

INVESTIGATION OF THE PHYSICAL AND CHEMICAL CHARACTERISTICS
OF AMBIENT COARSE PARTICULATE MATTER IN INDOOR AND
OUTDOOR ENVIRONMENTS

by

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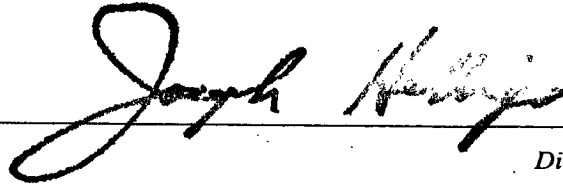
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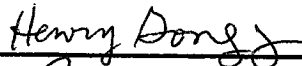
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ABSTRACT

Atmospheric coarse particles have been studied thoroughly but have recently come back into the spotlight due to a combination of bioterroristic threats, new technologic discoveries, and health effects studies. The longtime standard for sampling and measuring coarse PM, the 24-hour time-integrated filter sample, has been questioned for accuracy due to possible measurement error. This thesis is intended to alleviate the paucity of information on both the short-term variation of ambient coarse PM and to what extent humans are exposed to it. An indoor versus outdoor study in a desert location was conducted to demonstrate that even in environments with high outdoor coarse PM concentrations, indoor home exposure to coarse particles is almost entirely influenced by indoor sources and not penetration of outdoor coarse PM. Due to the relatively low ambient levels of coarse PM in many locations, a coarse particle concentrator was developed and evaluated. This device can concentrate ambient levels up to 30 times for in vivo exposure studies or sample collections over much shorter time intervals. Another device designed to measure coarse PM over short time intervals is also presented. The Continuous Coarse Particle Monitor measures real-time coarse particle mass concentrations and thus can be used for simple monitoring or detailed human or animal exposure studies. A PM₁₀ size-selective inlet was modified to operate at 50 LPM, the designed flow rate of the Continuous Coarse Particle Monitor. This inlet was tested in a laboratory wind tunnel and an outdoor field location and found to have a very sharp cutpoint near 9 μm . The final chapter of this work is dedicated to the overlap

between the ambient coarse and fine PM modes. A study was conducted to determine the effect of the tail of the coarse PM mode on the intermodal size range, or particles between 1 and 2.5 μm . Results indicate that in Los Angeles, intermodal PM is very similar to PM_{10} and shows nearly no correlation with coarse PM.

Chapter 1

INTRODUCTION

1.1 Background

1.1.1 Characteristics of Ambient Particulate Matter

Ambient particulate matter (PM) is a general name given to an atmospheric aerosol, which is a suspension of solid particles and/or liquid droplets in the atmosphere. PM is the keyword and not “aerosol” because the particulate mass and volume in an aerosol is too insignificant to discern from the air in which it is contained. Thus, researchers must focus on the each individual particle’s properties to acquire and understanding of the complete mixture of particles.

The sources of PM are many, and each source can change on a daily basis. Sources can be divided into anthropogenic and natural, after which they can be divided into mobile and stationary. Natural sources tend to be stationary and include volcanoes, wind-blown dust, and salt from sea-spray. Anthropogenic sources can be either stationary or mobile. Examples of the former are coal-fired power plants, wood-burning stoves, and soil disturbance from man-made construction projects. The largest category of mobile sources of PM is the combined contribution of vehicle exhaust from the millions of automobiles and trucks driven throughout the world.

Particles can be formed by a variety of processes, but the two on which most air pollution scientists focus are direct emission and secondary formation. Secondary formation can occur so close to a source that the particles are actually

considered to be directly emitted. This is the case in automobile exhaust because high concentrations of gaseous pollutants, such as nitrogen oxides, sulfur dioxide, and a host of organic gases, at very high temperatures mix with ambient air upon exit from the tailpipe. The result of this rapid cooling is condensation of vapors onto very small nuclei, and particles are formed. Particles are directly emitted from vehicles as well as any combustion source, resuspension of soil and road dust, and from plants in the form of pollen and spores. Secondary formation occurs by many processes that occur in the atmosphere and is driven by vapor concentration, particle concentration, temperature, relative humidity, and chemical reaction kinetics.

The source and formation of a particle determines its size. Mechanically produced particles arise from disintegration of liquids and solids and are usually larger than $1\text{ }\mu\text{m}$ (10^{-4} cm) in diameter while particles formed from gas phase vapors normally have sub-micron diameters. The distance between the large particles and smaller particles is spanned by growth of the smaller particles by condensation of vapors onto their surface and coagulation of two or more particles (Friedlander, 2000).

Because of the variety of sources, chemical composition, and sizes of particles, it has become useful to divide them into three size ranges. The largest particle size range considered in modern aerosol science is the coarse mode and consists of particles with aerodynamic diameters between $2.5\text{ }\mu\text{m}$ and $10\text{ }\mu\text{m}$. Coarse particles are windblown dust, salt particles from sea spray, bioaerosols (e.g. pollen, mold), and mechanically generated man-made particles (Hinds, 1999). The

latter originates from agriculture, surface disturbances (e.g. mining, construction development), disintegration of tires and brake linings from cars, etc.

The size range of 0.1 μm to 2.5 μm is termed the accumulation mode. Some also call this the fine mode while others define the fine mode as 0-2.5 μm . Accumulation mode particles are the products of combustion, atmospheric chemical reactions (smog), and particles with diameters less than 0.1 μm that have coagulated with these larger particles. Many combustion particles may originally be less than 0.1 mm in diameter, but they reach thermodynamic equilibrium quickly upon release from the combustion source. While equilibrating, these particles serve as condensation nuclei and thus grow as vapors concentrate on their surfaces. Fine particles can exist in the atmosphere on the order of days to weeks, which enables them to be transported long distances (Hinds, 1999). For this reason fine PM is responsible for regional and global air pollution.

The smallest PM size range is that of the ultrafine or nuclei mode, which includes all particles with aerodynamic diameters less than 0.1 μm . These particles form from both homogeneous and heterogeneous nucleation. The former is the process by which a high concentration of vapor is rapidly cooled and condenses into a liquid droplet while the latter is the process by which vapors are cooled and condense on a solid pre-existing particle. Some speculate that particles this small are either sulfate or elemental carbon. Because ultrafine particles are almost as small as gas molecules, they behave similarly. Thus, they are dominated by diffusion and

will either coagulate with larger particles or grow by condensation. The result is that their lifetimes as ultrafine particles are very short.

1.1.2 Health Effects of Particulate Matter

In 1970 the United States Environmental Protection Agency (USEPA) began regulating total suspended particulates (TSP) in the atmosphere. After health researchers began to study respiratory deposition of PM, the upper bound was set at 10 μm because particles larger than this are not respirable, which means that they cannot travel into the alveolar region of the lungs. Particles between 10 and 35 μm can still be inhaled, but they are removed by the nose, throat, and bronchi (Yeh and Schum, 1980; Yeh et al., 1996). The USEPA, in turn, modified its regulatory criteria in 1987 and developed a National Ambient Air Quality Standard (NAAQS) for PM_{10} at 50 $\mu\text{g}/\text{m}^3$ annually averaged and 150 $\mu\text{g}/\text{m}^3$ daily averaged (Wark et al., 1998).

In 1997 a new standard for $\text{PM}_{2.5}$ was set at 15 $\mu\text{g}/\text{m}^3$ and 65 $\mu\text{g}/\text{m}^3$ annually averaged and daily averaged, respectively, due to the huge variation between the coarse and fine modes and recent experimental results that demonstrate greater toxicity of the fine mode. Cohort studies, such as the Harvard Six City Study, that began in the 1970s published results in the early 1990s, which prompted regulators to establish the $\text{PM}_{2.5}$ standard. This study concluded that mortality was strongly associated with fine PM (Dockery et al., 1993). Other studies in the since the Harvard Six City Study have concluded the same results: fine PM is highly correlated with daily mortality (Pope et al., 1995; Schwartz and Neas, 2000; Tsai et

al., 2000). A recently published study, however, found that coarse mode particles increased the biological markers associated with alveolar macrophage response in the lungs more than the fine and ultrafine size fractions (Becker et al., 2003).

Current studies are now finding that ultrafine PM has the largest toxic response per unit mass in animals and cells. Oberdorster found that ultrafine particles induced an immune response in rats more than larger particles per unit mass (2000, 2001). Ultrafine particles can enter the cell and cause oxidative stress by damaging the mitochondria, which are cells' energy producers (Li et al., in press).

1.2 Rationale for the proposed research

Although of the three size fractions coarse PM has been studied for the longest amount of time, it is still not completely understood. The reasons for problems in characterizing coarse PM are: 1) coarse PM concentrations are very variable and heavily depend on changes in wind speed and direction; 2) sampling coarse PM can be difficult because the particles can settle out and/or are removed by impaction in the inlet before collection; 3) current measurement of coarse PM is conducted by the difference method, in which PM_{10} and $PM_{2.5}$ are collected on a filter and the difference between the two equals the coarse PM concentration.

For the same reasons listed above, it has also become very complex to determine the human exposure to coarse PM. Coarse particles are generally thought to originate from local sources and have very short residence times in the atmosphere, thus a centralized monitoring site will not accurately reflect the

concentrations to which someone living miles away will be exposed (Wallace et al., 1997). Additionally, the penetration of coarse PM indoors is very low, so indoor sources of coarse particles are more important when assessing human exposure.

Many health studies have been conducted to determine the health effects of coarse PM (Becker et al., 2003; Kleinman et al., 2003; Li et al., 2002). While these have involved the exposure of cell cultures and animals to coarse PM, little to no research has been conducted on human subjects. The development of a coarse particle concentrator with the potential to deliver concentrated coarse PM at flow rates required for humans is a necessity for future particle research. This is much more important for coarse PM exposure to health effect extrapolation because of the difficulty in determining ambient coarse PM exposure.

The objective of this thesis is to demonstrate the intricacies involved in characterizing coarse PM by presenting technologies that measure and concentrate coarse particles with the intention of reducing collection time. By doing this coarse PM can be studied on shorter time scales, and errors from variables such as wind speed and direction can be reduced. Further study of the relationship between coarse and fine PM is also investigated in order to determine the composition of the intermediate PM mode and the contribution of coarse PM to this submode of fine PM.

1.3 Theory

In order to understand the basics of aerosol science, a few equations must be presented. Because the focus of the research presented herein centers around the coarse size fraction, certain laws that are not relevant (i.e. diffusion) will not be discussed. Because an aerosol is a mixture of particles in air, it can be described by the equations of fluid motion. The Reynolds number is a dimensionless number that is characteristic of fluid flow around an object or objects. In the case of aerosols, the fluid is air and the objects are particles. Simply stated, the Reynolds number is the ratio of inertial forces to viscous (or frictional) forces acting on each small part of a fluid. The Reynolds number is commonly used as a yardstick to determine whether fluid flow is laminar or turbulent. When Reynolds number is expressed in terms of aerosols, it is written

$$Re = \frac{\rho V d}{\eta}$$

where ρ = density of the fluid

V = relative velocity between the fluid and particle

d = diameter of the particle

η = viscosity of the fluid

A general differential equation that describes fluid dynamics is the Navier-Stokes equation for incompressible flow. By neglecting gravity and buoyancy forces, it is written as

$$\rho \left(\frac{\partial U}{\partial t} \right) + u \left(\frac{\partial U}{\partial x} \right) + v \left(\frac{\partial U}{\partial y} \right) + w \left(\frac{\partial U}{\partial z} \right) = - \left(\frac{\partial p}{\partial x} \right) + \eta \left(\frac{\partial^2 U}{\partial x^2} + \frac{\partial^2 U}{\partial y^2} + \frac{\partial^2 U}{\partial z^2} \right)$$

in the x direction. Stoke's law is a solution to the above equation under the assumption that the inertial forces acting on a particle are negligible compared with the viscous forces on that particle. This is a valid supposition for particulate matter in air because the particles in question are very small and are subject to low velocities (Hinds, 1999). Stoke's Law can be solved from the equation and assumption above to yield:

$$F_D = 3\pi\eta Vd$$

By setting the above equation equal to the gravitational force, the terminal settling velocity of a particle can be determined. The simplified form after mathematical manipulation and assuming $d < 1 \mu\text{m}$ and $\text{Re} < 1$ is:

$$V_{ts} = \frac{\rho_p d^2 g}{18\eta}$$

Since the majority of this research deals with coarse PM, the equations above will serve as an introduction to the behavior of these particles in air.

1.4 Thesis Overview

The purpose of this thesis is to demonstrate the importance of accurate sampling and measurement of coarse PM by developing technologies to characterize it. Furthermore, the variability of coarse PM depending on location will be validated in order to discourage large-scale averaging and generalizing of coarse PM on a

regional basis. Seven chapters compose this thesis with the first being the introduction and brief layout of the fundamentals of aerosol science.

Chapter two will present a study of indoor versus outdoor concentrations of PM in the California desert during a time of maximum penetration. The aim of this study is to prove that exposure to coarse PM is not well represented by a centralized monitoring station that measures PM₁₀. Another benefit of this survey is the analysis of the chemical composition of coarse PM in a desert environment that is also influenced by the plume that is advected from the LA basin into the desert that lies to the east.

In contrast to the measurement of ambient and indoor coarse PM discussed in the second chapter, chapter three will describe the development and characterization of a technology to concentrate coarse PM in order to deliver a concentrated aerosol to the subject of a controlled exposure. The coarse particle concentrator was developed to determine the toxicity of coarse particles on human and animal subjects. Consideration was given to the ratio of the minor to total flow through each of ten virtual impactors in order to maximize the efficiency of the coarse particle collection. Another obstacle that must be overcome is the joining of ten working virtual impactors via air ducts without creating pressure and velocity fluctuations. Any changes in velocity or pressure drop in the collection manifold will lead to losses of coarse PM because of their high mass and thus high inertia and settling velocities.

Chapter four shifts gears once again as a methodology for measuring continuous coarse PM is developed and characterized. The relevance of this device is based on the finding that coarse PM is very localized and influenced by events that occur over time scales on the order of minutes to hours, such as wind speed and direction. The instrument is the combination of a virtual impactor and an already proven mass measurement technology—the Tapered-Element Oscillating Microbalance (TEOM™ 1400A, Rupprecht and Patashnick, Albany, NY). Since this device is the first continuous coarse-only PM monitor, it was characterized with time-integrated samples and compared with a time-of-flight particle counter by assuming the density of ambient particles.

Because the virtual impactor's flow rate is set at fifty liters per minute (LPM) for the continuous coarse monitor described by the previous chapter, a new PM₁₀ inlet (a device which removes particles larger than 10 µm in aerodynamic diameter) is discussed in chapter five. A PM₁₀ inlet with a sharp fifty percent cutpoint at 10 µm is necessary for accurate measurement of coarse PM because any particles larger than this that escape into the device can severely bias the total mass concentration. The reason for this is that a particles mass increases with the cube of its diameter. This chapter presents the development and characterization of a 50 LPM PM₁₀ inlet in both laboratory and field conditions.

Chapter six concerns an emerging topic in the arena of PM regulation and monitoring. Recent studies have shown that a significant fraction of coarse PM is collected with fine PM because the coarse mass distribution has a tail that does not

reach a negligible amount until around 1 μm . This coupled with the large masses of coarse particles compared with those of fine particles has ignited a debate over whether or not to establish a new PM_{10} standard. The sixth chapter of this thesis presents data collected over two years in the Los Angeles basin at various sites. This data includes monitoring of coarse and fine PM but also incorporates mass concentrations of PM in the size ranges of 0-1 μm and 1-2.5 μm . The latter size range has been termed the intermediate mode, or intermodal. While rural and desert community studies have proven that the intermediate mode is highly influenced by coarse PM, the data collected in the Los Angeles basin suggest that the intermediate mode is in fact also heavily influenced by fine particles that grow by condensation into the 1-2.5 μm size range.

Chapter seven of this work is the concluding chapter and ties together the ideas presented herein. Further research and new directions are also presented to the reader. The cohesiveness of the topics outlined above will become apparent as the characterization of and technologies to concentrate and monitor coarse particulate matter are presented.

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Chapter 2

INDOOR /OUTDOOR RELATIONSHIP AND CHEMICAL COMPOSITION OF FINE AND COARSE PARTICLES IN THE SOUTHERN CALIFORNIA DESERTS

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2.1 Abstract

The work presented in this paper examines the characteristics, chemical composition and relationship between indoor and outdoor particulate matter (PM) in the Coachella Valley, a unique desert area in southern California. Fine (0 - 2.5 μm) and coarse (2.5 - 10 μm) PM concentrations were measured concurrently indoors and outdoors in 13 residences during the winter and spring of 2000. Maximum outdoor PM penetration in indoor environments was expected during this period in the California deserts, as the mild climate minimizes the use of heating and/or air conditioning. Filter and impaction substrates were analyzed for mass, selected trace elements and metals, as well as elemental and organic carbon content (for fine PM only). Fine PM concentrations accounted, on average, for 74.3 (± 11.0)% of the total PM_{10} concentrations indoors, whereas fine PM contributed to 61.3 (± 13.1)% of the outdoor PM_{10} concentrations. The indoor-to-outdoor mass concentration ratios were 0.66 (± 0.27) and 1.03 (± 0.29), for coarse and fine PM, respectively. Chemical analysis of the filters revealed well-correlated indoor-to-outdoor concentrations of trace elements and metals in the fine PM mode, while lower correlations were obtained for the coarse PM mode. Elemental carbon concentrations indoors were

0.84 (\pm 0.32) of those measured outdoors, whereas organic carbon concentrations indoors were on the average 77% higher than outdoors, presumably due to the contributions of indoor sources. Coarse PM concentrations based on mass, trace elements and metals showed similar trends, with the average indoor-to-outdoor concentrations varying from about 50 to 70%. Although the outdoor air of the specific study area has been traditionally considered to be rich in coarse particles, the results of this study suggest that indoor PM concentrations are still dominated by the contribution of fine particles.

2.2 Introduction

Epidemiological evidence associating ambient particulate pollution with adverse health effects in humans is extensive (ATS, 1996; US EPA, 1996). Nevertheless, fundamental uncertainty and disagreement persist regarding which physical and chemical properties of particles influence health risks, which pathophysiological mechanisms are operative, and what air quality regulations should be adopted to address the health risks (Vedal, 1997). This lack of understanding stems, in part, from the paucity of reliable data linking personal exposure to observed health outcomes in large-scale epidemiological studies.

People spend most of their time indoors. Yet, the majority of particle concentration data is based on measurements conducted outdoors, in one or more central monitoring sites. Outdoor particulate concentrations may not be reliable indicators of indoor and personal particulate exposures (Wallace et al., 1997). For

example, poor associations between outdoor and indoor or personal levels may result from the presence of indoor particulates sources.

The work presented in this paper therefore examines the indoor and outdoor relationships of particulate matter in the Coachella Valley (hereinafter "the Valley"), a unique desert area in southern California. The Valley is located approximately 80 miles southeast of Los Angeles, between the Mojave and Colorado deserts. Bordered by mountains on the north, east, and west and by the Salton Sea on the south, the Valley intermittently accumulates high particle concentrations, sufficient to warrant designation by the EPA as one of five areas in serious non-attainment with the 24-hour ambient air quality standard for PM_{10} . The Valley is also home to many retirees and attracts large numbers of winter tourists because of its warm climate.

Recently, Ostro and Lipsett (Ostro et al., 1999) found that ambient concentrations of particulate matter smaller than $10\ \mu m$ (PM_{10}) in California's Coachella Valley are associated with an increased risk of daily mortality. Given that about 50-60% of the total PM_{10} mass concentration in that area measured in fixed-site monitoring stations was found to be in the coarse fraction (i.e., 2.5 to $10\ \mu m$ in aerodynamic diameter), the results of that study raised concerns on the mortality and morbidity effects of coarse particles.

The purpose of this field investigation was to determine the chemical characteristics of outdoor coarse and fine particles in the Valley and compare them to

those measured in the epidemiological study subjects' residences (the study is conducted by the California Environmental Protection Agency). This is a cross-sectional field study, investigating the indoor-outdoor PM characteristics in several different residences over three 24-hour periods. Data collected from the study presented here examined the following questions:

1. What are the relationships, for both coarse and fine particles, between ambient and indoor concentrations?
2. What are the major chemical constituents of indoor and outdoor particles?

2.3 Methods

2.3.1 *Study Design*

This investigation of the indoor/outdoor relationships of coarse and fine particles was designed for the unique desert climate in the winter and spring of 2000 for two reasons. First, geologic particles comprise a significant percentage of the total particulate mass throughout the year in the Valley, especially during gusty wind episodes (SCAQMD, 1990). Second, during the winter and spring seasons, typically from January to early May, outdoor PM may have marked influence on indoor air quality in residences whose occupants tend to open windows for prolonged time periods and do not use air conditioning.

Thirteen homes of volunteers who concurrently were participating in the epidemiological study noted above were included in this study. Seven locations were in Palm Springs (at the northwest end of the populated corridor) and six in

Indio, about thirty miles southeast of Palm Springs. The characteristics of each sampling site are shown in Table 2.1.

These residences were all within five miles of the fixed site air quality monitors at the north (Palm Springs) and south (Indio) ends of the Valley. These locations were targeted since the Indio area, which is in the Valley's wind belt, typically has higher concentrations of PM_{10} and coarse particles (Ostro et al., 1999), while the Palm Springs area historically has had a mix of coarse and fine particles, including materials transported from the Los Angeles basin, but lower overall concentrations of PM_{10} .

The principal sampler utilized in residences of this study was the USC Personal Particle Sampler (PPS), designed for coarse and $PM_{2.5}$ sampling at 5 LPM (Sioutas et al., 1999). A major feature of this sampler is the separation from the air sample and collection of coarse (2.5-10 μm) particles by impaction on an uncoated quartz substrate, without any particle bounce. The substrate is a quartz fiber filter disk, 0.8 cm in diameter. Collection efficiency of coarse particles as large as 10 μm in aerodynamic diameter exceeds 95% with a quartz fiber filter used as an impaction surface (Chang et al., 1997). Using this uncoated substrate for particle collection is a particularly attractive feature of the PPS, as adhesive coating materials typically used to reduce particle bounce in impactors would likely interfere with the chemical analysis of the substrate. Fine (i.e., <2.5 μm in aerodynamic diameter) particles in the PPS are collected on either a 37-mm Teflon filter (PTFE Teflon, 2 μm pore, Gelman Science, Ann Arbor, MI) or a 37-mm quartz filter (Pallflex Corp., Putnam,

CT), depending on the type of chemical analysis to be performed after sample collection. Teflon filters were used for gravimetric and elemental analysis, whereas quartz filters were used for gravimetric and organic analysis, described below.

TABLE 2.1. Characteristics of Coachella Valley Indoor/ Outdoor Sampling Locations. (P.S. stands for Palm Springs). Sampling period; January – May 2000

Residence	No. of occupants	City	Stove Type	Heater Type	Type of Analysis ^a
A	1	Indio	Gas	Electric	EC/OC, Elements
B	1	P.S.	Electric	Electric	EC/OC, Elements
C	1	Indio	Electric	Gas	EC/OC, Elements
D	1	P.S.	Electric	Electric	EC/OC, Elements
E	4	P.S.	Gas	Gas	EC/OC, Elements
F	1	Indio	Gas	Gas	EC/OC, Elements
G	1	Indio	Electric	Electric	EC/OC, Elements
H	2	P.S.	Electric	Gas	EC/OC, Elements
I	2	Indio	Gas	Electric	EC/OC, Elements
J	1	Indio	Electric	Electric	EC/OC, Elements
K	1	P.S.	Electric	Electric	Elements
L	1	P.S.	Gas	Gas	EC/OC
M	3	P.S.	Gas	Gas	EC/OC

^a EC/OC = elemental and organic carbon analysis

At each home a PPS was placed immediately outdoors, such as in the front yard, in a courtyard, or on a balcony. The indoor PPS was placed in either the living room or family room where the residents spent the majority of their time at home.

Efforts were made to secure the PPS inlet at a height of 1.0-1.5 m above the ground in each residence in order to avoid potential interferences from excessive resuspension of particles due to residential activities and to also sample aerosol concentrations that would reflect those in a “typical” breathing zone. Each set of indoor/outdoor PPS sampling lasted twenty-three hours in order to incorporate time needed for filter collection and replacement. Two to four 23-hour experiments were conducted in each residence to capture the intra-home variability.

2.3.2 Sample Analysis

For mass concentration measurements, the Teflon and quartz filters (for fine particles) as well as the quartz substrates (coarse particles) of the indoor and outdoor PPS were weighed before and after each field test, using a Mettler 5 Microbalance (MT 5, Mettler-Toledo Inc., Highstown, NJ), under controlled relative humidity (e.g., 40-45%) and temperature (e.g., 22-24 °C) conditions in the facilities of the Aerosol Laboratory at the University of Southern California. Filters were weighed after a 24-hour equilibration period. Laboratory and field blanks were used for quality assurance.

Subsequent to weighing, the PPS substrates, collecting coarse PM, were analyzed for trace element and metal content, whereas half of the PPS filters, collecting PM_{2.5}, were analyzed for trace elements and metals (Teflon filters) and half for elemental carbon (EC) and organic carbon (OC) concentrations (quartz filters).

The Teflon filters were analyzed by means of x-ray fluorescence (XRF) to determine fine particle concentrations of selected trace elements and metals. Trace element and metal concentrations for coarse particles were determined by analyzing the quartz PPS substrates by means of inductively coupled plasma-mass spectroscopy (ICP/MS). These analyses were conducted by the Monitoring and Laboratory Division of the California Air Resources Board.

The indoor and outdoor elemental and organic carbon (EC/OC) concentrations of fine particles were determined by thermo-analysis of the quartz PPS filters. This analytical method is described more elaborately by Fung (1990). It should be noted that particle collection using quartz filters for measurements of the OC content of PM may be prone to artifacts, mostly related to adsorption of gas-phase organics onto the quartz filter. Given the relative similarity between the sampling conditions (i.e., type of sampler, flow rate, duration, mass loading) indoor and outdoors, we expect that these artifacts (if they occurred), would not differ substantially between the outdoor and indoor samples collected concurrently, and thus would have little effect on the I/O comparisons for OC. Moreover, because many atmospherically relevant organic compounds, such as polycyclic aromatic hydrocarbons (PAH) partition between gas and particulate phases, and the gas-to-particle partitioning is temperature dependent, total (i.e., gas plus particle) measurements might be more desirable for source apportionment (Carlton et al., 1999).

2.4 Results and Discussion

2.4.1 Indoor and Outdoor Coarse and Fine PM Mass Concentrations

Results from the field tests comparing indoor to outdoor particle concentrations based on mass and chemical composition are shown in Figures 2.1-2.6 and summarized in Tables 2.2 and 2.3. Similar to previously published studies on the relationship between indoor-outdoor PM (Colome et al., 1992; Clayton et al., 1993), the value of the coefficient of determination (R^2) between the indoor and outdoor data was used as an indicator of the degree to which a PM species measured indoors is attributed to infiltration from outdoors.

In Figures 2.1 and 2.2, indoor mass concentrations for both coarse and fine particles were plotted against their respective outdoor concentrations. Table 2.2 presents a summary of the indoor and outdoor measurements for coarse and fine particle concentrations. Fine PM concentrations accounted on the average for 74.3 (± 11.0)% of the total PM_{10} concentrations indoors, whereas fine PM contributed to 61.3 (± 13.1)% of the outdoor PM_{10} concentrations. Previously published SCAQMD data indicated that geologic (which are primarily coarse) particles in the California deserts constitute about 50-60% of the total PM_{10} (SCAQMD, 1990), thus somewhat higher than those observed in our study. It needs to be emphasized, however, that the outdoor measurements collected in the SCAQMD study were taken in a variety of nonresidential locations at which intermittent gusty winds caused substantial resuspension of particles. Such resuspension may not occur in the immediate

proximity of residences, which usually have planted courtyards and regular daily watering of the ground.

Figure 2.1 shows that coarse indoor concentrations are markedly lower than those outdoors. Pairwise comparisons between indoor and outdoor coarse PM concentrations indicated that outdoor concentrations were significantly higher ($p=0.005$) than those indoors, with the average indoor-to-outdoor mass concentration ratio equal to 0.66 (± 0.27). Figure 2.1 also shows a relatively weak correlation between the outdoor and indoor data ($R^2 = 0.35$). The weak indoor-to-outdoor PM association suggests that a substantial fraction of coarse particles are generated by indoor sources and activities, such as dusting, cleaning, washing and resuspension, all of which depend on the residents of each individual home.

Our results are in agreement with the findings of a recent study by Abt et al. (2000), in which indoor activities, such as vacuuming, dusting, washing and carpet cleaning, contributed from 50% to 80% of the indoor concentrations of 2-10 μm particles. The same study also showed that the penetration of outdoor 2-10 μm particles indoors varies from 10% to 40% and generally decreases with size. These two factors would be responsible for decreasing the R^2 between the indoor and outdoor data. Our results (excluding the one outlier, which increases R^2 to 0.53) are also in very good agreement with those in a study by Monn and Becker (1999), in which the indoor-to-outdoor coarse PM ratio was 0.7 with the coefficient of multiple determination equal to 0.55.

Figure 2.2 shows a plot of the indoor versus outdoor concentrations for fine particles. Pairwise comparisons between these concentrations ($p = 0.7$) indicate that the indoor fine PM levels are very similar to those measured outdoors. The average

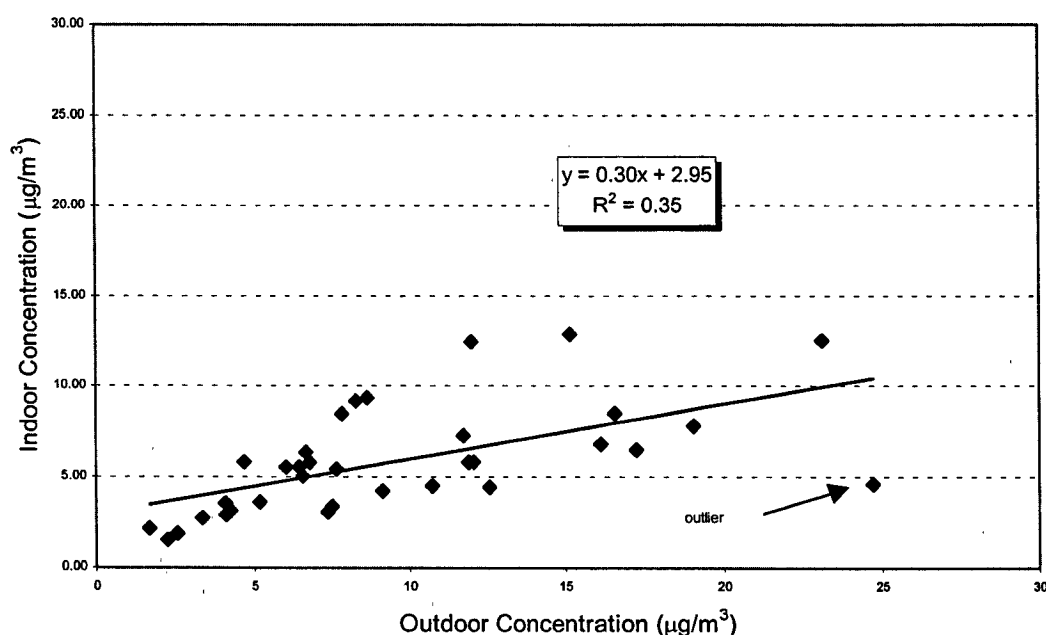


Figure 2.1. Indoor versus outdoor coarse particle mass concentrations.

indoor-to-outdoor fine particle mass concentration ratio was $1.03 (\pm 0.29)$. However, the data plotted in Figure 2.2 indicate that outdoor concentrations can explain only about 37% of the variation of the indoor concentrations, thereby suggesting that there may be significant contributions by indoor sources to the overall $PM_{2.5}$ concentrations in the 13 residences monitored in this study. [Excluding the one outlier shown by the arrow in Figure 2.2 increases the indoor-outdoor correlation to $R^2 = 0.51$, while the resulting regression line changes to $y = 0.81 x + 3.4$].

Additional differences in the home structural characteristics, number of occupants and activity patterns of individuals in each of the 13 residences also contribute to the overall variability in the indoor PM concentrations.

