from HDVs. The lowest  $E_{OC}$ and  $E_{EC}$  values were obtained for LDVs during the dynamometer tests by Fujita et al. (2007), because LDVs emit in general significantly lower quantities of OC and EC than HDVs. The somewhat higher  $E_{OC}$  measured at the CA-110 may be related to absorption of vapor-phase organics in the sampling filter during collection (Turpin et al., 2000; Subramanian et al., 2004). Unlike the OC measurements reported by Grieshop et al. (2006), our OC concentrations obtained at the CA-110 and at the I-710 were not corrected for this positive artifact and the correspondent  $E_{OC}$  might be slightly overestimated. This positive artifact would be associated with only a portion of our PM<sub>2.5</sub> OC emission rate, (i.e., the ultrafine range), given that about half of the measured  $PM_{2.5}$ OC was in the accumulation mode ( $0.18-2.5 \mu m$ ), which was collected by impaction and should not be affected by positive artifacts induced by adsorption of organic vapors on quartz filters. Nonetheless, the relatively higher OC emission factors of our study suggest that our data may be biased by this phenomenon, and our reported OC emission rates thus need to be interpreted with some caution.

An important factor that may influence the comparison between  $E_{OC}$  and  $E_{EC}$  data from the two dynamometer studies is the analytical method used to determine OC and EC. While Schauer et al. (1999; 2002) employed a NIOSH thermal-optical transmittance (TOT) protocol in a Sunset Laboratory OC/EC analyzer, Fujita et al. (2007) used an IMPROVE thermal-optical reflectance (TOR) method in a DRI carbon analyzer (Chow et al., 2001). Because EC and OC are operationally defined by the analytical method, the use of different thermal evolution protocols can greatly influence the "split" between OC and EC and, thus, the OC/EC ratio (but not the amount of total carbon, TC = OC + EC, detected). For dynamometer studies, differences in speed and acceleration in the test cycles will lead to different emissions of OC, EC, and TC and will certainly impact the EC/OC ratio.

#### 3.4.4 Comparisons in the emission factors of PAHs, hopanes and steranes

Figure 3-5 presents a comparison among emission factors of PAHs, hopanes, and steranes for HDVs (5a) and LDVs (5b), obtained or reconstructed: a) during our roadway measurements at the I-710 and the CA-110, b) from recent chassis dynamometer experiments (Schauer et al. 1999; Riddle et al. 2007) and c) in the course of several tunnel studies conducted in different parts of the United States (Fraser et al. 1998; Chellam et al. 2005; Phuleria et al. 2006). All considered PAHs were sorted into three groups based on their molecular weights (i.e. low MW  $\leq$  228, medium MW=252, and high MW $\geq$  276). At the outset of this discussion, we need to emphasize that perfect agreement between our roadway measurements and those reported in previous works should not be expected a priori, mostly because emissions of organics from motor vehicles depend on many factors that are likely to vary significantly among these studies. These include vehicle age and engine load (for chassis dynamometer tests) as well as fleet mix, tunnel up-or downhill grade and ambient temperature conditions (for tunnel and roadway measurements). For example, some of the highest values in Figure 3-5a are associated with emissions from old motor vehicles employed by Fraser et al. (1998) and by Miguel et al. (1998) in their tunnel studies (conducted in 1993 and 1996, respectively).

In this regard, the comparisons presented in this paragraph are mainly intended to provide a range of emissions factors for each organic species and the degree to which the results of the present study lie within that range.

The data shown in Figure 3-5a indicate that for all of the organic species the emission factors determined from our measurements at the I-710 and those reconstructed for the HDVs contribution to the freeway traffic emissions (equation 3) are well within the values reported from previous studies, reflecting the impact of a mixed HDVs fleet in real-world freeway environments. In particular, our emission factors of hopanes and steranes are in close agreement with those from the various tunnel and dynamometer studies. For almost all of the organic species, a closer agreement is observed between our data and those from the tunnel measurements compared to the dynamometer tests. This is because the emissions factors based on tunnel studies incorporate the contributions of thousands of vehicles, similarly to our work at the I-710, while those derived from dynamometer experiments are representative of a rather limited number of vehicles. In addition to the results of our study, the light- and medium-MW PAHs factors reported by the rest of the studies are higher for HDVs compared to LDVs, probably because the higher engine loads and hotter combustion temperatures in the HDVs engines tend to break down the PAHs with the highest MW (Riddle et al., 2007a). Finally, although coronene has been proposed as a potential tracer for gasoline motor vehicle exhaust (Schauer et al., 1996; Cass et al., 1998) this species was detected in significant amounts (and comparable to those from LDVs) in our study at the I-710, as well as in the tunnel studies by Phuleria et al. (2006) and the dynamometer experiments on HDVs operated

under low speed driving conditions by Riddle et al. (2007). (The latter study proposed the use of large PAHs with MW of 326 and 350 Daltons as tracers of LDVs emissions instead of coronene).

Figure 3-5b shows that for all of the organic species the emission factors determined from our measurements at the CA-110 are very comparable to those reported from previous studies, , especially for PAHs with a MW≥ 276, hopanes and steranes. The lower emission factors of light- and medium-MW PAHs obtained at the CA-110 further validates the argument that the higher temperature and dilution conditions in the freeway environment may be shifting the gas-particle equilibrium of these organic compounds towards the gaseous phase (Mader and Pankow 2002), thus decreasing the correspondent emission factors. Our results indicate that among all measured PAHs emitted by LDVs those with the highest MW (i.e. indeno-(cd)-pyrene, benzo-(ghi)-perylene and coronene) are characterized by the highest emission factors. These 3 PAHs are found both in gasoline and diesel vehicles exhausts, but only in used gasoline vehicle motor oil, and not in fresh or used diesel engine oil (Fujita et al., 2007). The fact that the concentration of these species in gasoline vehicle motor oil increases with the age of the oil, may be the main reason why the magnitude of their emission factors for LDVs varies considerably among studies (Figure 3-5b). Emissions of high-MW PAH from HDVs are likely to be dominated by "smoking" vehicles characterized by poor combustion conditions. Finally, our results suggest that LDVs exhaust contain a more even distribution by molecular weight of hopanes and steranes than HDVs exhaust, which seems to be dominated by higher amounts of low-MW hopanes.



Note: <sup>a</sup> 2004 HDV data from the Caldecott tunnel; <sup>b</sup> 1996 HDV data from the Caldecott tunnel; <sup>c</sup> Run on hot-start FTP urban driving cycle, 2 medium HDVs (Model year 1995); <sup>d</sup> Run on 56k pounds load test cycle, 1998 HDV; <sup>e</sup> 2000 Washburn tunnel mixed fleet data in Houston with %HDVs=3.4; <sup>f</sup> 1993 Los Angeles tunnel mixed fleet data with %HDVs=2.7.



Note: <sup>a</sup> 2004 LDV data from the Caldecott tunnel; <sup>b</sup> 1996 LDV data from the Caldecott tunnel; <sup>c</sup> Run on cold-start FTP driving cycle, 9 catalyst-equipped LDVs (Mode year 1981-1994); <sup>d</sup> Run on California UDC cycle; 5 catalyst-equipped LDVs (Model year 1993-1996); <sup>e</sup> Run on FTP driving cycle; 6 Three-way catalyst equipped LDVs (Model year 1988-1999); <sup>f</sup> Run on unified warm test cycle; 4 LDVs (Model year 1995-1997); <sup>g</sup> Run on warm start driving cycles; 24 nonsmoker LDVs (Model year 1985-1994).

Figure 3-5 Comparison among  $PM_{2.5}$  emission factors of PAHs, hopanes and steranes for HDVs (a) and LDVs (b) from roadway measurements and tunnel and dynamometer studies. All values are expressed in mg kg<sup>-1</sup> of fuel burned.

#### **3.5** Summary and Conclusions

The emission factors of several important organic and inorganic fine particle species, and of particle number (PN) were estimated by integrating roadside speciated chemical data and carbon dioxide (CO<sub>2</sub>) concentrations collected at the CA-110 highway (where only gas-fuelled light-duty vehicles, LDVs, are allowed) and at the I-710 freeway (where about 20% of the traffic is characterized by heavy-duty diesel vehicles, HDVs). Emission factors at these two roadways were compared to those reconstructed from source emission data obtained at the Caldecott tunnel by Phuleria et al. (2006) and those reported from several other roadway tunnel and chassis dynamometer studies. Very good overall agreement was found between estimated and reconstructed emission factors (Ep and Ep,rec, respectively) for PN, elemental carbon (EC), Sulfate (S), high MW polycyclic aromatic hydrocarbons (PAHs), hopanes and steranes. The fact that our Ep and *Ep,rec* values for almost all non-labile particle species agree within 30% or less is encouraging in using roadway-based emission factors as a reliable proxy of vehicle exhaust characterization. Very good agreement among studies was obtained for Phosphor (P), Potassium (K), Manganese (Mn), Copper (Cu), Molybdenum (Mo), Lead (Pb) and Barium (Ba), while the largest differences were observed for Magnesium (Mg), Sulfur (S), Calcium (Ca) and, especially, Iron (Fe), probably because the atmospheric concentrations of these latter metals/trace elements are associated with both traffic and non-traffic sources, and the relative abundances of Mg, Ca, and Fe in road dust varies considerably across locations. Highest and lowest emission factors of OC and EC were

associated with HDVs and LDVs, respectively. For PAHs, hopanes, and steranes the emission factors determined from our roadway measurements were well within the values reported in the literature from tunnel and dynamometer studies, which provides further corroboration to our results. The ability to determine reliable roadway-based Ep and Ep, rec data for any particulate species could be further improved if more accurate information about the fleet composition and the total carbon content in motor-vehicle emissions were available. Results similar to those obtained herein could be used in epidemiological studies to assess human exposure to PM and its components both inside vehicles and in the immediate proximity of roadways.

#### 3.6 Acknowledgments

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### Chapter 4 Photochemical reactions and formation of secondary aerosols in the atmosphere

#### 4.1 Daily variation in physical characterization of urban ultrafine aerosol

#### 4.1.1 Abstract

A summer air quality monitoring campaign focusing on the evolution of ultrafine (< 180 nm in diameter) particle concentrations was conducted at an urban site in Los Angeles during June – July 2006. Previous observations suggest that ultrafine aerosol at this site are generally representative of the Los Angeles urban environment. Continuous and intermittent gas and aerosol measurements were made over 4 weeks with consistent daily meteorological conditions. Monthly averages of the data suggest the strong influence of commute traffic emissions on morning observations of ultrafine particle concentrations. By contrast, in the afternoon our measurements provide evidence of secondary photochemical reactions becoming the predominant formation mechanism of ultrafine aerosols. The ultrafine number concentration peak occurs in the early afternoon, before the maximum ozone concentration is observed. It is possible that some secondary semi-volatile components of the aerosol re-volatilize due to the elevated peak temperatures observed (ca. 30-35°C) combined with the increased atmospheric dilution during that time.

#### 4.1.2 Introduction

Ambient aerosol research has been motivated by many purposes. Prominent among these are the impacts of atmospheric aerosols, particularly ultrafine (ca. 100 – 180 nm in

diameter) aerosol, on human health and climate. There is increasing evidence that ambient ultrafine particles (UFP) are associated with adverse human health effects. For example, due to their small size, direct cellular uptake of UFP is possible as well as translocation to other sensitive target organs such as the heart and central nervous system (Oberdorster et al. 2005). Particle composition, size and surface area are all possible metrics affecting the health outcomes associated with UFP, although the dominant mechanisms for these outcomes remain largely unknown (Nel 2005). Ultrafine particles dominate ambient particle number concentrations but contribute very little to the total mass. Several studies, however, suggest that UFP disproportionately induce oxidative stress in cells and are more toxic compared to larger particles of similar (Li et al. 2003; Nel 2005; Nel et al. 2006). Finally, atmospheric processing of ultrafine particles tends to increase their size. These larger diameter particles may then affect the radiation balance of the Earth directly and indirectly by the production of cloud condensation nuclei (Facchini et al. 1999; Chung and Seinfeld 2002; Kulmala et al. 2004).

