

EXPOSURE ASSESSMENT AND SOURCE APPORTIONMENT OF SIZE
FRACTIONS OF AIRBORNE PARTICULATE MATTER

by

Mohammad Arhami

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Dedication

To my Family

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Abstract

The aim of this thesis is to enhance the knowledge on exposure to size fractions of airborne particulate matter and their components and to find more intensive information on sources of indoor and outdoor size fractionated particles. In the first part of the study, the physical and chemical characteristics of indoor, outdoor, and personal quasi-ultrafine ($<0.25\mu\text{m}$), accumulation ($0.25\text{-}2.5\ \mu\text{m}$), and coarse ($2.5\text{-}10\ \mu\text{m}$) mode particles and gaseous pollutant were measured at two phases (warmer and colder phase) of four different retirement communities in Southern California in 2005-2007. Overall, the magnitude of indoor and outdoor measurements was similar, due to high influence of outdoor sources on indoor particle and gas levels. Secondary organic aerosol showed to be able to comprise a major fraction of organic carbon (more than 40% were estimated at some phases). Outdoor and indoor concentrations of gaseous pollutant were more positively correlated to personal quasi-UF particles than larger size fractions. Indoor sources were not significant contributors to personal exposure of PM, which is predominantly influenced by primary emitted pollutants of outdoor origin. Vehicular sources had the highest contribution to $\text{PM}_{0.25}$ among the apportioned sources for both indoor and outdoor particles at all sites. The contribution of mobile sources to indoor levels was similar to their corresponding outdoor estimates, thus even if people generally spend most of their time indoors, a major portion of the submicron particles to which they are exposed to, comes from outdoor mobile sources.

In the following, we characterized the physicochemical properties and sources of size fractionated PM and their spatial and seasonal variability at the Los Angeles-Long Beach harbor community, which is the busiest harbor in the US and the fifth in the world. The major mass contributions in the quasi-UF fraction were particulate organic matter, non-sea salt sulfate and elemental carbon; in the accumulation mode fraction were non-sea salt sulfate, sea salt, particulate organic matter and nitrate; and in the coarse fraction were sea salt and insoluble soil. In general, PM and its components in accumulation mode showed relatively lower spatial variability compare to the quasi-UF and the coarse modes. The vehicular sources accounted for almost all of quasi-ultrafine PM and more than 50% fine PM, whereas ship contribution was lower than 5% of total PM mass. Our results clearly indicate that, although ship emissions can be significant, PM emissions in the area of the largest US harbor are dominated by vehicular sources.

The results obtained in this study have been/will be used to examine the relationships between outdoor (or ambient), indoor and personal measurements of atmospheric particulate air pollution and health outcomes and to link health effects to certain sources of particulate matter. Such information would be highly valuable for targeting control strategies that protect human health and life.

Chapter 1.

Introduction

1.1. BACKGROUND

1.1.1. Air Pollution and Ambient Particulate Matter

Air pollution is the presence of any substances in sufficient quantities to cause harm to environment, human, plant, animal life or property (Bishop, 1957). The air pollutant can have natural origin such as smoke, fumes, ash, and gases from volcanoes and forest fires or can be anthropogenic such as combustion emitted pollutant. The air pollutants are in form of gas, solid and liquid and their pathway involves a sequence of events: the generation of pollutants, their release from the source, transport and removal from the atmosphere and their effects on human beings, materials and ecosystems (Flagan and Seinfeld, 1988). Ambient particulate matters (PM) are a major portion of the air pollutant which refers to suspended solid and/or liquid aerosols in the atmosphere. Ambient particulate matter varies greatly in their ability to affect visibility, climate, health and life quality (Hinds, 1999). PM can be directly emitted into the atmosphere or formed indirectly by chemical reactions the term primary and secondary PM are referred to the aerosol made from former and later process respectively. National Ambient Air Quality Standards (NAAQS) set primary and secondary standards for ambient particulate matters to protect environment and human health from adverse effect of these pollutants.

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 major characteristic particles relevant to their behavior and health outcome which is usually identified by aerodynamic diameter. Aerodynamic diameter is diameter of a sphere that behaves aerodynamically like the actual particle (Heinsohn et al.1999). Aerosol has a size range of larger than a single small molecule (about 0.002 μm in diameter) and smaller than about 500 μm . Particulate matters are divided into different groups based on their aerodynamic diameter. Particles with aerodynamic diameter bigger than 10 microns are not usually point of interest in the environmental and health studies because of their short life time in the atmosphere and their deposition efficiency of about 100% in nose (Hinds, 1999). PM_{10} is generally defined as all particles equal to and less than 10 microns in aerodynamic diameter which are inhale-able and important in air pollution studies. These particles are grouped into two different size ranges, $\text{PM}_{2.5}$ with an aerodynamic diameter of 2.5 μm or less and particles with aerodynamic diameter between $\text{PM}_{2.5}$ and PM_{10} , these particles are named “fine” and “coarse” PM respectively. This grouping is because they showed different behavior emission sources, formation mechanism, chemical composition, residence times in the atmosphere, distance traveled due to atmospheric transport processes and removal mechanisms and different standards were set to them to protect public health and environment. 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, 1999). The fine particles are grouped into two groups: particles

with a diameter of less than about 0.1 micrometers are considered as the *ultrafine* particle fraction (UFP) whereas the range between 0.1 to 2.5 μm is referred to as the *accumulation* mode (Whitby and Sverdrup 1980 and Ibal-Mulli et al., 2002). Typical particle size distribution is presented in Figure 1.1. Ultrafine particles dominate the number distribution while accumulation mode particles dominate the mass distribution.

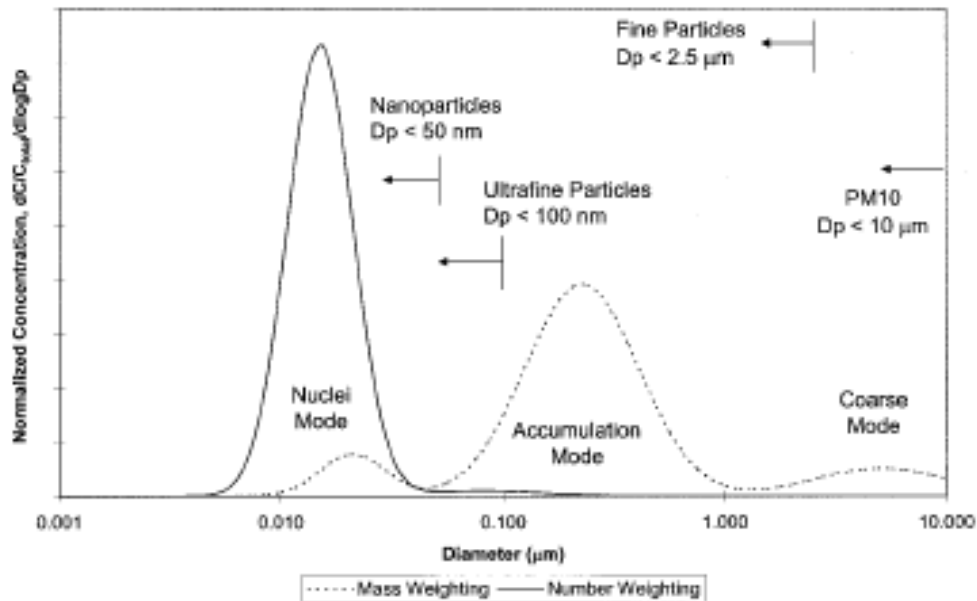


Figure 1.1. Typical particle size distribution by mass and number showing different size modes

These particles according to their sizes have different sources. Coarse particles are generated mechanically by crushing or grinding operations and are often dominated by crustal material and resuspended dusts from soil, paved or unpaved roads, construction and mining activities, farming, transportation and sea salt breeze. Accumulation mode particles are mainly direct products from combustion processes, formed by photochemical reaction or condensation of the gases or coagulation of the smaller

particles in the atmosphere as well as wood combustion and high temperature processes such as smelters and steel mills, contribute to accumulation mode particle emissions. Nucleation and automobiles emit most of the ultrafine particles and they can be produced by both natural and anthropogenic sources (Kavouras et al. 1998; Whitby and Svendrup 1980; Kotzick and Niessner 1999).

Different size range particles have different removal mechanisms. The removal of coarse particles is due to gravitational deposition while diffusion is the primal cause of removal of ultrafine particles. The accumulation mode particles are too large to be removed by diffusion and too small to be settling down by gravity and generally has a long life time in the atmosphere.

1.1.2. Health Effects of Particulate Matter

Associations of daily ambient air pollution and PM with mortality (Samet et al., 2000) and cardiovascular hospital admissions (Morris, 2001) as well as respiratory hospital admissions and mortality (EPA, 1996) and its adverse health outcome have been shown in numerous studies (Dockery et al., 1993, Pope et al., 1995). Initially total suspended solids in 1970 were considered as one of the eight criteria air pollutant. Studies proved more correlation between smaller size particles and adverse health effect and in 1987, as the result TSP was replaced by PM_{10} with $50\mu m/m^3$ and $150\mu m/m^3$ in annual and daily mean standards respectively. More studied showed the need of a standard for $PM_{2.5}$, so U.S. EPA added the annual and daily mean standard of $15\mu m/m^3$ and $65\mu m/m^3$ for fine

particulate air pollutant in 1997. The fine particles travel deeper to the alveolar region due to their high penetration efficiency characteristic, while the coarse particles can be removed more easily by impaction or settling in upper respiratory tract (Hinds, 1999).

Recent studies have demonstrated that UF particles (less than ~100 microns in diameter) are toxic and capable of penetrating cellular membranes and causing cell damage. This is due to major characteristics of ultrafine particles, including, high particle number, high pulmonary deposition efficiency, and a surface chemistry involving a high surface area that can carry adsorbed or condensed toxic air pollutants (oxidant gases, organic compounds and transition metals). These toxic air pollutants have all been identified as having pro-inflammatory effects. Ultrafine particles coated with neutralized strong acids may, upon deposition, cause tissue damage due to their acidity (Ferin et al., 1991). Trace metals transferred to the lung on ultrafine particles could catalyze the formation of oxidants within the lung which in turn produce tissue damage (Ghio et al., 1996). Heyder et al., (1996) and Peters et al., (1997) have shown strong association between adverse health effects and ultrafine exposure.

A large proportion of urban ultrafine particles in southern California is made up of primary combustion products from mobile source emissions (particularly diesel and automobile exhaust), and includes organic compounds, elemental carbon (EC) and metals (Kim et al. 2001). Experimental data show that compared with larger particles, ultrafine PM is better able to avoid phagocytosis by alveolar macrophages and gain entry to

pulmonary interstitial sites, including the endothelium. Therefore, ultrafine PM may induce pulmonary inflammation at both epithelial and interstitial sites, as well as enter the circulation to reach other target sites, including cardiovascular tissue (Oberdorster 2001). Additionally, diesel exhaust particles (DEP) in ultrafine mode have been shown to induce a broad polyclonal expression of cytokines and chemokines in respiratory epithelium possibly due to the action of polycyclic aromatic hydrocarbons (PAH) and related compounds that lead to the production of cytotoxic reactive oxygen species (ROS) (Nel et al., 1998; 2001).

1.2. RATIONALE OF THE PROPOSED RESEARCH

As it was stated earlier, epidemiological studies have shown significant exposure-response relationships for the adverse health effects in association with particulate matter (Pope and Dockery 2006). Particulate matter chemical composition and properties (such as mass, number, surface area and especially size) influence the adverse health effect and toxicity of particulate matter. Due to insufficient knowledge about the composition and properties of particulate matter and their exposure it has been difficult to address which component of particulate influences the health risk and what air quality regulation should be adopted. If health effects can be linked to certain sources of particulate matter, such information would be highly valuable for targeting control strategies.

The size of the particles has a strong influence on the type and intensity of health effect caused. Fine PM has been more strongly associated with mortality and morbidity,

although coarse particles have also been associated with respiratory hospital admissions (Brunekreef and Forsberg 2005). Ultrafine particles penetrate deep into the alveolar region of the respiratory system and have the ability to translocate in other parts of the human body (Elder et al. 2006). Toxicological data suggest that these particles are more strongly associated with cardiovascular and respiratory health outcomes (Araujo et al. 2007) compared to larger particles. Moreover, quasi-ultrafine PM ($PM_{0.25}$; particles with an aerodynamic diameter smaller than $0.25\ \mu m$) had the strongest and most significant association with circulating biomarkers of inflammation, antioxidant activity, and platelet activation measured in study subjects, which used some findings from current research (Delfino et al. 2008). So far, there is little research to support this finding (reviewed by Delfino et al. 2005; Weichenthal et al. 2007). Another problem is that the importance of particle size and chemistry has been limited by reliance on government monitoring of particle mass at two size cuts, PM_{10} and $PM_{2.5}$. Size fractionated indoor, outdoor and personal PM exposure measurement and exposure studies will be highly desirable to address this need.

Although air quality standards have been established for outdoor / ambient environments, a significant portion of human exposures to PM occurs indoors, where people spend around 85-90% of their time (Klepeis et al. 2001). One difficulty in identifying causal pollutant components driving associations to adverse health effect has been due to using the air pollution data from outdoor (ambient) sites which has led to exposure misclassification. So understanding the exposure to indoor and personal PM and its

component is very important. Fundamental uncertainty and disagreement persist regarding the composition, behavior and sources of indoor and personal PM so more studies are required in order to characterize and mitigate indoor exposure. To the best of our knowledge, only few studies on indoor PM source apportionment have been conducted in the past few years. These were mainly focused on examining the influence of outdoor sources on the measured outdoor concentrations of fine PM without any further size fractionation (Olson et al. 2008). Furthermore, there are no studies on sources and composition of indoor sub-micron particles. In addition not many continuous and semi continuous measurement of indoor PM and its component are obtained. Furthermore, recent epidemiologic studies have linked exposure to secondary organic aerosol (SOA) to respiratory inflammation through the generation of reactive oxygen species. Also, volatile and non-volatile PM_{2.5} components are characterized by different infiltration factor and indoor sources of PM_{2.5} and OC might be significant. Thus, the composition of indoor and outdoor particles is different and outdoor PM_{2.5} concentrations may not adequately represent personal exposure to PM_{2.5} in indoor environments. Thus, investigating the composition and sources of both indoor and outdoor PM and their relationships is desired.

Ascertaining the true risk associated with exposure to PM is difficult, mainly because the concentrations of ambient particles and those of their gaseous co-pollutants are often well correlated, and estimates of the health risks associated with PM exposure may be confounded by these gaseous species (Sarnat et al. 2000; Green et al. 2002; Sarnat et al.

2005). The National Research Council (1998) listed the investigation of the potential confounding effect of gaseous co-pollutants on PM health effects as one of their research priorities.

The Los Angeles Basin is a megalopolis of about 15 million inhabitants, and has one of the most polluted atmospheres in the US due to the contributions of a multitude of traffic and other combustion sources. One of the areas of particular concern regarding PM pollution is the communities near the Los Angeles-Long Beach harbor which constitutes the busiest harbor in the US and the fifth in the world, and therefore the area is affected by several PM sources. The potential for complex pollutant concentration gradients and high exposure conditions cannot be identified by conventional monitoring approaches. Accordingly, it is crucial to assess the exposure gradient of the community in the surrounding environment. Some studies have shown that using only community PM average concentrations to determine the health effects resulting from PM exposure may lead to non accurate results and therefore it is important to measure the variability of PM levels and sources within a community (Jerrett et al. 2005). For the development and implementation of PM policies that will be protective of the environment and human health, regulators require scientific knowledge of the strengths, spatial distribution and variability of the major sources of this pollutant. This information allows to design effective mitigation strategies on the local- and meso-scale level, and to evaluate human exposure to this pollutant and thus assess its health-related risks (Watson et al. 2002; Hopke et al. 2006).

Studies in Los Angeles Basin examining atmospheric aerosols at multiple locations across the basin have been conducted since the early 1970s (Cass et al. 2000; Christoforou et al. 2000; Hughes et al. 1999; Russell and Cass, 1986; Sardar et al. 2005). Most of these campaigns in Los Angeles have included only a few days or a week or two of sampling or were not concurrent at all the sites. However, concurrent and more extensive sampling in such a complex urban air basin would be highly desirable. In context of source apportionment, previous studies have been carried out to identify PM₁₀ sources in the aforementioned area (Kleeman et al. 1999; Manchester-Neesvig et al. 2003). These studies were spatially constrained by the fact that they were based on data collected in one sampling site in Long Beach. Moreover, source apportionment of fine and ultrafine fractions has not been conducted in this area. Nonetheless, there are not many studies on the micro-environmental spatial variations of chemical components and physical characteristics of particles in such complex environments.

My endeavor in this thesis is to enhance the knowledge on exposure to size fractions of airborne particulate matter and their components, to find more intensive information on sources of indoor and outdoor size fractionated particles and their variations. The results obtained in this study have been/will be used to examine the relationships between indoor, outdoor and personal measurements of atmospheric particulate air pollution and health outcomes and to link health effects to certain sources of particulate matter. Such

information would be highly valuable for targeting control strategies. To this end, the specific aims to address the abovementioned needs are:

- Improve the measurement methods of the particulate carbonaceous content, in order to get an insight in the characteristics of fine and ultrafine particles for better assessing the human exposure in this study
- Find the relationships between indoor and outdoor $PM_{2.5}$, its components and their seasonal variations as well as their association with gaseous co-pollutants
- Discover the contributions of primary OC and SOA to measured outdoor OC
- Evaluate the relative importance of indoor and outdoor PM sources to measured indoor OC, EC, $PM_{2.5}$ and PN concentrations
- Evaluate the associations between indoor, outdoor, and personal size-fractionated PM and its components of both indoor and outdoor origin
- To assess the role of gaseous co-pollutants as surrogates of personal size-fractionated PM exposures
- To evaluate the organic composition of quasi-ultrafine PM ($PM_{0.25}$) in both indoor and outdoor environments throughout the calendar year

- To identify the most important sources of these sub-micrometer particles
- To quantify their contribution to the total PM mass concentrations in both indoor and outdoor environments
- Characterize the chemical composition of ultrafine, accumulation mode and coarse particles across the Los Angeles-Long Beach harbor community
- Provide new insight into the variation of size-segregated PM and its properties and chemical composition over the harbor area
- Identify and quantify size fractionated particulate matter sources in the Los Angeles-Long Beach harbor area, and identify, if any, the spatial and seasonal differences in PM patterns and composition

1.3. THESIS OVERVIEW

The thesis consists of 8 chapters with Chapter 1 being the introduction. This section provides a general overview and background on air pollution, significance and characteristics of particles and their related health effects. It also describes the rationale of this thesis and outlines a brief layout.

In Chapter 2 the performance of new state-of-the-art Sunset Lab semi-continuous EC/OC field analyzer was assessed and evaluated in the field. The methods of examining artifacts which cause overestimation or under estimation in OC measurements were analyzed and improved. This instrument was used in rest of the study to get an insight in the characteristics of fine and ultrafine particles to better assess the human exposure to the carbonaceous components of particles.

Chapters 3, 4 and 5 are focused on exposure assessment to size fractionated particulate matter and their composition and sources. These chapters were conducted within the Cardiovascular Health and Air Pollution Study (CHAPS), a multi-disciplinary project whose goals were to investigate the effects of micro-environmental exposures to PM on cardiovascular outcomes in elderly retirees affected by coronary heart disease (CHD). The elderly population with CHD is likely to be among the most vulnerable to the adverse effects of particulate air pollutants. In this study the physical and chemical characteristics of indoor, outdoor, and personal quasi-ultrafine ($<0.25\mu\text{m}$), accumulation ($0.25\text{-}2.5\ \mu\text{m}$), and coarse ($2.5\text{-}10\ \mu\text{m}$) mode particles were studied at two phases (warmer and colder phase) in four different retirement communities in southern California between 2005 and 2007. Personal coarse, accumulation, and quasi-ultrafine PM samples were collected for 67 elderly retirees with a history of coronary artery disease. All participants were 71 years of age or older, nonsmokers, and with no home exposure to environmental tobacco smoke (ETS). Each subject was followed for two 5-day sampling periods during the 2 different phases of the study. Concurrent to personal

sampling, daily size fractionated PM samples were collected. In addition, real time concentration of fine particulate matter mass, OC, and EC, particle number (PN), ozone (O_3), carbon monoxide (CO) and nitrogen oxides (NO and NO_2) were measured at indoor and outdoor of these communities. Indoor and outdoor samples were analyzed to find their chemical composition and toxicological properties. This study provided one of the most extensive data set of its type for air pollution studies.

In chapter 3 the indoor/outdoor relationship, trends and carbonaceous content of fine particulate matter were intensively analyzed. The continues indoor and outdoor measured data in CHAPS were used to provide new insight into: a) the relationships between indoor and outdoor $PM_{2.5}$ measurements, its components and their seasonal variations as well as their association with gaseous co-pollutants, b) the contributions of primary OC and SOA to measured outdoor OC and c) the relative importance of indoor and outdoor PM sources to measured indoor OC, EC.

Chapter 4 evaluates the association between indoor, outdoor, and personal size-fractionated PM, OC, EC, PN, O_3 , CO, NO, NO_x , and other important pollutants of both indoor and outdoor origin. Furthermore, the role of gaseous co-pollutants as surrogates of personal size-fractionated PM exposures was assessed in this section.

Chapter 5 focuses on the quasi-ultrafine fraction of PM in both indoor and outdoor environments of the retirement communities. The main objectives of this study are: a) to

evaluate the organic composition of quasi-ultrafine PM in both indoor and outdoor environments throughout the calendar year, b) to identify the most important sources of these sub-micrometer particles, and c) to quantify their contribution to the total PM mass concentrations in both indoor and outdoor environments. The significance of this result magnifies since in an earlier investigation, also part of CHAPS study (not a part of this thesis) (Delfino et al. 2008), we reported that indoor PM of outdoor origin (mostly from combustion sources) was more significantly associated with systemic inflammation, platelet activation, and decreases in erythrocyte antioxidant activity than uncharacterized indoor PM that included particles of indoor origin.

In Chapter 6 and 7 we characterize the physicochemical properties and sources of size fractionated PM and their spatial and seasonal variability. Size fractionated PM samples were collected concurrently at 7 sites in the southern Los Angeles basin for two different phases throughout the year. The studied region was the Los Angeles Ports complex consisting of the port of Long Beach and the port of Los Angeles which together is the busiest harbor in the US and the fifth in the world.

The objective of Chapter 6 is to characterize the chemical composition of ultrafine, accumulation mode and coarse particles across this community. Results from the gravimetric and chemical analysis are verified by means of chemical mass closure (CMC). Subsequently, the paper focuses on organic species and elemental components and their distribution in PM size fractions among the sites. These results provide new

insight into the variation of size-segregated chemical composition of PM over the studied area.

Chapter 7 identify and quantify fine and quasi-ultrafine particulate matter sources in the Los Angeles-Long Beach harbor area, and identify, if any, the spatial and seasonal differences in PM patterns and composition. The results from this study will provide useful information for control strategies and will assist future toxicological studies that are planned in this area.

Chapter 8 comprises of summary and major conclusions of the thesis extracted from individual chapters. Finally, the potential research areas based on the findings of this work are addressed.

1.4. CHAPTER 1 REFERENCES

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Chapter 2.

Effect of Sampling Artifacts and Operating Parameters on the Performance of a Semi-continues Particulate EC/OC Monitor

2.1 ABSTRACT

The carbonaceous component of atmospheric particulate matter (PM) is considered very important with respect to the observed adverse health effects of PM. Elemental carbon (EC) is emitted from incomplete combustion occurring in sources such as diesel engines and biomass burning, while organic carbon (OC) is a component of particles emitted from almost every primary particle source. A significant fraction of particulate organic carbon can also be secondary organic aerosol (SOA), formed by atmospheric photochemical reactions of organic vapor precursors. The OC and EC components of PM have traditionally been measured off-line subsequent to daily, time-integrated particle collection on filters. However, the sub-daily or hourly variability of EC and OC can help to assess the variability of sources, ambient levels, and human exposure. In this study, the performance of the Sunset Laboratory Inc. semi-continuous EC/OC monitor was assessed in a field setting. The monitors were deployed near downtown Los Angeles, in a location representing typical urban pollution. An inter-monitor comparison showed high precision (R^2 of 0.98 and 0.97 for thermal OC and EC, respectively). By changing the inlet configurations of one of the monitors (adding a denuder, a Teflon filter, or both), the influences of positive and negative sampling artifacts were investigated. The positive artifact was found to be relatively large ($7.59 \mu\text{g}/\text{m}^3$ on average), more than 50% of measured OC, but it was practically eliminated with a denuder. The negative artifact was much smaller (less than 20% of the positive artifact) and may be neglected in most cases. A comparison of different temperature profiles, including a fast 3-minute analysis using

optical EC correction, showed good agreement among methods. Finally, a novel configuration using a size selective inlet impactor removing particles greater than 250 nm in diameter allowed for semi-continuous size-fractionated EC/OC measurements. More EC was observed in the sub-250 nm particle range, and similar levels of OC were seen in both the sub- and super-250 nm PM ranges. Evolution of OC at different temperatures of the thermal analysis showed higher volatility of OC in larger particles.

2.2 INTRODUCTION

While the link between ambient fine particle mass ($PM_{2.5}$) and adverse health outcomes has now been repeatedly established (NRC 2004), it is still not fully understood which properties of airborne particles are most responsible for these observations. Various studies have implicated sulfate (Clarke et al. 2000; Batalha et al. 2002), toxic elements such as vanadium (Saldiva et al. 2002), silicon (Wellenius et al. 2003), iron, nickel and zinc (Burnett et al. 2000), elemental carbon (EC) (Mar et al. 2000; Metzger et al. 2004), organic compounds such as polycyclic aromatic hydrocarbons (Dejmek et al. 2000), ultrafine particles (diameters less than ~ 180 nm) (Oberdörster 2001; Li et al. 2003), wood smoke (Tesfaigzi et al. 2002), and diesel exhaust (Seagrave et al. 2004), to name only a few. Therefore, accurate and convenient instruments, which measure detailed particle characteristics, are necessary to better assess ambient concentrations and human exposures. Continuous or semi-continuous monitors, providing data on hourly or sub-hourly time scales, are generally preferred over off-line analyses. Such monitors can not only capture important short-term variations in particle properties, but also can prove

more economical to operate by reducing sampling site visits and eliminating the need for laboratory facilities and analysis costs.

The carbonaceous component, elemental carbon (EC), organic carbon (OC) and carbonate (Birch and Cary 1996; Chow and Watson 2002), has been considered one of the most relevant PM fractions with respect to observed adverse health outcomes. Carbonate does not comprise a significant portion of PM_{2.5}, and is not suspected of being toxicologically active. Elemental carbon, similar to black carbon or refractory carbon (Chow et al. 1993; Birch and Cary 1996), is emitted from incomplete combustion occurring in sources such as diesel engines and biomass burning. It has been shown to produce adverse health responses when inhaled in both laboratory and ambient studies (Mar et al. 2000; Oberdörster et al. 2002; Metzger et al. 2004). Organic carbon is a component of particles emitted from almost every known primary particle source (Hildemann et al. 1994), but also can consist of secondary organic aerosol (SOA) (Griffin et al. 2002) which lead to low-volatility products. Both primary and secondary OC consist of hundreds of organic species, many of which are known to be toxic (i.e. PAH, nitro-PAH, etc.) (Schauer et al. 1996; Reisen and Arey 2005). The particle size distributions of both EC and OC are generally shifted to lower particle diameters relative to the total PM mass size distribution (Hughes et al. 1999).

The OC and EC components of PM have traditionally been measured off-line subsequent to particle collection on filters (Chow et al. 1993; Birch and Cary 1996). Numerous analytical methods have been developed, including thermal evolution techniques that heat

the filter to high temperatures and measure the total carbon that evolves off the filter. During heating, a portion of organic carbon pyrolyzes to form elemental carbon. Some of the methods use both non-oxidizing and oxidizing atmospheres, and by optically monitoring filter appearance, attempt to correct for this pyrolysis (Chow et al. 1993; Birch and Cary 1996), and several studies have examined the accuracy of these methods (Birch 1998; Chow et al. 2001; Schmid et al. 2001; Schauer et al. 2003; Chow et al. 2004). For the pyrolysis corrected techniques, it was found that the temperature profile (NIOSH vs. IMPROVE methods) and the laser configuration, thermal optical reflectance (TOR) vs. thermal optical transmittance (TOT) affected the results. All off-line analysis techniques are applied to time-integrated filters that typically collect PM for 24 hours or longer. However, these methods do not provide potentially useful information on the variability of EC and OC found in sub-daily or hourly data. Such data provided on finer temporal scales can help to assess the variability of sources, ambient levels and human exposure to EC and OC.

Collecting particles on filters, whether part of an on-line or off-line measurement, potentially leads to sampling artifacts. A positive organic carbon artifact arises from organic vapor adsorption onto quartz-fiber filter material and previously collected particles (matrix), leading to an overestimation of particle phase OC (McDow and Huntzicker 1990; Subramanian et al. 2004). A negative artifact can be caused by volatilization of organic particle-phase semi-volatile compounds from the particles into the gas phase, leading to an underestimation of OC (Subramanian et al. 2004).

To address this need, several in-situ continuous or semi-continuous particle measurement instruments have been developed for the measurement of EC, OC, or both. Black carbon can be measured continuously with Aethalometer, which measure the absorption of single-wavelength light through a filter collecting airborne particles (Hansen et al. 1984). Thermal evolution carbon monitors have been deployed in the field as well (Lim et al. 2003; Bae et al. 2004). The Sunset Laboratories Inc. semi-continuous EC/OC monitor was evaluated in a field study in St. Louis (Bae et al. 2004). In that study, OC levels were shown to agree very well with off-line OC measurements of 24-hour time-integrated filters using the laboratory based Sunset Lab analyzer ($R^2 = 0.90$, slope = 0.93). EC comparisons showed less agreement, most likely due to the very low ambient EC concentrations encountered at that sampling site. Since these instruments require an analysis cycle during which sample is not collected, this study used two monitors to sample alternating hours to achieve full 24-hour collection. The study also showed, however, that a single instrument sampling every other hour also yields good agreement with 24-hour time-integrated offline methods.

The objective of our study was to further assess the performance of the Sunset Lab semi-continuous EC/OC monitor in a field setting. Unlike the St Louis study, two identical and collocated instruments were run concurrently on a cycle consisting of 45 minutes of sampling and a 15 minute analysis period. The monitors were deployed near downtown Los Angeles at the Southern California Supersite Particle Instrumentation Unit (PIU) trailer. The location is about 100 m downwind of a major freeway, is surrounded by multi-story buildings, is near a construction area, and thus represents a good urban

pollution mix (Sardar et al. 2005). The collocated identical configurations allowed for the evaluation of the inter-monitor precision and the effects of monitor maintenance such as filter changes. By changing the inlet configurations of one of the monitors (adding a denuder, a Teflon filter, or both), the influences of positive and negative sampling artifacts were investigated. The temperature profiles were also varied between instruments, including a fast 4-minute analysis using an optical EC calibration rather than the thermal EC measurements. Finally, a novel configuration using a size selective inlet impactor removing particles greater than 250 nm in diameter allowed for semi-continuous size-fractionated EC/OC measurements. Observations of the evolution of OC at different temperatures of the thermal analysis also provided data on the relative volatility of OC in particles of different sizes.

2.3 EXPERIMENTAL METHODS

2.3.1 Semi-continuous OC/EC Field Instruments

Two identical OC/EC field instruments (Model 3F, Sunset Laboratory, Inc., Portland, OR) were deployed for monitoring the carbonaceous components of PM between December 2004 and May 2005. These instruments provide for automated sample collection and analysis of OC and EC on a semi-continuous basis (Bae et al. 2004). Samples are collected by drawing a sample flow of 8 l/min through two round 16 mm quartz filters, which are mounted back to back in an oven inside the instrument. After sample collection, the sample remains in the oven where it is heated in two different atmospheres. In the first part of the analysis, the oven is purged with Helium and the temperature is increased in multiple steps based on the programmed temperature profile.

The evolved organic carbon flows through a manganese dioxide (MnO_2) oxidizing oven and all carbon is transformed to carbon dioxide (CO_2) (Bae et al. 2004; Jeong et al. 2004). The CO_2 is then quantified by a self-contained non-disperse infrared (NDIR) detector system (Manual 2004). The oven is cooled prior to the second part of the analysis, when the oven is purged with a mixture of 10% Oxygen in Helium and the sample is again heated in steps (Bae et al. 2004; Jeong et al. 2004). During this stage, all remaining carbon on the filter, including elemental carbon, is oxidized, flows through the MnO_2 oven, and is detected by NDIR as CO_2 .

During the first part of analysis a fraction of organic compounds may pyrolyze and form EC (Bae et al. 2004; Jeong et al. 2004). This pyrolytic conversion is monitored by continuous measurement of the light absorbance of a red laser (wavelength of 660 nm) passed through the filter. The light absorbance increases as some OC is pyrolyzed to EC during the first analysis stage, then the absorbance declines as EC (from both pyrolyzed OC and sampled particles) is oxidized and leaves the filter during the second stage. The point at which the laser absorbance equals the initial value is used as the split point between OC and EC (Bae et al. 2004). CO_2 detected before the split point is considered OC, and CO_2 detected after the split point is considered EC (Turpin et al. 1990; Birch and Cary 1996).

The instruments also provide an optical determination of EC. The laser transmission is measured before and after the analysis cycle, and the difference is related to EC concentration via calibration. A pre-determined calibration factor, based on numerous

ambient measurements is used to convert laser attenuation to EC mass on the filter (Jeong et al. 2004). This optical EC is subtracted from the thermally measured total carbon ($TC = EC + OC$) to determine a parameter known as optical OC. All the EC and OC results presented in this study are thermal OC and EC unless stated otherwise.

Since the same quartz filters are re-used in every subsequent sampling and analysis cycle, some refractory inorganic particle components not removed in the heating process will accumulate on the filters. This is observed in the diminished initial laser transmittance through the filter over several days of sampling. The effect of using a week-old filter versus a fresh filter on the measured OC and EC was examined in this study and shown to be negligible. However, the filters were changed once a week as recommended by the manufacturer. The instruments were initially calibrated by injecting 1 cm^3 of calibration gas into the analyzers two times during the analysis period. The stability of the analyzers was checked by the same method later during the study period. Good internal instrumental stability was observed, as was also shown in a previous study (Bae et al. 2004).

2.3.2 Sampling Description

The instruments were operated in a sampling trailer, and sampled ambient air from a common inlet located on its roof. Inside the trailer, the common intake flow was split between the two instruments. Each instrument was operated downstream of its own $PM_{2.5}$ cyclone (provided by the manufacturer) at a flow rate of 8 l/min. The analyzers were run concurrently in coordinated hourly cycles, which included a 45-minute

sampling period and a 15-minute analysis period. A previous study using the same monitors showed good agreement between measurements made every other hour and 24-hour time-integrated off-line methods with $R^2 = 0.89$ and a slope of 0.94 for OC (Bae et al. 2004). Thus, missing half of the sampling time did not significantly bias 24-hour results. By extension, the 15-minutes of analysis during which sampling is interrupted should not significantly bias what is subsequently referred to as hourly readings.

The sampling location was on the University of Southern California campus at the Southern California Supersite Particle Instrumentation Unit (PIU) trailer. This site is located near downtown Los Angeles with a major freeway located about 100 m upwind (Sardar et al. 2005). The site is surrounded by several multistory buildings and is near a construction area. The air at this site represents a typical urban mix of mobile, industrial, and construction sources (Sardar et al. 2005). An Aethalometer (Model AE-21 (UV+BC), Thermo Andersen, Smyrna, GA) was deployed at the same location and measured black carbon (BC) in 5-minute averages.

The different sampling configurations used in this study are presented in Figure 2.1. Two of these five configurations (configuration A to E) were run concurrently during each of the sampling periods. The OC and EC measured via these configurations are referred to as OC_A , OC_B , ... OC_E and EC_A , EC_B , ... EC_E based on the inlet configuration employed. All configurations used the manufacturer supplied $PM_{2.5}$ cyclone

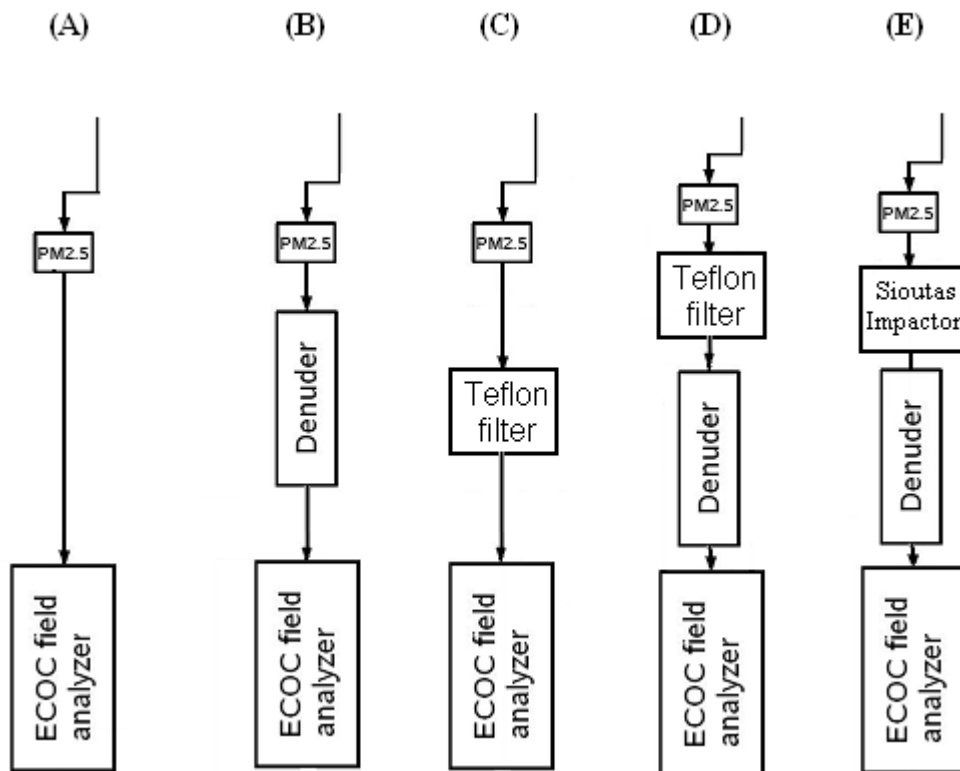


Figure 2.1 Inlet configurations implemented for sampling, A) bare, B) denuded, C) filtered, D) denuded/filtered and E) quasi-ultrafine.

2.3.2.1 Precision Evaluation

The precision of the instruments was tested via side-by-side operation, using only the cyclone on the inlet (bare configuration, Figure 2.1a). Each instrument collected 182 hourly samples in January 2005 and the OC and EC measured with the two analyzers were compared. Also, an evaluation of the optical EC and OC measurements were compared to their thermal counterparts using the instruments in the bare configuration. As shown in previous studies, the BC measurements from the Aethalometer are often comparable to EC measurements (Hansen et al. 1984; Turpin et al. 1990; Lavanchy et al.

1999; Ballach et al. 2001; Lim et al. 2003). The hourly averages of BC measured by Aethalometer were also compared to the EC results of the Sunset Laboratory monitors.

2.3.2.2 Denuder Breakthrough Determination

A carbon-paper denuder (provided by the manufacturer) was used to remove gas-phase OC that is known to cause positive adsorption artifacts (Turpin et al. 2000). The efficiency of a denuder can be less than 100%, allowing some organic gases to penetrate through the denuder (breakthrough) (Subramanian et al. 2004). The denuder breakthrough was measured by installing a 47 mm Teflon filter (PTFE, Gelman, 2 μ m pore, Ann Arbor, MI) followed by the carbon-paper denuder upstream of the samplers (Figure 2.1d). The Teflon filter removes the particles and the denuder removes organic vapors from air stream (Turpin et al. 2000; Bae et al. 2004; Subramanian et al. 2004). EC measurements under this configuration (EC_D) were practically zero, demonstrating complete removal of particles by the Teflon filter. Thus, the measured value of organic carbon (OC_D) is due to organic gases penetrating through the denuder and adsorbing on the quartz filter. Since the measured OC_D values were fairly consistent (see Results and Discussion section), the average of the breakthrough level was subtracted from all subsequent OC measurements using the denuder. The denuder breakthrough value found is specific to this type of denuder; different breakthrough values are expected if other denuder types are used. The effect of the age of the carbon paper strips in the denuder on breakthrough was assessed by side-by-side comparison of a denuder with fresh strips and one with two-month old strips. Using configuration D on both instruments, 24 samples were collected in February 2005 and analyzed. The results did not show a significant

change after denuder strips were changed. Denuder strips were deployed a maximum of three months before replacement with fresh strips.

2.3.2.3 Artifact Measurements

Two different methods were used for examining the magnitude of positive and negative sampling artifacts: a denuder method and a filter method. For the denuder method, an instrument with the denuder setup (configuration B, Figure 2.1b) was run side-by-side with the other instrument in the bare configuration A (Figure 2.1a) in January 2005. The denuder removes the organic vapors that may cause a positive adsorption artifact (Bae et al. 2004; Subramanian et al. 2004). However, it may increase the magnitude of negative volatilization artifacts since lowered organic vapor pressures favor volatilization of organic carbon from particles already collected on the filter (Eatough 1990; Turpin et al. 1994). The measured organic carbon by the denuder configuration (OC_B), after correction for breakthrough, would be equal to actual particulate OC (OC_{actual}) minus the negative artifact. The measured organic carbon via the bare measurement (OC_A) is OC_{actual} plus the positive artifact since no significant negative artifact is expected for the bare configuration during such short sampling periods (Subramanian et al. 2004). Thus, the difference between OC_A and OC_B is an estimate of the positive artifact plus the negative artifact, and is referred to as the total artifact determined via the denuder method ($OC_{artifact,denuder} = OC_A - OC_B$).

In the filter method, a 47 mm Teflon filter was installed downstream of the cyclone of one of the EC/OC analyzers (configuration C, Figure 2.1c) and run side-by-side with the

other instrument in the bare configuration in December 2004. The Teflon filter prevents particles from entering the instrument so that the measured carbon content is entirely due to adsorbed gas-phase organics (Turpin et al. 2000; Bae et al. 2004; Subramanian et al. 2004). It is therefore a direct measure of the positive artifact as determined with the filter method ($OC_{\text{artifact,filter}} = OC_C$) (Bae et al. 2004; Subramanian et al. 2004). Near zero EC_C levels confirmed the effectiveness of the filter. The measured OC_C was subtracted from the concurrent OC_A and the results are taken as actual particulate OC ($OC_{\text{actual}} = OC_A - OC_C$). Teflon filters were changed about once a week even though it was shown (see below) that the amount of loading on the Teflon filter did not significantly affect the results. Additional artifact measurements were made by sampling with configurations B and C concurrently.

2.3.2.4 Analysis Protocol Comparison

Three different temperature profiles, a modified-NIOSH protocol, a modified-IMPROVE protocol, and a FAST-ramp protocol, were employed for analyzing samples and the inter-comparability was assessed. Temperature profiles and purge gases in each analysis stage of these methods are presented in Table 2.1. In the modified-NIOSH and modified-IMPROVE methods the first temperature ramp consists of four heating steps in a helium atmosphere. The modified-NIOSH method is adapted from the NIOSH temperature profile (Birch and Cary 1996; NIOSH 1996) and was used by Schauer et al. (Schauer et al. 2003). The modified-IMPROVE method is adapted from the IMPROVE protocol (Chow et al. 1993; Schauer et al. 2003). The methods differ only in the temperatures

Table 2.1 Temperature profiles used for EC/OC analysis

Gas	Hold time (s)	Modified-NIOSH Temperature (°C)	Modified-IMPROVE Temperature (°C)
He	10	No heating	No heating
He	60	310	120
He	60	480	250
He	60	615	450
He	90	840	550
He	35	No heating	No heating
He+Ox	35	550	550
He+Ox	105	850	850

Gas	Hold time (s)	FAST-ramp Temperature (°C)
He+Ox	10	No heating
He+Ox	210	850

used in the He atmosphere of the first analysis part. The FAST-ramp method requires an analysis step of only 4 minutes and takes advantage of the optical measurements to enable this shorter analysis time. In this method, the sample is heated up quickly to 850 °C in a 10% oxygen in helium atmosphere in only one step (see Table 2.1) and TC is

quantified from the total NDIR response. EC is measured optically, based on initial and final laser transmittance, and is then used to determine OC via subtraction from TC. Not only does a faster analysis reduce the time when sampling is interrupted, it also increases the sensitivity dramatically since all carbon evolves in one narrow peak. Thus, it may allow for shorter sub-hourly sampling times.

First the modified-NIOSH protocol was compared to modified-IMPROVE protocol via side-by-side operation of the instruments employing these two methods. Then the FAST-ramp temperature profile was compared to the modified-NIOSH profile. For all the temperature profile comparisons, denuders were used on both monitors (configuration B) since, as described later, this was shown to provide near artifact free sampling. Except for these temperature protocol comparisons, all other samples in this study were analyzed using the modified-NIOSH protocol. In both the modified-NIOSH and modified IMPROVE methods, the four temperature steps in the He atmosphere allow for division of OC into different NDIR response peaks representing different volatility fractions of OC (Kirchstetter et al. 2001). These four OC peaks are designated and recorded as peak 1 to peak 4 (OC^1 to OC^4). For the purposes of this study, OC^2 , OC^3 , and OC^4 were summed (OC^{2-4}) and considered a less volatile OC fraction compared to OC^1 , a more volatile OC fraction.

2.3.2.5 Comparison of Quasi-Ultrafine Particles with Accumulation Mode Particles

Two collocated instruments provided the opportunity for simultaneous semi-continuous EC/OC measurements of different PM size fractions. The PM_{0.25} stage of a Sioutas™

impactor (SKC Inc, Eighty Four, PA) (Misra et al. 2002; Singh et al. 2003) was operated downstream of the PM_{2.5} cyclone of one of the instruments to remove particles greater than 250 nm in aerodynamic diameter (configuration E, Figure 2.1e). The rationale for these experiments was to obtain near continuous, concurrent measurements of the concentrations of the ultrafine (“freshly” emitted”) and accumulation (“aged”) mode PM. The Sioutas™ impactor was chosen because of its ability to remove super-250 nm particles at a flow rate that matches that of the Sunset Laboratory monitor with a low pressure drop (i.e., 1 kPa), an essential requirement for any sampler to be used as a pre-selective particle inlet in conjunction with this monitor. Considering that the upper size cuts that have been traditionally used to define the ultrafine mode (100–180 nm) are somewhat lower than the cutpoint of the Sioutas™ impactor (Kim et al. 2002; Chakrabarti et al. 2004; Fine et al. 2004), particles less than 250 nm are designated quasi-ultrafine (UF) for the purposes of this paper (OCE = OCuf, ECE = ECuf). A denuder was used downstream of the impactor to minimize sampling artifacts. The particles between 0.25 and 2.5 µm are defined here as accumulation mode particles. The instrument with the UF inlet configuration was run concurrently with an instrument with the denuder configuration B, which collected PM_{2.5}. The measurements with UF inlet configuration were subtracted from the concurrent measurements with denuder configuration to obtain accumulation mode values (OCacc = OCB - OCE, ECacc = ECB - ECE).

2.4 RESULTS AND DISCUSSION

2.4.1 Precision Evaluation

The time series plots of OC and EC measured concurrently by two collocated Sunset Laboratory semi-continuous OC/EC field analyzers using the bare configuration (A) are shown in Figure 2.2. Thermal OC measurements between the two instruments were very highly correlated with a correlation coefficient, R^2 , of 0.98, a slope of 1.01 ± 0.02 , and y-intercept of $0.12 \pm 0.16 \mu\text{gC/m}^3$. The R^2 , slope, and y-intercept of measured EC with the two instruments were 0.97, 0.82 ± 0.02 and $0.2 \pm 0.04 \mu\text{gC/m}^3$ respectively. The results show excellent inter-instrument precision for OC, but a systematic bias in EC reflected in the slope of 0.82. The reason for this discrepancy might be a result of a systematic difference in the split point determination between OC and EC, and as the EC values are a much lower fraction of TC, EC is affected to a greater degree than OC. The split point between OC and EC of the instrument with overall higher EC measurements (instrument #2) occurred on average 17 s before the split point of the other instrument (instrument #1). Also, there were periods with relatively low levels of EC during the comparison, which were close to the detection limit of the instrument ($0.2 \mu\text{gC/m}^3$ according to manufacturer), which may cause additional uncertainty in the readings. At some of these low EC levels when the EC level was lower than the detection limit, the instrument was unable to properly detect the split between EC and OC. In this case, the split point between OC and EC for at least one of the monitors occurred at the end of analyzing period, which resulted in artificially lower EC measurements (practically zero EC levels). Therefore, the EC measurements for which the split point occurred at the end of

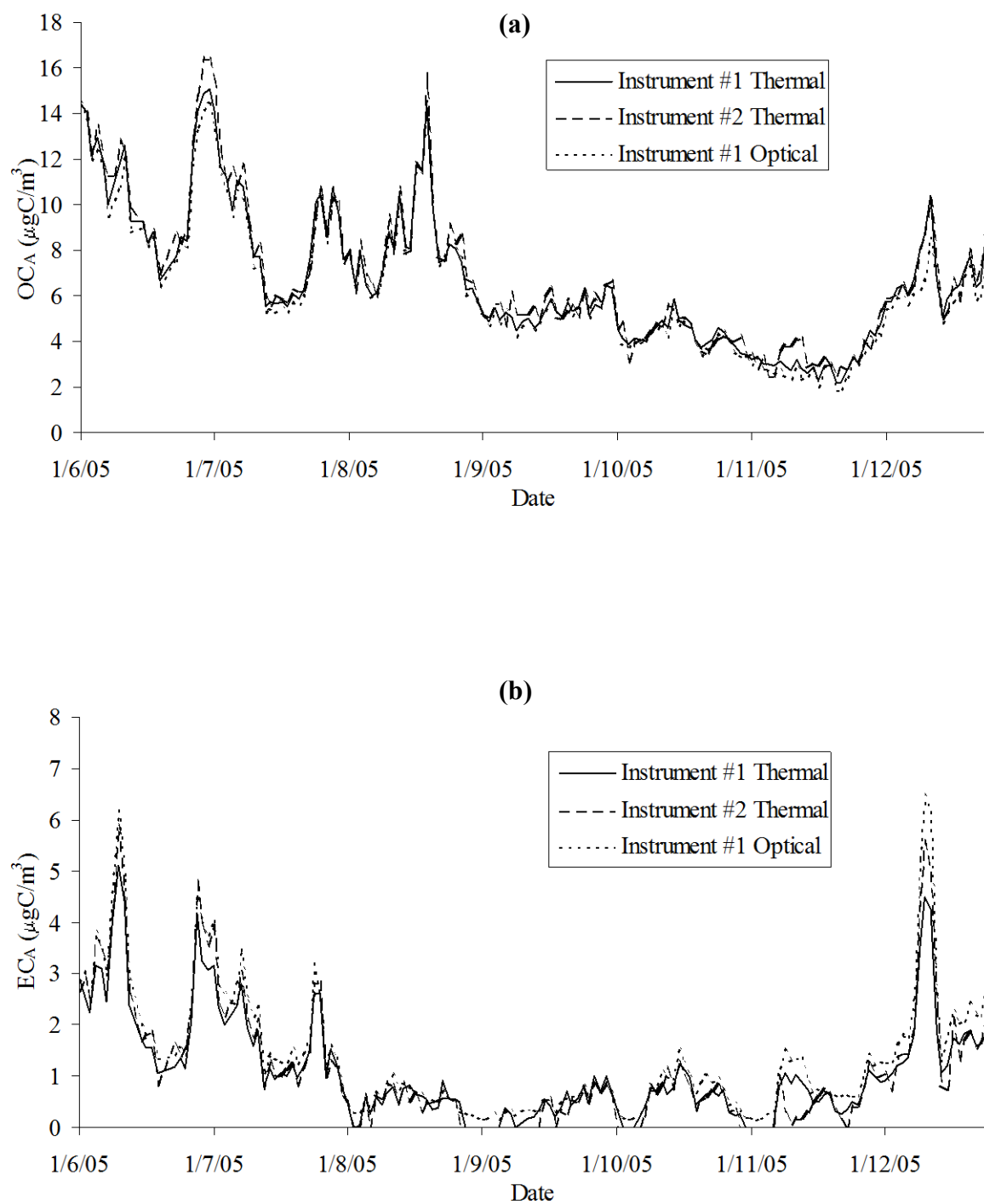


Figure 2.2 Test of instrumental precision results for a) OC measurements, b) EC measurements.

analyzing period were considered outliers and excluded from the analysis. This occurrence was infrequent, resulting in exclusion of less than 5% of data. Total carbon measured by the two instruments correlated well with each other, with R^2 and slope of 0.99 and 0.94 ± 0.02 respectively. Slightly lower TC measurements occurred on the same instrument with the overall higher split point. The lower TC measurements in this unit combined with the effect of the higher split point, resulted in lower EC measurements. For OC, these two effects approximately cancel each other out since lower EC now corresponds to higher OC.

The ability of the analyzers to measure EC (and by subtraction OC) optically was also assessed by comparing the thermal data of each instrument to its own optical data. The R^2 and slope of thermal versus optical OC correlation were 0.98 and 1.04 ± 0.02 for one unit, and 0.99 and 0.98 ± 0.02 for the other unit. Comparisons of thermal and optical EC yielded an R^2 and slope of 0.97 and 0.77 ± 0.04 for one unit and 0.97 and 0.98 ± 0.05 for the second instrument. These results indicate very strong correlation between optical and thermal measurements. However, in one of the instruments, the optical EC values seem to be higher compared to thermal EC, and because optical OC is determined by subtraction, the optical OC values are lower than thermal OC on the same instrument. As optical EC measured by two units correlated well with each other with a slope close to one (R^2 and slope of 1.00 and 1.07 ± 0.03 respectively) the observed difference in optical and thermal EC measurements in one of the units is caused by the lower thermal EC measurements of this unit mentioned above. The EC concentrations measured thermally with each unit

were also compared to BC measurements with the Aethalometer. The R^2 and slope of correlation between BC and EC were 0.96 and 1.39 ± 0.06 , respectively, for one unit and 0.95 and 1.17 ± 0.05 for the other. This indicates a high correlation between EC and BC measurements which was also shown in several previous studies (Hansen et al. 1984; Turpin et al. 1990; Lavanchy et al. 1999; Ballach et al. 2001; Lim et al. 2003), but systematically lower EC measurements than BC.

2.4.2. Denuder breakthrough

Denuder breakthrough was assessed using configuration D (Figure 2.1d). The average OC, EC, OC1 and OC2-4 measured with this configuration are presented in Table 2.2. The fact that no EC was measured implies the perfect removal of particles by Teflon filter, so the measured value of OC originated solely from the organic gases penetrating through the denuder and adsorbing to the quartz filter (Turpin et al. 2000; Bae et al. 2004; Subramanian et al. 2004). The average of OC measurements was $0.82 \pm 0.31 \mu\text{gC}/\text{m}^3$ and the R^2 between the bare OC measurements and OCD was 0.01, with a slope of 0.01 ± 0.07 , which together indicate a fairly constant degree of breakthrough adsorption, unrelated to ambient particulate OC levels. The average denuder breakthrough of $0.82 \mu\text{gC}/\text{m}^3$ was therefore subtracted from all the OC measurements obtained by using the denuder. The average denuder breakthroughs for OC1 and OC2-4 were $0.43 \pm 0.10 \mu\text{gC}/\text{m}^3$ and $0.37 \pm 0.17 \mu\text{gC}/\text{m}^3$ respectively. As was done for total OC, the average OC1 breakthrough was subtracted from all the OC1 measurements and the average OC2-4 breakthrough was subtracted from OC²⁻⁴ measurements of samples collected with a denuder upstream. The sum of OC¹ and OC²⁻⁴ breakthrough is smaller than the average of

total OC breakthrough because of the small amount of pyrolyzed OC included in total OC but not in OC peaks 1-4.

Table 2.2 Average denuder breakthrough values, which were subtracted from all denuded samples (all values in $\mu\text{gC}/\text{m}^3$)

Parameter	Average	Standard Deviation
OC	0.82	0.31
EC	0.00	0.00
OC ¹	0.43	0.10
OC ²⁻⁴	0.37	0.17

2.4.3 Sampling Artifacts

Using the filter method to determine the OC sampling artifact as described above, the positive artifact ($\text{OCC} = \text{OC}_{\text{artifact,filter}}$) ranged from 5.1 to 8.9 $\mu\text{gC}/\text{m}^3$, while the concurrent OCA from the bare configuration ranged from 7.2 to 24.7 $\mu\text{g}/\text{m}^3$. The average ECC was less than 10-2 $\mu\text{gC}/\text{m}^3$, which demonstrated the high efficiency of particle removal by the Teflon filter. The results of actual particulate OC ($\text{OC}_{\text{actual}} = \text{OCA} - \text{OCC}$) obtained by Teflon filter method and concurrent bare OC measurements (OCA) are shown in Figure 2.3. A fairly high correlation with R^2 of 0.89 was found between $\text{OC}_{\text{actual}}$ and OCA with a high non-zero intercept. Since the bare OCA consists of both positive artifacts and particulate OC, the high correlation and slope near unity show that the variation of OCA is driven by variations in particulate OC.

approximate estimate of the level of positive artifact is indicated by the intercept at 6.4 $\mu\text{gC}/\text{m}^3$.

Operating one instrument with a denuder configuration (B) concurrently with the other instrument with the bare configuration (A) provides another measure of magnitude of sampling artifacts. In this case, the artifact will include potentially enhanced negative artifacts caused by the denuder (Eatough 1990; Turpin et al. 1994; Subramanian et al. 2004). If an initial assumption is made that the negative artifact is negligible, then $\text{OC}_{\text{actual}} = \text{OCB}$, and the positive artifact is then $\text{OC}_{\text{artifact,denuder}} = \text{OCA} - \text{OCB}$. As shown, the filter method arrives at the same parameters ($\text{OC}_{\text{actual}} = \text{OCA} - \text{OCC}$, $\text{OC}_{\text{artifact,filter}} = \text{OCC}$) and the results from both artifact determination methods are plotted in Figure 2.4. The amount of positive artifact does not correlate well with the actual particulate OC ($R^2 = 0.26$), and only a slight increase in positive artifact was observed for increasing actual OC level (slope = 0.22). The average of the positive artifacts measured with both methods was $7.59 \pm 1.52 \mu\text{gC}/\text{m}^3$, with average $\text{OC}_{\text{artifact,denuder}}$ and $\text{OC}_{\text{artifact,filter}}$ of $8.14 \pm 1.49 \mu\text{gC}/\text{m}^3$ and $6.86 \pm 1.21 \mu\text{gC}/\text{m}^3$ respectively. The average positive artifact determined using denuder method is about 1.3 $\mu\text{gC}/\text{m}^3$ higher than the artifact using the filter method, but within the standard deviation of the measurements. This difference could be due to the negative artifact associated with the denuder, which would lead to an overestimation of the positive artifact by that method. However, it should also be noted that the measurements using the two methods were conducted over two different sampling periods, with higher particulate OC levels during the denuder method sampling.