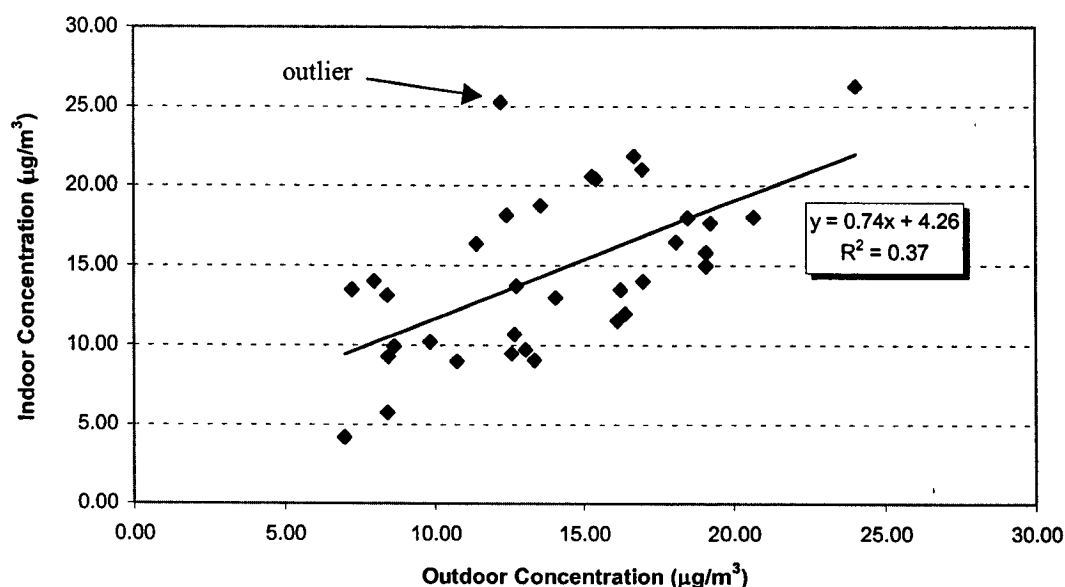


Figure 2.2. Indoor versus outdoor fine particle mass concentrations.

2.4.2 Indoor and Outdoor Elemental and Organic Carbon Concentrations for Fine PM

Figure 2.3 shows a plot of indoor-to-outdoor elemental carbon concentrations. Indoor EC concentrations are generally lower than those outdoors (with one notable exception observed for one of the 13 residences), with the average indoor-to-outdoor EC concentration being equal to $0.85 (\pm 0.46)$. The coefficient of multiple determination between indoor and outdoor EC concentrations, R^2 , is 0.45. It should be noted that omission of the outlier increases R^2 to 0.71, suggesting that a

substantial fraction of the variation in indoor EC concentrations can be attributed to that of the outdoor EC concentrations, at least in all but one residence. At this moment, we have no explanation for the elevated EC levels observed in the “outlier” residence. For the remaining data, the high R^2 value indicates that a substantial fraction of indoor elemental carbon penetrates from outdoors. This is consistent with results reported by Jones et al. (2000), who found that elemental carbon originates outdoors, mostly from vehicular emissions, except in homes in which smokers are present. (Sampling in our study was conducted exclusively in non-smoking residences.)

Elemental carbon (soot) is a byproduct of incomplete combustion emitted primarily in exhaust from road traffic (QUARG, 1993). These carbon particles can exist singly or as agglomerates with aerodynamic diameters mostly in the ultrafine range, between 0.05-0.2 μm (Seinfeld and Pandis, 1998). According to the recently published data by Abt et al. (2000), this size range has the highest outdoor-to-indoor penetration, varying generally from 75-100%; hence, in the absence of smoking and wood burning, most of the elemental carbon measured indoors would be expected to originate outdoors.

Figure 2.4 shows a plot of the indoor to outdoor concentrations of organic carbon, including the linear regression line. Organic carbon was the most significant component of both outdoor and indoor $\text{PM}_{2.5}$ mass concentrations, accounting for 0.41 (± 0.14) and 0.61 (± 0.17) of the total fine PM mass concentrations measured outdoors and indoors, respectively. Indoor organic carbon concentrations were

found to be substantially higher than those outdoors in all 13 residences of this study, with the average indoor to outdoor PM_{2.5} organic carbon concentration ratio being 1.77 (± 0.36). The high indoor concentrations are undoubtedly due to the

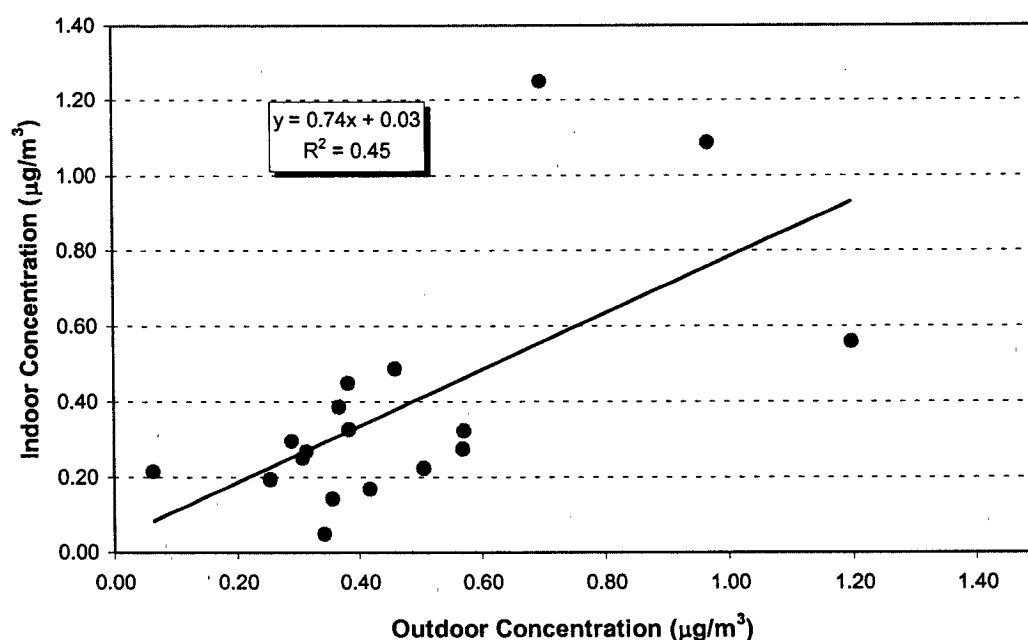


Figure 2.3. PM_{2.5} elemental carbon (EC) indoor/outdoor comparison by home.

contribution of indoor sources, including cooking, waxes, cleaners/polishes, plasticizers, and pesticides. Abt et al. (2000) reported that cooking was the predominant source of indoor particles smaller than 0.5 µm in diameter, contributing on average about 0.27 µm³/cm³/min. The same study showed that cooking generated substantial amounts of super-micrometer particles. However, such particles have also significantly higher decay rates than those smaller than 0.5 µm.

The data plotted in Figure 2.4 also indicate that a substantial fraction of the variability in the indoor data can be explained by the outdoor concentrations ($R^2=0.63$), thereby suggesting that a relatively high percentage of outdoor organic carbon also penetrates the home. The majority of particle-bound organic compounds

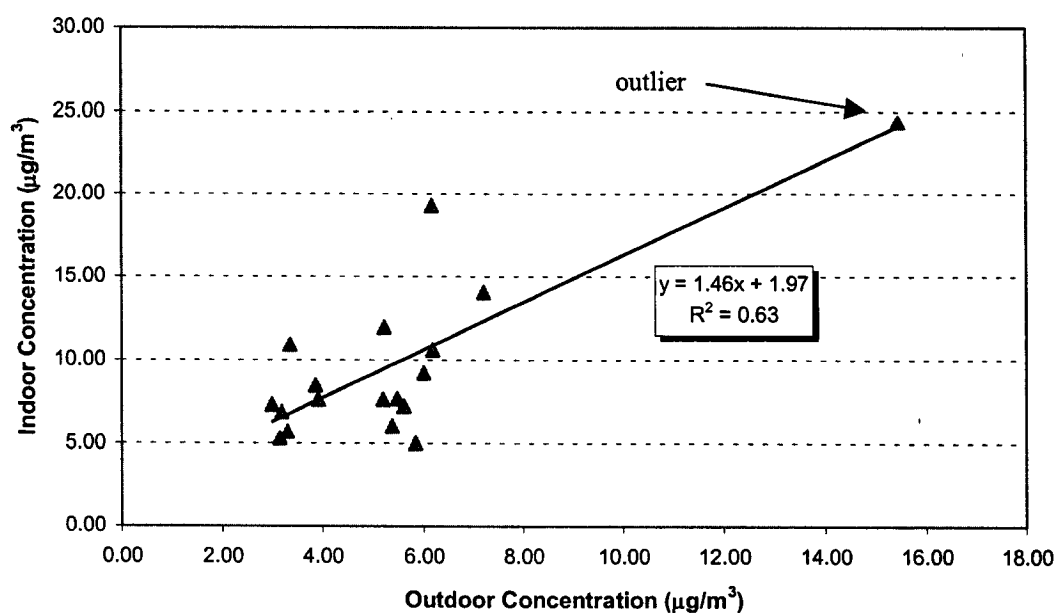


Figure 2.4. PM2.5 organic carbon (OC) indoor/outdoor comparison by home.

exist typically as submicrometer particles (McMurry and Zhang, 1989), often partitioned in a bimodal distribution with one peak in the 0.4-1.0 µm range and another between 0.1-0.2 µm (Pickle et al., 1990; Mylonas et al., 1991). The latter mode normally dominates the ambient OC size distribution (Hildemann et al., 1991; Hildemann et al., 1993). The fraction of outdoor particles in this size range reported to penetrate indoors varies between 80% and 100% (Abt et al., 2000). Thus, in addition to the considerable contribution of indoor sources to the overall organic

carbon in fine PM, a substantial fraction of the particle-bound organic carbon measured indoors infiltrates from outdoors.

2.4.3 Indoor and Outdoor Trace Element and Metal Concentrations for Fine PM

Only these trace elements and metals in fine PM found in concentrations greater than three times the XRF limit of detection were included in this analysis. Thus, results for only the following metals are available: aluminum, silicon, sulfur, potassium, calcium, titanium, iron, and zinc. The indoor concentrations were plotted against the outdoor concentrations and are shown in Figures 2.5a-h. Of these particle-bound metals, sulfur, titanium, zinc, iron and aluminum show high correlations (R^2 ranging from 0.59 to 0.85), which suggests that a significant fraction of their indoor concentrations can be attributed to infiltration of outdoor particles containing these metals. Similar conclusions can be drawn for silicon, calcium and potassium, which have lower yet still significant correlations (R^2 of 0.50, 0.48, and 0.46 respectively).

Sulfur is a classic marker of atmospheric outdoor aerosols (Jones et al., 2000; Clayton et al., 1993) with no known indoor sources, which explains the very high correlation obtained between its indoor and outdoor concentrations ($R^2 = 0.85$). Sulfur exists mostly as sulfate fine particles ($<1 \mu\text{m}$) that form from the oxidation of sulfur dioxide (Clayton et al., 1993; US EPA, 1975; Moschandreas et al., 1979). The indoor-to-outdoor (I/O) concentration ratio of sulfur was calculated to be 0.80 (\pm

0.18), which is consistent with the findings of Jones et al. (2000) and the PTEAM study (Clayton et al., 1993). The somewhat lower indoor levels are due to some particle removal during penetration indoors. The I/O sulfur ratio probably provides a reasonable estimate of the I/O species ratios for species that infiltrate indoors from the ambient. The near-equality of the indoor and outdoor fine PM concentrations obtained in this study is probably a coincidence occurring because of the higher OC concentrations measured indoors, which compensate for the particles lost during infiltration.

Similarly, the results shown in Figure 2.5b indicate that the indoor concentrations of aluminum are highly correlated with those measured outdoors ($R^2 = 0.85$), but on the average $0.64 (\pm 0.23)$ times the outdoors values. The high correlation between the indoor and outdoor data indicates that this metal likely originates outdoors; however, probably because of the larger particle size associated with Al, a smaller fraction infiltrates the house relative to sulfur. Particle-bound metals of crustal origin, such as silicon and calcium, are also expected to display indoor-to-outdoor characteristics similar to those observed for aluminum (Clayton et al., 1993). This probably explains the similar indoor-to-outdoor concentration ratios obtained for silicon and calcium (i.e., 0.69 ± 0.31 and 0.66 ± 0.24 , respectively). Since we expect all of these metals to be found primarily in the coarse mode, the sizes of these particles in the fine PM mode are probably greater than $1 \mu\text{m}$, thus representing a “tail-end” of the coarse outdoor mode. Coarse particles settle inside

and do not become resuspended except transiently, so indoor concentrations of the associated metals are expected to be lower than those outdoors.

The high correlations between indoor and outdoor concentrations obtained for iron, titanium and zinc indicate that these metals are also more likely to originate from outdoor sources with approximate indoor-to-outdoor concentration ratios of 0.69 (± 0.22), 0.63 (± 0.25), and 0.91 (± 0.29), respectively. Moschandreas et al. (1979) reported similar results. That study, however, did not find a strong correlation between PM₁₀ indoor and outdoor iron concentrations, probably because of the substantial fraction of iron in the coarse PM mode, both indoors and outdoors, which would tend to decrease these correlations. The higher indoor-to-outdoor Zn concentration ratio is probably due to the higher infiltration rate of outdoor particle-bound Zn indoors. Jones et al. (2000) and Clayton et al. (1993) found similar indoor-to-outdoor ratios for zinc. Zinc is also primarily an outdoor metal, whose only known indoor source is smoking (Wallace et al., 1997; Jones et al., 2000). Zinc is known to exist in very small particles (mostly smaller than 0.5 μm) that originate from anthropogenic sources such as fossil fuel combustion (Seinfeld and Pandis, 1998). The small size of these particles explains the high penetration values from outdoors.

Indoor and outdoor potassium concentrations were moderately correlated ($R^2 = 0.46$), with an average indoor-to-outdoor concentration ratio of 0.79 (± 0.27). These results are inconsistent with those of Moschandreas et al. (1979) who observed variations of potassium to be dependent mostly on indoor activities, such as smoking

and wood burning (hence no correlations were found between indoor and outdoor K concentrations). A possible explanation for this difference might be related to differences in the study locations, as potassium may be a soil constituent of the deserts and is also a marker for burning organic matter (i.e. cooking) (Moschandreas et al., 1979).

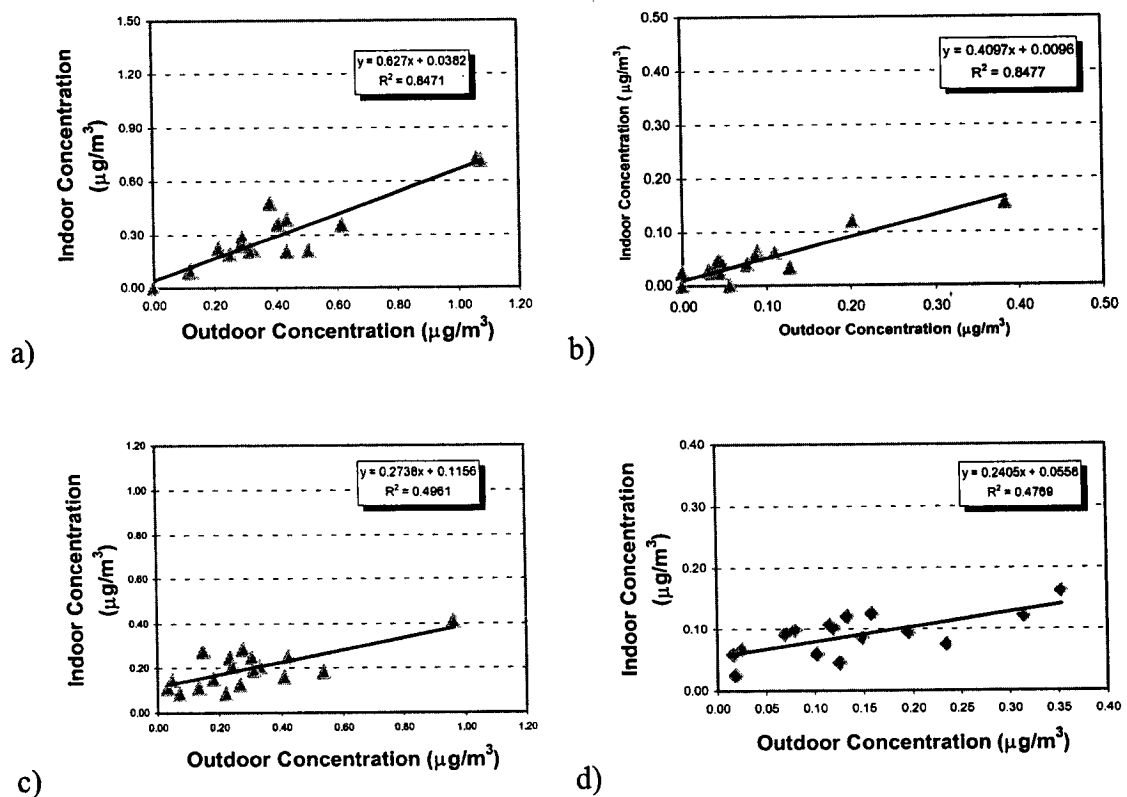


Figure 2.5. PM_{2.5} trace element and metal indoor/outdoor comparison by homes: (a) sulfur, (b) aluminum, (c) silicon, (d) calcium, (e) iron, (f) titanium, (g) zinc, (h) potassium.

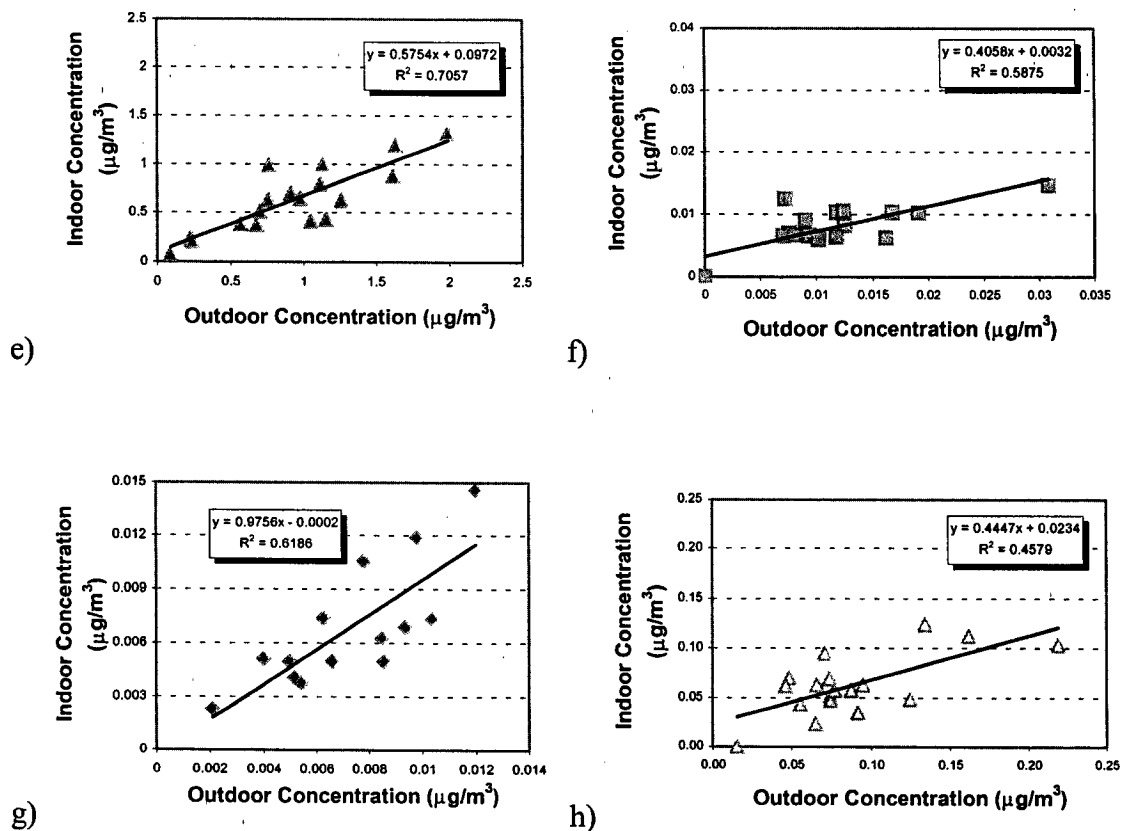


Figure 2.5. Continued.

2.4.4 Indoor and Outdoor Trace Element and Metal Concentrations for Coarse PM

To ensure accuracy, similar to the analysis of fine particles, the concentrations of metals in coarse PM were only included if greater than three times the limit of detection of ICP-MS. The results for magnesium, aluminum, silicon, sulfur, potassium, calcium, and iron are summarized in Figures 2.6 a-g, with the average ratios of indoor-to-outdoor coarse PM concentrations listed in Table 2.3.

Indoor to outdoor concentrations for coarse PM metals display considerably lower correlations than those observed for fine particles. Nevertheless, indoor concentrations still moderately depend on their outdoor concentrations. Silicon and magnesium have the highest indoor/outdoor correlations with R^2 values of 0.47 and 0.48, respectively, while the rest of the metals, except sulfur, have remarkably similar R^2 values, ranging between 0.37 – 0.42. The R^2 values for most metals are in agreement with that obtained for mass concentration ($R^2 = 0.35$). The data listed in

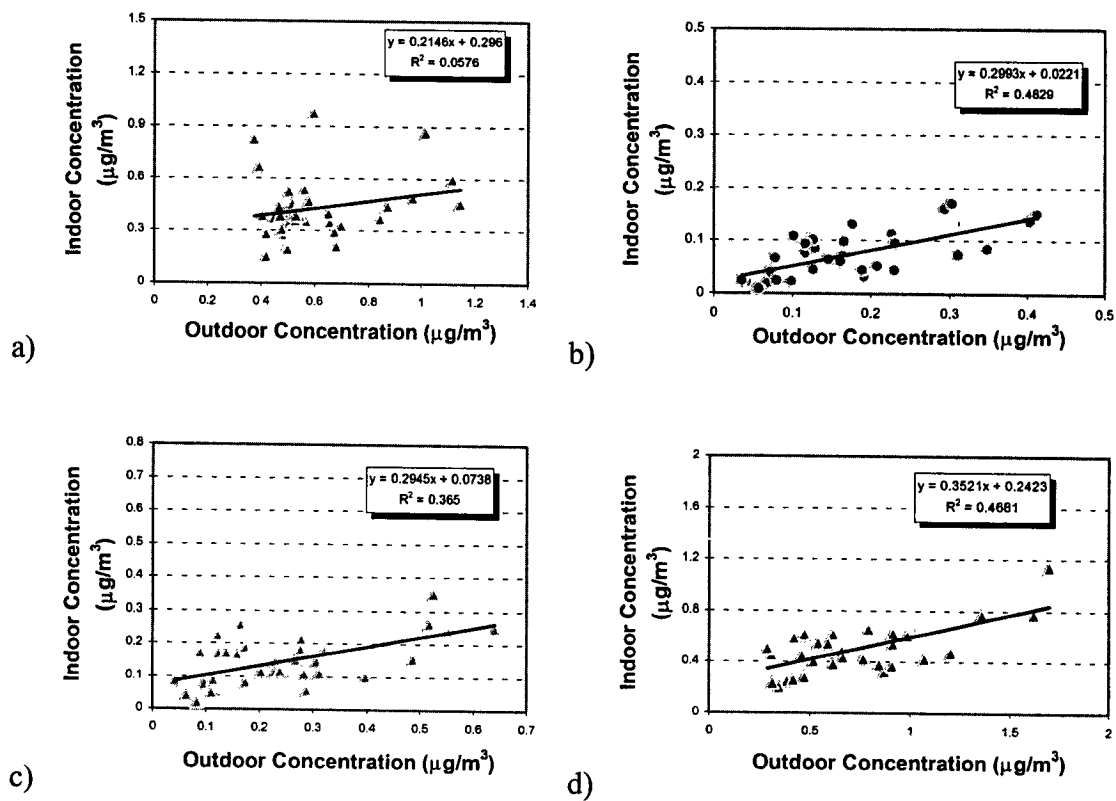


Figure 2.6. Coarse particle trace element and metal indoor/outdoor comparison by homes: (a) sulfur, (b) magnesium, (c) aluminum, (d) silicon, (e) calcium, (f) iron, (g) potassium.

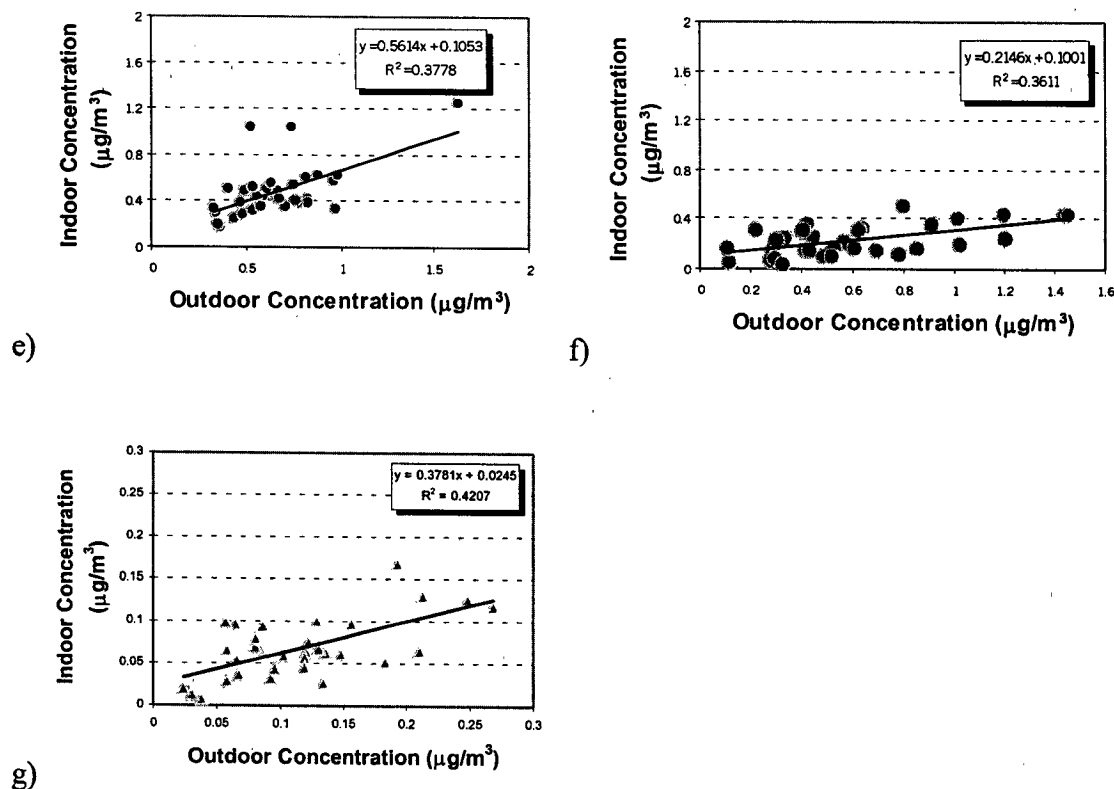


Figure 2.6. Continued.

Table 2.3 also indicate that the indoor-to-outdoor ratios for aluminum, silicon, sulfur, potassium and calcium are remarkably similar, varying from about 0.57 to 0.69. The indoor-to-outdoor concentration ratios for magnesium and iron are substantially lower (i.e., 0.42 and 0.38, respectively), suggesting that these two metals might be associated with somewhat larger particles than the rest of the particle-bound metals measured indoors.

TABLE 2.2. Descriptive Statistics for PM with Respect to Sampling Location and Size Cut.

Location and PM type	No. samples	Mean Mass Conc. $\mu\text{g}/\text{m}^3$	Median Mass Conc. $\mu\text{g}/\text{m}^3$	Range
Indoor--Fine PM	39	15.45	13.50	4.21-49.30
Outdoor--Fine PM	39	15.02	14.63	3.66-34.43
Indoor--Coarse PM	39	5.63	4.55	0.57-20.22
Outdoor--Coarse PM	39	8.61	8.42	0.64-24.71

The data plotted in Figure 2.6 show that there is no correlation between coarse particle-bound sulfur concentrations measured indoors and outdoors. Sulfur in ambient air of the Coachella Valley was mostly found in the fine PM mode (which accounted for approximately $80 \pm 5\%$ of total S by mass). The lack of correlation between the indoor and outdoor sulfur data suggests that indoor sources, such as gypsum found in certain wallboards or resuspension of previously deposited sulfate particles may be important contributors to sulfur measured in coarse PM indoors.

The considerably lower metal concentrations measured indoors compared to outdoors are undoubtedly due to the lower infiltration rates as well as higher deposition velocities of these particles (Abt et al., 2000). Many processes taking place within a house such as cleaning, dusting, washing, and vacuuming have been shown to affect coarse particle concentrations. As these processes vary randomly between individual homes, correlations between indoor and outdoor coarse particles would be expected to be low.

TABLE 2.3. Average (\pm standard deviation) ratio of indoor-to-outdoor particle concentrations for selected trace elements and metals. N = number of paired indoor and outdoor data collected simultaneously

PM species	N	Indoor to Outdoor Fine PM Ratio	N	Indoor to Outdoor Coarse PM Ratio
Mass	35	1.03 (\pm 0.29).	35	0.66 (\pm 0.27).
Elemental	17	0.85 (\pm 0.46)	N/A	
Carbon				
Organic	18	1.77 (\pm 0.36)	N/A	
Carbon				
Magnesium	N/A		33	0.42 (\pm 0.14)
Aluminum	18	0.64 (\pm 0.23)	34	0.58 (\pm 0.22)
Silicon	18	0.69 (\pm 0.31)	34	0.69 (\pm 0.20)
Sulfur	18	0.80 (\pm 0.18)	35	0.68 (\pm 0.21)
Potassium	18	0.79 (\pm 0.27)	33	0.57 (\pm 0.18)
Calcium	17	0.66 (\pm 0.24)	35	0.68 (\pm 0.15)
Titanium	17	0.63 (\pm 0.25)	N/A	
Zinc	14	0.91 (\pm 0.29)	N/A	
Iron	18	0.69 (\pm 0.22)	33	0.38 (\pm 0.15)

2.5 Summary and Conclusions

This study identified the concentrations and composition of both indoor and outdoor air in 13 residencies of the Coachella Valley, CA during the winter and spring of 2000, a period during which maximum outdoor PM penetration in indoor environments was expected. These data will be incorporated in an ongoing epidemiological study to examine associations between any of the PM measurements and health effects of elderly people who live in this area. Fine PM concentrations

indoors, whereas fine PM contributed to 61.3 (\pm 13.1)% of the outdoor PM₁₀ concentrations. The indoor-to-outdoor mass concentration ratios were 0.66 (\pm 0.27) and 1.03 (\pm 0.29), for coarse and fine PM, respectively. Although the outdoor air of the specific study area has been traditionally considered to be rich in coarse particles, the results of this study suggest that indoor PM₁₀ concentrations are still dominated by the contribution of fine particles.

Acknowledgements

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Chapter 3

DEVELOPMENT AND EVALUATION OF A COMPACT, HIGHLY EFFICIENT COARSE PARTICLE CONCENTRATOR FOR TOXICOLOGICAL STUDIES

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3.1 Abstract

A high-efficiency Coarse-mode Particle Concentrator (CPC) has been developed and evaluated in the laboratory as well as validated by performing field experiments at the University of Southern California, in Los Angeles, CA, and in Bilthoven, the Netherlands. The CPC operates with a total intake flow of 1000 LPM. The minor flow rate, containing the concentrated coarse-mode particles (2.5 – 10 μm), can be adjusted from 33 to 120 LPM in order to enrich ambient coarse PM concentrations by a factor of 8 to 30, depending on the desirable exposure level and flow rate needed. The laboratory evaluation of the virtual impactors at three minor flow rates (3.3, 7 and 10 LPM, respectively) indicated that extremely efficient concentration enrichment was obtained for 2.5 – 10 μm particles. In the field tests, the CPC operated at a minor flow rate of 33 LPM, and the mass obtained was compared to the mass collected by a reference sampler, a (rotating) Micro-Orifice Uniform Deposit Impactor (MOUDI), which sampled at 30 LPM. Concentration enrichment factors in the range of 26-30 were achieved based on particle mass, sulfate, nitrate as well as selected trace element and metal concentrations (Al, Si, Ca,

Fe, K, Mn, Cu, Zn, Ti). CPC and MOUDI concentrations were highly correlated for all species, with R^2 in the range of 0.74 to 0.89. The use of round (compared to rectangular geometry) nozzle virtual impactors in the CPC results in a high concentration efficiency, which reduces the CPC size as well as the power requirement that is required for its operation. The compact size of the CPC makes it readily transportable to desired locations for exposures to coarse-mode particles derived from different sources and thus of a varying chemical composition.

3.2 Introduction

Abundant epidemiological literature has indicated a significant relationship between ambient particulate matter (PM) and important clinical end-points, such as respiratory symptoms (including asthma attacks), respiratory-related clinic/emergency room encounters and hospitalization, as well as cardiovascular morbidity and mortality (Dockery et al., 1989; Pope et al., 1991; Koenig et al., 1993;). An average $10 \mu\text{g}/\text{m}^3$ increase in PM_{10} is typically associated with a 1-10% increase in respiratory symptoms at PM_{10} levels near or even below $150 \mu\text{g}/\text{m}^3$ and with lung function declines of as much as 7% during 24-hr PM_{10} concentrations exceeding $150 \mu\text{g}/\text{m}^3$ (Ostro, 1993; Pope et al., 1995). Despite the growing evidence of particulate-related health effects, the paucity of information about specific biological mechanisms remains a critical missing link.

Although a few studies using artificial multi-component fine particle aerosols (Amdur and Chen, 1989; Anderson et al., 1992; Kleinman et al., 1995 and 2003; Bolarin *et al.*, 1997; Arts *et al.*, 2000) have demonstrated mild effects in animals, they have not consistently provided support for a causal relationship between serious health effects in humans and realistic exposure levels. This discordance between the outcomes of laboratory and epidemiological studies may indicate that such artificial particles do not truly replicate the adverse effects of the complex and heterogeneous mixtures that occur in ambient air.