There are both primary and secondary sources of ambient UFP in urban atmospheres, and the dominant contributors are combustion products found in motor vehicle exhaust (Shi et al. 1999; Cyrys et al. 2003). Atmospheric oxidation of gas-phase exhaust species can produce lower vapor pressure compounds that readily condense onto existing particles. Particle composition and size can also evolve due to interaction/reaction of gas- and liquid- or solid-phase species at the particle surface or in the bulk solution, as well as through coagulation of existing particles. In some conditions, photochemical oxidation of gas-phase species can directly produce new UFP (Kulmala et al. 2004). Relatively few

studies have characterized the detailed physical and chemical properties of ultrafine particles. In Los Angeles, Sardar et al. (2005) reported ca. 4-5  $\mu$ g m<sup>-3</sup> for summertime UFP at a downtown site composed by mass of ca. 70% Organic Carbon (OC), 10% Elemental Carbon (EC), 10-15% sulfate and trace metals, and negligible nitrate. The high UFP mass concentrations at this site were attributed to the influence of a busy freeway nearby. An organic tracer study at this same site using time-resolved data showed that hopanes – a tracer for motor vehicle exhaust – were found mostly in the ultrafine (UFP) mode, and evidence for secondary organic aerosol production was found mostly in larger, accumulation mode, particles (Fine et al. 2004). These observations were similar to those reported by Cass et al. (2000) over a slightly different size range also in summertime Los Angeles. Observations in Pittsburgh, Pennsylvania during another recent summer study were similar (Zhang et al. 2005b), with hydrogenated carbon species dominating the UFP mode during the morning commute and oxygenated carbon species, the accumulation mode.

In addition to these direct UFP composition measurements, several studies have investigated particle properties in the vicinity of Los Angeles freeways to infer aerosol chemical composition (Zhu et al. 2002b; Kuhn et al. 2005a). Particle volatility was observed adjacent to, upwind and downwind of freeways. These studies suggest that sub-40 nm diameter particles are generally internally-mixed and external mixing tends to increase with UF particle size. High volumes of heavy duty diesel vehicle traffic were associated with higher relative fraction of non-volatile UF aerosol and more external mixing (Biswas et al. 2007) compared to freeways with no such traffic (Kuhn et al. 2005a). Depending upon the prevailing conditions, particle number concentrations reached urban background levels ca. 300 – 500 m downwind of freeways (Zhu et al. 2002a; Zhu et al. 2002b; Zhu et al. 2004). Motor vehicle exhaust thus directly impacts observations near the freeways as well as contributes to the urban background aerosol downwind.

In order to investigate the temporal evolution of ambient ultrafine atmospheric aerosol, we recently conducted a summertime study at an urban background site in Los Angeles, California. The temporal evolution of UFP tracers at "source" and "receptor" sites (Fine et al. 2004) has been reported as have chemical transformations in Lagrangian studies where fine aerosol were repeatedly observed as they moved downwind in the Los Angeles basin (Hughes et al. 2000; Hughes et al. 2002). Here we focus on changes occurring at a traditional "source" site. Several different aerosol measurement techniques were used to characterize the physical and chemical properties of the aerosol. This paper will focus primarily on the physical properties and volatility of the ultrafine aerosol with some supporting gas- and particle-phase composition data. The ultrafine aerosol composition data are reported in a companion paper (Ning et al. 2007). These data in combination with available concentrations of gaseous co-pollutants suggest that morning observations of UF aerosol, associated with the commute, are consistent with minimal atmospheric processing, but a large UFP fraction in the afternoon is composed of secondary material.

#### 4.1.3 Experimental Methods

This study was conducted at the University of Southern California's Particle Instrumentation Unit (PIU) located on the University Park campus near downtown Los Angeles, California. Some additional data were obtained from a nearby monitoring site (described below). The study was conducted over 4 consecutive 5-day weeks from June 28 through July 27, 2006. Sampling was conducted on weekdays only. The PIU is located within  $\approx$  150 m of a routinely-congested freeway (Interstate 110) and near construction and parking facilities. Previous observations have characterized the site as an urban background site heavily influenced by motor vehicle traffic (Sardar et al. 2005). Aerosol sampling inlets are at ca. 4 m in elevation at the PIU. All aerosol instrumentation inlets are co-located within a few meters horizontally of each other. Table 4-1 summarizes the sampling equipment, parameters obtained and sampling periods used.

Parameter	Sampling period	Dates
Meteorology Wind speed, wind direction, temperature, relative humidity <sup>a</sup>	Continuous 15 min average	27/6-28/7/2006
Aerosol measurements Ultrafine aerosol size distributions via SMPS <sup>b</sup>	Continuous 2-5 min scans	28/6-24/7/2006 (10 study days)
Mass concentration via APS <sup>e</sup>	Continuous 20 s average	14/7-27/7/2006 (10 study days)
MOUDI (Teflon substrates) <sup>e</sup>	Composite 5-day 6–9 a.m. and 1–4 p m samples	28/6–27/7/2006 (15 study days) 28/6–27/7/2006
Ultrafine aerosol volatility via TDMA <sup>f</sup>	Composite data, 6–9 a.m. and 1–4 p.m.	27/6-28/7/2006 (22 study days)
PM <sub>2.5</sub> mass via ARB <sup>g</sup>	Continuous hourly average	28/6-27/7/2006
Gas measurements O <sub>3</sub> , NO <sub>2</sub> /NO <sub>x</sub> , CO, SO <sub>2</sub> via $ARB^{g}$ CO <sub>2</sub> <sup>h</sup>	Continuous hourly average Continuous 1 min average	28/6-27/7/2006 30/6-27/7/2006 (18 study days)

#### Table 4-1Observations summary

#### 4.1.3.1 Site Meteorology

Standard meteorological parameters – wind speed and direction, temperature and relative humidity (RH) – were recorded as 15 minute average values, and subsequently processed to hourly means (Table 4-1). Conditions within the PIU during sampling were on average reasonably consistent throughout the study ( $\approx 25 \pm 2^{\circ}$ C,  $\approx 52 \pm 4\%$  RH) and should not have affected instrument performance.

#### 4.1.3.2 Gas composition measurements

Selected –  $NO_2$ ,  $NO_x$ ,  $O_3$ , CO,  $SO_2$  – hourly average gas concentration data observed at the Los Angeles – North Main Street monitoring site were obtained using the California Air Resources Board's Real-Time query tool (Table 4-1). The North Main Street location is ca. 3 km to the NE of the PIU, and is downwind for the prevailing conditions during the study. The archived data were converted to Pacific Daylight Time (PDT) to conform with the rest of the analysis. Carbon dioxide concentrations were measured at the PIU in 1 minute interval and converted to hourly averages (Table 4-1).

#### 4.1.3.3 Aerosol measurements - Continuous measurements

Several different continuous aerosol measurement techniques were used to characterize the properties of ambient particulate matter during the study (Table 4-1). Ambient ultrafine size distribution was measured using a Scanning Mobility Particles Sizer (SMPS) operated at a balanced sheath/excess flow rate of 15 liters min<sup>-1</sup> (lpm) and an aerosol in/out flow rate of 1.5 lpm. Twelve to thirty size distributions from 6 – 225 nm mean diameter were obtained per hour and averaged together. Total ultrafine number and volume concentrations were derived from the size distributions as well as ultrafine particle mass assuming a density of 1.6 g cm<sup>-3</sup> (Sioutas et al. 1999a; Geller et al. 2002). Within the ultrafine mode, particles < 50 nm in diameter are designated as the "nucleation" mode representing newly formed/relatively young atmospheric particles. Additional mass data were obtained using the Aerodynamic Particle Sizer for particles larger than ca. 500 nm in diameter and from the North Main Street location (PM<sub>2.5</sub> mass concentrations) (Table 4-1). An Aethalometer provided the sole continuous aerosol composition measurement – Black Carbon (BC) content (Table 4-1). Data were recorded every two minutes and averaged hourly.

#### 4.1.3.4 Aerosol measurements - Intermittent measurements

Two filter-based techniques were used to collect data for the study. The first was a custom-built high volume sampler (Misra et al. 2003; Phuleria et al. 2006), which operated at 450 lpm and was designed to separate particles into coarse (> 2.5  $\mu$ m in diameter), accumulation (180 nm – 2.5  $\mu$ m) and ultrafine (< 180 nm) modes. Accumulation mode aerosols are collected on quartz-fiber impaction strips (cut from Pallflex Tissuquartz 2500QAT-UP-8x10, Pall Corp., East Hills, NY) and ultrafine aerosols are collected on a TFE-coated glass fiber filter (Pallflex Fiberfilm T60A20-8x10, Pall Corp., East Hills, NY) held in a commercially-available ca. 20 x 25 cm high-volume filter holder. The quartz substrates and coated glass fiber filters were cleaned and prepared for sampling using the methods described by Fine et al. (Fine et al. 2004) and Phuleria et al. (Phuleria et al. 2006). Composite "morning" (6 – 9 am PDT) and "afternoon" (1 – 4 pm PDT) samples were obtained over all five days of each sampling

week. Weekly composite morning and afternoon samples were also obtained using a MOUDI operated at 30 lpm to size-segregate particles into the same modes as the high volume sampler. The MOUDI was operated with Teflon substrates. Total collected mass was obtained by weighing each Teflon substrate before and after the completion of weekly sampling in a temperature and humidity-controlled location after allowing for equilibrium to be achieved over 24 hours.

#### 4.1.4 Results and Discussion

#### 4.1.4.1 Meteorology

Throughout the month-long study, the weather conditions at the PIU were reasonably stable. The prevailing wind direction was from the SE (mean 226° range 206° – 242°, hourly average), although the winds were generally light (< 2.5 m s<sup>-1</sup>) and variable (hourly sigma values are relatively large (ca. 50°)). Diurnal patterns are readily evident in the wind speed, temperature and relative humidity. In the early morning, winds were light (< 1 m s<sup>-1</sup>). After 9 am, the wind speed increased to a maximum of 2.4 m s<sup>-1</sup> from 2 – 4 pm, before gradually declining into the evening. Therefore concentrations observed in the morning are more affected by nearby sources than in the afternoon. Ambient temperatures were about 20°C through 8 am, increasing rapidly to about 27°C at 10 am and becoming stable near 29-32 °C from 11 am – 5 pm before tapering off into the evening with an overall ca. 10°C decrease in temperature. Not surprisingly, RH follows the opposite pattern and is lowest (ca. 35%) in the middle of the day and peaks overnight

at 70% on average. The consistency of this weather on a daily basis ensures that representative results were obtained when averaging across all 4 weeks of the study.

#### 4.1.4.2 MOUDI/SMPS mass concentration comparison

The weekly average ultrafine mass concentrations observed by the MOUDI and the SMPS during the morning ("AM") and afternoon ("PM") sampling periods are comparable (Figure 4-1). Ambient ultrafine concentrations varied from ca.  $3 - 7 \mu g m^{-3}$  and are approximately 4  $\mu g m^{-3}$  on average with no consistent discernible difference between the two time periods. The average MOUDI concentration was  $0.96 \pm 0.18$  that of the SMPS. UFP mass concentrations on this order have been observed previously in Los Angeles (Fine et al. 2004; Sardar et al. 2005). With the exception of the first week's PM data, mass concentrations by the two methods during the other sampling periods agree within 1  $\mu g m^{-3}$  and are within the uncertainty of the measurement.



Figure 4-1 MOUDI- and SMPS-derived ultrafine mass concentrations byweek (week 1: 28–30 June, 5–6 July; week 2: 7, 10–13 July; week 3: 14, 17–20 July; week 4: 21, 24–27 July 2007). The error bars show the standard error of the mean.

#### 4.1.4.3 Hourly average gas- and aerosol-phase concentrations

Selected hourly average concentrations ( $\pm$ SD) for CO, NOx, BC and PM<sub>2.5</sub> are shown in Figure 4-2. All species observed exhibited a diurnal variation in concentration with minimum values typically exhibited in the middle of the afternoon and overnight.



Figure 4-2 Selected representative (CO,  $NO_x$ ,  $PM_{2.5}$ , black carbon (BC)) hourly average gas and aerosol data. The error bars show the standard error of the mean.