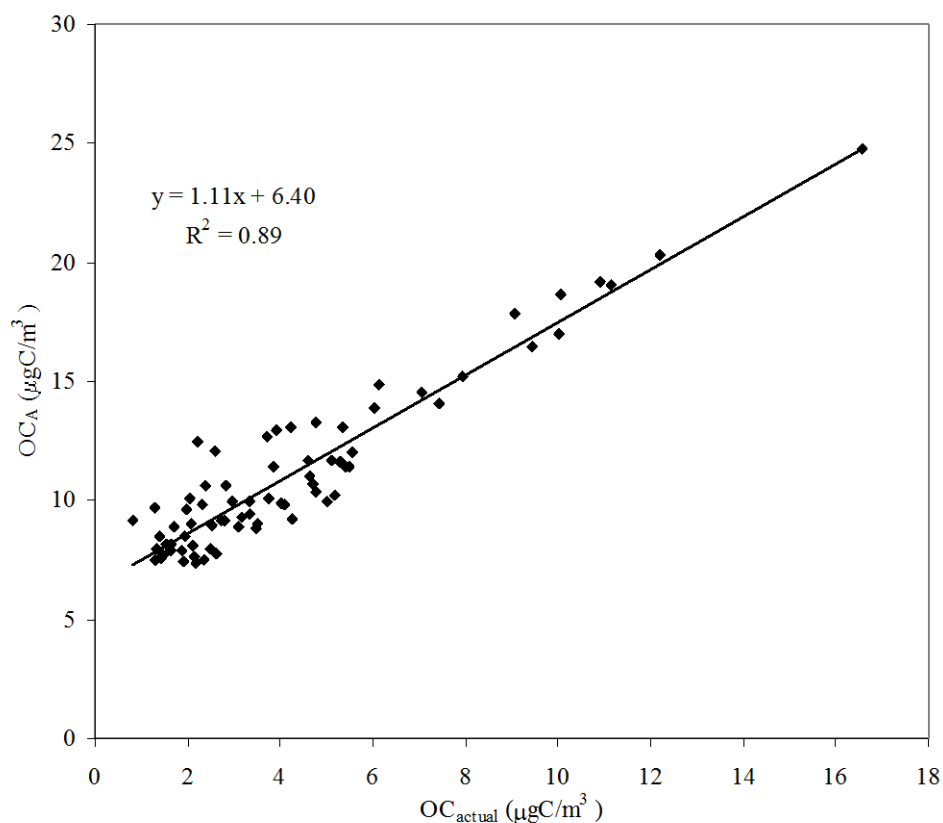


Figure 2.3 The comparison between the bare OC (OC_A) and the particulate OC obtained from Teflon filters method (OC_{actual}) concurrently.

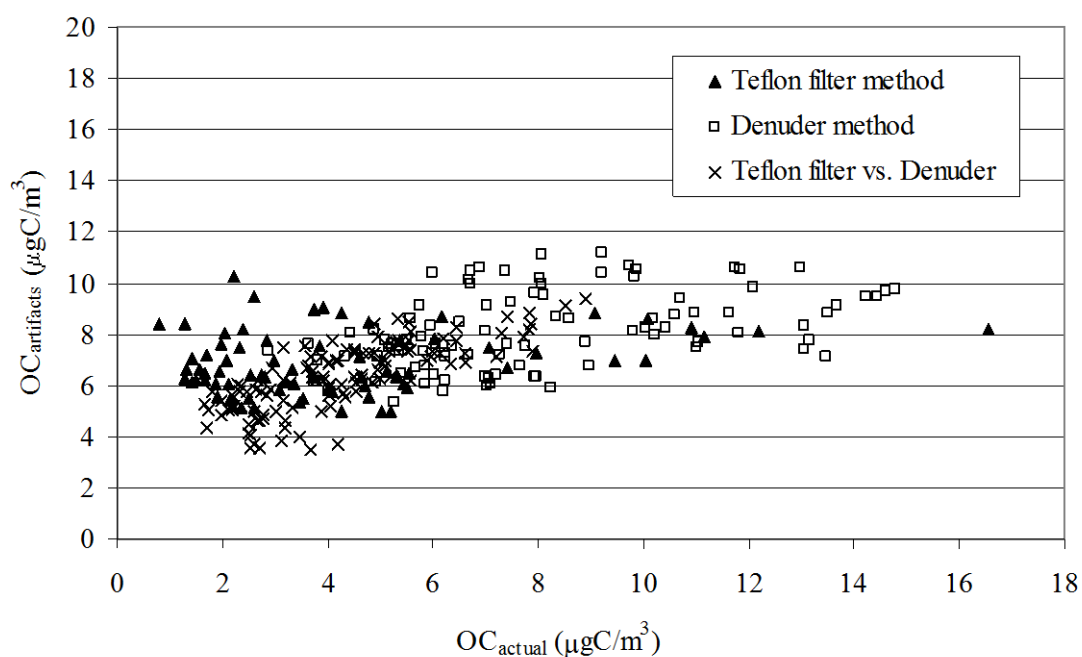


Figure 2.4 Comparison between OC_{artifact} and OC_{actual} determined by Teflon filter method (configuration A vs. C), denuder method (configuration A vs. B) and concurrent usage of Teflon filter and denuder (configuration C vs. B).

The average bare OC during the denuder method measurements was $16.24 \mu\text{gC}/\text{m}^3$ compared to $11.14 \mu\text{gC}/\text{m}^3$ during the filter method. Higher OC levels during the denuder method sampling period could lead to slightly higher artifacts due to possibly higher organic vapor concentrations on more polluted days, and/or possible matrix adsorption effects (Kirchstetter et al. 2001). The observed differences between the two methods does provide a rough upper estimate of the negative artifact of approximately $1 \mu\text{gC}/\text{m}^3$, less than 20% of the positive artifact on average. Other studies have demonstrated similar results for negative artifacts on 24 hour samples e.g. less than 10% of particulate OC by Subramanian et al. (Subramanian et al. 2004). However, higher negative artifacts (up to 80% of particulate OC) were also measured in other studies, which indicates a wide range of negative artifacts based on site and sampling conditions (Eatough et al. 1993; Modey et al. 2001; Anderson et al. 2002; Ding et al. 2002; Subramanian et al. 2004). Also shown in Figure 2.4 are results from measurements with one of the instruments operating with a Teflon filter (configuration C) concurrently with the other instrument operating with a denuder (configuration B). The measured OCC ($\text{OC}_{\text{artifact,filter}}$) is plotted as function of the measured OCB ($\text{OC}_{\text{actual}}$). An average positive artifact of $6.33 \pm 1.34 \mu\text{gC}/\text{m}^3$ was observed, which was consistent with our results using the filter and denuder methods separately, as can be seen in Figure 2.4.

The positive artifact was relatively high compared to actual particulate OC, comprising approximately 50% of OC_A on average. This large value for positive artifacts is attributable to the short 45-minute sampling time. Organic gases will adsorb on the filter until the filter is fully saturated (Subramanian et al. 2004). The longer sampling continues

after saturation occurs, the lower the positive artifact will be relative to actual particulate OC. Thus, a 24-hour sample would have a lower artifact relative to actual particulate OC than a 45-minute sample, assuming filter saturation is reached within 24-hours. The high percentage of artifact observed here indicates that the bare configuration of these instruments cannot directly measure actual particulate OC reliably.

If the sampling time is long enough for the quartz filter to saturate with adsorbed organic vapors, then the artifact mass will remain constant (Subramanian et al. 2004). For a short sampling time of 45 min, it is assumed that gas-phase organic concentrations do not vary sufficiently to cause additional adsorption or volatilization of organic material due to changing vapor pressures of these gases. As stated above, the average $7.59 \mu\text{gC}/\text{m}^3$ positive artifact was measured for a 45-minute sampling period. This corresponds to an adsorption artifact on the filter of $0.68 \mu\text{gC}/\text{cm}^2$ (2 back-to-back 16 mm filters, 8 l/min and a 45 min sample). In a previous study in the Los Angeles basin, the average measured positive artifact was $1.3 \mu\text{g}/\text{m}^3$ for 24 hr sampling on 37 mm quartz filters with 30 l/min flow rate (Sardar et al. 2005). This corresponds to $5.22 \mu\text{gC}/\text{cm}^2$, which is about 7.7 times the artifact value determined in this study. In another study in the same basin, an average positive artifact of $2.17 \mu\text{gC}/\text{m}^3$ was obtained (Kim et al. 2001), this time based on a flow rate of 20 l/min, 24 h sampling and using 47 mm filters. This value corresponds to $3.6 \mu\text{gC}/\text{cm}^2$ of positive OC artifact, which is about 5.3 times the artifacts measured here. Comparison of our results with both of these studies indicates that probably the saturation condition was not achieved in 45 min of sampling. In order to verify whether saturation was achieved, the samples were collected for 165 min of

sampling period and analyzed in 15 min (total cycle of 3 h) using configurations B and C concurrently. The average positive artifacts of 54 samples collected in May 2005, was $4.51 \pm 0.94 \mu\text{gC}/\text{m}^3$, corresponding to a $1.62 \mu\text{gC}/\text{cm}^2$ of positive OC artifact, which is 2.4 times higher than the artifacts measured for a sampling period of 45 min. This result further indicates that the filters were not saturated within 45 min. While the sampling period was increased about 3.7 times, the artifacts were enhanced only 2.4 times, suggesting that the adsorption rate of gas-phase organics slows as sampling continues. In a previous study in Pittsburgh (Subramanian et al. 2004) an average positive artifact of $0.53 \mu\text{g}/\text{m}^3$ and $0.71 \mu\text{g}/\text{m}^3$ were found respectively for 24 h and 4–6 h of sampling with 47mm quartz filters and a 16.7 l/min flow rate, corresponding to filter artifacts of $0.75 \mu\text{gC}/\text{cm}^2$ and $0.21 \mu\text{gC}/\text{cm}^2$, respectively. In that study, filter saturation was not achieved after 6 hours of sampling. As in our case, the artifact concentration on the filter increased with increasing sampling time, but the adsorption rate slows down as it approaches saturation conditions. Differences in the magnitude of the positive artifacts and adsorption rates at different locations indicate that the amount of OC artifact can vary significantly with sampling conditions. This is probably due to differences in concentrations of gas-phase organics at different sites and seasons.

An over-correction of positive artifacts using the filter method was predicted in previous studies (Chow et al. 1996; Subramanian et al. 2004) due to organic particulate matter collected on the Teflon filter volatilizing and then adsorbing to the quartz filter downstream. This effect was examined by operating two instruments side-by-side using

configuration C, initially both having new Teflon filters. After about 60 hours, sufficient time for Teflon filters to be heavily loaded with particulate matter, the Teflon filter on one of the instruments was changed while the other one remained unchanged, then 20 samples were collected on each instrument. The average difference between OC measured by the two instruments before the filter change was low ($0.55 \pm 0.52 \mu\text{gC/m}^3$) and nearly identical to the difference after the filter change ($0.58 \pm 0.57 \mu\text{gC/m}^3$). The similarity indicates that this effect may not be important for the current study, and that an overestimation of positive artifacts by using a loaded Teflon filter upstream has not occurred.

The relationship between particulate OC obtained by Teflon method and bare OC_A (shown in Figure 2.3) may provide a correction to estimate actual particulate OC in cases when the denuder is not deployed. The validity of this correction is demonstrated in Figure 2.5, where particulate OC, calculated from OC_A and the linear relationship in Figure 2.3, is compared to particulate OC measured concurrently with a denuder (OC_B , ignoring the negligible negative artifact). The time series (Figure 2.5a) confirms the good agreement. Figure 2.5b compares the calculated and measured OC in a scatter plot, showing a high correlation with slope of 0.98 ± 0.08 . This good agreement shows that it may be possible to obtain good particulate OC results in a bare configuration, using a

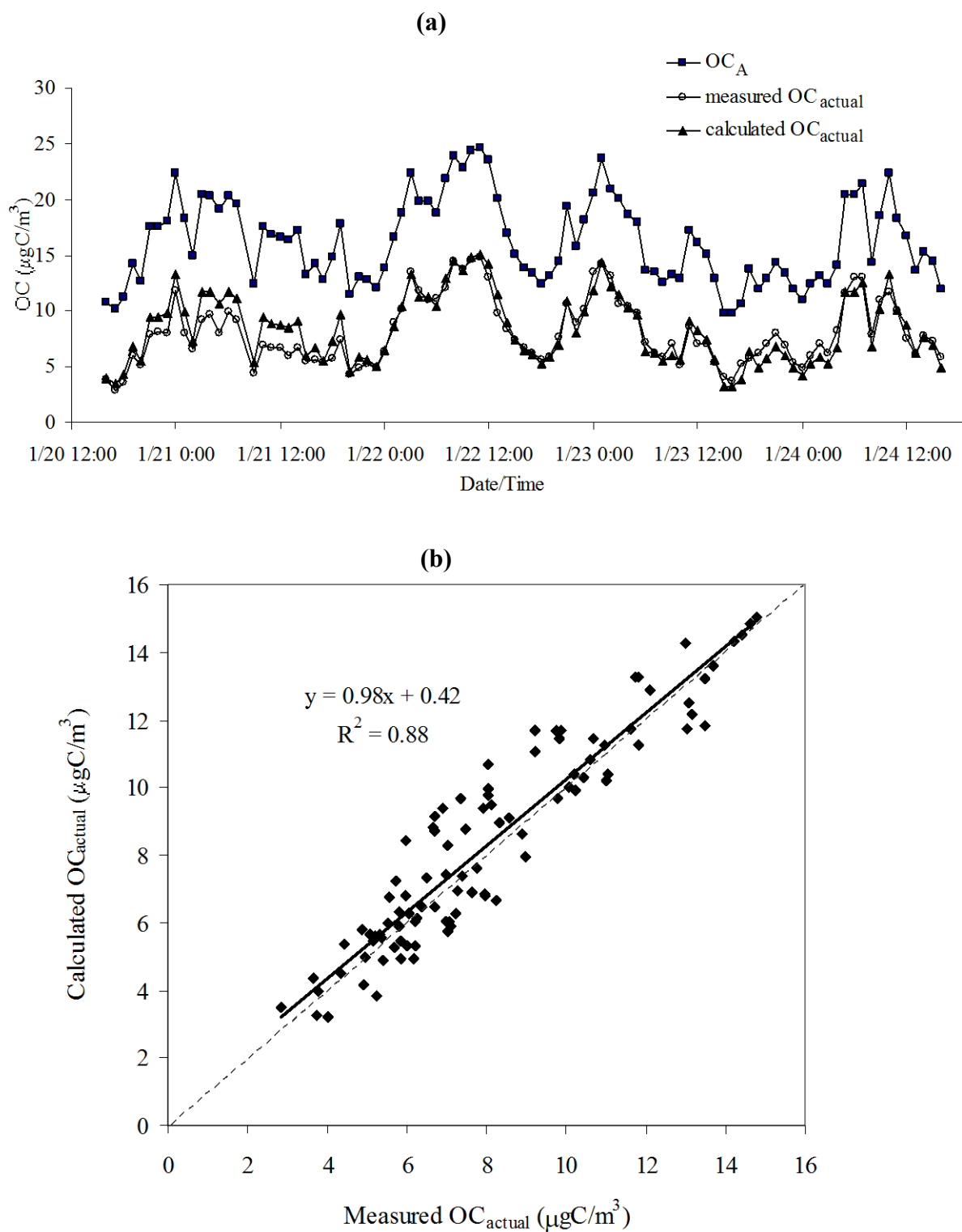


Figure 2.5 Calculated OC_{actual} from bare configuration measurements (applying the relationship found with Teflon filter method) compared to OC_{actual} measured with a denuder, a) time series data including the uncorrected bare OC (OC_A), and b) correlation plot.

previously derived correction. The derived linear relationship between the particulate OC and the bare OC may be specific to particular sampling site, instrument configuration, and/or sampling duration. The excellent agreement in Figure 2.5b also shows that the negative artifact caused by using a denuder is minor and does not significantly effect the particulate OC measurements. Therefore, the denuder configuration provides the best measure of actual particulate OC without significant associated artifacts.

2.4.4 Temperature profiles

Table 2.3 shows the statistical analysis of measurements made with the modified-IMPROVE and the FAST-ramp methods run concurrently with the modified-NIOSH method. The OC analyzed by modified-IMPROVE protocol showed a good agreement with the OC measured by using the modified-NIOSH protocol with an R^2 of 0.93 and slope of 1.04, consistent with a pervious study by Chow et al.(Chow et al. 2001). The main difference between methods is the maximum temperature reached in the first analysis stage; 550°C for the modified-IMPROVE and 850°C in the modified-NIOSH method. This shows that a temperature of 550°C is enough to evolve almost all of the OC. The EC temperature steps in both methods are the same, so any observed difference is the result of a difference between the split points affected by potentially more pyrolysis of OC at the higher temperatures of the modified-NIOSH method. Considering the R^2 of 0.92 and slope of 1.05 for EC measurements, and similar results for OC and TC, the two methods compare very well under the conditions of our experiments.

Table 2.3 Comparison between measured carbonaceous components of PM_{2.5} by different methods (units in µgC/m³)

Protocol	# of samples	Compared Parameter	R^2	Slope (95% intervals)	Intercept (95% intervals)
Modified-IMPROV. vs. Modified NIOSH	114	OC	0.93	1.04 (0.99,1.10)	0.09 (-0.11,0.30)
		EC	0.92	1.05 (1.11,1.00)	0.24 (0.17,0.31)
		TC	0.95	1.08 (1.04,1.13)	0.13 (-0.10,0.35)
FAST-ramp vs. Modified NIOSH	236	OC	0.92	0.90 (0.87,0.94)	0.05 (-0.2,0.09)
		EC	0.98	1.38 (1.35,1.4)	-0.14 (-0.17,-0.11)
		Optical OC	0.91	1.13 (1.08, 1.18)	-0.59 (-0.42,-0.77)
		Optical EC	1.00	0.99 (0.99,1.00)	-0.08(-0.09,-0.07)
		TC	0.98	1.08 (1.05,1.10)	-0.59 (-0.71,-0.47)

The OC measured using FAST-ramp temperature program (TC – optical EC) also correlated well with concurrent thermal OC measurements by the modified-NIOSH method with a correlation coefficient of 0.92. The slope of 0.90 (0.87,0.94) indicates slightly lower OC measurements compared to the modified-NIOSH method. The EC measurements in contrast were higher than those of the modified-NIOSH method with a slope of 1.38 but a high correlation coefficient of 0.98. TC measurements were also fairly consistent, with an R^2 of 0.98 and slope of 1.08. The FAST-ramp relies on the optical EC measurement to determine both EC and OC levels. The optical EC measurement is based on a manufacturer calibration, derived from relating differences in laser transmission to thermally measured EC levels over many samples using the modified NIOSH profile.

Comparing the optical EC measurements via the FAST method with optical EC measurements via NIOSH method, an R^2 of 1.00 and slope of 0.99 (0.99,1.00) were obtained. This excellent correlation is a result of using the same procedure for determining optical EC in both instruments in either of the methods. The systematic bias between optical and thermal EC measurements of about 30 % in one of the units (used for the modified-NIOSH method in this comparison) observed earlier during the instrumental precision tests can explain most of the difference between EC by the FAST-ramp and thermal EC by modified-NIOSH. The OC measurements by the FAST method are also highly correlated with optical OC via NIOSH method with R^2 and slope of 0.91 and 1.13 respectively, which are close to the correlation between TC measurements of these two methods ($R^2 = 0.98$ and slope =1.08). This indicates that the difference between these two optical OC values mainly originates from the difference between TC measurements, since optical EC values showed to be similar. The high correlation between EC measured with the NIOSH and FAST protocol suggest that a new calibration would bring the results into better agreement. Given these encouraging results, the shorter analysis time in the FAST-ramp method will potentially allow for nearly continuous sampling or shorter sampling periods.

2.4.5 Size-fractionated Measurements

The instrument with a quasi-ultrafine inlet and denuder configuration (configuration E) was run concurrently with the other instrument with a PM_{2.5} denuder configuration (configuration B), and 387 hourly samples were collected in March and May of 2005. The hourly OC measured in the quasi-ultrafine (UF) mode ranged from 0.03 to

5.80 $\mu\text{gC}/\text{m}^3$ with average of 1.59 $\mu\text{gC}/\text{m}^3$. Similar results were found in the accumulation mode, with OC ranging from 0.07 to 8.49 $\mu\text{gC}/\text{m}^3$ with an average of 1.37 $\mu\text{gC}/\text{m}^3$. The hourly EC in the quasi-ultrafine mode varied from 0.32 to 5.20 $\mu\text{gC}/\text{m}^3$ with an average of 1.16 $\mu\text{gC}/\text{m}^3$. EC in the accumulation mode was significantly less, varying from 0.0 to 2.78 $\mu\text{gC}/\text{m}^3$ with an average of 0.49 $\mu\text{gC}/\text{m}^3$. The average diurnal variations of particulate OC and EC in the both size ranges are presented in Figure 2.6. The diurnal variations of particulate EC as well as OC in these two size-fractions generally track each other well. The significant morning peak indicates the effect of morning rush hour. The UF concentrations of OC reached the maximum about 1 h earlier than the accumulation mode concentrations. A possible explanation is that UF particles are freshly emitted particles, originating directly from nearby emissions of mobile sources, and thus have diurnal patterns that follow traffic volume. By contrast, accumulation mode PM, which may have been emitted earlier as smaller particles in locations upwind of our sampling site, may be reaching the site after aging in the atmosphere, a process that allows for condensation of organic vapors onto pre-existing particles and thus an increase in particle size. The OC1 concentration (more volatile OC) in the UF mode varied between 0.01 and 3.26 $\mu\text{gC}/\text{m}^3$ with an average of 0.67 $\mu\text{gC}/\text{m}^3$, while OC1 in the accumulation mode was higher, ranging from 0.07 to 4.78 $\mu\text{gC}/\text{m}^3$ with an average of 0.96 $\mu\text{gC}/\text{m}^3$. The OC2-4 (less volatile OC) in the UF mode ranged from 0.02 to 2.54 $\mu\text{gC}/\text{m}^3$ with an average of 0.93 $\mu\text{gC}/\text{m}^3$, with lower values in the accumulation mode between 0.0 and 3.68 $\mu\text{gC}/\text{m}^3$ with the average of 0.41 $\mu\text{gC}/\text{m}^3$. The average ratios of OC1 and OC2-4 to total particulate OC in the UF and accumulation

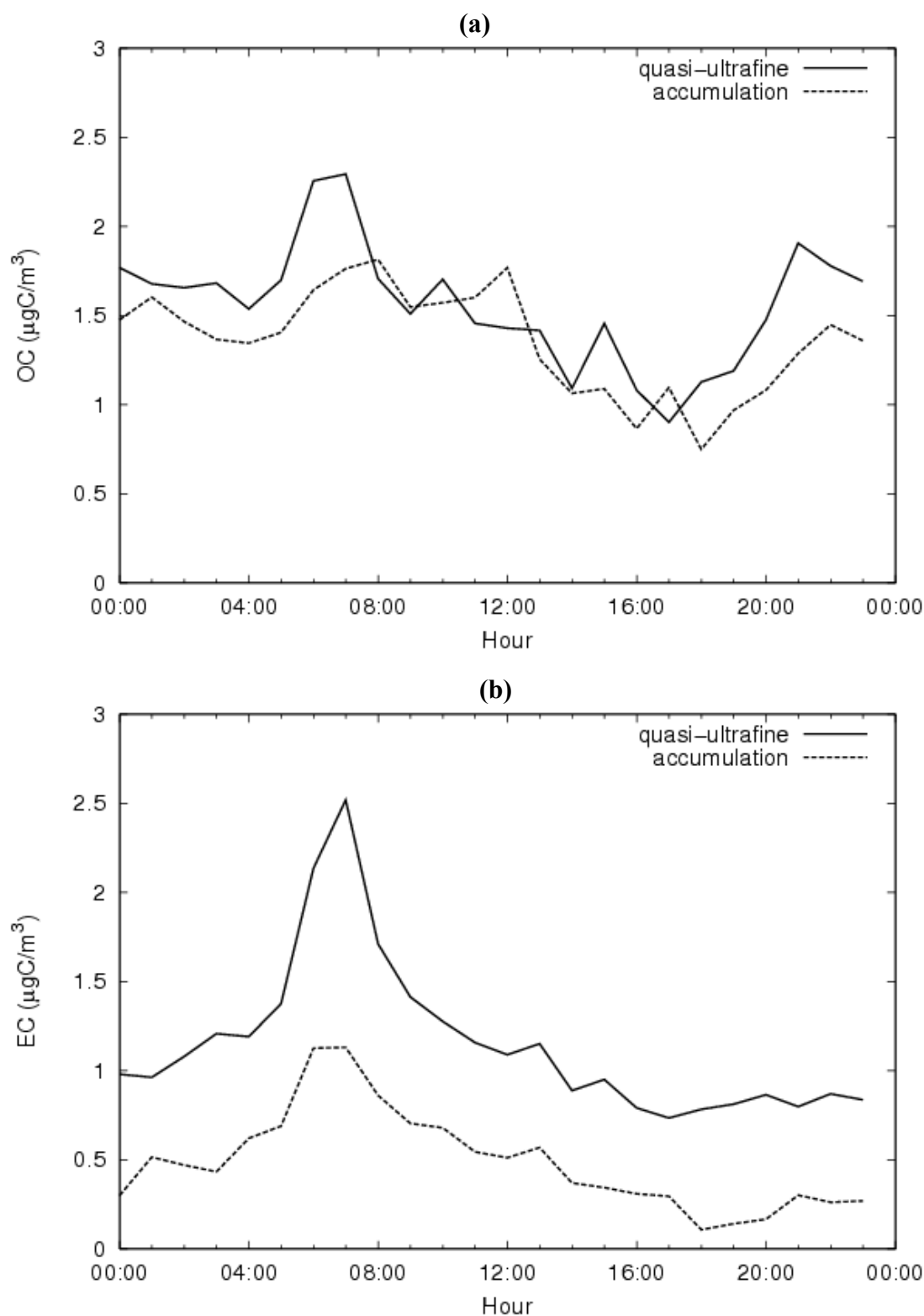


Figure 2.6 The diurnal pattern of carbonaceous component of particles in quasi-ultrafine and accumulation mode, a) OC and b) EC.

modes are presented in Figure 2.7. The average EC/OC ratios of particles in the UF and accumulation mode are also displayed in the same Figure. The considerably higher EC to OC ratio in the UF mode is due to the different sources and formation process of the two particle size ranges. EC from mobile sources (in the form of soot) is emitted primarily in smaller particles (Kittelson 1998; Kleemann 1999). While OC is also emitted in smaller particles from mobile sources, a portion of accumulation mode OC is formed by the condensation of organic gases which were either directly emitted from mobile sources or formed by photochemical secondary reactions (Kleemann 1999). The higher OC¹/OC and lower OC²⁻⁴/OC in the accumulation mode compared to the UF mode indicates higher OC volatility in the accumulation mode. This is consistent with OC condensation

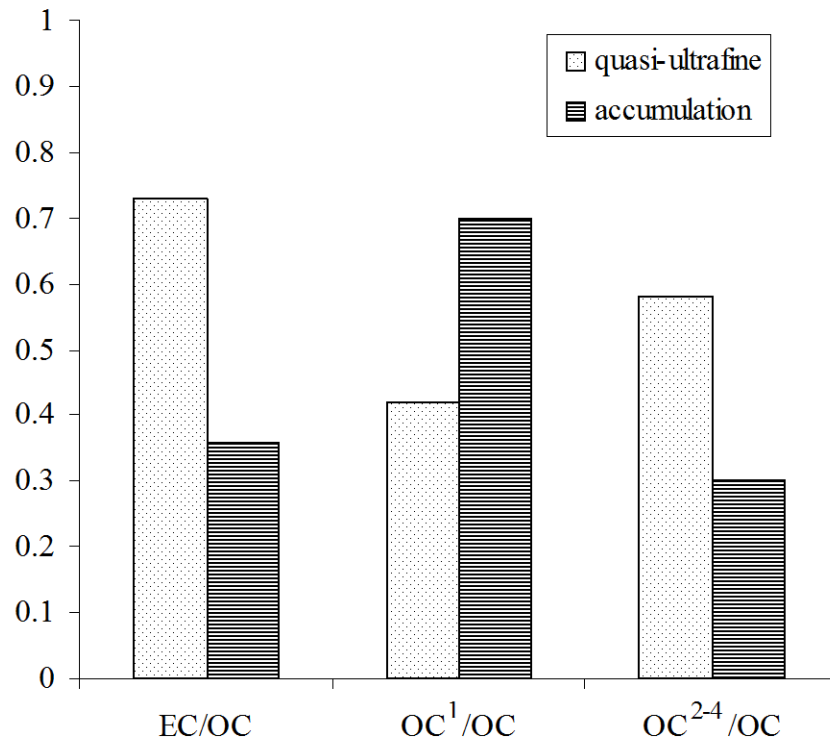


Figure 2.7 The ratio of particulate EC, OC¹ and OC²⁻⁴ to particulate OC in quasi-ultrafine and accumulation modes.

In this mode since both photochemical products and condensable vapors from vehicles are often semi-volatile species which will partition to pre-existing particle surface area (Kleemann 1999).

The results show that the semi-continuous EC/OC field analyzer is a reliable instrument for the measurement of the carbonaceous component of PM. The positive artifacts were almost constant and relatively high for the short sampling time of 45 min; more than 50% of un-denuded OC concentrations could be attributed to artifacts. These artifacts were virtually eliminated with the use of a denuder. EC and OC measurements using different temperature profiles, i.e., the modified-NIOSH, modified-IMPROVE, and FAST-ramp for analyzing the samples were highly correlated with one another. The FAST-ramp method offers the potential for reducing the time and increasing the sensitivity of the analysis step, thus allowing for more continuous measurements and shorter sampling periods. Finally, the inlets of the EC/OC analyzers can be easily modified to sample different particle size fractions. Thus, multiple instruments allow for time-resolved, size-fractionated measurements of the carbonaceous components of PM.

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Chapter 3.

Indoor/Outdoor Relationships, Trends and Carbonaceous Content of Fine Particulate Matter in Retirement Homes of the Los Angeles Basin

3.1. ABSTRACT

Hourly indoor and outdoor fine particulate matter ($PM_{2.5}$), organic and elemental carbon (OC and EC, respectively), particle number (PN), ozone (O_3), carbon monoxide (CO) and nitrogen oxides (NO_x) concentrations were measured at two different retirement communities in the Los Angeles area as part of the Cardiovascular Health and Air Pollution Study (CHAPS). Site A (group 1, or G1) was operated from 07/06/2005 to 08/20/2005 (phase 1, or P1) and from 10/19/2005 to 12/10/2005 (P2), while site B (G2) was operated from 08/24/2005 to 10/15/2005 (P1) and from 01/04/2006 to 02/18/2006 (P2). Overall, the magnitude of indoor and outdoor measurements was similar, probably because of the major influence of outdoor sources on indoor particle and gas levels. However, G2 showed a substantial increase in indoor OC, PN and $PM_{2.5}$ between 06:00 and 09:00 am, probably from cooking. The contributions of primary and secondary OC (SOA) to measured outdoor OC were estimated from collected OC and EC concentrations using EC as a tracer of primary combustion-generated OC (i.e. “EC tracer method”). The study average outdoor SOA accounted for 40% of outdoor particulate OC (40-45% in the summer and 32-40% in the winter). Air exchange rates (AER; h^{-1}) and infiltration factors (F_{inf} ; dimensionless) at each site were also determined. Estimated F_{inf} and measured particle concentrations were then used in a single compartment mass balance model to assess the contributions of indoor and/or outdoor sources to measured indoor OC, EC, $PM_{2.5}$ and PN. The average percentage contributions of indoor SOA of

outdoor origin to measured indoor OC were about 35% (during G1P1 and G1P2) and about 45% (for G2P1 and G2P2). On average, 36 (G2P1) to 44% (G1P1) of measured indoor OC was comprised of outdoor-generated primary OC.

3.2. INTRODUCTION

Numerous epidemiological studies have found associations between atmospheric aerosol concentrations and both acute and chronic adverse respiratory and cardiovascular effects (USEPA, 2004). Exposure to fine PM ($PM_{2.5}$) and its components have also been investigated in many toxicological studies on a) human volunteers exposed to concentrated outdoor PM under controlled conditions (Ghio and Devlin, 2001), b) in-vivo laboratory animal studies and c) in-vitro tissue studies using well characterized particles containing individual compounds or source mixtures (Dye et al., 2001). $PM_{2.5}$ properties and components that are believed to be responsible for the observed adverse health effects include: mass, surface area, size, metals, acids, organic compounds, elemental carbon (EC), sulfate and nitrate salts, peroxides, soot and bioaerosols (USEPA, 2004; McClellan, 2004).

The air quality standards established by the USEPA in 1997 were primarily based upon epidemiological studies conducted at stationary outdoor monitoring sites. However, a significant portion of human exposures to $PM_{2.5}$ occurs indoors where people spend approximately 85-90% of their time (Robinson et al., 1995; Klepeis et al., 2001). Thus, understanding the composition, behavior and origin of indoor $PM_{2.5}$ is important to exposure characterization and mitigation. Typically, indoor $PM_{2.5}$ consists of ambient

(outdoor) particles that have infiltrated indoors, particles emitted indoors (primary), and particles formed indoors (secondary) from precursors emitted both indoors and outdoors (Weschler and Shields, 1997; Weschler 2004; Meng, 2005). Because of indoor sources such as cooking, smoking, gas stoves, cleaning, washing, and other human activities, PM_{2.5} concentrations can be substantially higher indoors than outdoors (USEPA, 2004; Weschler and Shields, 1997). A few recent studies have demonstrated that indoor sources make a substantial contribution to the indoor concentrations of PM_{2.5} and its components, often higher than 50% (USEPA, 2004; Meng et al., 2005; Wallace, 1996; Polidori et al. 2006). Since outdoor particles can enter the building envelope by convective flow (e.g. open windows) or by diffusional flow/infiltration (e.g. cracks and fissures), outdoor PM_{2.5} is also a major contributor to indoor particle concentrations (USEPA, 2004; Thatcher et al., 1995; Abt et al. 2000). Recent epidemiologic panel studies have demonstrated the usefulness of separating total personal particle exposures into their ambient (outdoor origin) and non-ambient (indoor-generated) components. Typically, only associations between adverse health outcomes and ambient particle exposures have been found (Ebelt et al., 2005; Koenig et al., 2005).

Organic compounds make an important but poorly understood contribution to indoor and outdoor PM_{2.5}, and are believed to be a key factor in causing adverse health effects¹. They consist of organic carbon (OC) and EC and are comprised of hundreds of individual compounds with different physical and chemical properties. While EC is produced only during incomplete combustion and emitted directly in the particle phase, indoor and outdoor OC are both emitted from combustion sources (primary organic aerosols) and

formed from semi- and low volatility products of chemical reactions involving reactive organic gases (secondary organic aerosols, or SOA) (Turpin et al., 2000). Quantifying the SOA contribution to measured OC both indoors and outdoors is important to linking the organic PM concentration to its emissions and precursors, and to developing effective control strategies for PM.

The present work was funded by the National Institute of Health (NIH) and was conducted within the Cardiovascular Health and Air Pollution Study (CHAPS), a multi-disciplinary project whose goals are to investigate the effects of micro-environmental exposures to PM on cardiovascular outcomes in elderly retirees affected by coronary heart disease (CHD). The elderly population with CHD is likely to be among the most vulnerable to the adverse effects of particulate air pollutants.

In this paper, hourly indoor and outdoor $PM_{2.5}$, OC, EC, particle number (PN), ozone (O_3), carbon monoxide (CO) and nitrogen oxides (NO_x) concentrations were measured at two different retirement communities in the Los Angeles area and used to provide new insight into: a) the relationships between indoor and outdoor $PM_{2.5}$, its components and their seasonal variations as well as their association with gaseous co-pollutants, b) the contributions of primary OC and SOA to measured outdoor OC and c) the relative importance of outdoor and indoor PM sources to measured indoor OC, EC, $PM_{2.5}$ and PN concentrations. The results obtained in this paper will be used to determine personal exposure to outdoor-infiltrated $PM_{2.5}$ and its particulate components and to indoor-generated $PM_{2.5}$ and its particulate components in elderly retirees with a history of CHD.

3.3. METHODS

3.3.1. Study Design

As a part of CHAPS, the physical and chemical characteristics of indoor and outdoor $PM_{2.5}$ were investigated at two different retirement communities in southern California. Site A for subject group 1 (G1) was located about 30 miles east of downtown Los Angeles, in a residential area, approximately 2 miles away from any major freeways and close to a construction site. Site B for subject group 2 (G2) was located about 5 miles east of downtown Los Angeles, approximately 0.1 miles south of a major freeway. Two 6-week sampling campaigns were conducted at each site; site A (G1) was operated from 07/06/2005 to 08/20/2005 (Phase 1, or P1) and from 10/19/2005 to 12/10/2005 (Phase 2, or P2), while site B (G2) was operated from 08/24/2005 to 10/15/2005 (P1) and from 01/04/2006 to 02/18/2006 (P2). Thus, we were able to study the seasonal variations in the indoor/outdoor relationships of $PM_{2.5}$ and its components.

Two identical sampling stations were installed at each location, one indoors and one outdoors. The indoor sampling station at site A was located in a recreational area of the first community's main building, adjacently to a construction site where work was ongoing. The indoor sampling area at site B was situated in the dinning room of the second community's main building. At both sites the outdoor station, set-up inside a movable trailer, was positioned within 300 m from the indoor station.

3.3.2. Instrumentation

At both indoor and outdoor sampling areas a water-based condensation particle counter (CPC Model 3785, TSI Inc, Shoreview, MN), providing continuous (1-min) PN concentrations (operating flow-rate = 1 lpm), and a semi-continuous OC_EC analyzer (Model 3F, Sunset Laboratory Inc., Tigard, OR) were operated side-by-side. The two CPCs were examined at the USC lab before being deployed in the field and showed high internal precision. The OC_EC analyzers were placed downstream of a PM_{2.5} cyclone and collected samples at an approximate flow-rate of 8 lpm. Particulate OC and EC were measured in hourly cycles (i.e. sampling time = 45-min; analysis time = 15-min). A multi-channel parallel carbon plate diffusion denuder (provided by the manufacturer) was placed upstream of the OC_EC instrument to remove most of the organic vapors in the sampled air. The setup and the standard operating procedure for the semi-continuous carbon analyzer are described in more details in Arhami et al., 2006. A modified-NIOSH analysis protocol was used here to evolve particulate OC and EC. This protocol consists of four temperature steps in the He-analysis segment and allows for the separation of particulate OC into four response peaks representing different volatility fractions of OC (Birch and Cary, 1996; Kirchstetter, 2001). These four OC peaks are designated and recorded as peak 1 to peak 4 (OC₁ to OC₄). For the purposes of this study, OC₂, OC₃, and OC₄ were summed (OC₂₋₄) and considered as the least volatile OC fraction, while OC₁ represented the most volatile OC fraction. The internal precision of the two OC_EC analyzers (examined prior the beginning of CHAPS by running them side by side) was high (R^2 of 0.98 and 0.97 for thermal OC and EC, respectively). A detailed description of all quality control and quality assurance analyses performed with the semi-continuous

carbon analyzer is reported in the Supplemental Information along with the corresponding results.

Hourly $PM_{2.5}$ mass concentrations were measured by Beta-Attenuation Mass Monitors (BAM, Model 1020, Met One instruments Inc., OR) at a flow-rate of 16.7 lpm. Two BAMs were used at each of the indoor and outdoor sampling stations in order to examine the uncertainty of the collected data. Continuous (1-min) NO and NO₂ measurements were obtained both indoors and outdoors by using Thermo Environmental NOx Analyzers (Model 42, Thermo Environmental instruments Inc, Franklin, MA). Dasibi Carbon Monoxide Analyzers (Model 3008, Dasibi Environmental Corp, Glendale, CA) were implemented to measure continuous (1-min) indoor and outdoor CO levels. Continuous (1-min) outdoor ozone (O₃) concentrations were also monitored at each sampling station by using API Ozone Analyzers (Model 400A, Teledyne Technologies Inc, Los Angeles, CA).

3.3.3. Data Analysis

To match the OC, EC and $PM_{2.5}$ measurements, only hourly arithmetic averages of the highly resolved PN and gaseous co-pollutant (CO, NO_x, O₃) concentrations were considered. Then, a comprehensive indoor and outdoor database was constructed for each group (G) and phase (P) of CHAPS to analyze the relationships between measured indoor and outdoor particulate and gaseous species, and to facilitate the overall data analysis.

The contributions of primary OC and SOA to measured outdoor OC were estimated from collected OC and EC concentrations using EC as a tracer of primary combustion-generated OC (i.e. “EC tracer method”) (Turpin et al., 1995; Lim et al., 2003; Cabada et al., 2004; Polidori et. al., 2006). This method assumes that primary OC and EC are emitted from the same combustion sources. Data-points characterized by high CO and NO peaks, mainly observed during rush hour traffic, were used to identify periods dominated by primary sources, when SOA is less likely to be formed. By regressing the OC and EC data collected during these time-periods the characteristic primary OC/EC ratio for each month of CHAPS was determined. Because a conventional linear least-squares regression assumes that there are uncertainties only in the dependent variable, a Deming linear least-squares regression (Deming, 1943; Cornbleet et al., 1979) was used instead, and the uncertainties in OC and EC were assumed equal. Thus, primary OC (OC_{pri}) and SOA can be estimated by the following expressions:

$$OC_{pri} = a \times EC + b \quad (3.1)$$

$$SOA = OC - OC_{pri}, \quad (3.2)$$

where, $a = (OC/EC)_{pri}$ = characteristic primary OC/EC ratio for the study area, and b = non-combustion primary OC. Typically, the SOA values estimated through this method vary with season and location and are generally higher during the afternoon hours of summertime photochemical smog episodes (e.g. in the Los Angeles basin) and at locations that are recipients of long distance transport (e.g., the eastern US).

The indoor-outdoor air exchange rates (AER; h^{-1}) at each site were estimated from indoor CO measurements collected during periods affected by a dominant indoor source. Only time-periods when the CO concentration peaked at values significantly higher than the background CO level and was followed by a non-source period (mostly observed in the morning and probably associated with cooking activities) were considered in our calculations. Assuming an exponential decay of particles, that AER and outdoor concentrations are constant during the decay period, and that indoor concentrations are well mixed, then:

$$C_t = e^{-(\text{AER}+k)t} C_0 \quad (3.3)$$

or

$$\ln C_t = -(\text{AER}+k)t + \ln C_0 \quad (3.4)$$

where, C_t is the indoor CO concentration after time t (after the decay period), C_0 is the initial peak CO concentration (right after CO emission) and k is the indoor loss rate for particles or gases (h^{-1}) (Abt et al., 2000). Since k is rather negligible for CO, it was possible to estimate the AERs for the two sites directly from the above-mentioned eq (3.4) by regressing $\ln C_t$ over $\ln C_0$.

The infiltration factor (F_{inf} , defined as the equilibrium fraction of ambient particles that penetrate indoors and remain suspended (Long et al., 2001) is a key determinant of the indoor concentrations of particulate species. F_{inf} is described by the following eq:

$$F_{inf} = P(AER)/(AER+k) \quad (3.5)$$

where, P is the penetration coefficient (dimensionless). F_{inf} for $PM_{2.5}$ varies with particle composition, particle size and volatility, surface to volume ratio of the indoor sampling location and indoor air-speed. F_{inf} is typically highest for non-volatile species such as EC (Lunden et al., 2003; Sarnat et al., 2006). In order to estimate F_{inf} for OC, EC, $PM_{2.5}$ and PN two different techniques were used: 1) an analysis of the indoor/outdoor concentration ratios, and 2) the recursive model (RM) developed by Allen et al., 2003. In the first approach hourly indoor/outdoor ratios (I/O) for each particulate species were determined at times when no indoor particle sources, such as cooking or cleaning, were likely to be present (i.e. only I/O ratios ≤ 1 were considered) . Daily F_{inf} estimates were then obtained by averaging these segregated hourly I/O ratios. Mean F_{inf} for each group and phase of the study were also determined by averaging the corresponding daily values. To verify these results the same analysis of the I/O concentration ratios was then repeated by using only nighttime data (from 00:00 to 06:00 am), for at this time resident activities causing indoor particle generation were expected to be minimal. Conversely, the RM method, which has been recently validated for estimating F_{inf} for $PM_{2.5}$ from hourly light scattering data (Allen et al., 2006) states that, for a particular species of interest, the average indoor concentration during hour t (C_t^{in}) is equal to the sum of a fraction of the

average outdoor concentration during the same hour (C_t^{out}), a fraction of the average indoor concentration remaining from the previous hour (C_{t-1}^{in}), and the contribution from indoor sources (S_t^{in}):

$$C_t^{in} = a_1 C_t^{out} + a_2 C_{t-1}^{in} + S_t^{in} \quad (3.6)$$

where

$$a_1 = F_{inf} (1 - a_2) \quad (3.7)$$

and

$$a_2 = \exp[-(AER + k)\Delta t] \quad (3.8)$$

Algorithms are used to identify and minimize the influence of hours when the indoor concentration is influenced by indoor sources, thus eliminating the S_t^{in} term from eq (3.6):

$$C_t^{in} = a_1 C_t^{out} + a_2 C_{t-1}^{in} \quad (3.9)$$

The coefficients a_1 and a_2 are then estimated via multiple linear regression of eq (3.9) and F_{inf} is calculated from a_1 and a_2 using the following relationship:

$$F_{inf} = \frac{a_1}{1 - a_2} \quad (3.10)$$

Finally, a single compartment mass balance model (Meng et al., 2005; Wallace, 1996; Polidori et al. 2006) was used to assess the mean contributions of indoor and outdoor sources to measured indoor OC, EC, PM_{2.5} and PN concentrations. Under the assumption of perfect instantaneous mixing and that the factors affecting the indoor concentrations are constant or change slowly with time, the steady state indoor concentration of any particulate species can be described by the following eq:

$$C_{in} = \frac{P(AER)C_{out}}{AER + k} + \frac{Q_i / V}{AER + k} = F_{inf}C_{out} + C_{ig} = C_{og} + C_{ig} \quad (3.11)$$

where, C_{in} is the indoor concentration of the species of interest ($\mu\text{g}/\text{m}^3$), C_{out} is the corresponding outdoor concentration ($\mu\text{g}/\text{m}^3$), F_{inf} is the corresponding infiltration factor (estimated for each species as described previously; dimensionless), C_{ig} is the indoor-generated concentration for the same species found indoors and C_{og} is the outdoor-generated concentration for the same species found indoors. Typically, in the mass balance model, F_{inf} is given by eq (3.5) and C_{ig} is expressed by $Q_i/V(a+k)$, where Q_i is the indoor source strength ($\mu\text{g}/\text{h}$), and V is the house volume (m^3).

3.4. RESULTS AND DISCUSSION

3.4.1. Particle and Gaseous Measurements

The minimum, maximum, average and standard deviation of all hourly particle and gas data obtained for all groups (G) and phases (P) of CHAPS are presented in Table 3.1. Overall, the magnitude of indoor measurements was similar to that of outdoor measurements for most phases of the study, which highlights the major effect of outdoor sources on indoor levels (Meng et al., 2005; Polidori et al., 2006; Naumova et al., 2002; Naumova et al., 2003). Although at site B (G2) a wider range in indoor PM_{2.5}, PN and OC concentrations was observed compared to the outdoor levels, the average indoor and outdoor concentrations were still comparable. The difference between indoor and outdoor average concentrations was lowest for CO and NO_x (except NO_x in G2P1), which suggests the absence of an important indoor source of these two gases and that their penetration losses were not significant. Conversely, the differences between indoor and outdoor particle levels were higher, probably because of the presence of indoor sources and/or changes in concentration due to transportation of particles indoors from outdoors.

The average hourly diurnal variations for data collected during the first phase of CHAPS at site A (G1P1; from 07/06/2005 to 08/22/2005) are shown in Figure 3.1. Generally, indoor and outdoor particle and gas concentrations tracked each other well, with a better agreement for gases. Slightly higher OC levels were measured indoors, mainly because of indoor contributions of the most volatile OC fraction (OC₁; not shown). Indoor EC, PM_{2.5} and PN concentrations slightly increased from 10:00 am to 12:00 pm, probably because

of the emission contributions of a construction site located right outside the indoor sampling area. Significant EC, PN, PM_{2.5}, CO and NO_x peaks occurred concurrently outdoors and indoors during the morning rush hour traffic, suggesting that outdoor primary pollutants were important contributors to the indoor air. Indoor and outdoor OC concentrations increased from 12:00 to 04:00 pm probably as a result of photochemical OC formation in the afternoon. This mechanism of particle generation may also explain the increase in outdoor PN and PM_{2.5} between 03:00 and 05:00 pm, not observed for EC, CO and NO_x.

The average indoor and outdoor diurnal patterns at site A during the second phase of the study (G1P2; from 10/17/2005 to 12/13/2005), generally followed the same trends as those observed during G1P1 (Figure 3.1), which strengthen the hypothesis that at this location the majority of indoor particles and gases originated from outdoor sources. During G1P2 the CO and NO_x outdoor concentrations increased at midnight, most likely because of a lowered mixing height. This caused a subsequent increase in indoor gaseous levels.

Measurement results at site B during the first phase of CHAPS (G2P1, from 08/23/2005 to 10/15/2005) showed a substantial morning peak in indoor OC, PN and PM_{2.5} (Figure 3.2) between 06:00 and 09:00 am, probably from cooking activities in the kitchen adjacent the indoor sampling site where breakfast, lunch and dinner were all cooked at this time by using gas stoves/ovens. Interestingly, cooking did not affect EC, CO and NO_x, whose indoor and outdoor levels were mostly influenced by morning rush hour

Table 3.1 Average $\pm 1\sigma$ (standard deviation), minimum (min) and maximum (max) of all hourly particle and gas data obtained for all groups (G) and phases (P) of CHAPS.

	G1P1		G2P1		G1P2		G2P2	
	INDOOR	OUTDOOR	INDOOR	OUTDOOR	INDOOR	OUTDOOR	INDOOR	OUTDOOR
Average $\pm 1\sigma$ Min - Max								
OC ($\mu\text{gC}/\text{m}^3$)	5.91 $\pm$ 2.06 2.26 - 16.35	5.21 $\pm$ 1.80 1.72 - 18.17	6.75 $\pm$ 4.55 2.24 - 61.75	7.07 $\pm$ 3.13 1.54 - 22.20	5.46 $\pm$ 2.68 0.67 - 26.92	5.43 $\pm$ 2.89 0.97 - 29.10	5.25 $\pm$ 3.86 0.92 - 73.21	7.06 $\pm$ 3.32 0.45 - 23.20
EC ($\mu\text{gC}/\text{m}^3$)	1.43 $\pm$ 1.03 0 - 8.53	1.42 $\pm$ 0.73 0 - 5.98	1.24 $\pm$ 0.76 0 - 5.5	1.76 $\pm$ 1.21 0.05 - 10.03	1.42 $\pm$ 0.84 0 - 5.61	1.65 $\pm$ 1.05 0 - 8.87	1.18 $\pm$ 0.79 0 - 5.76	1.68 $\pm$ 1.16 0 - 6.48
OC₁ ($\mu\text{gC}/\text{m}^3$)	2.97 $\pm$ 1.03 1.47 - 8.53	2.27 $\pm$ 0.76 0.52 - 6.54	3.3 $\pm$ 2.1 1.25 - 34.08	3.16 $\pm$ 1.34 0.91 - 9.98	2.35 $\pm$ 0.99 0.12 - 10.47	2.23 $\pm$ 1.24 0.49 - 12.79	2.41 $\pm$ 1.77 0.62 - 38.13	2.82 $\pm$ 1.32 0.43 - 8.66
OC₂₋₄ ($\mu\text{gC}/\text{m}^3$)	2.88 $\pm$ 1.34 0 - 10.74	2.78 $\pm$ 1.36 0 - 11.57	3.32 $\pm$ 2.58 0 - 27.65	3.41 $\pm$ 2.25 0.91 - 15.47	2 $\pm$ 2.07 0 - 17.57	2.67 $\pm$ 1.94 0.49 - 17.29	2.44 $\pm$ 2.24 0 - 35.07	3.83 $\pm$ 2.38 0 - 15.04
PN (ptcl#/cm ³)	10643 $\pm$ 4826 2166 - 43140	13044 $\pm$ 3442 2577 - 23854	13424 $\pm$ 24776 307 - 2E+05	14017 $\pm$ 6297 738 - 61001	13724 $\pm$ 9871 2517 - 2E+05	13542 $\pm$ 5499 2649 - 44523	19000 $\pm$ 28400 2191 - 4E+05	22732 $\pm$ 8923 3524 - 62588
PM_{2.5} ($\mu\text{g}/\text{m}^3$)	19.73 $\pm$ 9.66 1 - 194	30.83 $\pm$ 11.43 6 - 72	37.51 $\pm$ 27.26 5 - 197	24.86 $\pm$ 13.47 0 - 81	22.16 $\pm$ 15.15 0 - 136	24.82 $\pm$ 22.42 0 - 132	12.66 $\pm$ 9.58 0 - 82	19.65 $\pm$ 17.07 0 - 100
CO (ppm)	0.64 $\pm$ 0.23 0.1 - 2.1	0.68 $\pm$ 0.32 0 - 2	0.78 $\pm$ 0.42 0.1 - 3.9	0.65 $\pm$ 0.39 0.1 - 3	0.71 $\pm$ 0.39 0 - 2.9	0.7 $\pm$ 0.4 0 - 4.2	0.98 $\pm$ 0.61 0 - 4	0.81 $\pm$ 0.56 0.1 - 3.4
NO_x (ppb)	38.81 $\pm$ 24.66 5 - 163	40.57 $\pm$ 22.92 8 - 184	35.56 $\pm$ 34.53 0 - 254	58.79 $\pm$ 44.02 6 - 300	59.19 $\pm$ 36.34 2 - 260	57.58 $\pm$ 38.73 3 - 272	84.63 $\pm$ 65.03 1 - 484	84 $\pm$ 61.85 2 - 356
Ozone (ppb)		30.25 $\pm$ 26.97 2 - 122		22.3 $\pm$ 20.6 1 - 112		14.08 $\pm$ 12.77 0 - 66		22.66 $\pm$ 12.46 12 - 61

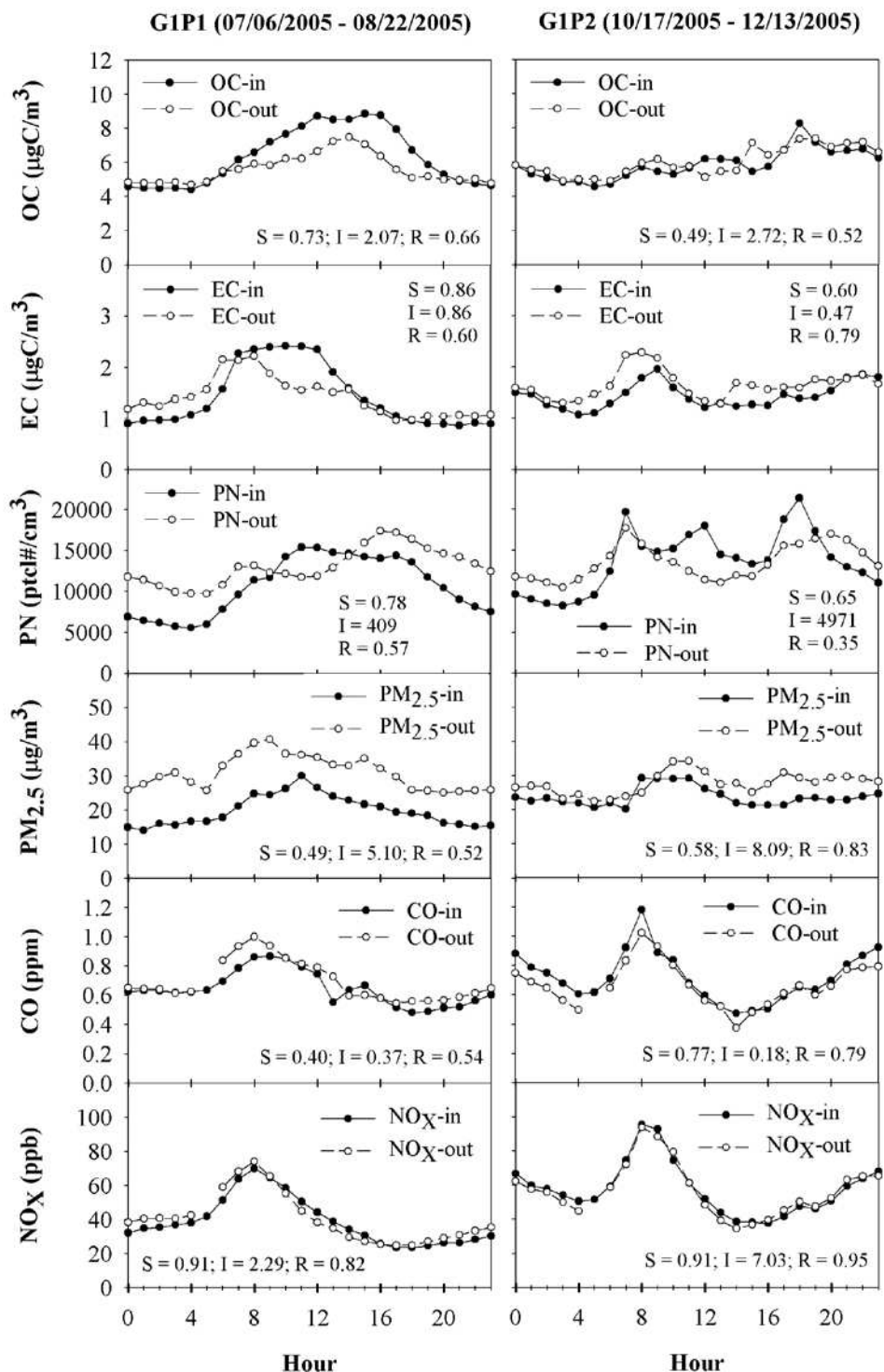


Figure 3.1 Hourly diurnal variations for particle and gas data collected during the first and the second phase of CHAPS at site A (G1P1 and G1P2, respectively). The slope (*S*), intercept (*I*) and Pearson correlation coefficient (*R*) for indoor versus outdoor concentrations are also reported.

traffic. With the exception of these morning peaks, indoor and outdoor particle and gas concentrations tracked each other well, although indoor levels were generally lower than outdoor levels. This suggests that indoor sources of OC, PN and PM_{2.5} were not significant other than during the morning cooking events, and that indoor EC mainly originated from outdoor sources. Indoor cooking affected the concentrations of the least and the most volatile OC fractions (OC₁ and OC₂₋₄, respectively) equally (not shown).