The recent development of fine particle concentrators based on the principle of virtual impaction (Sioutas et al., 1995a,b; Sioutas et al., 1997) or centrifugation (Gordon et al., 1999) has made it possible to perform laboratory exposures with “real-life” ambient aerosols at highly increased, yet still environmentally realistic, particle concentrations. Some preliminary results using these technologies have been reported (Godleski et al., 1996; Clarke et al., 1999; Gavett et al., 1999; Ghio and Devlin, 1999; Urch et al., 1999), suggesting physiological toxic responses to concentrated ambient particle exposures in laboratory animals and subtle responses in human volunteers. This new line of investigation will hopefully eventually lead to coherence between in vivo studies and epidemiological evidence.

The aforementioned particle concentrator technologies primarily concentrate the accumulation mode (i.e., 0.2 – 2.5 μm) of atmospheric aerosols. Coarse PM may

also consist of several potentially toxic components, such as resuspended particulate matter from paved and unpaved roads, industrial materials, brake linings, tire residues, trace metals, and bioaerosols. A considerable fraction of these particles may deposit in the upper airways and to a lesser extent into the lower airways, and may be responsible for the exacerbation of asthma. Recent data from a small number of epidemiological studies indicate that, apart from--or in addition to--the fine PM fraction, health effects may also be closely associated with the coarse PM fraction and sometimes even to a larger extent (Ostro et al., 1999, Kleinman et al., 2003) than PM_{2.5}. In vitro studies with human monocytes (Monn and Becker, 1998; Becker et al., 1996) show that cellular toxicity and inflammation may also be associated with the coarse fraction (2.5-10 µm) and its biological components. Also, in vitro data from Hornberg *et al.* (1998a,b) on genotoxicity of ambient fine and coarse mode PM collected from an urban area characterized by a high traffic density suggests that coarse mode PM may have comparable or even higher activity. Collectively, these studies indicated that the coarse mode PM might still contribute to a certain extent to observed health conditions, especially those occurring in the higher airways, like asthma.

To investigate real world ambient coarse mode particles in experimental studies, the research presented here describes the development of a high concentration efficiency coarse particle concentrator (CPC), extended from a previously developed single-nozzle, portable coarse particle concentrator (Kim et al.,

2000). The scaled up CPC maintains the advantage of portability and compact size (80cm×75cm×45cm) while increasing coarse particle concentrations by a factor up to 40, and it can be readily used for human and/or animal exposure studies. Detailed comparisons between concentrated and ambient coarse aerosols based on mass, sulfate, nitrate, and selected trace elements and metals were performed. The flexibility of varying the minor-to-total flow ratio of the CPC allows for alternating the desired exposure concentration level for animal exposures as well as for higher output flow rates needed when conducting human exposures.

3.3 Methods

The CPC consists of ten single-nozzle virtual impactors (Figure 3.1) developed by the department of Civil Engineering of the University of Southern California. These single-nozzle virtual impactors are placed in a 2 by 5 array (Figure 2a and 2b). A 90° elbow with inside diameter of 1.8 cm is connected to the inlet of each virtual impactor. Each virtual impactor operates at an intake flow rate of 100 LPM and therefore comprised a total intake flow rate of 1,000 LPM. The dimensions of the 90° elbow inlet were chosen to yield a theoretical 50% removal efficiency of 10 µm particles (PM₁₀) at a flow rate of 100 LPM based on the well-established impaction theory (Marple and Liu, 1974). The 50% cut point can be estimated from the Stokes number, St , defined as (Hinds, 1982):

$$St = \frac{\rho_p U_i d_p^2 C_c}{9 \mu d_0} \quad (1)$$

where d_p , ρ_p , C_c are the particle diameter, density and slip correction, μ is the air viscosity (1.81×10^{-4} g/cm•sec), U_i is the velocity through the 90° elbow, and d_0 is the inside diameter of the elbow ($d_0 = 1.8$ cm). The St corresponding to 10 μ m particles is 0.24, based on the nozzle dimensions and the flow rate through each nozzle, which is close to the value typically corresponding to the 50% cut point of round-nozzle impactors (Marple and Liu, 1974).

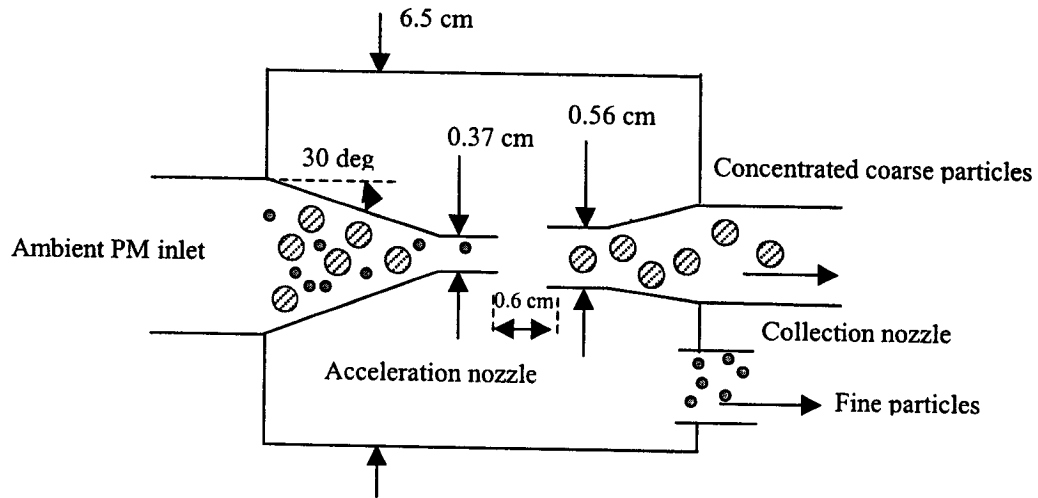


Figure 3.1 Schematic of the round jet impactors of the multinozzle CPC.

Particles smaller than 10 μm in aerodynamic diameter are drawn through the virtual impactor and become accelerated through a circular nozzle, which was designed to have a theoretical 50% cut point at about 2.0 μm for an intake flow rate of 100 LPM (Sioutas et al., 1999; Kim, et al., 2000). Coarse-mode particles (2.5 – 10 μm) cross the deflected air streamlines and are drawn through the collection nozzle (minor flow). Particles smaller than the cut point of the virtual impactor are diverted through the major flow. The ten minor flows are joined at the center of the CPC and lead to a 5-cm diameter tube, which can be connected to an animal or human exposure chamber (Figures 3.2a and 3.2b). The minor flow rate can vary from 3~20% of the intake flow rate, depending on desired exposure concentration level and/or exposure flow rate needed. Two major flow ducts, each 2.54 cm in diameter, were each connected to five of the virtual impactor major flows (i.e., 500 LPM) and placed on either side of minor flow, as shown in Figures 3.2a and 3.2b.

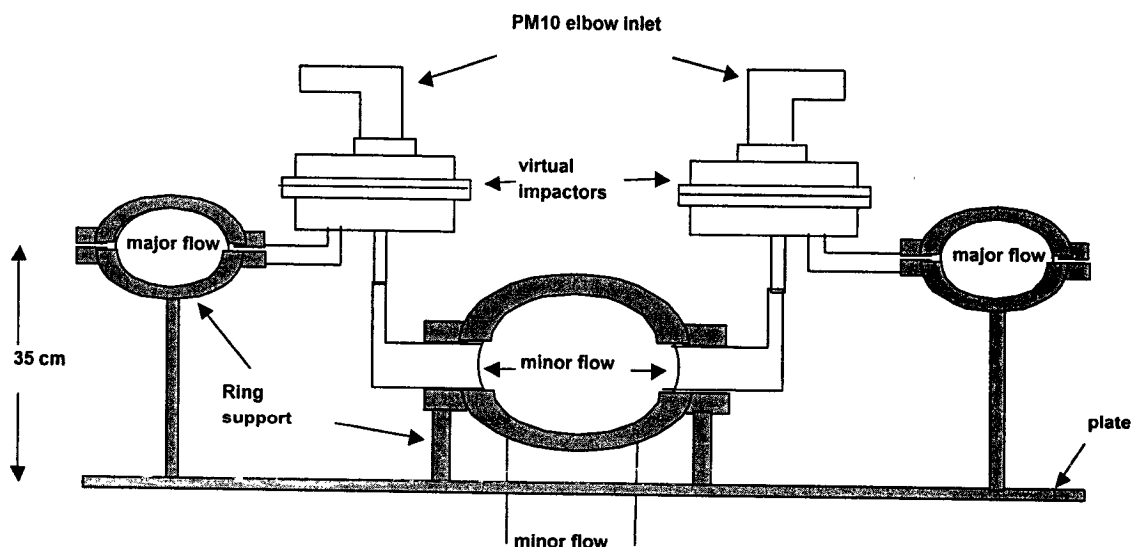


Figure 3.2a. Side view of the 10-nozzle Coarse Particle Concentrator.

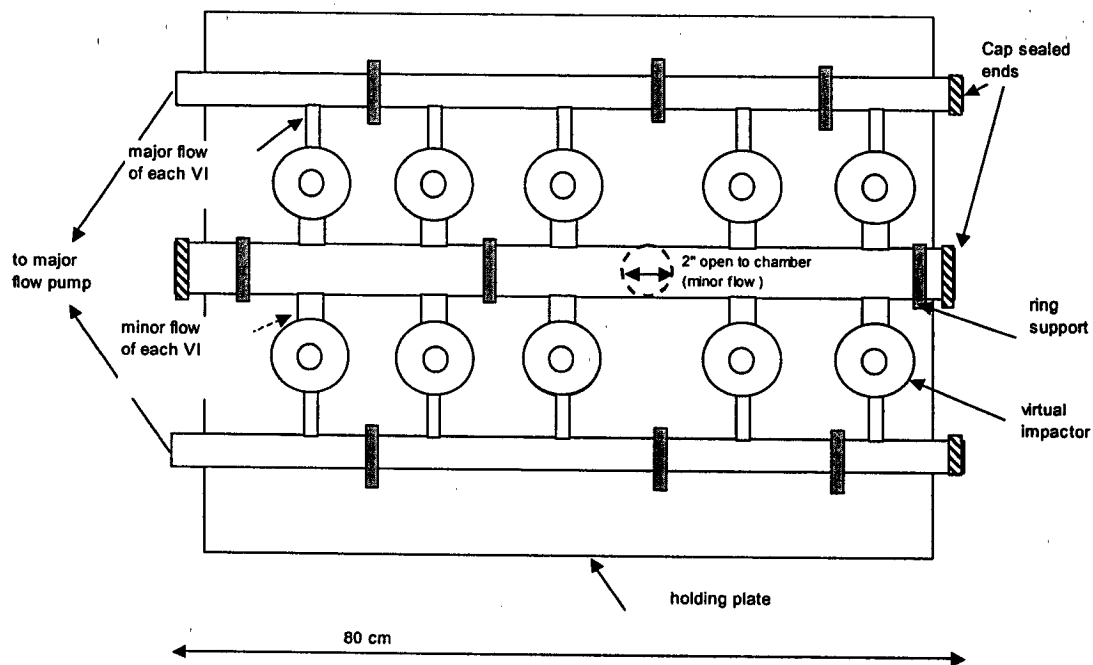


Figure 3.2b. Side view of the 10 nozzle CPC.

3.3.1 Laboratory Characterization of the Virtual Impactors

The first series of experiments was conducted in the laboratory to investigate the relationship between the concentration enrichment as a function of particle size and minor-to-total flow ratio. This relationship was investigated for each individual virtual impactor. Briefly, monodisperse aerosols in the size range of 1 to 10 μm were generated by atomizing dilute aqueous suspensions of fluorescent polystyrene latex particles (Polysciences Inc., Warrington, PA) with a constant output nebulizer

(HEART, VORTRAN Medical Technology, Inc., Sacramento, CA) at a rate of 15 LPM. The generated particles were drawn through a 1-liter bottle to remove the excess moisture and subsequently mixed with dry room air. The dry aerosol was then drawn through a tube containing ten Po-210 neutralizers that reduce particle charges prior to entering the virtual impactor. Monodisperse particles were subsequently drawn through the 90° elbow and entered the virtual impactor. For particles in the range of 1 to 5 μm , a nephelometer (DataRAM, RAM-1, MIE, Inc., Billerica, MA) was used to first measure the mass concentration of the generated aerosols prior to entering the 90° elbow of virtual impactors. The DataRAM was subsequently connected downstream of the minor flow of the virtual impactor to measure the mass concentration of the aerosols after concentration enrichment. The measurements were repeated at least three times, and the average concentration enrichment was determined as a function of particle size. The contributions from background ambient concentrations before and after the enrichment were recorded and subtracted from those of the input and concentrated aerosols prior to determining the collection efficiencies at the given particle size. It should be noted that indoor air levels were on the order of 7 – 15 $\mu\text{g}/\text{m}^3$, and substantially smaller than those of the generated aerosols (prior to concentration), which varied from 170 to about 500 $\mu\text{g}/\text{m}^3$. Therefore the contributions of the indoor aerosol to the overall concentrations measured upstream of- and in the minor flows of the virtual impactors were considered insignificant.

Concentration enrichment for 5 to 9 μm particles was determined by comparing the mass collected on a glass fiber filter (2 μm pore, Gelman Science, Ann Arbor, MI) connected to the minor flow of a virtual impactor, and the mass of a similar glass fiber filter in parallel to the test system to measure the concentration of the generated aerosol. The filter sampling in parallel was connected to a pump operating at 30 LPM. At the end of each run, each glass fiber filter was placed in 5 ml of ethyl acetate to extract the fluorescent dye from the collected particles. The quantities of the fluorescent dye in the extraction solutions were measured by a Fluorescence Detector (FD-500, GTI, Concord, MA) to determine particle concentration. Concentration enrichment for each particle size was defined as the ratio of the concentration measured in the minor flow of the virtual impactor to that of the aerosol immediately upstream of the virtual impactor inlet.

Each virtual impactor was tested at three different minor-to-total flow ratios. The total flow was kept constant at 100 LPM, whereas the minor flows were adjusted to 3.3, 7 and 10 LPM, resulting in ideal enrichment factors of 30, 15 and 10, respectively.

3.3.2 Field Evaluation of the Scaled-up Coarse Particle Concentrator

Following laboratory characterization, the CPC was evaluated in collocation with a modified Micro-Orifice Uniform Deposit Impactor (MOUDI, MSP Corporation, Minneapolis, MN) at two locations: University of Southern California,

in downtown Los Angeles (13 samples in mid August, 2000) and at the National Institute of Public Health and the Environment (RIVM, Bilthoven, The Netherlands, 6 samples in late September, 2000). The ten 90° elbow CPC inlets were arranged at 360° to ensure isokinetic sampling. In the field tests, the CPC operated at a total flow rate of 1,000 LPM and with a minor flow rate adjusted to 33 LPM. The ideal enrichment factor corresponding to this minor-to-total flow ratio is 30. Of the 33 LPM minor flow, 11 LPM were drawn into a 4.7 cm filter (2µm, PTFE, Gelman, Ann Arbor, MI) through an isokinetic sampling probe inserted in the 5 cm tube leading to the exposure chamber while the remaining 22 LPM were drawn by a separate pump. The reason for using only 11 LPM through the filter was to minimize potential coarse particle losses due to the flow contraction through the filter holder inlet. The pressure drops through the minor and major flows were about 2" H₂O and 110" H₂O, respectively. The MOUDI sampled at 30 LPM and was modified (from its original 8-stage configuration) to include only 3 stages, collecting size-segregated particles in aerodynamic diameter ranges of 0-2.5, 2.5-10 and 10-18 µm, respectively. 4.7 cm PTFE filters were used as impaction substrates in coarse PM MOUDI stages. The CPC 90° elbows and MOUDI stage 10-18 µm were coated with a thin layer of silicone grease to reduce potential particle bounce. The sampling flow rates of the MOUDI and CPC minor flows were measured before and after the sampling with calibrated flow meters (Cole-Parmer, #EW-32458-64 and #EW-32458-58, Cole-Parmer Instrument Company, Vernon Hills, IL 60061). Additionally

during sampling, the CPC minor flow filter sampler and the major flow were monitored by means of inline rotameters.

Particle mass, sulfate, nitrate concentrations as well as concentrations of trace elements and metals were determined for both ambient and concentrated aerosols. The sampling periods varied from 3 to 12 hours depending on observed PM levels. To determine particle mass concentrations, the PTFE filters of the MOUDI and minor flow were pre-weighed and post-weighed using a Microbalance (MT 5, Mettler-Toledo Inc., Highstown, NJ; Sartorius microbalance MC-5, Sartorius AG, Goettingen, Germany) in a room with controlled temperature of 21-24 °C and relative humidity of 40-50%. Filters were weighed twice in order to increase precision. In case of a difference of more than 3 µg between consecutive weighings, the filter was weighed a third time or reweighed until two consecutive weighings differed by less than 3 µg.

Thirteen out of nineteen pairs of PTFE filter samples collected by the CPC and MOUDI were then analyzed by means of x-ray fluorescence (XRF) to determine concentrations of selected elements and metals. These samples as well as the remaining six pairs (corresponding to samples collected in the Netherlands) were subsequently extracted with 0.15 ml of ethanol and 5 ml of ultrapure water. Ethanol was used in order to wet the hydrophobic Teflon filter. The samples were sonicated for 15 minutes and analyzed for sulfate and nitrate ions by means of ion chromatography (IC). Samples that were lower than three times the lower limits of

detection (LOD) of either XRF or IC were excluded. Using XRF prior to IC is a procedure that is typically not recommended for analysis of $PM_{2.5}$ because it might cause volatilization of ammonium nitrate. However, nitrate in the coarse mode in both the Netherlands (ten Brink et al., 1997) as well in Los Angeles (Solomon et al., 1988; Liu et al., 2000) is mostly associated with the non-volatile sodium nitrate (Solomon et al., 1988; Liu et al., 2000), the concentrations of which are not expected to be altered by XRF.

3.4 Results and Discussion

3.4.1 *Laboratory Characterization of the Virtual Impactors*

The results of the evaluation of the virtual impactors are shown in Figure 3.3. The concentration of generated monodisperse particles was in the range of 170-500 $\mu\text{g}/\text{m}^3$ and was enriched to 580-13,000 $\mu\text{g}/\text{m}^3$, and thus several orders of magnitude higher than the lower limit of detection of the DataRAM (1-5 $\mu\text{g}/\text{m}^3$) while below the instrument's upper limit (40 mg/m^3). It should be noted here that mass concentrations obtained by the DataRAM are quite dependent upon particle size (Sioutas et al., 2000). Therefore, particle concentrations measured by the DataRAM upstream and downstream of the virtual impactor were only used for determining the concentration enrichment of monodisperse particles, which is the ratio of the

downstream to the upstream concentrations and not for representing actual mass concentrations in the air stream.

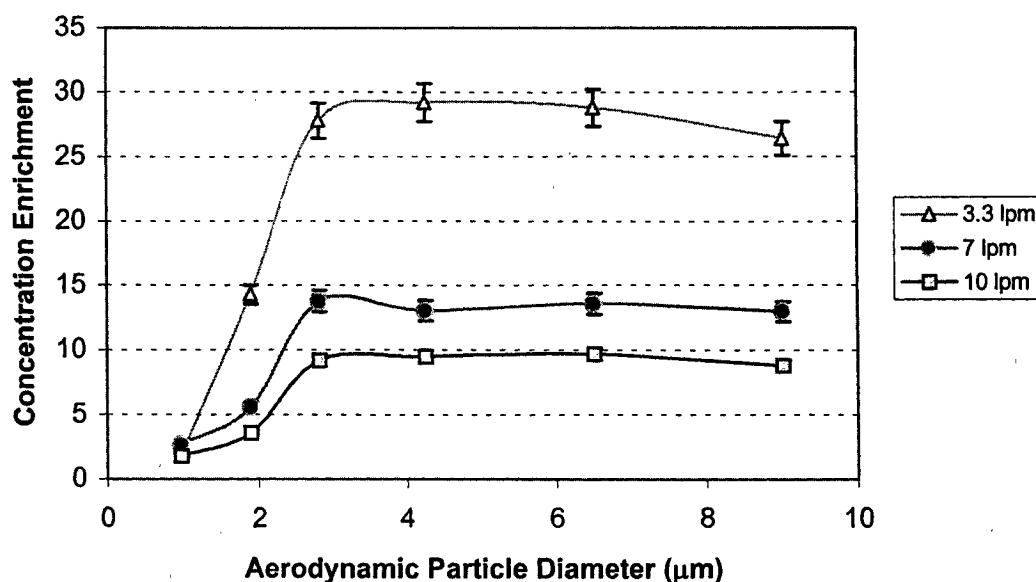


Figure 3.3. Concentration enrichment of each individual virtual impactor at three different minor flow rates. Total Intake Flow rate/impactor; 100 l/min.

Figure 3.3 shows the concentration enrichment for each individual virtual impactor at three minor flow rates as a function of aerodynamic particle diameter. The plotted data correspond to the averages of the ten virtual impactors, whereas the error bars represent the standard deviation in the enrichment values between the ten impactors. For a minor flow of 3.3 LPM, the concentration enrichment increases sharply from about 2 to about 28 as particle aerodynamic diameter increases from 1 to 2.5 μm . The enrichment is practically the same for particles in the aerodynamic

diameter range of 2.5 to 9 μm . Similarly, for a minor flow of 7 LPM, the concentration enrichment increases sharply from 2.7 to approximately 13.5 as particle aerodynamic diameter increases from 1 to 2.5 μm . For particles having aerodynamic diameters in the range of 3 to 9 μm , the enrichment value is about 13 to 14 and practically independent of particle size. The same trends can also be observed for the 10 LPM minor flow configuration. The data shown in Figure 3 also indicate that the 50% cut point of the virtual impactor (defined as the aerodynamic particle size at which the enrichment factor is half of its ideal value) is approximately 2.0 μm and does not seem to depend significantly on the minor-to-total flow ratio. The slight decrease in concentration enrichment values (still higher than 85% of the ideal value) observed at 9 μm particles is probably due to some internal losses through the collection nozzle. The overall high concentration efficiencies of 9 μm particles, however, prove that there is no significant loss of these particles due to the 90° elbow. More importantly, these tests imply that the size distribution of enriched coarse particles in the CPC was the same as that of the ambient air, since the concentration enrichment does not depend on particle size—at least for particles larger than 2.5 μm in aerodynamic diameter.

The near-ideal concentration enrichment factors for particles larger than 2.5 μm in aerodynamic diameter clearly illustrate the impressive performance of round nozzle virtual impactors, which have been proven to be superior to those having

acceleration and collection nozzles of rectangular geometry. Experimental flow visualization studies by Masuda et al. (1988) and Gotoh and Masuda (2000) as well as modeling studies by Marple and Chien (1980) showed that end effects associated

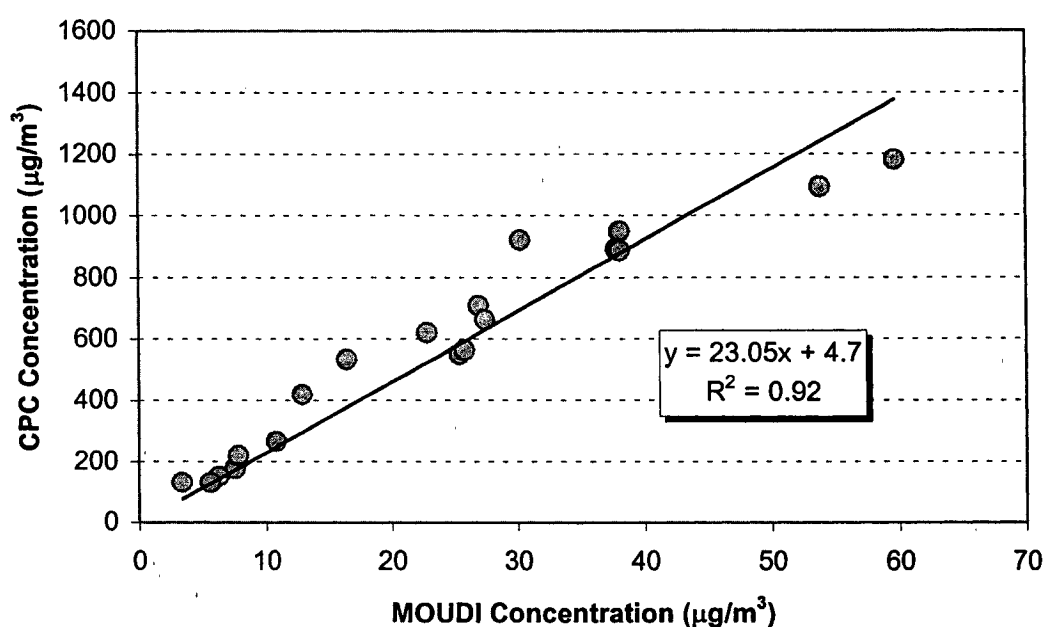


Figure 3.4. Comparisons between the coarse particle concentrator and MOUDI coarse PM mass concentrations.

with rectangular geometry virtual impactors result in excessive particle losses and decrease in the sharpness of the particle collection efficiency curve. The previously mentioned studies also indicated that particle losses become particularly high as the minor-to-total flow ratio decreases. Our laboratory experiments indicate that even at a minor- to -total flow ratio of 3.3 %, the collection efficiency of the virtual impactors of the CPC are high and internal losses are very low.

3.4.2 Field Evaluation Tests

Results of concentration comparisons based on mass, sulfate, nitrate, and selected trace elements and metals between Coarse Particle Concentrator and MOUDI are shown in Figures 3.4 to 3.8 and summarized in Tables 3.1 and 3.2.

Table 3.1 Comparisons between Coarse Particle Concentrator (CPC) and MOUDI based on mass, sulfate and nitrate concentrations (in $\mu\text{g}/\text{m}^3$).

	Range of Ambient Concentration	Range of Minor Flow Concentration	Mean E.F. ^a	Coefficient of Determination (R^2)
Mass	3.4 – 59.7	131.9 – 1,181.2	25.9 ± 4.6	0.92
Sulfate	0.32 - 2.04	9.60 – 65.24	30.0 ± 2.9	0.90
Nitrate	1.1 – 15.4	29.4 – 325.8	25.9 ± 4.2	0.81

^a Ideal Enrichment Factor (EF) determined by the flow ratio of total flow rate to minor flow rate, 1000 LPM to 33 LPM in this case.

Figure 3.4 shows that ambient coarse particle mass concentrations ranged from 3 to 60 $\mu\text{g}/\text{m}^3$ and were enriched from roughly 132 to 1,200 $\mu\text{g}/\text{m}^3$. The average concentration enrichment factor obtained for mass was 25.9 with standard deviation of 4.6 (Table 3.1). CPC and MOUDI mass concentrations were also very highly correlated, with the coefficient of determination (R^2) based on linear

regression being equal to 0.92. Given that the ideal enrichment factor for this minor-to-total flow rate configuration would be 30, these enrichment factor values indicate that the CPC operates with extraordinary collection efficiency (0.86 ± 0.15) and very few internal particle losses. Even though lower coarse particle mass concentrations ($3.5\text{--}10 \mu\text{g}/\text{m}^3$) were generally observed in the Netherlands during the field evaluation, there seems to be no significant difference between the actual enrichment factors obtained in Los Angeles and Bilthoven. This overall agreement is important, considering that these two locations have substantially different meteorological conditions (weather, temperature, and relative humidity) as well as aerosol sources; hence, they are expected to have coarse PM with different chemical composition.

The results of comparing coarse particulate nitrate and sulfate concentrations collected by the CPC and MOUDI are shown in Figures 3.5-3.6 and Table 3.2. The average amounts of sulfate and nitrate in the coarse mode were 4.6% and 19.6% by mass, respectively. The average enrichment factor obtained for nitrate was $25.9 (\pm 4.2)$ with R^2 of 0.81. Both enrichment and correlation coefficient values are very close to those based on mass concentrations. A slightly, but not statistically significant ($p=0.29$), higher enrichment factor of $30.0 (\pm 2.9)$ was observed when comparing sulfate concentrations between the CPC and MOUDI.

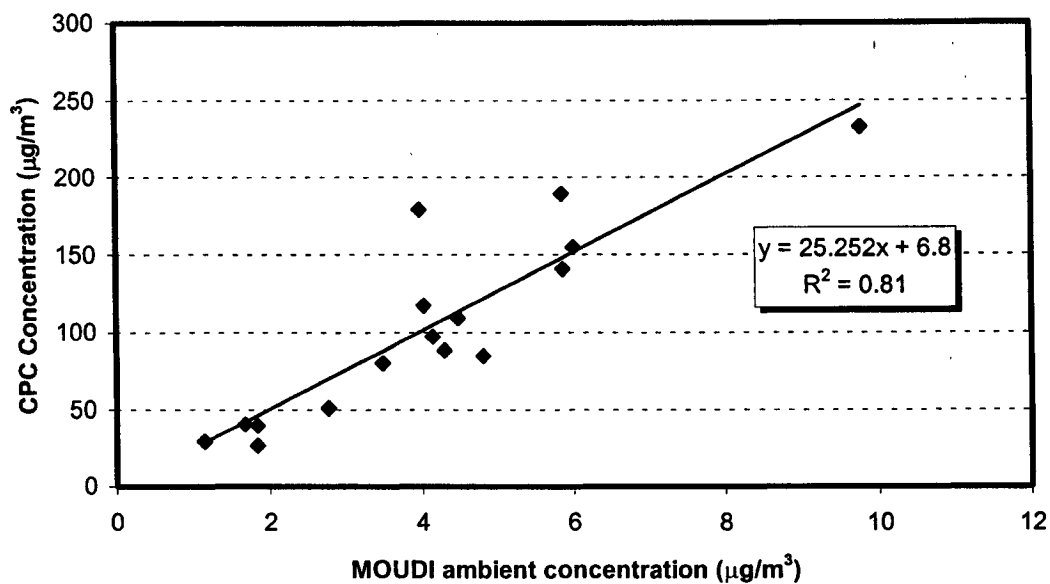


Figure 3.5. Field Comparisons of coarse PM nitrate concentrations between CPC and MOUDI.

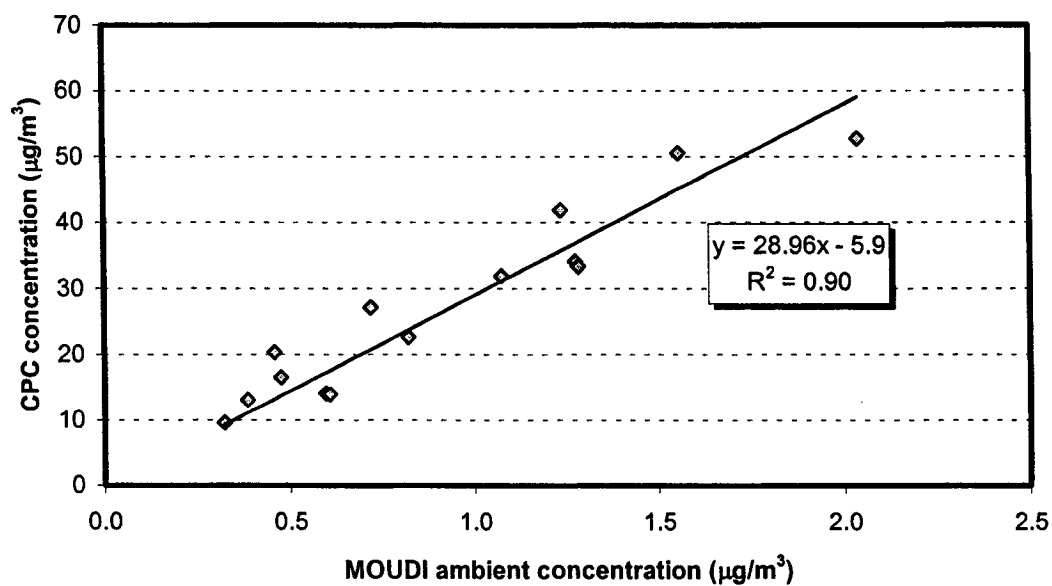


Figure 3.6. Field comparison of coarse PM sulfate concentrations between CPC and MOUDI.