NO<sub>X</sub> and CO concentrations reach 0.8 and 0.1 ppm, respectively, during the 6 – 10 am morning commute (ca. 200% of the daily mean value). They drop sharply in the early afternoon (2 – 3 pm), reflecting their common source at the nearby freeway and the decrease in traffic post-commute as well as the increase in atmospheric mixing height. SO<sub>2</sub> concentrations follow a pattern similar to CO's, consistent with diesel vehicle emissions being the dominant source. PM<sub>2.5</sub> mass concentrations exhibit a less steep peak
- up to 150% of the daily mean value or 40  $\mu$ g m<sup>-3</sup> –during the morning commute, and then degrade slowly into the evening reaching minimum values at 7 - 8 pm. PM<sub>2.5</sub> data extracted from the APS data exhibit a similar profile. The more gradual decline may reflect the influence of the increase in the atmospheric mixing height in the Los Angeles basin during the day partially counterbalanced by daylight emissions and photochemical production of new PM mass in that range. Aerosol Black Carbon (BC) mass concentrations exhibit behavior somewhat intermediate to these two patterns - while there is a sharp peak (up to 3.8  $\mu$ g m<sup>-3</sup> (200% of the daily mean)) in the morning, concentrations decrease slowly reaching a minimum concentration overnight of ca. 0.9 µg m<sup>-3</sup>. The sharp peak is also associated with motor vehicle emissions during the morning commute. The more gradual decay after the commute illustrates that BC becomes part of the urban background signal. Hourly average ultrafine particle size distributions (Figure 4-3) also show the strong impact of the morning commute period of 6 - 9 am – a sharp increase in concentrations with a mode at around 30 nm and broadening of the distribution to ca. 100 nm. Following the commute from 9 am to 2 pm, the mode diameter remains near 30 nm, but the peak concentration exceeds  $220 \ \text{# cm}^{-3}$ , increasing from 150 # cm<sup>-3</sup> earlier in the day. This concentration increase in the early afternoon is consistent with photochemical activity being responsible for the increase in particle number concentration, particularly as BC concentrations - a surrogate for primary UF particles from motor vehicles – do not similarly rise. A similar size distribution pattern has been observed previously as this site (Fine et al., 2004). These patterns show the influence of the morning commute at this urban background site on

UFP concentrations and suggest the influence of both primary and secondary sources on ambient UFP in summertime conditions.



### Hourly mean HSPMS contour plot (dN, # cm<sup>-3</sup>)

Figure 4-3 Hourly mean ultrafine aerosol number concentration contour plot (monthly average),  $dN/d(\log d_p)$ .

Ozone – a key marker for secondary photochemical activity – concentrations reach their maximum value from 2 – 4 pm (Figure 4-4) when temperatures reach nearly 30°C. Following its first morning peak related to traffic, the total ultrafine particle number concentration starts increasing in the late morning-early afternoon period in a trend similar to  $O_3$  concentrations, but unlike ozone, it subsequently decreases rapidly in the middle of the afternoon. Oxidation of ambient volatile organic gases from motor vehicle

exhaust by  $O_3$  and/or hydroxyl radical is likely to produce many of the semi-volatile species that partition to the particle-phase and contribute to the size and concentration of ultrafine aerosol particles.





sampling time period

Figure 4-4 Hourly mean  $O_3$ ,  $NO_x$ , temperature and ultrafine aerosol number concentrations (monthly average). The error bars show the standard error of the mean.

Recent observations during the summer in Tokyo, Japan (Takegawa et al. 2006) for similar meteorlogical conditions suggest the peak in largely accumulation mode secondary organic mass occurs simultaneously with the ozone peak. Given the increase in ambient temperature and atmospheric mixing height later in the afternoon, however, it is possible that re-volatilization of the semi-volatile secondary aerosol may occur from the relatively smaller particles at these elevated temperatures with subsequent redeposition onto and growth of larger particles. Recent modeling work investigating the effect of temperature (Sheehan and Bowman 2001) suggests this may occur for ambient conditions like those encountered in our study.

Further insights into the formation mechanisms of UFP may be inferred by examining the diurnal profiles of the mass (or volume) –based concentrations of BC, nucleation mode UFP and accumulation mode aerosol. The diurnal profiles of particle volume in the nucleation mode shows a main peak occurring well after the peak in BC concentrations (Figure 4-5), and a smaller peak discernible in the morning commute at 7 - 8 am. These peaks are indicative of two distinctly different processes, one related to traffic emissions and the other due to secondary production.



Figure 4-5 Hourly mean nucleation ( $V_{\rm UFN}$ , <50 nm) and accumulation ( $V_{\rm UFA}$ , 50–180 nm) mode ultrafine particle volume, accumulation mode ( $V_A$ , 180–2500 nm) particle volume and black carbon concentrations (monthly average). The error bars show the standard error of the mean.

In contrast, the particle volume in the accumulation mode aerosol shows a peak from 7 - 8 am and concentrations remain high and relatively stable until approximately 1 - 2 pm when they start to decline (Figure 4-5), following the peak in the nucleation mode volume. This suggest that these particles are mainly emitted by vehicles and do not seem to be affected by secondary processes. The minimums in nucleation and accumulation mode concentrations observed in the late afternoon are consistent with the relative persistence of these particles and the mixing height reaching a maximum prior to falling after dark.

All of the average hourly data shown are consistent with a morning commute peak in UFP with a strong primary emission component. As the day progresses, secondary atmospheric processes and changes in the mixing height are responsible for changing the distribution of UFP altering its composition and physical properties as well.

# 4.1.5 Conclusions

The combined gas concentration and aerosol physical and chemical concentration data noted in the previous sections support the following interpretation of UFP at this urban background site. During the morning, UFP levels are heavily impacted by fresh motor vehicle emissions and follow the trends of species originating from mobile sources (i.e.,  $NO_X$ , CO, and BC). Oxidizing photochemical reactions occur as the day progresses into the late morning and early afternoon. Ozone concentrations increase as does the concentration of ultrafine particles in the nucleation mode due to photochemical activity. As the mixing height increases, particle mass ( $PM_{2.5}$ ) and number concentrations decrease. Although the local emission strength is reduced, the sampling site is also observing substantial photochemical changes in the ultrafine particle population. As temperatures and ozone concentrations peak in the late afternoon, the number of nucleation mode particles has already started decreasing due to the high temperature as the smallest particles preferentially volatilize and condense onto larger particles. These observations at a single site are consistent with previous observations in the Los Angeles basin measuring the evolution of the aerosol plume as it moved downwind (Gard et al. 1998; Hughes et al. 2000; Hughes et al. 2002). It appears to be possible to observe UF aerosol evolution at a single location as long as the meteorological conditions are consistent. These results also emphasize the importance of obtained temporally-resolved data.

# 4.1.6 Acknowledgements

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# 4.2 Daily Variation in Chemical Characteristics of Urban Ultrafine Aerosols and Inference of Their Sources

# 4.2.1 Abstract

A summer air quality monitoring campaign focusing on daily variation of ultrafine (< 180 nm in diameter) particle chemical characteristics was conducted in a typical urban site in Los Angeles during June – July 2006. Ultrafine particles (UFP) were collected weekly for two 3-hr periods each day—one to capture the morning commute (06:00-09:00 PDT) (Pacific Daylight Time) and one to investigate photochemically-altered particles (13:00-16:00 PDT). Samples were analyzed for ionic compounds, metals, trace elements, elemental carbon, and organic carbon. In addition, measurements of individual organic species and their variation with time of day at the urban site were conducted. The relative abundances of alkanes, PAH, and hopanes in the morning denote a strong influence of commute traffic emissions on ultrafine particle concentrations. By contrast, afternoon concentrations of oxygenated organic acids and sulfate rose, while other species were diluted by increased mixing height or lost due to increasing temperature. These are clear indicators that secondary photochemical reactions are a major formation mechanism of ultrafine aerosols in the afternoon. The concentrations of organic species originating from vehicular emissions measured in this study compare favorably to those from freeway-adjacent measurements by using CO<sub>2</sub> concentrations to adjust for dilution, demonstrating the effectiveness of this tool for relating sites affected by vehicular emissions.

# 4.2.2 Introduction

Increasing epidemiological and toxicological evidence associates adverse human health effects with exposure to atmospheric ultrafine particles (UFP). Although ultrafine particles only constitute a small fraction of total ambient particulate matter (PM) mass concentration, they contribute significantly to the surface area concentration and dominate the number concentration. Several studies have demonstrated the ability of ultrafine particles to induce oxidative stress and inflammation in cells, which may contribute to cardiovascular diseases (Li et al. 2003; Nel 2005). The inherent large surface area-to-mass ratio of UFP may result in increased adsorption of organic molecules and the induction of oxygen radicals (Donaldson et al. 2002; Lippmann et al. 2003).

Ambient UFP in urban areas originate from both primary and secondary formation mechanisms. The former is direct emission from sources, such as vehicles and other anthropogenic activities (Kim et al. 2002; Cyrys et al. 2003), while the latter incorporates physical and chemical reactions such as condensation on the primary particles and photochemical reactions in the atmosphere (Donaldson et al. 1998; Jones et al. 2000; McMurry et al. 2000). These secondary formation mechanisms can substantially change particle size and chemical composition as they evolve in the atmosphere (Cass et al. 2000) as well as directly produce new UFP (Kulmala et al. 2004).

Several studies have addressed ambient UFP chemical composition. Cass et al. (2000) reported average mass concentration of  $0.55 - 1.16 \,\mu gm^{-3}$  for particles in the size range of

56 nm-100 nm in Southern California, which consisted of 65% organic matter, 7% elemental carbon, 7% sulfate, 4% trace elements, and small amounts of sodium, chloride and nitrate. Similarly, Sardar et al. (2005) found UFP mass concentration of 4-5 µgm<sup>-3</sup> at a major freeway site in downtown Los Angeles, with 70% of organic matter, 10% elemental carbon, 10-15% of sulfate and trace metals, and negligible nitrate. The high UFP mass concentrations at this site reflect the influence of the nearby freeway (CA-110). An organic tracer study at this same site using time-resolved data showed that hopanes – tracers for motor vehicle exhaust - were found mostly in the ultrafine (UFP) mode, and evidence for secondary organic aerosol production was found mostly in larger, accumulation mode particles (Fine et al. 2004). These observations were similar to those reported by Cass et al. (2000) over a slightly different size range also in summertime Los Angeles. Observations in Pittsburgh, Pennsylvania during another recent summer study were similar (Zhang et al. 2005b), with hydrogenated carbon species dominating the UFP mode during the morning commute and oxygenated carbon species prevailing in the accumulation mode. In addition to these generalized measurements of UFP composition, few studies have investigated the detailed UFP composition in the atmosphere. Fine et al. (2004) studied the diurnal and seasonal variation of several individual organic tracers of both ultrafine and accumulation particles at an urban site near downtown Los Angeles and an inland site in Riverside, CA. The results showed higher secondary organic compound concentrations in summer than in winter and during the day rather than at night, which was attributed to photochemical reactions.

In the present paper, we focus on the chemical composition of UFP in a typical urban site in Los Angeles, near the downtown area. The evolution of carbonaceous compounds and various organics species from morning to afternoon has been measured in order to investigate the contributions of primary emissions and secondary photochemical reactions. A comparison of polycyclic aromatic hydrocarbons (PAH) and hopanes/steranes between a nearby freeway and the sampling site was carried out by applying dilution ratios based on  $CO_2$  concentrations (Ntziachristos et al. 2007c). Additionally, an inorganic ion balance was used to investigate the acidity of ultrafine particles during the morning and afternoon periods. The present paper will provide insight into short-term variation of UFP chemical properties due to changes in source strength as well as atmospheric conditions.

# 4.2.3 Experimental methods

### 4.2.3.1 Sampling location

The present study took place between June 28 and July 27, 2006 over 4 consecutive weeks with sampling conducted only on weekdays. The sampling site was located at the Particle Instrumentation Unit (PIU) of the Southern California Particle Center and Supersite (SCPCS) near the University Park campus of the University of Southern California near downtown Los Angeles, CA. The PIU is within 150 m of a major freeway (Interstate-CA-110) and adjacent to a six level parking structure and various construction sites. An instrumented trailer is maintained inside PIU and the aerosol sampling inlets were located at an elevation of ca. 4 m fixed on top of the trailer and within ca. 3 m

horizontally of each other. Previous studies carried out in the same sampling site have described it as being affected by a typical mixture of urban pollution sources, including motor vehicle traffic (Sardar et al. 2005).