Similar indoor and outdoor trends in particle and gas concentrations, including a morning increase in OC, PN and PM_{2.5} due to cooking, were also observed in the second phase of the study at site B (G2P2, from 01/04/2006 to 02/21/2006; Figure 3.2). Indoor and outdoor diurnal patterns for EC, CO and NO_x were virtually identical (no significant indoor sources) and peaked in the morning during rush hour traffic. Ground-level concentrations of all particulate and gaseous species increased significantly at midnight because of a decrease in the mixing height and an increase in the atmospheric stability, typical of wintertime conditions. Indoor particle mass levels were lower during G2P2 than during G2P1; the reasons for this discrepancy are unclear.

Despite the substantial morning increase in indoor OC, PN and PM_{2.5} at site B due to cooking, the average indoor concentrations of these three species were not much higher than those measured outdoors (Table 3.1). This was the result of the smaller contribution of indoor sources during the rest of the day, which lowered the average indoor concentrations. Also, these observations are consistent with the low AER and F_{inf} values estimated in this work and discussed in a subsequent section.

Figures 1 and 2 also include the slope (S), intercept (I) and Pearson correlation coefficient (R) for indoor versus outdoor concentrations of all measured particulate and gaseous species and for all groups and phases of CHAPS. At site B, where indoor cooking significantly affected $PM_{2.5}$, PN and OC concentrations, the morning data (05:00 to 09:00 am) were not considered in the calculation of S , I and R . Indoor gas concentrations usually showed the highest degree of correlation with the corresponding outdoor levels with S close to 1 in most cases, confirming that indoor NO_x and CO were mostly of outdoor origin. For OC, EC, $PM_{2.5}$ and PN a positive I was obtained, suggesting the presence of significant indoor background concentrations for all particulate species. Indoor OC, OC_1 and OC_{2-4} measurements correlate well with the corresponding outdoor data, confirming the important effect of outdoor OC sources on indoor levels. A high R for the EC indoor/outdoor correlations was always observed, for indoor sources of EC were negligible at both sites.

The highest slopes for EC were found during G1P1, probably because of a substantial outdoor contribution from the diesel vehicles operating at the construction site located right outside the indoor sampling station and between the retirement community building and the outdoor monitoring site. Therefore, the concentration of EC impacting the building shell was greater than that measured by the outdoor site. This, rather than an indoor source of EC, is thought to explain the indoor EC being higher than the outdoor EC for G1P1. Representative hourly diurnal variations of the $PM_{2.5}$, OC and EC concentrations ($\mu g/m^3$) (non-averaged data) measured during each group (G) and phase (P) of CHAPS are reported in the Supplemental Information.

The correlation between gas levels, PM_{2.5} and PN concentrations for indoor and outdoor data are presented in Table 3.2. Overall, the results show a weak Pearson correlation coefficient between particles and gases indoors. However, some modest correlations ($R \sim 0.4-0.5$) between PN and NO_x and between PN and CO are observed outdoors during most phases of CHAPS, probably because these three species were mainly emitted from the same source (e.g. motor vehicles emission). These correlations are slightly higher at site B, which was located closer to a freeway.

3.4.2. Primary OC and SOA Estimations Outdoors

Figure 3.3 shows all semi-continuous outdoor OC and EC values obtained on July 2005 (G1P1). Data points were segregated into measurements dominated by primary emissions (grey) and measurements affected by SOA formation (black). Similar plots were obtained for each month of the study. By regressing OC on EC using only data dominated by primary emissions we estimated the characteristic primary OC/EC ratios (a in eq 3.1) and non-combustion primary OC (b in eq 3.1) for each month during CHAPS (Table 3.3). Carbon data corresponding to time periods affected by rain were not considered in the determination of a and b because of the possibility of differential wet scavenging (Lim et al., 2003; Cabada et al., 2004). The average coefficient of determination (R^2) for all monthly regressions was 0.87 ± 0.06 (1σ), which adds confidence to our results.

Thus, using eqs 3.1 and 3.2 and the estimated a and b values monthly averaged outdoor primary OC and SOA concentrations were obtained (Table 3). Polidori et al., 2006. calculated that the variability in primary OC and SOA determined by using the method

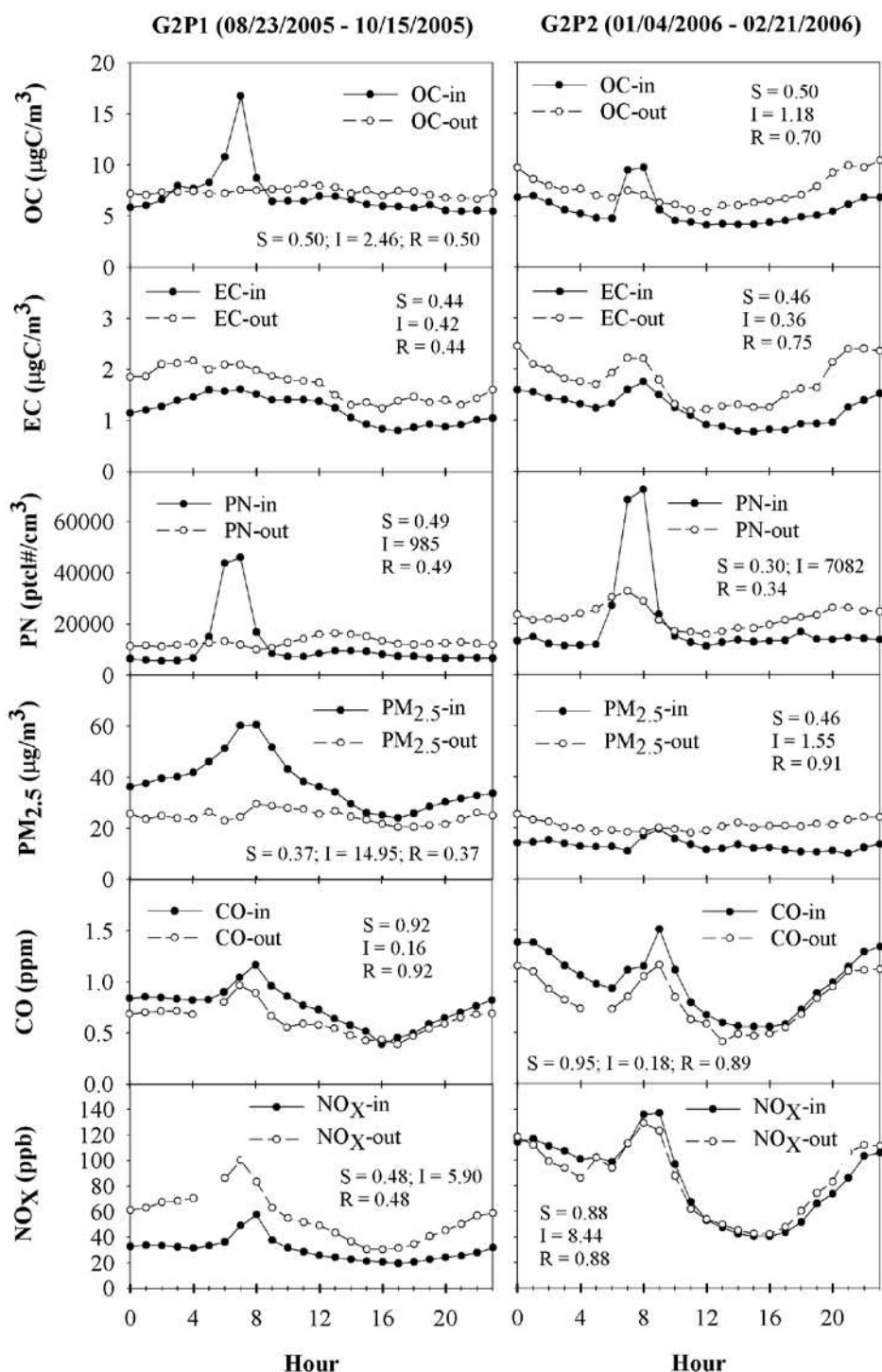


Figure 3.2 Hourly diurnal variations for particle and gas data collected during the first and the second phase of CHAPS at site B (G2P1 and G2P2, respectively). The slope (*S*), ntercept (*I*) and Pearson correlation coefficient (*R*) for indoor versus outdoor concentrations are also reported.

Table 3.2 Correlation between particle concentrations (PM_{2.5} and PN) gas levels (CO and NO_x) for all indoor and outdoor data collected during CHAPS.

	PN-CO		PM _{2.5} -CO		PN-NO _x		PM _{2.5} -NO _x	
	IN	OUT	IN	OUT	IN	OUT	IN	OUT
G1P1	0.37	0.21	0.22	0.05	0.33	0.22	0.10	0.15
G1P2	0.07	0.38	0.40	0.28	0.15	0.49	0.04	0.07
G2P1	0.28	0.45	0.32	0.21	0.40	0.47	0.15	0.07
G2P2	0.11	0.49	0.37	0.44	0.19	0.57	0.15	0.35

described above is around 10%. This estimate of precision only includes “model” uncertainties and it would be higher if measurement uncertainties were also taken into account. Typically, uncertainties for primary and secondary OC calculations are on the order of 10-40% (Cabada et al., 2004; Polidori et al., 2006).

During CHAPS the average SOA concentration was 2.50 ± 1.94 (1 σ) $\mu\text{gC}/\text{m}^3$, which represents $40\% \pm 22$ (1 σ) of the study average particulate OC. These results are likely to be representative of the entire San Gabriel Valley, for the SOA estimations presented in this work only refer to outdoor data and none of the two CHAPS sites was affected by

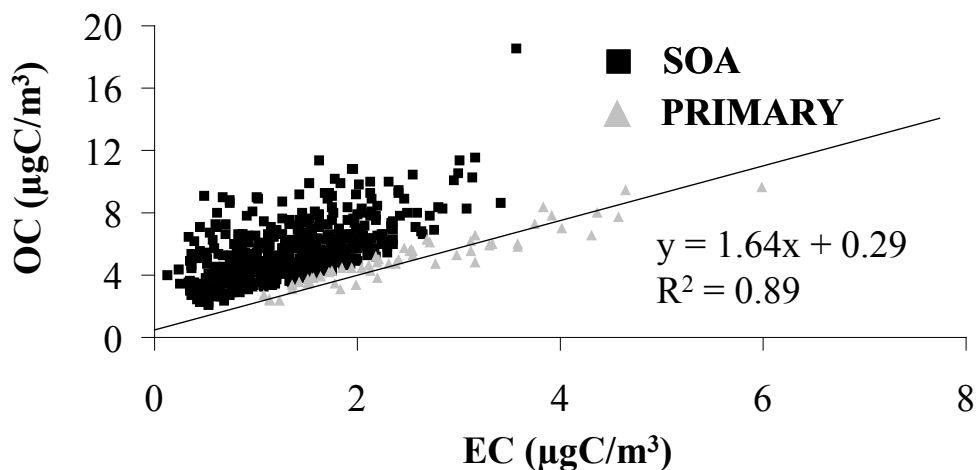


Figure 3.3 Particulate OC and EC semi-continuous carbon measurements made from 07/06/05 to 07/31/05 at site A (G1P1). Black rectangles represent measurements with a moderate or high probability of SOA formation. Grey triangles are measurements dominated by primary emissions. The regression line, equation and coefficient of determination (R^2) were obtained by Deming regression of measurements labeled “PRIMARY”. Similar scatter plots were obtained for each month of CHAPS.

any specific local sources other than traffic emissions. The highest monthly average SOA concentration ($3.30 \mu\text{gC}/\text{m}^3$, or 40% of measured OC) was estimated between 02/01/06 and 02/16/06 (G2P2), while the lowest average SOA concentration ($1.88 \mu\text{gC}/\text{m}^3$, or 35% of measured OC) was estimated between 11/01/05 and 12/09/05 (G1P2) (see Table 3 for details). Interestingly, the summertime percentage contributions of SOA to particulate OC obtained during CHAPS (40-45%) are higher than those estimated by Turpin and Huntzicker in Claremont, CA (where SOA exceeded 40% of the daily OC only during the afternoon photochemical smog episodes), but are in good agreement with those obtained in Atlanta by Lim and Turpin, 2002 (44%) and in the Pittsburgh area, PA, by Cabada et al., 2004 (35%) and Polidori et al., 2006 (38%). In each case a similar decision strategy was used to identify time periods dominated by primary OC and to estimate SOA. Thus,

these recent results are quite consistent and suggest that in the summertime SOA represents a substantial fraction of measured OC both in the East and in the West of the United States. Figure 3.4a shows the time averaged diurnal pattern for estimated primary OC and SOA concentrations during G1P1 (typical of summertime conditions). The corresponding measured outdoor CO and O₃ concentrations are also reported. As expected, primary OC, CO and NO (not shown) peaked between 05:00 and 11:00 am because of rush hour traffic, while SOA and O₃ peaked between 01:00 and 07:00 pm because of the high photochemical activity occurring locally. CO and NO are considered tracers of local and regional combustion, while O₃ is used as a tracer for photochemical reactions. During the wintertime, both the average SOA concentration (2.36 µgC/m³ in January, and 3.30 µgC/m³ in February) and the average percentage contributions of SOA to particulate OC (32% in January and 40% in February; G2P2) were comparable to the corresponding average values estimated in the summertime (2.18 µgC/m³ or 43% of measured OC in July, and 2.16 µgC/m³ or 40% of measured OC in August; G1P1) (Table 3), but had very different diurnal patterns. These wintertime SOA results are significantly higher than those reported for the San Joaquin Valley, CA, by Strader et al., 1999, where SOA formation accounted for roughly 25% of wintertime OC, and for Pittsburgh, PA,

Table 3.3 By regressing (Deming regression) OC on EC using only outdoor data dominated by primary emissions we estimated the characteristic primary OC/EC ratios (a = slope), non-combustion primary OC (b = intercept) and coefficient of determination (R^2) for each month of CHAPS. a and b were then used to estimate outdoor primary OC and SOA concentrations, and the percentage contribution of SOA to measured outdoor OC.

	From	To	a	b ($\mu\text{gC}/\text{m}^3$)	R^2	Primary OC ($\mu\text{gC}/\text{m}^3$)	SOA ($\mu\text{gC}/\text{m}^3$)	SOA (%)
G1P1	07/06/05	07/31/05	1.64	0.29	0.89	2.64	2.18	43
G1P1	08/01/05	08/19/05	2.27	0.00	0.87	3.06	2.16	40
G2P1	08/23/05	09/30/05	2.08	0.19	0.86	3.39	3.01	45
G2P1	10/01/05	10/14/05	2.21	0.04	0.94	4.95	3.10	42
G1P2	10/17/05	10/31/05	2.04	0.10	0.93	2.88	2.55	45
G1P2	11/01/05	12/09/05	1.86	0.00	0.85	3.18	1.88	35
G2P2	01/05/06	01/31/06	2.46	0.00	0.91	4.62	2.36	32
G2P2	02/01/06	02/16/06	2.39	0.18	0.74	4.32	3.30	40

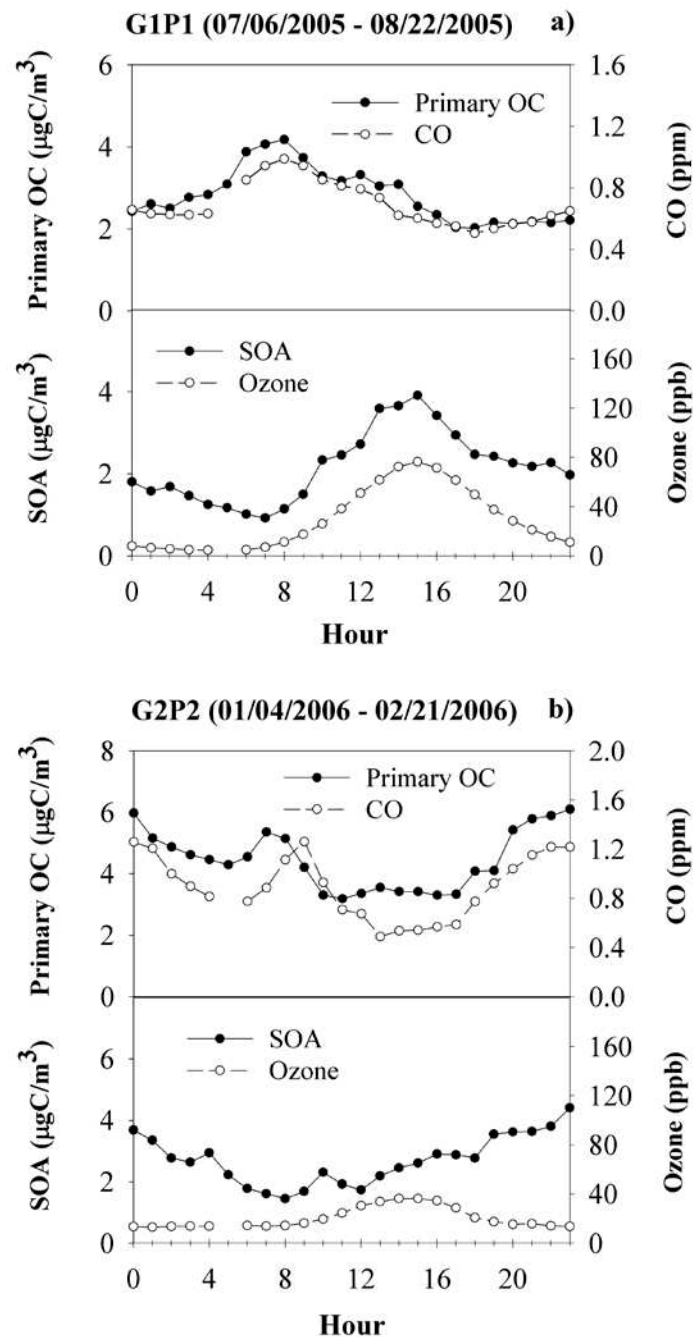


Figure 3.4 Time averaged diurnal pattern for estimated primary OC and SOA concentrations during G1P1 (typical for summertime conditions) (a) and G2P2 representative of wintertime conditions) (b). The corresponding measured CO and O₃ concentrations are also reported.

where the average wintertime SOA concentration was 24% of measured OC (Polidori et al., 2006). The time averaged diurnal pattern for estimated primary OC and SOA concentrations during G2P2 (representative of wintertime conditions) is shown in Figure 3.4b. The corresponding measured CO and O₃ concentrations are also reported. Typically, the concentrations of primary OC, CO and NO (not shown) tracked one another well across the day and peaked in the early morning (between 05:00 and 11:00 am; because of rush hour traffic) and late at night (between 08:00 pm and 02:00 am; most likely because of increased stability and low mixing heights). The average primary OC concentrations were higher during G2P2 (4.62 µgC/m³ and 4.32 µgC/m³ for January and February, respectively) than during G1P1 (2.64 µgC/m³ and 3.06 µgC/m³ for July and August, respectively) suggesting that primary combustion sources of OC were dominant in the wintertime. Periods of high wintertime SOA concentrations (as high as 9-12 µgC/m³) typically occurred in the late afternoon or at night (Figure 3.4b). Strader et al., 2005 suggested that under suitable conditions (clear skies, low horizontal winds, and low mixing height) SOA concentrations to levels as high as 15-20 µgC/m³ could be produced in the wintertime, mainly due to the oxidation of aromatics. Species such as toluene, xylenes, trimethylbenzenes, naphthalenes, and 1,3,5-trimethylbenzene are predicted to produce roughly 75% of all SOA under these conditions.

The meteorological conditions observed during G2P2 (especially in February) were extremely favorable for SOA production with afternoon temperatures that reached 30 °C on several occasions and nighttime temperatures as low as 5 °C. Under these circumstances, if highly reactive SOA precursors were accumulated within the San

Gabriel Valley, significant amounts of SOA could be formed in the afternoon because of photochemical activity, and at night because of a shifting of the gas-particle partitioning equilibrium towards the particulate phase due the temperature decrease (Pankow, 1994). In addition, a decrease in the mixing height could also contribute to the accumulation of SOA precursors at night, accelerating the rate of SOA formation. However, it has to be recognized that these high wintertime SOA values could be, at least in part, an artifact of the EC-tracer method, for the primary OC/EC ratio is in fact not constant, as assumed by the method, but varies between sources and is influenced by meteorology, diurnal fluctuations in emissions, and the influence of local sources. For example, an overestimation of the SOA concentrations could occur when the influence of a large primary source with no temporal regularity and a high OC/EC ratio (e.g., wood burning) were not taken into account in the determination of the primary OC/EC ratio. In fact, the OC/EC ratio for biomass burning can be greater than 10 (Hays, 2002). Although CO was considered as a primary combustion tracer in the determination of the primary OC/EC ratios, the possibility that a fraction of the estimated wintertime SOA is really primary OC from biomass combustion cannot be entirely ruled out. The contribution of other processes such as nighttime chemistry and fog/cloud processing to SOA formation remains uncertain.

The fall period (most of G2P1 and G1P2 measurements) was characterized by average SOA concentrations ranging between $3.10 \mu\text{gC}/\text{m}^3$ (10/01/05 to 10/14/05) and $1.88 \mu\text{gC}/\text{m}^3$ (11/01/05 to 12/09/05), corresponding to 42 and 35% of measured OC, respectively (Table 3). The daily primary OC and SOA concentration dynamics for G2P1

were more comparable to those observed in the summer (G1P1), with similar afternoon O_3 and SOA maxima, but slightly higher nighttime SOA increases and higher CO and primary OC morning and nighttime peaks (not shown). Likewise, G1P2 concentration dynamics were more comparable to those observed in the winter (G2P2), but with smaller nighttime SOA increases and smaller CO and primary OC morning and nighttime peaks (not shown).

3.4.3. Air Exchange Rate Estimates

The average AER for each group and phase ($0.25 \text{ h}^{-1} \pm 0.04$ (1σ), $0.28 \text{ h}^{-1} \pm 0.06$, $0.33 \text{ h}^{-1} \pm 0.07$ and $0.31 \text{ h}^{-1} \pm 0.10$ for G1P1, G2P1, G1P2 and G2P2, respectively) were quite constant throughout the year and similar for both G1 and G2 retirement communities. The generally low estimated AERs are consistent with the structural characteristics of the sampling sites (G1 was a recreational area and G2 a dining hall, both in the middle of the retirement homes), the low number of open windows and doors, and the presence of central air conditioners. These results are comparable to overnight AER high-resolution (3-min) measurements obtained by Sarnat et al., 2006 in 17 Southern California homes using a constant sulfur hexafluoride (SF_6) source in conjunction with SF_6 monitors. By using the same methodology, the median summertime AER measured in Pennsylvania residences were $\sim 0.30 \text{ h}^{-1}$ for air-conditioned homes and $\sim 2 \text{ h}^{-1}$ for non-air-conditioned homes (Suh, 1994). The R^2 for the regression lines used to calculate the AERs presented here (see eq 3.4) was always higher than 0.9, which adds confidence to our results.

3.4.4. Infiltration Factor Estimates

The average F_{inf} estimates (calculated by both the I/O concentration ratio and the RM approaches) for OC, EC, PM_{2.5} and PN concentrations for each group (G) and phase (P) of CHAPS are reported in Table 3.4. In general, for G1 and G2 the F_{inf} results were similar across P1 (summer and fall) and P2 (fall and winter), which is consistent with no seasonal changes in home dynamics and ventilation conditions as indicated by the rather constant AERs calculated throughout the study and discussed above. The average F_{inf} results were highest for EC (ranges across methods were 0.70-0.82, 0.67-0.74, 0.77-0.80 and 0.64-0.69 for G1P1, G2P1, G1P2 and G2P2, respectively) and OC (ranges were 0.83-0.98, 0.74-0.77, 0.82-0.87 and 0.61-0.67 for G1P1, G2P1, G1P2 and G2P2, respectively). For EC, this is likely due to the fact that EC is non-volatile, is found mostly in the 0.1-0.4 μm range (Miguel et al., 2004; Sardar et al., 2005) and, thus, is capable of infiltrating through the building envelope with great efficiency. The equally high F_{inf} estimated for OC suggests that the particle size range of this important PM_{2.5} component was probably similar to that of EC, and that it was mainly comprised of organic compounds with relatively low vapor pressure. This is also consistent with our observations throughout the study that a substantial fraction of outdoor OC consisted of SOA, whose size distribution is generally concentrated in the lower sizes of the accumulation mode (Zhang et al., 2005) (characterized by a nighttime F_{inf} of ~ 0.7 (Long et al., 2001, Sarnt et al., 2006), and is typically comprised of highly polar organics (Saxena et al., 1996; Kiss et al., 2002; Carlton et al., 2006). It should be noted that lower F_{inf} (OC) values may have been obtained if our indoor sampling sites had been located in environments characterized by a higher surface to volume ratio (S/V) (e.g. a fully furnished apartment as opposed to a

recreational area or a dining room), for the depositional loss rate (k) increases with increasing S/V of the studied indoor location (Thatcher et al., 2002). During CHAPS, for particulate species that are known to be comprised of both semi-volatile and volatile compounds (e.g. OC) this might translate in an overestimation of the corresponding F_{inf} . A somewhat lower average F_{inf} was obtained for $PM_{2.5}$ (ranges across methods were 0.52-0.74, 0.45-0.60, 0.52-0.62 and 0.38-0.45 for G1P1, G2P1, G1P2 and G2P2, respectively) reflecting the possible effects of volatile and semi-volatile species on F_{inf} . For example, particulate compounds such as ammonium nitrate, which accounts for 35–49% of the outdoor $PM_{2.5}$ mass in the Los Angeles basin (Chow et al., 1994; Christoforou et al., 2000; Kim et al., 2000; Tolocka, 2001), volatilize upon building entry and contribute to lower the average F_{inf} of $PM_{2.5}$. The average F_{inf} for ammonium nitrate reported by Sarnat et al., 2006 in a recent study conducted in Southern California homes was 0.18.

Finally, the F_{inf} estimates for PN concentration were 0.59-0.69, 0.46-0.55, 0.77-0.80 and 0.54-0.63 during G1P1, G2P1, G1P2 and G2P2, respectively. We hypothesize that the somewhat lower F_{inf} (PN) calculated at site B (G2) were caused, at least in part, by a higher fraction of sub-100 nm particles in the sampled aerosol due to the close proximity (less than one mile) of this site to a major highway. Lower F_{inf} values for PN at site B (G2) are consistent with the lower penetration of sub-100 nm particles indoors due to diffusional losses (Long et al., 2001, Sarnt et al., 2006) as well as losses due to evaporation of volatile species associated with this size range (Zhu et al., 2005).

With the exception of F_{inf} for PN concentration, the average F_{inf} results for OC, EC and $PM_{2.5}$ estimated during CHAPS are in good agreement with those obtained in several previous studies conducted in other parts of the United States (Polidori et al., 2006; Lunden et al., 2003; Sarnat et al., 2006). Because F_{inf} varies with both aerosol composition (e.g. changes in the outdoor concentration of labile species such as ammonium nitrate) and the AER, diurnal variations of these variables are likely to affect particle infiltration. However, the standard deviation of the daily averaged F_{inf} estimates for OC, EC, PN, and $PM_{2.5}$ (also reported in Table 3.4) were small within each group and phase of the study, probably because of the structural characteristic of the G1 and G2 sampling sites (e.g. presence of central air conditioners and low number of open windows and doors). Most importantly, our findings indicate that $PM_{2.5}$ and its carbonaceous components (e.g. OC and EC, both of which comprise a substantial portion of the $PM_{2.5}$ mass¹¹) are characterized by different F_{inf} values. This implies that the composition of indoor and outdoor particles is different and that ambient $PM_{2.5}$ concentrations may not adequately represent personal exposures to outdoor-infiltrated $PM_{2.5}$ in indoor environments (Polidori et al., 2006; Ebelt et al., 2005; Lunden et al., 2003; Naumova et al., 2002; Naumova et al., 2003).

3.4.5. Indoor and Outdoor Contributions to Measured Indoor Species concentrations

By multiplying the measured outdoor 1-hr OC, EC, $PM_{2.5}$ and PN concentrations (C_{out}) by the corresponding average F_{inf} estimates reported in Table 3.4, we determined the indoor contribution of outdoor origin for each particulate species (C_{og}) and for each group

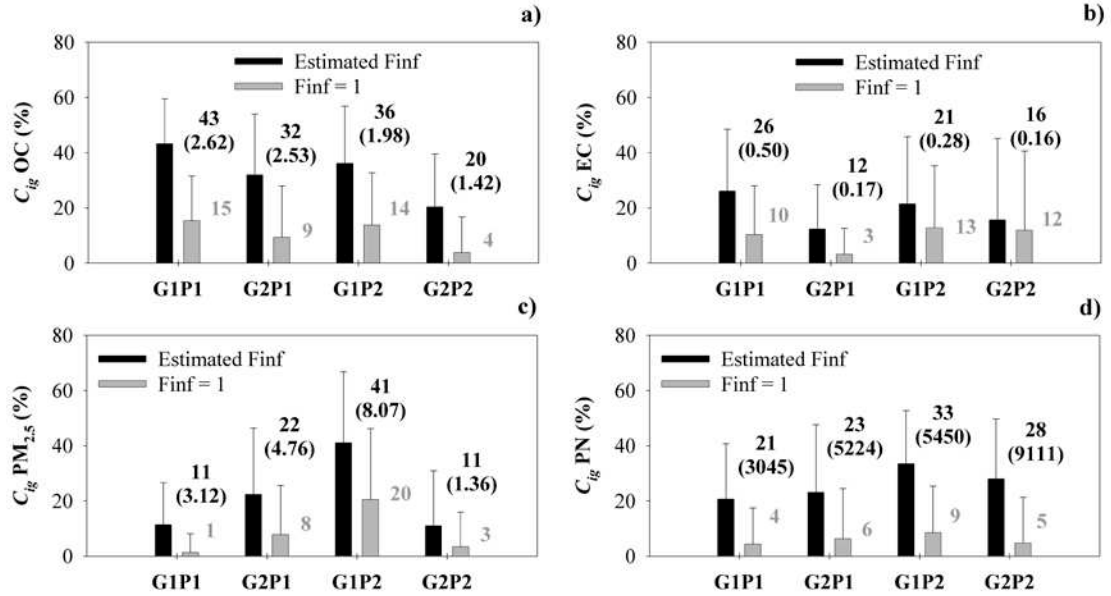


Figure 3.5 Calculated indoor concentrations of indoor origin (C_{ig}) for OC (5a), EC (5b), $PM_{2.5}$ (5c) and PN (5d) expressed as a percentage of the corresponding measured indoor concentrations (C_{in}), and averaged throughout G1P1, G2P1, G1P2 and G2P2 (black columns). The lowest possible C_{ig} estimations for the same species (grey columns) were obtained by assuming $F_{inf}=1$. Error bars represent $+1\sigma$ (1 standard deviation) of all C_{ig} estimates obtained within each group (G) and phase (P).

(G) and phase (P) of CHAPS. The resulting indoor contributions of indoor origin (C_{ig}) were then estimated by subtracting C_{og} from C_{in} on a sample-by-sample basis. Figure 3.5 shows the calculated C_{ig} concentrations for OC (5a), EC (5b), $PM_{2.5}$ (5c) and PN concentrations (5d) expressed as a percentage of the corresponding measured indoor concentrations (C_{in}), and averaged throughout G1P1, G2P1, G1P2 and G2P2. Columns refers to C_{ig} values obtained by using F_{inf} estimates from the indoor/outdoor ratio method considering all hourly I/O data ≤ 1 (black), the I/O method accounting only for nighttime ratios ≤ 1 (grey), and the RM approach (darker grey).

Our results indicate that, on average, 16 to 26% (1.06-1.63), 18 to 20% (1.69-1.80), 20 to 23% (1.17-1.33) and 13 to 17% (1.03-1.23) of measured indoor OC was emitted or formed indoors during G1P1, G2P1, G1P2 and G2P2, respectively (the corresponding ranges of average indoor-generated OC concentrations in $\mu\text{gC}/\text{m}^3$ are reported in parenthesis) (Figure 3.5a). These calculations suggest that although the G2 indoor site was characterized by higher indoor morning OC peaks due to cooking, the overall contribution of indoor sources to measured indoor OC was actually higher at the G1 site. These results are lower than those obtained by Polidori et al., 2006 during the Relationship of Indoor, Outdoor and Personal Air (RIOPA) study, where the average C_{ig} for OC varied between 40 and 70%. The lower C_{ig} OC estimates obtained here are consistent with the prevailing use of central air conditioning at both G1 and G2 indoor sites, and may also be due to differences in home dynamics between the RIOPA and the CHAPS sampling locations (personal residences and common areas for retirees, respectively) and exposure groups. The CHAPS subjects consisted of retirees with compromised health, whose indoor activity levels are likely to be much lower than those of the RIOPA group.

The average percentages of measured indoor EC that was generated indoors were 17 to 25% (0.37-0.48), 11 to 16% (0.16-0.22), 21 to 23% (0.27-0.30) and 20-22% (0.23-0.27) for G1P1, G2P1, G1P2 and G2P2, respectively (ranges of average indoor-generated EC in $\mu\text{gC}/\text{m}^3$ in parenthesis) (Figure 3.5b). These values are quite close to the detection limit for EC for semi-continuous carbon measurements, typically around 0.15-0.35 $\mu\text{gC}/\text{m}^3$ (as determined by Lim et al.²¹), and suggest that indoor sources of EC were not

an important contributor to measured indoor EC during CHAPS. These outcomes are consistent with indoor/outdoor EC ratios close to or slightly lower than unity obtained in several previous studies conducted both in California (Geller et al., 2002; Na et al., 2006) and around the world (Funasaka et al., 2000; Ho et al., 2004).

The mass balance model results also showed that on average 6 to 21% (1.85-5.33), 24 to 38% (5.02-7.47), 42 to 51% (8.26-10.31) and 21 to 30% (2.82-4.03) of measured indoor $PM_{2.5}$ was emitted or formed indoors during G1P1, G2P1, G1P2 and G2P2, respectively (the corresponding ranges of average indoor-generated $PM_{2.5}$ concentrations in $\mu g/m^3$ are reported in parenthesis) (Figure 3.5c). These outcomes are somewhat difficult to interpret and suggest that the seasonal emission/formation of indoor $PM_{2.5}$ from indoor sources was highly variable. It is important to recognize that the $PM_{2.5}$ concentrations measured indoors during G2P2 were unusually low compared to the corresponding outdoor $PM_{2.5}$ concentrations and to the G2P1 $PM_{2.5}$ data. Whether or not this was due to a malfunctioning of the indoor BAMs or to seasonal changes in home dynamics and ventilation conditions between G2P1 and G2P2 remains unclear.

The average percentage of measured indoor PN concentration that was emitted/formed indoors were 14 to 22% (2235-3169), 17 to 26% (4618-5493), 17 to 19% (3258-3527) and 13 to 21% (6841-8010) for G1P1, G2P1, G1P2 and G2P2, respectively (ranges of average indoor-generated PN/ cm^3 reported in parenthesis) (Figure 3.5d). These results suggest that the PN concentration of indoor origin increased from summer to fall (at the G1 site) and from fall to winter (at the G2 site). The seasonal increase in C_{ig} for PN

concentration was probably due to the use of indoor fan heaters during the wintertime. A recent study conducted by He et al., 2004, in 15 Australian houses demonstrated that the use of a fan heater elevates the indoor sub-micrometer PN concentration levels by more than five times over a 48-hr period but does not affect significantly the levels of indoor PM_{2.5} mass. Other indoor activities such as cooking might have increased the indoor levels of PN concentrations by a substantial amount.

By using the same mass balance approach, we also estimated the average amount of outdoor SOA and outdoor primary OC that penetrated inside G1 and G2 indoor sites (C_{og} SOA and C_{og} primary OC, respectively) during each phase of CHAPS. For these calculations we assumed that F_{inf} for SOA was equal to 0.86, the average summertime value for OC during G1P1 (see Table 3.4). As illustrated in Figure 3.6, the average percentage contribution of indoor SOA of outdoor origin to measured indoor OC, C_{og} SOA (%), was rather constant throughout the study within each group, varying from 33% (1.89) to 35% (1.60) for G1P1 and G1P2, respectively, and from 46% (2.60) to 45% (2.34) for G2P1 and G2P2, respectively (the corresponding average concentrations in $\mu\text{gC}/\text{m}^3$ are reported in parenthesis). When varying F_{inf} for SOA of ± 0.1 , the corresponding average C_{og} SOA (%) for all groups and phases fluctuated by 5% or less. Figure 3.6 also shows that, on average, 44%, 36%, 42% and 40% of measured indoor OC was comprised of outdoor-generated primary OC during G1P1, G2P1, G1P2 and G2P2, respectively. These C_{og} primary OC (%) values were determined from the mass balance equation as follows:

$$C_{og} \text{ primary OC (\%)} = 100 - C_{ig} \text{ OC (\%)} - C_{og} \text{ SOA (\%)} \quad (3.12)$$

To the best of our knowledge, these results are among the first to quantify the contributions of outdoor-generated SOA and primary OC to indoor OC and to demonstrate their importance in indoor environments. These outcomes will be used by CHAPS investigators to clarify the links between exposure to PM_{2.5} of indoor and outdoor origin and its effects on cardiovascular outcomes. In the Los Angeles basin

Table 3.4 By regressing (Deming regression) outdoor hourly overnight OC, EC, PM_{2.5} and PN concentrations over the correspondent indoor data we determined the infiltration factor (F_{inf} = slope), the background source strength (intercept) and the coefficient of determinations (R^2) for these four particle species during CHAPS (see text for details).

	Species	F_{inf}	Background source*	R^2
G1P1	OC	0.62	1.17	0.60
	EC	0.68	0.02	0.74
	PN	0.60	-126.83	0.73
	PM _{2.5}	0.64	-0.17	0.61
G2P1	OC	0.59	1.07	0.71
	EC	0.72	0.05	0.88
	PN	0.49	849.46	0.84
	PM _{2.5}	0.62	1.27	0.85
G1P2	OC	0.65	0.06	0.75
	EC	0.79	0.05	0.90
	PN	0.60	1568.40	0.86
	PM _{2.5}	0.63	1.56	0.89
G2P2	OC	0.66	0.05	0.71
	EC	0.80	0.08	0.87
	PN	0.48	1264.40	0.84
	PM _{2.5}	0.60	0.85	0.94

* OC and EC in $\mu\text{gC}/\text{m}^3$; PN in ptcl/cm^3 ; $\text{PM}_{2.5}$ in $\mu\text{g}/\text{m}^3$

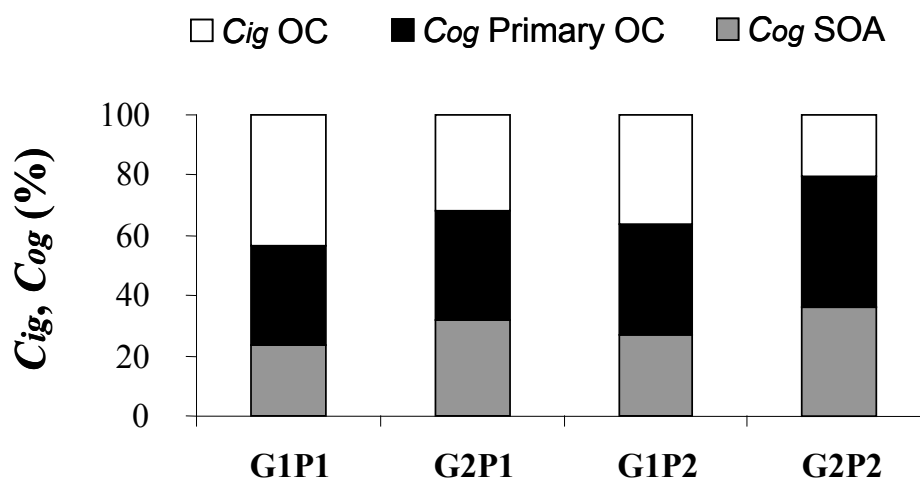


Figure 3.6 Estimated indoor primary OC and indoor SOA concentrations of outdoor origin (“Cog Primary OC” and “Cog SOA”, respectively) expressed as a percentage of the corresponding measured indoor concentrations (C_{in}), and averaged throughout G1P1, G2P1, G1P2 and G2P2. Estimated indoor OC concentrations of indoor origin (Cig OC) are also reported.

outdoor primary OC particles are mainly emitted from motor-vehicle exhausts, are mostly found in the ultra-fine mode, are comprised of well known carcinogenic components/species such as diesel particles and polycyclic aromatic hydrocarbons (PAHs), and are more likely to deposit in the lower airways than coarse particles (Daigle et al., 2003; Kaiser et al., 2005; Nel, 2005). On the other hand, a growing body of evidence is suggesting that exposure to SOA (mostly comprised of highly polar organic compounds) are linked to respiratory inflammation through the generation of reactive oxygen species (ROS) (Nel, 2005; Xiao et al., 2003).

The single compartment mass balance model presented in this work allows for a straightforward estimation of the C_{ig} and C_{og} concentrations for a given F_{inf} value. Although the uncertainties inherent in the approach proposed here must be acknowledged (e.g. F_{inf} was considered to be constant within each group and phase of the study), the estimated C_{ig} and C_{og} values for OC, EC, PM_{2.5}, PN, SOA and primary OC seem reasonable when compared to the relatively limited data in the available literature.

3.5. CONCLUSIONS

This study was conducted in the Los Angeles basin at two retirement communities. Measured indoor and outdoor concentrations of PM_{2.5}, OC, EC, PN, O₃, CO and NO_x were generally comparable, although at G2 a substantial peak in indoor OC, PN and PM_{2.5} (probably from cooking) was typically observed between 06:00 and 09:00 am. The study average percentage contribution of outdoor SOA to outdoor particulate OC (representative for the San Gabriel Valley) was 40%, and varied between 40-45% in the summer (during G1P1) and 32-40% in the winter (during G2P2). Quantifying the SOA contribution to measured OC is important: a) to test evolving predictive SOA models, b) to link the organic PM concentration to its emissions and precursors, and c) to develop effective control strategies for PM. The low AERs (0.25 to 0.33 h⁻¹) calculated for G1 and G2 are consistent with the structural characteristics of the sampling sites, the low number of open windows and doors and the presence of central air conditioners. F_{inf} values were determined for OC, EC, PM_{2.5} and PN by using different methods, including the recursive model (RM) developed by Allen et al., 2003. Here the RM approach, recently validated for estimating F_{inf} for PM_{2.5} from light scattering data, has been

applied to OC, EC and PN data for the first time. F_{inf} estimates were highest for EC (a non-volatile species mostly found in the 0.1-0.4 μm range (Miguel et al., 2004; Sardar et al., 2005) and also for OC (probably because of the substantial percentage mass contribution from SOA throughout CHAPS). Lower F_{inf} values were obtained for $\text{PM}_{2.5}$ and PN, for these compounds are comprised of both volatile and non-volatile inorganic and organic components. Estimated F_{inf} and measured particle concentrations were then used in a single compartment mass balance model to assess the mean contributions of indoor and outdoor sources to measured indoor OC, EC, $\text{PM}_{2.5}$ and PN. We found that 13-17% (G2P2) to 16-26% (G1P1) of measured indoor OC was emitted or formed indoors. Although the G2 indoor site was characterized by higher indoor morning OC peaks due to cooking, the overall contribution of indoor sources to measured indoor OC was higher at the G1 site. These results are consistent with low indoor activity levels at both retirement communities and with the prevailing use of central air conditioning. Our modeling results also showed that the measured indoor $\text{PM}_{2.5}$ emitted or formed indoors was highly variable (from 6-21% at G1P1 to 42-51% at G1P2). The average percentage contribution of indoor SOA of outdoor origin to measured indoor OC varied from about 35% (at site 1) to about 45% (at site 2). Also, outdoor-generated primary OC comprised, on average, 36 to 44% of measured indoor OC during G2P1 and G1P1, respectively. These results are among the first to quantify the contributions of outdoor-generated SOA and primary OC to indoor OC and to demonstrate their importance in indoor environments. The outcomes presented here will be used by CHAPS investigators to determine the relationship between cardiovascular outcomes and hourly retirement community exposures by each resident to $\text{PM}_{2.5}$ of indoor and outdoor origin.

3.6. CHAPTER 3 REFERENCES

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Chapter 4.

Associations between Personal, Indoor, and Residential Outdoor Pollutant Concentrations for Exposure assessment to Size Fractionated PM

4.1. ABSTRACT

The physical and chemical characteristics of indoor, outdoor, and personal quasi-ultrafine ($<0.25\mu\text{m}$), accumulation ($0.25\text{-}2.5\ \mu\text{m}$), and coarse ($2.5\text{-}10\ \mu\text{m}$) mode particles were studied at four different retirement communities in southern California between 2005 and 2007. Linear mixed effects models and Spearman's correlation coefficients were then used to elucidate the relationships among size segregated PM levels, their particle components, and gaseous co-pollutants. Seasonal and spatial differences in the concentrations of all measured species were evaluated at all sites based on p-values for product terms. Outdoor quasi-UF and, to a lesser extent, accumulation mode particles were the two fractions that best correlated with outdoor concentrations of CO, NO₂, NO_x (during both phases of the study) and O₃ (only during the warmer months). Outdoor and indoor concentrations of CO, NO₂ and NO_x were more positively correlated to personal quasi-UF particles than larger size fractions. In spite of these findings, it seems unlikely that these gaseous co-pollutants could confound epidemiologic associations between quasi-UF particles and adverse health effects. Overall, measured gaseous co-pollutants were weak surrogates of personal exposure to accumulation mode PM, at least for subjects with similar exposure profiles and living in similar urban locations. Indoor sources were not significant contributors to personal exposure of accumulation and quasi UF PM, which is predominantly influenced by primary emitted pollutants of outdoor

origin. Correlations between personal coarse mode PM and both outdoor and indoor gaseous co-pollutant concentrations were weak at all sites and during all seasons.

4.2. INTRODUCTION

Several epidemiological and toxicological studies have found positive associations between levels of atmospheric fine particulate matter ($PM_{2.5}$; D_p = aerodynamic diameter $\leq 2.5 \mu m$) and acute or chronic adverse health effects (Pope and Dockery 2006). The PM components that are believed to be responsible for the adverse health outcomes include transition metals, organic species (often reported using surrogate measurements such as organic and elemental carbon, or OC and EC, respectively), sulfate and nitrate salts, and bioaerosols (McClellan 2002; Chakrabarti et al. 2004). In addition, PM properties such as mass, number, surface area and, especially, size are important in evaluating particle toxicity. Besides having the highest potential to penetrate deeply into the human lungs, ultra-fine (UF) particles ($D_p \leq 0.10 \mu m$) collected in urban environments include particularly toxic species such as polycyclic aromatic hydrocarbons (PAHs). In a recent study conducted by Ntziachristos et al. (Ntziachristos et al. 2007), size-fractionated ambient PM samples (i.e. quasi-UF, $D_p \leq 0.25 \mu m$, accumulation, $D_p \leq 2.5 \mu m$, and coarse, $2.5 \mu m \leq D_p \leq 10 \mu m$, mode particles) were collected at four different locations in the Los Angeles basin, and analyzed for their chemical composition and redox potential (an indicator of particle toxicity). The quasi-UF fraction had the highest redox activity on a per-PM mass basis, which was correlated with the higher mass fractions of

particulate OC and PAHs (some of which are well-known carcinogens(Kaiser 2005; Nel 2005) for this size range.

Although the link between PM exposure and adverse health effects has become widely accepted, ascertaining the true risk associated with exposure to PM is difficult, mainly because the concentrations of ambient particles and those of their gaseous co-pollutants (e.g. carbon monoxide, CO, nitrogen oxides, $\text{NO}_x = \text{NO} + \text{NO}_2$, ozone, O_3 , and sulfur dioxide, SO_2) are often well correlated, and estimates of the health risks associated with PM exposure may be confounded by these gaseous species (Sarnat et al. 2000; Green et al. 2002; Sarnat et al. 2005). The National Research Council(Press 1998) listed the investigation of the potential confounding effect of gaseous co-pollutants on PM health effects as one of their research priorities.

Sarnat et al. explored these confounding effects both in Baltimore, MD(Sarnat et al. 2000), and in Boston, MA(Sarnat et al. 2005), using integrated (24-hr) ambient and personal exposure data (i.e. $\text{PM}_{2.5}$, O_3 , NO_2 , and SO_2 concentrations) collected in the summertime and in the wintertime. In both cities, ambient gaseous levels were more strongly correlated with personal exposure to $\text{PM}_{2.5}$ and SO_4^{2-} , than with their respective personal gas exposures. Only the results obtained in Boston showed an occasional association between ambient $\text{PM}_{2.5}$ and personal O_3 and NO_2 . Although the strength of these cross-pollutant associations was not as substantial as between ambient and personal $\text{PM}_{2.5}$, these findings suggest that at times, ambient pollutant gases can also serve as

surrogates for personal exposures to PM_{2.5}. In addition, these studies showed that between-subject differences might exist in the strength of the personal-ambient association for gases, probably due to differences in house characteristics and ventilation conditions (Rojas-Bracho et al. 2000; Sarnat et al. 2000; Polidori et al. 2007). While in Boston personal-ambient gaseous correlations were moderately strong, in Baltimore ambient gas concentrations were not associated with their respective personal exposures. This implies that changes over time for some gaseous pollutants (O₃, for example) measured at central sites reflect corresponding changes in personal exposures only at some locations.

In this study, we expanded the work by (Sarnat et al. 2005) by including size segregated PM data in our analysis. Associations between indoor, outdoor, and personal size-fractionated PM and OC, EC, particle number (PN), O₃, CO, NO, NO_x, and other important pollutants of both indoor and outdoor origin were evaluated, and the role of gaseous co-pollutants as surrogates of personal size-fractionated PM exposures assessed. Data were collected at four retirement communities of the Los Angeles Basin during the Cardiovascular Health and Air Pollution Study (CHAPS), a multi-disciplinary project whose goals are to investigate the effects of micro-environmental exposures to PM on cardiovascular outcomes in elderly retirees affected by coronary artery disease (Delfino et al. 2008).

4.3. METHODS

4.3.1. Study Design

The physical and chemical characteristics of indoor, outdoor, and personal quasi-UF, accumulation, and coarse PM were studied at four different retirement communities in southern California between 2005 and 2007. Three of these communities were in the San Gabriel Valley, CA (here referred to as sites San Gabriel 1, San Gabriel 2 and San Gabriel 3) and the fourth in Riverside, CA. Site San Gabriel 1 was located about 50 Km east of downtown Los Angeles, in a residential area, approximately 3 Km away from any major freeways and close to a construction site. Site San Gabriel 2 was situated about 8 Km east of Los Angeles, approximately 300 m south of a major freeway (see Polidori et al. (Polidori et al. 2007), for details). Site San Gabriel 3 was about 55 Km east of downtown Los Angeles, 2.5 Km away from 2 busy freeways and in close proximity (150 m) of a major street. The Riverside site was about 110 Km east of Los Angeles and 15 Km southeast of downtown Riverside. The closest freeway and a major street were approximately 3 and 1 Km away, respectively, and downwind of the site. The abundant vegetation surrounding this last community may be a potential source of precursors of biogenically generated PM (e.g. organic particles from the photo-oxidation of terpenes).

Two 6-week sampling campaigns were conducted at each location. Phase 1 (P1) of each campaign was conducted during a warmer season (including summer and early fall), whereas phase 2 (P2) was conducted during a cooler season (including late fall and

winter). Site San Gabriel 1 was operated from 07/06/2005 to 08/20/2005 (P1) and from 10/19/2005 to 12/10/2005 (P2); sampling at site San Gabriel 2 was conducted from 08/24/2005 to 10/15/2005 (P1) and from 01/04/2006 to 02/18/2006 (P2); site San Gabriel 3 was operated from 07/05/2006 to 8/17/2006 (P1) and from 10/18/2006 to 12/01/2006 (P2); sampling at site Riverside was conducted from 8/23/2006 to 10/13/2006 (P1) and from 01/04/2007 to 02/16/2007 (P2). Thus, we were able to study the seasonal variations in indoor, outdoor, and personal relationships between size-segregated PM and its components.

Two identical sampling stations were installed at each site, one indoors and one outdoors. The indoor sampling station at site San Gabriel 1 was located in a recreational area of the first community's main building, adjacently to a construction site where work was ongoing. The indoor sampling area at site San Gabriel 2 was situated in the dining room of the community's central building. The indoor station at site San Gabriel 3 was set up in a recreational area of the main retirement community complex, adjacent to a gym and to an activity room. The indoor area at the Riverside site was located in the hallway of the main building with a dining room, activity room and numerous apartment units nearby. At all sites the outdoor station, set-up inside a movable trailer, was positioned within 300 m from the indoor station.

Personal PM concentrations were measured for 67 elderly retirees (18, 14, 17, and 18 subjects at sites San Gabriel 1, 2, 3, and Riverside, respectively) with a history of

coronary artery disease. All subjects, except one, also participated in at least some part the epidemiologic part of this study including ambulatory ECG and blood pressure monitoring. All participants were 71 years of age or older, nonsmokers, and with no home exposure to environmental tobacco smoke (ETS). Each subject was followed for two 5-day sampling periods during the 2 phases of the study. Throughout this time, size fractionated PM levels were measured daily. A more detailed description of the study design can be found in Delfino et al. (Delfino et al. 2008)

4.3.2. Instrumentation

Continuous (1-min) PN concentrations were measured using water-based condensation particle counters (CPC Model 3785, TSI Inc, Shoreview, MN) at both indoor and outdoor sampling stations. Indoor and outdoor particulate OC and EC were measured in hourly cycles (i.e. sampling time = 45-min; analysis time = 15-min) by mean of 2 semi-continuous OC_EC analyzers (Model 3F, Sunset Laboratory Inc., Tigard, OR). Hourly PM_{2.5} mass concentrations were measured by Beta-Attenuation Mass Monitors (BAM, Model 1020, Met One instruments Inc., OR). Continuous (1-min) NO and NO₂ measurements were obtained both indoors and outdoors by using Thermo Environmental NOx Analyzers (Model 42, Thermo Environmental instruments Inc, Franklin, MA). Dasibi Carbon Monoxide Analyzers (Model 3008, Dasibi Environmental Corp, Glendale, CA) were implemented to measure continuous (1-min) indoor and outdoor CO levels. Continuous (1-min) outdoor ozone (O₃) concentrations were also monitored at each sampling site by using API Ozone Analyzers (Model 400A, Teledyne Technologies Inc,

Los Angeles, CA). For more details about the continuous/semi-continuous instruments employed during the sampling campaign see Polidori et al. (Polidori et al. 2007)

In addition, integrated (24-h) size segregated indoor and outdoor particle samples were collected at all sites by means of SioutasTM Personal Cascade Impactors (SKC Inc, Eighty Four, PA) (Misra et al. 2002; Singh et al. 2003) from Monday to Friday. Coarse, accumulation, and quasi-UF ($PM < 0.25 \mu m$) mode PM were sampled on Zefluor filters (3 μm pore-size, Pall Life Sciences, Ann Arbor MI) and analyzed gravimetrically using a microbalance (Mettler-Toledo, Columbus, OH; weight uncertainty $\pm 2 \mu g$). Personal environmental monitors (PEM) were deployed concurrently with the indoor and outdoor PM samplers to obtain integrated (24-h) personal PM exposure data. Each PEM consists of an inlet, a SioutasTM impactor and a Leland Legacy pump (SKC Inc, Eighty Four, PA) operating at 9 lpm, all enclosed in a personal carry-on bag, then assigned to each subject.

4.3.3. Data Analysis

In order to match all continuous (or semi-continuous) measurements to the corresponding filter based data, only daily averages of the concurrently measured $PM_{2.5}$, OC, EC, PN, NO_x , CO and O_3 concentrations were considered. The contributions to outdoor OC by primary OC (OC_{pri}; emitted directly from combustion sources such as vehicular exhaust and wood smoke) and secondary organic aerosol (SOA; formed from semi- and low-volatility products of chemical reactions involving reactive organic gases) were estimated from measured OC and EC concentrations using EC as a tracer of primary combustion-generated OC (i.e. “EC tracer method”; see Polidori et al. (Polidori et al. 2007)). Because

one of the aims of this study is to evaluate the effects of outdoor air pollutants on indoor and personal exposure, we estimated air exchange rates (AER; from CO measurements during periods affected by a dominant indoor source; Abt et al.¹⁶) and infiltration factors (F_{inf} ; defined as the equilibrium fraction of the outdoor species of interest that penetrate indoors and remain suspended) at each site.

Assuming an exponential decay of particles, that AER (hr^{-1}) and outdoor concentrations are constant during the decay period, that CO is conservative, and that indoor concentrations are well mixed, then:

$$C_t = e^{-(\text{AER})t} C_0 \quad (4.1)$$

where, C_t is the indoor CO concentration after time t (after the decay period), C_0 is the initial peak CO concentration (right after CO emission). The infiltration factor (F_{inf} , defined as the equilibrium fraction of ambient particles that penetrate indoors and remain suspended¹⁷) is described by the following eq:

$$F_{inf} = P(\text{AER})/(\text{AER}+k) \quad (4.2)$$

where, P is the penetration coefficient (dimensionless). F_{inf} for OC, EC, $\text{PM}_{2.5}$ and PN were calculated using the recursive model (RM) developed by Allen et al.¹⁸. In this method, for a particular species of interest, the average indoor concentration during hour is equal to the sum of a fraction of the average outdoor concentration during the same hour, a fraction of the average indoor concentration remaining from the previous hour, and the contribution from indoor sources. More details on the F_{inf} and AERs estimation methods are described in Polidori et al. (Polidori et al. 2007). The average AERs calculated during CHAPS at the 4 retirement communities ranged from 0.21 to 0.4 hr^{-1}

(Table 4.1). The generally low estimated AERs are consistent with the structural characteristics of the sampling sites, the low number of open windows and doors, and the presence of central air conditioners. The average F_{inf} results were highest for EC (0.64-0.82) and OC (0.60-0.98) compared to those of $PM_{2.5}$ (0.38-0.57) and PN (0.41-0.78). In general, the F_{inf} results were similar across P1 (summer and fall) and P2 (fall and winter), which is consistent with no seasonal changes in home dynamics and ventilation conditions as indicated by the rather constant AERs calculated throughout the study. Estimated F_{inf} and measured particle concentrations across all hours were then used in a single compartment mass balance model to assess the contributions of indoor and outdoor sources to measured indoor EC, OC_{pri}, SOA, and PN (Wallace 1996; Meng et al. 2005; Polidori et al. 2007). The average amounts of indoor- and outdoor-generated PM and PM species (here denoted with “ig” and “og” subscripts, respectively) inside the studied homes were determined by this approach.