The CPC and MOUDI comparison based on concentrations of trace elements and metals is shown in Figures 3.7 a-j and summarized in Table 3.2. For each element a total of thirteen reliable CPC-MOUDI paired data were obtained. The following metals and elements were selected based on their relative high amounts in the coarse mode relative to the fine mode PM: Al, Si, Ca, K, S, Fe, Cu, Mn, Zn and Ti. Results from our field tests indicated that the concentrations of Al, Si and Ca, which originate from crustal material, contributed on average by 2.0%, 5.4% and 2.4% to the overall coarse PM mass, respectively (Table 3.2). Table 3.2 also shows

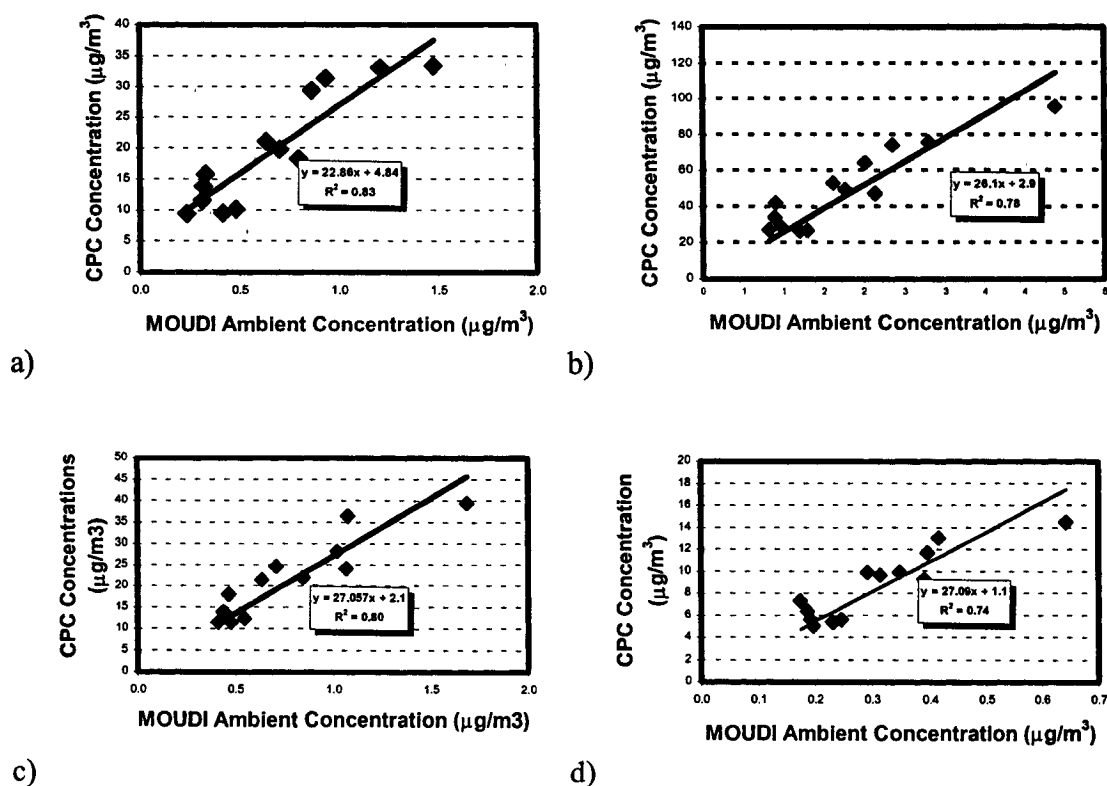


Figure 3.7. Comparisons of coarse PM concentrations between CPC and MOUDI for selected trace elements and metals: (a) Al, (b) Si, (c) Ca, (d) K, (e) S, (f) Fe, (g) Cu, (h) Mn, (i) Zn, (j) Ti.

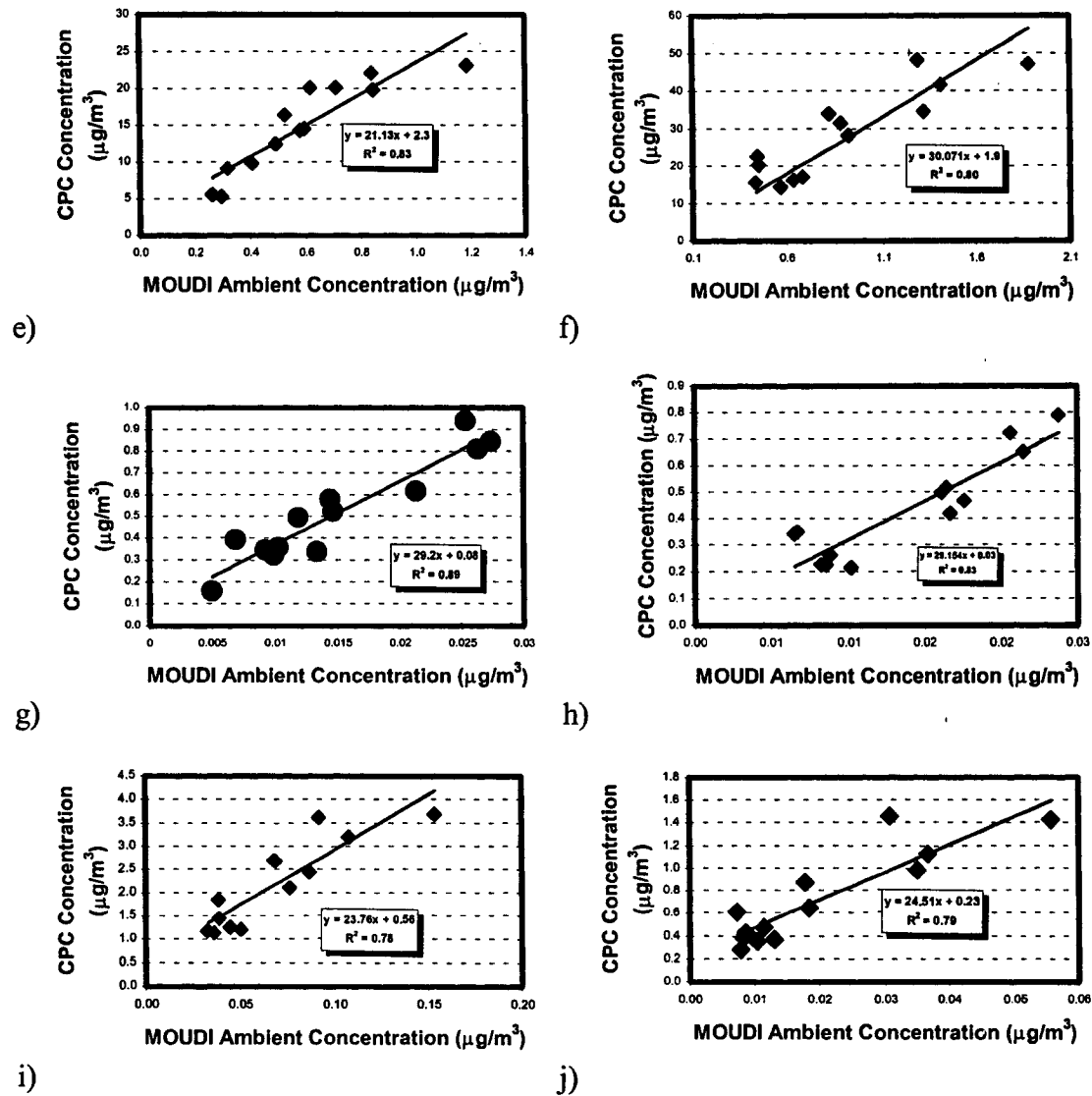


Figure 3.7. Continued.

that the average concentration enrichment factors of Al, Si, and Ca were $30.5 (\pm 3.6)$, $28.8 (\pm 4.4)$, and $28.9 (\pm 5.2)$, respectively. Based on linear regression between the CPC and ambient metal concentrations, the coefficients of correlation (R^2) were 0.83, 0.78, and 0.80, respectively, as displayed in Figures 3.7 a-c. The coarse mode

particles also contained K, S, and Fe with mass percentages of 1.0%, 0.8% and 2.8%, respectively. The enrichment factors for K, S, and Fe ranged from 24 to 32 (Table 3.2) with standard deviations between 3.3 and 5.6, and thus similar to the results obtained for Al, Si, and Ca. Figures 3.7d-f show CPC and MOUDI concentrations for K, S and Fe were also highly correlated, with R^2 values of 0.74, 0.83, and 0.80, respectively. Slightly higher enrichment factors (30-33) were obtained for trace elements (Cu, Mn, Zn, and Ti), which may be in part due to some uncertainty generated by the very small (but detectable) amounts collected in the MOUDI samples. The total contributions of Cu, Mn, Zn, and Ti were less than 0.5% of the coarse mode mass. Nevertheless, the comparison of concentrations between the CPC and MOUDI of Cu, Mn, Zn, and Ti (shown in Figures 3.7 g-j) indicate consistency with other species in terms of concentration enrichment.

Particle separation and concentration by means of virtual impaction is a technique based on particle inertia; therefore, the enrichment factor should be solely dependent on particle aerodynamic diameter and not chemical constituents. The CPC concentrations for all ten metals/elements are plotted against those measured by the MOUDI in Figure 3.8. Integration of all data in one graph was done to reduce potential analysis errors due to the XRF limits of detection.

The linear regression of this integrated comparison indicated an overall average enrichment factor of 27 ± 7.6 for the CPC. Figure 3.8 also indicates that a very high correlation was obtained between the ambient and concentrated coarse

aerosols ($R^2=0.93$) and that this correlation is independent of the amount of the chemical constituent in the aerosol.

Table 3.2 Ambient concentrations ($\mu\text{g}/\text{m}^3$) and enrichment factor (E.F.)^a for selected metal/elements based on 13 sets of comparisons between CPC and MOUDI.

	Al	Si	Ca	K	S	Fe	Cu	Mn	Zn	Ti
Min. Conc. ($\mu\text{g}/\text{m}^3$)	0.24	0.82	0.41	0.17	0.26	0.4	0.00 5	0.00 7	0.00 7	0.03
Max. Conc. ($\mu\text{g}/\text{m}^3$)	1.48	4.4	1.69	0.64	1.19	1.90	0.03	0.02	0.06	0.15
Average Mass Fraction (%)	2.0	5.4	2.4	1.0	0.8	2.8	0.05	0.04	0.06	0.21
Mean E.F.	30.5	28.8	28.9	28.5	24.8	32.2	33.4	30.0	31.4	32.4
E.F. Standard Deviation	3.6	4.4	5.2	5.6	4.3	3.3	2.8	3.5	2.7	3.1
Slope of Regression Line	22.9	26.1	27.1	27.1	21.1	30.1	29.2	29.2	24.5	23.8

^a Ideal Enrichment Factor (EF) determined by the flow ratio of total flow rate to minor flow rate, 1000 LPM to 33 LPM in this case.

3.5 Conclusions

A compact, portable coarse particle concentrator (CPC) with a flow capacity of 1,000 LPM was assembled by connecting ten virtual impactors in parallel. Characterization of the CPC in the laboratory and field-testing in two locations confirmed that the CPC enriches coarse particles by a factor of approximately 26 (± 5) when operating with a minor flow of 33 LPM. This enrichment factor is based on

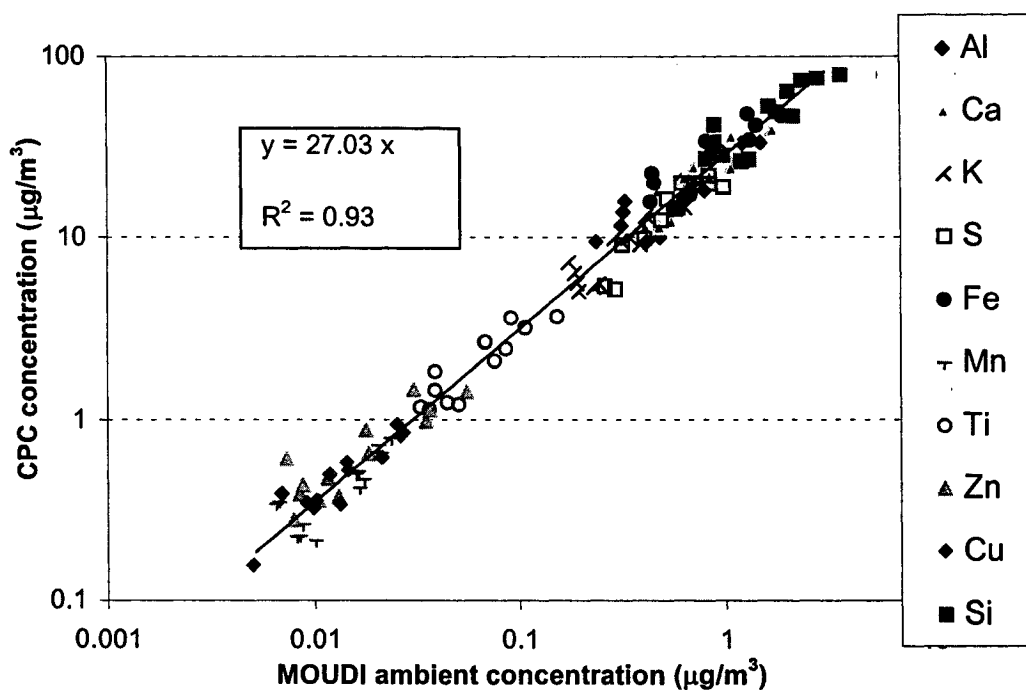


Figure 3.8. Field Comparison of multi metal/elemental concentrations between CPC and MOUDI.

the gravimetric analysis of mass, ion chromatography analysis of sulfate and nitrate, and x-ray fluorescence analysis of trace elements and metals.

Ambient coarse PM levels as low as a few micrograms per cubic meter can be concentrated for exposure to humans and animals as well as for rapid collection of samples for chemical analyses. The system itself, while compact and easily transportable, is variable in design and can be configured to fit many existing systems (sampling, exposure, etc.). The flow rates, also highly adjustable, determine the enrichment of the aerosol and thus, give the researcher latitude in exposure

studies. Therefore, the system can be adapted for human exposures by simply increasing the minor flow rate (or increasing the minor-to-total ratio) until a desired concentration is attained. The compact size of the CPC (bulk dimensions 80cm×75cm×45cm) makes it readily transportable to desired locations for exposures to coarse particles of varying chemical composition.

Acknowledgements

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Chapter 4

DEVELOPMENT AND EVALUATION OF A CONTINUOUS COARSE (PM₁₀ - PM_{2.5}) PARTICLE MONITOR

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4.1 Abstract

In this paper, we describe the development and laboratory and field evaluation of a continuous coarse (2.5 – 10 µm) particle mass (PM) monitor that can provide reliable measurements of the coarse mass (CM) concentrations in time intervals as short as 5-10 minute. The operating principle of the monitor is based on enriching CM concentrations by a factor of about 25 by means of a 2.5 µm cutpoint round nozzle virtual impactor, while maintaining fine mass, i.e., mass of PM_{2.5} (FM) at ambient concentrations. The aerosol mixture is subsequently drawn through a standard TEOM™, the response of which is dominated by the contributions of the CM, due to concentration enrichment. Findings from the field study ascertain that a TEOM™ coupled with a PM₁₀ inlet followed by a 2.5 µm cutpoint round nozzle virtual impactor can be used successfully for continuous CM concentration measurements. The average concentration-enriched CM concentrations measured by the TEOM™ were approximately 26-27 times higher than those measured by the time-integrated PM₁₀ samplers (MOUDI™ and Partisol™ sampler), and highly correlated. CM concentrations measured by the concentration-enriched TEOM™ were independent

of the ambient FM-to-CM concentration ratio, due to the decrease in ambient coarse particle mass median diameter (MMD) with an increasing FM-to-CM concentration ratio. Finally, our results illustrate one of the main problems associated with the use of real impactors to sample particles at relative humidity (RH) values lower than 40%. While PM_{10} concentrations obtained by means of the MOUDI™ and Partisol were in excellent agreement, CM concentrations measured by the MOUDI™ were low by 20%, while FM concentrations were high by a factor of 5, together suggesting particle bounce at low RH.

4.2 Implications

Several researchers have raised the issue of the quality of CM concentrations data used in PM exposure assessment and epidemiological studies. Poor CM precision could lead to potential biases in exposure-health effect models that include both FM and CM exposure variables, and make it more difficult to properly assess the spatial correlations of CM over metropolitan areas. Since these issues may be important in evaluating the health effects of CM relative to PM_{10} or $PM_{2.5}$, it is desirable to have CM measurements that are sufficiently precise to resolve the uncertainty surrounding existing PM studies that include CM data. This paper describes the development and performance evaluation of a CM monitor that can provide reliable measurements in time intervals as short as 5 minutes. The simplicity and reliability of this monitor makes it ideal for use in large scale monitoring networks.

4.3 Introduction

Ambient particles in the size range 2.5 to 10 μm are referred to as coarse particles or coarse mode (CM) aerosols. Coarse particles may consist of several potentially toxic components, such as resuspended particulate matter from paved and unpaved roads, industrial materials, brake linings, tire residues, trace metals, and bioaerosols. Since a considerable fraction of these particles may deposit in the upper airways and to a lesser extent into the lower airways, they may be responsible for the exacerbation of asthma. Recent data from a small number of epidemiological studies indicate that, apart from--or in addition to--the fine fraction (FM) of particulate matter (also called $\text{PM}_{2.5}$), health effects also may be closely associated with the CM fraction and sometimes even to a larger extent than FM (Ostro, 1993; Mar et al., 1999; Ostro et al., 1999). In vitro studies with human monocytes show that cellular toxicity and inflammation also may be associated with the CM and its biological components (Becker et al., 1996; Hornberg et al., 1998; Monn and Becker, 1998).

Several researchers have raised the issue of the quality of CM concentrations data used in PM exposure assessment and epidemiological studies (Lipfert and Wyzga, 1995; Wilson and Suh, 1997; White, 1998). These researchers state that poor CM precision could lead to potential biases in exposure-health effect models that include both FM and CM exposure variables, and make it more difficult to properly assess the spatial correlations of CM over metropolitan areas. Since these issues may be important in evaluating the health effects of CM relative to PM_{10} or

PM_{2.5}, it is desirable to have CM measurements that are sufficiently precise to resolve the uncertainty surrounding existing PM studies that include CM data.

According to the Federal Reference Method (FRM), current measurements of both the PM₁₀ and PM_{2.5} mass concentrations are based on gravimetric analysis of particles collected on filters over a period of 24 hours (Federal Register, 1997). Gravimetric analysis was selected because most of the particle data used for the epidemiological studies investigating associations between mortality and morbidity outcomes and ambient particle exposures are based on PM concentrations (Dockery et al., 1989; Pope et al., 1995). Typically, a time-integrated sample (e.g., over 24 hours) is collected on the filter, which is later equilibrated at designated temperature and RH conditions, and subsequently weighed to determine the mass of the deposited PM. Dividing by the amount of air sample yields the atmospheric concentration. Since the values of atmospheric parameters influencing ambient particle concentration, hence human exposure, such as the emission strengths of particle sources, temperature, RH, wind direction and speed and, mixing height, fluctuate in time scales that are substantially shorter than 24 hours, a 24-hour measurement may not reflect an accurate representation of human exposure. Thus, more accurate, better quality data on the physico-chemical characteristics of particles are needed to understand their atmospheric properties and health effects.

Methods that are capable of providing continuous or near continuous measurements (i.e. 1-hour average or less) are highly desirable because they can provide accurate information on human exposure and atmospheric processes in short

timer intervals. Over the past decade, a significant number of state-of-the-art methods were developed for continuous PM_{10} and $PM_{2.5}$ mass concentration measurements. These include the Tapered Element Oscillating Microbalance (TEOM™ 1400A; Rupprecht and Patashnick, Albany NY), a host of nephelometers, such as the DataRAM™ (RAM-1, MIE Inc., Billerica, MA), and the DUSTTRACT™ (Model 8520, TSI Inc., St. Paul, MN), and the Continuous Ambient Mass Monitor (CAMM™, Thermo Andersen, Smyrna, GA) (Babich et al., 1999). The latter method can only provide measurements of FM. Mass concentration measurements using photometers or nephelometers are based on light scattering, and are dependent on particle size and chemical composition showed that variations in particle size and chemical composition may introduce considerable errors in predicting the response of nephelometers such as the DataRAM (Sloane, 1984; McMurry et al., 1996; Sioutas et al., 2000).

The TEOM™ measures either PM_{10} or $PM_{2.5}$ (but not directly CM) by recording the decrease in the oscillation frequency of a particle-collecting element due to the increase in its mass associated with the depositing particles. In its standard configuration, the TEOM™ collects particles at a flow rate of 2-4 liter per minute (lpm) on an oscillating filter heated to 50 °C. The TEOM™ filter is heated to eliminate interferences from changes in RH that can change the amount of particle-bound water associated with the collected PM (Allen et al., 1997). Determining CM concentrations by difference, as currently proposed by EPA introduces significant uncertainties in cases where FM account for a large fraction of the PM_{10} (Wiener and

Bachmann, 2000). Moreover, since much of the semi-volatile particulate matter (which is mostly associated with FM) is expected to be lost from the TEOMTM filter during and after collection at 50 °C, there is the potential for a substantially different measurement of PM₁₀ mass between the TEOMTM and FRM. This is most likely to occur in urban areas (or areas affected by urban plumes) where volatile compounds, such as ammonium nitrate and organic compounds can comprise a substantial fraction of the FM. Heating is not likely to affect the mostly non-volatile constituents of coarse particles, thus the accuracy of CM concentrations determined as the difference between PM₁₀ and PM_{2.5} will be compromised by the generally random loss of volatile compounds from FM.

In theory, continuous measurements of CM concentrations also could be conducted by means of optical, electrical, and time-of-flight monitors. These monitors measure size-resolved particle concentrations based on particle numbers, which could be subsequently converted to volume concentrations assuming spherical particles and an assumption about particle density; both assumptions are required to convert particle volume to mass concentrations. As in most air sampling applications, information on particle density is generally not available and assumptions about its value will introduce uncertainties in the resulting mass concentrations estimates. A far more important limitation of the aforementioned particle number-based monitors results from the sharply decreasing number of ambient particles with increasing particle size. The ambient particle size distribution, by number, is dominated by ultrafine particles (i.e., smaller than 0.1

μm). As well, when converting a number to volume distribution, a 1.0 μm particle weighs as much as 10^3 times a 0.1 μm particle and 10^6 times a 0.01 μm particle. Consequently, counting errors associated with this conversion, which may be substantial for large particles, due to their relatively low numbers combined with electronic noise, may lead to significant uncertainties in volume and consequently mass as a function of particle size. This was demonstrated in a recent study by Sioutas et al., which showed that the mass concentrations obtained with the Scanning Mobility Particle Sizer/Aerodynamic Particle Sizer system (SMPS, Mode 3936, TSI Inc., St. Paul, MN; APS, Model 3320, TSI Inc., St. Paul, MN) were higher by 70-200% than those determined with a reference gravimetric method (1999).

In this paper, we describe the development and laboratory and field evaluation of a Continuous Coarse Particle Monitor (CCPM) that can provide reliable measurements of the CM concentrations in time intervals as short as 5-10 minute. The operating principle of the monitor is based on enriching the CM concentrations by a factor of about 25 while maintaining FM at ambient concentrations. The aerosol mixture is subsequently drawn through a standard TEOM™, the response of which is dominated by the contributions of the CM due to concentration enrichment. This paper also presents a comparison between the CM and FM concentrations obtained different time-integrated samplers (i.e., filters and impactors), which was conducted during the field evaluation study of the CCPM.

4.4 Methods

4.4.1 Description of the Continuous Coarse Particle Monitor

The CCPM, shown schematically in Figure 4.1, operates at an intake flow of 50 lpm, and consists of three main components: a) a PM₁₀ inlet; b) a 2.5 µm cutpoint round nozzle virtual impactor (or, coarse particle concentrator), and; c) TEOM™.

Particles are drawn at 50 LPM through a circular nozzle, 1.1 cm inside diameter, attached to a 90° aluminum duct elbow, 3.2 cm in diameter. The nozzle protrudes 3 cm from the rest of the inlet section of the continuous monitor and extends up to a distance of 1.5 cm from the inside wall of the 90° elbow, as shown in Figure 4.1. The nozzle has been designed with a cutpoint of approximately 10 µm aerodynamic diameter (AD). During the field tests, a thin layer (approximately 1 mm) of silicon grease (Chemplex™ 710, NFO Technologies, Kansas City, KS) was applied periodically to the inside wall of the elbow to prevent particle bounce.

The collection efficiency of the PM₁₀ inlet was evaluated in field tests by measuring the mass-based concentrations of ambient particles in the 2.5 to 20 µm range by means of an APS™. For these tests, the TEOM™ was disconnected from the virtual impactor and the minor flow was drawn directly the APS™. The sampling flow of the APS™ is 5 lpm, thus higher than the minor flow of the CCPM (2 LPM). Since the cutpoint of the PM₁₀ inlet does not depend on the minor-to-total flow of the virtual impactor but on the total aerosol flow entering the impactor-inlet,

the major flow of the virtual impactor was adjusted to 45 LPM in order to maintain the total flow entering the PM₁₀ inlet and virtual impactor at 50 lpm.

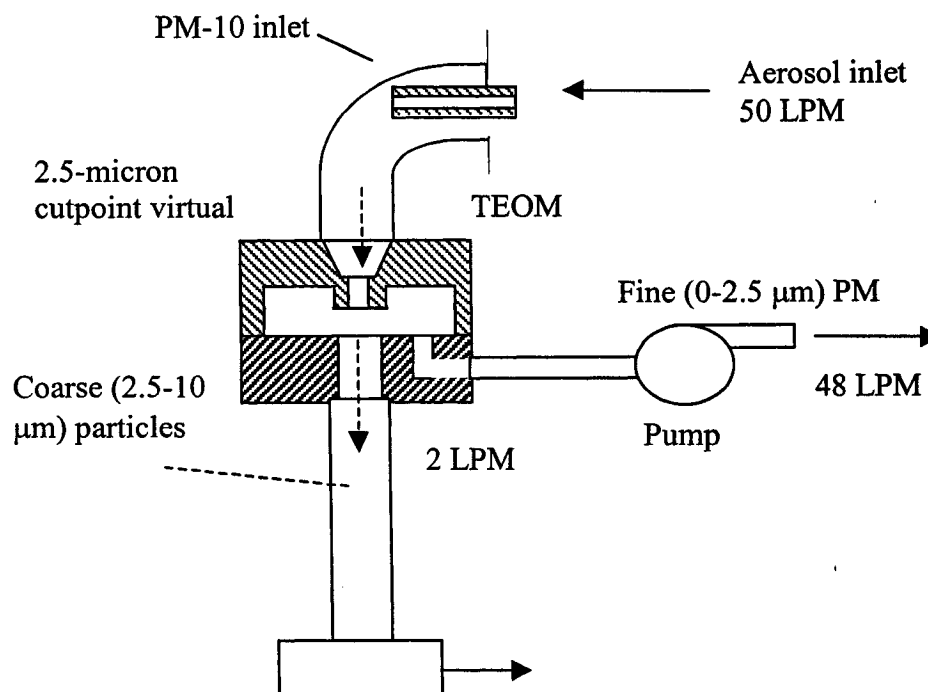


Figure 4.1. Schematic of the Continuous Coarse Particle Monitor

The concentration of particles in the 2.5 to 20 μm (enriched by a factor of approximately 10) was obtained for a sampling period of 3 minutes. Subsequently, the PM₁₀ inlet was removed and the mass-based concentration of 2.5 to 20 μm particles was obtained for a period of 3 minutes. The above test sequence was repeated five times. Particle penetration through the PM₁₀ inlet was determined for each size by dividing the average concentration (based on five tests) obtained with the PM₁₀ inlet connected to the sampler to the concentration without the inlet. The

wind speed (a crucial parameter in for the performance evaluation of the inlet) was recorded during these experiments and varied from 1 to 7 miles per hour (mph), which is a typical range for Los Angeles.

Particles smaller than 10 μm in AD are drawn through the virtual impactor, which was designed to have a theoretical 50% cut point at about 2.5 μm for an intake flow rate of 50 LPM. This is single-stage, round-jet nozzle virtual impactor with an acceleration nozzle diameter of 0.37 cm and collection nozzle diameter of 0.56 cm. The distance between the acceleration and collection nozzles is 0.7 cm.

The flow field in a virtual impactor is determined by the Reynolds number, which, is defined as:

$$\text{Re} = \frac{U W \rho}{\mu} \quad (1)$$

where U is the average jet velocity through the acceleration nozzle of the impactor, W is the diameter of that nozzle, and μ and ρ are the dynamic viscosity and density of air, respectively. The value of Re corresponding to the operating configuration of the virtual impactor is 18,927. Coarse particles follow the minor (concentrated) flow, while particles smaller than the cutpoint of the virtual impactor follow the major flow. The minor flow in these experiments was set at 2 LPM to achieve a nominal enrichment factor of 25. Concentrated CM, including a small fraction of FM (about 4%) are drawn through the TEOM, whose flow was adjusted to 2 LPM. In its

most common configuration, the aerosol is heated to 50 °C before collection on the TEOM™ filter, which is attached to the oscillating element. Our experiments were performed at sample temperatures of 50 °C and 30 °C to determine whether differences in these temperatures would result in significant differences in the response of the CCPM. While the standard configuration of the TEOM™ is to operate it at 50 °C, due to loss of semi-volatile species at this temperature, many TEOMs are being operated at 30 °C with a nafion dryer to remove water vapor prior to the collection substrate. No nafion dryer was used in our configuration. The remaining 48 LPM (major flow) through the virtual impactor is drawn through a separate, lightweight, rotary vane pump (Gast, Model 1023, Gast Mfg. Corp., Benton Harbor, MI). The pressure drops across the major and minor flows of the virtual impactor are 5.8 and 0.25 kPa, respectively.

4.4.2 Laboratory Evaluation of 2.5 µm Cutpoint Round Nozzle Virtual Impactor

The first series of experiments were conducted in the laboratory to investigate the relationship between the concentration enrichment achieved by the 2.5 µm cutpoint round nozzle virtual impactor as a function of particle size. Briefly, monodisperse aerosols in the size range of 1 to 10 µm were generated by atomizing dilute aqueous suspensions of fluorescent polystyrene latex particles (Polysciences Inc., Warrington, PA) with a constant output nebulizer (HEART™, VORTRAN Medical Technology, Inc., Sacramento, CA). The generated particles were mixed with dry room air in a 1-liter bottle to remove the excess moisture. The dry aerosol

was then drawn through a tube containing ten Po-210 neutralizers that reduced particle charges prior to entering the virtual impactor. For each of the monodisperse particles in the range of 1 to 5 μm , the DataRAM was used to first measure the mass concentration of the generated aerosols prior to entering the 90° elbow of virtual impactor. The DataRAM was subsequently connected downstream of the minor flow of the virtual impactor to measure the mass concentration of the aerosols after concentration enrichment. The measurements were repeated at least three times, and the average concentration enrichment was determined as a function of particle size. The contributions from background ambient concentrations before and after the enrichment were recorded and subtracted from those of the input and concentrated aerosols prior to determining the collection efficiencies at the given particle size. It should be noted that indoor air levels were on the order of 7 – 15 $\mu\text{g}\cdot\text{m}^{-3}$, and substantially smaller than those of the generated aerosols (prior to concentration enrichment), which varied from 170 to about 500 $\mu\text{g}\cdot\text{m}^{-3}$. Therefore the contributions of the indoor aerosol to the overall concentrations measured upstream of- and in the minor flow of the virtual impactor were considered negligible.

Concentration enrichment for 5 to 10 μm particles was determined by comparing the mass collected on a glass fiber filter (2 μm pore, Gelman Science, Ann Arbor, MI) connected to the minor flow of the virtual impactor, and the mass of a similar glass fiber filter in parallel to the test system to measure the concentration of the monodisperse aerosol. The filter sampling in parallel was connected to a pump operating at 30 LPM. At the end of each run, each glass fiber filter was placed

in 5 ml of ethyl acetate to extract the fluorescent dye from the collected particles. The quantities of the fluorescent dye in the extraction solutions were measured by a Fluorescence Detector (FD-500, GTI, Concord, MA) to determine particle concentration. Concentration enrichment for each particle size was defined as the ratio of the concentration measured in the minor flow to that of the aerosol immediately upstream of the virtual impactor inlet.

4.4.3 Field Study

Following the completion of the laboratory experiments, the performance of the CCPM was evaluated in a field study which was part of the Los Angeles Supersite project at the Rancho Los Amigos National Rehabilitation Center in Downey, CA. Situated near the Los Angeles "Alameda corridor", Downey has some of the highest inhalable PM₁₀ concentrations in the US, very often exceeding the 24-hour National Ambient Air Quality Standard for PM₁₀ of 150 µg.m⁻³. The field experiments were performed during the period of October to December 2000.

Concentrated CM were provided directly to the TEOM™ from the minor flow (2 LPM) of the 2.5 µm cutpoint round nozzle virtual impactor. Measurements of concentration-enriched CM measured by the TEOM™ were compared to direct measurements with a co-located Microorifice Uniform Deposit Impactor (MOUDI™, MSP Corp. Minneapolis, MN) and Dichotomous Partisol-Plus™ (Model 2025 Sequential Air Sampler, Rupprecht and Patashnick Co. Inc., Albany, NY). The MOUDI™ sampled at 30 LPM. Instead of using all available MOUDI™ stages, only

those having cut-points of 10 μm and 2.5 μm were used. Thus the first MOUDI™ stage (2.5-10 μm) was used as a reference sampler for CM concentrations and the last stage (i.e., the after-filter) was used to determine the ambient FM concentrations. Teflon filters with diameters of 4.7 and 3.7 cm (2 μm pore size, Gelman Science, Ann Arbor, MI) were used to collect CM and FM in the two MOUDI™ stages, respectively.

The Partisol™ uses a PM_{10} inlet operating at 16.7 LPM to remove particles larger than 10 μm in AD. The remaining PM_{10} aerosol is drawn through a virtual impactor, or, “dichotomous splitter”, located after the inlet. Two separate flow controllers maintain the CM at 1.67 LPM and the FM stream at 15 LPM. CM and FM are collected on two 4.7cm Teflon filters, placed in the minor and major flows of the Partisol virtual impactor, which are housed in reusable cassettes.