#### 4.2.3.2 Sampling protocol

Aerosol sampling was accomplished by deploying two filter-based techniques: a custombuilt high volume sampler (Geller et al. 2002) and Micro-Orifice Uniform Deposit Impactors (MOUDI, MSP, Inc., Minneapolis, MN). The high volume sampler has a nominal flow rate of 450 l min<sup>-1</sup> and separates particles into coarse ( $D_p > 2.5 \mu m$ ), accumulation (0.18 <  $D_p$  <2.5  $\mu m)$  and ultrafine (D\_p<0.18  $\mu m)$  modes. Accumulation mode aerosols were collected on quartz-fiber impaction strips (cut from Pallflex Tissuquartz 2500QAT-UP-8×10, Pall Corp., East Hills, NY), and ultrafine aerosols were collected on TFE-coated glass fiber filters (Pallflex Fiberfilm T60A20-8x10, Pall Corp., East Hills, NY) seated in a specially-designed  $20 \times 25$  cm high-volume filter holder. The coated filters have been used to minimize organic vapor adsorption artifacts associated with quartz-fiber filters (Fine et al. 2004; Phuleria et al. 2006). Parallel to the high volume sampler, two MOUDIs sampled concurrently at 30 lpm to collect size-segregated particles in the accumulation mode ( $0.18 < D_p < 2.5 \mu m$ ) and ultrafine mode ( $D_p < 0.18$  $\mu$ m). PTFE and quartz 37 mm filters were used as impaction substrates to collect ultrafine particles, whereas PTFE filters and Aluminum 47mm substrates were used to collect accumulation mode particles in the two MOUDIs. Quartz and aluminum substrates were prebaked at 550 °C for 8 hours, and TFE-coated glass fiber filters were precleaned with a

solvent mixture as described by Fine et al. (Fine et al. 2004). All were stored in baked aluminum-foil-lined containers prior to sampling.

Composited aerosol samples were collected in the "Morning" (6:00-9:00 PDT) and "Afternoon" (13:00-16:00 PDT) periods over the five days of each sampling week for four consecutive weeks. Each weekly sample encompassed 15 hours (5 days multiplied by 3 hours per day) sampling for respective time periods. "Morning" period corresponds to rush hour traffic times when the ambient aerosols in the sampling site are dominated by particles freshly emitted from vehicles on the nearby freeway. "Afternoon" period represents the mixture of primary particles from traffic and secondary particles undergoing physical and chemical changes (i.e. photochemistry and possible volatilization if they contain labile species) during the day. Although the present study mainly focuses on UFP properties, accumulation mode particles were also collected in the last week of sampling in order to put the data into perspective. All filters were sealed in annealed, foil-lined Petri dishes and stored in a freezer between sampling intervals.

# 4.2.3.3 Sample analysis

The PTFE filter samples from MOUDI were weighed three times before and after the weekly sampling using a microbalance (Model MT-5, Mettler Toledo, Inc., Highstown, NJ) after allowing at least 24 hours of equilibration in a controlled environment with temperature of 22-24°C and relative humidity of 40-45%. The mass concentrations of aerosol particles were determined by the net filter weight gained after sampling. Quartz filter samples of ultrafine particles and aluminum substrate samples of accumulation

mode particles from MOUDI were then cut into 3 fractions for chemical composition analysis. Half of the filters were used for analysis of inorganic ions by means of ion chromatography to determine the PM concentrations of inorganic ions, including sulfate, nitrate, ammonium, potassium, sodium, and chlorine, according to Kerr et al. (Kerr et al. 2004). Another fraction of 1 cm<sup>2</sup> punches from the other half of the filters was analyzed for elemental carbon (EC)/organic carbon (OC) using the Thermal Evolution/Optical Transmittance (TOT) analytic method as described by Birch and Cary (Birch and Cary 1996). The remaining portions of samples were retained for future analyses. The PTFE filter samples from MOUDI were analyzed by means of inductively coupled plasma mass spectroscopy (ICPMS) to determine the trace element and metal content. Details of the digestions, analysis and method detection limits have been presented by Lough et al. (2005).

The analysis methods of the quantification of individual organic compounds in the collected aerosol samples were based on earlier established solvent extraction methods (Sheesley et al. 2004). Procedures for sample extraction and molecular quantification for the organic tracers have been described in detail by Phuleria et al. (Phuleria et al. 2006), and only a brief summary is presented here. The filter samples from the high-volume sampler were spiked with known amounts of isotope labeled internal standard compounds, including three deuterated PAH, three deuterated alkanoic acids, four deuterated alkanes, deuterated cholestane, deuterated cholesterol, and  $C^{13}$  labeled galactosan. Samples were extracted in dichloromethane and methanol and were combined and reduced in volume to 100-250 µL by rotary evaporation followed by pure nitrogen

evaporation. The final target volume was determined based on the amount of organic carbon mass in each sample (Phuleria et al. 2006). The extracts were derivatized using diazomethane to convert organic acids to their methyl esters and run on the GCMS. An aliquot of the sample extract was then silylated and run on the GCMS to measure levoglucosan.

The methylated and silylated samples were analyzed by auto-injection into a GC/MSD system (GC model 5890, MSD model 5973, Agilent). A 30 m  $\times$  0.25 mm DB-5MS capillary column (Agilent) was used with a splitless injection. Along with the samples, six dilutions of authentic quantification standard solutions were also injected and used to determine calibration curves for the compounds of interest. While some compounds are quantified based on the response of a matching compound in the standard mixtures, others for which matching standards were not available are quantified using the response factors of compounds with similar structures and retention times. Analytical errors for these methods were calculated by compound using spike recovery and the standard deviation of blank filter analysis.

# 4.2.4 Results and discussion

### 4.2.4.1 Mass concentration and mass balance

Throughout the entire campaign the meteorological conditions at the sampling site were typical of Southern California summer, with stable wind speeds at  $1.64 \pm 0.74$  m/s and wind direction of  $223 \pm 28$  degrees, which placed the sampling site directly downwind of

the nearby freeway (and at ~150m). The distance to the sampling site from the freeway is sufficiently long to place it outside the immediate "zone of influence" of the freeway, based on our previous work in Southern California (Zhu et al. 2002a; Zhu et al. 2002b). Temperature and relative humidity showed strong diurnal profiles with higher temperature and lower humidity in the afternoon. Elevated afternoon ambient ozone concentrations further support enhanced photochemical activity during afternoons of this study. Detailed average and standard deviation of meteorological parameters and associated gases concentrations in the morning and afternoon periods are described in Table 4-2.

Meteorological parameters	Morning <sup>1</sup>	Afternoon <sup>1</sup>
Temperature (°C)	$25\pm3$	$38 \pm 3$
Humidity (%)	$70 \pm 10$	$35\pm7$
Wind speed (m/s)	$0.96\pm0.28$	$2.32\pm0.29$
Wind direction (degree)	$213\pm35$	$233\pm15$
Gas species		-
CO (ppm)	$0.75\pm0.34$	$0.22\pm0.09$
$NO_2$ (ppb)	$38.4 \pm 14.7$	$17.8\pm4.2$
$NO_x(ppb)$	$95.4\pm46.9$	$17.8\pm4.7$
$O_3$ (ppb)	$5.6 \pm 5.8$	$57.3 \pm 21.6$

<sup>1</sup>: Presented data are the average and standard deviation during the time period.

# Table 4-2Meteorological parameters and measured gases concentrations in the<br/>morning and afternoon periods during the study

Weekly and average UFP mass concentrations as well as measured species concentrations in the morning and afternoon periods are shown in Figure 4-6. Mass concentrations of ultrafine particles (UFP, in the context of this paper defined as  $PM_{0.18}$ ) ranged from 2.63 to 7.26 µg/m<sup>3</sup> with an average value of 4.35 ± 0.22 µg/m<sup>3</sup> in the

morning and  $4.95 \pm 0.26 \ \mu\text{g/m}^3$  in the afternoon. Average UFP concentration is slightly higher (14%) in the afternoon than morning, which may suggest secondary aerosol formation and growth by condensation of low-volatility atmospheric oxidation reaction products onto pre-existing particles (Shimmo et al. 2002).



Figure 4-6 Weekly and average mass concentrations of ultrafine (U) particles and mass balance of measured species in the morning (AM) and afternoon (PM).

Chemical mass balance results show very good agreement between the reconstructed mass by summing the measured chemical species concentrations and the gravimetricallydetermined mass concentration. On average  $78 \pm 14\%$  and  $94 \pm 29\%$  of UFP mass can be explained by the measured chemical constituents in the morning and afternoon periods, respectively. The unidentified mass is primarily composed of carbon-associated atoms (O, H, etc.) in the organic compounds (Sardar et al. 2005).

For organic mass (OM) concentrations, conversion factors have been applied to the measured organic carbon concentrations to account for additional mass of the H, O, S and N in the organic compounds of typical urban atmospheric organic aerosols (Gray et al. 1986). Typically, a conversion factor of 1.4 has been used in the previous studies by Cass et al. (2000) and Sardar et al. (2005). However, Turpin and Lim (2001) reported that this factor may vary widely from 1.2 to 2.6 due to the variety of organic constituents. Bae et al. (2006) estimated a conversation factor of 1.8 for urban aerosols by using both chemical mass balance and source apportionment methods in a two-year study around St. Louis, MO. In the present study, a conversion factor of 1.4 has been applied for morning aerosols and 1.8 for afternoon aerosols to represent the increased contribution of oxygenated organic compounds in the afternoon (Huebert and Charlson 2000).

UFP chemical composition varied to a slight extent during the study, with 50-73% OM, 1-11% EC, 6-23% nitrate and 9-23% sulfate. Similar chemical composition of UFP has been reported by Sardar et al. (2005) in Los Angeles (32-69% OM, 1-34 % EC, 0-4% nitrate and 0-24% sulfate) and by Cass et al. (2000) in other Southern California locations (37-67% OM, 3.5-17.5% EC, 0-19% nitrate and 1-18% sulfate). Other reported ions include ammonium, sodium, potassium, chlorine and phosphate, which will be discussed in a subsequent section of this paper. Average contribution of nitrate to UFP mass decreased from 16% to 10% due to its volatilization from particle- to- gas phase as

temperature increases in the afternoon (Buckley et al. 1991; Chang et al. 2000). EC fraction decreased from 5% to 2%, suggesting the decline of freeway traffic volume from morning to afternoon combined with the increase in mixing height of the atmosphere during that time. However, OC and sulfate contributions to UFP increased from 59% to 65% and 14% to 18%, respectively, indicating elevated secondary aerosol formation when higher photochemical activity occurs in the afternoon (Pandis et al. 1993; Barth et al. 2000). Detailed chemical composition data will be further discussed in the subsequent sections.

# 4.2.4.2 Inorganic Ions

Figure 4-7 presents the ratio of sulfate, nitrate and ammonium concentrations to the total UFP mass concentrations of UFP in morning and afternoon periods. The measured average UFP sulfate concentrations were 0.47  $\mu$ g/m<sup>3</sup> and 0.84  $\mu$ g/m<sup>3</sup> in morning and afternoon, respectively. Similar concentrations have been observed by Sardar et al. (2005) in Los Angeles.



Figure 4-7 Mass fractions of sulfate, nitrate and ammonium in total mass of ultrafine (U) particles in the morning (AM) and afternoon (PM) periods.

Sulfate concentrations and mass fraction for both UFP and accumulation mode particles increased in the afternoon due to the photochemical origin by condensation of gaseous sulfuric acid from the oxidation of sulfur oxide gases (Barth et al. 2000). Average UFP nitrate concentrations were 0.53  $\mu$ g/m<sup>3</sup> and 0.44  $\mu$ g/m<sup>3</sup> in morning and afternoon, respectively. The decrease of nitrate concentrations in the afternoon reflects the increase in its dissociation constant with increasing temperature and decreasing relative humidity (Hering et al. 2004). The most abundant cation was ammonium, with average concentrations of 0.09  $\mu$ g/m<sup>3</sup> and 0.17  $\mu$ g/m<sup>3</sup> in morning and afternoon, respectively. The increase in ammonium by nearly the same percentage as sulfate from morning to afternoon indicates that a small amount of the photochemically produced sulfuric acid aerosol is neutralized by ammonia.