The following four associations (models) were then used to study the relationships between pollutant concentrations and size segregated PM levels:

- Associations between outdoor co-pollutant concentrations and outdoor size fractionated PM levels (“outdoor-outdoor associations”).
- Associations between indoor co-pollutant concentrations and indoor size fractionated PM levels (“indoor-indoor associations”).

- Associations between outdoor particle and gaseous species concentrations and personal exposure to size fractionated PM (“outdoor-personal associations”).
- Associations between indoor particle and gaseous species concentrations and personal exposures to size fractionated PM (“indoor-personal associations”).

Linear mixed-effects regression parameters (slopes, or *S*) and Spearman’s correlation coefficients (*R*) were calculated for the above mentioned correlations.

Table 4.1 Estimated air exchange rate (AER) and infiltration factors F_{inf} over the studied sites and phases of the study

		AER, h ⁻¹			F_{inf}			
		(mean ± <i>SD</i>)			OC	EC	PN	PM _{2.5}
Phase 1 (summer and fall)	San Gabriel 1	0.25	±	0.04	0.98	0.82	0.66	0.52
	San Gabriel 2	0.28	±	0.06	0.74	0.74	0.46	0.45
	San Gabriel 3	0.40	±	0.12	0.67	0.68	0.41	0.42
	Riverside	0.21	±	0.06	0.60	0.72	0.57	0.49
Phase 2 (fall and winter)	San Gabriel 1	0.33	±	0.07	0.87	0.79	0.78	0.52
	San Gabriel 2	0.31	±	0.10	0.61	0.64	0.55	0.38
	San Gabriel 3	0.26	±	0.08	0.81	0.75	0.43	0.57
	Riverside	0.31	±	0.09	0.90	0.82	0.45	0.41

4.3.4. Mixed Models

Data were analyzed with linear mixed-effect models, which expand the capabilities of linear regression by accounting for the correlation present in repeated measures data. In matrix notation, the mixed-effects model can be expressed as:

$$Y = X\beta + Zu + \varepsilon \quad (4.3)$$

where Y is a vector of outcomes, X is a known matrix of covariates, β is a vector of fixed effect parameters, and ε is a vector of normally distributed errors. These terms parallel the standard linear regression model. To account for correlation within subjects, the linear mixed-effects model includes an additional covariate matrix Z and a vector of subject-specific random effects, u , (Laird and Ware 1982). In our models, random intercepts were estimated for each subject, and an autoregressive covariance structure was selected based on best fit from Akaike's information criteria. Residual and influence diagnostics were used to identify potentially outlying and influential observations. To allow for a fair comparison of the regression slopes, all regression parameter estimates were standardized by the interquartile range (IQR) of the considered independent variable. Thus, the mixed model coefficients for the dependent variable correspond to an IQR change in the independent variable.

In addition to linear mixed-effects models, Spearman's correlation coefficients (R) were reported as an additional indicator of the association strength among indoor, outdoor, and

personal data for the studied associations. Subjects having fewer than 5 valid days of observations in any of the size fractions (out of 10 per size fraction) were excluded from the analysis. Prior to regression and correlation analyses, outliers were detected at three standard deviations beyond the mean and individually inspected for influence in regression models.

All data collected at sites San Gabriel 1 to 3 were combined and considered to be representative of the entire San Gabriel Valley, and compared to the measurements generated at the Riverside site. This division was based on the observation that diurnal and seasonal patterns of indoor and outdoor PM pollutants in Riverside (in particular OC, OCpri, and SOA) were distinctly different from those recorded at the other 3 sites. The San Gabriel Valley sites are closer to downtown Los Angeles, are impacted to a higher degree by fresh traffic emissions and, thus, exemplify the characteristics of typical “source” sites. Conversely, site Riverside is designated as a “receptor” location, where the aerosol is mostly comprised of advected, aged and photochemically processed particles from the central Los Angeles area, as well as of some local emissions²².

Finally, seasonal differences in phase-average concentrations of all measured species were estimated at all sites, and assessed using p-values for product terms between phase and the predictor. These “Phase Interaction” terms allowed us to study possible temporal variations in the associations between the variables considered during phase 1 (summer and early fall) and phase 2 (late fall and winter). Similarly, regional interactions between

the San Gabriel Valley and the Riverside sites were calculated to highlight possible spatial differences in the considered associations.

4.4. RESULTS

4.4.1. Data Overview

Mean personal and mean indoor PM mass concentrations were similar at all sites, during all phases and for all size fractions (Table 4.2), probably because most subjects spent the majority of their time indoors. Mean outdoor PM levels were higher than the corresponding personal and indoor concentrations across all size modes (especially for accumulation and coarse mode particles), sites and phases of the study (Table 4.2). This suggests that the overall loss of outdoor particles during penetration through the building envelope was higher than the particle generation from indoor sources. Fine PM levels (Table 4.1) were calculated in two different ways, by combining the filter based quasi-UF and accumulation mode PM gravimetric masses, and from continuous BAM measurements. The resulting Fine PM concentrations were always within $1.7 \mu\text{g}/\text{m}^3$ across all sites and during all phases of the study. The estimated average indoor concentrations of outdoor origin of fine PM, OC, EC and PN (Fineog, OCog, ECog and CPCog, respectively) were higher than the correspondent mean indoor generated levels (Fineig, OCig, ECig and CPCig, respectively), which confirms that outdoor sources were the most important contributors to the measured indoor pollutant concentrations.

Table 4.2 Descriptive statistics for residential outdoor, indoor and personal concentrations

			San Gabriel Valley						Riverside					
			Phase 1			Phase 2			Phase 1			Phase 2		
			Mean ± SD	IQR ¹		Mean ± SD	IQR ¹		Mean ± SD	IQR ¹		Mean ± SD	IQR ¹	
Gases Concentration	CO (ppm)	Outdoor	0.59 ± 0.23	0.37		0.69 ± 0.31	0.36		0.31 ± 0.13	0.25		0.12 ± 0.11	0.17	
		Indoor	0.64 ± 0.23	0.29		0.78 ± 0.35	0.37		0.46 ± 0.11	0.16		0.60 ± 0.11	0.17	
	NO ₂ (ppb)	Outdoor	32.55 ± 9.47	12.20		33.33 ± 9.05	10.72		15.25 ± 5.83	7.14		15.37 ± 7.14	9.42	
		Indoor	25.70 ± 9.99	16.21		31.02 ± 9.51	15.09		11.41 ± 2.48	3.89		13.03 ± 2.93	4.09	
	NO _x (ppb)	Outdoor	48.36 ± 21.07	21.77		68.63 ± 35.59	39.06		18.52 ± 7.29	10.08		18.77 ± 9.58	12.47	
		Indoor	41.02 ± 21.39	25.45		69.32 ± 37.71	40.77		15.58 ± 3.97	5.84		19.66 ± 5.65	6.81	
	O ₃ (ppb)	Outdoor	31.52 ± 10.98	15.65		18.31 ± 7.13	7.77		38.05 ± 10.40	13.82		28.69 ± 6.26	8.62	
Particulate Mass (µg/m ³)	Quasi-UF PM	Personal	8.52 ± 4.21	4.09		8.77 ± 7.83	4.30		6.97 ± 3.10	5.04		4.58 ± 2.75	2.60	
		Outdoor	9.87 ± 3.02	4.13		9.95 ± 4.40	5.46		11.42 ± 4.92	7.06		7.29 ± 3.54	6.49	
		Indoor	8.93 ± 2.86	3.77		8.89 ± 3.66	4.62		8.99 ± 3.26	4.24		6.05 ± 2.95	2.47	
	Accum. mode PM	Personal	6.03 ± 3.69	4.43		5.01 ± 4.87	3.75		4.86 ± 3.16	3.64		1.98 ± 1.64	1.30	
		Outdoor	13.30 ± 6.05	8.01		10.94 ± 9.23	10.39		9.75 ± 6.34	8.65		5.07 ± 3.81	4.61	
		Indoor	7.31 ± 3.41	4.42		6.28 ± 4.72	5.14		4.55 ± 2.36	1.49		2.21 ± 1.68	1.17	
	Coarse PM	Personal	3.33 ± 2.40	2.68		3.42 ± 4.80	2.11		3.14 ± 1.90	2.34		1.61 ± 1.01	0.89	
		Outdoor	11.48 ± 3.61	4.35		8.58 ± 5.21	5.89		12.52 ± 6.95	7.95		4.62 ± 2.55	3.15	
	*	Indoor	2.62 ± 2.91	3.16		4.14 ± 5.49	3.93		2.88 ± 2.64	1.94		2.85 ± 1.40	1.54	
	Fine PM	Personal	14.54 ± 6.60	7.87		13.77 ± 10.93	8.20		11.77 ± 5.50	8.13		6.50 ± 3.66	3.53	
		Outdoor	24.48 ± 8.30	10.56		20.10 ± 13.75	18.35		22.06 ± 7.94	12.52		11.57 ± 7.65	11.85	
		Indoor	15.09 ± 5.95	9.88		12.78 ± 7.21	8.94		9.30 ± 2.83	3.94		5.31 ± 2.31	3.30	
	Fine _{og} ²	Indoor	12.73 ± 6.02	10.43		9.95 ± 7.54	8.86		7.50 ± 2.52	4.56		3.79 ± 2.17	3.20	
	Fine _{ig} ³	Indoor	3.42 ± 2.10	1.81		4.85 ± 3.39	5.24		3.39 ± 1.21	1.31		2.53 ± 1.46	1.12	
Particles Number (ptel #/cm ³)	PN	Outdoor	12100 ± 4717	5646		17357 ± 6424	10334		6947 ± 1077	1133		9574 ± 2038	3243	
		Indoor	8910 ± 7120	8383		13866 ± 7930	11196		4676 ± 907	997		4373 ± 969	1343	
	PNig ³	Indoor	3021 ± 4112	2386		4311 ± 5912	4336		1239 ± 847	662		970 ± 849	1086	
	PNog ²	Indoor	6459 ± 3621	5757		9695 ± 4147	7782		3504 ± 487	569		3412 ± 627	533	
Organic Carbon (µg/m ³)	OC	Outdoor	6.24 ± 1.90	2.60		7.70 ± 3.55	6.94		10.50 ± 1.14	1.31		15.39 ± 1.74	2.90	
		Indoor	5.62 ± 1.42	1.70		6.78 ± 3.12	5.72		8.46 ± 1.68	2.47		14.27 ± 1.95	3.11	
	OCig ³	Indoor	1.16 ± 0.70	1.15		1.21 ± 1.10	1.32		2.32 ± 1.65	2.55		1.41 ± 0.52	0.69	
	OCog ²	Indoor	4.49 ± 1.28	1.49		5.69 ± 2.99	5.76		6.14 ± 0.65	0.85		13.64 ± 1.44	2.37	
	OCpri ⁴	Outdoor	2.85 ± 0.82	1.11		5.13 ± 3.27	6.17		8.23 ± 1.09	1.65		11.25 ± 0.78	0.97	
	OCpri _{og} ^{2,4}	Indoor	2.19 ± 0.80	1.04		4.07 ± 2.28	4.11		4.42 ± 0.68	1.07		10.07 ± 0.61	0.87	
	SOA ⁵	Outdoor	2.81 ± 1.45	1.93		2.76 ± 1.43	2.13		2.28 ± 0.90	1.19		4.14 ± 1.55	1.98	
	SOAog ^{2,5}	Indoor	2.38 ± 1.23	1.53		2.37 ± 1.22	1.83		1.82 ± 0.72	1.05		3.56 ± 1.33	1.70	
Elemental Carbon (µg/m ³)	EC	Outdoor	1.66 ± 0.44	0.55		1.71 ± 0.74	1.09		1.22 ± 0.48	0.56		0.82 ± 0.31	0.39	
		Indoor	1.39 ± 0.44	0.65		1.32 ± 0.54	0.83		1.37 ± 0.23	0.21		1.01 ± 0.25	0.41	
	ECig ³	Indoor	0.31 ± 0.23	0.25		0.25 ± 0.20	0.15		0.48 ± 0.26	0.35		0.34 ± 0.10	0.14	
	ECog ²	Indoor	1.08 ± 0.30	0.42		1.10 ± 0.49	0.73		0.89 ± 0.29	0.37		0.65 ± 0.24	0.31	

1 IQR = Interquartile range

2 og = Outdoor generated penerated indoor

3 ig = Indoor generated

4 OCpri = Primary fraction of particulate organic carbon

5 SOA = Secondary organic aerosol

* Calculated as the sum of quasi-UF and accumulation mode PM integrated measurements (personal Fine PM), and from continuous BAM data (indoor and outdoor Fine PM).

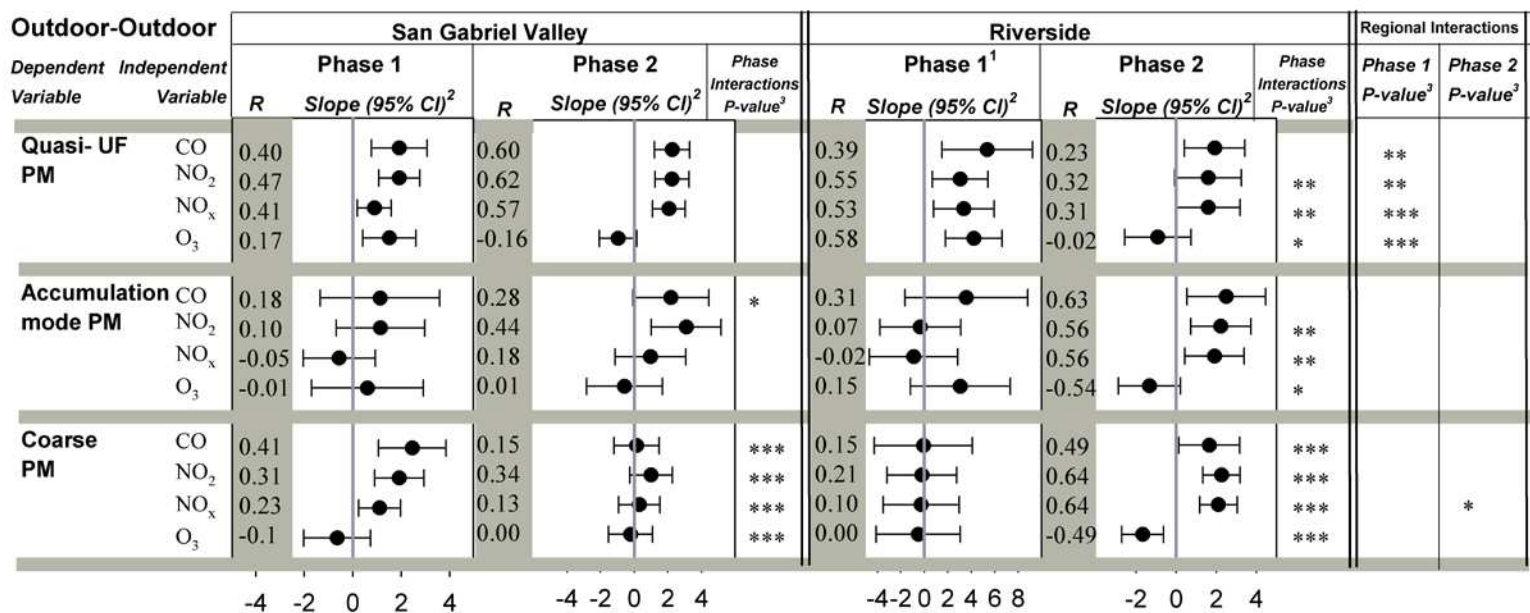
The San Gabriel Valley sites were closer to freeways than the Riverside site (located in a desert region) and were impacted by higher levels of CO, NO₂ and NO_x, mainly emitted from primary combustion sources (e.g. motor-vehicle emissions). Conversely, OC and O₃ levels were generally higher in Riverside. The latter site was approximately 110 Km east (and downwind) of downtown Los Angeles, with prevailing westerly winds blowing from the Pacific Ocean. The plume of pollutants generated in the Los Angeles area includes several reactive organic species that are likely to form OC through secondary processes (i.e. SOA formation) as the air mass ages and is transported eastwards. The higher average OC, O₃ and SOA levels and the smaller diurnal OC variation in Riverside (compared to the characteristic afternoon increase in OC, O₃ and SOA in the San Gabriel Valley) confirm that the latter is a typical receptor area, where the contribution of SOA to total measured OC is substantial. In addition, the vegetation surrounding the Riverside community is a potential source of biogenic gas-phase precursors, which form secondary organic aerosols through photochemical reactions (e.g., photochemical oxidation of terpenes (Kanakidou et al. 2005)).

4.4.2. Outdoor - Outdoor Associations

Outdoor quasi-UF PM was positively (and moderately) correlated with CO, NO₂ and NO_x at all locations and during all seasons, mainly because all of these species are emitted by the same combustion sources, and also because their atmospheric transport and removal is affected by similar meteorological processes (Chen et al. 1999; Wallace 2000) (Figure 4.1). Outdoor quasi-UF PM was positively correlated with O₃ only

during phase 1 (warmer season), both in the San Gabriel Valley ($R = 0.17$; Regression slope = $1.5 \mu\text{g}/\text{m}^3$ [95% confidence interval = 0.4 to 2.6]) and, especially, in Riverside ($R = 0.58$; Slope = $4.2 \mu\text{g}/\text{m}^3$ [1.8 to 6.6]). For an interquartile increase in the average O_3 concentration measured in Riverside during phase 1, the correspondent quasi-UF PM increased by $4.2 \mu\text{g}/\text{m}^3$, reflecting the important contribution of photochemical processes to the production of SOA. The same associations were negative and non-significant during phase 2 (cooler months) ($R=-0.16$; $S = -1.0 \mu\text{g}/\text{m}^3$ [-2.1 to 0.2] in the San Gabriel Valley; $R=-0.02$; $S = -1.0 \mu\text{g}/\text{m}^3$ [-2.6 to 0.7] in Riverside). Based on p -values for product terms, the prediction of quasi-UF particles by gaseous co-pollutants was significantly different between phase 1 and phase 2 in Riverside, and between phase 1 in Riverside and phase 1 in the San Gabriel Valley (see the “Regional Interaction” column in Figure 4.1 for details, and note the scale difference for slopes in phase 1 for Riverside).

Accumulation mode particles had generally smaller correlations and mixed model slopes with CO , NO_2 and NO_x compared to quasi-UF PM, probably because their outdoor levels are influenced by a combination of primary and secondary sources. However, these associations were stronger in phase 2, when the production of accumulation mode particles and their corresponding co-pollutants from primary combustion sources is typically the highest and the contribution of secondary formation mechanisms to the measured PM mass are decreased.



- 1 Sclae is different for phase 1 at Riverside
- 2 Mixed model coefficients for the dependent variable correspond to an interquartile range change in the independent variable
- 3 * = p-value < 0.1 (sufficient evidence for a difference)
 ** = p-value < 0.05
 *** = p-value < 0.01 (significantly different)

Figure 4.1 Mixed model and Spearman correlation results for outdoor-outdoor associations

With the exception of phase 2 in the San Gabriel Valley and phase 1 in Riverside, positive and moderately strong correlations between coarse particles and CO, NO₂ and NO_x were observed at all sites. Although not consistent, this association is not surprising, since coarse PM is emitted from re-suspended soil and road dust, and the latter mechanism shares the same anthropogenic sources responsible for the production of these gaseous co-pollutants. The product term models for phase showed a significant phase interaction at all sites ($p < 0.01 = ***$ in Figure 4.1), indicative of the seasonal effect of primary sources on the associations between outdoor coarse PM and the corresponding gaseous co-pollutants. Interestingly, slopes for the prediction of coarse particles by these gases were greater in phase 2 than phase 1 in Riverside. The opposite situation was observed in the San Gabriel Valley.

Strong and positive associations between outdoor EC and outdoor CO, NO₂ and NO_x were found both in the San Gabriel Valley and in the Riverside (average $R = 0.45$ to 0.91 and average $S = 0.4$ to $0.8 \mu\text{g}/\text{m}^3$). Similarly, PN and OC concentrations were well correlated with primary gaseous co-pollutants levels measured at all sites and during all phases. EC consists of graphite-like material emitted from the incomplete combustion of organic fuels (Chow et al. 1993; Birch and Cary 1996). Combustion sources are also the major contributor to the ambient PN and OC concentrations, although a substantial amount of OC is also formed from secondary processes. A significant phase interaction for PN was observed at the San Gabriel Valley sites, but not in Riverside. PN concentrations were both higher and more strongly associated with CO, NO₂ and NO_x

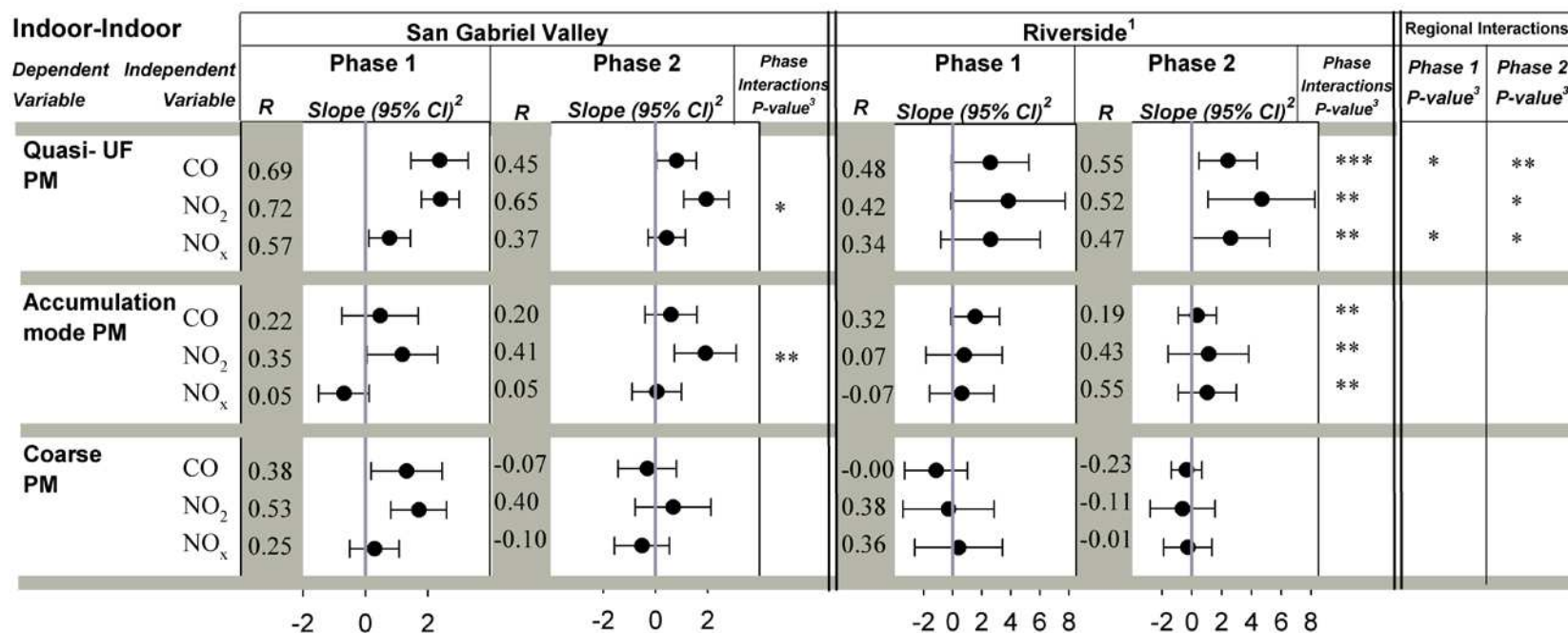
during the period of air stagnation (phase 2). This finding highlights the seasonal effect of primary sources on the associations between PN and primary gaseous co-pollutants.

4.4.3. Indoor - Indoor Associations

Indoor quasi-UF particles were strongly and positively associated with indoor gaseous co-pollutants at all sites and during all phases (R values ranged from 0.34 to 0.72 for this size fraction) (Figure 4.2). The strength and regression slopes of these correlations are similar to the corresponding outdoor-outdoor associations (Figure 4.1).

Accumulation mode particles were more weakly associated with gaseous co-pollutants than quasi-UF PM, probably because this size fraction contains a higher percentage by mass of SOA that might condense on existing indoor particles, or volatilize in the indoor environment (depending on the vapor pressure of the considered organic species and/or the home characteristics). It is well known that changes in the physical and chemical properties of fine PM occur as they penetrate indoors from outdoors. For example, ammonium nitrate (NH_4NO_3), which accounts for 35–50% of the outdoor $\text{PM}_{2.5}$ mass in the Los Angeles basin (Christoforou et al. 2000; Kim et al. 2000; Sardar et al. 2005), volatilizes upon building entry and results in altering the PM size and chemical composition indoors.

In most cases, indoor coarse PM was not correlated with indoor gaseous co-pollutants because, unlike CO , NO_2 and NO_x , the coarse fraction is characterized by very low



1 Sclae is different for Riverside graph

2 Mixed model coefficients for the dependent variable correspond to an interquartile range change in the independent variable

3 * = p-value < 0.1 (sufficient evidence for a difference)

** = p-value < 0.05

*** = p-value < 0.01 (significantly different)

Figure 4.2 Mixed model and Spearman correlation results for indoor-indoor associations

infiltration indoors (F_{inf}), and may also be emitted from re-suspension of existing particles deposited on indoor surfaces and floors (Chakrabarti et al. 2004). The product term analysis showed a significant phase interaction at the Riverside site for indoor quasi-UF and accumulation mode PM, implying a seasonal variability in the associations between these two fractions and the corresponding indoor gaseous co-pollutants (Figure 4.2).

Indoor OC was weakly associated with indoor gases, except during phase 1 (warmer months) at the San Gabriel Valley site, where strong positive associations ($R = 0.69$ to 0.81 ; Average regression slopes = 0.6 to $1.4 \mu\text{g}/\text{m}^3$) were found. These overall weak associations could be explained by changes in the OC characteristics as it penetrates indoors from outdoors, or by the presence of indoor OC sources, such as cooking, particularly for the retirement community here referred to as group 2 (see Polidori et al. (Polidori et al. 2007), for details). A significant phase interaction between indoor EC and indoor gaseous co-pollutants was observed at all locations, similarly to the findings for outdoor-outdoor associations. This indoor correlation may be because EC, CO, NO_2 and NO_x all share the same primary combustion sources coupled with the size range of EC particles (0.1 - $0.3 \mu\text{m}$) (Sardar et al. 2005) that allows them to penetrate indoors with great efficiency³¹. Moreover, EC is formed indoors in negligible amounts (Geller et al. 2002; Na and Cocker 2005; Polidori et al. 2007).

In Riverside, correlations between indoor PN and indoor gaseous species were weaker than the correspondent outdoor-outdoor associations, probably due to the presence of indoor sub-micrometer PN particles from fan heaters (particularly during phase 2), which tend to increase PN concentrations, but not the overall PM mass level (He et al. 2004).

4.4.4. Outdoor – Personal Associations

At all sites, personal quasi-UF particles correlation with outdoor quasi-UF PM (Figure 4.3a), were weaker compare to corresponding correlations for accumulation mode particles (discussed below). Weaker quasi-UF correlations is consistent with the relatively low penetration of sub-100 nm particles indoors due to diffusional losses³¹(Long et al. 2001; Sarnat et al. 2006) as well as losses due to evaporation of volatile species associated with this size range (Zhu et al. 2005).

This is further confirmed by the relatively small average regression slopes for the personal-outdoor associations ($S = 0.1$ to $1.4 \mu\text{g}/\text{m}^3$). Personal quasi-UF particles were not well correlated with either the larger outdoor PM fractions, or OC and most of its components (e.g. SOA and OC_{pri}), but were positively associated with EC and tracers of primary combustion (CO and NOx). The low correlations (R) between personal quasi-UF PM and OC_{pri} might be because OC_{pri} includes components with a relatively high vapor pressure, which volatilize upon building entry. Most importantly, this data

a) Quasi-UF PM

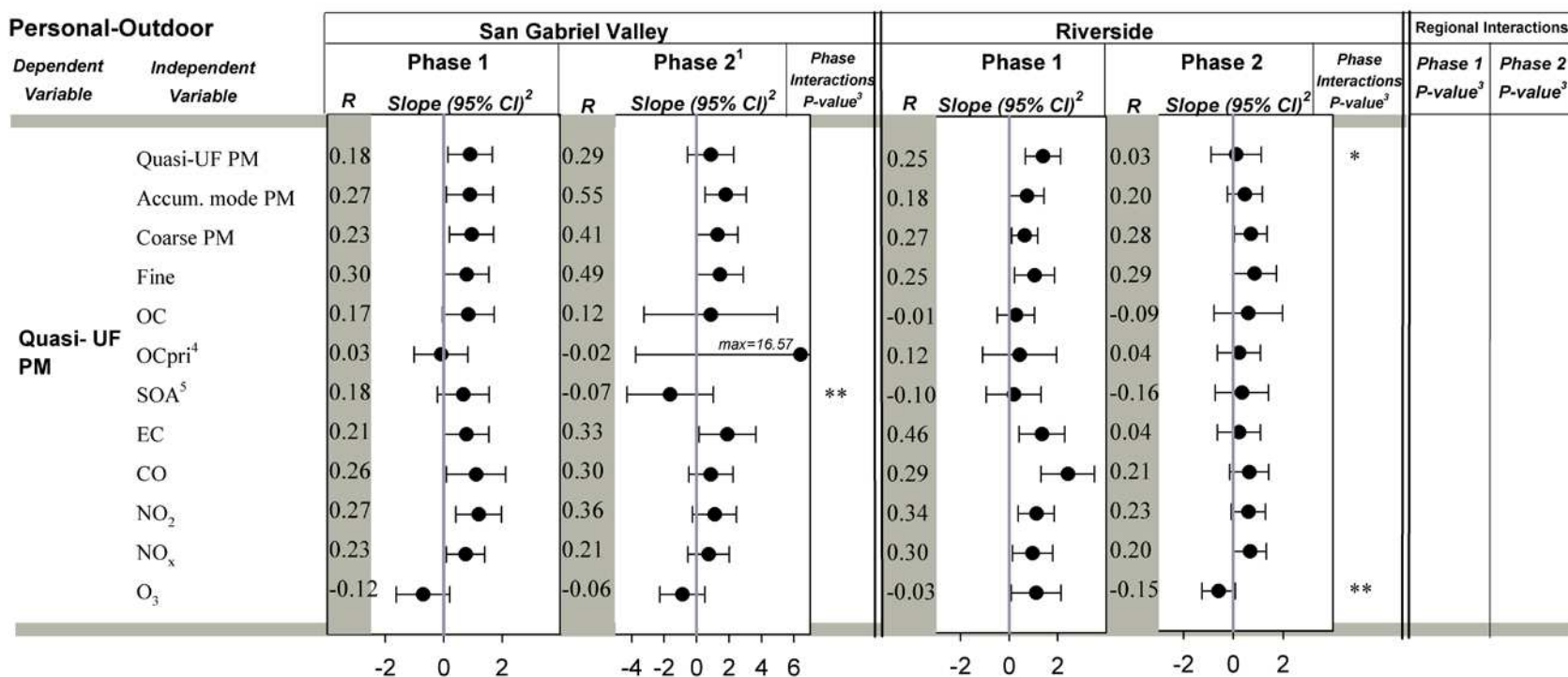


Figure 4.3 Mixed model and Spearman correlation results for outdoor pollutants with: a) personal quasi-UF PM, b) personal accumulation mode PM and c) coarse PM

b) Accumulation mode PM

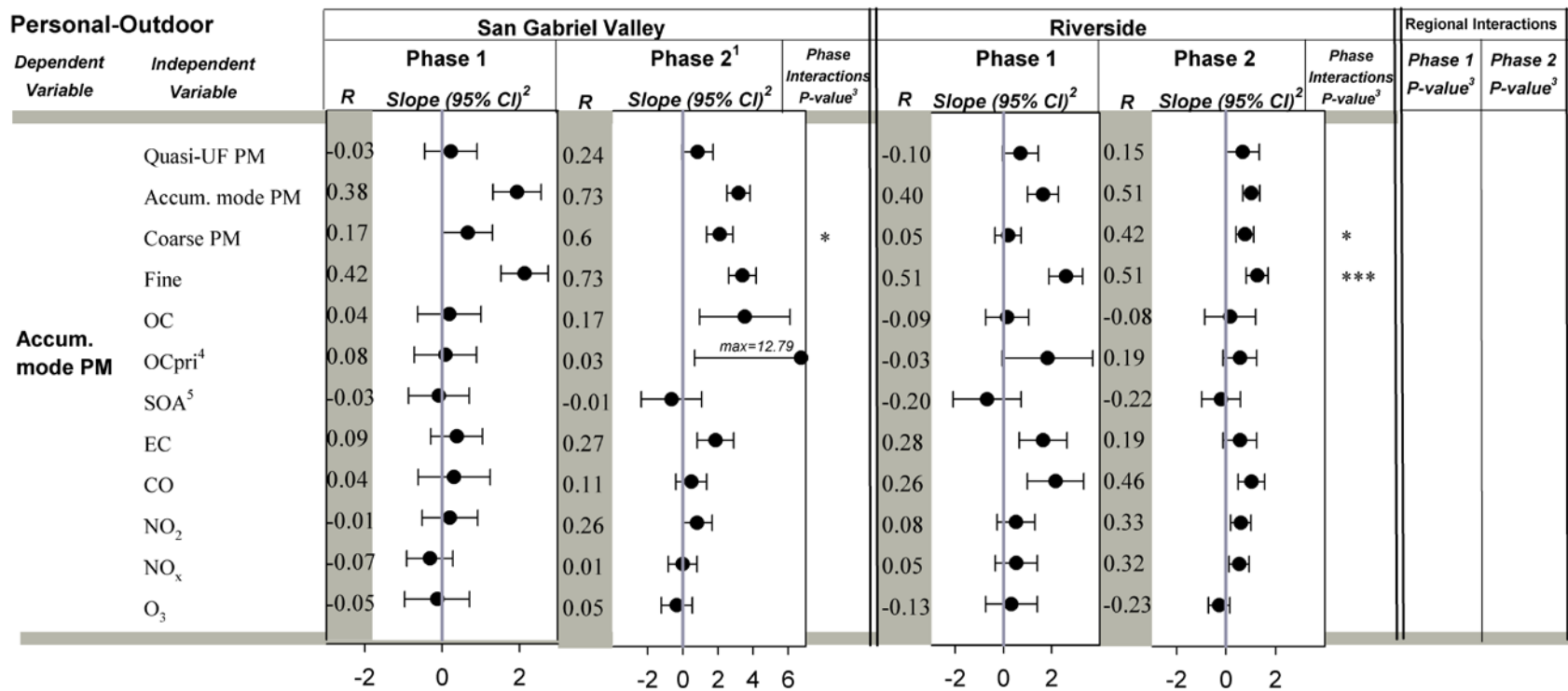
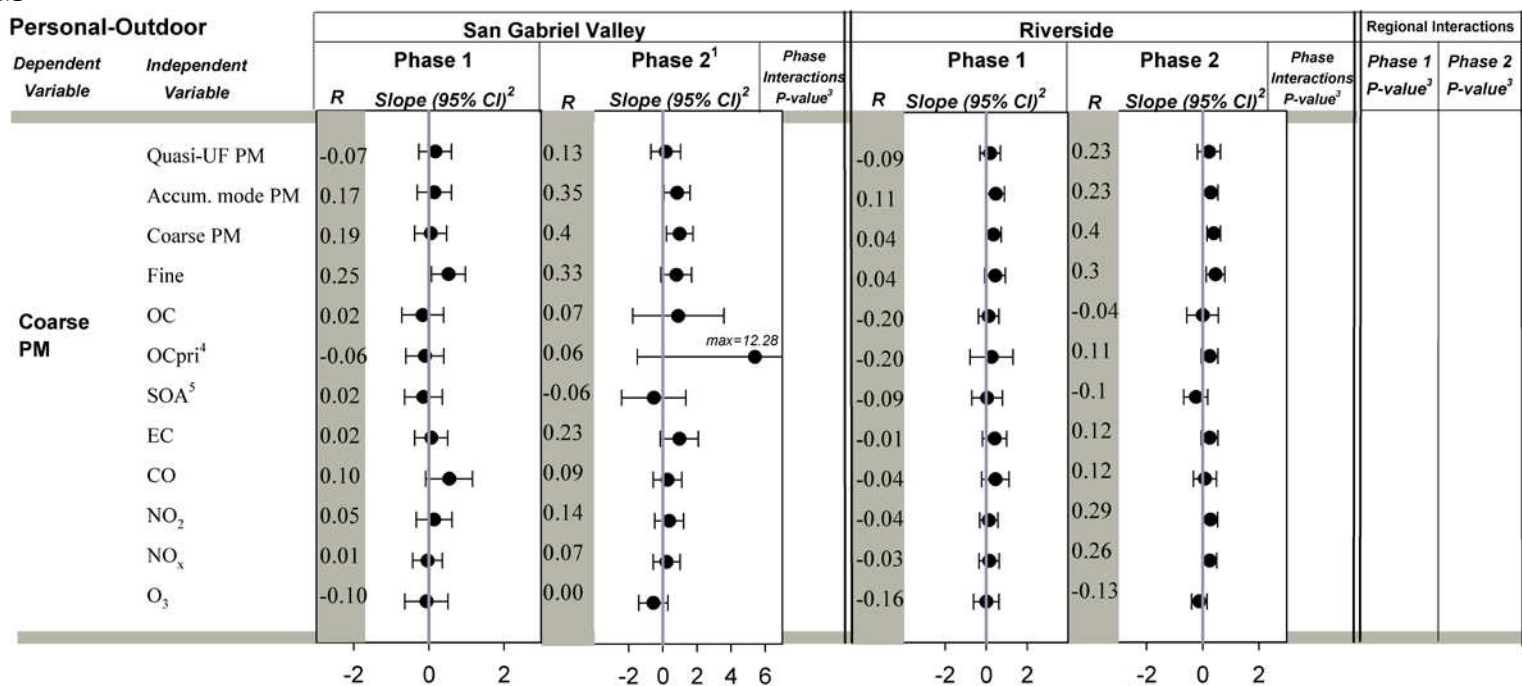


Figure 4.3 Continued

c) Coarse PM



- 1 Scal is different for phase 2 at San Gabriel Valley
- 2 Mixed model coefficients for the dependent variable correspond to an interquartile range change in the independent variable
- 3 * = p-value < 0.1 (sufficient evidence for a difference)
 ** = p-value < 0.05
 *** = p-value < 0.01 (significantly different)
- 4 OC_{pri} = Primary fraction of particulate organic carbon
- 5 SOA = Secondary organic aerosol

Figure 4.3 Continued

suggest that personal exposures to quasi-UF PM were significantly associated with EC at all CHAPS sites except during phase 2 in Riverside. This has important implications for the potential health effects of personal PM because EC is a good surrogate for diesel particles and a well known carcinogenic compound class (IARC 2005).

Outdoor accumulation mode PM (as well as $PM_{2.5}$) were well correlated with personal accumulation mode particles (R-values ranged between 0.38 and 0.73), and the magnitude of the regression parameter estimates was also relatively high. In particular, an interquartile increase in outdoor accumulation mode PM was associated with increases in personal accumulation mode particles of 1.9 and 3.1 $\mu\text{g}/\text{m}^3$ (for phases 1 and 2, respectively) in the San Gabriel Valley, and of 1.6 and 1.0 $\mu\text{g}/\text{m}^3$ (for phases 1 and 2, respectively) in Riverside (see Figure 4.3b for details). This size fraction is not as easily lost by diffusion/coagulation as quasi-UF PM when entering indoors, or by inertial deposition mechanisms (like coarse particles) and, hence, has a high penetration efficiency. Outdoor OC and its sub-fractions, were generally not well associated with personal accumulation mode particles. However, in the cooler seasons, stronger correlations (and generally higher regression slopes) were found with EC and other combustion products, such as CO, NO₂, and NO_x. Based on product term models, a significant phase interaction ($p < 0.01$) was found at the Riverside site for the prediction of personal accumulation mode particles by outdoor $PM_{2.5}$, highlighting the seasonal effect of primary sources on these associations. between these two PM size fractions. Overall, personal coarse mode particles were not well correlated with any of

the outdoor PM fractions/components, or outdoor gases, suggesting that none of these species was a good surrogate for exposure to personal coarse PM. This is because of the lower F_{inf} values for larger particle sizes, coupled with the fact that indoor coarse particles are mostly generated by mechanical processes and/or re-suspended from previously deposited particles on indoor surfaces. P-values showed no significant phase or regional interactions for personal coarse particles at the San Gabriel Valley and Riverside communities (see the “phase interactions” and “regional interactions” columns in Figure 4.3c), which implies that factors affecting the associations between personal coarse PM and its outdoor gaseous and particle co-pollutants were similar at all sites and phases.

4.4.5. Indoor – Personal Associations

Personal and indoor quasi-UF PM levels were best correlated in the San Gabriel Valley ($R = 0.38$; average regression slope = $1.6 \mu\text{g}/\text{m}^3$ [0.8 to 2.3] in the warmer season; $R = 0.40$; slope = $2.3 \mu\text{g}/\text{m}^3$ [0.7 to 4.0] in the cooler months) than in Riverside (Figure 4.4a). At the San Gabriel Valley sites, moderate correlations and significant regression parameter estimates were also observed between personal quasi-UF particles and fine PM. Associations between personal quasi-UF particles and indoor OC (and its sub-components) varied with location (from strong and positive in the San Gabriel Valley, to poor and negative in Riverside). Although there are different possible mechanisms leading to the production of particulate OC (e.g. photochemical reactions, condensation of organic vapors on existing particles, and primary emission from combustion sources),

a) Quasi-UF PM

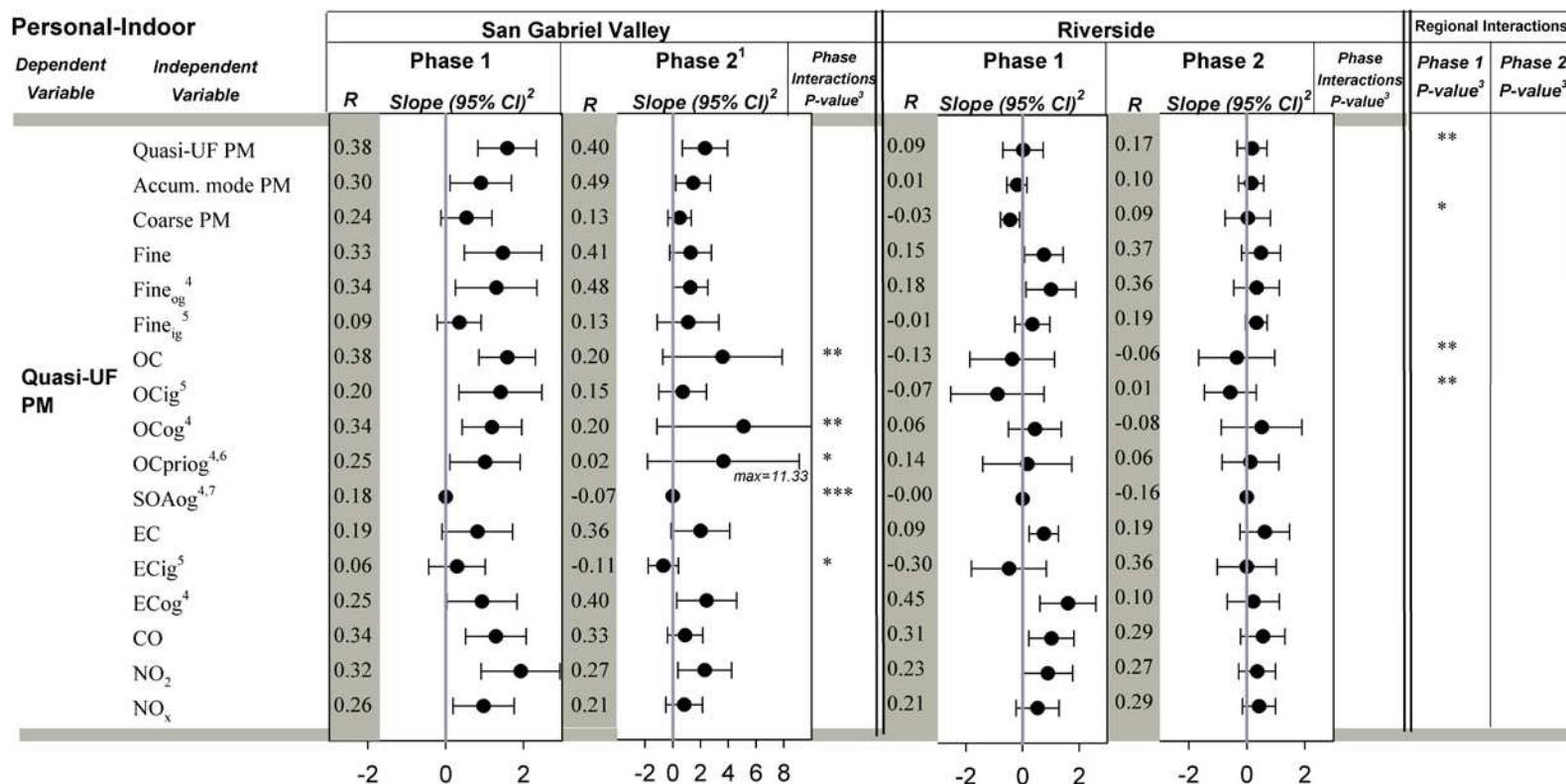


Figure 4.4 Mixed model and Spearman correlation results for indoor pollutants with: a) personal quasi-UF PM, b) personal accumulation mode PM and c) coarse PM

b) Accumulation mode PM

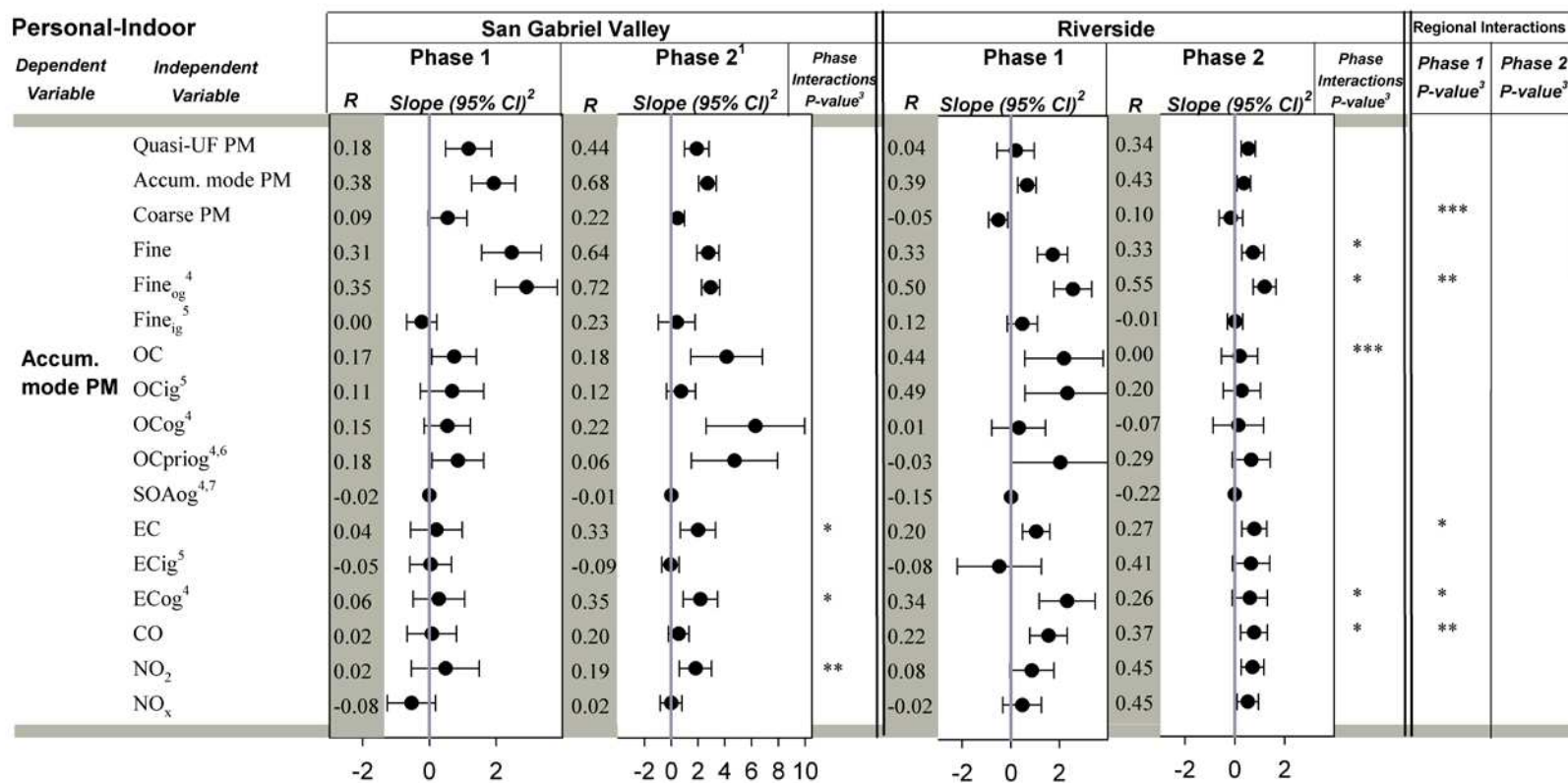


Figure 4.4 Continued

c) Coarse PM

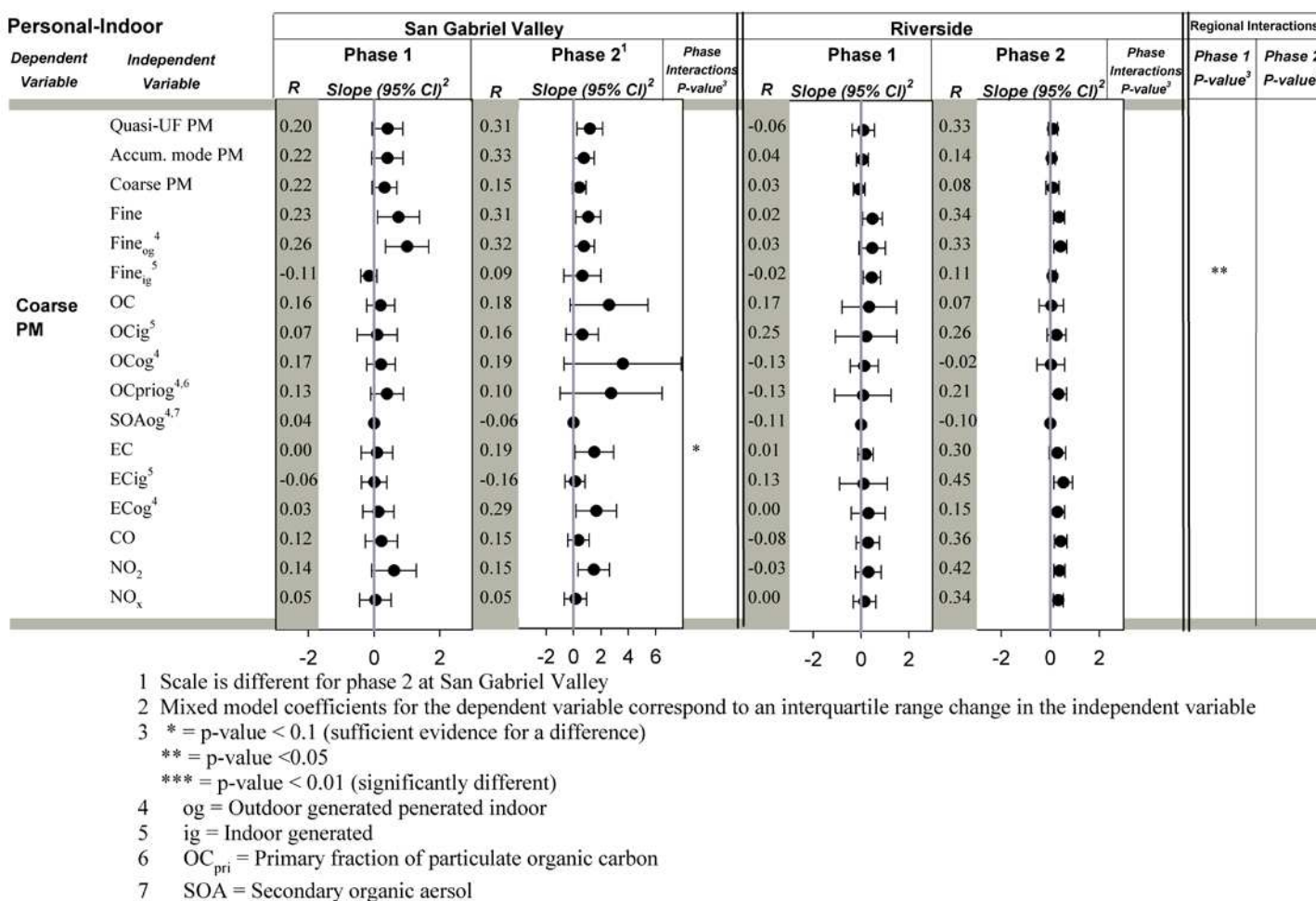


Figure 4.4 Continued

organic particles in the quasi-UF mode are generally formed by combustion processes (Fine et al. 2004; Sardar et al. 2005), which are more dominant in the San Gabriel Valley than in Riverside. Indoor EC and outdoor generated EC found indoors (ECog) were better associated with quasi-UF personal PM than indoor generated EC (ECig), indicating that indoor sources of EC were not substantial. For each interquartile increase in ECog the personal quasi-UF PM concentration increased of 0.9 and 2.4 $\mu\text{g}/\text{m}^3$ (during phases 1 and 2, respectively) in the San Gabriel Valley, and of 1.6 and 0.2 $\mu\text{g}/\text{m}^3$ (during phases 1 and 2, respectively) in Riverside (see Figure 4.4a for details). Similarly, indoor concentrations of outdoor origin of other important particle species, such as fine PM, OC, and OCpri (“Fine_{og}”, “OCog”, and “OCpri(og)”, respectively; see Figure 4.4a) were generally strongly and positively correlated with personal quasi-UF PM, compared to their corresponding indoor concentrations of indoor origin (“Fine_{ig}” and “OCig”, respectively; “OCpri(ig)”, estimates were not reported). This observation suggests that indoor sources were probably not significant contributors to personal exposure, which is predominantly influenced by primary emitted pollutants produced/emitted outdoors. Indoor gaseous co-pollutants (most likely originating outdoors) were more positively correlated to quasi-UF particles ($R = 0.21$ to 0.34 ; average regression slopes = 0.4 to $2.3 \mu\text{g}/\text{m}^3$) than larger size fractions (discussed below), likely due to similarities in sources, transportation and deposition mechanisms for these two classes of pollutants. Positive and fairly well correlation of indoor (and outdoor) concentrations of CO, NO₂ and NO_x with personal quasi-UF PM levels, reflects the possibility that these gaseous co-pollutants could confound epidemiologic associations between quasi-UF particles and adverse health

effects. However, this seems questionable because CO is neither a respiratory irritant nor a moderator of immune response in the respiratory tract (Sarnat et al. 2000), and NO₂ is probably not responsible for adverse health effects despite, given its low concentrations in personal and ambient air (Delfino et al. 2006; Delfino et al. 2008). Thus, we speculate that the observed association between personal quasi-UF PM concentrations and measured indoor co-pollutant levels do not reflect the corresponding personal-personal relationships (personal gaseous measurements were not performed during CHAPS).

At all sites and during all seasons, personal accumulation mode particles were well associated with indoor accumulation PM and with PM_{2.5} (Figure 4.4b). Moreover, personal accumulation mode PM was more strongly correlated with Fineog, OCog (only at the San Gabriel sites) and ECog than with the corresponding indoor levels of indoor origin (Fineig, OCig, and ECig, respectively). In contrast, personal accumulation mode PM was always negatively associated to SOAog. These results reinforce the idea that outdoor primary emission sources are of great importance in terms of personal exposure to PM_{2.5}. These findings support the epidemiologic results reported by Delfino et al. (Delfino et al. 2008) for the present panel of elderly people with a history of coronary artery disease. They concluded that the strongest associations were found between indoor PM of outdoor origin and increases in blood biomarkers of systemic inflammation and platelet activation, and decreases in erythrocyte antioxidant activity. In the same study, little evidence for biomarker associations with secondary PM_{2.5}, SOA or total OC was found, while robust

associations with emission sources of primary PM_{2.5}, OC and quasi-UF particles were observed. This is consistent with the weak and often negative correlations between personal quasi-UF and accumulation mode PM and indoor SOA of outdoor origin (SOA_{og}) obtained in our work.

Indoor CO, NO₂ and NO_x levels were not as well correlated to personal accumulation PM concentrations as quasi-UF mode particles, except during phase 2 at Riverside (R= 0.37 to 0.45; see Figure 4.4b). Generally, indoor CO and NO₂ were better associated with personal accumulation PM exposure than indoor NO_x. Overall, this suggests that the measured gaseous co-pollutants are weak surrogates of personal exposure to accumulation mode PM, at least for subjects with similar exposure profiles and living in similar urban locations. It is worth emphasizing that, while quasi-UF PM is mostly produced from primary combustion sources, accumulation mode particles originate from a combination of primary and secondary emissions. This might explain the relatively weaker correlations observed earlier between personal accumulation PM and outdoor CO (and EC, a tracer of primary combustion). For NO₂ (a rather non reactive gas), indoor sources may also weaken its association with personal PM.