The Teflon filters of both MOUDI™ and Partisol™ samplers were pre- and post-weighed using a Mettler Microbalance (MT5, Mettler-Toledo, Inc, Hightstown, NJ) after 24-hour equilibration under controlled humidity (35-40%) and temperature (22-24 °C).

The experiments were performed with simultaneous sampling from the TEOM™ and the MOUDI™ and/or the Partisol™. The sampling time varied from 90-minute to 210 minute depending on the ambient concentrations to allow sufficient mass to be collected on the time-integrated samplers. The majority of the experiments were for sampling periods of 120-minute. The volume concentration of ambient CM also was recorded in 15-minute intervals using an APS™ for a number

of experiments. In addition, in selected experiments, the time-weighted mass median diameter (MMD) of the ambient coarse particles was determined by means of the APS™. Temperature and RH data, for each experiment were also measured continuously by the Partisol™ and recorded automatically by the systems software. The mass concentration of the CCPM was determined both by the 1- or 2-hour time integrated TEOM™ readings and by directly dividing the mass deposited on the TEOM™ filter by the total air volume sampled. In all experiments, these two concentrations differed by less than 5%. CM and FM concentrations of the MOUDI™ were determined by dividing the total PM collected on the MOUDI™ substrates by the total sampled air volume. The CM concentration of Partisol was determined after dividing by the appropriate sample flow and subtracting 10% of FM concentration from it, which corresponded to the ratio minor flow to the total flow of the Partisol™I virtual impactor.

4.5 Results and Discussion

4.5.1 *Evaluation of the PM₁₀ Inlet*

Particle penetration values through the PM₁₀ are plotted as a function of AD in Figure 4.2. The data plotted in this figure indicate that particle penetration is 90% or higher for particles in the range of 2.5 to 8 µm. Penetration decreases sharply to about 50% at 10 µm and further to less than 10% for particles larger than 12 µm in AD. The sharpness of the particle penetration curve of an impactor can be defined in

terms of the geometric standard deviation (σ_g), which is the square root of the ratio of the particle AD corresponding to 16% penetration to that corresponding to 84 % penetration (Marple and Willeke, 1976). Based on this definition, the value of σ_g is approximately 1.2 (roughly the ratio of 11 μm / 8 μm) for the PM_{10} inlet, thereby indicating reasonably sharp aerodynamic particle separation characteristics.

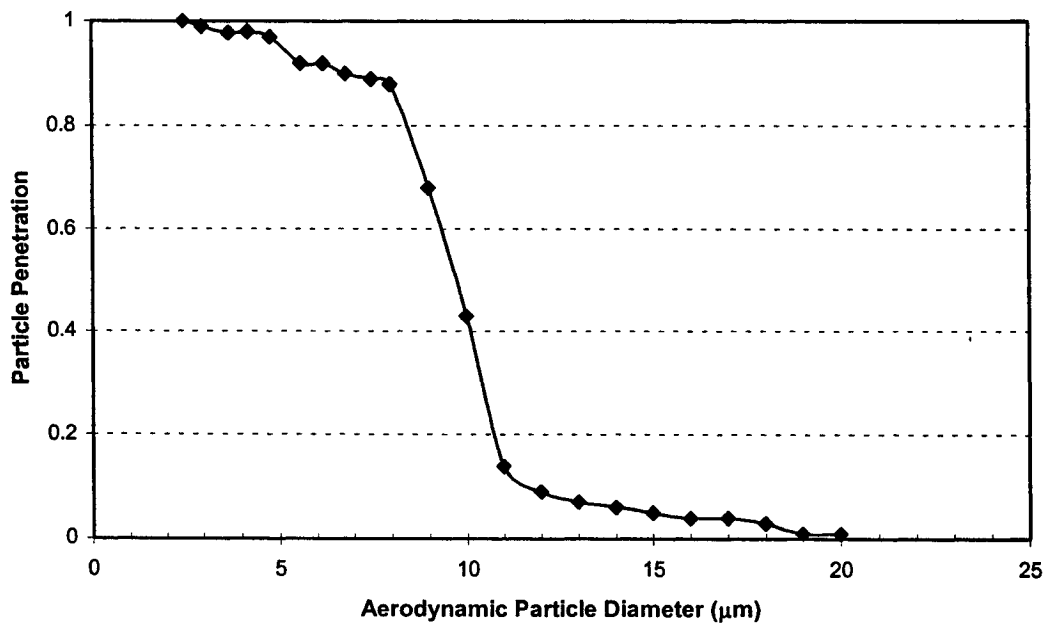


Figure 4.2. Particle Penetration Through the PM_{10} Inlet.

4.5.2 Laboratory Evaluation of the 2.5 μm Cutpoint Round Nozzle Virtual Impactor

Figure 4.3 presents the concentration enrichment of the 2.5 μm cutpoint round nozzle virtual impactor as a function of particle AD. The data in Figure 4.3 confirm the rise of the enrichment factor as a function of particle AD. As seen from

the figure, the enrichment factor increases sharply up to its ideal value of 25, as predicted based upon the intake and minor flow rates of 50 and 2 LPM, respectively. The plotted data correspond to the averages of at least three experiments per particle size, whereas the error bars represent the standard deviation in the enrichment values. The concentration enrichment factor increases sharply from about 2 to 23 as particle AD increases from 2 to 3 μm . The enrichment factor is practically the same

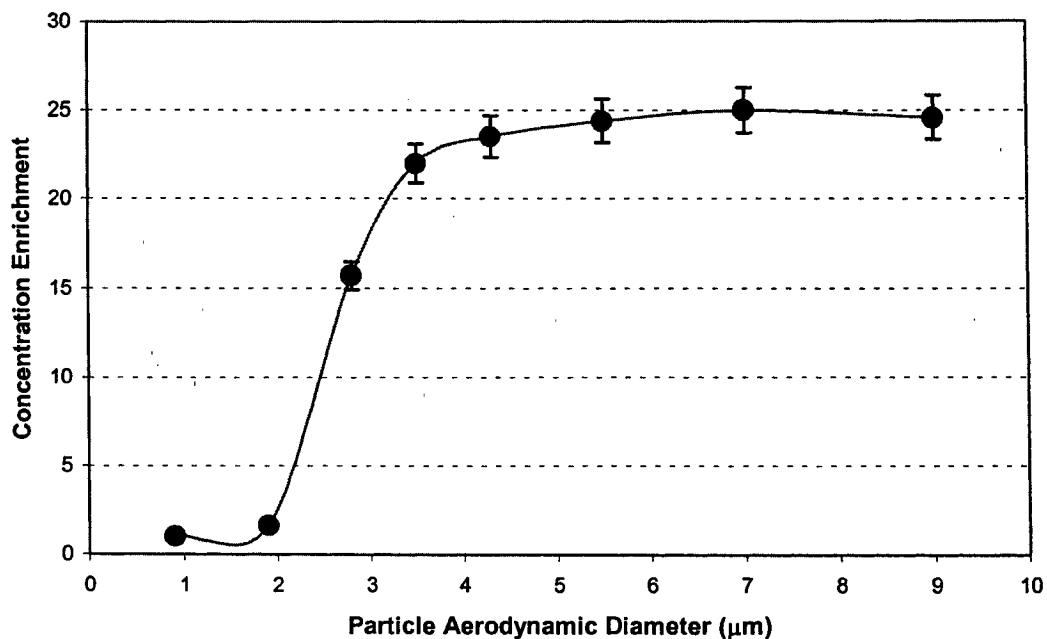


Figure 4.3. Concentration enrichment as a function of particle aerodynamic diameter, total flow rate = 50 LPM, minor flow rate = 2 LPM.

for particles in the AD range of 3 to 9 μm . The data shown in Figure 4.3 also indicate that the 50% cut point of the virtual impactor, defined as the aerodynamic particle size at which the enrichment factor is half of its ideal value (i.e. about 12.5) is approximately 2.4 μm . [The enrichment factor measured at 2.5 μm is about 15].

The overall high concentration efficiencies of 9 μm particles, proves that there are no significant losses of these particles in the 90° elbow of the PM_{10} inlet. More importantly, these tests imply that the size distribution of concentrated CM before entering the TEOM is the same as that of the ambient air, since the concentration enrichment factor does not depend on particle size—at least for particles larger than 2.5 μm in AD.

4.5.3 Field Evaluation of the Continuous Coarse Particle Monitor

The results of the field evaluation of the CCPM are shown in Figures 4.4 to 4.7 for experiments performed at a TEOM™ temperature of 50 °C. Figure 4.4 shows the comparison between the TEOM™ and MOUDI™ CM concentrations at 50 °C. As indicated, the data are highly correlated ($R^2=0.88$) with a slope of 25 and a near zero intercept. The ratio of concentrations equal to 26.1 (± 3.6) also is close to the expected value.. Figure 4.5 shows the comparison between the TEOM™ and Partisol™ CM concentrations at 50 °C. Again, these datas are highly correlated ($R^2=0.88$) with a slope of 24 and a near zero intercept. The ratio of concentrations equal to 25.8 (± 4.1) also is close to the expected value. It is worthwhile noting, that the TEOM™ concentrations are not corrected for the contributions of the FM, which is present in the inlet stream. The purpose of concentrating the CM by a factor of 25 is to eliminate the need for knowing *a priori* the FM concentration. Ideally, the mass concentrations measured by the CCPM are related to the actual ambient CM concentrations as follows:

$$\text{CCPM} = 25 \text{ CM} + \text{FM} \quad (2)$$

Thus a 1:1 FM-to-CM concentration ratio would result in the CCPM being 26 times higher than the actual CM concentration.

An important implication of equation (2) is that unusually high (but not impossible) FM-to-CM concentration ratios (i.e., 4 - 6) would lead to a positive bias

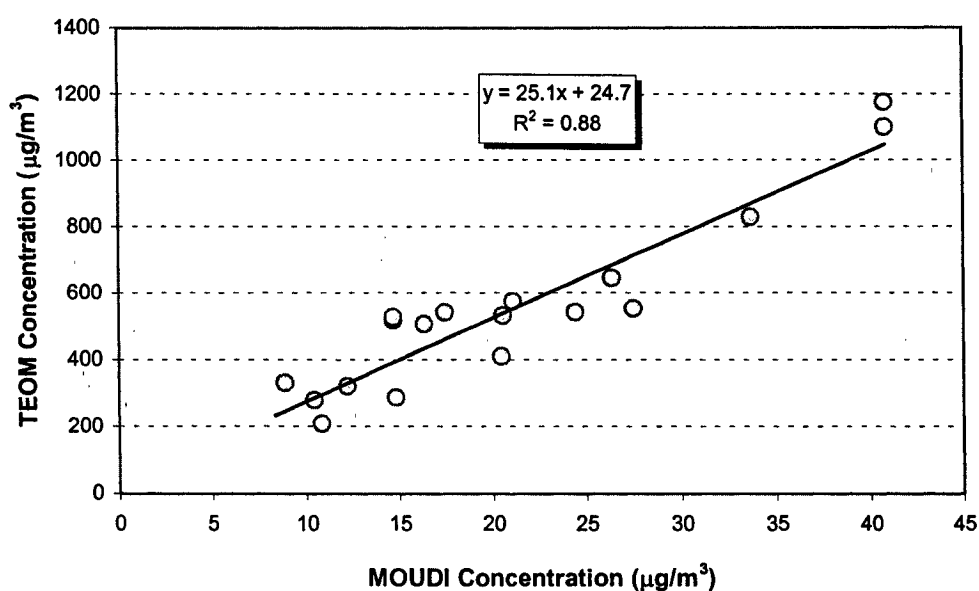


Figure 4.4. TEOM versus MOUDI coarse PM concentrations; TEOM at 50°C.

(or overestimation) of the CM concentration by the CCPM, if the concentrations are not corrected to account for the contribution of FM. To investigate the effect of the FM-to-CM concentration ratio on the response of the CCPM, the ratio of the concentration-enriched TEOMTM-to-MOUDITM and TEOMTM-to-ParisolTM concentrations were plotted as a function of the FM-to-CM concentration ratio. The

results, shown in Figure 4.6, clearly indicate that the ratio of TEOM™-to-MOUDI™ CM concentration and the ratio of TEOM™-to-Partisol™ CM concentration are, under the conditions of this experiment independent of the ratio of ambient FM-to-CM concentrations. ($R^2 = 0.0064$). This independence can be further explained by the data plotted in Figure 4.7, which shows the decrease in the ambient MMD (determined by the APS) as the FM-to-CM concentration ratio increases. There is a marked shift in MMD from 4.8 – 5 μm to 2.8 – 3 μm as the ratio of FM-to-CM concentration increases from 1 to 5, respectively.

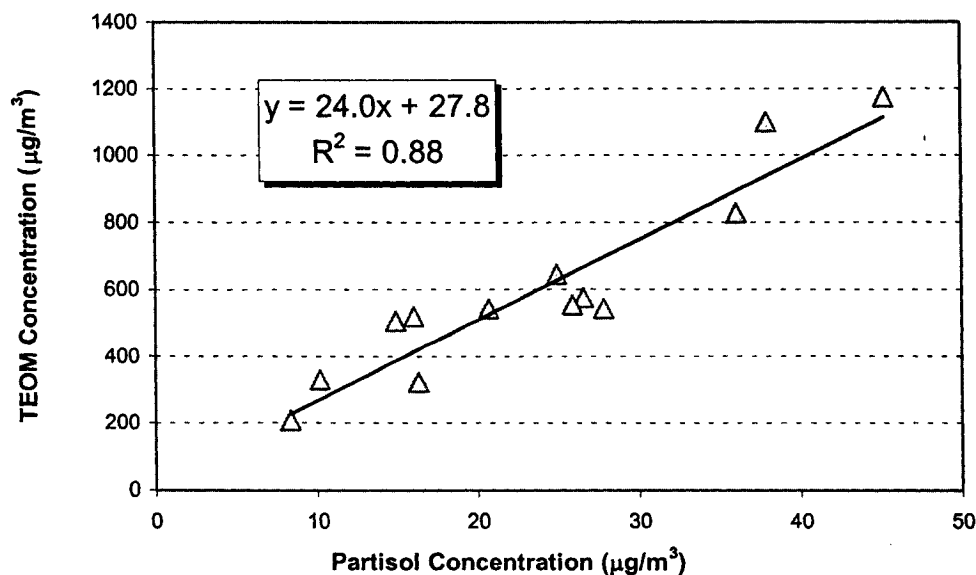


Figure 4.5. TEOM versus Partisol coarse PM concentrations; TEOM at 50°C.

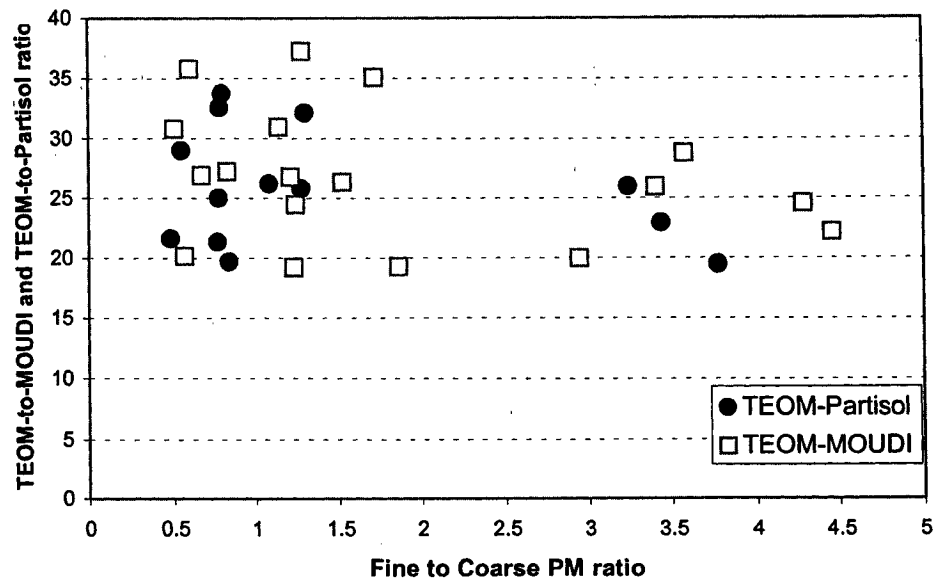


Figure 4.6. TEOM-MOUDI and TEOM-Partisol concentration ratio as a function of fine/coarse PM ratio; TEOM at 50°C.

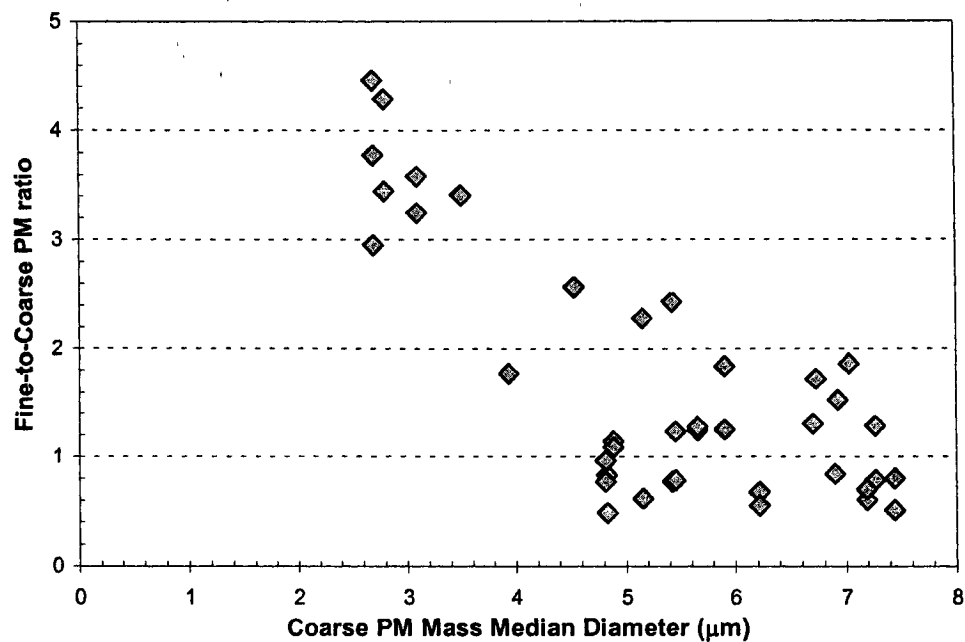


Figure 4.7. Relationship between coarse particle mass median diameter (MMD) and fine-to-coarse PM ratio.

The highest values of FM-to-CM concentrations, ranging from about 3.5 to 4.6, were obtained on October 20 and 21, 2000. During these two days, stagnation conditions occurred in Downey, with the average wind speed during the sampling periods being less than 1 miles per hour (mph). 2-hour averaged FM concentrations measured by either the MOUDI™ or Partisol™ during these two days ranged from 80 to 146 $\mu\text{g}\cdot\text{m}^{-3}$. These conditions are expected to result in high FM concentrations in locations such as Downey, which is primarily impacted by vehicular emissions from nearby freeways, while the relatively low CM concentrations may be explained by the lack of sufficient wind velocity to either generate or transport coarse particles. As the virtual impactor-particle concentrator preceding the TEOM™ has a 50% cutpoint at about 2.5 μm , particles in the 2.5 – 3 μm AD range would be concentrated somewhat less efficiently than those larger than 3 μm . For example, the laboratory evaluation of the 2.5 μm cutpoint virtual impactor (Figure 4.3) indicated that 2.5 to 3 μm particles are concentrated by a factor ranging from 16 to 22, compared to particles in the 3 – 10 μm range that are concentrated by a factor of 25. This slightly uneven concentration enrichment, combined with the intrinsic relationship between the coarse particle MMD and the FM-to-CM concentrations ratio, brings the CCPM-to-CM concentration ratio closer to the range of 25-26, and thus, compensates for the increase in the FM-to-CM concentration ratio. As a result, the CCPM can be used efficiently for measuring the ambient CM concentrations even in cases where the ratio of FM-to-CM concentration is unusually high.

The results of the field experiments conducted at a TEOM™ temperature at 30 °C are presented in Figures 4.8 to 4.11. Similar to the 50 °C configuration, highly correlated data ($R^2=0.85$) are obtained for the comparison of the TEOM™ and Partisol™ CM concentrations as shown in Figure 4.8. The ratio of concentrations is $27.4 (\pm 3.7)$, which is slightly higher, but not statistically different ($p=0.69$) than that at 50 °C.

No comparisons between the CCPM and the MOUDI™ concentrations were conducted for the 30 °C TEOM configuration, although MOUDI™ data were collected concurrently to the continuous monitor and the Partisol™. This is because the ambient RH was unusually low (even by the standards of the generally arid climate of the Los Angeles Basin), often below 20 to 30 %. As a result, while the comparison between TEOM™ and Partisol™ CM concentrations is robust, the CM concentrations measured by the MOUDI™ were low, resulting in unrealistically high ratios between the TEOM™ and MOUDI™ CM concentrations. This is confirmed by plotting the CM concentration ratio of Partisol™-to-MOUDI™ versus RH, as shown in Figure 4.9. From the data plotted in Figure 4.9 there is a well-defined inverse relationship between this ratio and the RH. This ratio achieves an ideal value of 1 as the RH reaches 45-50 %. For lower RH, this ratio increases sharply and becomes as high as 5 when the RH reaches the 10 to 15% range. To confirm that this phenomenon is related to particle bounce, which would be more pronounced at lower RH, the ratio of FM concentration of Partisol™-to-MOUDI™ vs RH was plotted, as shown in Figure 4.10. The reverse trend is observed, with the ratio of the FM

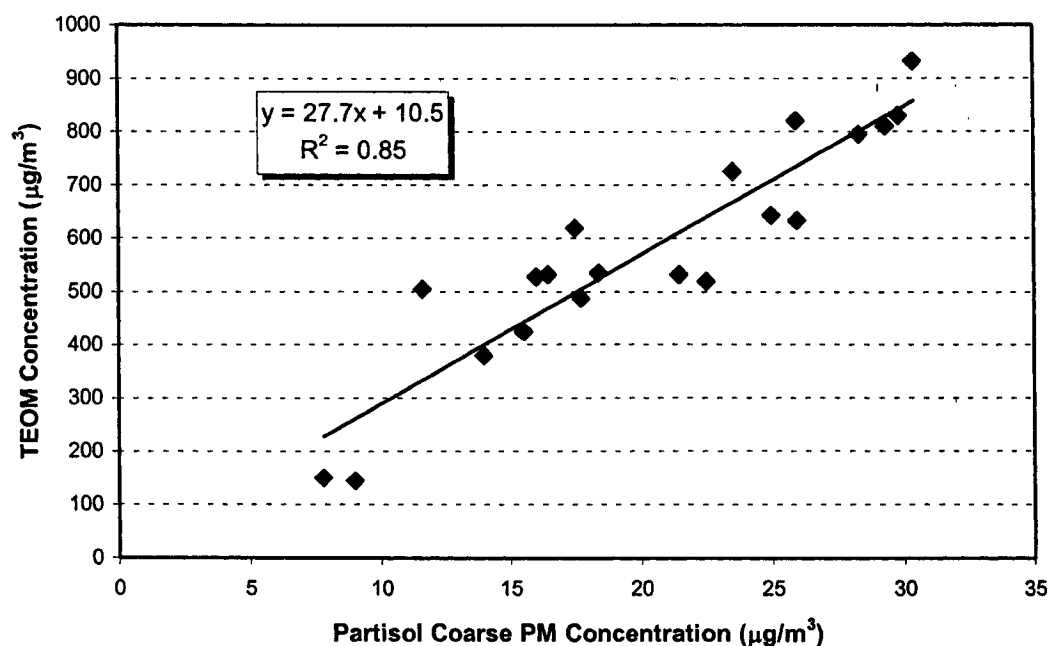


Figure 4.8. TEOM versus Partisol coarse PM concentrations; TEOM at 30°C.

concentration of the Partisol™-to-MOUDI™ increasing from 0.2 to about 1, as the RH increases from 10 to 50 %. Further, the total PM₁₀ Partisol™-to-MOUDI™ ratio was 0.99 (± 0.13) based on 30 field experiments, thereby suggesting that since both samplers agreed well for PM₁₀, the only difference is in the FM and CM concentrations measurements, that is, CM concentration is low and FM concentration is high at low RH, suggesting particle bounce. These field observations illustrate one of the main drawbacks of impactors, and raises serious implications on the appropriateness of using impactors with uncoated substrates to obtain the size distributions of aerosols under low (< 30%) RH conditions.

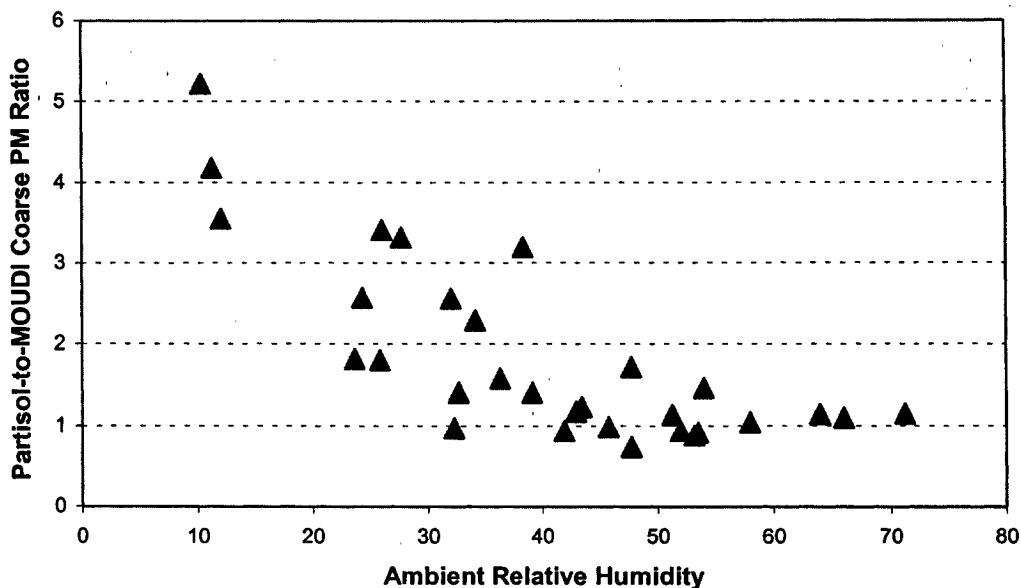


Figure 4.9. Plot of the Partisol-to-MOUDI coarse particle concentrations as a function of ambient relative humidity.

Experiments at a TEOM™ temperature setting of 30 °C also showed independence of the ratio of the TEOM™-to-Partisol™ CM concentrations to the ambient FM-to-CM concentration ratio (Figure 4.11). Data plotted in Figures 4.6 and 4.11 indicate that the mass concentration ratio of the concentration-enriched TEOM™ to either the MOUDI or Partisol™ is independent of the FM-to-CM concentration ratio over a range of values extending from about 0.2 to 5, thereby covering a broad spectrum of ambient sampling conditions, and thus, strengthening the applicability of the CCPM to other locations and times of the year.

During these experiments, ambient PM data for a few selected runs were recorded using an APS™. Figure 4.12 shows the time series in CM concentrations

measured by the TEOM™ and the APS™ during one day of the field experiments. A particle density of 1.6 g/m^3 was assumed in the APS™ data. The TEOM™ CM concentrations were converted to ambient CM concentrations by dividing by 26.

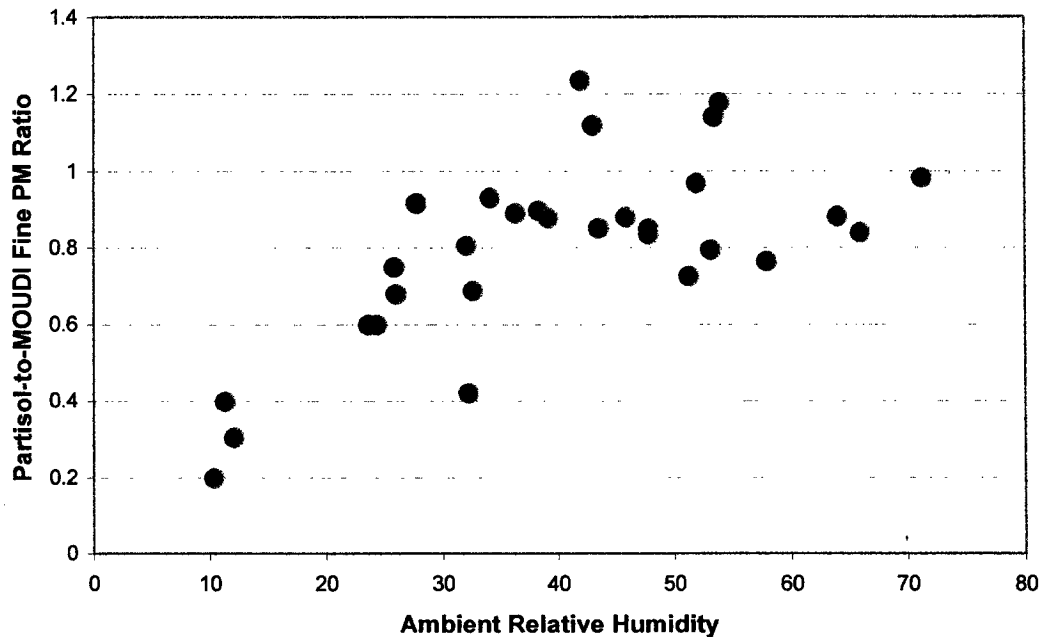


Figure 4.10. Plot of the ratio of Partisol-to-MOUDI fine PM concentrations as a function of relative humidity.

Direct comparison between the actual concentrations measured by the two monitors cannot be made, since knowledge of the real (as opposed to an assumed) density of ambient coarse particles is required in order to convert the APS™ concentrations to actual mass concentrations. However, the data plotted in Figure 4.12 clearly show that very good overall agreement is observed in the time series of the CM concentrations obtained by means of the two samplers.

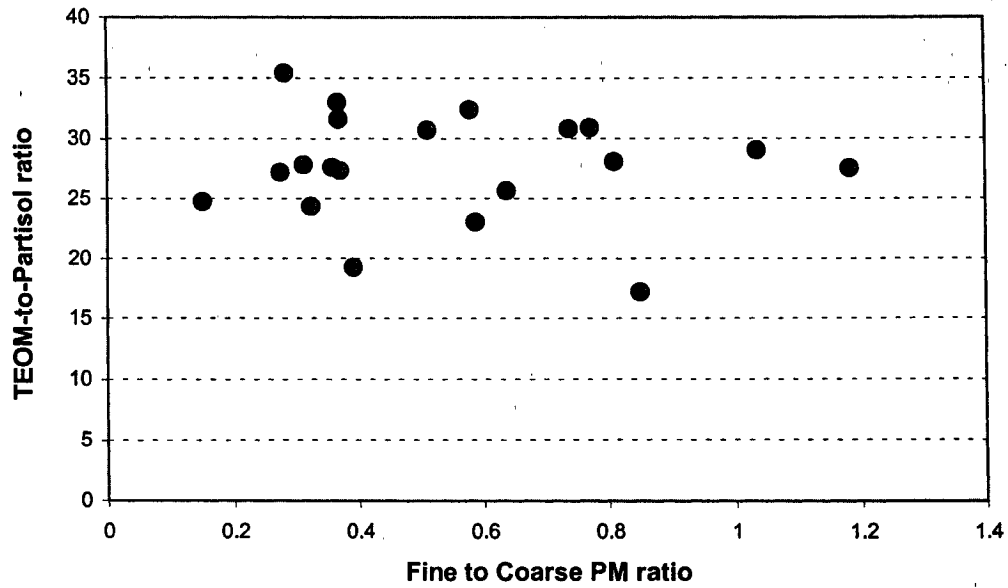


Figure 4.11. Dependence of TEOM-Partisol ratio on fine/coarse PM ratio; TEOM at 30°C.

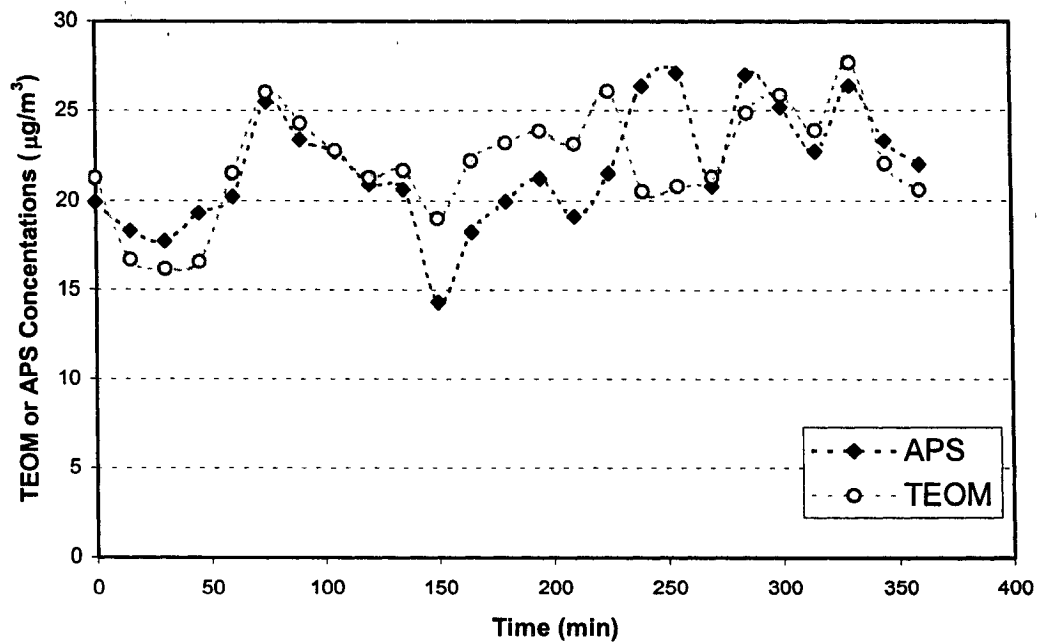


Figure 4.12. Time-series of TEOM and APS coarse particle concentrations.