The measured ion concentrations for UFP and accumulation mode particles allowed us to determine the degree to which particles in these two ranges are acidic or fully neutralized. Following the approach of Zhang et al. (2004), particle acidity was examined, based on the ratio of measured ammonium concentrations versus the concentration needed to fully neutralize the measured sulfate and nitrate. A value of unity suggests that sulfate and nitrate might be fully neutralized by ammonium in the form of  $(NH_4)_2SO_4$  and  $NH_4NO_3$ . A value close to zero suggests that the particles are predominately  $H_2SO_4$ . Figure 4-8 presents the ammonium ratio plots for weekly and average UFP and accumulation mode particles in the morning and afternoon. Accumulation mode PM are fully neutralized in both morning and afternoon periods, with the measured to the required for neutralization ammonium concentrations being very close to 1. On the other hand, UFP appear to be highly acidic during both sampling periods, with ammonium ratios of  $0.29 (\pm 0.09)$  and  $0.36 (\pm 0.14)$  in the morning and afternoon periods, respectively. The UFP acidity in the afternoon period is consistent with the findings of Zhang et al. (Zhang et al. 2004) in Pittsburgh showing that ultrafine particles are acidic during the initial stage of the photochemically induced nucleation. The UFP acidity during the morning traffic period corroborates previous findings of studies characterizing vehicle emissions, showing that the UFP sulfate in vehicle exhaust is mostly in the form of sulfuric acid or ammonium bisulfate rather than



Figure 4-8 Weekly and average ratios of measured ammonium to required ammonium concentration for complete neutralization of ultrafine (U) and accumulation (A) particles in the morning (AM) and afternoon (PM) periods.

ammonium sulfate (Grose et al. 2006). Previous investigators argued that UFP may be acidic in the immediate vicinity of the roadway, but they would become neutralized a short distance downwind since the reaction rate of ammonia with sulfuric acid particles is close to collision-controlled (Mcmurry et al. 1983) under excess ammonia conditions. A possible explanation for the observations in our site is that ammonia preferentially reacts with accumulation mode particles and is used up before it can react with UFP. In turn, the accumulation mode appears to be fully neutralized during both periods (Figure 4-7), a result that is also consistent with the fact that particles in that range represent an aged

aerosol, whose residence time in the atmosphere has been sufficiently long for it to be fully neutralized.

# 4.2.4.3 Carbonaceous compounds

Figure 4-9 presents the average concentrations of organic carbon (OC) and elemental carbon (EC) measured in ultrafine and accumulation mode particles in morning and afternoon. The concentrations for UFP are the average of four weekly samples, and uncertainties were determined by the combination of weekly variation of sample concentrations and analysis error. Accumulation mode data were collected for one week and are presented here for comparison purposes. The EC concentration of UFP decreased from 0.17  $\mu$ g/m<sup>3</sup> in the morning to 0.10  $\mu$ g/m<sup>3</sup> in the afternoon. The same trend was also found in the accumulation mode particles with 0.18  $\mu$ g/m<sup>3</sup> in the morning and 0.13  $\mu$ g/m<sup>3</sup> in the afternoon. Traffic emissions are the predominant source of elemental carbon to the atmosphere in Los Angeles (Schauer et al. 1996). In turn, higher EC concentration in the morning reflects higher traffic volume on the nearby 110 freeway during the morning sampling period. Decreased traffic and increased mixing height likely result in declining EC concentration in the afternoon. Similar observations have been found by Bae et al. (2004) and Sardar et al. (2005).



Figure 4-9 Average OC and EC concentrations of ultrafine (U) and accumulation (A) particles in the morning (AM) and afternoon (PM).

In contrast to UFP EC, average UFP OC concentrations increased from 1.41  $\mu$ g/m<sup>3</sup> to 1.66  $\mu$ g/m<sup>3</sup> from morning to afternoon, which suggests that EC and OC do not share the same sources in the afternoon. While vehicular traffic is responsible for a portion of EC and OC at the site, elevated photochemical activity augments OC concentration in the afternoon. Interestingly, accumulation PM mode OC concentration decreased from 4.78  $\mu$ g/m<sup>3</sup> to 3.24  $\mu$ g/m<sup>3</sup> in the afternoon, as shown in the figure. Decreasing accumulation mode OC concentrations are likely the result of a regional OC concentration being diluted as mixing height increases in the afternoon.

# 4.2.4.4 Organic speciation



Figure 4-10 Average organic species concentration of ultrafine particles in the morning and afternoon: (a) *n*-alkanes; (b) PAHs; (c) Hopanes and Steranes; (d) Organic acids.

Figure 4-10(a) presents the average mass concentrations of  $C_{24}$ - $C_{40}$  *n*-alkanes during the campaign. Sums of weekly averaged average *n*-alkanes ( $C_{24}$ - $C_{40}$ ) concentrations of ultrafine particles were 30.2 ng/m<sup>3</sup> and 11.7 ng/m<sup>3</sup> in the morning and afternoon,

respectively. Carbon preference index (CPI) can be used to determine the anthropogenic and biogenic sources of *n*-alkanes. It is defined as the sum of the concentrations of the odd carbon number alkanes divided by that of the even carbon number alkanes (Simoneit 1986). Previous studies have shown that *n*-alkanes attributed to anthropogenic emission (e.g., gasoline residues) have CPIs close to 1. In rural areas, CPIs are generally higher than 2.0 due to biogenic influence (Simoneit 1986; Zheng et al. 2000; Zheng et al. 2006). In the present study, CPIs of UFP *n*-alkanes are 1.1 and 1.0 in the morning and afternoon, respectively, indicating the strong influence of vehicular emissions to the sampling site during the campaign. As shown in the figure, the measured C<sub>24</sub>-C<sub>40</sub> n-alkanes species showed much higher concentrations in the morning, which can be explained by the strong source strength of vehicle exhaust from morning commute traffic. The drop in their concentrations in the afternoon may be due to the combined effects of decrease in traffic volume, increase in atmospheric mixing height and possible loss due to volatilization of some of these species, which results in gas-particle partitioning back into the gas phase and re-condensation onto larger particles when temperature increases (Mader and Pankow 2002; Kuhn et al. 2005c).

In the present study, 18 polycyclic aromatic hydrocarbons (PAH) have been identified and quantified in UFP. Figure 4-10(b) presents the average mass concentrations of different PAH species during the campaign. Sums of weekly average PAH concentrations were 1.93 ng/m<sup>3</sup> and 0.49 ng/m<sup>3</sup> in morning and afternoon, respectively. PAH are semivolatile organic compounds existing in both gas and particle phases, and their concentrations in the atmosphere depend on various factors such as source strength, meteorological conditions, gas-particle partitioning and wet/dry deposition (Bidleman et al. 1986; Bidleman 1988). PAH may come from both anthropogenic sources and natural processes, but the former dominate urban areas (Miguel et al. 1998). As shown in the figure, concentrations of PAH are higher in the morning period, when the nearby freeway is congested with vehicles during the morning commute. As in the case of n-Alkanes, the decrease in PAH concentration in the afternoon reflects the combined effects of reduction in traffic, increase in mixing height and also possible volatilization, especially of the lower molecular weight PAH, when temperature rises in the afternoon (Zheng and Fang 2000). Both roadway tunnel studies (Benner et al. 1989; Venkataraman et al. 1994) and dynamometer studies (Rogge et al. 1993; Geller et al. 2006b) have found that diesel vehicle emissions are enriched in lower molecular weight PAH (e.g., alkylated phenanthrenes, chrysene), whereas higher molecular weight PAH are associated with gasoline vehicle emission (e.g., benzo (ghi) perylene, coronene). The lower concentrations of PAH with molecular weight <228 compared to heavier molecular weight PAH are therefore consistent with the predominantly gasoline-vehicle traffic in the nearby CA-110 freeway (roughly 95-97%) (Caltrans- www.dot.ca.gov), as shown in the figure.

Sixteen hopanes and steranes in the UFP range have been identified and quantified in the present study. Sums of weekly average hopanes and steranes concentrations were 2.89 ng/m<sup>3</sup> and 2.15 ng/m<sup>3</sup> in morning and afternoon, respectively. Figure 4-10 (c) shows the average mass concentrations of the individual species in the morning and afternoon. Hopanes and steranes are found in lubricant oils used by both diesel and gasoline vehicles

(Schauer et al. 1996), so they have been used as organic tracers of particles emitted from motor vehicles (Cass 1998; Schauer and Cass 2000; Zheng et al. 2002). Similarly to alkanes and PAH, the majority of the hopanes and steranes exhibited lower concentrations in the afternoon with a decline by an average of 26%, compared to 61% for alkanes and 75% for PAH. These diurnal changes of concentrations reflect the combined changes in source strength and mixing height. The larger differences in alkanes and PAH may be due to their higher volatility compared to hopanes and steranes, which increases their partitioning from the PM to the gaseous phase as the temperature rises in the afternoon.

A total of 31 organic acids in UFP were identified in the present study. Sums of weekly average concentrations of *n*-alkanoic acids between  $C_{14}$  to  $C_{30}$  in UFP are 182.0 ng/m<sup>3</sup> and 372.1 ng/m<sup>3</sup> in morning and afternoon, respectively. Octadecanoic acid ( $C_{18}$ ) was the most abundant species, followed by hexadecanoic acid ( $C_{16}$ ) and tetradecanoic acid ( $C_{14}$ ), with significantly lower concentrations of other acid species. The results are consistent with observations in other locations by Park et al. (Park et al. 2006) and Simoneit (Simoneit 1986) for fine particles. Figure 4-10(d) presents the average mass concentrations of the three most abundant acid species in morning and afternoon. As shown in the figure, hexadecanoic acid and octadecanoic acid have much higher concentrations in the afternoon, resulting from photochemical formation (Pandis et al. 1993). However, tetradecanoic acid showed slightly lower concentration in the afternoon which may be explained by its partitioning in the gas phase in the afternoon due to its higher volatility than  $C_{16}$  and  $C_{18}$  acids. Although other measured organic acids have very

low concentrations in UFP, there is a discernible increase in concentrations from morning to afternoon. The most likely explanation for the increase of these species observed in the afternoon is that they are products of secondary photo-oxidation of either organic gases, and-or semi-volatile species evaporating from primary particles (Pandis et al. 1993). Food cooking is a source of some organic acids, but Rogge et al. (Rogge et al. 1991) argued that atmospheric chemistry is more likely responsible for their formation because food cooking alone cannot explain the entire mass of these compounds typically measured in the atmosphere. In a recent article on the origin of the secondary organic aerosol, Robinson et al. (2007) demonstrate how photo-oxidation of low volatility gas-phase species evaporating from primary particles emitted by vehicles rapidly generates organic aerosols, thereby greatly exceeding the contribution from known secondary organic aerosol precursors.

# 4.2.5 Acknowledgement

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# Chapter 5 Atmospheric processes of primary particles and inference to their impact on public exposure

# 5.1 Abstract

Combustion-generated aerosols, especially emissions of heavy and light duty vehicles, are the dominant contributors of ambient particulate matter (PM) in urban environments. This paper reviews the atmospheric processes (such as dilution, nucleation, condensation and coagulation) that dominate the dynamics of combustion aerosols following their emission, with a particular emphasis on PM from mobile sources. Atmospheric dilution affects the dynamic behavior of aerosols by shifting the gas-particle partitioning of the semivolatile component of these aerosols. Our paper discusses the roles of dilution in changing the physico-chemical properties of the ambient aerosols, such as particle size distribution and number concentration, and the degree to which it affects non-labile and semi-volatile PM components. This information is complemented with a discussion of secondary aerosol formation from atmospheric photochemical reactions that involve precursors emitted from traffic sources. Special focus is devoted to the role of gas-phase vapors formed from the evaporation of the semivolatile fraction of aerosols during dilution. Adding to the common recognition that volatile organic compounds (VOCs) are the major gaseous precursors, these vapors also actively participate in photochemical reactions and contribute to the formation of secondary aerosols. Following this discussion, we review recent findings that link PM semi-volatile components and their redox activity,

and we discuss the influence and importance of PM volatility on particle toxicity. Lastly, this paper discusses possible metrics to regulate PM emissions and establish ambient air quality standards that are pertinent to public health, and suggests future investigations aimed to improve our current understanding of the adverse health effects of population exposure to combustion -generated aerosols.