Personal coarse mode particles were more strongly associated with all indoor PM fractions in the San Gabriel Valley than in Riverside, although the strength of this correlation was rather low at all sites (Figure 4.4c). Associations between personal coarse PM and indoor EC (as well as indoor OC) were generally small. Indoor CO,

NO₂ and NO_x showed relatively poor associations with personal coarse PM at all sites, except in Riverside during the cooler months ($R = 0.34$ to 0.42 ; average regression slopes = 0.3 to $0.4 \mu\text{g}/\text{m}^3$).

4.4.6. Regional and Seasonal Correlations and Comparison with Other Studies

To the best of our knowledge, this study is one of the most extensive analysis to date of seasonal correlations between indoor, outdoor, and personal size-segregated PM concentrations and the corresponding gaseous levels/PM components. Despite the uniqueness of this data analysis, we considered it important to compare our results to those obtained from similar studies conducted previously in the U.S., in an effort to clarify the role of CO, NO₂, NO_x, and O₃ as surrogates of human exposure to PM_{2.5}. Figure 4.5 shows Spearman's correlation coefficients (R) for the associations between personal PM_{2.5} levels and the outdoor (residential or ambient) concentrations of PM_{2.5}, CO, NO₂, NO_x, and O₃, both in the warmer (Figure 4.5a) and cooler (Figure 4.5b) months. R values calculated at the San Gabriel Valley and Riverside sites (personal vs residential outdoor) were plotted against those obtained by Sarnat et al. in Baltimore (Sarnat et al. 2000) and Boston (Sarnat et al. 2005) (personal vs ambient).

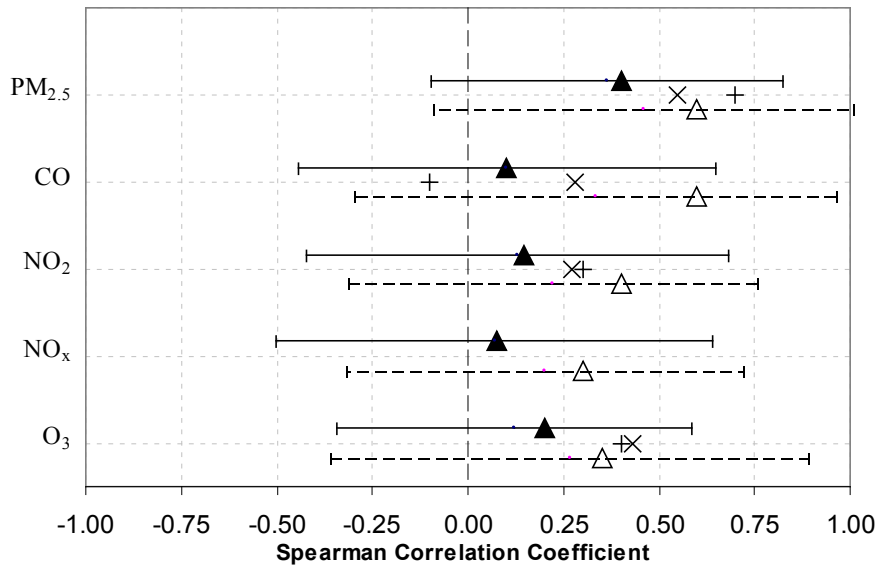
At all studied locations, personal PM_{2.5} was well correlated with outdoor/ambient PM_{2.5}, both in the warmer and the cooler seasons. This is also consistent with results from other recent longitudinal studies on PM exposure (Ebelt et al. 2000; Sarnat et al. 2000; Williams et al. 2000; Sarnat et al. 2005). Of particular interest are the moderately strong

associations observed at all sites between personal $\text{PM}_{2.5}$ and NO_2 (in both phases; see Figures 5a and 5b), personal $\text{PM}_{2.5}$ and O_3 (only in the phase 1; Figure 4.5a), and $\text{PM}_{2.5}$ and CO (only in the phase 2; Figure 4.5b). Variability in these correlations reflects the effects of seasonal changes on the formation mechanisms of PM.

In the warmer months, a considerable fraction of personal exposure to $\text{PM}_{2.5}$ might be related to particles originating from photochemical activities, while in the cooler months personal $\text{PM}_{2.5}$ levels are predominantly influenced by combustion processes. In addition, results from all studies indicate that outdoor/ambient NO_2 and O_3 (in the warmer season) and outdoor/ambient CO and NO_2 (in the cooler season) are moderately correlated with personal $\text{PM}_{2.5}$ exposure and, in each location, there may be differences in the strength of the personal-ambient associations, probably due to geographical variability in housing characteristics and ventilation conditions (Sarnat et al. 2000; Sarnat et al. 2005; Polidori et al. 2007).

Therefore, it might be incorrect to assume that outdoor/ambient gas measurements are consistent surrogates for personal $\text{PM}_{2.5}$ exposures, because correlations between personal $\text{PM}_{2.5}$ and outdoor/ambient CO, NO_2 , NO_x , and O_3 vary by both season and location (Figures 5a and 5b). Results from time-series epidemiologic studies that include both gaseous and particulate pollutant concentrations in the models should be interpreted with caution. As noted by Sarnat et al. (Sarnat et al. 2000), if ambient co-pollutant concentrations are surrogates (as opposed to confounders) of PM, using multiple particles

a) Summertime personal PM_{2.5} vs outdoor species associations



b) Wintertime personal PM_{2.5} vs outdoor species associations

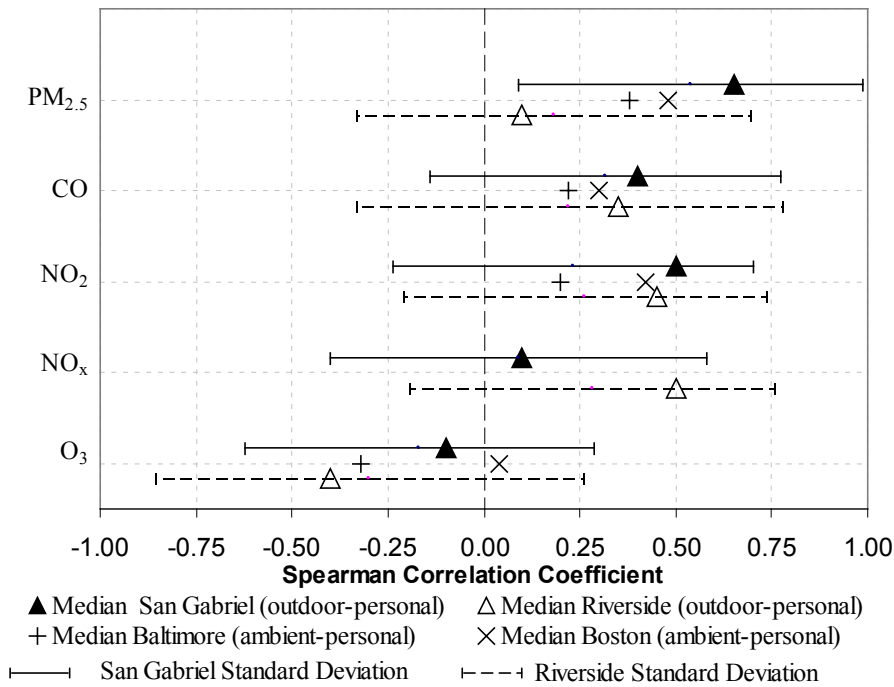


Figure 4.5 Spearman's correlation coefficients (R) for the associations between personal PM_{2.5} concentrations and outdoor (residential or ambient) particle/gaseous levels in the summer (a) and winter (b). The R values calculated in this work at the San Gabriel Valley and Riverside sites (personal vs residential outdoor) were compared to those obtained by Sarnat et al. in Baltimore (2001) and Boston (2005) (personal vs ambient). Error bars are referred to standard deviation of individual values

would lead to an erroneous significant association for the collinear co-pollutants. Previous environmental and occupational studies showed that O₃ and NO₂ exposures may elicit adverse health effects (Delvin et al. 1997; Devlin et al. 1997; Gong et al. 1998; Geyh et al. 2000; Mosqueron et al. 2002), thus have the potential to act as confounders of personal exposure to PM_{2.5}. However, two recent studies by Delfino et al. have suggested that NO₂ might be a surrogate of not only particle species, but also volatile and semivolatile compounds that may have important health effects independent of particle bound components (Delfino et al. 2006; Delfino et al. 2008).

4.5. CONCLUSIONS

Our modeling results have shown that outdoor and indoor levels of CO, NO₂ and NO_x were better correlated with measured indoor, outdoor and personal quasi-UF PM levels than accumulation mode and coarse mode PM. This better correlation is due to more similarity in sources and transportation mechanism. Indoor concentrations of outdoor origin of important carbonaceous species such as EC, OC, and OCpri (“ECog”, “OCog”, and “OCpri(og)”, respectively) were more strongly correlated with personal quasi-UF and accumulation mode PM, than their corresponding indoor concentrations of indoor origin (“ECig”, “OCig”, and “OCpri(ig)”). This is because indoor sources were probably not significant contributors to personal exposure of accumulation and quasi UF PM, which is predominantly influenced by primary pollutants produced/emitted outdoors. These results are important, because other CHAPS investigators have suggested that traffic-related emission sources of PM_{2.5} OCpri, and quasi-UF particles lead to increases in systemic

inflammation, platelet activation, and decreases in erythrocyte antioxidant activity in elderly people with a history of coronary artery disease.

Overall, our data analysis suggests that investigating the correlations among size-segregated indoor, outdoor and personal PM, their specific components, and concurrently measured gaseous co-pollutants is a challenging endeavor. These associations depend on a number of factors that vary in space and time, such as: the relative contribution of UF, accumulation and coarse mode PM to the measured PM concentrations, the seasonal variability of primary and secondary emission sources, the presence of indoor sources of PM and gaseous co-pollutants (e.g. cooking), home characteristics (e.g. ventilation conditions and household characteristics), and proximity to the emission sources. The analysis of these associations is further complicated by the amount of time spent indoors (highly variable among subjects, especially in the warmer season), which is also a critical component in determining exposure. Thus, results from time-series epidemiologic studies that include both gaseous and particulate pollutant concentrations in the models should be interpreted with caution. Future research should focus on how these specific factors affect the strength of between-pollutant associations for individuals living in different locations.

4.6. CHAPTER 4 REFERENCES

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Chapter 5.

Organic Compound Characterization and Source Apportionment of Indoor and Outdoor Quasi-ultrafine PM in Retirement Homes of the Los Angeles Basin

5.1. ABSTRACT

Quasi-ultrafine PM ($PM_{0.25}$) and its components were measured in indoor and outdoor environments at four retirement communities in the Los Angeles basin, CA, as part of the Cardiovascular Health and Air Pollution Study (CHAPS). The present paper focuses on the characterization of the sources, organic constituents and indoor and outdoor relationships of quasi-ultrafine PM. In contrary to n-alkanes and n-alkanoic acid, the average indoor/outdoor ratio of most of the measured PAHs, hopanes and steranes were close to- or slightly lower than 1, and indoor-outdoor correlation coefficients (R) were always positive and for most of these components moderate to strong (median R was 0.60 for PAHs and 0.74 for hopanes and steranes). This suggests that indoor PAHs, hopane and steranes were mainly from outdoor origin, whereas indoor n-alkanes and n-alkanoic acids were significantly influenced by indoor sources.

The Chemical Mass Balance (CMB) model was applied to both indoor and outdoor speciated chemical measurements of quasi-ultrafine PM. Vehicular sources had the highest contribution to $PM_{0.25}$ among the apportioned sources for both indoor and outdoor particles at all sites (on average 24-47%). The contribution of mobile sources to indoor levels was similar to their corresponding outdoor estimates.

In an earlier investigation, also part of this study, we reported that indoor infiltrated particles from mobile sources are more strongly correlated with the adverse health effects observed in the elderly subjects living in the studied retirement communities compared to indoor measured particles. The contribution of mobile sources to indoor levels was similar to their corresponding outdoor estimates, thus illustrating the significance of these sources on indoor PM concentrations. A major implication of these findings is that, even if people (particularly the elderly population of our study) generally spend most of their time indoors, a major portion of the $PM_{0.25}$ particles to which they are exposed comes from outdoor mobile sources.

5.2. INTRODUCTION

Positive associations between exposure to atmospheric particulate matter (PM) and adverse health effects have been shown by numerous epidemiological and toxicological studies (Pope and Dockery 2006). Particle size is an important parameter affecting the percentage of the inhaled aerosol that deposit in the human lung as well as the deposition site. Generally, smaller particles penetrate into the deeper regions of the human respiratory tract after being inhaled. Thus, fine PM ($PM_{2.5}$; particles with an aerodynamic diameter smaller than $2.5\ \mu m$) has been more strongly associated with mortality and morbidity, although coarse particles ($PM_{2.5-10}$; aerodynamic diameter between 2.5 and $10\ \mu m$) have also been associated with respiratory hospital admissions (Brunekreef and Forsberg 2005). Ultrafine particles, tenuously defined as those with diameters less than $0.1 - 0.2\ \mu m$ (see more discussion on the appropriate cutpoint of the ultrafine PM mode

in (Sioutas et al. 2005) penetrate deep into the alveolar region of the respiratory system and have the ability to translocation in other parts of the human body (Elder et al. 2006). Toxicological data suggest that these particles are more strongly associated with cardiovascular and respiratory health outcomes (Araujo et al. 2007) compared to larger particles. So far, there is little direct epidemiologic research to support this (reviewed by (Delfino et al. 2005); (Weichenthal et al. 2007). Along with particle size, chemical composition influences the toxicity of PM. Thus, exposure to several types of highly toxic organic particle components [including quinones, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls and other organochlorine compounds] may result in acute effects (Li et al. 2003).

Although air quality standards have been established for outdoor / ambient environments, a significant portion of human exposures to PM occurs indoors, where people spend around 85-90% of their time (Klepeis et al. 2001). Hence, it is important to understand the composition and sources of both indoor and outdoor PM and their relationships. Indoor PM consists of outdoor particles that have infiltrated indoors, particles emitted indoors (primary), and particles formed indoors (secondary) from precursors emitted both indoors and outdoors (Weschler 2004). To the best of our knowledge, only few studies on indoor PM source apportionment have been conducted in the past few years. These were mainly focused on examining the influence of outdoor sources on the measured outdoor concentrations of fine PM (without any further size fractionation), although indoor measurements of organic tracers that are typically used for source apportionment were

also conducted (Olson et al. 2008). Few studies have demonstrated that indoor sources can contribute up to 50% to the indoor concentrations of fine PM and its components (Wallace 1996; Meng et al. 2005), whereas other studies reported lower contributions (6-22%) (Yli-Tuomi et al. 2008).

The present papers has been conducted as part of the Cardiovascular Health and Air Pollution Study (CHAPS), a multidisciplinary project funded by the National Institutes of Health (NIH) and designed to investigate the effects of micro-environmental exposures to PM on cardiovascular outcomes in elderly retirees affected by coronary artery disease. The elderly population with coronary artery disease is likely to be among the most vulnerable to the adverse effects of particulate air pollutants. In an earlier investigation, also part of this study (Delfino et al. 2008), we reported that indoor PM of outdoor origin (mostly from combustion sources) was more significantly associated with systemic inflammation, platelet activation, and decreases in erythrocyte antioxidant activity than uncharacterized indoor PM that included particles of indoor origin. The present study focuses on the quasi-ultrafine fraction of PM ($PM_{0.25}$; particles with an aerodynamic diameter smaller than $0.25\ \mu m$) in both indoor and outdoor environments at four distinct retirement communities of the Los Angeles Basin, which were study sites of the CHAPS project. The main objectives of this study are: a) to evaluate the organic composition of quasi-ultrafine PM ($PM_{0.25}$) in both indoor and outdoor environments throughout the calendar year, b) to identify the most important sources of these sub-micrometer particles, and c) to quantify their contribution to the total PM mass concentrations in both indoor

and outdoor environments. The study focuses on $PM_{0.25}$ because we have shown in earlier publications from the CHAPS that this size range had the strongest and most significant association with circulating biomarkers of inflammation, antioxidant activity, and platelet activation measured in the study subjects (Delfino et al, 2008). Furthermore, to best of our knowledge, there are no other studies of sources and composition of indoor ultrafine or quasi-ultrafine particles. The results described in this paper will be used by the CHAPS investigators to evaluate associations between indoor and outdoor PM sources to cardiovascular outcomes.

5.3. METHODS

5.3.1. Sampling sites and schedule

Indoor and outdoor PM measurements were conducted at four retirement communities in southern California between 2005 and 2007. Three of these communities were in the San Gabriel Valley, CA (sites San Gabriel 1, 2 and 3) and the fourth in Riverside, CA. Site San Gabriel 1 was located in a residential area about 50 km east of downtown Los Angeles, approximately 3 km away from a major freeway. Site San Gabriel 2 was about 8 km east of Los Angeles, approximately 300 m away of a major freeway. Site San Gabriel 3 was situated about 55 km east of downtown Los Angeles, 2.5 km from two busy freeways and 150 m away from a major street. Site Riverside was located about 110 km east of Los Angeles, 15 km southeast of downtown Riverside, 3 km away from the closest freeway and 1 km from a major street (downwind of the site). The abundant

vegetation surrounding this last community may be a potential source of precursors of biogenically generated PM (Rogge et al. 1993).

Two identical sampling stations were installed at each site, one indoors and one outdoors. The indoor sampling station at site San Gabriel 1 was set-up in a recreational area of the community's main building, adjacently to a construction site. San Gabriel 2 indoor station was located in the dining room of the community's central building (see Polidori et al., 2007, for further details on sites San Gabriel 1 and 2). The indoor station at site San Gabriel 3 was in a recreational area of the main retirement community complex. The indoor station at site Riverside was in the hallway of the main building with a dining room, activity room and numerous apartment units nearby. Outdoor sampling equipment was set-up inside a movable trailer, positioned within 300 m from the indoor station at all sites.

Two 6-week sampling campaigns were conducted at each location, one during summer and early fall (warmer phase) and one throughout late fall and winter (colder phase); see Arhami et al. (2009) for more details.

5.3.2. Sampling method and chemical analyses

24-h size segregated PM samples were collected daily from Monday to Friday by means of SioutasTM Personal Cascade Impactors (SKC Inc, Eighty Four, PA). Coarse, accumulation, and quasi-ultrafine mode PM were sampled on Zefluor (3 µm pore-size,

Pall Life Sciences, Ann Arbor MI) filters (although the present study focuses only in the quasi-ultrafine fraction). The PM mass concentration was determined gravimetrically by weighing filters in a controlled temperature and relative humidity room, using a microbalance (Mettler-Toledo, Columbus, OH; weight uncertainty $\pm 2 \mu\text{g}$).

Filters were composited weekly (including 5 daily collected samples-from Monday to Friday) for chemical analyses. Composites were cut into 3 sections: 1 half and 2 quarter sections. The one half section was analysed for 92 different organic compounds using Gas Chromatography/Mass Spectrometry (GC/MS) (Stone et al. 2008). The first quarter section of such composited filters were digested with concentrated acid using microwave digestion and then analyzed by high resolution Inductively Coupled Plasma Mass Spectrometer (HR-ICPMS, Finnigan Element 2) to determine 52 trace elements (Herner et al. 2006). The second quarter was analyzed for water soluble organic carbon (WSOC) and used for a reactive organic species (ROS) assay. A General Electric Instrument (Sievers Total Organic Carbon, TOC; GE, Inc.) was used to determine WSOC concentrations. ROS will be used and described in other CHAPS papers.

Hourly elemental and organic carbon (EC and OC, respectively) levels in the fine PM fraction were measured using semi-continuous OC_EC analyzer (Model 3F, Sunset Laboratory Inc). The quasi-ultrafine EC was estimated from the measured fine EC using a factor of 0.70 ± 0.18 (quasi-ultrafine EC = fine EC $\times$ 0.70), which is based on recent size distribution data obtained over a 3 year period at 10 locations of the Los Angeles

Basin (Arhami et al. 2006; Minguillon et al. 2008; Arhami et al. 2009). Dasibi Carbon Monoxide Analyzers (Model 3008, Dasibi Environmental Corp, Glendale, CA) were implemented to measure continuous (1-min) indoor and outdoor CO levels.

5.3.3. Source Apportionment

The Chemical Mass Balance (CMB) model (version CMB8.2 from the US Environmental Protection Agency) was used for the apportionment of the total measured ambient organic carbon (OC). In order to apportion the most important quasi-ultrafine PM sources, all model results were converted to equivalent PM based on the correspondent OC/PM ratio of each of the considered sources. OC/PM ratios were calculated for source profiles assuming that quasi-ultrafine PM = Elemental Carbon (EC) + Organic Matter (OM) and that $OM = 1.4 * OC$ (Turpin et al. 2000; Polidori et al. 2008). Other contributors to PM considered in this study are: sulfate, estimated from S concentrations assuming that all measured S by ICP-MS was in the form of fully neutralized ammonium sulfate (Arhami et al. 2009); sea spray, calculated based on total Na as an estimate of water soluble Na concentrations and using a multiplication factor of 3.248 (Simoneit 1986); resuspended dust, calculated from Si, Al, Ca, Fe and K concentrations, assuming they appear predominantly as oxides (Brook et al. 1997) and Si was not measured but estimated assuming $Si = 3 * Al$ (Sillanpaa et al. 2006); and SOA estimations were based on measurements of WSOC. In polluted regions, compounds comprising water soluble organic carbon (WSOC) are either mainly emitted from biomass burning sources (Docherty et al. 2008) or formed via secondary atmospheric processes (Weber et al.

2007). Thus, measured WSOC concentrations, minus the OC fraction apportioned to biomass burning (from CMB output), was multiplied by a factor of 2.5 $\mu\text{gOM}/\mu\text{gOC}$ (Turpin and Lim 2001; Polidori et al. 2008) to convert it to SOA. The resulting SOA was then adjusted to account for the water-insoluble organic carbon (WISOC) fraction, assuming that 20% of the SOA concentration was water insoluble (Kondo et al. 2007). The uncertainty associated with this method is discussed in the results section.

A careful selection of OC sources is critical for the correct application of the CMB model, as demonstrated in previous sensitivity studies (Subramanian et al. 2006; Sheesley et al. 2007). Hence, after evaluating all potential pollutant emissions in the study area, the sources considered in this work were: light duty and heavy-duty vehicles (LDV and HDV respectively; (Kuhn et al. 2005; Ntziachristos et al. 2007; Phuleria et al. 2007), biomass burning in the Western US (Fine et al. 2004), and ocean vessels (Rogge et al. 1997; Agrawal et al. 2008). Vehicular profiles correspond to roadway data from studies carried out at the CA-110 and I-710 freeways in Los Angeles and, thus, they represent emissions from a mixture of vehicular sources (Phuleria et al. 2007). Other typical OC sources were included in the first modeling attempts, but were found to be non-quantifiable (meat cooking and natural gas) or their contribution was very low (candle smoke and cigarette smoke, with contributions <1% of OC). A set of fitting species was chosen based on: a) their chemical stability (Schauer et al. 1996), b) availability of their concentrations in different source profiles and in ambient data, and c) previous studies that identified markers for different sources (Schauer et al. 1996; Simoneit 1999; Schauer and Cass

2000). Thus, the following species were used as fitting species: EC, Benzo(k)fluoranthene, Benzo(e)pyrene, Benzo(b)fluoranthene, Benzo(ghi)perylene, Coronene, 17 α (H)-22,29,30-Trisnorhopane, 17 α (H)-21 β (H)-Hopane, 22S-Homohopane, 22R-Homohopane, Sitostane, Levoglucosan, Vanadium and Nickel.

Each model result was evaluated using the regression statistics parameters accompanying each CMB model output: correlation coefficient (R^2) and χ^2 , which were within the desired ranges (0.81-1.00 and 0.0-5.7, respectively). The chi-square is the weighted sum of squares of the differences between the calculated and measured fitting species concentrations (for more details and description of statistical parameters, see CMB8.2 manual by the US Environmental Protection Agency). Weekly source contributions were estimated and the results were averaged over each phase of study at each site.

5.3.4. Data Analysis

A number of relevant organic species were not detectable at several sites or during particular phases of the study. In order to make a fair comparison between sites and time phases, half of the detection limit for each species was used as its concentration with half of the detection limit as uncertainty (the detection limit varied from 1.7e-5 to 0.06 ng/m³ for different species). CO levels were used to estimate indoor-outdoor air exchange rates (AER; h⁻¹) at each site using a well established procedure developed by (Abt et al. 2000) (see (Polidori et al. 2007) for further details).

5.4. RESULTS AND DISCUSSION

5.4.1. Overview

The recorded meteorological data highlight the overall climatological stability of the Los Angeles basin, characterized by moderate differences in terms of temperature (T) and relative humidity (RH%) between colder and warmer phases (Table 5.1). These moderate meteorological variations may cause low variability in pollutants levels throughout the year. The average T and RH% were lower in Riverside than at the three San Gabriel sites. During the warmer phase of the study, the indoor and outdoor areas were generally characterized by similar T, whereas during the colder phases the average T was $\sim 10^{\circ}\text{C}$ higher indoors than outdoors. The higher differences between indoor and outdoor T values in the colder phase can potentially cause higher variability between indoor and outdoor concentrations compared to the warmer phase, especially for volatile (or semi-volatile) components. The air exchange rates (AER) at different sites were relatively similar to each other throughout the monitoring phases (Table 5.1), suggesting an overall similarity in home characteristics among different communities (Polidori et al. 2007). The magnitude of the AERs was generally low ($0.21\text{-}0.4\text{ h}^{-1}$), and consistent with the low number of open windows and doors, the presence of central air conditioners, and the overall structural characteristics of the studied retirement homes.

Table 5.1 Studied sites PM concentrations, meteorology and air exchange rates

		Quasi-UF PM ($\mu\text{g}/\text{m}^3$)		Temperature ($^{\circ}\text{C}$)		Outdoor Humidity (%)	AER* (h^{-1})
		<i>outdoor</i>	<i>Indoor</i>	<i>outdoor</i>	<i>Indoor</i>		
Warmer Phase	San Gabriel 1	9.9 $\pm$ 2.2	10.3 $\pm$ 1.6	25.1 $\pm$ 2.2	26.1 $\pm$ 1.2	60 $\pm$ 6	0.25 $\pm$ 0.04
	San Gabriel 2	9.3 $\pm$ 1.8	9.8 $\pm$ 1.6	21.5 $\pm$ 2.1	23.6 $\pm$ 0.9	58 $\pm$ 15	0.28 $\pm$ 0.06
	San Gabriel 3	10.4 $\pm$ 2.3	6.6 $\pm$ 1.3	25.9 $\pm$ 2.8	23.3 $\pm$ 1.1	58 $\pm$ 11	0.40 $\pm$ 0.12
	Riverside	11.5 $\pm$ 3.0	8.7 $\pm$ 2.3	21.1 $\pm$ 4.0	24.9 $\pm$ 1.7	53 $\pm$ 15	0.21 $\pm$ 0.06
Colder Phase	San Gabriel 1	8.8 $\pm$ 1.8	9.6 $\pm$ 3.1	15.4 $\pm$ 2.8	23.4 $\pm$ 1.2	58 $\pm$ 19	0.33 $\pm$ 0.07
	San Gabriel 2	10.4 $\pm$ 2.6	9.4 $\pm$ 2.6	14.9 $\pm$ 2.1	23.9 $\pm$ 0.8	49 $\pm$ 14	0.31 $\pm$ 0.10
	San Gabriel 3	10.7 $\pm$ 2.0	7.1 $\pm$ 2.6	16.6 $\pm$ 3.6	24.7 $\pm$ 1.2	55 $\pm$ 10	0.26 $\pm$ 0.08
	Riverside	7.2 $\pm$ 2.2	6.0 $\pm$ 1.5	11.2 $\pm$ 2.8	25.4 $\pm$ 0.7	42 $\pm$ 22	0.31 $\pm$ 0.09

Average $\pm$ Standard Deviation of weekly data are reported

* AER: Air Exchange Rate

The average outdoor quasi-ultrafine mass concentrations at all sites varied from 9.3 to 11.5 $\mu\text{g}/\text{m}^3$ in the warmer phases and from 8.9 to 10.7 $\mu\text{g}/\text{m}^3$ in the colder phases thus indicating relatively low seasonal variability. Similar to outdoor quasi-ultrafine PM levels, indoor levels were consistent throughout the year at all the sites. Mean indoor concentrations were generally lower than- or similar to the corresponding outdoor concentrations (average indoor levels were 63-107% of their outdoor values). This suggests that particle loss due to penetration of outdoor particles indoors, deposition of infiltrated PM on indoor surfaces, and/or evaporation of semi-volatile particle components is generally greater than or similar to the amount of PM generated indoors.

5.4.2. Outdoor Organic Species and Seasonal Variability

As shown in Figure 5.1a, the outdoor PAHs concentrations were similar in the warmer and the colder phases. However, medium and high molecular weight PAHs levels were slightly higher in the colder months compared to the warmer periods. PAHs are mainly products of incomplete combustion, including vehicular emissions (Manchester-Neesvig et al. 2003). The higher colder phase levels could be attributed to the influence of cold start spark-ignition from gasoline-powered vehicles, which emit higher amounts of high molecular weight PAHs, such as benzo(ghi)perylene and coronene, than hot-start conditions (Miguel et al. 1998; Fine et al. 2004; Lough et al. 2007). The average seasonal changes in hopanes and steranes were also quite small (Figure 5.1b), a result that can be explained by the low seasonal variability in the emission rates of their main source, i.e., engine lubricating oil of mobile sources (Rogge et al. 1993; Rogge et al. 1996; Schauer et al. 1996), which are independent of the driving conditions (e.g. cold-start, hot-start or steady state; (Schauer et al. 2002). Moreover, the low seasonal variability may reflect the low volatility of these organic species. A major portion of the analyzed n-alkanes was characterized by substantially higher and more variable concentrations in the colder months over the studied sites (Figure 5.1c), possibly because of the enhanced condensation of gas phase n-alkanes onto existing particles (Fraser et al. 1997; Kuhn et al. 2005). Conversely, the lower n-alkanes concentrations observed in the warmer phases could be due to volatilization of their most volatile fraction (Fraser et al. 1997; Kuhn et al. 2005) and to variations in the emission sources of these compounds.

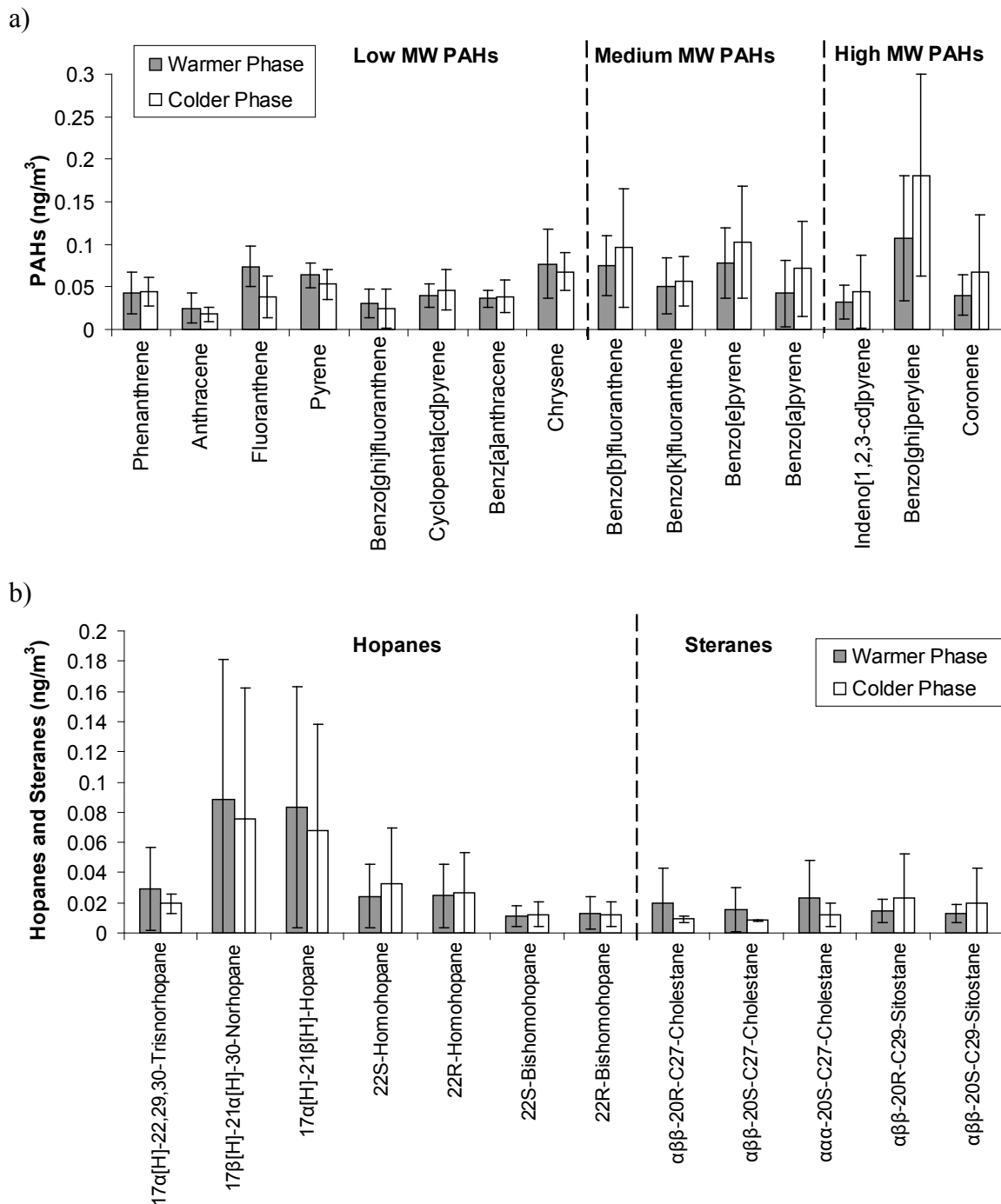
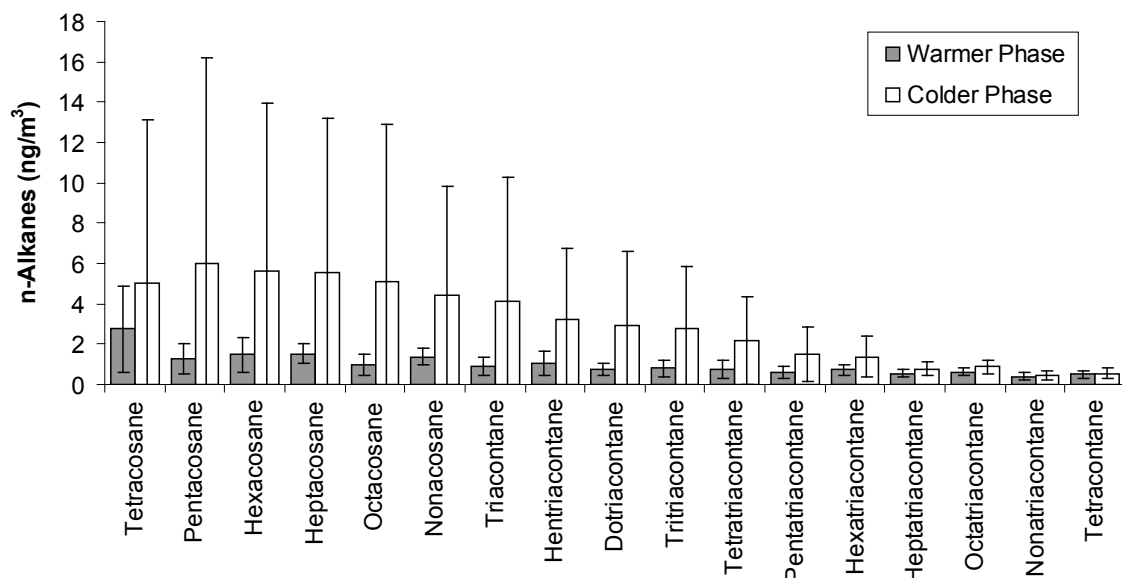


Figure 5.1 Outdoor concentrations of a) PAH's, b) Hopanes and Steranes, c) n-Alkanes and d) Acids. The presented values are average concentrations across all sites and error bars are standard deviation of these averages at each site.

c)



d)

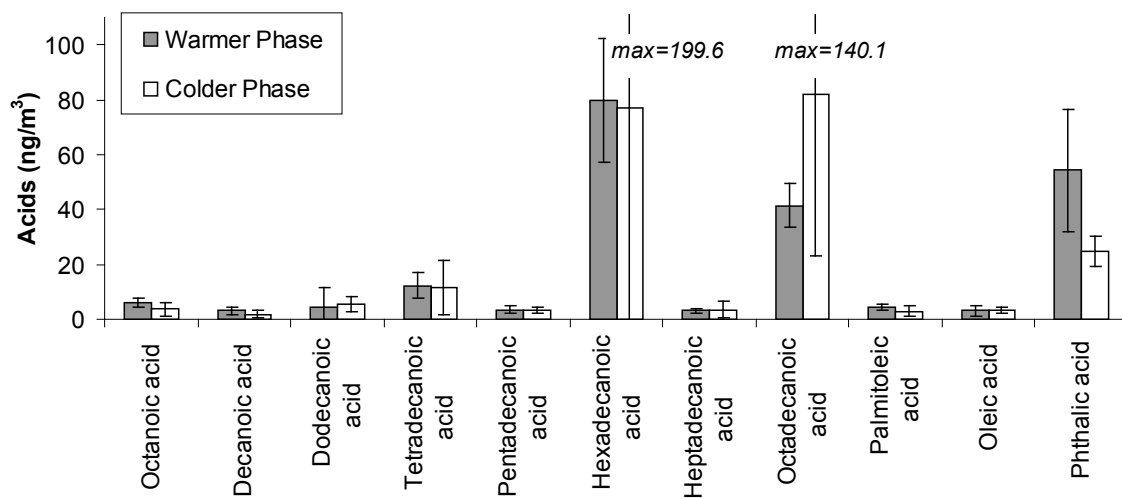


Figure 5.1 Continued

Hexadecanoic, octadecanoic and phthalic acids were the most dominant measured acids in quasi-UF PM (Figure 5.1d). Phthalic acid concentration in the warmer months was on average more than 2 times higher than in the colder periods. This variability is probably due to relatively higher photo-oxidation rates of organic gases in warmer conditions (Rogge et al. 1991; Pandis et al. 1993; Robinson et al. 2007).

5.4.3. Indoor-Outdoor Organics

Figures 2 and 3 present the relationship between indoor and outdoor concentrations for the studied organic compounds in the quasi-ultrafine particle range. Figure 5.2 shows the average indoor and outdoor levels of PAHs, hopanes and steranes, n-alkanes and organic acids at each site and phase of the study. Figure 5.3 shows the indoor / outdoor (IN / OUT) ratio and correlation coefficient of measured organic species for different phases of the study. The average outdoor level of the sum of all PAHs were lowest in Riverside (0.5 ng/m^3) and highest at San Gabriel 2 site (1.5 ng/m^3). The Riverside site was the most distant from the primary combustion sources (i.e. freeways and busy roadways), while the San Gabriel 2 site was closest to a major freeway (within 300 m) among all the sites. Typically, the average concentrations of the sum of all measured PAHs were similar, but slightly lower indoors than outdoors. Accordingly, the average IN / OUT ratio of most of the measured PAHs was close to or lower than 1 and correlation coefficients were always positive and generally high for most of the components (median R for all components = 0.60). These results suggest that most of the indoor PAHs in the quasi-ultrafine mode were of outdoor origin (mostly from motor-vehicle emissions), which is consistent with

previous studies (Ohura et al. 2004). PAHs generated by tobacco smoke were not expected indoors, since all of the studied retirement communities were non-smoking residences. Few individual PAH components, such as phenanthrene, anthracene and benz(a)anthracene, showed slightly higher than 1 average IN / OUT ratios and a relatively high standard deviation, hence indicating the possibility of indoor sources (e.g. natural gas appliances) for these species.

Similarly to PAHs, the sum of all measured hopanes and steranes concentrations was slightly higher outdoors than indoors at all sites. Average IN / OUT ratios were close to 1 (min=0.83, max=1.31 and median=0.94), accompanied by relatively high R values (median of R for all components = 0.74). As in the case of PAHs, these results highlight the dominant influence of outdoor sources to the measured indoor concentrations of hopanes and steranes, and the insignificant contributions from indoor sources. There were no clear seasonal patterns for the corresponding IN / OUT ratios and R values. As hopanes and steranes are more stable species compared to PAHs, the effect of temperature differences between indoor and outdoor environments on their indoor and outdoor associations becomes less significant. Similar relationships between the indoor-outdoor concentrations of hopanes and steranes (and also PAHs) were found in a recent study conducted in Tampa, FL (Olson et al. 2008).

The average indoor concentrations of the sum of all measured n-alkanes were typically higher than the corresponding outdoor levels. Exceptionally high indoor levels with large

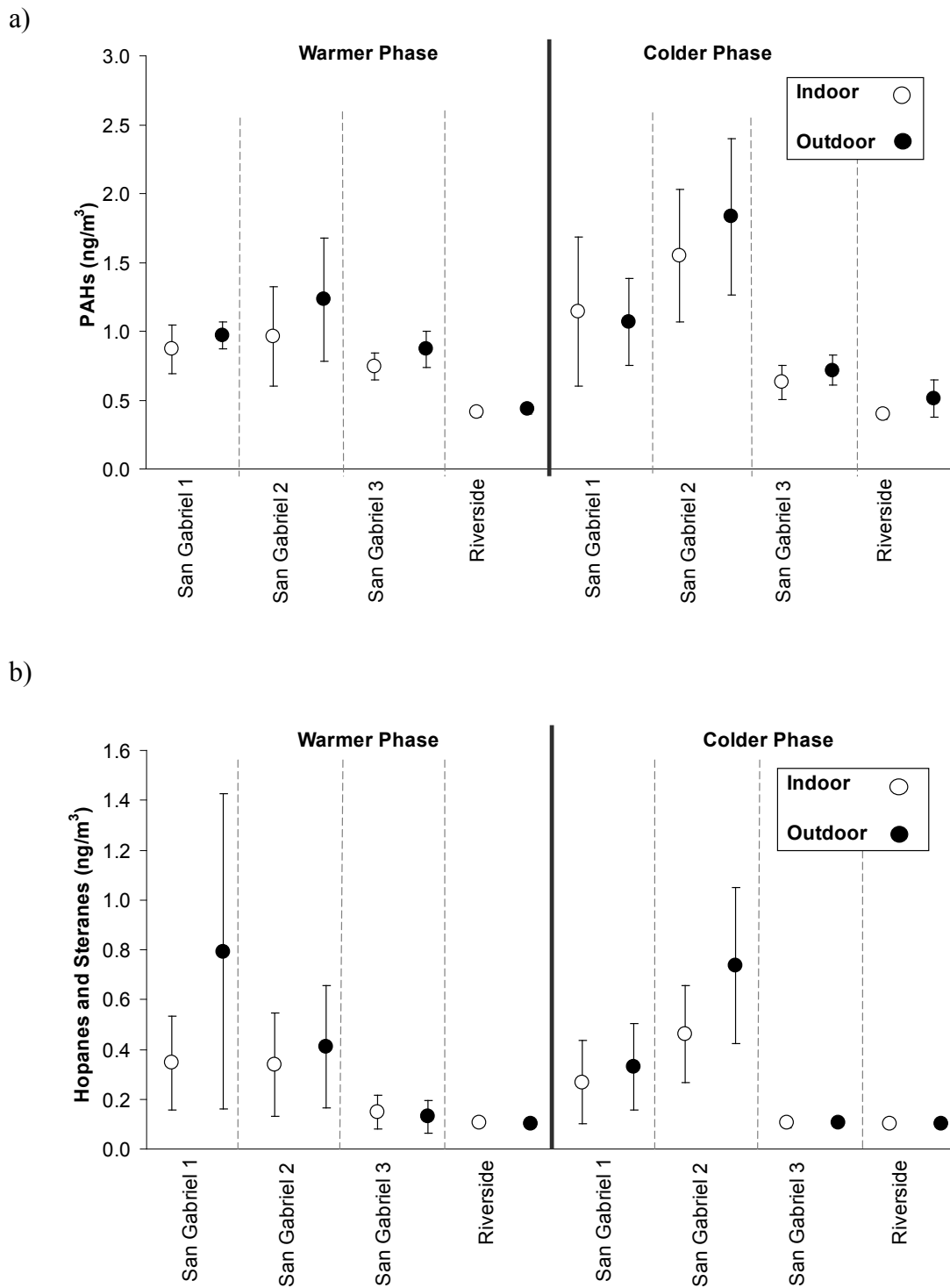
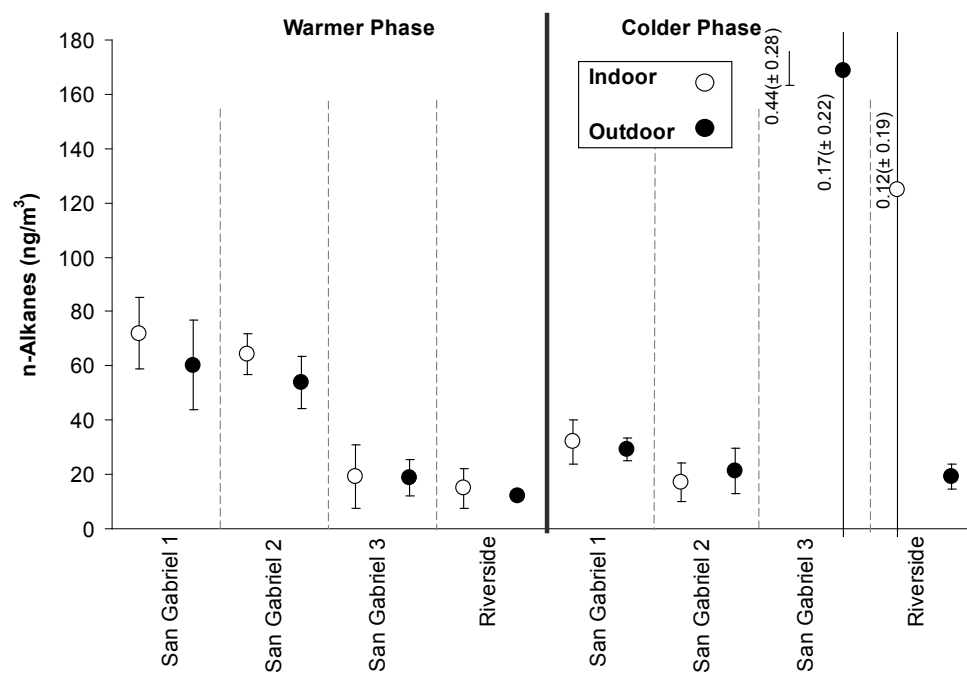


Figure 5.2 Concentration of total a) PAH's, b) Hopanes and Steranes, c) n-Alkanes and d) Acids. Dots are average of concentrations across all the sites and error bars are standard deviation of these averages at each site

c)



d)

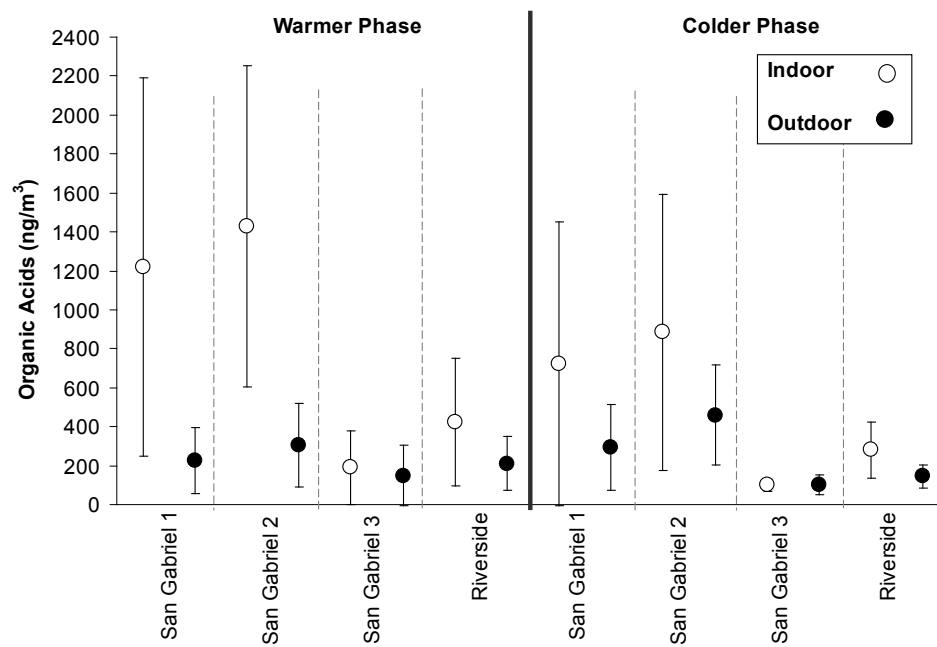


Figure 5.2 Continued

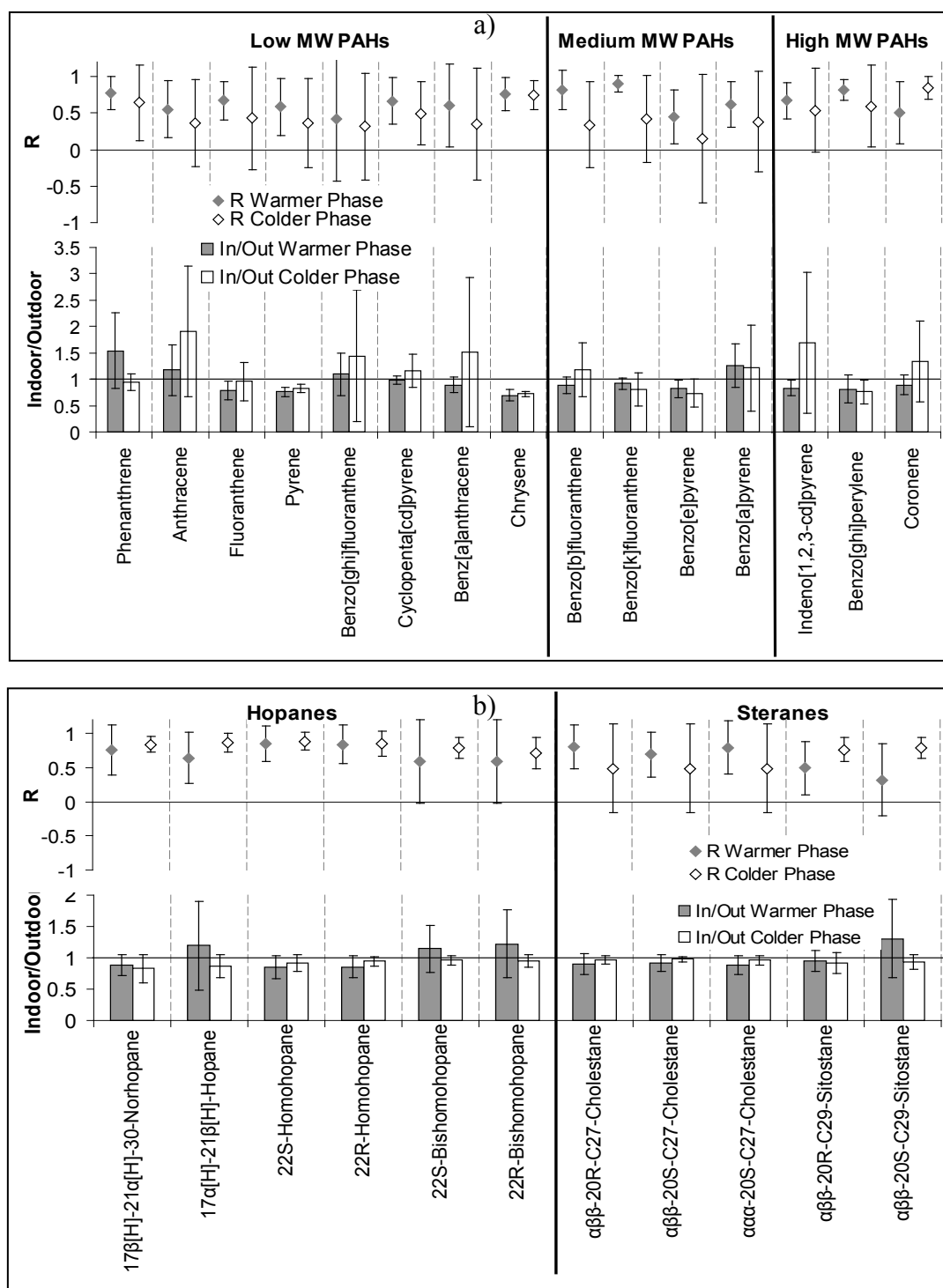


Figure 5.3 Correlation coefficient and indoor and outdoor ratios of a) PAHs, b) Hopanes and Steranes, c) n-Alkanes and d) Acids, values are averaged over the sites and bars are the standard deviation over the sites standard deviation, hence indicating the possibility of indoor sources for these species.

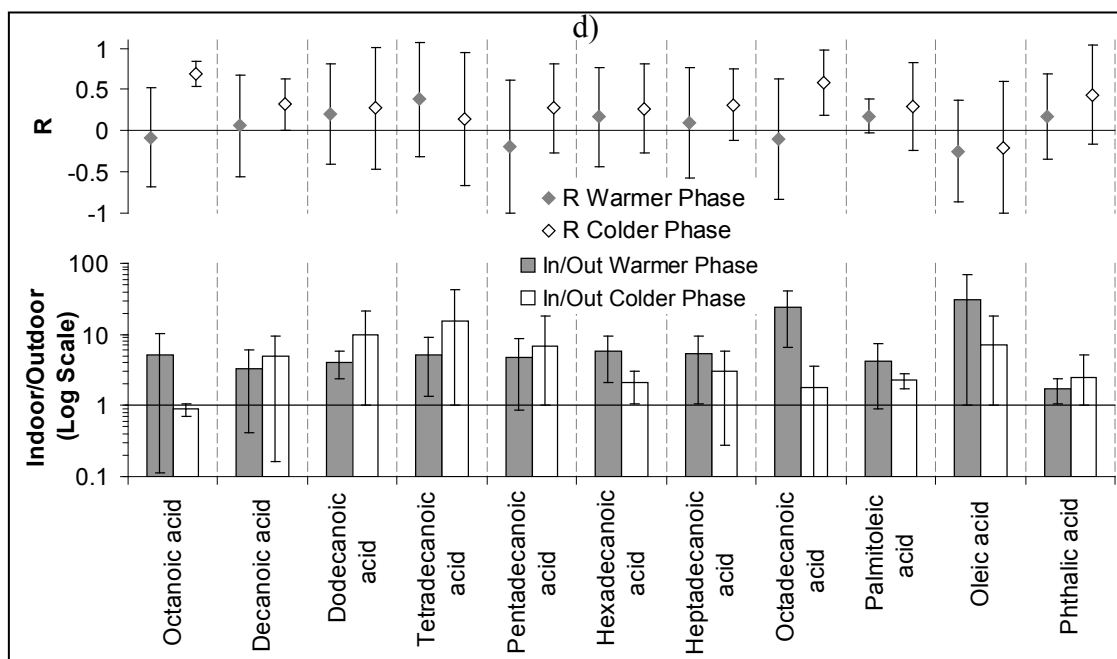
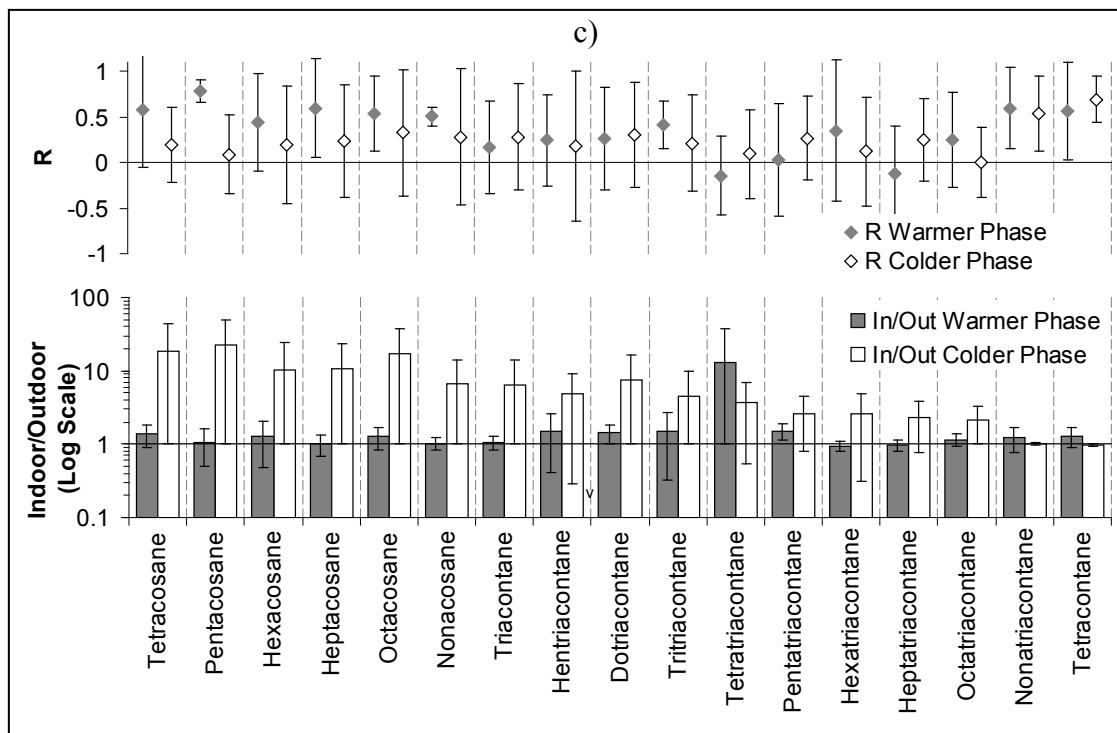


Figure 5.3 Continued

standard deviation were shown during the colder phase at San Gabriel 3 and Riverside sites. Most of the IN / OUT ratios of n-alkanes were much higher than 1 (up to 23 during the colder phase). R values were not always positive and, on average, were much lower than those found for PAHs, hopanes and steranes (min=-0.14, max=0.79 and median=0.41). The high IN / OUT ratios and low R values are indicative of the significant influence of indoor sources of n-alkanes. Considerably higher indoor n-alkanes levels compared to the outdoor levels were also found in a previous study (Olson et al. 2008). A variety of PM sources such as cooking, household products, dust, smoking and candle burning are known as indoor sources of n-alkanes (Fine et al. 1999; Schauer et al. 1999; Kleeman et al. 2008). The average indoor and outdoor concentrations of n-alkanes at the San Gabriel 3 site were substantially higher than those of at other sites.