4.6 Summary and Conclusions

This paper describes the development and laboratory and field evaluation of a CCPM that is based on enriching the CM concentrations by a factor of 25, while maintaining FM concentration at ambient concentrations. The aerosol mixture is subsequently drawn through a standard TEOM™, the response of which is dominated by the contributions of the CM due to enrichment of the coarse particles. The laboratory evaluation of the 2.5 µm cutpoint round nozzle virtual impactor confirms the rise in the enrichment factor as a function of particle AD. The concentration enrichment factor increases sharply from about 2 to about 25 as particle AD increases from 2 to 3 µm. The enrichment is the same, within the error of the measurement, for particles in the AD range of 3 to 9 µm.

Findings from the field study ascertain that the TEOM™ coupled with a 2.5 µm virtual impactor can be used successfully for continuous CM concentration measurements. The results indicate excellent correlation between the concentration-enriched TEOM™ and time integrated samplers (MOUDI™ and Partisol™), with the average TEOM™ CM concentration being approximately 26-27 times higher than those measured by the time-integrated samplers. No substantial differences in the response of the concentration-enriched TEOM™ are observed between TEOM™ operating temperatures of 30 and 50 °C. Results from the field experiments also show that the CM concentrations measured by the concentration-enriched TEOM™ are independent of the ambient FM-to-CM concentration ratio. This is due to the

decrease in ambient coarse particle MMD with increasing FM-to-CM concentration ratio, as might be expected, since FM concentrations tend to increase and coarse particle loadings tend to decrease during stagnation conditions. This also strengthens the applicability of the CCPM in cases where the FM-to-CM concentration ratio is very high. Finally, our results illustrate one of the main problems associated with the use of impactors to sample particles under conditions of RH values lower than 40%. While PM_{10} concentrations obtained by means of the MOUDI™ and Partisol™ are in excellent agreement, CM concentrations measured by the MOUDI™ are as low as 20% compared to those measured by the Partisol™, while MOUDI™ FM concentrations were high by as much as a factor of 5, together suggesting particle bounce at low RH.

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Chapter 5

DEVELOPMENT AND EVALUATION OF A PM₁₀ IMPACTOR-INLET FOR A CONTINUOUS COARSE PARTICLE MONITOR

Aerosol Science and Technology 37 (2003) 271-281

5.1 Abstract

Conventional PM₁₀ inlets available operate at a flow rate of 16.7 LPM. The purpose of this study was to develop and test a PM₁₀ inlet designed to operate at 50 LPM to be used with a recently developed Continuous Coarse Particle Monitor (Misra et al., 2001). Laboratory tests using polystyrene latex particles established the inlet's 50% cutpoint at 9.5 μm . Further evaluation of PM₁₀ inlet was performed in a wind tunnel at wind speeds of 3, 8 and 24 km/h. Tests showed that the 50% efficiency cutpoint as well as the very sharp particle separation characteristics of the inlet were maintained at these wind speeds. Field evaluation of the PM₁₀ inlet was performed in Riverside and Rubidoux, CA. A 2.5 μm cutpoint round nozzle virtual impactor was attached downstream of the developed PM₁₀ inlet. The Dichotomous PM₁₀ Partisol Sampler, operating at a flow rate of 16.7 LPM was used as a reference sampler. The Dichotomous Partisol uses an FRM PM₁₀ inlet operating at 16.7 LPM to remove particles larger than 10 μm in aerodynamic diameter. Commercially available 4.7 cm Teflon filters were used in both the Partisol and the PM₁₀ inlet to collect particulate matter (PM). Results showed good agreement between coarse PM (2.5-10 μm) mass concentrations measured by means of the PM₁₀ inlet and Partisol. Chemical analyses showed excellent agreement between coarse PM concentrations of Al, K, Si, Ca and

Fe obtained by the two samplers. The agreement also persisted for nitrate and sulfate. Finally, the excellent agreement between coarse concentrations of the PM_{10} inlet and Partisol persisted for wind speeds up to 19 km/h.

5.2 Introduction

Since the advent of the particulate matter (PM) standards by the United States Environmental Protection Agency (US EPA), particle sampling has been a primary goal of both scientists and lawmakers. The addition of the $PM_{2.5}$ (fine particle) and the soon to be developed PM_{10} - $PM_{2.5}$ (coarse particle) standards to the PM_{10} standard has created the need for reliable continuous coarse and fine PM measurement devices. One such device, a Continuous Coarse Particle Monitor (CCPM) is described by Misra et al. (2001).

An essential component of any modern PM monitoring device is a size pre-selective inlet. This is even more important when the size range to be removed prior to sampling consists of large particles. If the inlet allows even a small fraction of the undesirable PM into the measuring device, the error could be large. The reason for this is that large particles have large masses, which will heavily influence the measurement of a mass-based monitor.

Because of their large mass, hence inertia, coarse particles are difficult to sample and collect. When these heavy particles are accelerated in an impactor jet, their substantial inertia causes them to hit the impactor collection plate. Many times the particle will bounce off of this plate and become re-entrained in the air stream.

This causes overestimation of the mass downstream of the inlet. Another problem that occurs because of the inertia of these particles is the underestimation or overestimation of particle mass that results from anisokinetic sampling. Unlike the PM in smaller size ranges, coarse PM is not as uniformly dispersed in the atmosphere. It settles and becomes resuspended due to localized events (i.e. high wind episodes). The original inlet employed to characterize the CCPM (described in more detail by Misra et al., 2001) was subject to this error. That inlet consisted of a simple 90-degree elbow with a jet fashioned from a pipe with a preset diameter. Particles larger than about 10 μm impacted on the throat of that elbow. Among its problems were that it sampled from only one direction (thus was prone to substantial anisokinetic sampling errors if the wind direction was not in alignment with the inlet) and also needed to be re-greased periodically in order to prevent bounce of large particles. Additionally, the inlet's efficiency curve was not as steep as most commercially available PM₁₀ inlets.

Currently, several manufacturers have developed commercially available PM₁₀ inlets, some of which have received designation from the US EPA to be used as federal reference methods. These inlets operate at sampling flow rates ranging from 16.7 to 1133 LPM. A comprehensive review of PM₁₀ and other federal reference method inlets is given by Chow (1995). The SA (Thermo-Anderson, Smyrna, GA) or GMW (General Metal Works, Tisch Environmental, Village of Cleves, OH) Models 321A, 321B, 1200, and Wedging IP₁₀PM₁₀ operate at the highest flow rate. The SA 254 Medium-Volume PM₁₀ Inlet operates at a flow of 113

LPM, and the SA 246B operates at a design flow of 16.7 LPM (Chow, 1995). None of the devices listed above, however, is compatible with the CCPM's flow rate of 50 LPM.

To these ends, an efficient and low-maintenance PM_{10} inlet was designed and evaluated for a flow rate of 50 LPM. The inlet's design flow rate accommodates the CCPM developed by Misra et al. (2001). The goals of this newly developed inlet are to overcome anisokinetic sampling, sharpness of cutpoint, and limited capacity of other commercially available PM_{10} inlets.

5.3 Materials and Methods

5.3.1 *Description of the PM_{10} Impaction Inlet*

The inlet used in these tests is a modification of a commercially available PM_{10} inlet, from Rupprecht and Patashnick (Model P/N 57-00596, R&P Inc., Albany, NY), which operates at a flow rate of 16.7 LPM. This inlet is described in detail in Federal Register, 1996. To adapt the inlet so that it could operate at 50 LPM, the nozzle was modified by widening the nozzle diameter and also shortening the nozzle length so as to increase the jet-to-plate distance. The schematic of the inlet is shown in Figure 5.1a. The modifications along with the new dimensions are given in Figure 5.1b. The nozzle design parameters were modified so that the predicted cutpoint of the impactor is about 10 μm at the flow rate of 50 LPM.

The principal parameter determining particle capture is the Stokes number of a particle having a 50% probability of impacting, St , defined as the ratio of the

particle stopping distance to the characteristic dimension of the impactor (Hinds, 1982):

$$St = \frac{\tau U}{W} = \frac{\rho_p C_c d_p^2 U}{9 \mu W} \quad (1)$$

where W is the diameter of the impactor's nozzle, U is the average velocity of the impactor jet, ρ_p is the particle density, μ is the dynamic viscosity of the air and C_c is the Cunningham slip correction factor, given by the following equation (Hinds, 1982):

$$C_c = 1 + \frac{2}{P d_p} [6.32 + 2.01 \exp^{(-0.1095 P d_p)}] \quad (2)$$

where P is the pressure at the location of the particle in the flow (in cm Hg) and d_p is the particle diameter in μm . The acceleration nozzle diameter of the impactor was 1.7 cm and the corresponding jet velocity for a flow of 50 LPM was 367 cm/s. The gap between the impaction jet and the collection plate was 1.1 cm. The Stokes number corresponding to 10 μm was approximately 0.135.

5.3.2 Laboratory Tests for Determination of Cutpoint

The schematic diagram of the experimental setup for testing the cutpoint of the PM_{10} inlet is shown schematically in Figure 5.2. Monodisperse aerosols in the range of 2.6 to 12 μm were generated by atomizing dilute aqueous suspensions of

polystyrene latex particles (PSL, Bangs Laboratories Inc., Fisher, IN), using a constant output nebulizer (HOPE, B&B Medical Technologies, Inc., Orangevale, CA). The generated particles were drawn through a 2-liter glass container in which they were mixed with dry room air in order to remove excess moisture. The dry aerosols were then passed through a series of Po-210 neutralizers (NDR Inc., Grand Island, NY) to bring the particle charge distribution to Boltzmann equilibrium. Particle penetration through the impactor was measured as a function of particle size by means of a nephelometer, DataRAM (RAM-1, MIE Inc., Billerica, MA), which was used to measure the mass concentrations of the monodisperse aerosols upstream and downstream of the PM₁₀ inlet. The upstream and downstream measurements were repeated at least three times. The contributions from background ambient concentrations before and after the PM₁₀ inlet were recorded and subtracted from those of the input and concentrated aerosols prior to determining the collection efficiencies at the given particle size. It should be noted that indoor air levels were on the order of 7-12 µg/m³, and substantially smaller than those of the generated aerosols (prior to entering the PM₁₀ inlet), which varied from 95 to about 300 µg/m³. Therefore the contributions of the indoor aerosol to the overall concentrations measured upstream of- and downstream of- PM₁₀ inlet were considered negligible.

5.3.3 Wind Tunnel Tests

The performance of the PM₁₀ inlet was evaluated in the wind tunnel facility of School of Public Health, UCLA. The wind tunnel is described in detail by Hinds

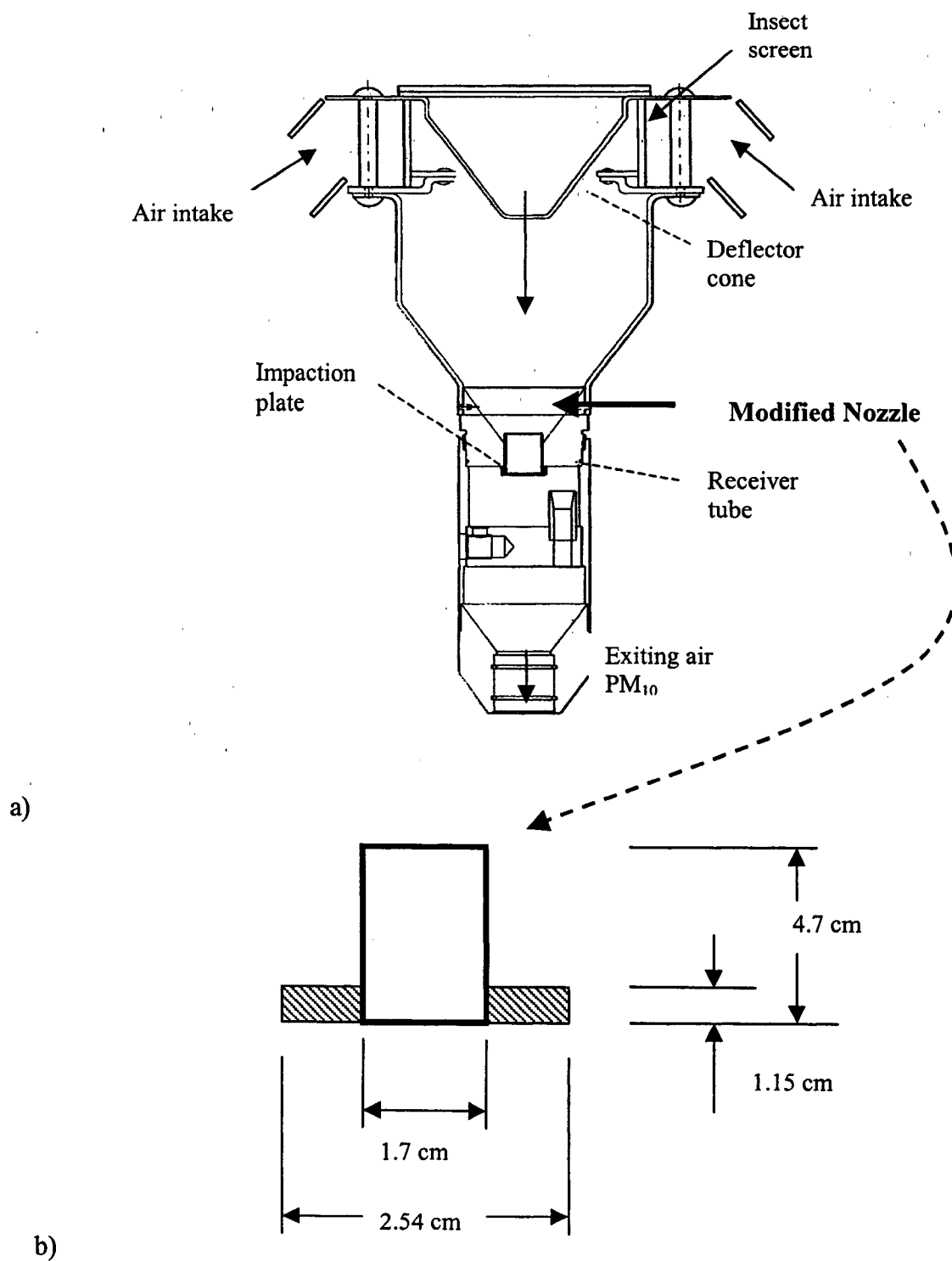


Figure 5.1. a) Modified PM_{10} inlet for CCPM. b) Dimensions of modified acceleration jet nozzle.

and Kuo, 1995. In its original design, the wind tunnel has a 1.6 x 1.6 m cross-section and was operated at two wind speeds (3 and 8 km/h). The blower downstream of the sampler test area was capable of driving the wind tunnel speed up to 8 km/h (Kennedy et al., 2001). The cross-section of the wind tunnel was modified later to achieve a wind speed of 24 km/h. A plywood baffle was placed about 0.5 m upstream of the aerosol generation system to promote mixing. The vibrating aerosol orifice (VOAG) (Model 3450, TSI Inc., St. Paul, MN) was itself mounted on a shaft, which moved both up and down and sideways to promote uniform injection. Three isokinetic samplers were placed around the PM₁₀ inlet. The PM₁₀ inlet was placed such that it was equidistant from the three isokinetic samplers. Two of these samplers were lateral to the PM₁₀ inlet while the third one was above the PM₁₀ inlet. The positioning of the isokinetic samplers corresponded to uniformity in concentration around the inlet. The earlier work by Hinds and Kuo, 1995 describes the positioning of isokinetic samplers in detail.

The sampling characteristics of the PM₁₀ inlet were determined by comparing the mass concentration obtained by the PM₁₀ inlet to that measured by isokinetic samplers. Seven different particle sizes - 5, 7, 9, 10, 12, 15 and 20 µm were selected to evaluate the performance of the PM₁₀ inlet.

A vibrating orifice aerosol generator (VOAG) (Model 3450, TSI Inc., St. Paul, MN) was used to generate monodisperse particles. It is known that when a solution containing a non-volatile solute is sprayed through an orifice, the solvent

eventually evaporates from the droplets and non-volatile particles of solute are obtained. The diameters for these non-volatile solute particles are given by:

$$D_p = C^{1/3} D_d \quad (3)$$

where C is volumetric concentration of the non-volatile solute in the solution and D_d is the initial droplet diameter.

A vibrating orifice produces one droplet per cycle and the D_d is given by:

$$D_d = (6Q/\pi f)^{1/3} \quad (4)$$

where Q is the liquid flow rate and f is the disturbance frequency (Berglund and Liu, 1973). The droplet size primarily depends on the orifice size for a given solution feed rate and the frequency. For these experiments, a 20 μ m orifice was used for generating particle sizes of 5 and 7 μ m while a 35 μ m orifice was chosen for generating particles in size ranges of 9, 10, 12, 15, 20 μ m. Typical VOAG operating parameters were 0.150 mLPM of feed rate at 65-70 kHz utilizing a 20 μ m orifice. A feed rate of 0.3 mLPM at an operating frequency of 35 kHz was found to be optimum for a 35 μ m orifice.

Uranine tagged oleic acid was used as a non-volatile solute for generating particles with acetone as the solvent. Approximately, 2 g of uranine dye was dissolved in 50 mL of methanol to prepare the tracer solution and was left overnight to dissolve the dye in the solution with concomitant settling of the undissolved uranine dye. A 20-40 % of this solution was then added to the oleic acid-acetone solution to generate particles of a desired size using Equations 3 and 4. The

monodispersity of the generated aerosols was confirmed by observing the generated particles under a microscope, which also corroborated the size of the particles.

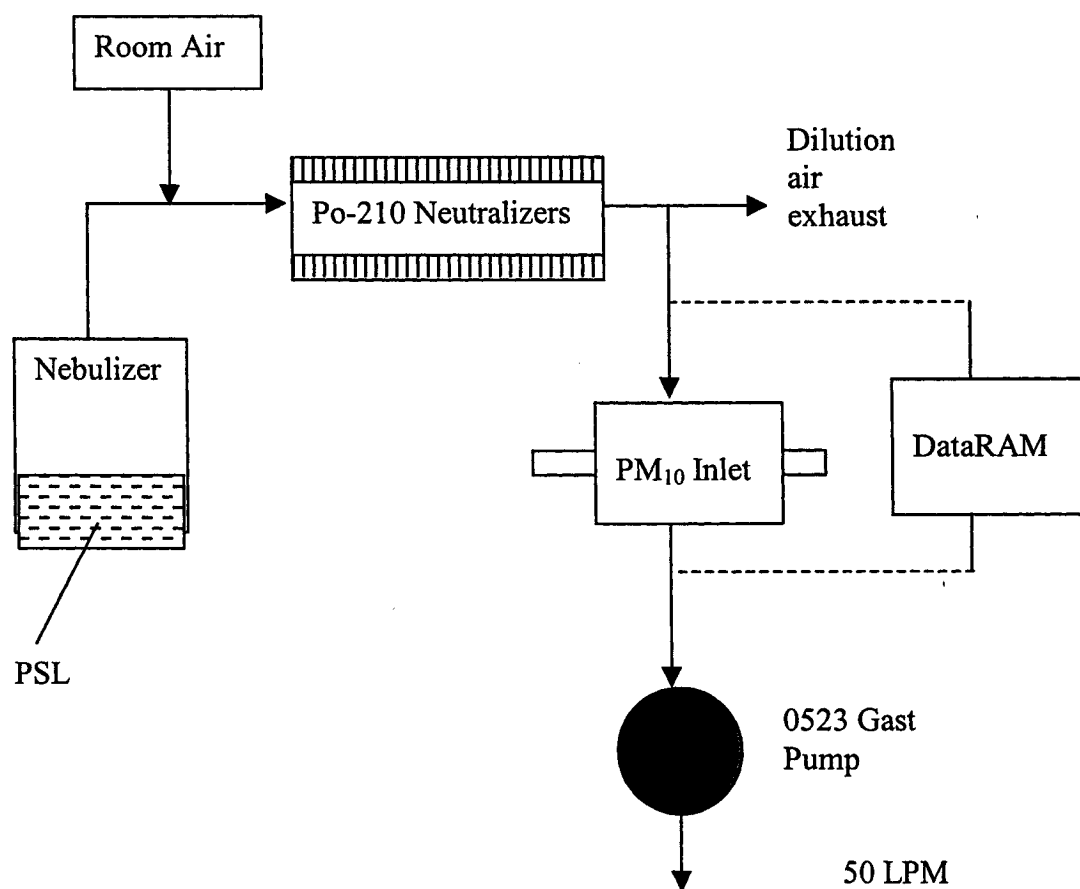


Figure 5.2. Schematic of the experimental set-up used for the laboratory characterization of the PM₁₀ inlet.

The isokinetic samplers and the PM₁₀ inlet were positioned at the same distance from the sample injection point (same axial plane). These samplers were constructed from 2.5 cm in-line stainless steel filter holders (P/N 1209, Gelman Sciences Inc., Ann Arbor, MI) fitted with 8.5 mm ID brass probes that extended 32

mm from the face of the filter holder and sampled at a flow rate of 10 LPM for wind speeds of 3, 8 and 24 km/h. Millipore membrane filters (SMWP 02500, Millipore, Bedford, MA) were placed downstream each of the isokinetic samplers to collect the generated monodisperse uranine tagged oleic acid particles. A 4.7 cm Millipore membrane filter (SMWP 04700, Millipore, Bedford, MA) was placed after the PM₁₀ inlet in order to collect the oleic acid particles. Each of the experiments was characterized by particle size and wind speed and lasted for about 10-15 min, which was sufficient to obtain detectable mass on the filters.

Detection of the deposited uranine tagged oleic acid particles on the Millipore filters was performed using a fluorescence detector (Model FD-500, Programmable Fluorescence Detector, GTI, Concord, MA). Prior to their fluorescence detection, the extraction of the uranine was done using a buffer solution. The buffer solution was prepared by dissolving 12.4 g of boric acid in 1000 mL of water (solution A) and 19.05 g of sodium borate in 1000 mL of water (solution B). Diluting 50 mL of solution A and 59 mL of solution B to 200 mL using distilled water yielded the buffer solution.

The Millipore filters were then extracted in glass vials using the buffer solution. Most of the extractions were done using 5-10 mL of solution. Standard uranine dye solutions of 0.005, 0.01, 0.025, 0.05, 0.075 and 0.1 ppm were used to plot the calibration curve.

For each wind speed, comparison between the mass concentrations obtained by means of the three isokinetic samplers and the PM₁₀ inlet was performed. For

each particle size, the averaged value of the mass concentration for the three isokinetic samplers was used. Finally, the particle penetration through the PM₁₀ inlet was plotted against the particle diameter for each wind speed.

5.3.4 Field Evaluation of the PM₁₀ Inlet

The performance of the PM₁₀ inlet was evaluated in Riverside and Rubidoux, CA in the months of May and July, 2001. For these tests, a virtual impactor with a cutpoint of 2.5 µm at 50 LPM was attached downstream of the PM₁₀ inlet. This is the same virtual impactor used in the continuous coarse PM monitor (CCPM) described by Misra et al., 2001 to separate coarse from fine PM. [The concentrated coarse PM in the minor flow of this impactor is drawn into a Tapered Element Oscillating Microbalance (TEOM Mode 1400A, Rupprecht and Pataschnick Inc., Albany, NY) for near-continuous measurement of coarse mass concentration]. A thin film of silicone grease (Chemplex 710, NFO Technologies, Kansas City, KS) was applied to the impaction plate of the PM₁₀ inlet to prevent particle bounce. Coarse PM follows the minor flow, while particles smaller than the cutpoint of the virtual impactor follow the major flow. The minor flow in these experiments was set at 2 LPM to achieve a nominal enrichment factor of 25. This minor flow also corresponds to the inlet flow of the CCPM. Concentrated coarse particles, including a small fraction of fine PM (about 4%), were drawn in the minor flow (2 LPM), which was pulled by an oil-less pump (Model DOA-V191-AA, Gast Manufacturing Inc., Benton Harbor, MI). The remaining 48 LPM (major flow) through the virtual impactor was drawn by a separate, oil less, light-weight, rotary vane pump (Model 0523-101Q-G588DX,

Gast Manufacturing Inc., Benton Harbor, MI). Concentrated coarse particles in the minor flow stream were collected on a 4.7 cm Teflon filter (2 μ m pore size, Gelman Science, Ann Arbor, MI). Measurements of concentration-enriched coarse particle mass were compared to measurements with a Dichotomous Partisol-Plus sampler (Model 2025 Sequential Air Sampler, Rupprecht and Patashnick Co. Inc., Albany, NY). The Dichotomous Partisol uses a Federal Reference Method (FRM) PM₁₀ inlet operating at 16.7 LPM to remove particles larger than 10 μ m in aerodynamic diameter. The remaining PM₁₀ aerosol is drawn through a virtual impactor, or, “dichotomous splitter”, located after the inlet. Two separate flow controllers maintain the coarse particle stream at 1.67 LPM and the fine particle stream at 15 LPM. Coarse and fine PM were collected on two 4.7 cm Teflon filters, placed in the minor and major flows of the Partisol virtual impactor, which are housed in reusable cassettes.

The Teflon filters of PM₁₀ inlet and Partisol samplers were pre- and post-weighed using a Mettler Microbalance (MT5, Mettler-Toledo, Inc, Hightstown, NJ) after 24-h equilibration under controlled humidity (35-40%) and temperature (22-24 °C). The experiments were performed with simultaneous sampling from the PM₁₀ inlet and the Dichotomous Partisol. The sampling time was around 120 min for each experiment to ensure sufficient mass was collected on the filters.

The coarse concentration of PM₁₀ inlet was determined after dividing by the appropriate sample flow and subtracting 2.5% of fine concentration from it, which corresponded to the ratio of minor flow to the total flow of the PM₁₀ inlet virtual

impactor. Similarly, the coarse concentration of Dichotomous Partisol was determined after dividing by the appropriate sample flow and subtracting 10% of fine concentration from it, which corresponded to the ratio of minor flow to the total flow of the Partisol virtual impactor.

In addition to mass concentrations, comparisons were made between coarse PM concentrations of selected trace elements as well as particulate nitrate and sulfate measured by the PM₁₀ inlet and Partisol. Ten of twenty-one pairs of PTFE filter samples collected by the PM₁₀ inlet and Partisol were analyzed by means of x-ray fluorescence (XRF) to determine concentrations of selected elements and metals. The remaining eleven pairs were extracted with 0.15 ml of ethanol and 5 ml of ultrapure water. [Ethanol was used in order to wet the hydrophobic Teflon filter]. The samples were sonicated for 15 minutes and analyzed for sulfate and nitrate ions by means of ion chromatography (IC). Samples that were lower than three times the lower limits of detection (LOD) of either XRF or IC were excluded.

5.4 Results and Discussion

5.4.1 *Experimental Determination of Cutpoint*

Particle penetration, the ratio of downstream to upstream mass concentration, through the PM₁₀ inlet is plotted as a function of aerodynamic diameter in Figure 5.3. The data shown in this figure indicate that particle penetration is 90% or higher for particles in the range of 2.5 to 8 μm . Penetration decreases sharply to about 50% at 9.5-9.7 μm and further to less than 10% for particles larger than 11 μm in

aerodynamic diameter. An estimate of the “sharpness” of the particle penetration curve of an impactor can be defined by means of a geometric standard deviation (σ_g), which is the square root of the ratio of the aerodynamic particle diameter corresponding to 16% penetration to that corresponding to 84 % penetration (Marple and Willeke, 1976). Based on this definition, the value of σ_g is approximately 1.1 (roughly the square root ratio of 11 μm / 9 μm) for the PM_{10} inlet, thereby indicating very sharp aerodynamic particle separation characteristics.

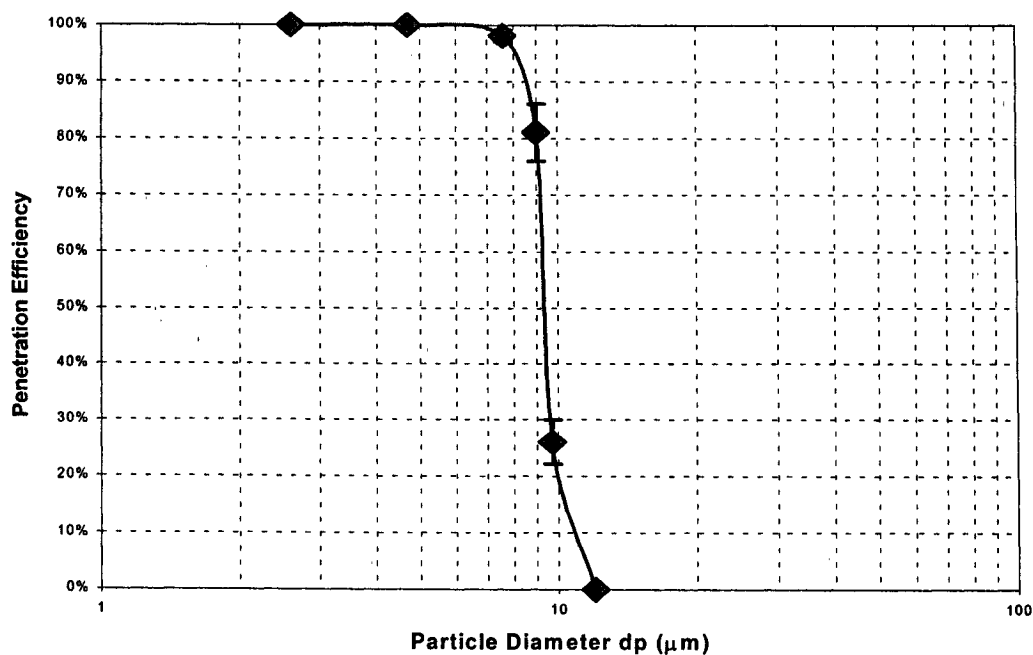


Figure 5.3. PM_{10} Inlet Particle Penetration Curve

5.4.2 Wind Tunnel Evaluation of the PM_{10} Inlet

The results of the wind tunnel test are summarized in Figure 5.4. As evident from the figure, the particle penetration characteristics of the PM_{10} inlet are

unaffected by the wind speeds. The penetration for all the wind speeds tested, viz., 3, 8 and 24 km/h show a very close agreement. This is a particularly important result because it demonstrates that the inlet can be used throughout the various ambient conditions found in all normal environments. The wind tunnel tests show that the 50% cut is slightly shifted left at around 9-9.5 μm . The shift may be due to the limited resolution in that data of Figure 5.4, considering that experiments were conducted for particles with aerodynamic diameters of 9 and 10 μm and data in-between were fitted by the graph.

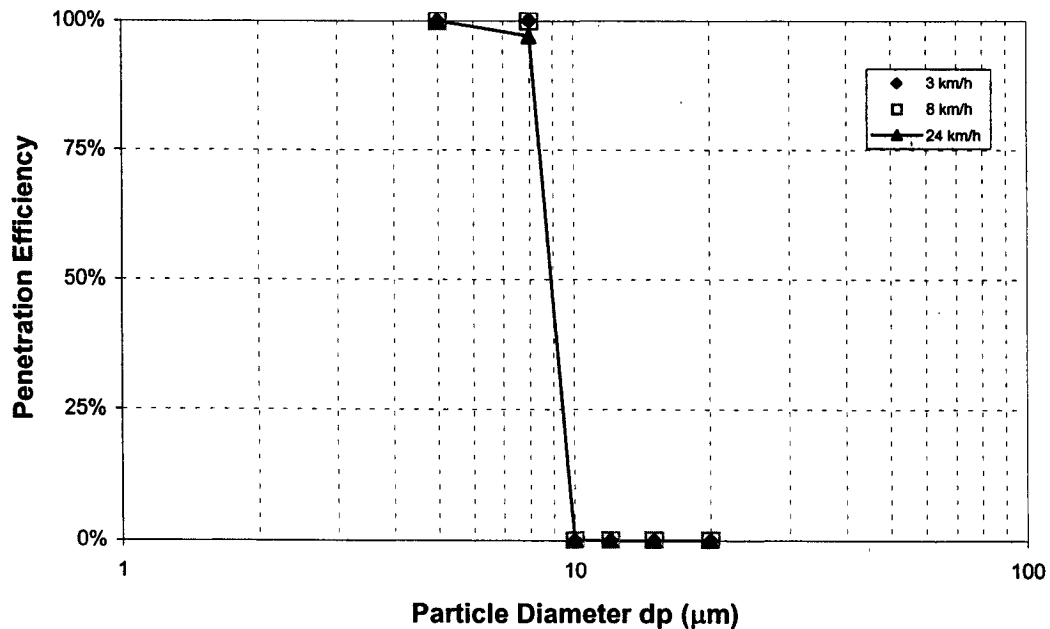


Figure 5.4. Plot of Penetration vs Particle Diameter for Various Wind Speeds

5.4.3 Field Evaluation of the Inlet

The results of the field evaluation of the PM₁₀ inlet are shown in Figures 5.5 to 5.8. Figure 5.5 shows comparison between coarse PM mass concentrations obtained from the Partisol and the PM₁₀ inlet. The figures display a very good agreement between the two samplers. The geometric mean ratio of PM₁₀ inlet to Partisol coarse PM concentration is around 0.94. Coarse PM concentrations determined by both samplers appear to be also well correlated with R²=0.91. It should be mentioned that for all the mass calculations, the contributions of the fine PM was subtracted from the coarse PM, both for Partisol and the PM₁₀ inlet. The calculations were performed using equations 5 and 6:

$$\text{Actual Coarse Mass (Partisol)} = \text{Coarse Mass (Partisol)} - 0.1 \times \text{Fine Mass (Partisol)} \quad (5)$$

Similarly,

$$\text{Actual Coarse Mass (PM10)} = \text{Coarse Mass (PM10)} - 0.025 \times 50 \times \text{Fine Mass (Partisol)} / 16.7 \quad (6)$$

The Teflon filters after gravimetric analysis were analyzed for elements using XRF. Five major crustal metals were chosen to see the correlation between their coarse PM concentrations between the two samplers. Figure 5.6 and Table 5.1 show the comparisons and correlations between coarse concentrations of Al, Si, K, Ca and Fe obtained by the two samplers.