# 5.2 Introduction

In the last decades, several epidemiological studies have linked adverse health effects of populations exposed to increased ambient fine ( $d_p$ <2.5 µm) and ultrafine ( $d_p$ <180 nm) particles concentrations (Dockery et al. 1993; Laden et al. 2000; Peters and Pope 2002; Schulz et al. 2005). Particle size determines its deposition site and fraction in human lungs and its potential translocation to other target organs (Oberdorster 2003; Kreyling et al. 2006). Particle toxicity studies have also linked individual particle chemical components with different adverse health effect. Organics and transition metal PM components have been identified as capable of inducing proinflammatory effects in the lung due to their ability to produce oxidative stress (Nel et al. 1998; Saldiva et al. 2002). Polar organic compounds such as quinones can act as catalysts to produce reactive oxygen species (ROS) directly (Monks et al. 1992) whereas polycyclic aromatic hydrocarbons (PAHs) can induce oxidative stress indirectly, through biotransformation to generate redox active quinones (Penning et al. 1999).

Particles in the atmosphere can be divided into two broad categories: primary and secondary particles. Primary particles are directly emitted from combustion sources, such

as light-duty and heavy-duty vehicles, wood smoke, off- road vehicles, oil combustion of refineries and marine vessels, and stationary sources, such as power plants. In urban areas, vehicular emissions constitute the majority of the primary particles in the atmosphere. These particles are mostly sub-micrometer agglomerates of solid carbonaceous materials residing mainly in accumulation mode (Morawska et al. 2008). Secondary particles are largely composed of sulfate, nitrate, ammonium and secondary organic aerosols (SOA). The inorganic secondary aerosols are formed in the atmosphere from the oxidation of gas-phase precursors such as sulfur dioxide (SO<sub>2</sub>) (Seinfeld and Pandis 1998), nitric oxide (NO) and nitrogen oxides (NO<sub>x</sub>) (Pinder et al. 2004). By comparison, SOA formation mechanisms have not been fully understood. Generally, SOA may be formed by the oxidation of high molecular weight volatile organic compounds (VOCs) to produce low-volatility products, which subsequently condense onto the existing aerosols (Seinfeld and Pandis 1998). Particle phase heterogeneous reactions, including those occurring in clouds and fog, may also contribute the SOA formation in the atmosphere (Jang and Kamens 2001; Jang et al. 2003). Moreover, the gas-particle partitioning of semi-volatile organic aerosols may produce the gas-phase organic compounds in the atmosphere, which subsequently participate in the SOA formation (Robinson et al. 2007).

Atmospheric dynamic processes change the physical and chemical characteristics of combustion generated aerosols after their emission in the atmosphere. Particles from vehicle emissions often display a bi-modal size distribution with a large number fraction of the particles residing in nucleation mode ( $d_p$ <30 nm) (Kittelson 1998). Ambient measurements showed similar bimodal distributions in the proximity of freeways with

diesel traffic (Zhu et al. 2002a; Ntziachristos et al. 2007c) or when following a diesel vehicle on the road (Vogt et al. 2003; Ronkko et al. 2006). The profile of ambient particle size distribution tends to change significantly with elevated numbers of nucleation mode particles during photochemical episodes due to the formation of secondary aerosols (Moore et al. 2007). Photochemical reactions in the atmosphere also lead to the alteration of particle chemical composition, thus creating seasonal and diurnal variations in the chemical characteristics of ambient aerosols. This review discusses the major atmospheric processes that dominate the dynamics of combustion related aerosols and synthesizes the current understanding of particles toxicity in the context of their adverse health effect of public exposure.

# 5.3 Atmospheric processes and combustion related aerosols

Following almost immediately the emission of PM from primary combustion sources, atmospheric processes dominate the dynamics of their behavior in the atmosphere and influence their characteristics. These processes include direct particle formation involving nucleation of gaseous precursors and-or their condensation onto pre-existing particles, gas-particle partitioning of primary semi-volatile PM with atmospheric dilution, and further secondary particle formation by means of photochemical reactions. The following sections review our current understanding of the major processes that influence combustion aerosol dynamics based on observations and findings reported in the recent literature.

# 5.3.1 Nucleation and condensation

Combustion sources, such as vehicle engines, emit a complex mixture of gas vapors and particulate matter (PM). Nucleation and condensation are the dominant processes controlling the dynamics of the mixture shortly after their emissions from vehicles. During the dilution phase, the hot mixture of vapors and particles of the exhaust is rapidly cooled , resulting in super- saturation of low volatility gaseous compounds in the exhaust and the formation of new particles by nucleation of these vapors and – or their condensation are two competing processes. The availability of a pre-existing particle surface area and the dilution rate determine the degree to which each of these processes dominates. Low aerosol concentrations favor new particle formation by nucleation and their growth to larger sizes (Kulmala et al. 2000), while high PM concentrations promote condensation of the vapors onto the pre-existing particles (Kerminen et al. 2001).



Figure 5-1 Number and mass emission factors from different vehicles (Biswas et al. 2008a).

For vehicles retrofitted with diesel particulate filters and other after treatment control devices, the emitted primary particles are efficiently removed resulting in an overall reduction of total PM mass emission rates. However, the reduced particle surface area also facilitates the formation of nucleation mode particles from organic vapors under favorable temperature and dilution conditions. Dynamometer studies have reported enhanced formation of nuclei mode particles, consisting of a mixture of sulfate and organic compounds, in vehicles equipped with control devices (Grose et al. 2006). Figure 5-1 shows an indicative graph comparing particle mass and number emission factors from older (baseline) diesel vehicles, operating without after treatment devices, and vehicles retrofitted with control devices (Biswas et al. 2008a). There is a clear trend of increased particle number emissions with decreasing PM mass in vehicles operating with control devices. Similar results were also reported in several other studies (Vaaraslahti et al. 2004; Kittelson et al. 2006).



Figure 5-2 Particle size distributions at different sampling locations near freeway (Zhu et al. 2002a)

In the ambient environment, particles formed from nucleation processes mostly reside in the size range below 30 nm, and they usually dominate the particle number concentrations near freeways (Zhu et al. 2002a; Ntziachristos et al. 2007c). Figure 5-2 shows typical particle size distributions near a busy freeway with a high fraction of diesel traffic. At the sampling locations close to freeway, small particles dominate in numbers and they gradually grow to larger sizes as they move away from freeway, indicating the effects of coagulation and condensation.

Nucleation processes involve binary (such as sulfuric acid and water) and ternary (such as sulfuric acid, ammonia, and water) formation mechanisms (Kulmala et al. 2000). Organic vapors may also participate in nucleation, but they contribute mostly to the growth of freshly formed particles (Kulmala et al. 2004), without being the nucleating agent themselves. Some studies also proposed that the presence of atmospheric ions might affect the nucleation process by stabilizing the nucleating species (Yu and Turco 2001; Enghoff and Svensmark 2008). In polluted urban atmospheres, particle formation by nucleation is less favorable than the condensation of vapors of low volatility onto existing particles due to the high particle surface area available for condensation of these vapors (Alam et al. 2003). Charron and Harrison (2003) measured the evolution of particle size distributions near a busy road and showed that semi-volatile vapors from vehicle exhausts favored new particle formation by nucleation and their growth to detectable sizes in the early morning hours, with low pre-existing particle surface areas of 300 to 500  $\mu$ m<sup>2</sup> cm<sup>-3</sup>. However, condensation of condensable vapors onto pre-existing

particles dominated during daytime, when the particle surface area increased to 800 to  $1100 \ \mu m^2 \ cm^{-3}$ .

# 5.3.2 Role of atmospheric dilution

Following their emission from mobile sources, particles disperse into the atmospheric background in two distinct dilution stages: 1) tailpipe-to-road dilution by the strong turbulence generated by traffic, lasting about 1-3 seconds, causing dilution up to a factor of1000, and: 2) atmospheric turbulence-induced dilution caused by the wind and atmospheric instability, which lasts 3-10 min, resulting in an additional dilution ratio of about 10 (Zhang and Wexler 2004). For non-labile PM species, dilution changes their atmospheric concentrations in the ambient by dispersion. During dilution and cooling, gaseous precursors nucleate or condense onto pre-existing particles. For semi-volatile aerosols, dilution affects their gas-particle phase partitioning and alters the physical (size distribution, concentrations etc) and chemical properties (semi-volatile fraction) of the aerosol.

The dilution ratio (DR) can be calculated based on the ratio of the fleet-average exhaust carbon dioxide (CO<sub>2</sub>) concentration over the incremental ambient CO<sub>2</sub> increase, as shown in the following equation (Zhang and Wexler 2004; Phuleria et al. 2007):

$$DR = \frac{[CO_2]_{exhaust} - [CO_2]_{background}}{[CO_2]_{measured} - [CO_2]_{background}}$$
(1)

This method has been used to derive the dilution ratio in different environments with significant influence of vehicle emissions, including tunnel environment (Kirchstetter et
al. 1999; Phuleria et al. 2006), on- freeway sites (Kurniawan and Schmidt-Ott 2006) and ambient sites near freeways (Ntziachristos et al. 2007c).

#### 5.3.2.1 Dilution effects on non-labile PM components

For non-labile PM species, such as elemental carbon (EC) or black carbon (BC), organic molecular tracers, heavy molecular weight organic compounds and metals, dilution is the dominant mechanism that determines their ambient concentration levels. For traffic emissions, fuel-based emissions rates are a reliable measure of comparing measurements made at different dilution ratios on a consistent basis. (Lipsky and Robinson 2006) measured the fuel-based emission rates of EC from low-load diesel, medium-load diesel vehicles and wood smoke at various dilution ratios. A summary of their results is shown in Figure 5-3. EC emission rates from different combustion sources are independent of dilution ratios, appearing as horizontal lines in the figure, which indicates the direct relationship between their ambient concentrations levels and atmospheric dilution ratios.



Figure 5-3 Fuel-based OC and EC emissions from low-load diesel (left column), medium-load diesel (middle column), and wood smoke (right column) experiments (Lipsky and Robinson 2006).

Another study by Ntziachristos et al. (2007c) compared the ambient BC concentrations measured at locations with different dilution ratios, including the vicinity of freeway, infreeway measurement with a mobile platform and a tunnel environment. Table 5-1 summarizes their results. After correcting for dilution, BC concentrations agreed overall quite well among the different environments, especially considering the experimental uncertainties involved in each of these studies. Similar results were also observed for carbon monoxide (CO), which is an inert gaseous pollutant, and often used as an indicator of atmospheric dispersion.

	2006 study			Westerdahl et al. ( <i>10</i> )	Geller et al. ( <i>24</i> )	
location sampling site period	l-710 20 m from freeway median strip Feb-Apr 2006		n strip	I-710 Caldecott Tur mobile lab following traffic tunne Feb-Apr 2003 Aug 2		ott Tunnel (Bore 1) tunnel exit Aug 2004
sampling hours passenger cars (h <sup>-1</sup> ) light-duty trucks (h <sup>-1</sup> )	12 pm—4 pm 8359 600	5 pm-7 pm 10250 360		7580ª	12 pm-6 pm 4041 91	
heavy-duty trucks (h <sup>-1</sup> ) temperature (°C) BH (%)	1630 21.4 42	1225 14.4 60		1040ª 21	64 23.3 59	
wind speed (m/s)	2.2	1.2		2.0		
	measured	measured	measured	d corrected for DR <sup>b</sup>	measured	corrected for DR <sup>b</sup>
CPC (cm <sup>-3</sup> ) CO (ppm) BC (µg/m <sup>3</sup> ) relative dilution ratio	75000 0.27 4.6 1:1	98500 0.11 2.8	190000 1.9 12	36600 (5400) 0.28 (0.05) 3.4 (0.6) 1:10.2 (1.22)	637500 8.78 27.5°	92600 (10100) 2.18 (0.21) 6.8 (1.4) 1:7.3 (0.82)

<sup>a</sup> Daily averages from CalTrans. <sup>b</sup> Values in parentheses correspond to calculation uncertainty (see Supporting Information). <sup>c</sup> Elemental carbon.

## Table 5-1Comparison of concentrations at different environments(Ntziachristos et al. 2007c).

#### 5.3.2.2 Dilution effects on semi-volatile PM components

During the first dilution stage, nucleation, condensation and coagulation are mainly responsible for the evolution of overall particle size distribution of emissions in which semi-volatile species play an important role (Zhang and Wexler 2004).