Similarly to n-alkanes, average indoor concentrations of the sum of all measured n-alkanoic acids were higher than the corresponding outdoor levels. The indoor concentrations were substantially enriched (i.e, more than 3 times of outdoor levels) with a large variation in indoor concentrations during both phases at San Gabriel 1 and 2 sites. IN / OUT ratios of measured organic acids were higher than 1 (except for octanoic acid in the colder months) with average IN / OUT ratios of 4.8 (IN/OUT ratios of up to ~30 were found for oleic acid in the warmer phases). The high IN / OUT ratios were accompanied by low R-values (median R values = 0.19; lowest R = -0.27 for oleic acid in the warmer phases), indicating the influence of indoor sources for organic acids. Cooking is a major indoor source of these acids, and oleic and palmitoleic acid had often been used as

biomarkers of food cooking (Robinson et al. 2006). Throughout the study, no specific seasonal trends were observed for the association between indoor and outdoor organic acids.

The carbon preference index (CPI), i.e., the ratio of the concentrations of odd-carbon-to-even-carbon n-alkanes, is a parameter used to differentiate between anthropogenic and biogenic source contributions to PM (Simoneit 1986). Previous studies have shown that n-alkanes originating from anthropogenic sources have a CPI close to 1, whereas the CPI is generally higher than 2 when the biogenic sources are dominant (Simoneit 1986). The average indoor and outdoor CPIs at sampling sites varied from 0.60 to 0.95, suggesting that anthropogenic emissions (originated from fossil fuel) are the dominating sources in the studied area.

5.4.4 Spatial Variability

The coefficient of variance, which is also called coefficient of variation, ($CV = \text{standard deviation} / \text{mean}$) was determined for several measured components to investigate their spatial variation over the studied area (Figure 5.4). A limitation to the calculated coefficient of variations is that the sampling at different sites were not concurrent which can affect the calculated CVs in some extent, however CV was calculated separately for colder and warmer phases to reduce this effect. In general, colder phases were characterized by a higher CV values compared to the warmer phases, probably due to the

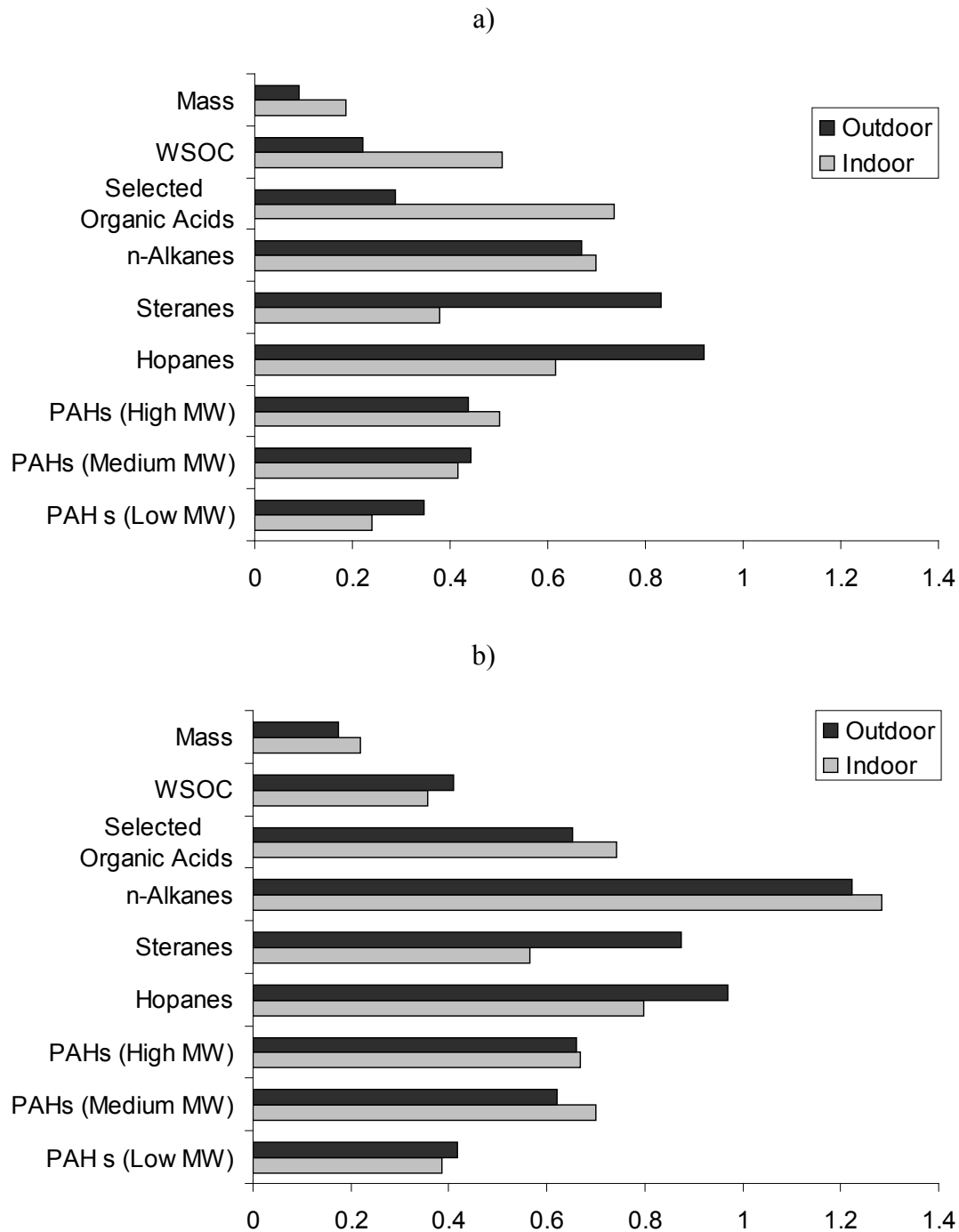
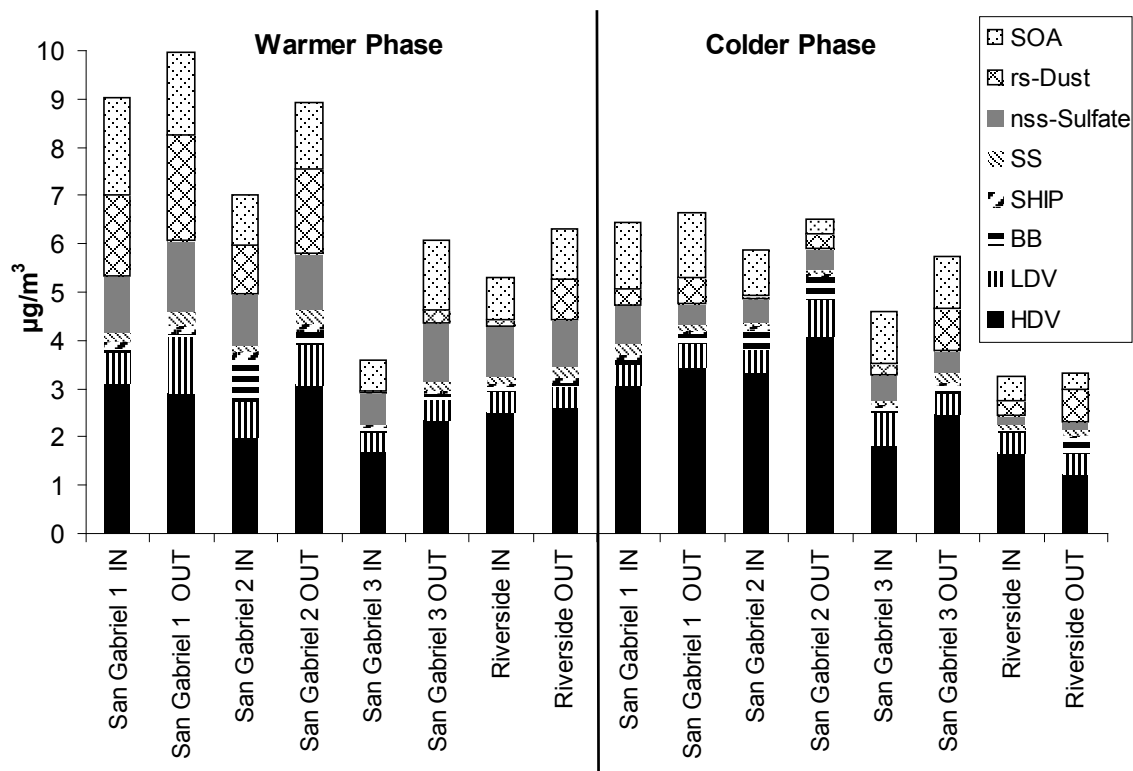


Figure 5.4 Coefficient of variance (CV) for indoor and outdoor organic groups for:
a) warmer and b) colder period of the study

lower regional atmospheric mixing and increased atmospheric stability during cold meteorological conditions. Quasi-UF mass concentrations showed relatively low variability over the studied sites for both indoors and outdoors (CV= 0.09 to 0.22). Outdoor WSOC was less variable in the warmer phases compared to colder phases. That can be explained by the seasonal variability of the main WSOC sources, i.e. secondary atmospheric processes and biomass burning (Weber et al. 2007). Secondary quasi-UF OC formation is expected to be higher in warmer periods due to higher photochemical activity, whereas higher biomass burning formation of OC is expected in colder conditions in the absence of wildfire. Biomass burning has localized effects on OC compared to secondary photo-oxidation formation of OC, which can influence the concentrations of several carbonaceous compounds on a regional scale. Although particulate OC formation by biomass burning is generally not significant (at least in the absence of wildfires) in the polluted Los Angeles basin (Minguillon et al. 2008), it may still affect the spatial variability of WSOC levels. Regarding indoor CVs of WSOC, the relatively high values in the warmer months may be due to the high levels of indoor WSOC at the San Gabriel 1 and 2 sites during these periods. The spatial variance (CV) of outdoor hopanes and steranes was 0.83 and 0.97, respectively, of the highest among all organic species. This variability originates from differences in the local traffic sources and their influence on each sampling site. Spatial variability in indoor and outdoor PAHs was similar, due to the significant contribution of outdoor originated PAHs to indoor PM.

5.4.5. Source Contribution Estimations

The results of the source apportionment of quasi-ultrafine particle mass are presented in Figure 5.5. Vehicular sources, including both HDV and LDV, showed the highest contribution for both indoor and outdoor particles at all sites (on average 1.67-4.86 $\mu\text{g}/\text{m}^3$ or 24-47% of the quasi-UF mass). Estimations of the HDV contribution were higher than those from LDV. This could be due to the location of the study sites, all situated in the eastern region of Los Angeles, where the traffic fleet has a higher fraction of HDV compared to the typical urban area of Los Angeles. The average percentage contribution of HDV to the total vehicle fleet (HDV + LDV) at the I-10, I-210 and I-60 freeways in eastern Los Angeles counties (San Bernardino and Riverside counties), where most of the sites were located, was ~10 to 15%, which is ~2-3 times higher than the corresponding percentage in Los Angeles urban area (values were estimated from data obtained from the Caltrans website; <http://traffic-counts.dot.ca.gov>). As we stated in the methods section, the LDV source profile used for CMB analysis is from a study conducted near the I-110 freeway, between downtown Los Angeles and Pasadena, CA (Phuleria et al. 2007). However, in the study areas, the emissions of EC from older vehicles can be higher than that at the I-110 (Schauer et al. 2002). This could bias the results obtained by the CMB analysis by underestimating the LDV contribution, because in this model, EC is a key determinant for discriminating between HDV and LDV. Therefore, higher EC levels emitted from old LDV can artificially increase the source contribution estimations for HDV.



SOA = secondary organic aerosol

rs-Dust = resuspended dust

nss-Sulfate = non sea salt sulfate

SS = sea salt

BB = biomass burning

LDV = light duty vehicles

HDV = heavy duty vehicles

Figure 5.5 Source apportionment of quasi-UF PM in the four sites and during the two sampling periods

The relative contribution of biomass burning to the measured indoor and outdoor quasi-UF mass was low (on average, from 0.06 to 0.87 $\mu\text{g}/\text{m}^3$, across all sites and phases of the study, with the exception of San Gabriel 2 site). The differences between indoor and outdoor contributions were low, except at the San Gabriel 2 site in the warmer phase. Average outdoor biomass burning contribution was 1.4 to 3.8 times higher in the colder phases compared to the warmer phase. Sea spray and ship emission contributions to PM were negligible, as it is expected for sites located far away from the ocean (median sea spray and ship contributions were 0.12 and 0.08 $\mu\text{g}/\text{m}^3$, respectively, over all sites and phases). Estimated indoor and outdoor non-sea salt sulfate contributions tracked each other at most of sites, suggesting that a substantial portion of indoor sulfate originates from outdoors (median = 0.72 $\mu\text{g}/\text{m}^3$ indoors and 0.74 $\mu\text{g}/\text{m}^3$ outdoors). Outdoor non-sea salt sulfate was, on average, 33% higher in warmer phases compared to colder phases, confirming the secondary origin of this pollutant (Rodhe 1999).

Candle and cigarette smoke sources were also used as an input for the CMB model, but the resulting contributions were negligible (no more than 0.02 $\mu\text{g}/\text{m}^3$ at all sites and during all phases of the study). Our CMB model was not able to apportion the contribution of cooking using common meat cooking source profiles (Schauer et al. 1999; Kleeman et al. 2008). This does not necessarily imply that the contribution of cooking to the quasi-UF particle mass was negligible, but it can indicate that the cooking source profile used is not representative of the specific food cooking emissions at our study sites. The influence of food cooking emissions on indoor PM is evidenced by the elevated

levels of indoor organic acids such as oleic acid and palmitoleic acid, frequently used as biomarkers of food cooking (Robinson et al. 2006). The same study also showed that significant inconsistencies exist between ambient data and published source profiles for cooking, which makes it difficult to obtain reliable estimates of the relative contribution of cooking to ambient PM. Resuspended dust contributions were 0.02 to 1.66 $\mu\text{g}/\text{m}^3$ to indoor, and 0.27 to 2.17 $\mu\text{g}/\text{m}^3$ to outdoor quasi-ultrafine PM across all sites. Road dust and indoor activities are respectively main outdoor and indoor sources of resuspended dust. Warmer phase resuspended dust was on average more than 100% higher than corresponding colder phase levels over all outdoor stations. Estimated SOA accounted for 0.23 to 1.62 $\mu\text{g}/\text{m}^3$ of the indoor and outdoor quasi-ultrafine PM at all sites and phases. At some sites (e.g. colder phase of San Gabriel 2), estimated SOA concentrations were higher indoors than outdoors (up to ~ 3 times), which can be partially due to the formation of secondary particles in indoor environments from reactions of household products with ozone and to a lesser extent hydroxyl radicals (Destailats et al. 2006; Weschler and Nazaroff 2008). The average SOA contribution in the warmer phase was about 2 times higher than during the colder phase at all outdoor sites, which highlights the important role of photo-oxidation in the formation of SOA. The average un-apportioned fraction of quasi-UF PM was $33 \pm 15\%$ among all sites and phases. A fraction of this un-apportioned mass could be attributed to ammonium nitrate, which was not measured, but could account for as much as 2-3 $\mu\text{g}/\text{m}^3$ in the $\text{PM}_{0.25}$ mass concentrations, especially in the Riverside area (Kleeman et al. 1999; Hughes et al. 2002; Sardar et al. 2005). Moreover, there are uncertainties associated with the calculations of SOA. Part of this uncertainty

originates from the multiplication factor used to convert WSOC to SOA (2) and from the assumed fraction of WSOC in SOA (20%), as they both can vary with time and location; (Turpin and Lim 2001; Docherty et al. 2008). A study carried out in Tokyo showed that 6 to 26% of summer oxygenated organic carbon was water-insoluble (Kondo et al. 2007), whereas water-insoluble SOA fractions as large as 60% have recently been reported for urban environments (Favez et al. 2008). In a recent study by (Docherty et al. 2008) SOA was reported to comprise 45 to 90% of the organic fine aerosol mass in the Los Angeles basin.

Lastly, the estimated indoor LDV and HDV source contributions were similar to those calculated outdoors during both phases and at all retirement communities. This is indicative of the significant role of outdoor mobile sources on indoor environments and illustrates the high indoor infiltration of particles generated by mobile sources. This finding has important exposure and health implications considering that in an earlier publication generated from the CHAPS study, we found that traffic-related particles had much stronger associations with adverse health effects in the elderly retirees of the studied communities compared to uncharacterized indoor particles (Delfino et al. 2008).

5.5. CONCLUSIONS

The mass and chemical composition of indoor and outdoor quasi-UF PM levels generally did not show a clear seasonal pattern. However, the concentrations of most n-alkanes and n-alkanoic acid were higher in the colder periods and in the warmer months, respectively.

No major seasonal differences were found for PAHs, hopanes and steranes. High influence of outdoor sources (mainly vehicular sources) and insignificant contributions from indoor sources were observed for PAHs, hopanes and steranes. By contrast, indoor sources (e.g. cooking) impacted the measured indoor concentrations of n-alkanes and organics acids significantly. Inside some studied retirement communities we observed evidence of secondary organic aerosol formation, probably from reactions of household products with indoor ozone.

Vehicular sources showed the highest contribution among the apportioned sources for both indoor and outdoor particles at all sites (on average 24-47% of the quasi-UF mass). The contribution of mobile sources to indoor levels was similar to their corresponding outdoor estimates, thus illustrating the significance of these sources on indoor PM concentrations. A major implication of these findings is that, even if people (particularly the elderly retired population of our study) generally spend most of their time indoors, a major portion of the PM_{0.25} particles to which they are exposed comes from outdoor mobile sources. The significance of this conclusion is supported by the fact that indoor infiltrated particles from mobile sources were more strongly associated with the adverse health effects observed in the elderly subjects living in the studied retirement communities compared to uncharacterized indoor particles.

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Chapter 6.

Size-Segregated Inorganic and Organic Components of PM in the Communities of the Los Angeles Harbor

6.1. ABSTRACT

The Los Angeles Ports complex consists of the port of Long Beach and the port of Los Angeles. Due to the high levels of particulate matter (PM) emitted from many sources in the vicinity of these ports and to their projected massive expansion, the Harbor area will be the focus of future governmental regulations. This study aims to characterize the physicochemical properties of PM at locations influenced by port-affiliated sources. PM samples were collected concurrently at six sites in the southern Los Angeles basin for a 7-weeks period between March and May 2007. Four sites were set-up within the communities of Wilmington and Long Beach; one site was located at a background location near the harbors of the Los Angeles port; the sixth site, near downtown Los Angeles, was chosen to represent a typical urban area. Coarse (PM_{2.5-10}), accumulation (PM_{0.25-2.5}), and quasi-ultrafine (PM_{0.25}) mode particles were collected at each site. Samples were analyzed for organic and elemental carbon content (OC and EC, respectively), organic species, inorganic ions, water soluble and total elements. The carbon preference index (CPI) for quasi-UF and accumulation mode particles varied from 0.65 to 1.84 among sites, which is in the range of previous findings in areas with high influence of anthropogenic sources. In sites located close to harbor the average n-Alkanes and PAHs levels were respectively about 3 and 5 times higher than their corresponding levels at a site located in vicinity of harbor, but upwind of most of local sources. The ratio of hopanes to EC and hopanes to OC over all the sites were in the range of previous

roadside measurements near freeways with variable volumes of diesel truck traffic. High overall correlation of vanadium with nickel ($R=0.9$) and a considerable gradient of vanadium concentrations with distance to the port, suggest marine vessels as the major sources of these elements.

6.2. INTRODUCTION

Epidemiological studies have shown significant exposure-response relationships for the adverse health effects in association with particulate mass concentrations (Samoli et al. 2005; Atkinson et al. 2001). Fine particles (aerodynamic diameter, $D_p < 2.5 \mu\text{m}$; $\text{PM}_{2.5}$) have been more strongly associated with mortality and morbidity than coarse particles ($2.5 \mu\text{m} < D_p < 10 \mu\text{m}$; $\text{PM}_{2.5-10}$) (WHO 2003) whereas coarse particles have been associated more strongly with respiratory hospital admissions (Brunekreef and Forsberg 2005). Ultrafine particles ($D_p < 0.1 \mu\text{m}$; $\text{PM}_{0.1}$) are of particular interest in health-related studies due to their high number concentration in urban environments and ability to penetrate deep into the alveolar region of the lung (Delfino et al. 2005). Recent toxicological studies suggest that adverse responses per unit mass are associated more strongly with ultrafine particles than fine or coarse particles (Donaldson et al. 2002; Li et al. 2003; Oberdörster et al. 2001; Xia et al. 2004).

Along with the particle size, the chemical composition influences the toxicity of particulate matter (Oberdörster 1996; Anderson 2000). There are several types of highly toxic organic compounds in the atmosphere including quinones, polycyclic aromatic

hydrocarbons (PAHs), polychlorinated biphenyls and other organochlorine compounds, which may have acute effects (USEPA 2004; Li et al. 2003). Pollen spores and proteins (in the super micron fraction) are known allergens, whereas some components of bacteria and viruses are biologically generated toxins (Lighty et al. 2000). Carbonaceous matter and transition metals such as iron, copper, chromium and vanadium have been shown to generate reactive oxygen species and can contribute to oxidative DNA damage (Dreher et al. 1997). Secondary inorganic ions and sea salt as well as soil-related material are thought to be relatively benign, but they may affect the toxicity or bioavailability of other particulate components. In addition, endotoxins (mostly in coarse PM) are believed to play an important role in the development of organic-dust related diseases (e.g. Salonen et al. 2004). Because the atmospheric aerosols form a highly multi-component system, it is very difficult to discern a clear association between adverse health effect and specific chemical components. If health effects can be linked to certain sources of particulate matter, such information would be highly valuable for targeting control strategies.

The Los Angeles Basin is a megalopolis of about 15 million inhabitants, and has one of the most polluted atmospheres in the US due to the contributions of a multitude of traffic and other combustion sources. Studies in Los Angeles Basin examining atmospheric aerosols at multiple locations across the basin have been conducted since the early 1970s (Cass et al. 2000; Christoforou et al. 2000; Hughes et al. 1999; Russell and Cass, 1986). Most of these campaigns in Los Angeles have included only a few days or a week or two of sampling. Recently, a more comprehensive, longer term campaign was operated by the

Southern California Particle Center and Supersite (SCPCS), and the results are summarized by Sardar et al. (2005a). The focus of that campaign was to determine the size- fractionated and chemically speciated PM concentrations in the so-called “source” and “receptor” regions of the Los Angeles basin. The former are the central and western parts of the basin. In these regions, aerosols are mainly produced by primary emissions. By contrast, aged aerosols transported from the “source” regions dominate the eastern part of the basin, i.e. the “receptor” areas. PM samples in that campaign were not collected concurrently at the different sites, but were often apart by several years. To a certain degree, the consistent meteorology in Southern California may allow for seasonal comparisons between sites even if samples have been collected in different years. However, concurrent sampling in such a complex urban air basin would be highly desirable.

The focus of the present study is the area of the Los Angeles- Long Beach harbor. This is a unique area and quite disparate from the overall description of source and receptor sites of the basin that were discussed in the previous section. The Los Angeles port complex consisting of the port of Long Beach and port of Los Angeles is the busiest harbor in the US and ranks fifth in the world. In addition to the harbor activities (e.g. Marine vessels, heavy-duty trucks, locomotives, cargo handling equipments and harbor crafts), the local PM sources include some of the most heavily traveled freeways in southern California (CA-110, I710 plus local street traffic) and multiple petroleum refineries and other industrial facilities. Many smaller industrial and commercial businesses are also located

within the community. The Alameda Corridor runs through the eastern portion of the community. Thus, the surrounding area of the Los Angeles – Long Beach harbor constitutes arguably the most complex emission source scenario in California, and provides the potential for complex pollutant concentration gradients and high exposure conditions that cannot be identified by conventional monitoring approaches. Accordingly, it is crucial to assess the exposure gradient of the community in the surrounding environment. Nonetheless, there are not many studies on the micro-environmental spatial variations of chemical components and physical characteristics of particles in such complex environments.

The objective of this study is to characterize the chemical composition of ultrafine, accumulation mode and coarse particles across this community. Results from the gravimetric and chemical analysis are verified by means of chemical mass closure (CMC) (Sillanpää et al. 2006). Subsequently, the paper focuses on organic species and elemental components and their distribution in PM size fractions among the sites. These results provide new insight into the variation of size-segregated chemical composition of PM over the studied area.

6.3. EXPERIMENTAL METHOD

6.3.1. Sampling Sites

Size-segregated PM samples were collected concurrently at five sampling sites in the LA port area and one additional site further north (at USC), serving as a representative site of the urban Los Angeles air quality, sufficiently far from the harbor, thus not immediately impacted by the local sources of that area. Sampling was conducted daily from Monday to Friday over a 7-week period from March – May of 2007. The sampling site locations are shown in Figure 6.1 and their specifications and major potential emission sources are described in detail in subsequent paragraphs.

Site 1 and 2 were located in the communities of Wilmington to the west of Long Beach area. Site 1 was about 1.5 km east (mostly downwind) of a major freeway (CA-110) and about 1.5 km north of Pacific Ocean coast. The site was situated in an open field, at the intersection of a major street and a local residential street.

Site 2 was about 3 km north of the coast. It was located in the backyard of a single-family house in a residential area, at the intersection of two busy major streets. It was also next to the Alameda corridor, a 20 mile (32 km) freight rail "expressway", directly connecting the national rail system near downtown Los Angeles, to the ports of Los Angeles and Long Beach, running parallel to Alameda Street.

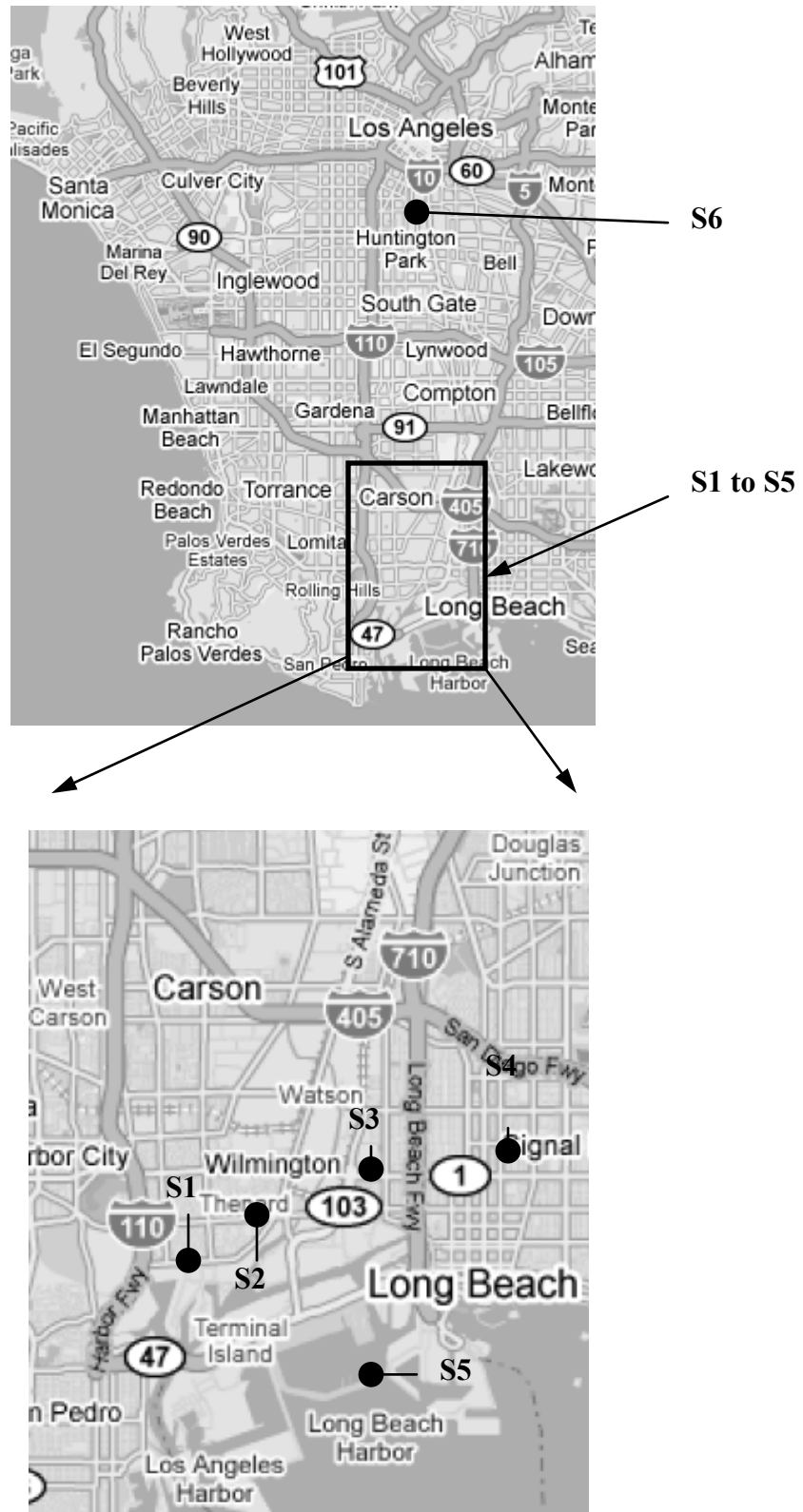


Figure 6.1 Sampling sites locations

Site 3 and 4 were located within the communities of Long Beach. Site 3 was about 3 km north of the coast with a major highway (CA-1) in less than 1 km to the south (hence upwind) of the site. The sampling site was located inside a semi-industrial area with one and two-story buildings around it.

Site 4 was about 7 km north of the coast and 1 km downwind (east) of a major freeway (I-710), which has the highest ratio (up to 25%) of heavy-duty diesel vehicles in the Los Angeles highway network (Ntziachristos et al. 2007a). Another major freeway (I-405) was located about 1 km to the south of this site. The samplers were placed on the rooftop of a one-story building right beside a major street. Industrial, commercial and residential one- and two-story buildings were surrounding the site. This site was thus influenced by an urban and industrial mix of sources.

Site 5 was located in Long Beach at a pier extending about 1.5 km toward Pacific Ocean upwind of Long Beach harbor. The sampling site was located in an open area at the end of the pier, which was surrounded by ocean at three sides, and a small tree-planted area on one side. This site served as the background area of Long Beach harbor. The maximum distance between Sites 1 to 5 was about 8 km.

Site 6 was located on the University of Southern California campus at the Southern California Supersite Particle Instrumentation Unit (PIU) trailer near downtown Los Angeles. The PIU is about 40 km north of the coast, 150 m east of a major freeway (CA-

110) and adjacent to a six level parking structure and various construction sites. This site represents a typical urban mix of downtown Los Angeles (Arhami et al. 2006) and was used for comparison to the harbor sites 1-5.

Sites 1-5 were located between latitudes of N33° 44' to N33° 48' and between longitudes of W118° 13' to W118° 15' and Site 6 were located at N34° 1' and W118° 17'.

6.3.2. Sampling Description

Two collocated Sioutas™ impactors (SKC Inc, Eighty-Four, PA), operated at a flow rate of 9 lpm (Misra et al. 2002; Singh et al. 2003), were implemented at each site to collect size fractionated PM samples. Zefluor filters (3 µm pore, Pall Life Sciences, Ann Arbor MI) were used in one impactor and quartz fiber filters (Pall Life Sciences, Ann Arbor MI) in the other impactor. Coarse (aerodynamic diameter, $D_p \geq 2.5 \mu\text{m}$; $\text{PM}_{2.5-10}$), accumulation mode ($D_p = 0.25-2.5 \mu\text{m}$; $\text{PM}_{0.25-2.5}$) and quasi-ultrafine ($D_p < 0.25 \mu\text{m}$; $\text{PM}_{0.25}$) particles were collected at each site. The impactors were placed inside temperature-controlled enclosures. The sampling inlet for each impactor was about 3 m in length (above the enclosure) and 0.95 cm in diameter and the vertical height of the inlet point from ground was at least 5 m. All sampling stations were mounted to the ground, except for Site 4, where the sampler enclosure was placed on the rooftop of a one-story building. Due to technical and weather-related problems, samples were not collected or were disregarded for week 7 at Sites 2, 4 and 5.

Local weather data, including temperature, relative humidity, wind speed and direction, were measured every minute at all sampling sites using a weather station (Vantage Pro2, Davis Instruments Corp., Hayward, CA). The meteorological data were not available for the weeks 1 to 5 at Site 1.

Prior to sampling, quartz filters were baked at 550°C for a minimum of 12 hours and Zefluor filters were cleaned using sequential flow through leaches of 2N HCl, 2N HNO₃ and high purity water. After cleaning the filters were air dried in a laminar flow hood in a trace metals clean room. At the end of each sampling period, all the filters and substrates were placed in petri dishes and quartz fiber filters were wrapped with aluminum foil. All the samples were kept frozen until chemical analysis.

6.3.3. Gravimetric and Chemical Analysis

Aerosol mass was determined by weighing the Zefluor filters before and after sampling with a microbalance (MT 5, Mettler-Toledo Inc., Highstown, NJ) having a sensitivity of 0.001 mg. The samples were allowed for equilibration in the weighing room at a relative humidity of 40–45% and a temperature of 22–24 °C for about 24 hours before weighing. The stability of mass readings was verified by weighting the laboratory blank filters before, after and during each weighing session. The electrostatic charges of substrate and filter materials were eliminated with a static neutralizer (500uCi Po210, NRD LLC, Grand Island, NY) before each weighing.

The chemical components of PM samples were analyzed at Wisconsin State Lab of Hygiene at University of Wisconsin-Madison. Daily (24 hr) samples from the each impactor were combined into weekly composites and analyzed for chemical speciation. Both the Zefluor and quartz fiber filters were cut into four equal parts. One quarter of the quartz fiber filters was analyzed by an Ion Chromatography (IC) for inorganic ions including chloride, nitrate, phosphate, sulfate, sodium, ammonium and potassium (Kerr et al. 2004). The second quarter of the quartz fiber filters was analyzed by the Thermal Evolution/Optical Transmittance (TOT) analysis (Schauer et al. 2003; Birch and Cary 1996) to determine the elemental and organic carbon (EC and OC) levels. The third set of the quartz fiber filters was composited for the whole 7-week period at each site and analyzed by a Gas Chromatography/Mass Spectrometry (GC/MS) for 92 different organic compounds (Zheng et al. 2002; Chowdhury, 2007; Schauer et al. 1999). The remaining quarter of quartz filter samples was archived for future analysis. Similarly, one of the four sets of Zefluor filters were composited for the whole 7-week period at each site and for each PM range and analyzed by Inductively Coupled Plasma Mass Spectrometer (ICP-MS) to determine 52 trace elements (Herner et al. 2006). The second set of Zefluor filters was also composited for the whole 7-week period at each site and analyzed for water-soluble elemental content. Samples were leached in high purity water and analyzed using a magnetic sector inductively coupled plasma mass spectrometer (HR-ICPMS, Finnigan Element 2). Three internal standards, gallium, indium and bismuth were used for the HR-ICPMS analysis along with authentic standards for each quantified elements. The remaining samples were archived for future toxicity analysis.

6.3.4. Chemical Mass Closure (CMC)

The sum of mass concentrations obtained from nine chemical components was used to assess the extent to which the gravimetrically measured particulate mass could be reconstructed from the sum of the measured chemical components (Sillanpää et al. 2006). The chemical constituents were grouped into nine components as follows: ammonium (NH_4^+), nitrate (NO_3^-), non-sea salt sulfate (nss-SO_4^{2-}), soil-derived compounds (crustal soil), sea salt, other elements, elemental carbon (EC), particulate organic matter (POM) and unidentified matter (UM). Table 6.1 summarizes the formula for calculating the grouped chemical components. The nss-SO_4^{2-} was calculated from the measured SO_4^{2-} , Na^+ and a standard seawater parameter; Sea salt concentrations were also estimated by multiplying Na^+ concentrations by a standard seawater parameter (3.25) (Brewer 1975). Si, Al, Ca, Fe and K, appear predominantly as oxides, used to calculate the soil-derived components (Brook et al. 1997). Sum of other elements, which include all the trace elements except major soil and sea salt elements, represents mostly the metal content of the particles. These elements are generated by a great diversity of sources, including metal industry, automotive vehicles (by abrasion of brakes, clutch etc.) and dust resuspension (containing minor soil elements). The POM was obtained by multiplying the thermo-optically measured OC by a factor of 1.4 (Turpin and Lim 2001; Russell 2003), which roughly converts the carbon mass of organic compounds to its total mass by including other elements. It should be noted that there are uncertainties associated with use of 1.4 as a multiplier for converting measured carbon to organic carbon, leading to uncertainties in estimating the total PM mass by means of CMC. The average organic

molecular weight per carbon weight is subject to change with location, season, and time, due to changes in the particular organic mixture (Turpin and Lim 2001). A higher multiplication factor than 1.4 is expected for more oxygenated organic compounds (Sardar et al. 2005b), which would be more prevalent in areas impacted by aged aerosols. In a previous study by Turpin and Lim (Turpin and Lim 2001), the range of 1.6 ± 0.2 was recommended to be used for urban areas, including that of Los Angeles. Thus, the factor of 1.4, which was used in this study, lies in the suggested range and has been used in previous recent studies in Los Angeles basin (e.g. Sardar et al. 2005b) as well as other urban areas (e.g. Sillanpää et al. 2006). The UM was obtained by subtracting the reconstructed mass (i.e., the sum of calculated chemical components) from the gravimetrically measured aerosol mass.

Table 6.1 The chemical components used in the mass closure studies

Component	Abbreviation	Formula
Non-sea-salt sulphate ^a	Nss-SO ₄ ²⁻	$[\text{Nss-SO}_4^{2-}] = [\text{SO}_4^{2-}] - 0.246 \times [\text{Na}^+]$
Nitrate	NO ₃ ⁻	
Ammonium ion	NH ₄ ⁺	
Sea salt ^a	SS	$[\text{SS}] = 3.248 \times [\text{Na}^+]$
Water-soluble soil ^b	WSS	$[\text{WSS}] = [\text{Fe}_2\text{O}_3] + [\text{Al}_2\text{O}_3] + [\text{CaO}] + [\text{K}_2\text{O}]$
Water-insoluble soil ^c	WIS	$[\text{WIS}] = [\text{Fe}_2\text{O}_3]_{\text{IS}} + [\text{SiO}_2]_{\text{IS}}^{\text{d}} + [\text{Al}_2\text{O}_3]_{\text{IS}} + [\text{CaO}]_{\text{IS}} + [\text{K}_2\text{O}]_{\text{IS}}$
Other elements	OE	$[\text{OE}] = \text{Sum of the analysed elements excluding soil elements}$
Elemental carbon	EC	
Particulate organic matter	POM	$\text{POM} = 1.4 \times [\text{OC}]$
Unidentified matter	UM	$[\text{UM}] = [\text{PM}_x] - [\Sigma \text{ identified components of PM}_x]$

^aBrewer (1975).

^bWSS is based on ICP-MS extraction of the soluble portion of these species

^cWIS is based on ICP-MS extraction of the total - soluble portion of these species.

^d[Si] has been estimated from [Al], $[\text{Si}] = 3 \times [\text{Al}]$ (Sillanpää et al, 2006).

6.4. RESULTS AND DISCUSSION

6.4.1. Overview of the Data

Weather station data collected during the sampling campaign at each site are presented in Table 6.2. Site 5, which was located at the pier, was somewhat colder (average $T=14.7$ °C), windier (average $WS=3.0$ m/s) and more humid (average $RH=75\%$) than the other sites, as one would expect. Averaged meteorological data over the sampling period were similar across the other sites, with the average temperature, relative humidity and wind speed varying in the ranges of 16.6-19.1 °C, 52-63% and 0.8-2.3 m/s, respectively. These meteorological data reaffirm the overall climatological stability of Los Angeles and show that weather conditions did not have a considerable effect on differences of the PM and its components between the sampling sites. In most of the sites, the prevailing wind was from the southwest, except at Sites 1 and 3, where a major part of wind directed from north and northwest, respectively. It should be mentioned that meteorological data was available for only the weeks 6-7 of sampling at Site 1.

The mean mass concentrations of three PM size ranges measured at the sampling sites are presented in Figure 6.2. The campaign mean PM_{10} concentrations varied in the range of 13.9-26.8 $\mu g/m^3$. The lowest PM_{10} concentrations were measured at Site 1 and Site 5 whereas the concentrations at the other sites were $\geq 22.8 \mu g/m^3$. The mass distribution between three measured size ranges was relatively different among sampling sites. Quasi-UF particles were the dominant PM fraction (49%) at Site 1, whereas Site 6 was

Table 6.2 Meteorological data during the sampling campaign at sampling sites

Site		Temperature (°C)	RH (%)	Wind Speed (m/s)	Wind Roses
1	Average	19.1	57	1.4	
	St Dev	5.4	21	1.2	
	Min.	12.2	12	0.0	
	Max	35.9	87	5.0	
2	Average	17.6	58	0.8	
	St Dev	4.6	19	0.7	
	Min.	9.2	12	0.0	
	Max	36.9	86	4.7	
3	Average	16.6	63	1.5	
	St Dev	4.0	21	1.3	
	Min.	8.5	10	0.0	
	Max	34.2	92	6.5	
4	Average	16.6	63	2.3	
	St Dev	4.4	26	1.3	
	Min.	9.2	3	0.4	
	Max	35.5	100	7.4	
5	Average	14.7	75	3.0	
	St Dev	1.6	16	1.9	
	Min.	10.9	24	0.0	
	Max	21.6	93	8.8	
6	Average	17.3	52	1.5	
	St Dev	4.2	22	0.8	
	Min.	10.9	5	0.1	
	Max	35.0	89	3.9	

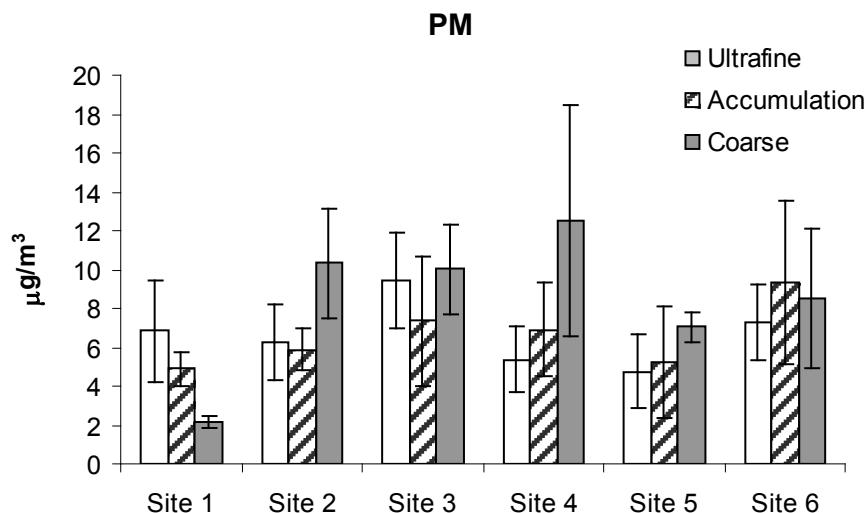


Figure 6.2 Particle mass concentrations in the quasi-UF, accumulation and coarse mode measured at six sampling sites. Error bars represent standard deviations, which are calculated for components on a weekly basis

dominated by accumulation mode particles (37%). The coarse particles had the highest contribution to PM_{10} in the other four sites (37% to 50%).

6.4.2. Chemical Mass Closure (CMC)

The mass closure results of different particle size ranges at each sampling site are shown in Figure 6.3. The major components of each size fraction and their contributions are described below.

Quasi-ultrafine mode. The POM was the dominant component of quasi-UF particles, followed by nss-sulfate and EC. The highest POM contribution was observed at Site 4 (50%) whereas its contribution was lowest at Site 3 (27%). The organic carbon consists

of both primary OC and secondary OC. The primary OC, emitted mainly from various combustion sources, is dominated by a mode around 0.1 to 0.2 μm (Maricq, 2007 ; Hildemann et al. 1991), which makes it fall mostly in the quasi-UF particle range of our study. The generally high correlation between OC and EC ($R^2=0.66$) in quasi-UF mode indicates that the majority of OC in that range is attributed to primary sources. The nss-sulfate is a secondary aerosol component that is predominantly formed in the atmosphere through the oxidation of sulfur dioxide (Rodhe 1999). The nss-sulfate contribution to total mass of quasi-UF varied in the range of 8.3-17%. Elemental carbon (EC) consists of graphite-like species and is formed by incomplete combustion of organic material (Seinfeld and Pandis 1998). The EC contributed 7.0-11% to the quasi-UF particle mass. Insoluble soil elements, ammonium, sea salt and nitrate, contributed 1.6-9.0% to the quasi-UF particle mass. The contribution of sea salt (7.4%) at Site 5 was more than two times higher than that at the other sites. Recent studies have shown that sea spray can generate primary particles even in the ultrafine range (O'Dowd and De Leeuw 2007). Elements associated with soluble soil had only a small impact (<0.60%) on the quasi-UF particle mass. The gravimetric mass was somewhat higher than the reconstructed $\text{PM}_{0.25}$ mass in each sampling site. The unidentified matter in Sites 1, 4, 5 and 6 ranged from 6.7% to 26%, which is within the methodological uncertainties as well as the uncertainties associated with the multiplication factor for OC. A higher fraction of unidentified matter was found in Site 2 (36%) and Site 3 (45%). The discrepancy may be due to the following factors: 1) the actual OC-to-POM ratio may differ from the applied factor (1.4) and it can vary between the sites and different size ranges; 2) as discussed

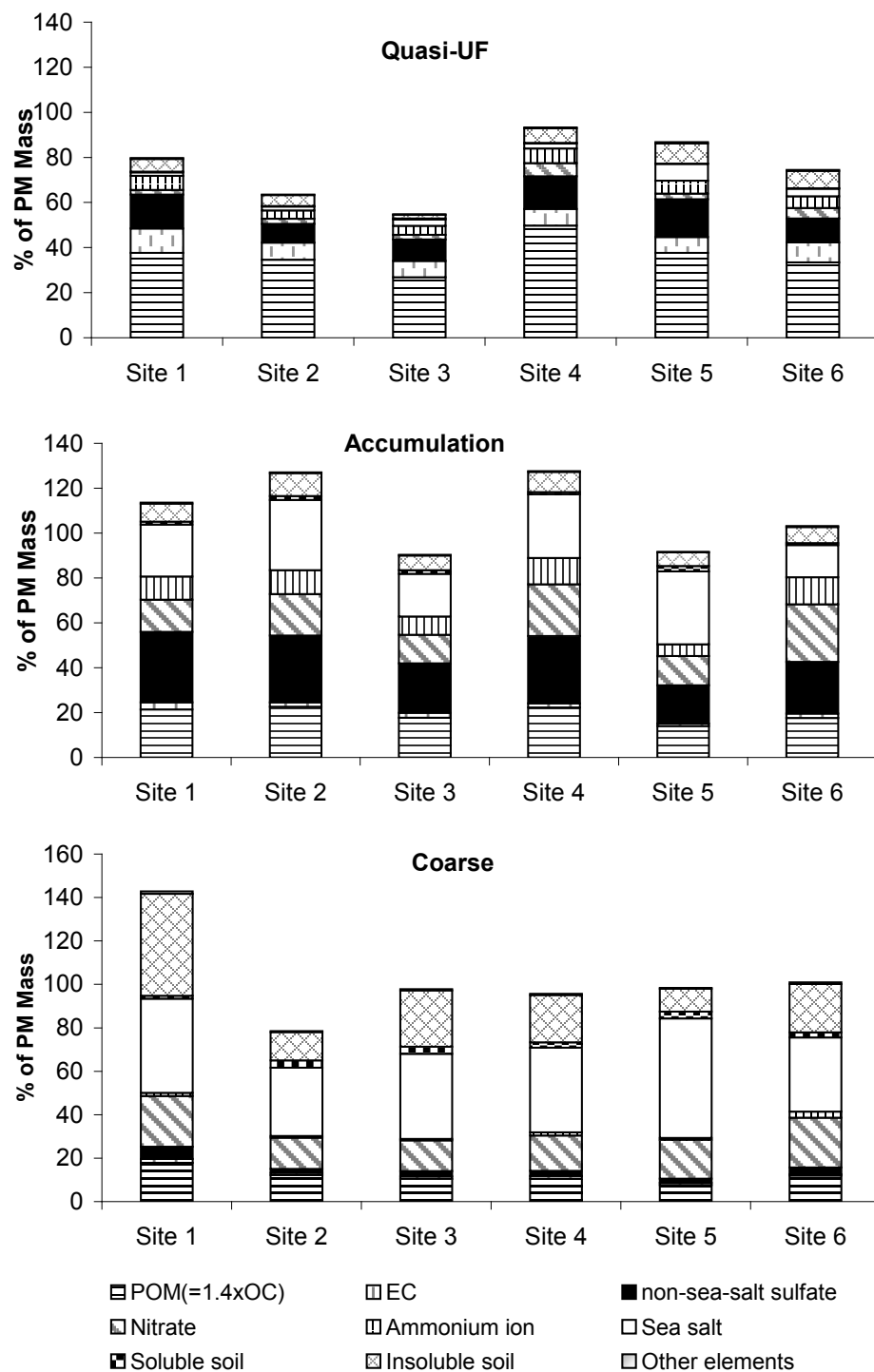


Figure 6.3 The contributions of nine chemical component-groups to the mass of quasi-UF, accumulation mode, fine and coarse particles measured at the six sampling sites. The chemical mass closure for fine particles is based on the sum of the concentrations measured in quasi-UF and accumulation mode

earlier, the sample collected on Zefluor filters was used for mass measurement, while the major chemical components of reconstructed mass were quantified from the samples collected on quartz fiber filters. The cutoff size (D_{50}) between quasi-UF and accumulation mode may also be slightly lower for the quartz fiber filter than the Zefluor filter, since other collection mechanisms in addition to inertial impaction play a role while using the porous impaction substrates (Saarikoski et al. 2008).

It should be noted that positive artifact due to adsorption of gaseous organic vapors on the quartz after-filter used to collect quasi-UF particles might have occurred during our sampling. In previous studies in the Los Angeles basin (Kim et al. 2001; Sardar et al. 2005), it was shown that the positive organic artifacts approached a nearly constant saturation value of 1-1.5 $\mu\text{g}/\text{m}^3$ of OC for 24 hr sampling periods at similar flow rates to those of our impactors, suggesting that these artifacts may be more important at lower PM mass concentrations than those reported in our study. Moreover, possible negative artifacts caused by volatilization of these organic vapors over a 24 hr sampling period may compensate for some of the adsorption artifacts (Sardar et al. 2005). Given the likely occurrence of these positive artifacts, however, the statements made in previous paragraphs regarding quasi-ultrafine OC (and POM) concentrations need to be qualified and put into perspective.

Accumulation mode. The major chemical components found in the accumulation mode were nss-sulfate, sea salt, POM and nitrate—each of them accounted for 15-30% of the mass. The contributions of these major components were rather evenly distributed over

the studied area. In contrast to quasi-UF and coarse particles, the accumulation mode particles remain longer in the atmosphere due to weak removal mechanics, which enables them to transport far from their sources and to disperse evenly through an urban area (Seinfeld and Pandis 1998). Both ammonium and insoluble soil accounted roughly for 10% of the accumulation mode mass. The contributions of EC and soluble soil were in the magnitude of a few percent, whereas that of other elements was less than half percent. In the site located at the pier (Site 5), the EC contribution was about half compared to that measured at the other sites. This site can be influenced by some primary EC emissions, mainly in quasi-UF mode, from nearby ships. The reconstructed mass was close to or higher than the measured mass (92-128%) in accumulation mode, contrary to quasi-UF mode. The relatively higher reconstructed mass may be explained by the differences in cutoff sizes mentioned above hence a part of large ultrafine particles were collected on quartz fiber substrate while bypassed this stage in Zefluor sampling. In addition the actual OC-to-POM ratio may differ from the applied factor (1.4), which results in the under- or overestimation of the particulate organic matter.

Coarse particles. Contrary to fine particles, coarse particles are typically composed of windblown dust, large sea salt particles from sea spray and mechanically generated anthropogenic particles, as well as biogenic particles (e.g. pollen, fungal spores and bacteria). The major contributors to coarse particles mass were sea salt (31-55%) and insoluble soil (11-47%), followed by nitrate (14-23%) and POM (8-18%). The coarse particles in Site 5 were heavily dominated by sea salt (55%). Due to their size, these

larger sea salt particles cannot be transported far from the source, which can be seen from the low sea salt concentration at Site 6. Among secondary inorganic ions, nitrate had clearly the highest contribution to coarse PM. Unlike the case of nitrate in fine particles, coarse particulate nitrate is predominantly formed in the reactions between nitric acid and sea salt or mineral compounds (Kerminen et al. 1998; Pio and Lopes 1998). Soluble nss-sulfate, soluble soil, ammonium, EC and other elements had a minor contribution to this PM size fraction (<3%). Excluding Site 1, the fraction of unidentified matter ranged from -0.9 % to 22%, which is within the methodological uncertainties. An underestimation in the reconstructed mass calculations is partly due to the assumption that the soil-related elements exist only as oxides, but other mineral compounds are likely present in the coarse PM fraction. The reconstructed coarse mass for Site 1 samples was 43% higher than the gravimetrically measured mass. This bias is likely due to the very low mass concentration of coarse particles ($2.2 \mu\text{g}/\text{m}^3$) at Site 1, which causes relatively high uncertainty in the result.

6.4.3. Organic Species Concentrations

Table 6.3 presents the size-fractionated concentrations of n-alkanes. n-Alkanes concentrations varied from 6.4 to $43.3 \text{ ng}/\text{m}^3$ in quasi-UF and from 2.3 to $27.4 \text{ ng}/\text{m}^3$ in accumulation mode particles at all six sites. Fraser et al. (1997) has shown that n-alkanes are emitted from both anthropogenic sources (mainly combustion process) and biogenic sources (e.g. plants and bacterial activities). Site 5 had substantially lower levels of fine particulate n-alkanes ($8.7 \text{ ng}/\text{m}^3$) than Sites 1 to 4 ($26.0\text{-}63.8 \text{ ng}/\text{m}^3$). Site 5 was located

upwind of local anthropogenic sources (e.g. vehicular sources), while Sites 1 to 4 were in the same vicinity as Site 5, but downwind of local anthropogenic sources. Site 2 had the highest particulate n-alkanes levels compare to other sites (63.8 ng/m^3 in fine mode), which indicates a significant influence of local combustion sources (likely surface street traffic, with frequent vehicle acceleration- deceleration) on this site.

Carbon preference index (CPI), i.e., the ratio of the concentrations of odd-carbon-to-even-carbon n-alkanes, is an indicator to differentiate between anthropogenic and biogenic source contribution to PM (Simoneit 1986). Previous studies have shown that n-alkanes originating from anthropogenic sources have a CPI close to unity, whereas the CPI is generally higher ≥ 2 when the biogenic sources are dominant (Simoneit 1986). The calculated CPIs at the six sampling sites are presented in Table 6.3. The CPIs varied from 0.74 (Site 2) to 1.36 (Site 6) in quasi-UF mode particles, and from 0.65 (Site 1) to 1.84 (Site 5) in the accumulation mode. These values confirm that anthropogenic emissions are the dominating sources of fine particulate matter emissions in the studied area. The relatively high CPI in accumulation mode at Site 5 (background site) implies a lower influence of anthropogenic sources. However, the low CPI of 0.9 in quasi-UF mode at this site could be due to primary emission of quasi-UF particles from ships located upwind of that site.

Table 6.3 Measured n-alkanes and calculated carbon preference index (CPI) for quasi-UF and accumulation mode particles at all sampling sites

		$\Sigma n\text{-alkanes (ng/m}^3\text{)}$	$C_{\max}$	CPI ^a
Quasi-Ultrafine	Site 1	20.66	C26 (1.24)	0.77
	Site 2	43.28	C28 (4.54)	0.74
	Site 3	19.67	C25 (2.78)	0.89
	Site 4	17.84	C24 (2.75)	0.81
	Site 5	6.42	C24 (1.08)	0.90
	Site 6	8.41	C25 (1.15)	1.36
Accumulation	Site 1	27.38	C34 (2.68)	0.65
	Site 2	20.47	C24 (1.47)	0.81
	Site 3	22.41	C31 (1.83)	0.85
	Site 4	8.11	C29 (1.10)	0.79
	Site 5	2.29	C27 (0.41)	1.84
	Site 6	4.52	C25 (0.62)	1.35

^aCPI = $\Sigma C(2n+1)/\Sigma C(2n)$, $n = 7-20$

PAHs are also products of incomplete combustion of different organic matter and their composition and emission rate are dependent on combustion processes and atmospheric conditions (Manchester-Neesvig et al. 2003). The PAH concentrations in quasi-UFP and accumulation mode are shown in Figure 6.4. In general, PAH concentrations were higher in quasi-UFP mode compared to accumulation mode, since they are species of primarily emitted aerosols, as it was shown in previous studies (Fine et al. 2004; Phuleria et al. 2007). Tunnel studies suggested that heavy molecular weight PAHs (e.g. coronene) are primarily originated from poorly operated gasoline-powered vehicles (Miguel 1998; Lough et. al. 2006; Phuleria et al. 2006). The highest coronene concentration was observed at Site 2 (0.07 ng/m³), suggesting a possible impact from poorly operating gasoline powered engines associated with the local street traffic in that site. The transient operation of the vehicle engines, which is characteristic of urban surface street driving conditions (compared to the more even cruise-mode driving conditions of the freeways) may have also contributed to the higher concentrations of almost all organic species

coming from combustion in that site. It should be noted that coronene was close to or under the detection limit of the GC/MS method in quasi-ultrafine particles at Sites 4, 5 and 6 and in accumulation mode at all the sites. Site 5 had the lowest level of particulate PAHs (0.1 ng/m^3) since it was upwind of most of combustion sources. The low, but still measurable levels of PAHs at this site may originate from ship and boat traffic upwind of this site. The fine particulate PAHs concentrations at the studied sites ranged from 0.1 to 0.4 ng/m^3 , and were close to but somewhat lower than the range reported in previous studies (Manchester-Neesvig et al. 2003; Ning et al. 2007; Lough et al. 2006). It should be noted the PAH levels in this study represent concentrations averaged over an entire day. However, diurnal variation of different molecular weight PAHs are generally substantial, especially during the morning rush hour, when they can be up to 5-6 times higher than the rest of the day (Ning et al. 2007).