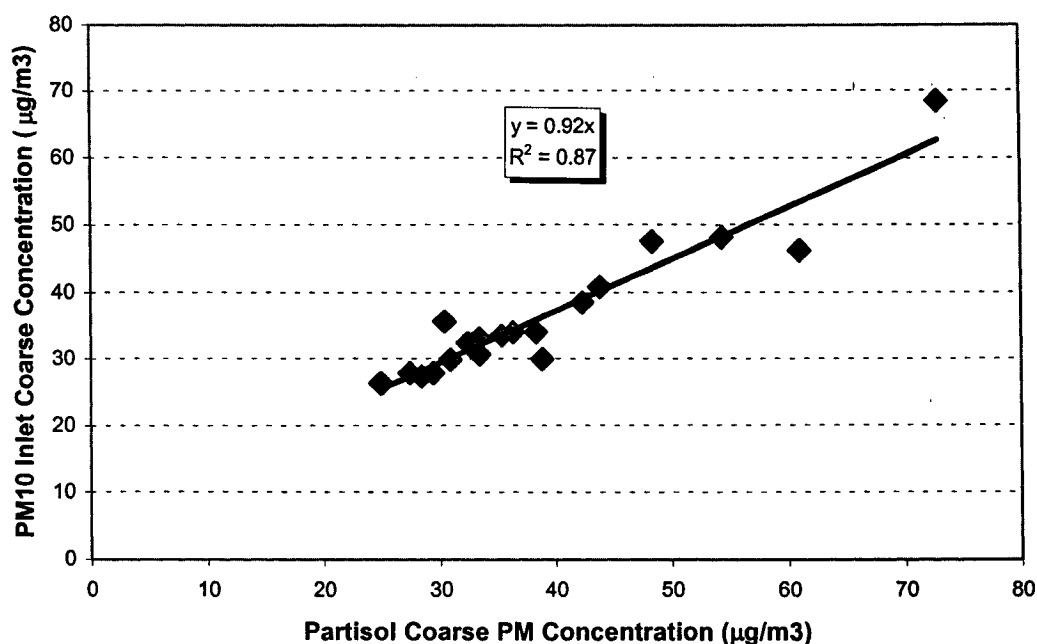


Figure 5.5. Coarse PM Concentrations Determined by the 50 LPM PM₁₀ Inlet and the R&P Partisol

The average (\pm standard deviation) ratio of the PM₁₀ inlet to Partisol coarse concentration for a given element and metal are shown in Table 5.1, along with the correlation coefficient between these concentrations obtained for the specific metal. Figure 5.6 depicts an overall comparison of all the five crustal metals. The results summarized in Table 5.1 as well as the data plotted in Figure 5.6 reveal excellent agreement between the metal concentrations of the two samplers. The mean PM₁₀ inlet- to- Partisol coarse PM concentrations vary from 0.98 to 1.19. The concentrations between the two samplers also appear to be highly correlated for each metal and element, with R^2 varying from 0.79 to 0.92. As seen in Figure 5.6, the

overall PM₁₀ inlet-to-Partisol ratio based on all metal concentrations is virtually identical to 1.

Table 5.1. Comparison between coarse PM concentrations of various crustal metals measured by the PM₁₀ inlet and Partisol

Element	Ratio of PM ₁₀ /Partisol Coarse Concentration [Average (± S.D.)]	Coefficient of Determination R ²
Aluminum	1.19 (± 0.23)	0.81
Silicon	1.06 (± 0.22)	0.79
Potassium	1.09 (± 0.19)	0.86
Calcium	1.07 (± 0.18)	0.92
Iron	0.98 (± 0.16)	0.85

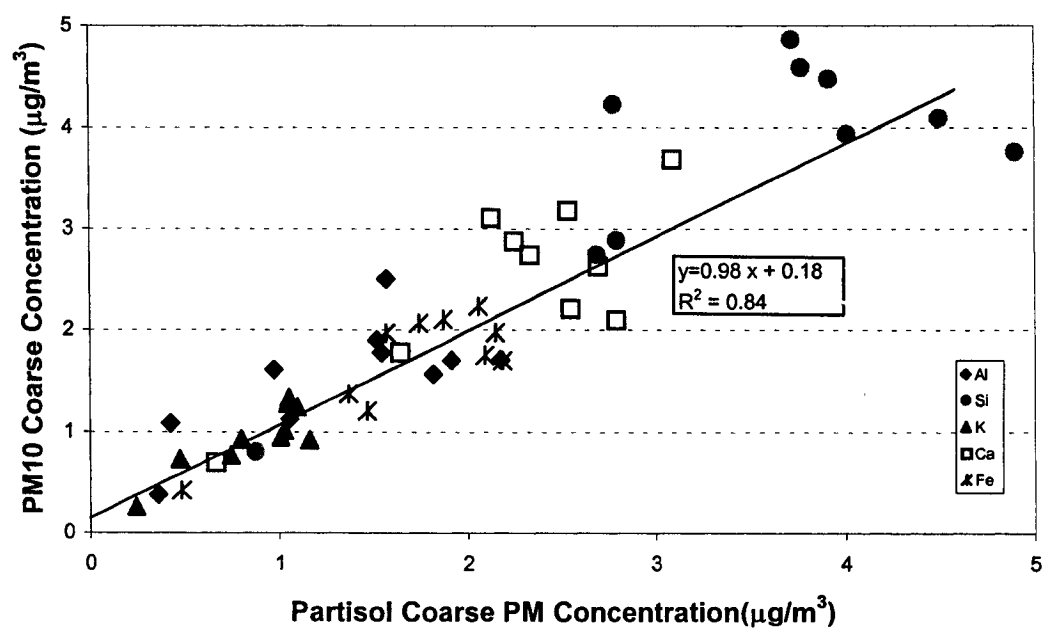


Figure 5.6. Overall comparison between coarse PM concentration of five crustal metal measured by Partisol and PM₁₀ inlet

The comparison of coarse PM nitrate and sulfate concentrations measured by Partisol and the PM₁₀ inlet are shown in Figures 5.7a and 5.7b, respectively. Fine PM contributions were subtracted using Equations 5 and 6, as in the case of the concentrations determined for metals. The results plotted in Figures 5.7a and 5.7b show also very good agreement between these two samplers, with the average PM₁₀ inlet-to-Partisol concentration ratios being 1.13 (± 0.15) and 1.08 (± 0.14) for nitrate and sulfate, respectively.

Finally, the coarse PM concentration ratios of PM₁₀ inlet and Partisol were plotted against the wind speed. The average ratio of PM₁₀ inlet to Partisol coarse PM concentration is around 0.91 (± 0.11). The slightly smaller PM₁₀ inlet concentrations may be due to its somewhat smaller cutpoint (about 9.5 μm estimated from Figure 5.3) compared to that of the Partisol inlet. The results shown in Figure 5.8 clearly indicate that the ratio is independent of the wind speed, thereby indicating that there is no systematic bias in the coarse particle concentrations measured by the PM₁₀ inlet when sampling is conducted at high wind speeds. This result further supports the findings of the wind tunnel tests and establishes the applicability of using the new 50 LPM PM₁₀ inlet in conditions of winds as high as 24 km/h.

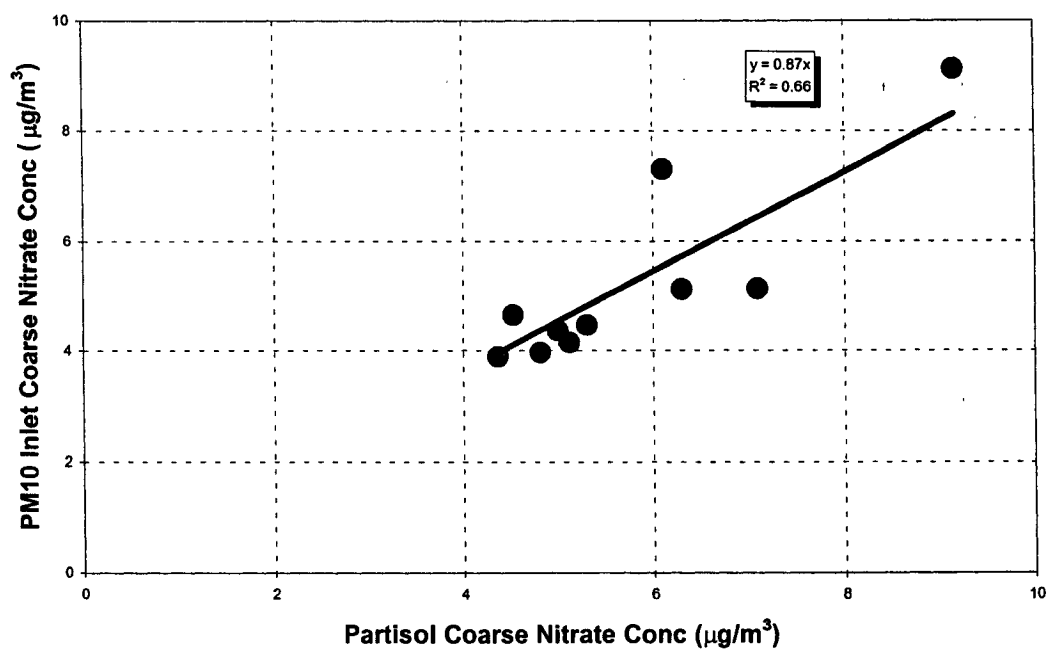


Figure 5.7a. Plot of coarse PM nitrate concentrations between PM₁₀ Inlet and Partisol.

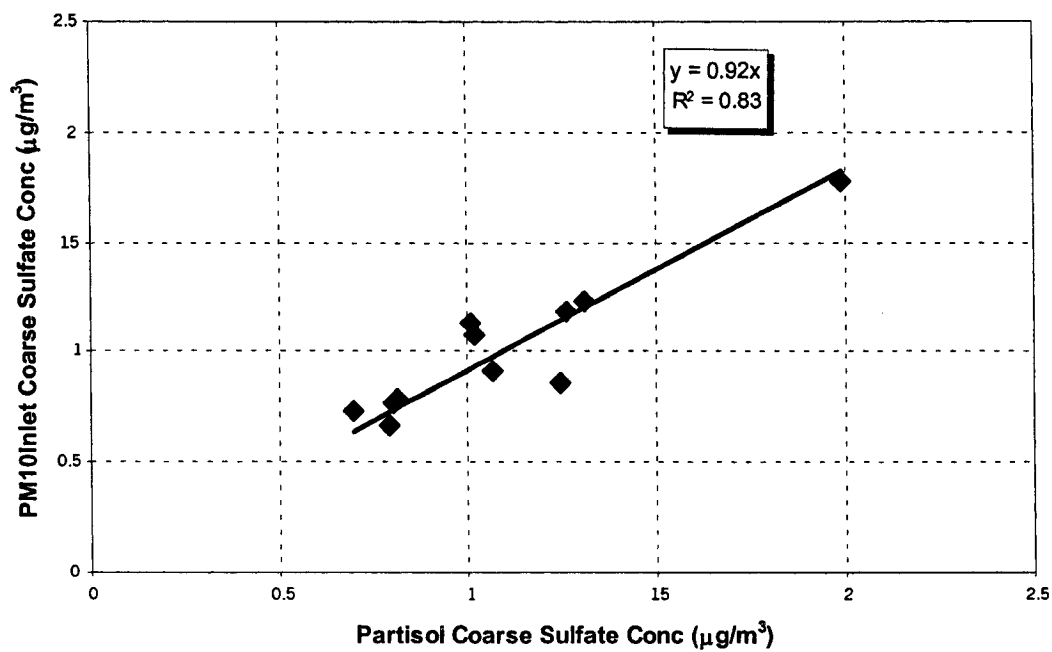


Figure 5.7b. Plot of coarse PM sulfate concentrations between PM₁₀ Inlet and Partisol.

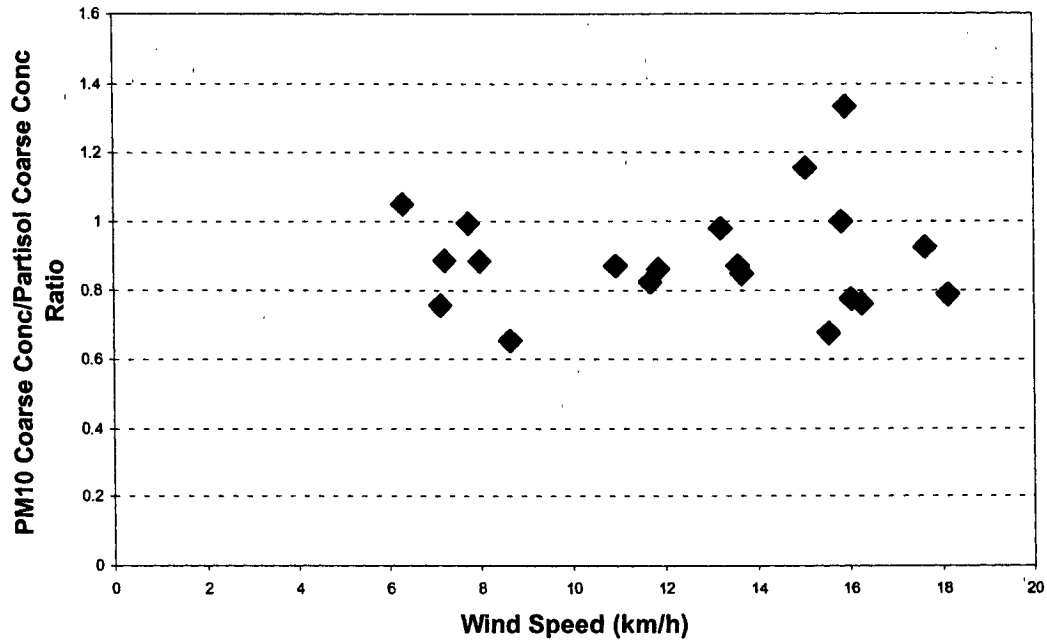


Figure 5.8. Plot of Ratio of PM10/Partisol Coarse Concentrations vs Wind Speed.

5.5 Summary and Conclusion

A PM₁₀ inlet was developed and evaluated for the Continuous Coarse Particle Monitor developed by Misra et al. 2001. Laboratory evaluation was done using polystyrene latex particles and the cutpoint was found to be approximately 9.5 μm . The steepness of the penetration curve, the value of σ_g , was calculated to be as 1.1. This indicated reasonably sharp aerodynamic particle separation characteristics. The PM₁₀ inlet sampling characteristics were then evaluated in a wind tunnel. Tests were performed at three different wind speeds, viz., 3, 8 and 24 km/h. 5, 7, 10, 12, 15 and 20 μm particles were generated for these tests. Results showed that the particle

penetration characteristics of the PM₁₀ inlet were unaffected by the wind speeds. The penetration for all the wind speeds tested, viz., 3, 8 and 24 km/h showed a very close agreement. The 50% cutpoint appeared to have shifted slightly left to around 9 µm. Field evaluation of the PM₁₀ inlet was performed in Riverside and Rubidoux, CA in the months of May and July, 2001. For the field evaluation, a 2.5 µm cutpoint round nozzle virtual impactor was attached downstream of the developed PM₁₀ inlet. Dichotomous Partisol was used as a reference sampler. Partisol has a preselective FRM PM₁₀ inlet to remove particles larger than 10 µm aerodynamic diameter. Results showed excellent correlation between coarse PM concentrations measured by the PM₁₀ inlet and the Partisol with slope of 0.94 with $R^2=0.93$. XRF analysis of filters was done and coarse PM concentrations of five different crustal metals measured by the PM₁₀ inlet and Partisol were determined. Excellent agreement between the two samplers was obtained, with the average PM₁₀ inlet to Partisol coarse concentration ratio for various crustal metals being between 0.98 and 1.19. The overall coarse PM metal concentration ratio for these five crustal metals was 0.98. Nitrate and sulfates were analyzed via ion chromatography. Coarse PM nitrate concentration agreed very well (e.g., within 15%) between the PM₁₀ inlet and the Partisol. Finally, the coarse PM concentration ratios of PM₁₀ inlet and Partisol were plotted against the wind speed and the results clearly showed that this ratio was independent of the wind speed. This further strengthens the wind tunnel tests and establishes the applicability of using the new 50 LPM PM₁₀ inlet in conditions of wind speeds at least as high as 24 km/h.

Acknowledgements

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Chapter 6

THE RELATIONSHIP BETWEEN BOTH REAL-TIME AND TIME-INTEGRATED COARSE (2.5-10 μm), INTERMODAL (1-2.5 μm), AND FINE (<2.5 μm) PARTICULATE MATTER IN THE LOS ANGELES BASIN

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6.1 Abstract

Population exposure to ambient particulate matter (PM) has received considerable attention due to the association between ambient particulate concentrations and mortality. Current toxicological and epidemiological studies and controlled human and animal exposures suggest that all size fractions of PM may be responsible for observed health effects. Recently, the governments of European countries and the U.S. have been discussing a new PM_{10} standard. The purpose of this standard is to preclude invasion of coarse particles into the fine PM mode. This notion is predicated on evidence that suggests that $\text{PM}_{10-2.5}$ is dominated by coarse PM.

In this study, coarse (PM_{10} - $\text{PM}_{2.5}$), intermodal ($\text{PM}_{1-2.5}$), and fine ($\text{PM}_{2.5}$) PM mass concentrations in four different sites are measured with both continuous and time-integrated sampling devices. Two source sites, USC and Downey, CA and two receptor sites, Claremont and Riverside, CA, were monitored for at least three months each. The main objective is to document both short-term and diurnal variations in ambient fine, intermodal, and coarse particulate mass concentrations

with respect to each other while considering the effects of sources, weather, wind speed, and wind direction. Of particular interest are the relationships between PM_1 and $PM_{1-2.5}$ and coarse PM with $PM_{1-2.5}$.

Results show strong correlations between PM_1 and intermodal PM in receptor sites. These two modes in source sites show moderate correlation ($R^2 \sim 0.5$). The contribution of $PM_{1-2.5}$ to $PM_{2.5}$ shows seasonal variation with the largest contribution in the summer months, most likely due to enhanced long range transport. Coarse PM is poorly correlated with intermodal PM in USC and Riverside. The correlation is dependent upon the mass concentration at Claremont, with smaller mass concentrations being moderately-to-well-correlated. This correlation becomes moderate in Downey, most likely because the local freeway is a source of all particle sizes. Continuous data yield insight into the possibility that PM_1 is growing into $PM_{1-2.5}$ via a complex process that involves stagnation of the ambient aerosol during high relative humidity conditions, followed by advection during daytime hours.

6.2 Implications

The regulatory community is currently deliberating the establishment of a PM_1 standard that would eventually replace the current $PM_{2.5}$ standard. The new standard is predicated on the assumption that the PM_1 component of $PM_{2.5}$ may be more reflective of the health effects associated with fine PM, based on the fact that PM_1 is mainly composed of combustion and atmospheric reaction byproducts, while $PM_{1-2.5}$

is dominated by crustal materials that are associated with the coarse PM mode. While a few studies have been conducted with results that support the change to a new standard, the study locations were not representative of all areas because they were surrounded by desert or rural areas and not downwind of metropolitan areas. This study presents the relationship between $PM_{1-2.5}$ and both fine and coarse PM in source and receptor sites in an urban region.

6.3 Introduction

Currently, ambient particulate matter (PM) is divided into three modes by both the regulatory and scientific communities. These modes are based on the aerodynamic diameter of the particles and were chosen due to convenience, physical properties, source, and to some extent the chemical composition. Coarse mode PM consists of particles with diameters between 2.5 and 10 μm and contains crustal metals (Al, Si, Ca, Fe, Ti) and bioaerosols (pollen, mold spores, etc.) Accumulation mode PM includes particles from 0.1 to 2.5 μm in diameter and is comprised of combustion aerosols and particles that grow from photochemical and physical processes that occur in the atmosphere. The remainder of particles (with diameters less than 0.1 μm) comprises the ultrafine PM mode, which consists of combustion-formed particles and nucleation of vapors in the atmosphere (Hinds, 1999).

Since the focus of PM regulation has switched from PM_{10} (particulate matter with aerodynamic diameters less than 10 μm) to $PM_{2.5}$ (particulate matter with

aerodynamic diameters less than 2.5 μm), both scientists and regulators have pondered whether or not another PM standard should be developed for smaller particles. The new standard in question is PM_{10} . The reason given to set the standard at 1- μm particles is due to the sources of these particles. One prevailing theory is that 1-2.5 μm particles primarily originate from the “tail” of the coarse mode PM mass distribution, thus these particles have the same sources as coarse particles and do not significantly contribute to the accumulation mode and more specifically to the health effects caused by fine ($\text{PM}_{2.5}$) particles. The evidence for this was seen in Spokane, WA and Phoenix, AZ, where coarse and intermodal PM ($\text{PM}_{10-2.5}$) were highly correlated (Haller et al., 1999; Kegler et al., 2001). Proponents of the standard argue that recent research demonstrates that PM_{10} has greater health implications due to its sources, size, chemical composition, and results of health studies. If the standard is approved and a sizable fraction of PM_{10} originates from the same sources as $\text{PM}_{10-2.5}$ and/or grows to particles in the 1-2.5 μm size range, $\text{PM}_{2.5}$ would essentially be studied in two halves. Dividing a mode in this fashion only complicates regulations and may ignore an important fraction of toxic PM.

The goal of this paper is to demonstrate the correlation between intermodal PM and PM_{10} in various areas of the Los Angeles basin. The existence of this correlation has extreme significance for regulators because intermodal PM cannot be discounted if it is both correlated with PM_{10} and comprises a substantial fraction of $\text{PM}_{2.5}$. Furthermore, a PM_{10} standard, if adopted, should reflect studies in multiple cities that have both urban and rural characteristics.

6.4 Methods

6.4.1 *Sampling Location*

The instruments described below were operated inside a mobile particle laboratory developed by the Southern California Particle Center and Supersite (SCPCS) measurement and monitoring program that is funded by the US EPA. During the period of this study, measurements were conducted at four sites for about 5-12 months each and across separate seasons. From October 2000 – February 2001, sampling was done in Downey, a typical urban site in south central Los Angeles impacted mostly by primary vehicular emissions. From mid-February through August 2001, sampling was conducted in Riverside/Rubidoux, and from September through August 2002 in Claremont. Riverside/Rubidoux and Claremont are both considered receptor areas in the eastern inland valleys of the basin because they lie downwind of the aerosol plume generated by the millions of vehicles in the western portion of the Los Angeles Basin. This plume is advected by the predominantly westerly winds after aging for several hours to a day (Pandis et al., 1992). Riverside/Rubidoux (unlike Claremont) also lies downwind of significant ammonia emissions from nearby farming and livestock, resulting in high concentrations of ammonium nitrate after atmospheric chemical reactions (Christoforou et al., 2000). From October 2002 through February 2003, sampling occurred near the University of Southern California (USC) at an urban site impacted by freeway emissions, local vehicle emissions, and construction site emissions due to a local sewer replacement project.

6.4.2 Instrumentation

Both continuous and time-integrated data were collected for coarse, fine, and intermodal PM. The sampling devices employed included the Aerodynamic Particle Sizer (APS™, TSI Model 3320), the Beta-Attenuation Monitor (BAM™, Met-One Instruments), the Micro-Orifice Uniform Deposit Impactor (MOUDI™, MSP Corp., Minneapolis, MN), the Dichotomous Partisol-Plus™ (Model 2025 Sequential Air Sampler, Rupprecht and Patashnick Co. Inc., Albany, NY), and the Harvard/EPA Annular Denuder System (HEADS, Koutrakis et al., 1993). Additionally, intensive studies were conducted for short time intervals in which the USC Continuous Coarse Monitor (Misra et al., 2001) and Cascaded ADI Continuous Nitrate Monitor (Stolzenburg et al., 2003) were collocated with the above instruments for a short time. All samples were drawn through conductive stainless steel pipes with diameters proportional to sample air velocities for each instrument.

Both the MOUDI and Partisol sampled approximately once per week and over time periods varying from 4 to 24 hrs, depending on location and observed pollution levels. Particles were classified by the MOUDI in the following aerodynamic particle diameter ranges: <0.10, 0.10-0.32, 0.32-0.56, 0.56-1.0, 1.0-2.5, and 2.5-10 μm . Teflon filters with diameters of 4.7 and 3.7 cm (2 μm pore size, Gelman Science, Ann Arbor, MI) were used to collect particles in the MOUDI stages and after-filter, respectively.

The Partisol uses a PM₁₀ inlet operating at 16.7 LPM to remove particles larger than 10 μm in aerodynamic diameter. The remaining PM₁₀ aerosol is drawn

through a virtual impactor, or, “dichotomous splitter”, located after the inlet. Two separate flow controllers maintain coarse aerosol velocity at 1.67 LPM and that of the fine aerosol stream at 15 LPM. Coarse and fine particles are collected on two 4.7 cm Teflon filters, which are housed in reusable cassettes placed in the minor and major flows of the Partisol virtual impactor. The Teflon filters of both the MOUDI™ and Partisol™ samplers were pre- and post-weighed using a Mettler Microbalance (MT5, Mettler-Toledo, Inc, Hightstown, NJ) after 24-hour equilibration under controlled humidity ($40 \pm 5\%$) and temperature ($24 \pm 3^\circ\text{C}$) to determine particle mass concentrations.

The Teflon filters were then used to determine sulfate and nitrate concentrations by ion chromatography. For measurement of metals and trace elements, a second set of Teflon filters was collected in a second MOUDI configured identically to the first. After weighing, filters were analyzed by X-ray fluorescence for metals and other trace elements. Samples to determine the size-fractionated concentrations of elemental carbon (EC) and organic carbon (OC) were obtained by simultaneous sampling with a third MOUDI. 47 mm aluminum substrates were used for the impaction stages and a 37 mm quartz fiber filter (Pallflex Corp., Putnam, CT) was used as the after-filter (ultrafine stage). EC and OC values were determined using the Thermal Evolution/Optical Transmittance (TOT) analysis of Birch and Cary (1996). Concurrent to the 24-hour MOUDI sampling, fine and coarse mass measurements were performed with 47 mm Teflon filters in a dichotomous sampler (Partisol-Plus™, Model 2025 Sequential Air Sampler, Rupprecht and Patashnick Co.

Inc., Albany, NY). Mass and elemental concentrations of coarse and fine size fractions were determined by the same methods as described previously for MOUDI sampling. Partisol results were compared to MOUDI data to check for consistency, and, in a few cases, used in the analysis when MOUDI results were not available.

In addition to time integrated chemical composition data, the USC Continuous Coarse Monitor (Misra et al., 2001) operated during a winter intensive study at the USC site. The operating principle of the monitor is based on enriching coarse particle concentrations by a factor of about 25 by means of a 2.5- μm cutpoint round nozzle virtual impactor, while maintaining mass of $\text{PM}_{2.5}$ at ambient concentrations. The aerosol mixture is subsequently drawn through a Tapered Element Oscillating Microbalance (TEOM™ 1400A, Rupprecht and Patashnick, Albany, NY), the response of which is dominated by the contributions of coarse PM due to concentration enrichment.

Another intensive study was conducted during the month of September 2001 in Claremont, in which the newly developed ADI Continuous Nitrate Monitor was located at the Claremont site for an intensive study. The operation and characterization of this device is described by Stolzenburg et al. (2003) and Fine et al. (2003).

6.5 Results and Discussion

$PM_{1-2.5}$ and $PM_{2.5}$ mass concentrations are very highly correlated ($R^2 = 0.76$) for all sites (Figure 6.1). Figure 6.1 also indicates that, contrary to the prevailing perception, the 1-2.5 μm range accounts for a substantial fraction of the total $PM_{2.5}$ mass, ranging from 20-45%, depending on location and season, as it will be discussed in following sections. The chemical characteristics of intermodal PM are displayed by site in Figure 6.2. These results are similar to those discovered by Hughes et al. (2000), in which they determined the chemical composition of the fine PM mode at four locations in Southern California. In contrast, the coarse size mode does not demonstrate as high of a positive correlation with intermodal PM. Intermodal PM tracks much better with PM_1 than the coarse mode in receptor sites,

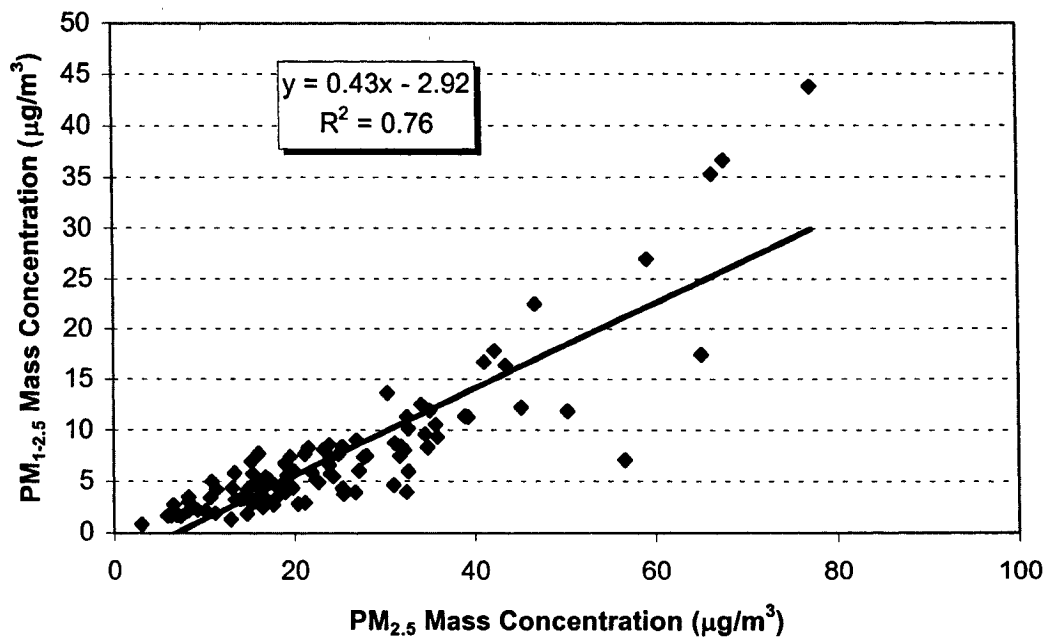


Figure 6.1. $PM_{1-2.5}$ Versus $PM_{2.5}$ at All Sites

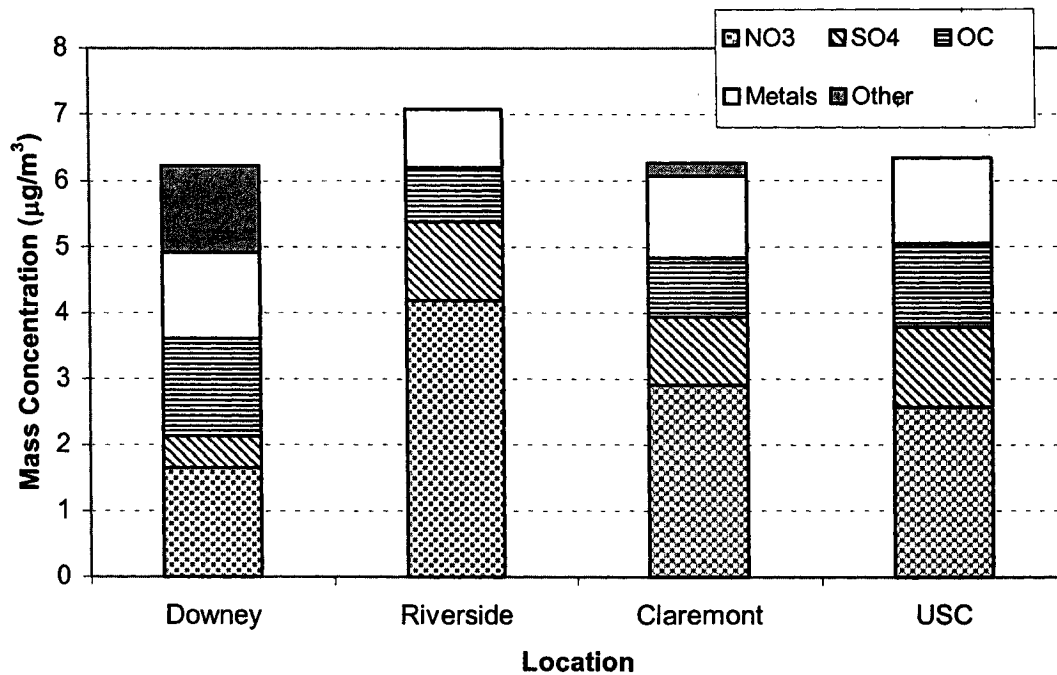


Figure 6.2. Chemical Composition of Intermodal PM Averaged By Location

while the correlations between coarse and intermodal PM as well as between PM_{10} and intermodal PM become closer in source sites. The following section will describe this in detail.