Zhu et al. (2002a) measured size-segregated particle number concentrations at different distances from several freeways in the Los Angeles basin, as shown in Figure 5-4. They observed that the number concentration close to freeway was dominated by very small particles. These particles are semi-volatile in nature and formed by nucleation. Their concentrations decreased dramatically with increasing distance from freeway due to the combined effects of atmospheric dilution, diffusion to available surfaces and evaporation. Coagulation may have also played a minor role in the reduction of particle number concentrations and shifted particles distributions towards larger sizes. As argued by Zhang et al. (2005a), the particle number concentrations even inside the freeway environments are not sufficiently high to lead to coagulation, including agglomeration induced by turbulence. However, limited heterogeneous coagulation of smaller semi volatile nano- particles on larger PM may be possible during the dilution process, as their size decreases and their diffusivity increases progressively when they disperse away from the freeway (Jacobson and Seinfeld 2004).



Figure 5-4 Normalized particle number concentration from different size ranges as a function of distance from the 710 freeway (Zhu et al. 2002a)

Further insights on the evolution of particle number concentrations and size distributions from roadway emission to the ambient were discussed by Zhang and Wexler (2004). Shortly after their emission from the tailpipe, highly concentrated gas vapors experience supersaturation due to their rapid cooling in the atmosphere, which causes them to nucleate and-or condense onto the pre-existing particles, thereby creating a chemically complex aerosol. Following this stage, dispersion from roadway to the ambient occurs, during which the gas-phase concentration decreases, leading to evaporation of some organic compounds in the exhaust whereas other compounds may continue condensing, depending on the relative magnitude of their partial pressure to vapor pressures. The dynamics of volatilization are more pronounced for smaller particles of the UFP range (i.e. < 20 nm), because due to the "Kelvin effect" a higher vapor pressure is required to keep them from volatilizing compared to larger particles.

By comparing the particle size distributions measured at different distances from freeway, Zhang and Wexler (2004) observed that a large number of particles grow into size larger than 50 nm around 30 to 90 m downwind of the freeways, while some particles shrink to sizes less than 10 nm beyond 90 m away from freeway, and others continue to grow to size larger than 100 nm due to evaporation and condensation, respectively.

Equally informative are the roadway and grid (i.e., urban background) level based emission factors in the study by Zhang et al. (2005a). The authors of that study computed on-road size-resolved particle number emission factors using concurrently measured carbon monoxide (CO) as a freeway dilution indicator and correlating roadside (i.e., 15 m from the freeway) particle measurements to CO measurements (this is essentially the same methodology illustrated in equation 1, but using CO instead of CO<sub>2</sub> as a tracer of atmospheric dilution). Zhang et al. (2005a) also extended this analysis to produce unique receptor-dependent, size-resolved, road and grid-level (defined in their case as 150-300 m away from the freeway and considered representative of the urban background) emission factor distributions.



Figure 5-5 Distance and fuel-based particle number emission factors in Highway 405 summer (a) and winter (b) studies. The error bars only denote those of distanced-based emission factors (Zhang et al. 2005a).

Both mileage- and fuel-based particle number emission factors at road and grid levels were determined. Indicative results are shown in figures 5-5a and 5-5b. The figures show emission factors for particle numbers as a function of particle size obtained at the I-405 freeway during summer (Fig 5-5 a) and winter (Fig 5-5 b) periods. In summer time, the emissions of sub-20 nm particles decreased with increasing distance to the freeway, while the emissions of ~50-100 nm particles increased with distance, a counter- intuitive observation that was attributed by the authors to evaporation of sub-20nm and recondensation on larger PM, due to increased mixing during the summer period. By

contrast, in wintertime we see similarities in road-level and grid level emission factors as a function of particle size, with somewhat lower emission factors fo very small (i.e, < 20nm) particles away from roadway, possibly due to some volatilization of these particles despite the relatively lower atmospheric dilution and mixing prevailing during that period. These results are a direct consequence of the aerosol dynamic processes described in the work of Zhang et al. (2005a)

The evolution of particle size distribution and number concentration is thus accompanied by changes in particle chemical composition, since the partitioning of semi-volatile species may change dramatically with changing dilution ratio to maintain gas-particle phase equilibrium. A large fraction of primary aerosols generated by combustion includes semi-volatile organic components. In the atmosphere, these organic aerosols may undergo gas-particle partitioning depending on their concentrations, meteorological conditions, ambient concentrations of their vapor and PM phases and the degree of dilution (Pankow 1987). Dilution influences directly the partitioning process by reducing the concentrations of both semi-volatile and sorptive species (in the case of adsorption of semi volatile species onto soot particles), which causes semi-volatile species to transfer from particle to gas phases to maintain equilibrium (Lipsky and Robinson 2006).



Figure 5-6 Fuel-based organic aerosols emission factor as a function of their concentrations and dilution ratios (Robinson et al. 2007)

Robinson et al. (2007) presented a rich set of diesel organic aerosols (OA) partitioning data measured at different levels of dilution, extending from conventional vehicle emission tests to typical atmospheric conditions. Figure 5-6 shows that the fuel-based emission factors of organic aerosols decrease with increasing dilution and decreasing concentration, more than what dispersion can explain alone, which indicates substantial evaporation of primary OA with the increasing dilution ratios. From the results reported in that study, only a quarter of the traditionally defined primary OA exists in the particle phase at the levels of ambient dilution conditions with atmospherically relevant concentrations. The measured data showed excellent agreement with the fit curve based on absorptive partitioning (Robinson et al. 2007), along with a 95% confidence interval (CI). In addition to the factors discussed earlier, the gas-particle partitioning of the complex and dynamic mixture of vehicular exhaust also depends on the volatility of

individual organic compounds, which is closely related to their molecular weights and functional groups. Ning et al. (2008) compared the fuel-based emission rates of particle phase polycyclic aromatic hydrocarbons (PAHs), hopanes and steranes measured in the near-freeway (black dots), tunnel environment (grey triangles) with different dilution conditions as shown in Figure 5-7. These organic compounds have been commonly used as organic tracers for vehicle emissions. By correcting the ratio of the fleet-averaged exhaust CO<sub>2</sub> concentration over the incremental ambient CO<sub>2</sub> increase, the near-freeway sites (Kuhn et al. 2005a; Ntziachristos et al. 2007c) and tunnel site (Phuleria et al. 2006) have an average dilution ratio of about 2500 and 300, respectively. The estimated emission rates of non-labile species, such as high molecular weight PAHs, hopanes and steranes, were in very good agreement between these environments. However, fuel based emission rates of light molecular weight PAHs measured near freeways only accounted for about 40-50% of those measured in the tunnel environment, suggesting the likelihood of evaporation of these semi-volatile organic aerosols due to the increasing dilution ratios in the ambient environment compared to the roadway tunnel. This dependence on dilution in the emission rates of semi volatile species raises significant difficulties in assessing accurately their overall emissions in the context of population exposure, considering that atmospheric mixing and dilution have strong local, seasonal and temporal variations because of their intrinsic dependence on meteorology. This is clearly one of the greatest challenges in the field of characterizing emissions from the exhaust of vehicles.



Note: <sup>a</sup> 2004 HDV data from the Caldecott tunnel; <sup>b</sup> 1996 HDV data from the Caldecott tunnel; <sup>c</sup> Run on hot-start FTP urban driving cycle, 2 medium HDVs (Model year 1995); <sup>d</sup> Run on 56k pounds load test cycle, 1998 HDV; <sup>e</sup> 2000 Washburn tunnel mixed fleet data in Houston with %HDVs=3.4; <sup>f</sup> 1993 Los Angeles tunnel mixed fleet data with %HDVs=2.7.



Note: <sup>a</sup> 2004 LDV data from the Caldecott tunnel; <sup>b</sup> 1996 LDV data from the Caldecott tunnel; <sup>c</sup> Run on cold-start FTP driving cycle, 9 catalyst-equipped LDVs (Mode year 1981-1994); <sup>d</sup> Run on California UDC cycle; 5 catalyst-equipped LDVs (Model year 1993-1996); <sup>e</sup> Run on FTP driving cycle; 6 Three-way catalyst equipped LDVs (Model year 1988-1999); <sup>f</sup> Run on unified warm test cycle; 4 LDVs (Model year 1995-1997); <sup>g</sup> Run on warm start driving cycles; 24 nonsmoker LDVs (Model year 1985-1994).

### Figure 5-7 Fuel-based emission factors of PAHs, hopanes and steranes in various environments with different dilution conditions (Ning et al. 2008).

# 5.3.3 Photochemical reactions of primary emissions and secondary aerosol formation

Secondary aerosols comprise a large fraction of fine particles in urban areas. The processes that govern the formation of secondary inorganic aerosols, such as sulfate, nitrate and ammonium, have been well understood; however, the sources and formation mechanisms of secondary organic aerosols have not been fully characterized due to the complex nature of organic compounds in the atmosphere.

Generally, SOA are formed by photo oxidation of gas phase volatile organic compounds (VOC) in the atmosphere. VOC are emitted from a variety of natural biogenic and anthropogenic sources, least of which is combustion processes. Approximately 50% of anthropogenic VOC are emitted by combustion related sources (Barthelmie and Pryor 1997). Generally, VOC that are capable of forming SOA have more than six carbon atoms since the oxidation products of organic compounds with lower carbon numbers are too volatile to condense at ambient temperature conditions (Hung and Wang 2006). These high molecular weight VOC species react with photochemical oxidants, such as hydroxyl radicals and ozone, and produce low-volatility oxidation products, such as organic acids, nitro-polycyclic aromatic hydrocarbons (nitro-PAH), etc (Seinfeld and Pandis 1998). The added functional groups result in an increase in the compounds polarity and molecular weight, and thereby decrease their volatility. These compounds have sufficiently low volatilities to condense onto pre-existing particles or to establish equilibrium between the gas and particle phase (Odum et al. 1996). In the absence of

nuclei or ions, nucleation also occurs when the oxidation products with exceptionally low vapor pressure accumulate to reach high concentrations.

A recent study by Ning et al (2007) reported ambient organic compounds concentrations of ultrafine particles (defined as sub -180 nm particles in that study) in summer near a busy freeway near downtown Los Angeles, and discussed the formation of secondary organic aerosols by comparing the average organic compounds concentrations during morning rush hours and afternoon photochemically active periods, each representing primary and secondary aerosols, respectively. Figure 5-8 shows the average ambient concentrations of PAHs, n-alkanes and organic acids measured in the morning and afternoon. As discussed in the previous section, PAHs are semivolatile organic compounds and they exist in both gas and particle phases. The particle phase PAHs concentrations in the atmosphere are affected by the factors such as their source (or emission) strength, meteorological conditions and gas-particle partitioning (Bidleman et al. 1986). As shown in the figure, morning (6-9am) PAH concentrations were consistently higher, when the nearby freeway was busy with traffic during morning rush hours, the atmosphere was cooler and the mixing height was low. The decrease of afternoon PAH concentrations reflected the reduction in freeway traffic, increase in mixing height, and possible volatilization due to the increase in temperature. In addition, PAHs can also react with photo oxidants in the atmosphere such as ozone, hydrogen peroxide (Grosjean et al. 1983; Arey et al. 1988) that would also lower their levels in the afternoon. A similar diurnal pattern is also observed for the *n*-alkanes as shown in figure 5-8b. Figure 5-8c shows measured organic acids concentrations in the morning and

afternoon. In contrast to the diurnal pattern of PAHs and *n*-alkanes, the hexadecanoic (C<sub>16</sub>) acid and octadecanoic (C<sub>18</sub>) acid had much higher concentrations in the afternoon despite the increased mixing height, which is a clear indication of the formation of secondary organic aerosols from photochemical oxidation. However, tetradecanoic (C<sub>14</sub>) acid, also a photo oxidation product, showed slightly lower concentration in the afternoon, which may be explained by its evaporation through gas-particle partitioning process after formation since it has higher volatility than C<sub>16</sub> and C<sub>18</sub> acids. These ambient observations verify the formation of secondary organic aerosols in the atmosphere even in the quasi-ultrafine PM range (i.e., < 0.2  $\mu$ m)

Various air quality and atmospheric chemistry models have attempted to predict the ambient OA concentrations and simulate the formation of SOA from the photo-oxidation of VOCs. However, predicted OA levels from most of these models have shown persistent discrepancies with measured data, generally underestimating SOA formation (Heald et al. 2008; Russell 2008). Primary organic aerosols are commonly recognized as non-volatile in traditional emission inventories and air quality models. Based on the discussion of our previously sections, supported also by recent laboratory experiments (Lipsky and Robinson 2006; Robinson et al. 2007) and ambient measurements (Ning et al. 2008), with the increasing of dilution ratios to ambient conditions, some semi-volatile fraction in the primary OA emissions can also participate in the gas-particle partitioning process. As a result, the evaporation of primary OA may substantially contribute to the overall gas-phase organic compounds in the atmosphere in addition to the VOC that are emitted directly from combustion sources (Shrivastava et al. 2006).