Hopanes and steranes appear in the particulate emissions of gasoline- and diesel-powered vehicles due to their presence in engine lubricating oil (Rogge et al 1993 and 1996; Schauer et al. 1996 and 2002). These compounds are used as organic markers of vehicular emissions (Fine et al. 2004; Schauer et al. 1996, 1999, 2000 and 2002). Nonetheless, marine vessels may contribute to the urban concentrations of hopanes and steranes (Peter et al. 1992). More than 96% of the detected hopanes and all the detected steranes were contained in quasi-UFP mode (Figure 6.4). Sites 1, 2, 3 and 5, which were located within 3 km of the coast, had higher hopanes and steranes levels than site 4 (~7 km from the coast) and Site 6 (~40 km from the coast). This gradient of hopanes and

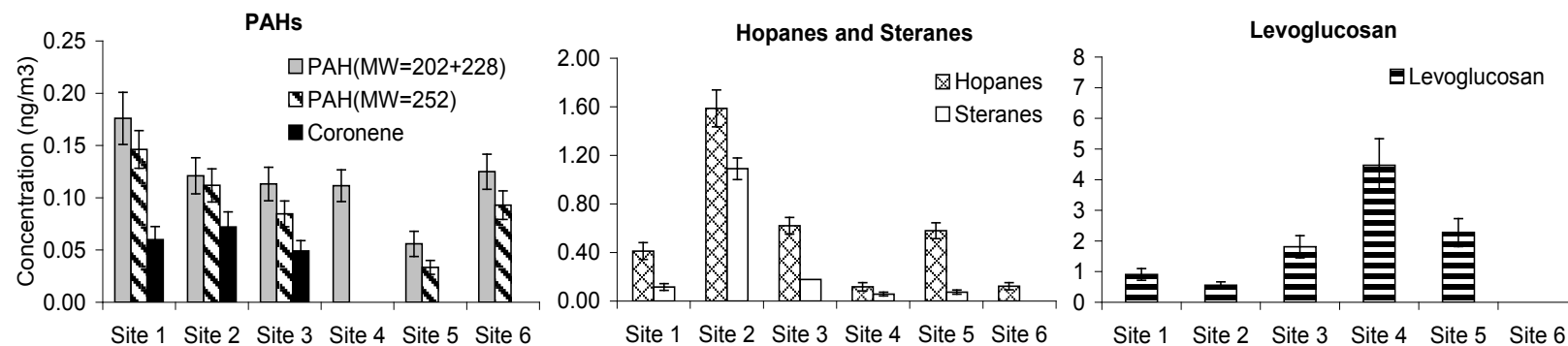
steranes concentrations may be due to impact of marine vessels in addition to that of vehicular emissions in each site. For example, non-negligible hopanes and steranes were measured at Site 5 (0.7 ng/m^3 of fine hopanes + steranes), although this site was clearly located upwind of most known vehicular sources in that area. The higher concentrations of hopanes and steranes were measured at Site 2 than all other sites (3.6 ng/m^3 of fine hopanes + steranes), which indicates a high vehicular emission from either gasoline or diesel-powered vehicles in addition to marine vessels emissions affecting this site. The total fine particulate hopanes and steranes concentrations at the studied sites ranged from 0.1 to 3.6 ng/m^3 and were consistent with the measured concentrations in previous studies in the Los Angeles area (Manchester-Neesvig et al. 2003; Fine et al. 2004).

The relative ratio of sum of hopanes to EC has been used in previous studies to distinguish between the influence of diesel and gasoline powered vehicles (Manchester-Neesvig et al. 2003; Fine et al. 2004). Diesel powered vehicles contribute generally to hopanes and steranes concentrations and higher amounts of EC, whereas gasoline powered vehicles contribute to hopanes and steranes and smaller amounts of EC (Manchester-Neesvig et al. 2003; Schauer et al; 1999; Fraser et al. 1997). Figure 6.5 shows the measured hopanes and EC levels (points) at all the sites compared to average levels measured near I-710 freeway (with the highest ratio of diesel powered vehicles in the entire state of California), shown as a solid line, and average levels measured near I-110 freeway (less than 3% diesel powered vehicles), shown as a dashed line (Phuleria et al. 2007). The plotted data points represent the fine fraction particles (i.e., the sum of

quasi-ultrafine and accumulation mode concentrations). Site 5, which is the background site, had the lowest level of EC compare to the other sites, as it was anticipated. For the rest of the sites located close to harbor, the data points lie closer to the previously measured EC –to- hopanes ratio for diesel vehicle emissions, except for Site 2. Site 2 had the highest hopanes level accompanied with a relative high EC level. As it was discussed earlier, Site 2 is not situated in an area with an obvious high diesel vehicle impact, unlike Sites 1, 3, 4 and 6. The high hopane, sterane and EC levels maybe attributed to poorly maintained gasoline vehicles impacting that site as well as to the transient (frequent acceleration and abrupt stops as well as accelerating from stop lights) driving on the busy arterial roads that surround this site. When gasoline-powered vehicles perform hard accelerations, they temporarily reduce the efficiency of the catalytic converter, due to deviations from the stoichiometric fuel-air ratio (Maricq et al. 1999). Under the more steady-state conditions such as freeway driving, catalytic converters remove CO, NO, volatile organic compounds, and UFP with high efficiency.

The average ratio of hopanes/OC over all the sampling sites was 0.21 ± 0.17 (ng/ μ g), which agrees reasonably well with data measured near highways with either highly impact from heavy-duty vehicles (I-710, hopanes/OC = 0.42 ng/ μ g), or from gasoline vehicles (I-110, hopanes/OC = 0.35 ng/ μ g) (Phuleria et al. 2007). These ratios support the notion that vehicular sources are the major OC contributors. The OC/EC ratios varies

a) Quasi-ultrafine



b) Accumulation mode

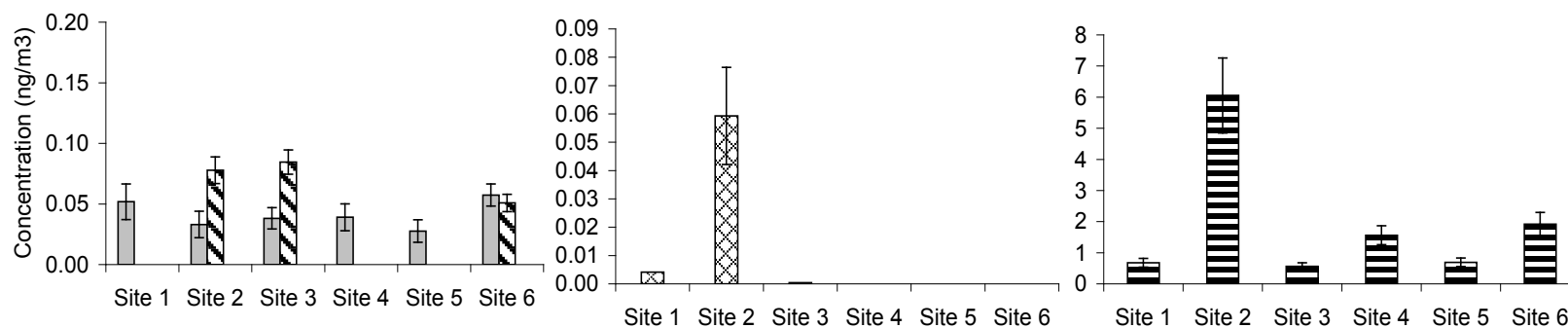


Figure 6.4 Concentration of PAHs (classified by molecular weight), Hopanes, steranes and Levoglucosan in a) quasi-UF and b) accumulation mode. Error bar represent the uncertainties in organics concentrations

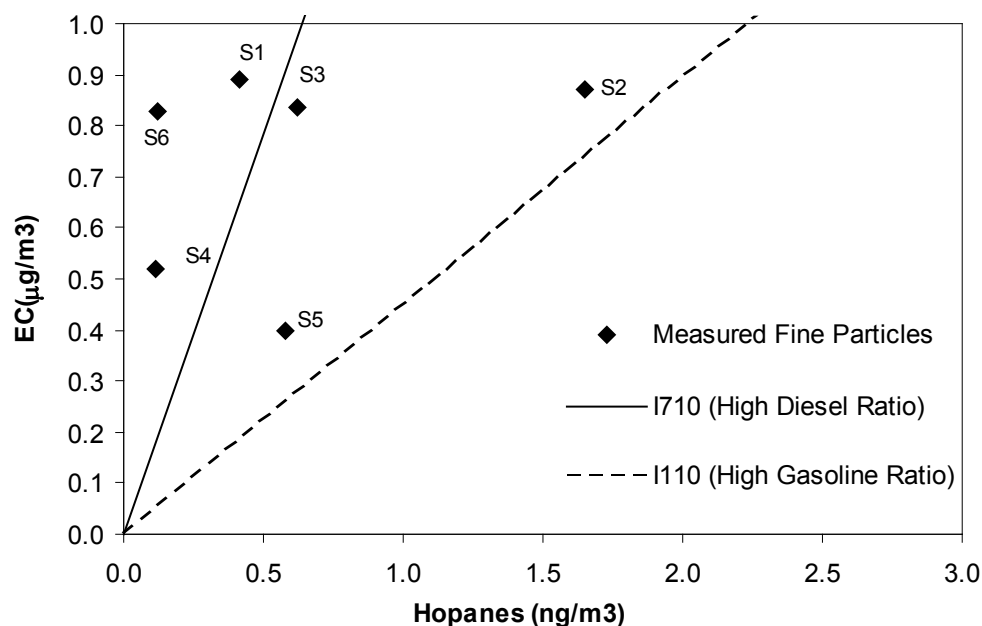


Figure 6.5 Relationship between hopanes and elemental carbon; Straight lines represent measured ratios in a previous study of urban PM_{2.5} in the proximity of freeways (Phuleria et al. 2007)

from 3.4 (Site 3) to 6.1 (Site 1), which lie within the ranges of those measured near the I-710 (OC/EC = 2.0) and near the I-110 freeway (OC/EC=7.7) (Phuleria et al 2007), inferring impacts from both diesel powered vehicles and gasoline vehicles. Levoglucosan is a pyrolysis product of cellulose and it is regarded as a good tracer for wood burning emissions (Schauer et al. 2000; Simoneit et al. 1999; Fraser et al. 1997). The quasi-UF-to-accumulation mode ratio of levoglucosan varied substantially across the sites, which suggests that local wood burning dominates the levels of levoglucosan in the investigated area (Figure 6.4). Site 2 and 4 had substantially higher levoglucosan levels than the other sites; however, levoglucosan at Site 2 mainly appeared in the accumulation mode (6.1 ng/m³ in accumulation and 0.6 ng/m³ in quasi-UF mode), while at Site 4 it was measured

in quasi-UFP mode (4.5 ng/m^3 in quasi-UF and 1.6 ng/m^3 in the accumulation mode). The levels of the fine PM levoglucosan during the sampling campaign (1.6 to 6.7 ng/m^3) were comparable to those reported by Manchester-Neesvig et al. (2003) and Fine et al. (2004) in Los Angeles. The levoglucosan- to- OC ratios for $\text{PM}_{2.5}$ varied from $0.6 \text{ ng/}\mu\text{g}$ (Site 1) to $2.0 \text{ ng/}\mu\text{g}$ (Site 2 and 4), which are far below the ratio reported for $\text{PM}_{2.5}$ influenced by biomass burning (about $44.0 \text{ ng/}\mu\text{g}$; Sheesley et al. 2007). These low ratios suggest that biomass burning is not a major source for particulate organic matter for the harbor communities.

6.4.4. Spatial Variance of Size Fractionated PM and its Components

The coefficient of variance ($\text{CV} = \text{standard deviation} / \text{mean}$) was determined for several measured species within each PM size range to investigate the spatial variation of these chemical components. To that end, during each week, mean concentrations across the six sampling sites (and standard deviations) were determined for PM, OC, EC and ions data where the concentrations were available concurrently at all the sites. The PAHs were classified into three groups on the basis of their molecular weight (MW) (Phuleria et al. 2007). The crustal material consisted of Al, Ca, Ti and Fe. Organic species with more than one missing data point (mainly due to concentrations lower than the detection limit) were excluded from the CV analysis. Figure 6.6 shows the CV of species for the three PM size ranges. PM mass in accumulation mode showed a relatively lower spatial variability ($\text{CV} = 0.25 \pm 0.06$) compared to the quasi-UFP mode ($\text{CV} = 0.47 \pm 0.16$) and the coarse mode ($\text{CV} = 0.46 \pm 0.01$). The accumulation mode particles have higher

residence times in the atmosphere, are subject to more intense atmospheric mixing and are thus more homogeneously dispersed over a large area. Conversely, the ultrafine and coarse mode PM tend to have local maxima closer to their emission sources and are removed faster from the atmosphere by diffusion and gravitational deposition (Seinfeld and Pandis 1998). In the quasi-UF particles, sodium and chloride are the most heterogeneously dispersed ions, with CV of 0.88 and 0.91, respectively. The high CV is mainly driven by the substantially higher concentration of these species at the background site (Site 5), which corresponds to high impact of sea salt generated by bubble bursting processes. EC, which is mainly emitted from diesel-powered vehicles, displayed relative high CV, which is indicative of the high variation of the influence of diesel vehicles on the six sites. By contrast, OC, which originates from most combustion sources (e.g. gasoline and diesel engine vehicles and wood smoke) showed relatively low CV values. Moreover, a fraction of OC can also be attributed to secondary formation processes in the atmosphere, which are regional in nature and result in a relatively homogenous dispersion of OC. Sulfate had the lowest CV values (hence the most homogeneous distribution over the investigated area) due to its mostly secondary origin. Steranes and hopanes showed also a high spatial variance (CV= 0.80 and 0.91, respectively), indicating a large variation in the impact of local traffic and marine sources on the different sites. The relative higher CV for these species was driven by the levels measured at Site 2, where the concentrations of hopanes and steranes were about 2-3 times higher than the rest of the sampling sites. PAHs had a low CV (0.2-0.3), at the same level with the CV of OC, and unlike the rest of the organic species in that size range.

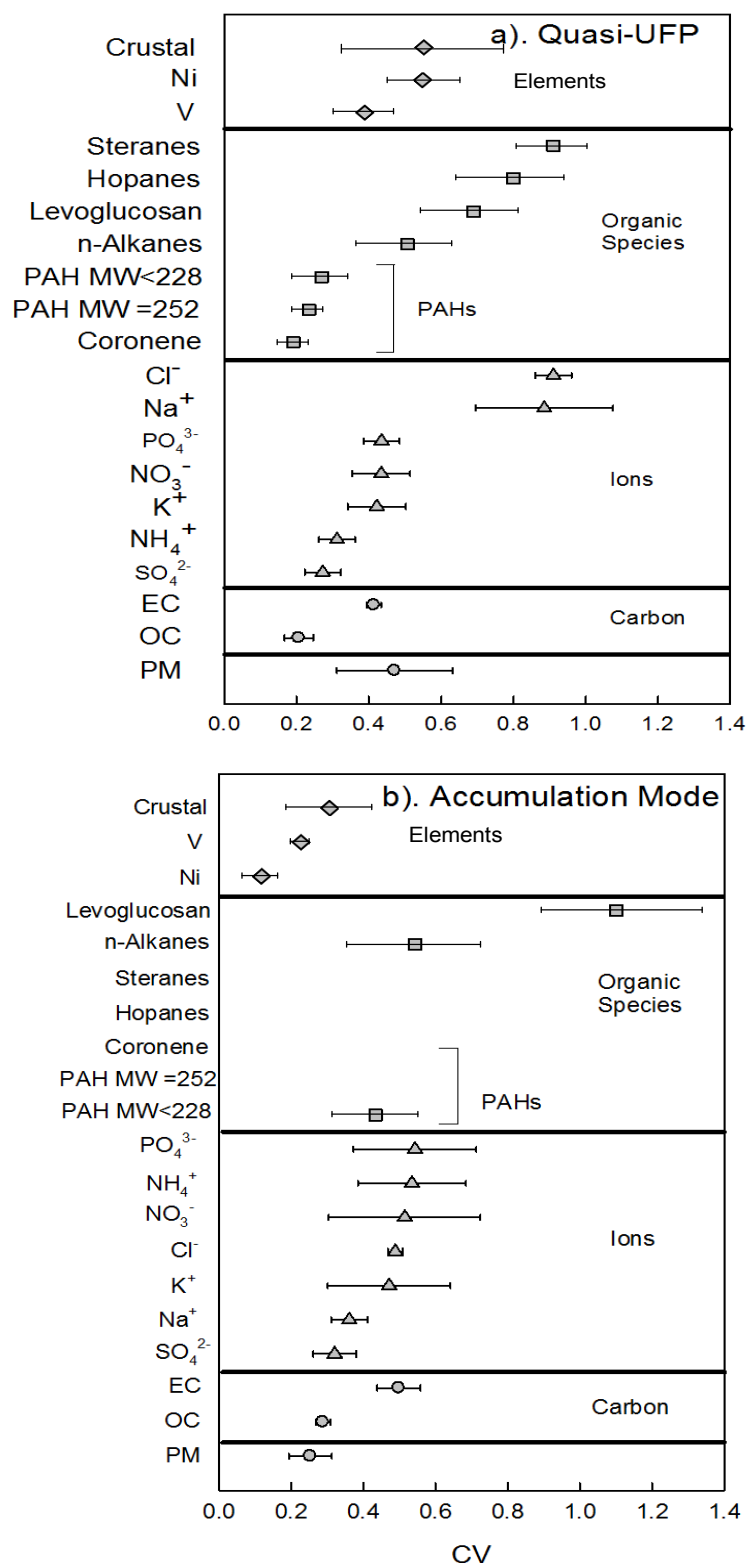


Figure 6.6 Coefficient of variances (CV) with standard deviation (SD) of selected chemical components at three size fractions: a) quasi-UF mode, b) accumulation mode and c) coarse mode. Error bars represent standard deviations

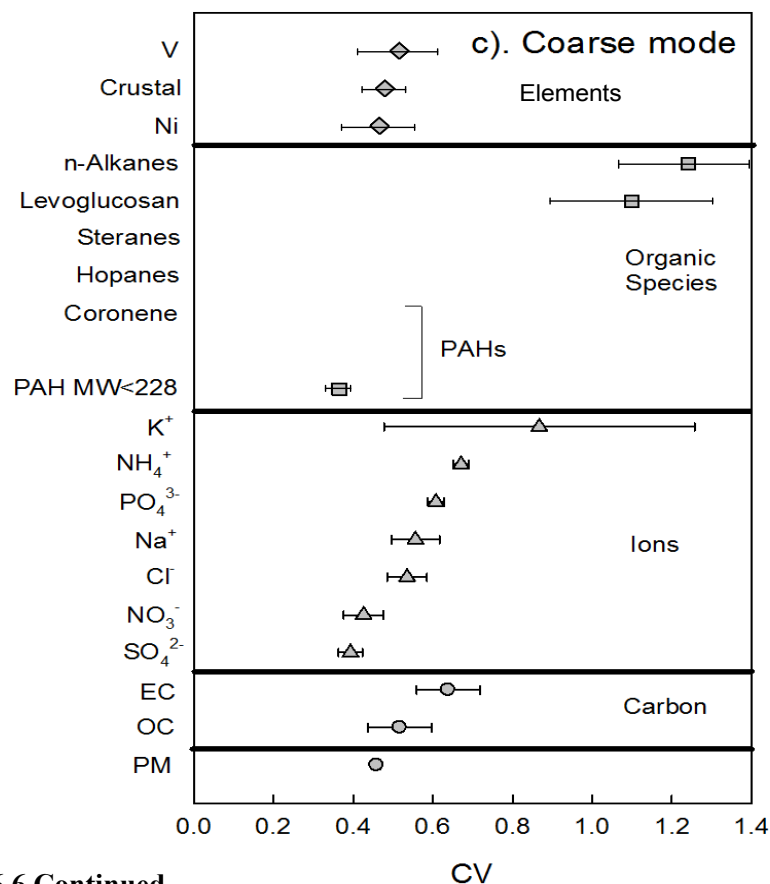


Figure 6.6 Continued

In the accumulation mode particles, levoglucosan was the most spatially heterogeneous species, with a CV of 1.1. The high variation was mainly due to substantially higher concentration at Site 2 than the other sites, probably due to the presence of a local wood-burning source near Site 2. The majority of the other species in accumulation mode are rather evenly distributed over the sites compared to other modes, with CV values varying from 0.2-0.6. In the coarse mode particles, levoglucosan and n-alkanes are the most spatially heterogeneous species with (CV =1.1 and 1.2, respectively). Potassium and EC also showed relatively high spatial variances (0.9 and 0.7, respectively). Crustal elements and inorganic ions in that size range had CV values varying from 0.5-0.7.

6.4.5. Elemental Constituents of PM

The concentration ranges of selected elements and their coefficient of variance (CV) over all the sites and for different size fractions are shown in Figure 6.7a. Na and S were the most abundant elements in all three size fractions, followed by Ca, Mg, K, Fe and Al. The calculated CV in the quasi-UF particles varied from 0.22 (P) to 1.63 (Cr); in the accumulation mode, they varied from 0.12 (Ni) to 0.81 (Cd); and in the coarse mode, they varied from 0.40 (Zn) to 0.79 (Sb). Figure 6.7b presents the size fractionated Upper Continental Crust (UCC) enrichment factors (EFs) (Ntziachristos et al. 2007b) for selected elements. The concentration of each element was normalized to Al and then was divided by the relative abundance of the same element over Al in UCC (Taylor and McLennan 1985). EFs in Figure 6.7b are averaged over the six sites; the error bars, denoting one standard deviation, suggest that the variability in EFs among sites was rather small. Trace elements were sorted in a decreasing order of their EF in fine PM mode. EFs close to 1 indicate crustal origin, while higher EFs indicate anthropogenic origin for a given element. For almost all the elements, the EF values were higher in the fine mode compare to the coarse mode, as the fine PM mostly originates from the anthropogenic sources. The lower coarse mode EFs were observed for Al, Fe, Ti, K, Mn, Cs, and K, indicating that these airborne species are products of resuspended soil dust. Even the fine PM fraction of these species had generally lower EFs compare to other elements, indicating again a crustal origin. High EFs for Sb, S, Cd, Mo, Zn, Pb and Cu were found in all the size fractions with higher values in fine mode (both quasi-ultrafine and accumulation mode). Most of these elements are generated from vehicular sources

and some are ingredients of lube oil (Ntziachristos et al. 2007b). Cu, Sb and Ba originate from vehicle brake abrasion (Sanders et al. 2003; Sternbeck et al. 2002). The concentrations of these three species were highly correlated across all size ranges, with R^2 values ranging from 0.90-0.95 for Ba vs Cu and Sb vs Ba, respectively, confirming their common source; in fact, EFs for the coarse mode of these species are substantially higher than 1, supporting this argument that these elements are not products of soil dust resuspension. Mo is a component of lube-oil combustion since it is used as additives in oils. Zn is mostly a product of tire attrition (Singh et al. 2002). Pb is attributed to wheel weights and gasoline exhaust in small amount (Sternbeck et al. 2002). High EFs of Sb, Mo, S, Sn, Pb, Zn, Cu, Ba, V and Ni were also reported at other urban locations (Ntziachristos et al. 2007b; Lin et al. 2005; Birmili et al. 2006). The high EF values for Na can be attributed to sea breeze as it is expected in coastal areas. High EFs were found for V and Ni, as these elements are generated by fuel oil combustion, mainly by marine vessels (Isakson et al. 2001; Lu et al. 2006; Cass and McRae 1983). Vanadium-to-nickel ratio has been used to distinguish between different emission sources so that the ratios higher than 1.5 mainly indicate fuel oil combustion, ratios around 1 indicate industrial sources (Isakson and Persson et al. 2001) and smaller ratios indicate diesel and gasoline engine emissions (Lin et al. 2005). Figure 6.8a presents the scatter plot of vanadium versus nickel in the fine particle modes. Excluding Site 6 (at USC) a strong association between the two species was obtained across all the sites ($r = 0.90$). This association suggests a common dominant source. A high slope of regression line ($V/Ni = 4.2$)

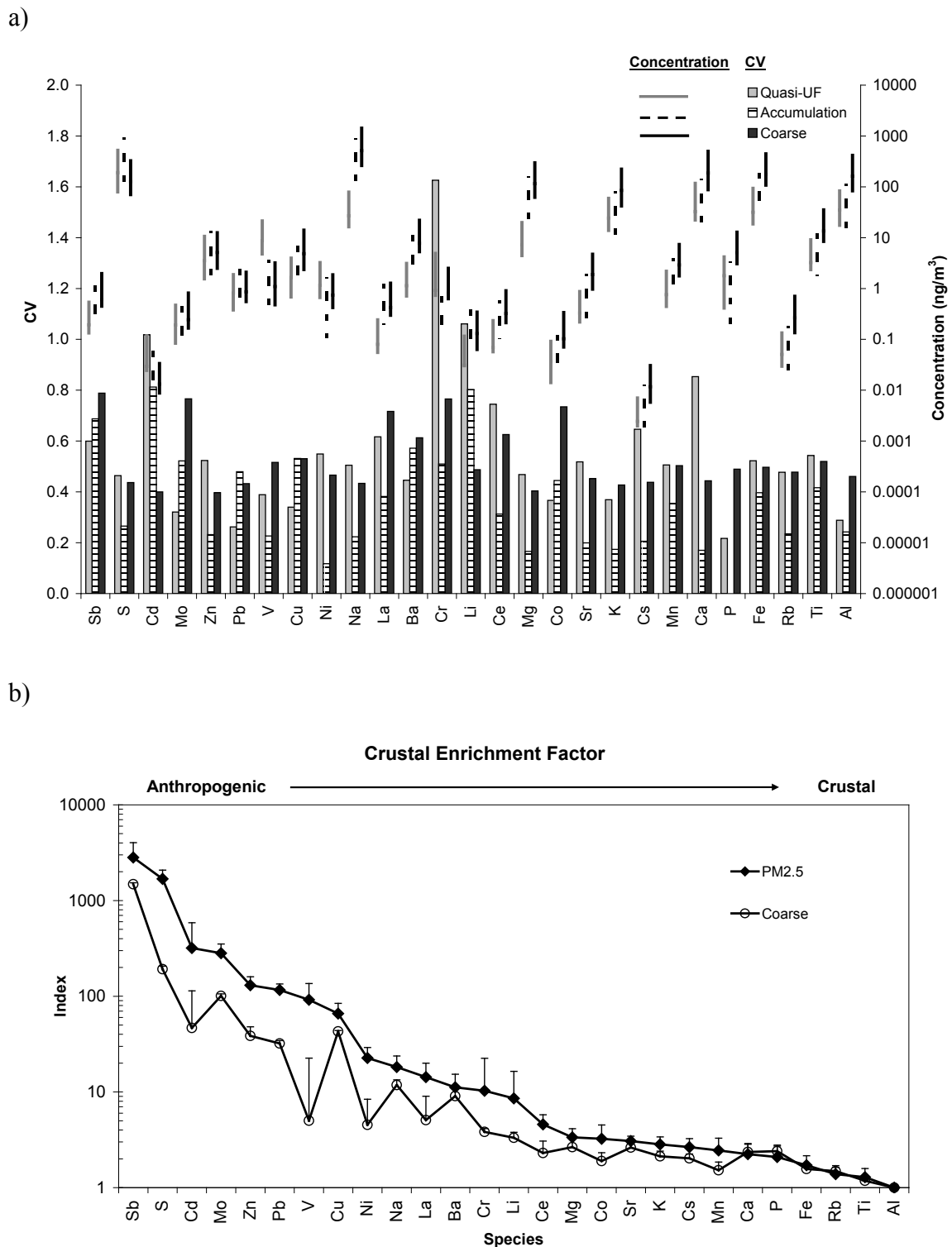


Figure 6.7 Size fractionated results of a) concentration ranges and coefficient of variances (CV) and b) crustal enrichment factor for selected. Error bars represent standard deviations.

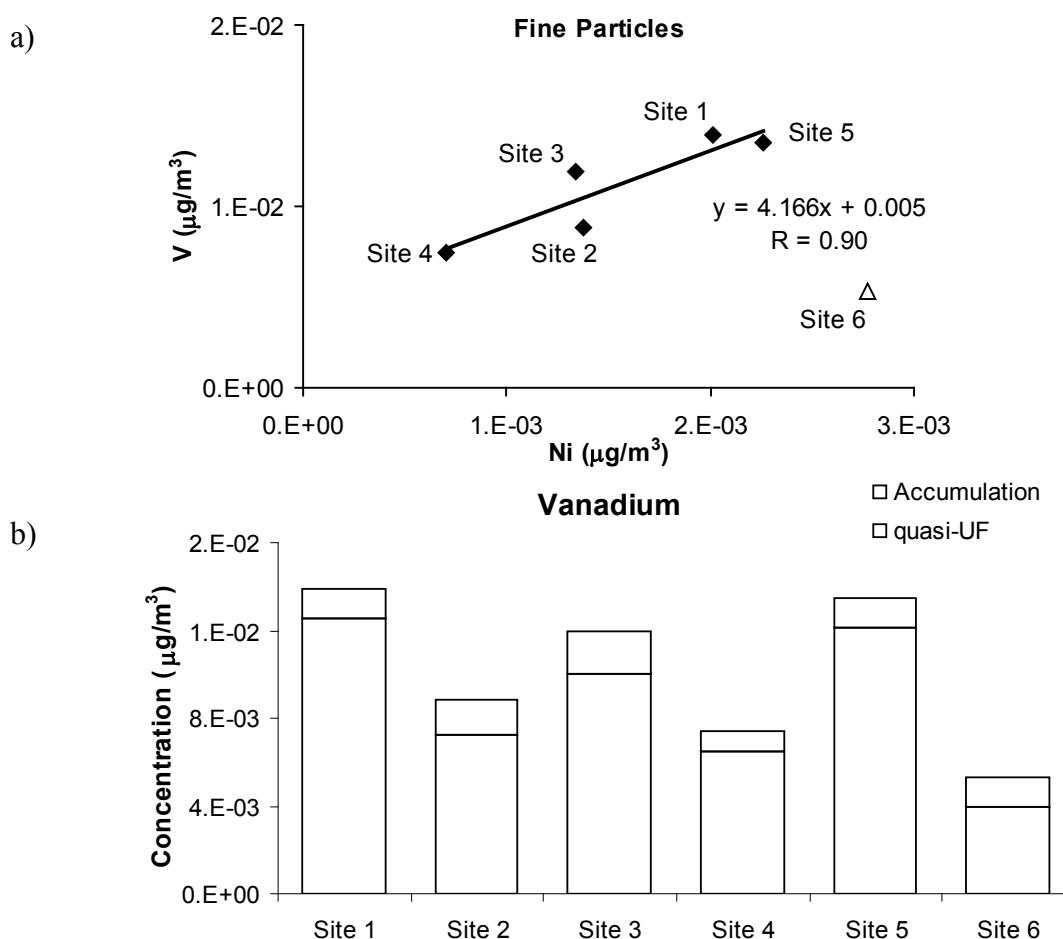


Figure 6.8 Vanadium concentrations a) plotted versus nickel concentrations and b) measured in quasi-ultrafine and accumulation mode at all the sites

indicates a fuel oil combustion source, (i.e. vessels). The distinctly lower ratio at Site 6 ($V/Ni = 1.9$) suggests the influence of other important local Ni source(s).

Figure 6.8b presents the variation of the vanadium concentrations measured over all the sampling sites. More than 80% of vanadium concentrations were in the quasi-UF mode. Site 5 and Site 1 showed the highest vanadium concentrations, followed by Site 3 and Site 2—all these sites were located within 3km from the coast. Relative to the vanadium concentration measured at the coastal site (Site 5), the concentrations dropped to about

62% at Site 4 (7km from the coast) and 49% at Site 6 (40 km from the coast). This gradient further confirms the major contribution of marine vessels to vanadium concentrations. Figure 6.9 presents the scatter plots and correlation coefficients of vanadium versus sulfur at all sites. Vanadium and sulfur were highly correlated in the quasi-UF mode ($r=0.72$), whereas there was lack of correlation in the accumulation mode ($r=0.03$). These results suggest that sulfur in quasi-UF mode mainly comes from similar sources to vanadium, i.e., mainly bunker-fuel combustion from marine vessels (Lin et al. 2005). By contrast, sulfur in accumulation mode is mainly in the form of ammonium sulfate which is produced by secondary reactions, hence the low correlation with V. There was no significant correlation ($p<0.05$) between V and Ni with OC and EC in different PM size fractions (Table 6.4). The weak association further supports the argument that marine vessels are probably not the major contributor to particulate EC and OC; even in areas proximal to the largest US harbor, the carbonaceous content of PM is generally emitted from vehicular sources. The V/OC ratio varied from 1.8 ng/ μ g (Site 6, Los Angeles Downtown Site) to 7.1 ng/ μ g (at Site 5, the background site, influenced by marine vessels). The Ni/OC ratio varied from 2.0 ng/ μ g (Site 5) to 12.0 ng/ μ g (Site 4). Yuan et al. (2006) reported V/OC and Ni/OC for residual oil combustion of about 160 and 70 ng/ μ g, respectively. This corroborates the minor overall contribution of residual oil combustion sources to the measured EC and OC concentrations. Slightly higher, but still not significant correlations were found between Ni and EC-OC in the accumulation mode, which may be due to the contribution of vehicular sources to airborne Ni in addition to marine vessels.

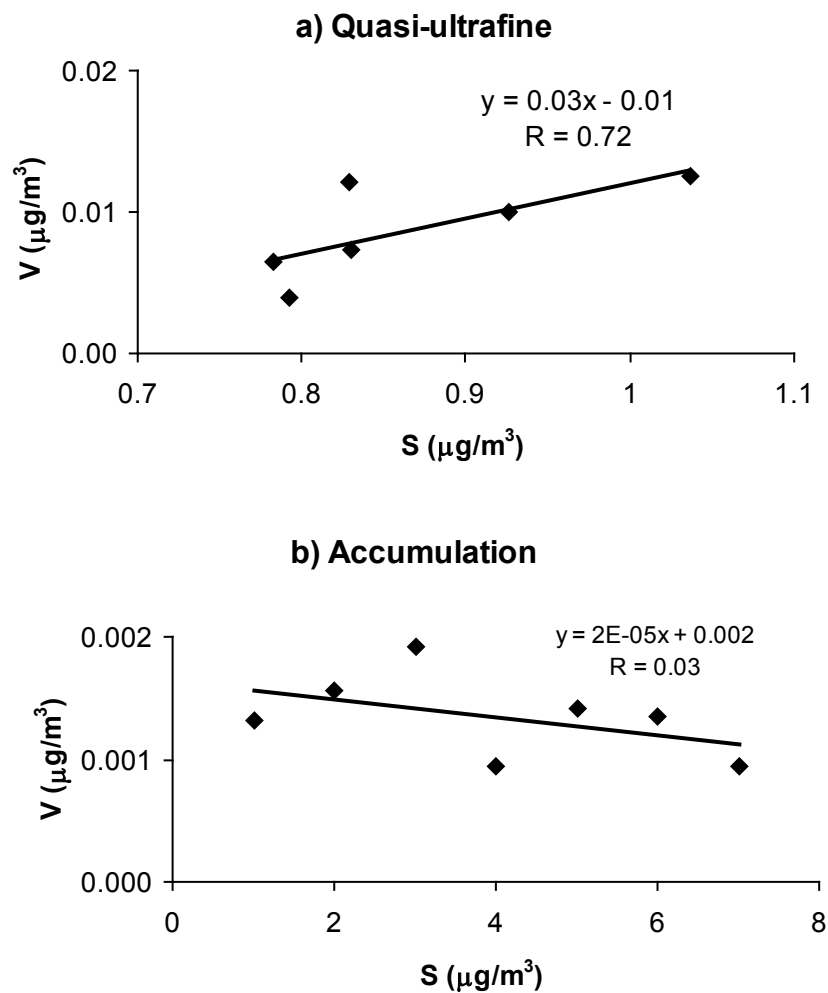


Figure 6.9 Relationships between vanadium and sulfur concentrations for (a) quasi-UF and (b) accumulation fractions

Table 6.4 Pearson number and P-values of correlation between V and Ni with EC and OC in different size fractions of PM

		Quasi-ultrafine		Accumulation Mode		PM _{2.5}	
		V	Ni	V	Ni	V	Ni
EC	R	-0.08	-0.17	0.15	0.58	-0.08	0.12
	P-Value	0.88	0.75	0.78	0.23	0.88	0.82
OC	R	-0.40	-0.57	-0.25	0.39	-0.66	-0.43
	P-Value	0.44	0.24	0.63	0.45	0.16	0.39

6.5. SUMMARY AND CONCLUSION

Size fractionated PM and its chemical compositions were investigated in the communities of Los Angeles harbor. The major mass contributions in the quasi-UF fraction were particulate organic matter (POM), nss-sulfate and EC; in the accumulation mode fraction were nss-sulfate, sea salt, POM and nitrate; and in the coarse fraction were sea salt and insoluble soil. In general, PM and its components in accumulation mode showed relatively lower spatial variability compare to the quasi-UF and the coarse modes. The carbon preference index (CPI) for quasi-UF and accumulation mode particles varied from 0.65 to 1.84 among sites, which is in the range of previous findings in areas with high influence of anthropogenic sources. In sites located close to harbor, the average n-Alkanes and PAHs levels were respectively about 3 and 5 times higher than their corresponding levels at a site located in vicinity of harbor, but upwind of most of local sources. The ratio of hopanes to EC and hopanes to OC over all the sites were in the range of previous roadside measurements near freeways with variable volume of diesel truck traffic. High overall correlations of vanadium with nickel ($R=0.9$), as well as a considerable gradient of vanadium concentrations with distance from the coast, suggests marine vessels as the major sources of these elements.

6.6. CHAPTER 6 REFERENCES

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Chapter 7.

Seasonal and Spatial Variations of Sources of Fine and Quasi-ultrafine Particulate Matter in Neighbourhoods near the Los Angeles-Long Beach Harbour

7.1. ABSTRACT

The Los Angeles – Long Beach harbor is the busiest port in the US. Levels of particulate matter (PM) are relatively high in this area, since it is affected by multiple PM sources. A Chemical Mass Balance (CMB) model was applied to speciated chemical measurements of quasi-ultrafine and fine particulate matter from seven different sites. Winter measurements were obtained during a 7-week period between March and May 2007, and summer measurements corresponded to a 6-week period between July and September 2007. Four of the sites were located within the communities of Wilmington and Long Beach, two sites were located at a background area in the harbor of Los Angeles and Long Beach, and one more site was located further downwind, near downtown Los Angeles, representing urban downtown LA, influenced by mostly traffic sources. The samples were analyzed for organic (OC) and elemental (EC) carbon content, organic species, inorganic ions, water soluble and total elements. The sources included in the CMB model were: light duty vehicles (LDV), heavy duty vehicles (HDV), road dust (RD), biomass burning and ship emissions. The model predictions of the LDV and HDV source contributions accounted, on average, for 83% of total fine OC in winter and for 70% in summer, whereas ship emissions contribution was lower than 5% of total OC at all sites. In the quasi-ultrafine mode, the vehicular sources accounted for 118% in winter and 103% in summer. Spatial variation of source contributions was not very pronounced

with the exception of some specific sites. In terms of total fine PM, vehicular sources together with road dust explain up to 54% of the mass, whereas ship contribution is lower than 5% of total fine PM mass. Our results clearly indicate that, although ship emissions can be significant, PM emissions in the area of the largest US harbor are dominated by vehicular sources.

7.2. INTRODUCTION AND OBJECTIVES

A large number of epidemiological studies have shown a relationship between exposure to ambient particulate matter (PM) and adverse effects on human health (Dockery et al., 1993; Atkinson et al., 2001; Samoli et al., 2005). The size of the particles has a strong influence on the type and intensity of health effect caused. Thus, fine particles (aerodynamic diameter, $D_p < 2.5 \mu\text{m}$; $\text{PM}_{2.5}$) have been more strongly associated with mortality and morbidity, whereas coarse particles ($2.5 \mu\text{m} < D_p < 10 \mu\text{m}$; $\text{PM}_{2.5-10}$) have been associated with respiratory hospital admissions (Brunekreef and Forsberg, 2005). Ultrafine particles ($D_p < 0.1 \mu\text{m}$; $\text{PM}_{0.1}$) penetrate deep into the alveolar region of the respiratory system (Delfino et al., 2005) and recent toxicological studies suggest that some adverse effects are associated more strongly with ultrafine particles than fine or coarse particles (Oberdorster, 2001; Donaldson et al., 2002; Li et al., 2003). Moreover, some studies have shown that using only community PM average concentrations to determine the health effects resulting from PM exposure may lead to non accurate results and therefore it is important to measure the variability of PM levels and sources within a community (Jerrett et al., 2005).

The communities near the Los Angeles-Long Beach harbor are of particular concern regarding PM pollution given that this harbor constitutes the busiest harbor in the US and the fifth in the world, and therefore the area is affected by several PM sources. In addition to the PM sources associated with harbor activities (marine vessels, heavy-duty trucks, locomotives, cargo handling equipments and harbor crafts), these communities are affected by other PM sources including road traffic from nearby freeways and local streets, multiple petroleum refineries and other industrial facilities. Thus, the surrounding area of the Los Angeles-Long Beach represents a highly complex urban airshed, and requires the application of sophisticated analytical and statistical tools to identify and quantify the major PM sources at different sites within the area.

For the development and implementation of PM policies that will be protective of the environment and human health, regulators require scientific knowledge of the strengths, spatial distribution and variability of the major sources of this pollutant. This information allows to design effective mitigation strategies on the local- and meso-scale level, and to evaluate human exposure to this pollutant and thus assess its health-related risks (Watson et al., 2002; Hopke et al., 2006).

In this context, previous studies have been carried out to identify PM₁₀ sources in the aforementioned area (Kleeman et al., 1999; Manchester-Neesvig et al., 2003). These studies were spatially constrained by the fact that they were based on data collected in one sampling site in Long Beach. Moreover, source apportionment of fine and ultrafine

fractions has not been conducted in this area. To the authors' knowledge, ship emissions' contribution to ambient PM has not been quantified before by means of receptor models and very few studies exist on source apportionment of the ultrafine PM fraction (Toner et al., 2008).

Hence, the objective of this study is to identify and quantify fine ($PM_{2.5}$) and quasi-ultrafine ($PM_{0.25}$) particulate matter sources in the Los Angeles-Long Beach harbor area, and identify, if any, the spatial and seasonal differences in PM patterns and composition. The results from this study will provide with useful information for control strategies and will assist future toxicological studies that are planned in this area.

7.3. METHODOLOGY

7.3.1. Sampling sites and schedule

Size-segregated PM samples were collected concurrently at seven sampling sites. Sites 1 and 2 were located in the community of Wilmington to the west of Long Beach area. Site 1 was about 1.5 km east (mostly downwind) of a major freeway (CA-110) at the intersection of a major street and a local residential street. Site 2 was at the intersection of two busy major streets, and next to the Alameda corridor, a 20 mile (32 km) freight rail "expressway" connecting the national rail system to the port. Site 3 and 4 were located within the communities of Long Beach. Site 3 was 1 km downwind of a major highway (CA-1), inside a semi-industrial area. Site 4 was 1 km downwind (east) of a major

freeway (I-710) with the highest ratio (up to 25%) of heavy-duty diesel vehicles in the Los Angeles highway network (Ntziachristos et al., 2007), and 1 km to the north of another major freeway (I-405). This site was influenced also by industrial sources. Sites 5 and 7 were located in an open area at the end of the pier of Long Beach and Los Angeles, respectively, upwind of harbor activities, hence serving as the background sites of the harbor.

Site 6 was located at the Southern California Particle Center (SCPC) Particle Instrumentation Unit (PIU) trailer near downtown Los Angeles. The PIU is about 40 km north of the coast, 150 m east of a major freeway (CA-110). This site represents a typical urban mix of downtown Los Angeles (Arhami et al., 2006) and was used as a reference to which the measurements in the harbor area would be contrasted. More details about these sites are described elsewhere (Arhami et al., 2008).

Sampling was conducted daily from Monday to Friday over a 7-week period from March to May 2007 (hereafter referred to as the winter period) and a 6-week period from July to September 2007 (hereafter referred to as summer period). Due to technical and weather-related problems, samples were not collected or were disregarded for week 7 at Sites 2, 4 and 5 in the wintertime. Moreover, sampling was not possible at Site 7 during the winter period.

7.3.2. Sampling methods

Only a brief description of the sampling methods is included in this paper. A detailed description can be found elsewhere (Arhami et al., 2008). Two collocated Sioutas™ impactors (SKC Inc, Eighty-Four, PA; (Misra et al., 2002; Singh et al., 2003)), operated at a flow rate of 9 lpm, were used in each site to collect size fractionated PM samples. In this study we only report data in the accumulation ($D_p = 0.25\text{-}2.5\ \mu\text{m}$; $\text{PM}_{0.25\text{-}2.5}$) and quasi-ultrafine ($D_p < 0.25\ \mu\text{m}$; $\text{PM}_{0.25}$) modes, although coarse ($D_p = 2.5\text{-}10\ \mu\text{m}$) PM were also collected and analyzed during these campaigns. Zefluor and quartz fiber filters were used as particle collection media.

Local weather data were measured every minute at all sampling sites by means of a weather station. The average temperature, relative humidity and wind speed varied in the ranges of 14.7-19.1 °C, 52-75% and 0.8-3.0 m/s in winter period and 20.9-23.9 °C, 58-82% and 0.5-2.2 m/s in summer period over all the sites. These meteorological data show that, on average, the winter period was 4.2-6.4 °C colder and that humidity and wind speed do not change much thorough the year. Generally, the prevailing wind was from southwest, where the ocean is located.

7.3.3. Gravimetric and chemical analyses

Mass concentration was determined by weighing the Zefluor filters before and after sampling with a microbalance (MT 5, Mettler-Toledo Inc., Highstown, NJ) having a sensitivity of 0.001 mg. A 24 hr equilibrating period under controlled temperature and

relative humidity was allowed prior to each filter weighing. A detailed description can be found elsewhere (Arhami et al., 2008).

Each filter was divided into 4 fractions for chemical analyses. Weekly composites (from daily samples) of quartz fiber filters were used for analyses of inorganic ions (chloride, nitrate, phosphate, sulfate, sodium, ammonium and potassium) by ion chromatography, and of elemental and organic carbon by the Thermal Evolution/Optical Transmittance (TOT) analysis. Seven (winter) or six (summer) weekly composites of quartz filters were used for analyses of 92 different organic compounds by Gas Chromatography/Mass Spectrometry (GC/MS). Seven (winter) or six (summer) week composites of Zefluor filters were used for analyses of 52 trace elements in soluble and insoluble fractions by means of a magnetic sector inductively coupled plasma mass spectrometer (HR-ICPMS, Finnigan Element 2). The remaining samples were used for toxicity analysis (results reported elsewhere (Hu et al., 2008)).

7.3.4. CMB model methodologies

General description of the model

The chemical mass balance receptor model has been widely used to determine source contribution estimates for PM₁₀ and PM_{2.5} (Watson et al., 1994; Schauer et al., 1996; Samara et al., 2003). Differently from other source apportionment models, CMB model requires knowledge of the emission sources and their chemical profiles, i.e. the fractional abundances of chemical species in the source emissions, in addition to the ambient data. In this paper we used the version CMB8.2 from the US Environmental Protection

Agency (US EPA), applied for apportionment to total OC (instead of total PM). Thus, the concentration of a general constituent i at a receptor site k , c_{ik} , can be expressed as:

$$c_{ik} = \sum_{j=1}^m a_{ij} s_{jk} + \varepsilon_{ik} \quad (7.1)$$

Where a_{ij} is the relative concentration of chemical constituent i in the emissions from source j ; s_{jk} is the increment to total OC mass concentration at receptor site k originating from source j ; and ε_{ik} is the error term with zero mean and standard deviation.

Source profiles

A careful selection of OC/PM sources is critical for the application of the CMB model, as demonstrated in previous sensitivity studies (Subramanian et al., 2006; Robinson et al., 2006; Sheesley et al., 2007; Lough et al., 2007). Hence, after evaluating the characteristics of the area, a selection of PM/OC sources was considered to run the CMB model. Source profiles were referenced to total OC (concentration ratio between the specific species and OC in the emission source), since the CMB model was run to apportion total OC as stated above. The sources considered were: road dust specific for the Long Beach area (Schauer, 1998; Amato et al., 2008) (only for the fine PM fraction); biomass burning characteristic from West US (Fine et al., 2004) for both fine and quasi-ultrafine fractions, although the source profile was only available for the fine fraction, it was assumed to be the same for the quasi-ultrafine fraction based on results from Kleeman et al. (2008); ocean vessels (Rogge et al., 1997; Agrawal et al., 2008) for fine and quasi-ultrafine fractions (again the quasi-ultrafine profile was assumed to be the same with the fine fraction); and light duty and heavy-duty vehicles, for fine and quasi-

ultrafine fractions (Kuhn et al., 2005a; Ntziachristos et al., 2007; Phuleria et al., 2007). The vehicular profiles correspond to roadway profiles (instead of the more commonly used exhaust profiles) from studies carried out in the CA-110 and I-710 freeways in Los Angeles, which are the closest freeways to the study area, and thus provide the most suitable and representative traffic source profiles for this area.

Other typical OC sources were not considered for different reasons. Meat cooking was not considered because cholesterol (main marker for this source) was not detected in most part of our ambient data set; nevertheless, its contribution was expected to be low in comparison with the rest of the sources in the area. Vegetative detritus and natural gas contributions were included in the first attempts but were found not quantifiable, moreover their contribution is expected to be very low since there is no obvious reason to believe that they have a substantial contribution to the air quality burden in that area. Refinery emissions were not included in the model due to lack of appropriate information on suitable profiles for refineries in the Long Beach area.

Fitting species

A set of fitting species was chosen based on: a) their chemical stability (Schauer et al., 1996); b) availability of their concentrations in the different source profiles and in the ambient data, and; c) previous studies that identify markers for different sources (Schauer et al., 1996; Rogge et al., 1997; Simoneit, 1999; Schauer and Cass, 2000; Cooper, 2001; Fine et al., 2004; Phuleria et al., 2007; Sheesley et al., 2007; Agrawal et al., 2008).

Thus, the following species were used as fitting species: EC, Benzo(e)pyrene, Coronene, 17 α (H)-22,29,30-Trisnorhopane, 17 α (H)-21 β (H)-Hopane, 22S-Homohopane, 22R-Homohopane, Cholestane, Sitostane, Levoglucosan, Aluminum, Vanadium and Nickel. When some of the species were not detected at some of the sites, they were not used as fitting species for the specific case.

Evaluation of the accuracy of the results

Each model result was evaluated by using the regression statistics parameters accompanying each CMB model output (Table 7.1). These are: the percent of measured ambient OC mass (%mass) accounted for by the sum of the source contribution estimates; the correlation coefficient (R^2) i.e. the variance in ambient species concentrations explained by the calculated species concentrations; the χ^2 representing the weighted sum of squares of the differences between calculated and measured fitting species concentrations. The R^2 and χ^2 were within the desired ranges (0.8-1 and 0-5, respectively) for the fine fraction. The % mass in summer was relatively low at some sites, probably due to the higher contribution of secondary organic compounds to the overall PM mass in the summer time. On the other hand, for the quasi-ultrafine fraction some parameters are not within the desirable ranges due to potential sampling artifacts associated with the reported OC concentrations both for ambient data and for the source profiles (Olson and Norris, 2005; Arhami et al., 2006; Polidori et al., 2006). These are typically due to the inadvertent collection of some vapor phase OC when using quartz filters for particle

Table 7.1 Regression statistics parameters

Period	Site	Quasi-ultrafine			Fine		
		R ²	χ^2	%mass	R ²	χ^2	%mass
winter	S1	0.92	2.5	124 ± 19	0.96	1.7	100 ± 19
	S2	0.82	4.6	162 ± 28	0.90	3.5	130 ± 26
	S3	0.80	5.9	115 ± 18	0.90	3.8	85 ± 17
	S4	0.90	4.2	60 ± 10	0.98	0.7	65 ± 12
	S5	0.93	1.6	144 ± 25	0.96	1.2	94 ± 19
	S6	0.92	3.3	60 ± 10	0.91	4.1	62 ± 10
summer	S1	0.97	1.1	102 ± 16	0.97	1.9	73 ± 14
	S2	0.94	1.9	72 ± 13	0.97	1.4	55 ± 12
	S3	0.97	0.9	73 ± 13	0.98	1.1	58 ± 11
	S4	0.92	2.2	91 ± 16	0.93	2.9	72 ± 14
	S5	0.91	2.3	141 ± 30	0.92	2.4	126 ± 31
	S6	0.90	3.4	82 ± 16	0.92	2.8	81 ± 16
	S7	0.94	1.7	156 ± 33	0.93	2.1	119 ± 29

sampling. Previous studies in Los Angeles (Kim et al., 2001; Sardar et al., 2005) showed that the positive artifact for a 24 hours period is on the order of 1-1.5 $\mu\text{g}/\text{m}^3$ of OC, thus on the order of 20% of our measured OC concentrations. Given the possible occurrence of these positive artifacts in our study as well as in previous studies creating source emissions profiles, statements made in the following paragraphs regarding quasi-ultrafine OC concentrations need to be qualified and put into perspective. The accumulation mode OC concentrations were determined by collecting particles via impaction, which diminishes the importance of this artifact.

Calculation of the source apportionment to total PM

Direct results from the model provide us with the source apportionment to ambient OC mass. To better assess the impact of the sources on total ambient PM, OC results were converted to PM based on the OC/PM ratio in each of the sources. For the quasi-ultrafine sources, the OC/PM ratio reported was higher than 1, which has no physical meaning, hence it was calculated assuming that $PM = EC + OM$ and that $OM = 1.4 * OC$ (Turpin et al., 2000; Arhami et al., 2008). To account for secondary inorganic aerosol contributions to PM, sulfate, nitrate and ammonium concentrations apportioned by the considered sources were subtracted from the ambient concentrations, and the difference was attributed mainly to secondary aerosol. The sea spray sulfate (calculated from Na concentration) was also subtracted. Sea spray contribution was calculated based on Na concentration (after subtracting Na apportioned by the considered sources) and a factor (3.248) including the chlorine and sulfate. The contribution from 'other organics' was calculated from the unexplained OC mass assuming it is mostly in the form of secondary OC and hence multiplied by a factor of two to be converted into organic matter (El-Zanan et al., 2005).

7.4. RESULTS AND DISCUSSION

7.4.1. Chemical composition of PM in winter and summer

The overall fine, quasi-ultrafine and accumulation mode PM mass were in relatively similar ranges in summer and winter (Figure 7.1). Higher OC levels in summer (Figure

7.1) can be due to the additional contribution of more intense photochemical activity leading to the formation of secondary OC (Seinfeld and Pandis, 1998). The average OC/EC ratios over all the sampling sites were 4.0 ± 1.1 in winter and 5.7 ± 1.0 in summer. The 30% higher OC/EC ratios in summer can be attributed to the higher OC levels because of the contribution of secondary OC as stated before. In a previous study the average ratio of OC/EC measured near highways with either highly impact from heavy-duty vehicles (I-710) or from gasoline vehicles (I-110) were 2.0 and 7.7, respectively (Phuleria et al., 2007). Our ratios are within this range, which could infer the high impact of vehicular sources on ambient OC concentrations.

Sum of all measured n-alkanes over the sampling sites in fine mode were 33.6 ± 21.4 ng/m³ in winter and 17.9 ± 7.0 in summer, reflecting 88% of higher winter period concentrations (Figure 7.2). The wintertime concentration of n-alkanes were 132% higher in accumulation mode and 62% higher in quasi-ultrafine compared to summer, showing a higher prevalence in accumulation mode. The lower levels of n-alkanes concentration in summer could be due to volatilization of the particulate phase into the gas phase (Kuhn et al., 2005b) and to variations in the emission sources of these compounds. Furthermore, more enhanced condensation of gas phase n-alkanes during the winter time onto the larger surface area of accumulation mode particles will result in increased concentrations of that size range in the winter (Kuhn et al., 2005b).

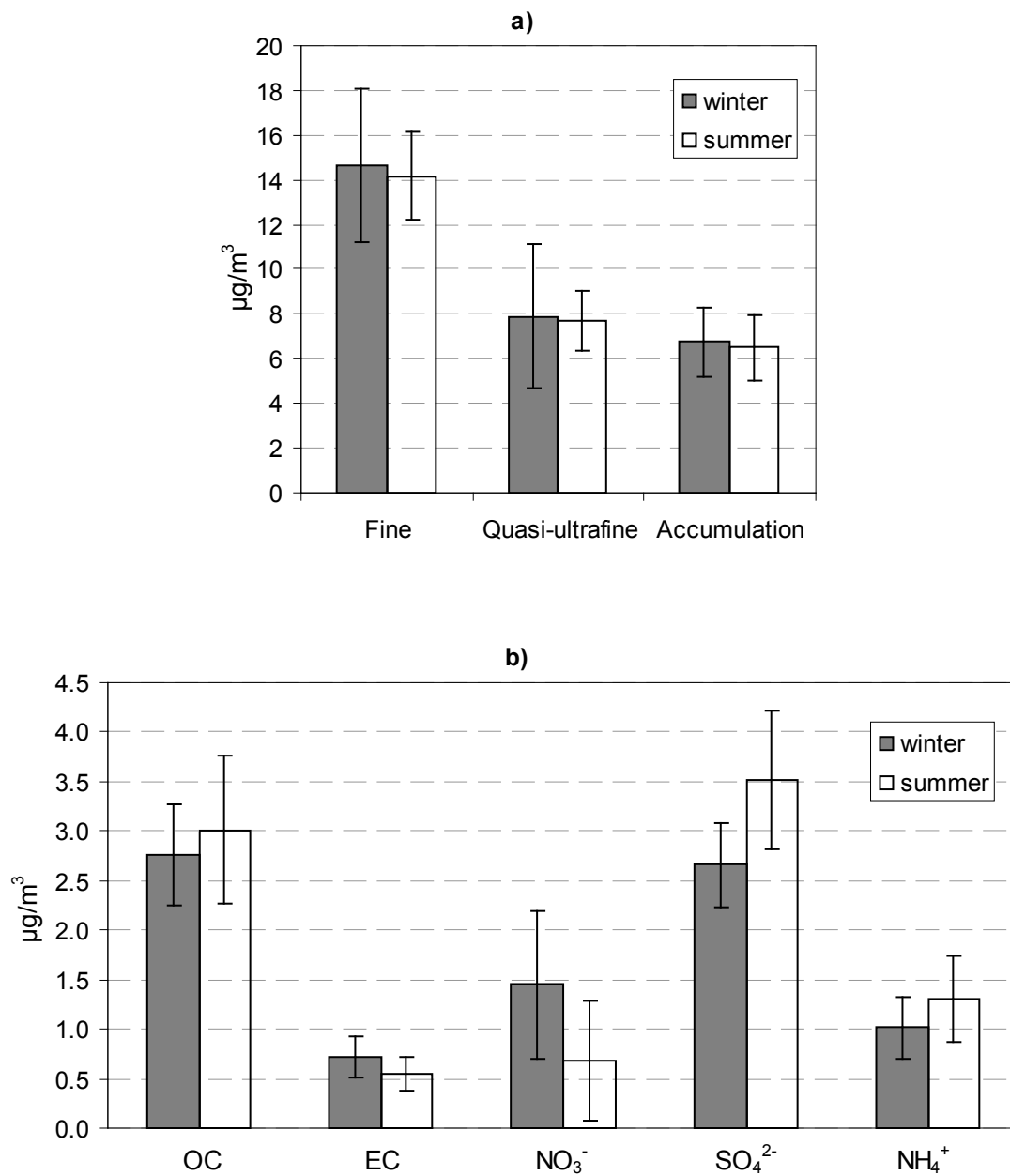


Figure 7.1. Overall comparison of measured PM species in winter and summer: a) mass concentrations of fine, quasi-ultrafine and accumulation mode PM, b) EC, OC, nitrate, sulfate and ammonium concentrations in fine particulate mode, error bars are the standard deviations of average measured concentration over the studied sites.

The sums of all measured fine particulate polycyclic aromatic hydrocarbons (PAH) were $0.32 \pm 0.15 \text{ ng/m}^3$ in winter and 0.23 ± 0.08 in summer over all the studied sites (Figure 7.2). PAH are mainly products of incomplete combustion of organic matter (Manchester-Neesvig et al., 2003). The composition and emission rate of PAH are dependent on combustion processes, atmospheric conditions (Manchester-Neesvig et al., 2003), gas particle partitioning and deposition (Mader and Pankow, 2002; Kuhn et al., 2005b). Also oxidizing gases such as ozone, nitrogen oxides, hydrogen peroxide can react with PAH and lower their concentrations (Grosjean et al., 1983), and these reactions are generally more pronounced in summer time. Hence, the slightly lower concentration of PAH in summer could be due to combine effect of volatilization and reaction with oxidizing gases. However, the decline in PAH levels is not as sharp as for n-alkanes levels, which could be due to the lower volatility of PAH compare to n-alkanes.

The sum of all measured hopanes and steranes were $0.86 \pm 1.00 \text{ ng/m}^3$ in winter and $0.78 \pm 0.23 \text{ ng/m}^3$ in summer in the fine PM fraction (Figure 7.2), thus quite similar during both seasons. This similarity may be due to the lower volatility of hopanes and steranes compared to PAH and n-alkanes, which showed a difference of 28% and 47%, respectively, between summer and winter.

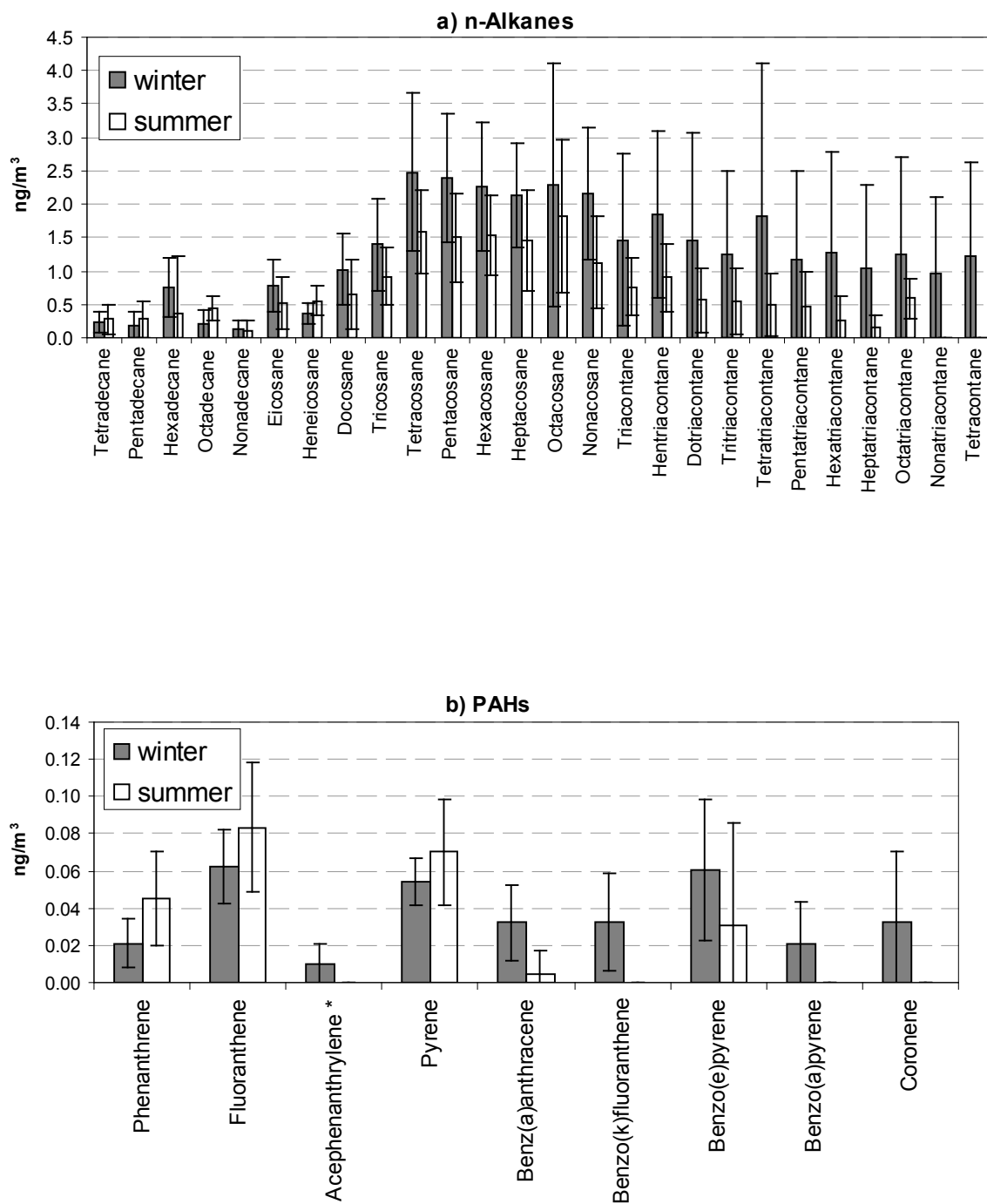


Figure 7.2. Average organic species concentration of fine particles in winter and summer: (a) n-alkanes; (b) PAH; (c) Hopanes and steranes and (d) Organic acids, error bars are the standard deviations of average measured concentration over the studied sites.

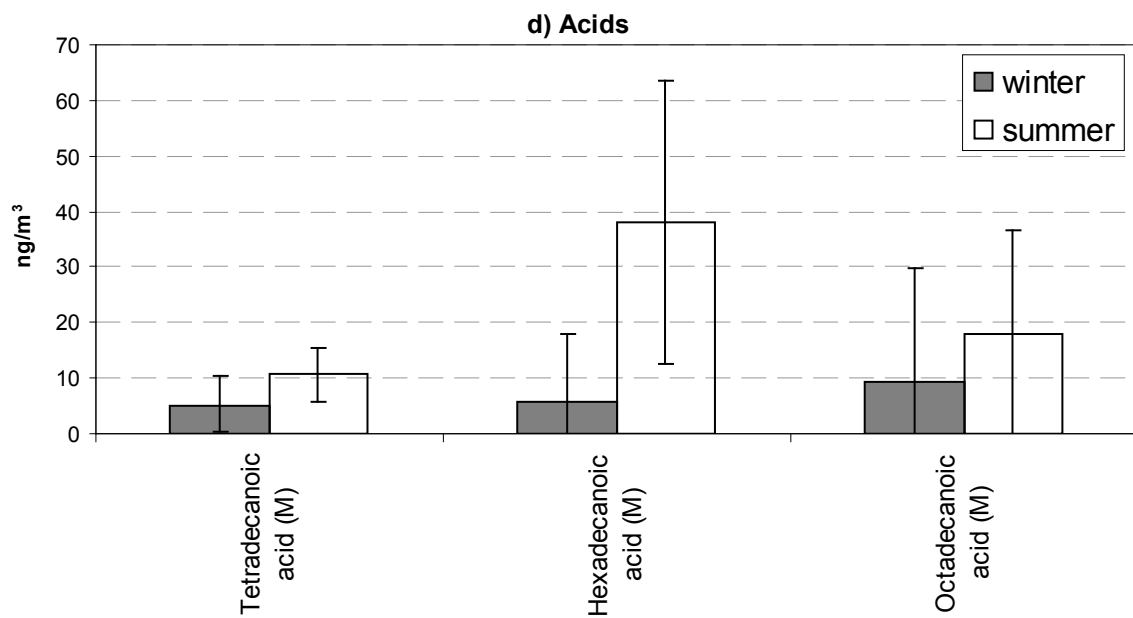
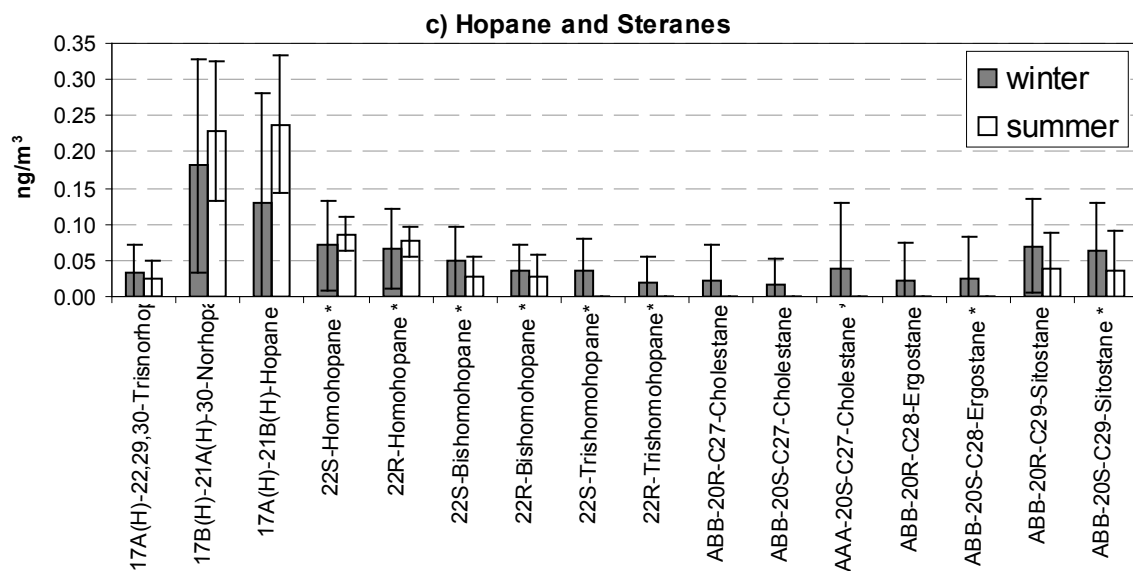


Figure 7.2. Continued

Particulate hopanes and steranes mainly come from lubricating oil of both diesel powered and gasoline-powered vehicles. In order to verify the origin of these compounds, EC concentration can be used as a reference, as EC is mainly attributed to diesel powered vehicles (Rogge et al., 1993; Schauer et al., 1996; Schauer et al., 2002). The average hopane to EC ratio over all the sampling sites were 0.82 ± 0.71 ng/ μ g in winter and 1.35 ± 0.55 ng/ μ g in summer, which lie within the ranges of those measured near the I-710 (0.64 ng/ μ g) and near the I-110 freeways (2.23 ng/ μ g) (Phuleria et al., 2007), inferring impacts from both diesel and gasoline powered vehicles. Moreover, hopane to OC ratios were 0.21 ± 0.17 ng/ μ g in winter and 0.24 ± 0.09 ng/ μ g in summer. These ratios are also reasonably comparable to roadway ratios measured near the I-110 (0.42 ng/ μ g) and I-710 (0.35 ng/ μ g) freeways (Phuleria et al., 2007). The impact of road traffic emissions will be confirmed and quantify by means of the CMB model in subsequent sections. The sum of concentrations of n-alkanoic acids in fine PM was 39.9 ± 51.6 ng/ m^3 in winter and 81.5 ± 54.1 ng/ m^3 in summer. The average concentration of Tetradecanoic acid (C18), Hexadecanoic acid (C16) and Octadecanoic acid (C14), which are among the most abundant measured organic acids (Ning et al., 2007) are presented in Figure 7.2. The average summer time concentration of fine mode Tetradecanoic acid, Hexadecanoic acid and Octadecanoic acid were respectively 2.1, 6.5 and 1.9 times of their corresponding concentrations in winter. In addition to food cooking, which is known to be a source of particulate organic acids, secondary photo-oxidation of organic gases and semi-volatile species volatilizing from particulate phase are reported to be a major source of these acids

(Rogge et al., 1991; Pandis et al., 1993; Robinson et al., 2007). The effect of secondary formation on the total concentration of these acids is thus evident.

The average concentrations of levoglucosan in fine PM measured in our sites were 3.6 ± 2.2 ng/m³ in winter and 2.2 ± 1.0 ng/m³ in summer. This compound is generated by pyrolysis of cellulose which is generally attributed to biomass burning emissions (Simoneit, 1999; Schauer and Cass, 2000; Fine et al., 2004). The relatively low measured levels indicate that biomass burning is not a major source of OC in the study area, as already pointed out by a previous study (Arhami et al., 2008) and confirmed by CMB model later in the present work.

Regarding inorganic compounds, average particulate sulfate and ammonium concentrations were 28% and 32% higher in summer than in winter due to the condensation of gaseous sulfuric acid from the oxidation of sulfur oxide gases through photochemical mechanisms (Hidy, 1994). A decline of 53% in nitrate concentrations in the summer reflects the partitioning of ammonium nitrate to its gaseous precursors with increasing temperature (Schaap et al., 2004) (Figure 7.1). From the group of trace elements analyzed, vanadium and nickel levels are considered more relevant in the study area and therefore discussed in detail due to their relationship with vessel emissions. V and Ni are mainly generated from fuel oil combustion (Cass and McRae, 1983), which in the study area can be assumed to be coming from ship emissions and refineries. A strong association between the two species in the fine mode was obtained across all the sites in

both winter and summer ($r = 0.90$ in winter and 0.89 in summer), with V/Ni slopes of 4.2 and 2.9 in winter and summer, respectively (Table 7.2). Vanadium concentration is highest at coastal sites (sites 5 and 7) and declines 55-62% at site 6 (USC, 40 km away from the coast). This gradient indicates the major contribution of marine vessels to vanadium concentrations, which will be confirmed with CMB model results explained later.

In wintertime, vanadium and sulfur were highly correlated in the quasi-ultrafine mode ($r=0.72$), whereas there was lack of correlation in the accumulation mode ($r=0.03$). These results suggest that sulfur in quasi-ultrafine mode mainly comes from similar sources to vanadium, i.e. marine vessels, , on the other hand in the accumulation mode it mainly has photochemical origin causing low correlation with V (Arhami et al., 2008). In summer time vanadium and sulfur were less correlated in the quasi-ultrafine mode ($r=0.46$) and similarly to wintertime there was no correlation in the accumulation mode ($r=0.09$) (Table 7.2). The low correlation in summer time even in lower mode particles can be attributed to higher overall spatial mixing and enhanced dispersion due to meteorological conditions in summer time.

There was no significant correlation between V and Ni with OC and EC in either summer or wintertime ($p>0.05$). The weak association further supports the notion that marine vessels are probably not the major contributor to particulate EC and OC as will be confirmed by the results from CMB model.

Table 7.2 Correlation of fine particulate OC, EC, V, Ni and S over a) winter and b) summer campaign (R is Pearson number and S is the slope of linear correlation).

a) Winter

		<i>Independent Variable</i>				
		OC	EC	V	Ni	S
<i>Dependent variable</i>	OC	R S	0.58 1.39	-0.67 -0.10	-0.44 -0.38	-0.48 0.00
	EC	R S		-0.11 -0.01	-0.08 -0.03	-0.06 0.00
	V	R S			0.90 4.17	0.24 0.01
	Ni	R S				0.54 0.00
	S	R S				

b) Summer

		<i>Independent Variable</i>				
		OC	EC	V	Ni	S
<i>Dependent variable</i>	OC	R S	0.71 3.11	-0.41 -0.11	-0.30 -0.25	0.28 0.00
	EC	R S		-0.09 -0.01	0.08 0.02	0.48 0.00
	V	R S			0.89 2.96	0.51 0.01
	Ni	R S				0.55 0.00
	S	R S				

7.4.2. Source apportionment

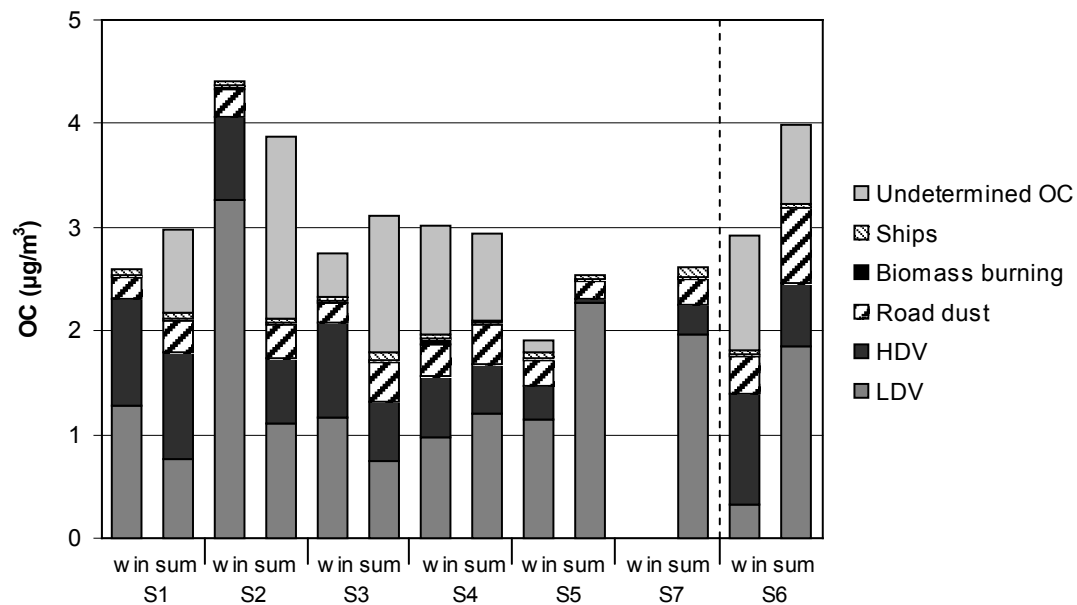
The collective contributions of the selected sources (LDV, HDV, road dust, ship emissions and biomass burning) calculated by means of CMB model accounts for $55\pm 12\%$ to $130\pm 26\%$ of measured ambient fine OC. The proximity of the total to 100% indicates that the selected sources are the main sources of organic matter in the study sites. The lower values (higher proportion of unaccounted OC) correspond to the summer period, probably not accounting for the higher contribution of secondary organic compounds in summer than in winter (Gelencser et al., 2007), which cannot be apportioned by the CMB model, given that it uses primary chemical profiles.

The total contribution of vehicular sources accounts for 52-120% of ambient fine OC at the harbor sites (Sites 1 to 4) in winter (Figure 7.3). These contributions are in general higher than in summer (42-60%) due to the higher stagnation of the atmosphere in winter, causing the accumulation of pollutants. The contributions of LDV and HDV are quite similar between sites located in the harbor area, with the exception of the higher LDV contribution at S2 in winter, probably due to the major influence of stop-and-go traffic at this site, which is more noticeable in winter with respect to summer owing to the higher stagnation. Moreover, contributions of light duty vehicles at the background sites (sites 5 and 7) in summer are relatively higher in comparison to the rest of the sites, and in comparison to the winter contribution at site 5 (site 7 data are not available for the winter). This could be due to the more enhanced mixing of pollutants in the atmosphere in the summer, which would increase the effect of traffic sources even in the coastal areas, as

well as to the additional contribution of off-road sources with similar chemical profile to light duty vehicles to these sites. These additional off-road sources could be recreational marine vessels, which would be used more often in the summertime, and therefore with higher impact on the sites nearest to the coast (background sites 5 and 7). The distinction between these on-road and off-road sources is difficult to be made by means of the CMB model.

The contribution of road dust is similar at all sites, explaining at most 13% of ambient fine OC either in summer or winter, with the exception of site 6 in summer, with a contribution of 18% to ambient fine OC. This can be explained by the proximity of that site to major freeways and sporadic higher wind speeds and drier conditions in summer than in winter, which would enhance resuspension of road dust. In the harbor sites, the summer-winter difference is not as pronounced because of the higher relative humidity in these areas due to their proximity to the ocean. Biomass burning contributes less than 1.5% to ambient fine OC. Finally, the contribution of ship emissions to ambient fine OC is also very low, between 0.04-0.07 $\mu\text{g}/\text{m}^3$ (1.1- 2.4 % of ambient fine OC) at the harbor sites, and slightly higher at the background harbor sites (0.05-0.09 $\mu\text{g}/\text{m}^3$, 2.3-4.1% of ambient fine OC). These results are consistent with previous findings in Hong Kong, showing that vessel contributions to ambient PM are very low (Yuan et al., 2006). Hence, despite the proximity to the harbor, the levels of particulate organic matter in the study area are controlled by traffic emissions rather than by ship emissions.

a)



b)

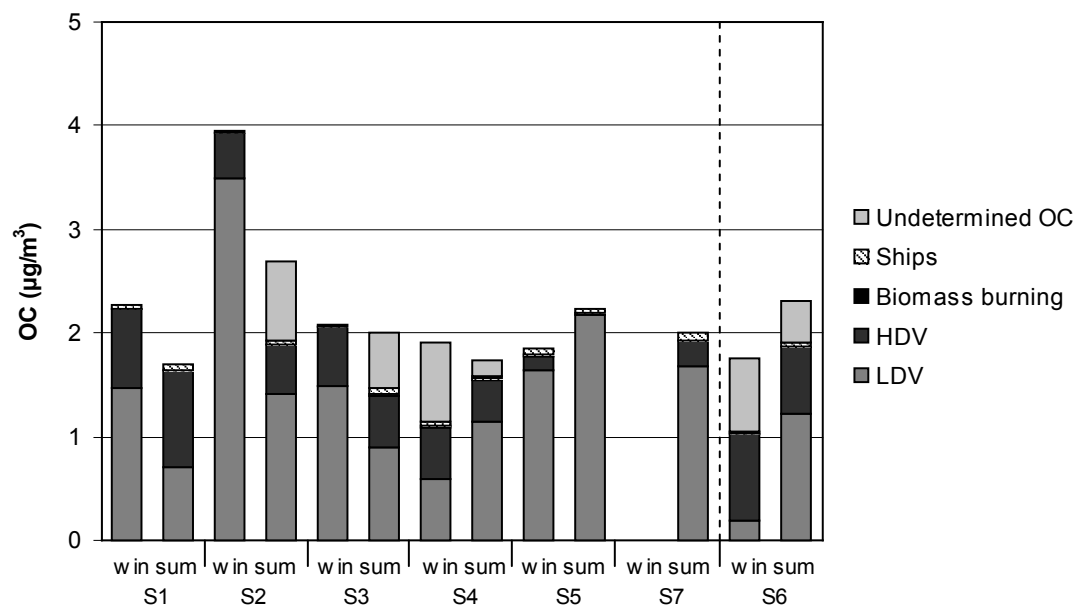


Figure 7.3. Source apportionment to total (a) fine and (b) quasi-ultrafine OC ($\mu\text{g}/\text{m}^3$) in winter and summer at the seven sampling sites.

Source contribution obtained for the quasi-ultrafine fraction of OC shows that vehicular sources are clearly predominant in this fraction (Figure 7.3). Although road dust was not included as a quasi-ultrafine source as stated before, the contribution from this source is expected to be very low according to the recorded Aluminum levels (i.e, the fitting species for road dust source). Moreover, the total contribution of the considered sources account for 60 ± 10 to $162\pm 28\%$ of total quasi-ultrafine OC, which indicates that no major sources are missing. The ratios of the LDV to HDV contributions in the quasi-ultrafine fraction at each of the sites are similar, but slightly higher than those found for the fine PM fraction, indicating that LDV have a higher impact on the quasi-ultrafine fraction. Only at the urban site (site 6), the ratio LDV/HDV contribution is higher for the fine fraction, indicating that HDV may have a higher impact on the quasi-ultrafine fraction at this site.

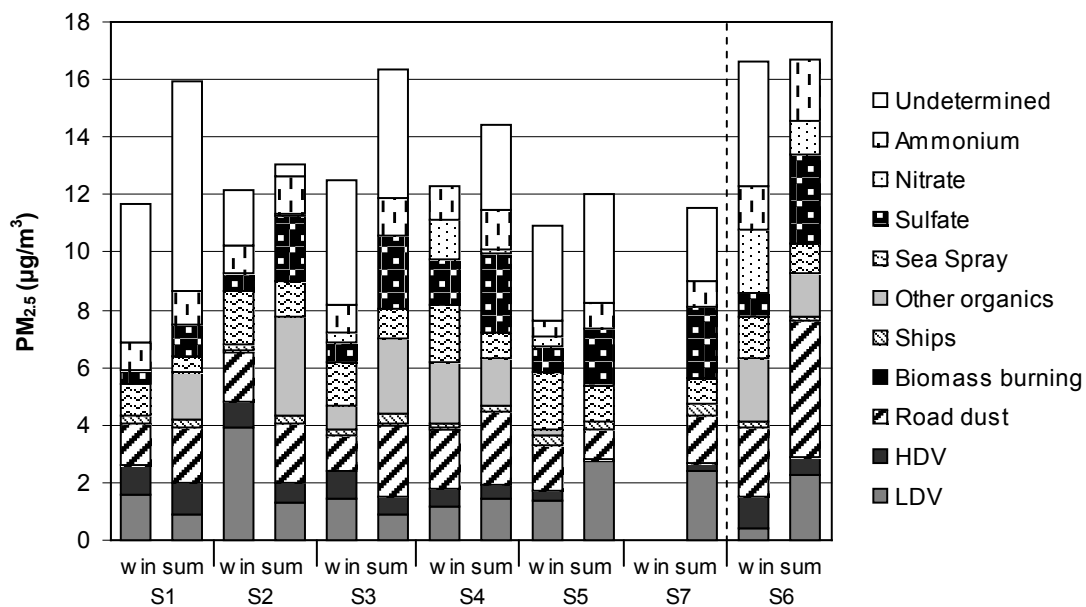
As discussed in the methodology section, source contribution to ambient PM was obtained from OC contributions and by considering secondary inorganic compounds (Figure 7.4). The vehicular sources (heavy and light duty vehicles) together with the road dust account for 24-54% of total fine PM at the harbor sites. This percentage increases up to 48% at site 6 in summer, 62% of which is due to road dust, which can be explained by sporadic increased wind speed and drier conditions in the summer, as noted earlier. The contributions of ‘other organics’ are higher in summer than in winter, and are assumed to be mostly in the form of secondary organic compounds. The contribution of sea spray accounts for 3.6-16% of total fine PM at the harbor sites, with higher values at the

background harbor sites (8-18% of ambient fine PM) due to their proximity to the ocean. As already discussed above, levels of nitrate are higher in winter due to the volatilization of nitrate at higher temperatures (Schaap et al., 2004), whereas levels of sulfate are higher in summer due to the higher photochemical activity that forms partially or fully neutralized ammonium sulfate salts (Hidy, 1994).

The total contribution of vehicular sources accounts for 36 to 100% of quasi-ultrafine PM in winter, whereas in summer it is in the range of 24-41%. The remaining mass is explained mainly by the contributions of secondary organic matter and sulfate. The contribution of sea spray and nitrate in the quasi-ultrafine fraction is very low compared to the fine fraction. Ship emissions contributions, although low, are similar in the quasi-ultrafine and fine fractions, indicating that these emissions are mainly in the quasi-ultrafine fraction, because they represent freshly emitted aerosols from a combustion source, as shown elsewhere (Petzold et al., 2008).

Results obtained in this study are consistent with previous results carried out in the same area for PM₁₀ fraction in 1995 (Manchester-Neesvig et al., 2003). Hence, in the present study vehicular sources (heavy duty + light duty vehicles) contribute to ambient fine OC levels by 1.6-2.3 $\mu\text{g}/\text{m}^3$ in the area of Long Beach (excluding site 2, with a very high contribution of light duty vehicles due to its specific location in a crossroad with traffic lights). These values are comparable to 1.8 $\mu\text{g}/\text{m}^3$ of total PM₁₀ OC found by Manchester-Neesvig et al. (Manchester-Neesvig et al., 2003) in winter. Vehicular

a)



b)

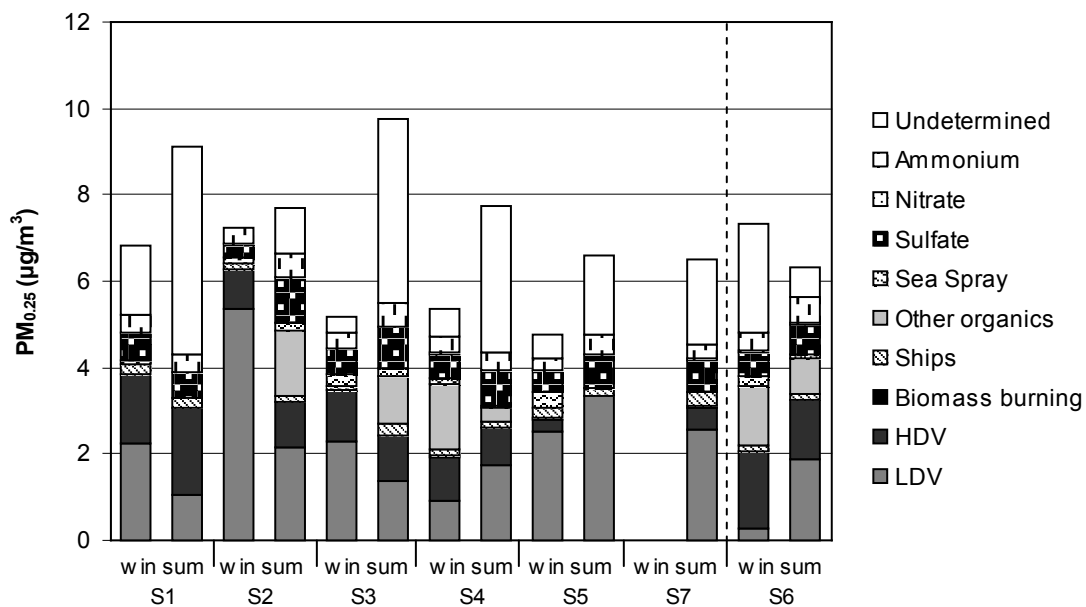


Figure 7.4. Source apportionment to total (a) fine and (b) quasi-ultrafine PM ($\mu g/m^3$) in winter and summer at the seven sampling sites.

contributions in summer season are also comparable, 1.3-1.8 $\mu\text{g}/\text{m}^3$ in our study and 1.4 $\mu\text{g}/\text{m}^3$ according to Manchester-Neesvig et al. (Manchester-Neesvig et al., 2003).

Regarding the source apportionment of different PM species, hopanes are mainly apportioned by light duty vehicles in the harbor area as well as in the marine background sites. Only in the urban site near downtown in winter they are apportioned to a major degree by heavy-duty vehicles (Figure 7.5). Benzo(e)pyrene is apportioned by LDV and HDV at all sites. In contrast, EC mainly comes from HDV. We should note, nevertheless, the relatively high contribution of LDV to ambient EC at the background sites. As we argued earlier, this could be due to the additional contribution of other off-road sources in the harbor with similar chemical profiles to LDV. Finally, the rest of the fitting species used are very specific to a given source, hence they are apportioned by more than 70% by one single source: levoglucosan from biomass burning, Al from road dust and V from ship emissions. The undetermined mass for Ni in summer is relatively high, which indicates that there are probably additional sources of this element during this season.

7.5. CONCLUSIONS

Some seasonal variations have been found regarding the concentration of different compounds: higher OC levels recorded in summer can be due to the additional contribution of more intense photochemical activity leading to the formation of secondary OC; higher levels of n-alkanes in winter than in summer are due to

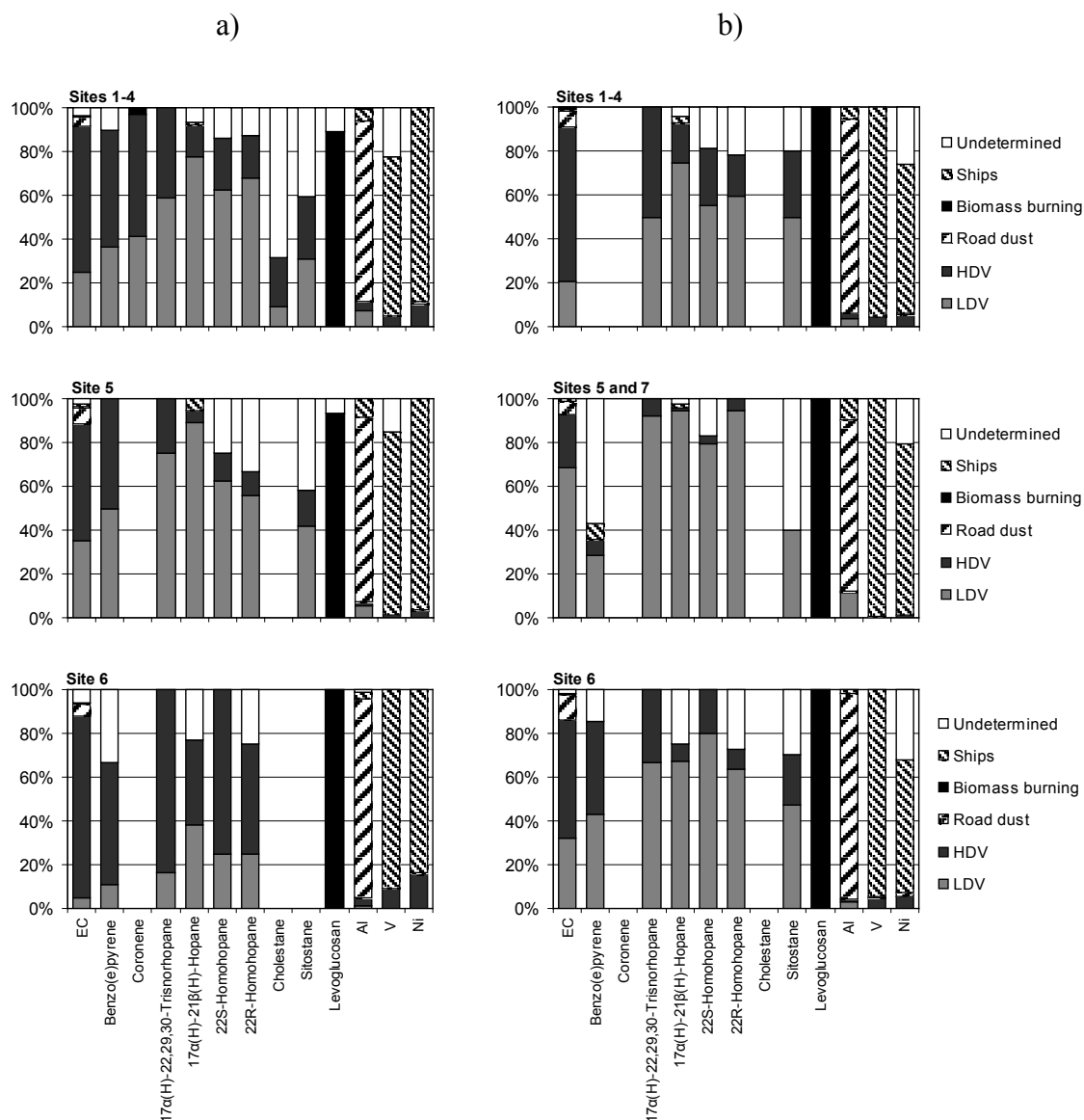


Figure 7.5. Source apportionment to ambient concentration of species in fine fraction used as fitting species in CMB model in (a) winter and (b) summer.

volatilization; higher levels of PAH in winter than in summer are due to volatilization and reaction with oxidizing gases; higher concentrations of n-alkanoic acids in summer than in winter evidence the effect of secondary formation; higher sulfate and ammonium

concentrations in summer are due to the condensation of gaseous sulfuric acid from the oxidation of sulfur oxide gases through photochemical mechanisms; lower nitrate levels in summer reflect the increase in the partitioning of ammonium nitrate to its gaseous precursors with increasing temperature.

The source contribution to OC is dominated by the vehicular sources (42-120% of total fine OC). The contribution of road dust is at most 13% of ambient fine OC and that of biomass burning is lower than 1.5%. The quasi-ultrafine mode is also dominated by vehicular sources. The contribution of ship emissions to ambient OC is less than 5% in both quasi-ultrafine and fine fractions. Hence, despite the proximity to the harbor, the levels of particulate organic matter in the study area are controlled by traffic emissions rather than by ship emissions.

The source contribution to total PM is also dominated by the vehicular sources, hence heavy and light duty vehicles together with road dust account for 24-54% of total fine PM and for 24-100% of total quasi-ultrafine PM. The remaining mass is explained by the contributions of secondary organic matter, secondary inorganic compounds (sulfate, nitrate and ammonium) and, in the case of fine PM, also by sea spray. The contribution of sea spray accounts for 3.6-16% of total fine PM, with higher values at the background harbor sites (8-18% of ambient fine PM) due to their proximity to the ocean. Ship emissions contributions, although low, are similar in the quasi-ultrafine ($0.12\text{-}0.33\text{ }\mu\text{g}/\text{m}^3$)

and fine (0.18-0.42 $\mu\text{g}/\text{m}^3$) fractions, indicating that these emissions are mainly in the quasi-ultrafine fraction.

7.6. CHAPTER 7 REFERENCES

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Chapter 8.

Conclusions and Future Research Directions

8.1. SUMMARY AND CONCLUSION

Although several epidemiological studies have shown adverse health effects of atmospheric particulate matter (PM), it has been difficult to address which component of particulate influences the health risk and what air quality regulation should be adopted. This difficulty is due to insufficient knowledge about the composition and properties of particulate matter and human exposure to them. Furthermore, if health effects can be linked to certain sources of particulate matter, such information would be highly valuable for targeting control strategies. A number of outstanding reasons that drives these important deficiencies in knowledge and were targeted in this thesis are:

- a) Because the atmospheric aerosols form a highly multi-component system, composition and properties of aerosols and their variations over time and space can not be ascertained by standard monitoring system.

- b) The size of the particles has a strong influence on the type and intensity of health effect caused. Particularly, ultrafine particles are shown to have more toxicity potential and more strongly associated with cardiovascular and respiratory health outcomes (Araujo et al. 2007) compared to larger particles. So far, there is little research to support this finding (reviewed by Delfino et al. 2005; Weichenthal et al. 2007). Another problem is that the importance of particle size and chemistry has been limited by reliance on

government monitoring of particle mass at two size cuts, PM_{10} ($<10\ \mu m$ and $PM_{2.5}$ ($<2.5\ \mu m$).

c) Although people spend around 85-90% of their time in indoor environment, air pollution data from outdoor (ambient) sites have been used for air quality standards which led to exposure misclassification. Accordingly, it is crucial to understand the composition and sources of both indoor and outdoor PM, their relationships and the association of indoor and outdoor concentrations with real personal exposure levels. Besides, no studies on apportionment of the sources of submicron indoor PM have been conducted.

d) Ascertaining the true risk associated with exposure to PM is difficult, mainly because the concentrations of ambient particles and those of their gaseous co-pollutants are often well correlated, and estimates of the health risks associated with PM exposure may be confounded by these gaseous species (Sarnat et al. 2000; Green et al. 2002; Sarnat et al. 2005).

The air pollution of the community near Los Angeles-Long Beach harbor is one of the areas of particular concern regarding PM pollution which constitutes the busiest harbor in the US and the fifth in the world, and therefore the area is affected by several PM sources. The potential for complex pollutant concentration gradients and high exposure conditions cannot be identified by conventional monitoring approaches. Accordingly, it is crucial to assess the exposure gradient of the community in the surrounding environment,

since using only community PM average concentrations to determine the health effects resulting from PM exposure may lead to non accurate results. In this context, previous studies have been carried out to identify PM sources, characterization and variations in the aforementioned area (Kleeman et al. 1999; Manchester-Neesvig et al. 2003). These studies were spatially constrained by the fact that they were based on data collected in limited number of sampling site in Long Beach or were not concurrent. Moreover, source apportionment of ultrafine fractions has not been conducted in this area. Nonetheless, there are not many studies on the micro-environmental spatial variations of chemical components and physical characteristics of particles in such complex environments. For the development and implementation of PM policies that will be protective of the environment and human health, regulators require scientific knowledge of the strengths, spatial distribution and variability of the major sources of this pollutant. This information allows to design effective mitigation strategies on the local- and meso-scale level, and to evaluate human exposure to this pollutant and thus assess its health-related risks (Watson et al. 2002; Hopke et al. 2006). Thus, concurrent and more extensive sampling and studies in such a complex urban air basin is desirable.

The conducted studies to address the above mentioned knowledge deficiencies and needs are summarized and their results and conclusions are briefed in the following. The measurements and studies were conducted in the Los Angeles Basin which is a megalopolis of about 15 million inhabitants and has one of the most polluted atmospheres in the US due to the contributions of a multitude of traffic and other combustion sources.

In first part of the study (Chapter 2), the performance of the Sunset Laboratory Inc. semi-continuous EC/OC monitor was assessed in a field setting and the influences of positive and negative sampling artifacts were investigated. The carbonaceous component of atmospheric particulate matter is considered very important with respect to the observed adverse health effects of PM. The organic carbon (OC) and elemental carbon (EC) components of PM have traditionally been measured off-line subsequent to daily, time-integrated particle collection on filters. However, the sub-daily or hourly variability of EC and OC can help to assess the variability of sources, ambient levels, and human exposure. The semi continuous monitors were deployed near downtown Los Angeles, in a location representing typical urban pollution. The results show that the semi-continuous EC/OC field analyzer is a reliable instrument for the measurement of the carbonaceous component of PM. The positive artifacts were almost constant and relatively high for the short sampling time of 45 min; more than 50% of un-denuded OC concentrations could be attributed to artifacts. These artifacts were virtually eliminated with the use of a denuder. The inlets of the EC/OC analyzers can be easily modified to sample different particle size fractions. Thus, multiple instruments allow for time-resolved, size-fractionated measurements of the carbonaceous components of PM. This instrument was used in rest of the study to get an insight in the characteristics of fine and ultrafine particles to better assess the human exposure to the carbonaceous components of particles.

Following part of the study (Chapter 3, 4 and 5) focused on exposure assessment and source characterization of size fractionated particulate matter and their. This part of the

study conducted within the Cardiovascular Health and Air Pollution Study (CHAPS), a multi-disciplinary project whose goals were to investigate the effects of micro-environmental exposures to PM on cardiovascular outcomes in elderly retirees affected by coronary heart disease (CHD). The elderly population with CHD is likely to be among the most vulnerable to the adverse effects of particulate air pollutants. In this study the physical and chemical characteristics of indoor, outdoor, and personal quasi-ultrafine ($<0.25\mu\text{m}$), accumulation ($0.25\text{-}2.5\ \mu\text{m}$), and coarse ($2.5\text{-}10\ \mu\text{m}$) mode particles were measured in four different retirement communities in southern California between 2005 and 2007. Three of these communities were in the San Gabriel Valley, CA (sites San Gabriel 1, 2 and 3 for groups G1, G2 and G3 respectively) and the fourth in Riverside, CA (group G4). Two 6-week sampling campaigns were conducted at each location. Phase 1 (P1 or warmer phase) of each campaign was conducted during a warmer period (including summer and early fall), whereas phase 2 (P2 or colder phase) was conducted during a cooler period (including late fall and winter). The San Gabriel Valley sites were closer to downtown Los Angeles and major freeways and Riverside site was further away from downtown Los Angeles and any major freeways.

Personal size fractionated PM samples were collected daily for 67 elderly retirees with a history of coronary artery disease. All participants were 71 years of age or older, nonsmokers, and with no home exposure to environmental tobacco smoke. Each subject was followed for two 5-day sampling periods during the 2 different phases of the study. Concurrent to personal sampling, daily indoor and outdoor size fractionated PM samples were collected. In addition, real time concentration of fine particulate matter mass, OC,

and EC, particle number (PN), ozone (O₃), carbon monoxide (CO) and nitrogen oxides (NO and NO₂) were measured at indoor and outdoor of these communities. Indoor and outdoor samples were analyzed to find their chemical composition and toxicological properties. This study provided one of the most extensive data set of its type for air pollution studies.

In Chapter 3 real time data collected at site San Gabriel 1 (G1) and San Gabriel 2 (G2) during 2005 and 2006 were analyzed. Measured indoor and outdoor concentrations of PM_{2.5}, OC, EC, PN, O₃, CO and NO_x were generally comparable, although at San Gabriel 2 a substantial peak in indoor OC, PN and PM_{2.5} (probably from cooking) was typically observed between 06:00 and 09:00am. The contributions of primary and secondary OC (SOA) to measured outdoor OC were estimated from collected OC and EC concentrations using EC as a tracer of primary combustion-generated OC (i.e. “EC tracer method”). The study average outdoor SOA accounted for 40% of outdoor particulate OC (40-45% in the summer and 32-40% in the winter). Air exchange rates (AER; h⁻¹) and infiltration factors (F_{inf} ; dimensionless) at each site were also determined. Estimated F_{inf} and measured particle concentrations were then used in a single compartment mass balance model to assess the contributions of indoor and/or outdoor sources to measured indoor OC, EC, PM_{2.5} and PN. The average percentage contributions of indoor SOA of outdoor origin to measured indoor OC were about 35% at San Gabriel 1 and about 45% at San Gabriel 2. On average, 36 to 44% of measured indoor OC was comprised of outdoor-generated primary OC.

Associations between indoor, outdoor, and personal size-fractionated PM and OC, EC, particle number (PN), O₃, CO, NO, NO_x, and other important pollutants of both indoor and outdoor origin were evaluated, and the role of gaseous co-pollutants as surrogates of personal size-fractionated PM exposures assessed (Chapter 4). Linear mixed effects models and Spearman's correlation coefficients were then used to elucidate the relationships among size segregated PM levels, their particle components, and gaseous co-pollutants. Seasonal and spatial differences in the concentrations of all measured species were evaluated at all sites based on p-values for product terms. Our modeling results have shown that outdoor and indoor levels of CO, NO₂ and NO_x were better correlated with measured indoor, outdoor and personal quasi-UF PM levels than accumulation mode and coarse mode PM. This better correlation is due to more similarity in sources and transportation mechanism. Indoor concentrations of outdoor origin of important carbonaceous species such as EC, OC, and OC_{pri} were more strongly correlated with personal quasi-UF and accumulation mode PM, than their corresponding indoor concentrations of indoor origin. This is because indoor sources were probably not significant contributors to personal exposure of accumulation and quasi UF PM, which is predominantly influenced by primary pollutants produced/emitted outdoors. These results are important, because other CHAPS investigators have suggested that traffic-related emission sources of PM_{2.5} OC_{pri}, and quasi-UF particles lead to increases in systemic inflammation, platelet activation, and decreases in erythrocyte antioxidant activity in elderly people with a history of coronary artery disease. Overall, our data analysis suggests that investigating the correlations among size-segregated indoor, outdoor and personal PM, their specific components, and concurrently measured gaseous co-

pollutants is a challenging endeavor. These associations depend on a number of factors that vary in space and time. Thus, results from time-series epidemiologic studies that include both gaseous and particulate pollutant concentrations in the models should be interpreted with caution.

Chapter 5 focuses on the characterization of the sources, organic constituents and indoor and outdoor relationships of quasi-ultrafine PM. In contrary to n-alkanes and n-alkanoic acid, the average indoor/outdoor ratio of most of the measured PAHs, hopanes and steranes were close to- or slightly lower than 1, and indoor-outdoor correlation coefficients (R) were always positive and for most of these components moderate to strong (median R was 0.60 for PAHs and 0.74 for hopanes and steranes). This suggests that indoor PAHs, hopane and steranes were mainly from outdoor origin, whereas indoor n-alkanes and n-alkanoic acid were significantly influenced by indoor sources. The Chemical Mass Balance (CMB) model was applied to both indoor and outdoor speciated chemical measurements of quasi-ultrafine PM. Vehicular sources had the highest contribution to PM_{0.25} among the apportioned sources for both indoor and outdoor particles at all sites (on average 24-47%). The contribution of mobile sources to indoor levels was similar to their corresponding outdoor estimates. A major implication of these findings is that, even if people (particularly the elderly retired population of our study) generally spend most of their time indoors, a major portion of the PM_{0.25} particles to which they are exposed comes from outdoor mobile sources. The significance of this conclusion is supported by the fact that indoor infiltrated particles from mobile sources were more strongly associated with the adverse health effects observed in the elderly

subjects living in the studied retirement communities compared to uncharacterized indoor particles.

In the final part of this study (Chapter 6 and 7) we characterize the physicochemical properties and sources of size fractionated PM and their spatial and seasonal variability. Size fractionated PM samples were collected concurrently at 7 sites in the southern Los Angeles basin for two different phases throughout the year. The studied region was the Los Angeles Ports complex consisting of the port of Long Beach and the port of Los Angeles which together is the busiest harbor in the US and the fifth in the world. Due to the high levels of particulate matter emitted from many sources in the vicinity of these ports and to their projected massive expansion, the Harbor area will be the focus of future governmental regulations. Four of the sites were located within the communities of Wilmington and Long Beach, two sites were located at a background area in the harbor of Los Angeles and Long Beach, and one more site was located further downwind, near downtown Los Angeles, representing urban downtown LA, influenced by mostly traffic sources. Winter measurements were obtained during a 7-week period between March and May 2007, and summer measurements corresponded to a 6-week period between July and September 2007. Coarse, accumulation, and quasi-ultrafine mode particles were collected at each site. Samples were analyzed for organic and elemental carbon content, organic species, inorganic ions, and water soluble and total elements.

Chapter 6 characterizes the chemical composition of ultrafine, accumulation mode and coarse particles across this community. Results from the gravimetric and chemical

analysis are verified by means of chemical mass closure (CMC). The major mass contributions in the quasi-UF fraction were particulate organic matter (POM), nss-sulfate and EC; in the accumulation mode fraction were nss-sulfate, sea salt, POM and nitrate; and in the coarse fraction were sea salt and insoluble soil. In general, PM and its components in accumulation mode showed relatively lower spatial variability compare to the quasi-UF and the coarse modes. The carbon preference index (CPI) for quasi-UF and accumulation mode particles varied from 0.65 to 1.84 among sites, which is in the range of previous findings in areas with high influence of anthropogenic sources. In sites located close to harbor, the average n-Alkanes and PAHs levels were respectively about 3 and 5 times higher than their corresponding levels at a site located in vicinity of harbor, but upwind of most of local sources. The ratio of hopanes to EC and hopanes to OC over all the sites were in the range of previous roadside measurements near freeways with variable volume of diesel truck traffic. High overall correlations of vanadium with nickel ($R=0.9$), as well as a considerable gradient of vanadium concentrations with distance from the coast, suggests marine vessels as the major sources of these elements. These results provide new insight into the variation of size-segregated chemical composition of PM over the studied area.

Finally (in Chapter 7) we identify and quantify fine and quasi-ultrafine particulate matter sources in the Los Angeles-Long Beach harbor area, and the spatial and seasonal differences in PM patterns and composition. A Chemical Mass Balance model was applied to speciated chemical measurements of quasi-ultrafine and fine particulate matter from seven different sites. The sources included in the CMB model were: light duty

vehicles (LDV), heavy duty vehicles (HDV), road dust (RD), biomass burning and ship emissions. The model predictions of the LDV and HDV source contributions accounted, on average, for 83% of total fine OC in winter and for 70% in summer, whereas ship emissions contribution was lower than 5% of total OC at all sites. In the quasi-ultrafine mode, the vehicular sources accounted for 118% in winter and 103% in summer. Spatial variation of source contributions was not very pronounced with the exception of some specific sites. In terms of total fine PM, vehicular sources together with road dust explain up to 54% of the mass, whereas ship contribution is lower than 5% of total fine PM mass. Our results clearly indicate that, although ship emissions can be significant, PM emissions in the area of the largest US harbor are dominated by vehicular sources.

Some seasonal variations have been found regarding the concentration of different compounds: higher OC levels recorded in summer can be due to the additional contribution of more intense photochemical activity leading to the formation of secondary OC; higher levels of n-alkanes in winter than in summer are due to volatilization; higher levels of PAH in winter than in summer are due to volatilization and reaction with oxidizing gases; higher concentrations of n-alkanoic acids in summer than in winter evidence the effect of secondary formation; higher sulfate and ammonium concentrations in summer are due to the condensation of gaseous sulfuric acid from the oxidation of sulfur oxide gases through photochemical mechanisms; lower nitrate levels in summer reflect the increase in the partitioning of ammonium nitrate to its gaseous precursors with increasing temperature. The results from this study will provide with

useful information for control strategies and will assist future toxicological studies that are planned in this area.

8.2. FUTURE RESEARCH DIRECTIONS

This thesis has put an effort to improve our scientific understanding of composition and properties of particulate matter, their sources and human exposure to them. Considering the complexity of PM metrics, several questions remained unanswered and should be areas of active research in future. These research areas are listed below.

- It is still not definitely known which component of particulate influences the health risk and what air quality regulation should be adopted and such information would be highly valuable for targeting control strategies. Some epidemiological studies have been performed (or are ongoing) to find the link of composition and properties found in this study to health effect (e.g. Delfino et al., 2008). However, considering the importance of ascertaining this link in protecting human health and life and current knowledge deficiency, more studies in this area are required.

- A major portion of this thesis focused on finding the real exposure to particulate matter, its composition and properties. In this regard, several findings were achieved which were discussed in previous sections. However, more air pollution and personal exposure studies are required to refine, verify and improve this finding for different locations, home environments, and population groups.

- Toxicity analysis (e.g. ROS and DTT assays) of the samples that were collected in this study to find the toxicity of different size fractions of PM, their correlations with organics, elements and other constituents of PM or gaseous pollutants and their link to different sources is recommended. This information will be very useful in targeting control strategies and regulatory applications.

- More research to find accurate and convenient instruments, which measure detailed particle characteristics, are necessary to better assess ambient concentrations and human exposures. In particular, continuous or semi-continuous monitors, providing data on hourly or sub-hourly time scales, are generally preferred over off-line analyses. Such monitors can not only capture important short-term variations in particle properties, but also can prove more economical to operate by reducing sampling site visits and eliminating the need for laboratory facilities and analysis costs.

- It was shown that even if people spend most of their time indoors, a major portion of the particles to which they are exposed can come from outdoor mobile sources. Also it was found that indoor infiltrated particles from mobile sources were more strongly associated with the adverse health effects observed in the elderly subjects living in the studied retirement communities compared to uncharacterized indoor particles. Thus, it is very important to implement more researches to improve the control technologies for vehicles. Also, more research to come up with new technologies to reduce the infiltration efficiency of particles to indoor environment is required. As an example filters have been implemented on air conditioning units to address this need; however more studies are

required to find the efficiency of this system, improve it and come up with better methods.

- The importance of particle size and real exposure has been limited by reliance on government monitoring and standards of only outdoor (ambient) PM_{10} and $PM_{2.5}$. Furthermore, the results of this study showed that the real exposure could vary with size of PM and could be different from outdoor levels. More size fractionated indoor, outdoor and personal PM exposure measurements and studies are necessary to improve the current regulations. In particular, submicron particles are shown to have more toxicity potential and more strongly associated with cardiovascular and respiratory health outcomes (Araujo et al. 2007) compared to larger particles. Thus, more studies to evaluate the need for new regulation for ultrafine particles are required.

- Studies are needed to advance mitigation technologies such as air purifier to remove the particles in indoor environment where the people spend most of their time. To this end, exposure studies to find the efficiency of available purifiers and technologies are required to be utilized in advancing the current technologies for better efficiency.

- More studies are required to find personal level chemical composition of size fractionated PM and to apportion the sources to personal levels. These results are very important for control strategies, and the extensive personal samples collected and archived during CHAPS (as a part of this thesis) can be used for such a study.

- Association of indoor, outdoor and personal levels depend on a number of factors that vary in space and time, such as: the relative contribution of UF, accumulation and coarse mode PM to the measured PM concentrations, the seasonal variability of primary and secondary emission sources, the presence of indoor sources of PM and gaseous co-pollutants (e.g. cooking), home characteristics (e.g. ventilation conditions and household characteristics), and proximity to the emission sources. The analysis of these associations is further complicated by the amount of time spent indoors (highly variable among subjects, especially in the warmer season), which is also a critical component in determining exposure. Thus, results from time-series epidemiologic studies that include both gaseous and particulate pollutant concentrations in the models should be interpreted with caution. Future research should focus on how these specific factors affect the strength of between-pollutant associations for individuals living in different locations
- Most of conducted toxicity studies have been focused on toxicity of outdoor generated particles, however not many studies are available on indoor generated particles and more studies are recommended. In this regard, the correlation between indoor generated particles which were estimated in this study and toxicity of indoor particles can be assessed and compared to the same correlation for outdoor generated particles.
- As a part of this thesis a source apportionment analysis was conducted only on the quasi-ultrafine fraction of samples collected during CHAPS. However, applying source apportionment on fine and coarse mode particles and compare it to the results for quasi-

ultrafine mode is desirable. Also other models than CMB (such as PMF) to identify the sources are suggested to compare with the results from this thesis.

- Studies to find better, more extensive and size fractionated source profiles are required to improve future source apportionment studies.
- A portion of particles could not be apportioned to any sources, which in some cases was more than 50% of particle mass (especially in ultrafine mode). Studies are required on origin and sources of this unapportioned fraction or refining source apportionment models to cover this fraction.
- There are other mega cities with complex air pollution environment around the world, which not many studies have been conducted there and they have been among most polluted city in the world (such as Tehran, Capital of Iran). Similar studies in these cities are highly desirable and the results can be compared to our findings to find better insight to the composition and properties of PM and their variation over space.

8.2. CHAPTER 8 REFERENCES

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