Figure 5-8 Average PAHs (a), *n*-alkanes (b), organic acids (b) concentrations of ultrafine particles in the morning (AM) and afternoon (PM) (Ning et al. 2007).

Traditional SOA formation mechanism models mostly account for the VOC, such as monoterpenes and light aromatics, as the dominant gas precursors of photochemical reactions in the atmosphere (Koo et al. 2003; Vutukuru et al. 2006). Robinson et al. (2007) proposed a modified OA prediction model which accounts for both gas-particle partitioning of semi-volatile OA and the oxidation of all low volatility gas-phase organic vapors to simulate the formation of SOA in the atmosphere. With the modified SOA formation framework, Robinson et al. (2007) compared the fraction of SOA in total OA as predicted by traditional model (Figure 5-9 A) that treated primary OA as nonvolatile, and revised model (Figure 5-9 B) that included the photo-oxidation of gas-phase organics from evaporation of semi-volatile OA. As shown in the figures, SOA fraction in the revised model showed substantially higher contribution to OA than in the traditional model, indicating the important role of semi-volatile primary OA in the formation of SOA in the atmosphere. The amendment of traditional model also brought the predicted urban to regional OA ratios to a closer agreement with the ambient measurement data as shown in Figure 5-9 D.



Figure 5-9 Predicted SOA fractions in OA from traditional and revised models, and their comparison with ambient measurement data (Robinson et al. 2007)

#### 5.4 PM volatility and its impact on public exposure and health

In the previous sections we offered extensive discussion of the complex nature of combustion generated aerosols, which contain both non volatile and semi volatile components (Scheer et al. 2005). The semi-volatile compounds may partition between gas and particle phase in the ambient conditions depending on their vapor pressure and degree of atmospheric dilution (Kuhn et al. 2005b), and participate in photochemical reactions in the atmosphere (Robinson et al. 2007). Consequently, the physical and chemical characteristics of combustion- generated aerosols change dramatically with atmospheric dilution and aging, which may alter their toxic properties and influence their role on population exposures and public health.

Semi-volatile PM contains a wide variety of organic compounds, many of which possess genotoxic and carcinogenic characteristics, such as dioxins, polycyclic aromatic hydrocarbons (PAHs) and their derivatives. Some of these semi-volatile organic species trigger a chain of biochemical reactions in cells, change its redox state and exert oxidative stress. Polar organic compounds, such as quinones, oxygenated PAHs and aldehydes induce oxidative stress in cells by inducing hemoxygenase-1 expression (Li et al. 2003). A number of bioassays have been formulated to quantify the PM toxicity based on the redox and electrophilic characteristics of PM species, including the dithiothreitol (DTT) consumption rate, ascorbate (reducing agent in lung fluid lining), and the dihydroxybenzylamine (DHBA, transition metal formation) assays (Donaldson et al. 1997; Mudway et al. 2004; Cho et al. 2005). These bioassays estimate the net chemical reactivity of PM without establishing specific mechanistic pathways for PM toxicity. For example, the DTT test measures the ability of particles to catalyze the reduction of oxygen to superoxide and DTT consumption rate gives a fair indication of the formation of reactive oxygen species (Cho et al. 2005).

Previous studies reported strong associations between the PAH content of atmospheric PM samples and DTT (Cho et al. 2005; Ntziachristos et al. 2007a). Biswas et al. (2008b) measured the chemical composition and redox activity of particles from a variety of diesel engines, and found that there is a strong association between water soluble organic carbon (WSOC), organic acids, and DTT. The DTT consumption rate per PM mass was correlated with the WSOC (R= 0.94, p< 0.001) and sum of organic acids (R= 0.81; p= 0.05) contents of PM. WSOC is a complex mixture of a diverse group of semi volatile

species, including dicarboxylic acids, poly acidic compounds, polyethers etc (Decesari et al. 2000).

Figure 5-10 compares the mass and number-based semi-volatile PM fraction and the redox activity from different diesel engine particle samples (Biswas et al. 2008b). As shown in the figure, there is remarkable reduction in redox activity as the aerosols are denuded of their semi-volatile fraction, and with the exception of one vehicle (operating without any control technologies) over 80% of the overall particle redox activity is found in the semi-volatile PM fractions (Biswas et al. 2008b).



Figure 5-10 Relationship between redox activity and semi-volatile PM fraction (Biswas et al. 2008b)

Atmospheric dilution directly affects the particle volatility distribution by shifting the gas-particle partitioning process of semi-volatile species. As we discussed in the previous section, the fraction of these semi-volatile species bound to the PM phase directly affects their toxicity, at least in the context of their ability to produce oxidative stress and cellular injury. Biswas et al. (2008b) reported particle redox activity data measured at various locations, where vehicle emissions were the major sources of ambient aerosols, including road tunnel environment with dilution ratios of 200 to 300, and ambient environment with dilution ratios in the range from 1500 to 4000. Figure 5-11 shows the redox activity expressed in DTT consumption rate with respect to the atmospheric dilution ratio (Biswas et al. 2008b). The PM redox potential very clearly decreases with increasing atmospheric dilution (thus decreased semi volatile components present in the PM phase) until it reaches a lower threshold value of ~0.02 n-moles min<sup>-1</sup>  $\mu g^{-1}$  of PM.



Figure 5-11 Redox activity from various studies with respect to atmospheric dilution ratio (Biswas et al. 2008b)

These observations corroborate the results reported from dynamometer tests, i.e, that an increased semi-volatile PM fraction leads to higher overall redox activity on a per PM mass basis. These findings further illustrate the significant role of semi-volatile aerosols in determining PM toxicity. Due to the association of dilution ratio and PM volatility, atmospheric dilution conditions may thus play a neglected yet important role in determining PM effects on human health and in assessing public exposure to combustion generated aerosols in the atmosphere.

### **Chapter 6 Conclusions and future recommendation**

#### 6.1 Conclusions

Combustion generated aerosols, especially vehicular PM emissions, are the dominant sources of ambient primary aerosols in the urban atmosphere. Upon emission from the vehicle tailpipes, the gas- particle mixture of exhaust undergoes various atmospheric dynamic processes, which may cause significant change of the physical and chemical characteristics of the ambient aerosols. These processes include dilution, nucleation, coagulation, evaporation and possible re-condensation of organic vapors onto preexisting PM, and the secondary aerosols formation with the presence of photo-oxidant radicals, all of which control the dynamics of the exhaust mixtures after their emissions from vehicles.

From vehicle tailpipe to ambient environment, dilution plays a key role in characterizing the exhaust aerosols. Non-labile PM components, such as black carbon, trace elements and metals and high molecular weight organic tracers, are mostly affected by dilution; their atmospheric concentrations are a function of the degree to which the exhaust is diluted by atmospheric dispersion and mixing. Cooling of the exhaust during dilution also enables the formation of nucleation particles from gaseous precursors, and changes the number concentrations and size distribution of the emitted aerosols. For semi-volatile species, increased dilution also shifts the gas-to-particle partitioning process towards the gas phase, and alters the PM volatility and chemical composition of the emitted aerosols as they reach the ambient level.

With the presence of photo oxidants in the atmosphere, gas phase volatile organic compounds (VOCs) participate in the photochemical reactions and form secondary aerosols via different pathways. In addition to the VOCs, the formation of secondary organic aerosols (SOA) is also significantly enhanced by the photo-oxidation of organic vapors evaporating from semi-volatile PM during ambient dilution, resulting in the different diurnal patterns of primary and secondary organic aerosols.

Semi-volatile PM contains a wide variety of organic compounds and their fraction in the total PM determines their overall toxicological potency, thus their ability to induce adverse health effects. Recent toxicity studies have shown a direct correlation between the semi-volatile PM fraction and PM redox activity, indicating the significance of PM volatility in effecting public exposure to ambient aerosols. This relationship is also reflected in the correlation between ambient dilution ratio, which affects the fraction of semi-volatile species in total PM, and their redox activity.

#### 6.2 Discussion and future recommendations

Current vehicular PM emission standards as well as ambient pollution standards are based on PM mass measurement. However, with the new advancement of emission control technologies and new findings in PM toxicology research linking adverse health effect with individual PM compositions, there is growing concern about the suitability of such a single metric as the standard for regulation.

Advanced vehicle emission control technologies are effective in reducing solid, nonlabile PM emissions by means of filtration. However, recent investigations have shown substantial increases (by one order of magnitude, and often more) of particle number emissions from retrofitted vehicles due to the formation of nucleation mode particles from organic vapors in the exhaust. The emission of these smaller particles in the atmosphere may pose a greater threat to public health, since they deposit deeper in the human respiratory system and their chemical composition appears to be intrinsically more toxic than the non-labile PM. Europe is adopting a new particle measurement program (PMP), which measures the 'solid' particle ( $d_p>20$  nm) number concentrations from diesel exhaust after removing the volatile PM fraction by heating the exhaust to 300 degree C. In light of recent toxicity findings discussed in our earlier sections, indicating the increased potency and redox activity of the semi volatile nanoparticles, such a measure would seem imprudent.

In ambient conditions, atmospheric processes may significantly change particle size distribution and number concentration by nucleation, condensation, coagulation and secondary reactions. These changes highlight the difficulty and uncertainty in establishing meaningful standards for both vehicle emissions and ambient air quality based on particle number or mass concentrations only. We thus recommend that a better understanding of the linkages between PM size, chemistry and toxicity should be

developed in order to adopt regulatory strategies that might be sufficiently protective to the public. Of particular note is the semi-volatile PM from vehicular exhaust because of its unique role in atmospheric processes leading to the formation of secondary aerosols. Moreover, the semi-volatile PM fraction is highly correlated with PM redox activity and its ability to induce oxidative stress, and it is therefore a key determinant of the overall PM toxicological potency. Given the increased toxicity of these semi-volatile species, efforts should be made to reduce their emissions from newer vehicles, including reductions in their gas-phase precursors formed during the combustion process. Atmospheric dilution plays a key role in determining the degree to which these semivolatile species are partitioned in the particulate phase, thus directly affecting their overall toxicity in the context of public exposure. It is recommended that more research efforts are needed to investigate the dynamics and atmospheric behavior of these semivolatile species. Air quality models and emission inventories will need to account for PM volatility distribution and their evolution in the atmosphere with photochemical aging.

It is also recommended that current emission testing procedures should be modified to reflect real-world conditions in characterizing PM emissions and evaluating their impacts of ambient exposure. Considering the impact of temperature on the semi-volatile PM fraction, the current strategy of diluting vehicle exhaust with particle free air at elevated (and mostly uncontrolled) temperatures needs to be seriously re-considered. We suggest that emissions testing should be conducted ideally with the inclusion of a range of dilution temperatures (e.g., at least 2-3 settings between 0 to 30 degrees C to cover typically encountered ambient conditions in most urban areas). The effect of atmospheric

aging also needs to be taken into consideration in characterizing emissions under realistic conditions. This may be done, for example, by replacing the current constant volume dilution sampler with an aging chamber under realistic temperature and humidity conditions, where the vehicle exhaust is allowed to age for several seconds to few minutes to equilibrate to ambient conditions before sampling of the exhaust emissions starts.

In summary, current mass-based PM emission regulations and ambient air quality standards will need to be re-considered to address the emerging literature findings on physico-chemical and toxicological characteristics of combustion-generated aerosols. New metrics, such as particle number concentrations, chemical composition and PM volatility will need to be considered in attempting to develop a better understanding of the adverse health consequences of public exposure to these aerosols. Current emission testing procedures also need to be modified to reflect the impact of atmospheric processes on combustion-generated aerosols in the real-world conditions.

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## Appendix

Peer-reviewed publications list:

- 1. Ning, Z., Sioutas, C. Atmospheric processes influencing aerosols generated by combustion and their impact on public exposure: A Review. *Aerosol and Air Quality Research*. Submitted for publications May, 2009.
- 2. Verma, V., **Ning, Z.,** Cho A. K., Schauer J. J., Shafer M. M. and Sioutas C. Redox activity of urban ultrafine particles from primary and secondary sources. Submitted to *Atmospheric Environment*, May 2009.
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