6.5.1 Site-by-Site Comparison

University of Southern California

Figure 6.3a shows the relationship between intermodal PM and the coarse mode at the USC sampling site 1 mile south of downtown Los Angeles. The correlation coefficient (R^2) of 0.11 reflects the divergence of these two modes in the ambient air near this site. Because the site is urban and crustal particles are not locally emitted, this result is not unusual. The site is also not directly impacted by a

freeway (unlike the Downey site), which would emit coarse particles in the form of road dust. Intermodal PM correlates moderately with PM_{10} , however, with an R^2 of 0.53 (Figure 6.3b). At a source site such as USC, this correlation is most likely driven by direct emission of both PM_{10} and intermodal particles from the same automobile sources.

The continuous data displayed in Figures 6.4a,b represent two weeks of intensive sampling at USC. Winter days are normally cool ($\sim 10^\circ\text{C}$) and humid ($>70\%$) in the mornings and dry ($<40\%$) and temperate ($\sim 19^\circ\text{C}$) in the afternoons. Figure 6.4a illustrates a week during early winter in which a Santa Ana wind event occurred from 11/25 to 11/29 and a rain event occurred from 11/29 to 12/1. From the graph it is apparent that coarse mode concentrations increase and wind becomes erratic at the beginning of the week. Intermodal PM tracks the coarse mode during this time because Santa Ana winds blow crustal particles from the California deserts while creating hot and dry conditions that do not favor particulate growth. The drastic mass concentration drop in all size modes marks the arrival of the rainstorm. Figure 6.4b presents a more typical winter week in December 2002. Intermodal PM concentration tracks with both $PM_{2.5}$ and coarse concentrations. The continuous data do not show whether intermodal PM is more closely associated with coarse or fine PM during this week as all modes appear interrelated. For the week of 12/02/02 to 12/09/02, a correlation was performed between the continuous intermodal mass data and both the coarse and fine PM data. The resulting Pearson correlation coefficients (R-values) were 0.35 and 0.64, respectively. This demonstrates the obvious

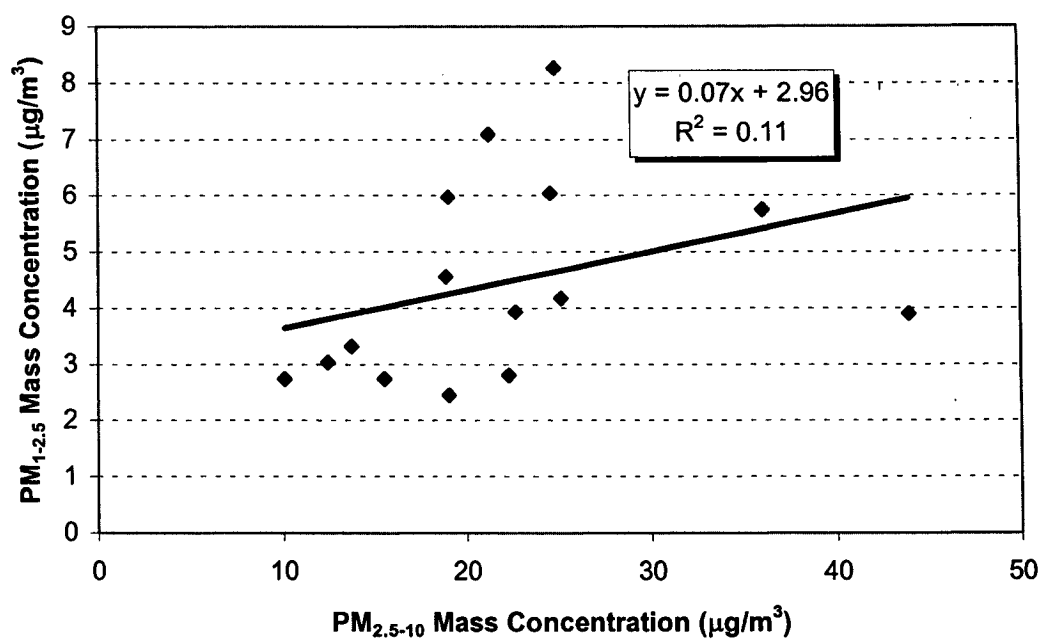


Figure 6.3a. Intermodal Versus Coarse PM at USC

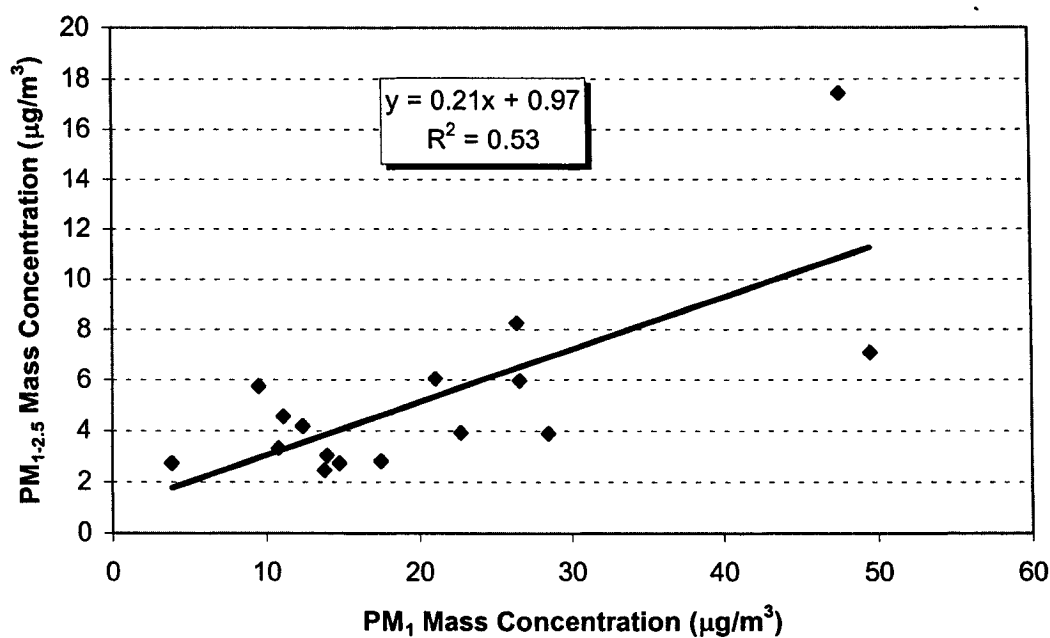


Figure 6.3b. Intermodal Versus PM_1 at USC

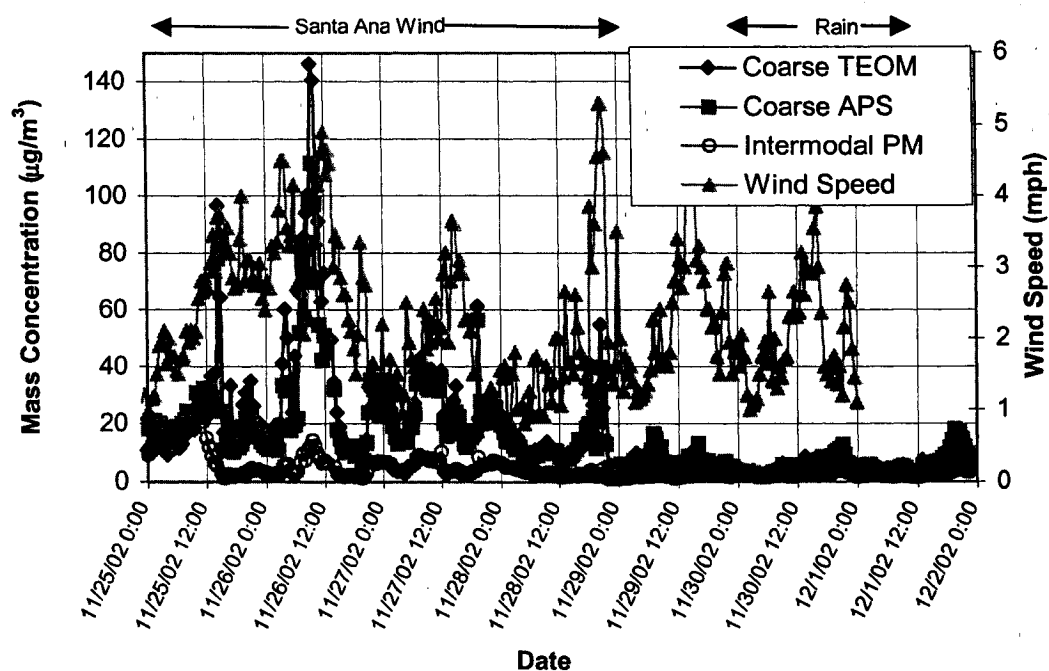


Figure 6.4a. Coarse, Intermodal, and Fine 11/25-12/1 2002

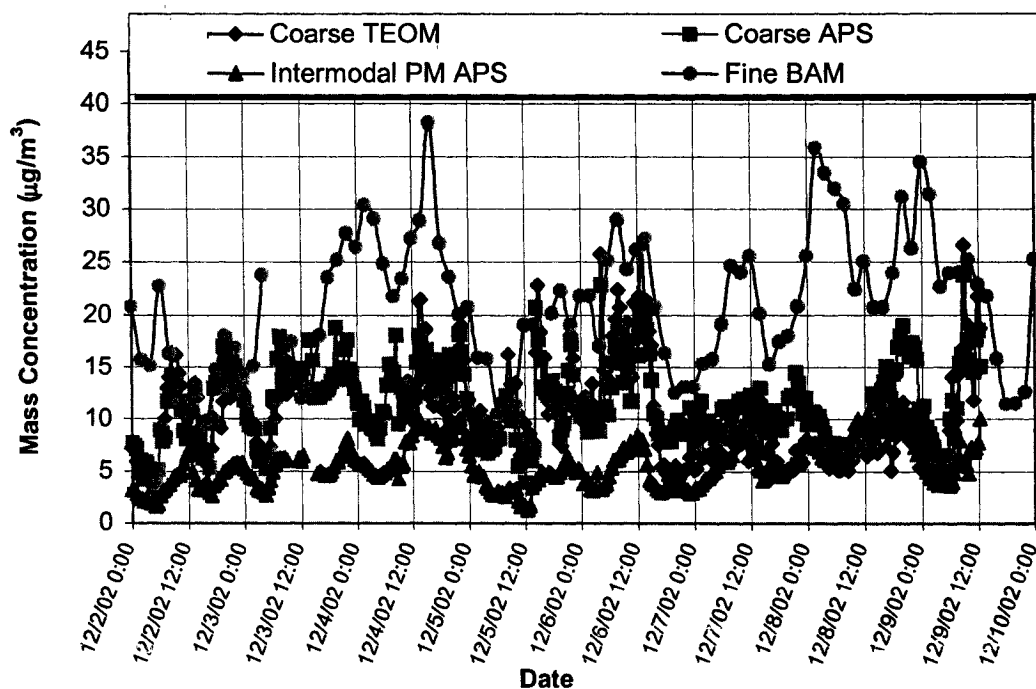


Figure 6.4b. Coarse, Intermodal, and Fine PM Mass Concentrations 12/02-12/09/2002

correlation between intermodal and fine PM while a much weaker one exists between intermodal and coarse PM.

Downey, California

Figures 6.5a,b demonstrate the correlations between intermodal PM and both coarse and PM_{10} mass concentrations, respectively. The correlations between intermodal PM and the other two modes are similar with $R^2=0.49$ for intermodal-coarse and $R^2=0.47$ for intermodal- PM_{10} . A possible explanation for this finding is that the site is located downwind of a high capacity freeway (I-710) with a large number of trucks and automobiles, and which may be the dominant particle source at that site for particles of all ranges. Coarse particles in Downey are dominated by resuspended road and tire dust while fine particles are a mixture of about 40% combustion emissions and 30% resuspended road and tire dust (Singh et al., 2002). Moreover, this site is not near any source of crustal particles (i.e. all nearby surfaces are paved), so intermodal PM correlation with coarse PM is most likely driven by road dust, which is known to contain toxic compounds (Chow et al., 2003).

Riverside, California

Intermodal PM is graphed versus coarse PM in Figure 6.6a. The R^2 of 0.14 is very surprising in this location because it is a rural site with local dust emissions. This result indicates that the tail of the coarse PM distribution is not significantly affecting intermodal concentrations and thus fine PM concentrations. The

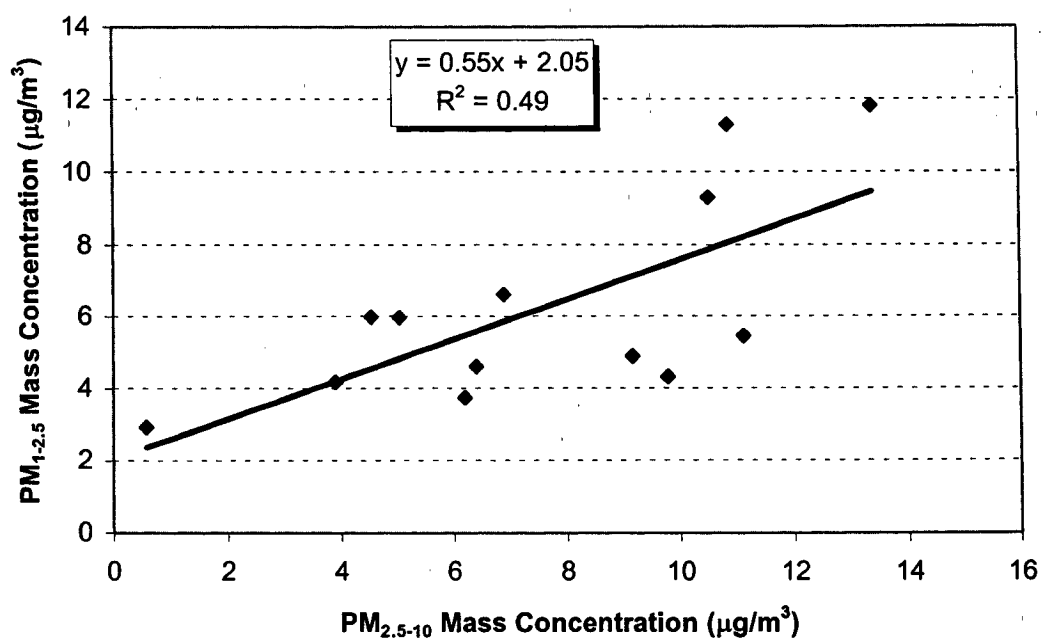


Figure 6.5a. Intermodal Versus Coarse PM at Downey, CA

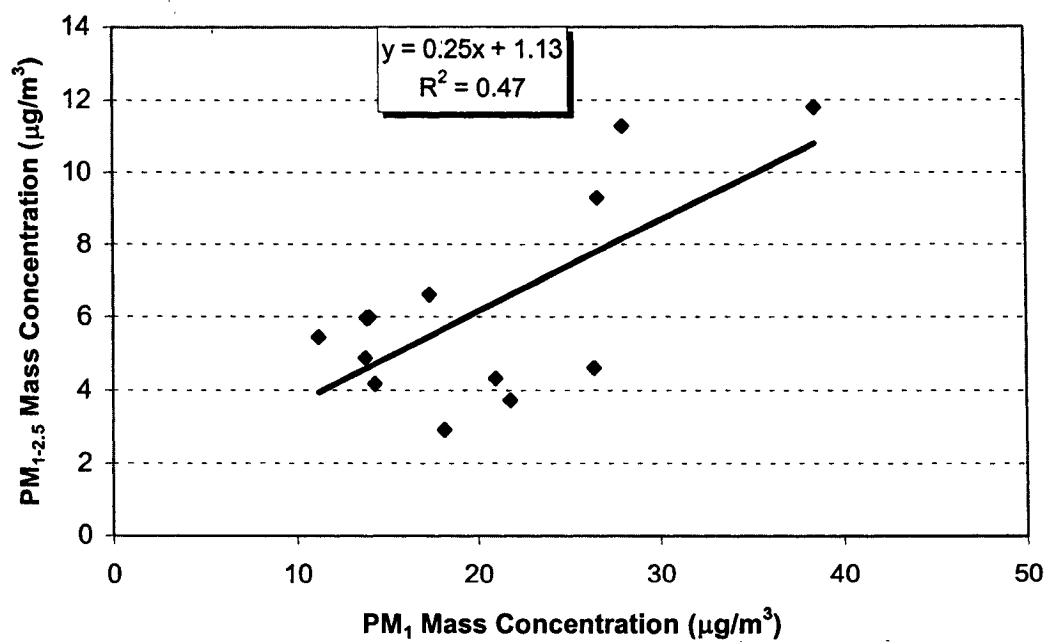


Figure 6.5b. Intermodal Versus PM_1 at Downey, CA

relationship between intermodal PM and PM₁ is strong at this site (Figure 6.6b). The R² of 0.74 is significant and may be explained by condensational growth of particles less than 1 µm in diameter to particles between 1 and 2.5 µm in diameter. The sub-micron particles are emitted west of Riverside in the Los Angeles area and grow while advection transports them to Riverside. This process often occurs over 6-12 hour time intervals (Allen et al., 2000).

While a linear correlation does provide a good fit, the data in Figure 6.6b appear to have an exponential trend. To explore this further, the data points for which chemical data were known were split into two regions. Group 1 (n = 5) included PM_{1-2.5} concentrations less than 5 µg/m³ and group 2 (n = 4) included those points in which PM_{1-2.5} was greater than 5 µg/m³. These groups were then statistically tested to determine whether their chemical compositions are significantly different based on the following three parameters: nitrate fraction, organic carbon fraction, and sulfate fraction. The non-parametric Wilcoxon Rank Sum test was employed because of small sample size and assumed non-normality of the distribution. The results of this test showed that the median nitrate fraction of intermodal concentrations less than 5 µg/m³ in Riverside is significantly lower than the median nitrate fraction of intermodal concentrations greater than 5 µg/m³ (p < 0.01). This test also confirmed that median organic carbon fraction of intermodal concentrations less than 5 µg/m³ in Riverside is significantly higher than the median organic carbon fraction of intermodal concentrations greater than 5 µg/m³ (p = 0.026). Median sulfate fraction was nearly significantly lower in group 1 than group

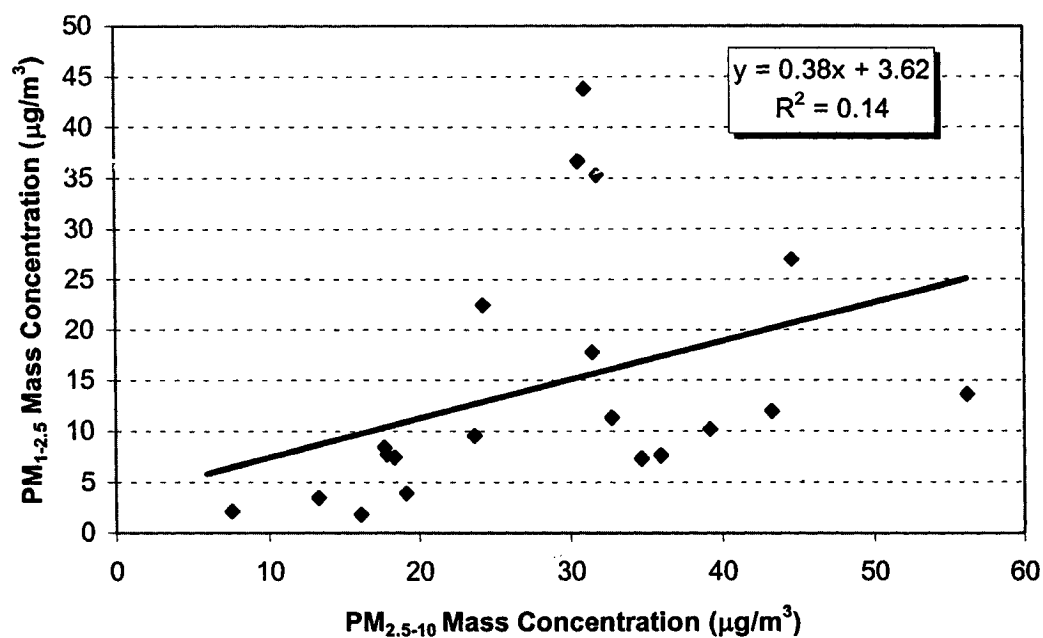


Figure 6.6a. Intermodal Versus Coarse PM for Riverside/Rubidoux, CA

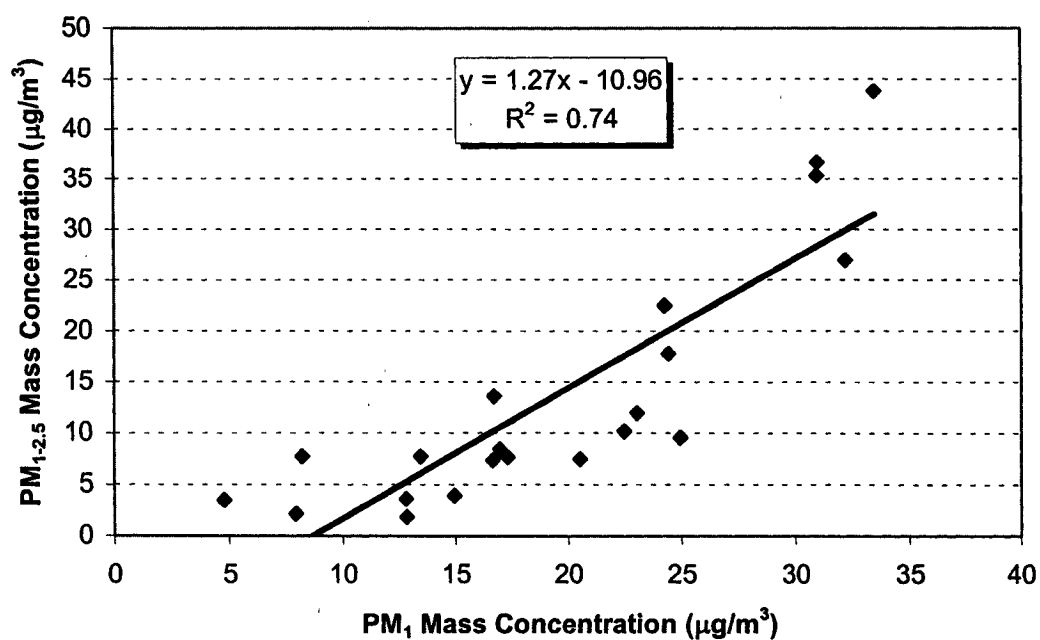


Figure 6.6b. Intermodal Versus PM_1 at Riverside/Rubidoux, CA

2 ($p = 0.111$). These results reinforce our hypothesis that higher $PM_{1-2.5}$ concentrations are due to increases in hygroscopic compounds such as nitrate and sulfate instead of the more hydrophobic organic carbon.

Claremont, California

At first glance, intermodal PM are not correlated with coarse mode PM with an $R^2 = 0.10$ (Figure 6.7a). However, the correlation increases to $R^2 = 0.43$ when all points with intermodal PM mass concentrations greater than $8 \mu\text{g}/\text{m}^3$ are excluded, suggesting that there is some association between coarse and intermodal PM in that location, but the highest concentrations in the $1 - 2.5 \mu\text{m}$ range are not associated with days during which coarse PM concentrations were high. This is counterintuitive to the argument that the tail of the coarse mode contributes to fine PM during times when high coarse concentrations are measured. Because Claremont is also a rural site, coarse PM would be expected to correlate with intermodal PM, but this is only true for relatively low coarse PM mass concentrations. Intermodal PM correlates well ($R^2 = 0.65$) with PM_{10} without excluding high mass concentrations (Figure 6.7b). Thus, at the receptor site Claremont, advection of fine PM outweighs the local coarse emissions with respect to contributions to intermodal PM.

6.5.2 Comparisons Between PM Modes Based on Chemical Composition

Particulate nitrate is the predominant chemical constituent of the $1-2.5 \mu\text{m}$ range, accounting (with the exception of the Downey site) for about 40 – 65% of the

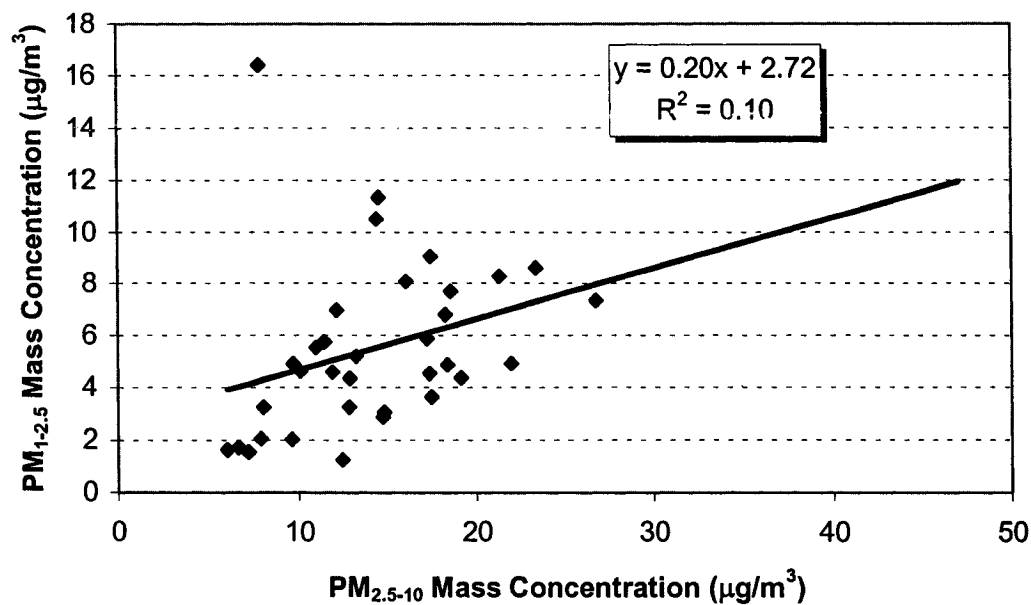


Figure 6.7a. Intermodal Versus Coarse PM in Claremont, CA

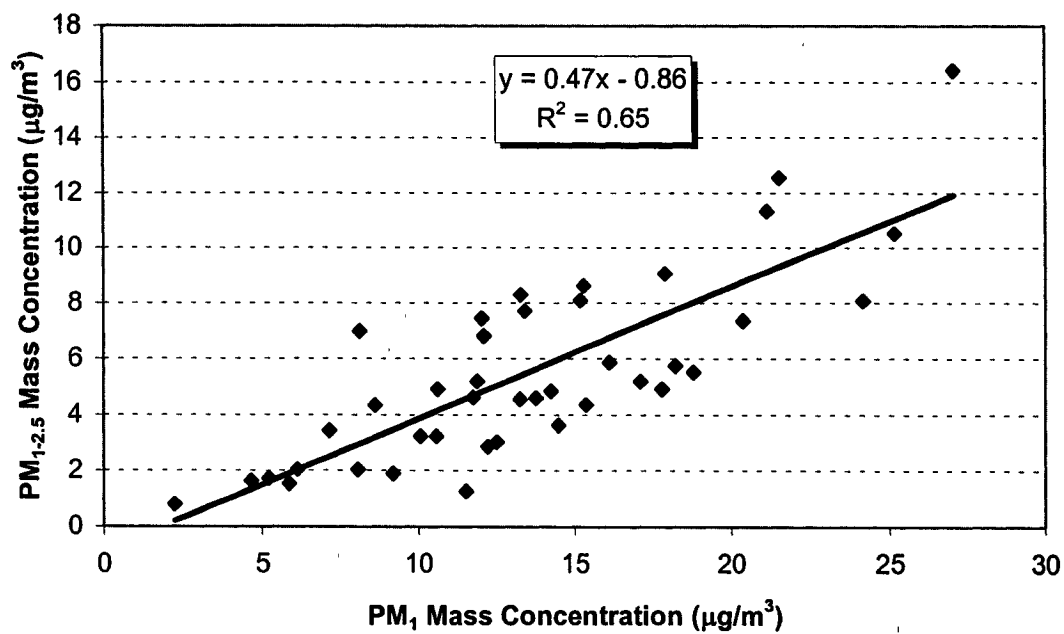


Figure 6.7b. Intermodal Versus PM₁ for Claremont, CA

total mass in that range (Figure 6.2). The relationship between coarse, intermodal and fine PM was also investigated for this species. The correlation between coarse and intermodal nitrate is weak ($R^2 = 0.13$), which demonstrates the divergence of the sources of these particles (Figure 6.8a). Previous studies in Southern California indicated that coarse mode nitrate is a mixture of sodium and ammonium nitrate, while nitrate in the fine mode is mostly ammonium nitrate (Kleeman et al., 1999). Figure 6.8b shows that intermodal nitrate is well correlated with $PM_{2.5}$ nitrate with $R^2 = 0.70$, and it also comprises a substantial fraction of $PM_{2.5}$ nitrate (slope = 0.32). A similarly high degree of correlation between continuously measured intermodal nitrate and PM_1 nitrate ($R^2 = 0.80$) is shown in Figure 6.9, using the data generated by the Cascaded ADI Continuous Nitrate Monitor (Stolzenburg et al., 2003). These two figures confirm that nitrate in the $PM_{1-2.5}$ is a significant portion of total $PM_{2.5}$ bound nitrate, probably originating from the sub-micrometer range by condensational growth. The exact mechanism through which accumulation mode PM grows to the micrometer range have been debated in several previous publications, including aqueous phase reactions (Hering and Friedlander, 1982) as well as activation of sub-0.5 μm particles to form fog or cloud droplets, followed by aqueous phase chemistry and fog evaporation (Meng et al., 1994). Growth of hygroscopic ambient PM beyond the 1 μm range has been observed in several other studies (Koutrakis et al., 1989; Kelly and Koutrakis, 1998) when relative humidities reach greater than ninety percent.

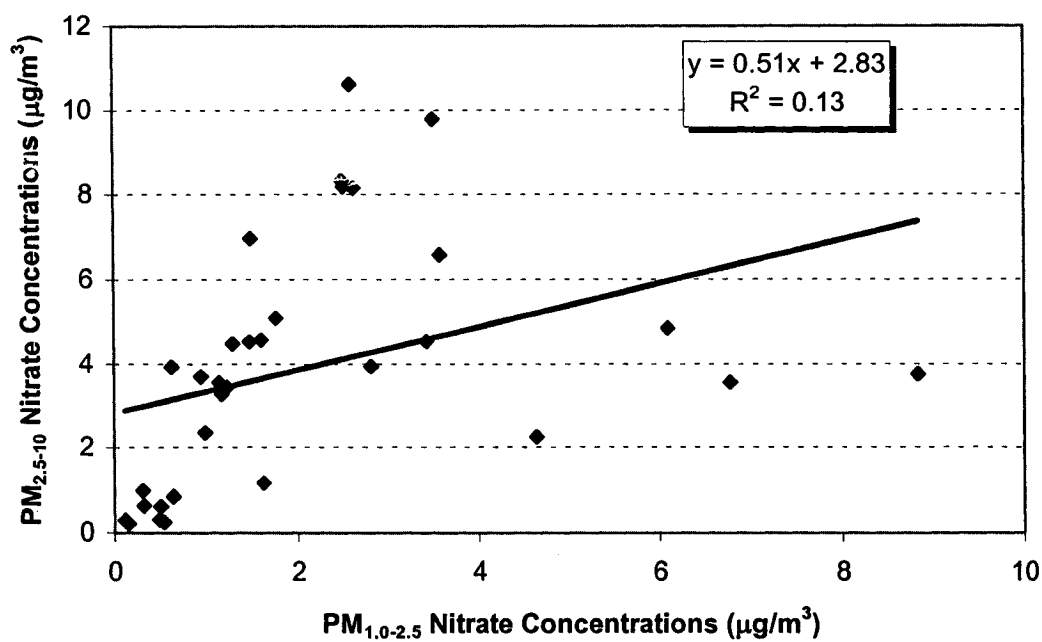


Figure 6.8a. PM_{2.5-10} Vs. PM_{1.0-2.5} Nitrate Mass Concentrations for Claremont, CA

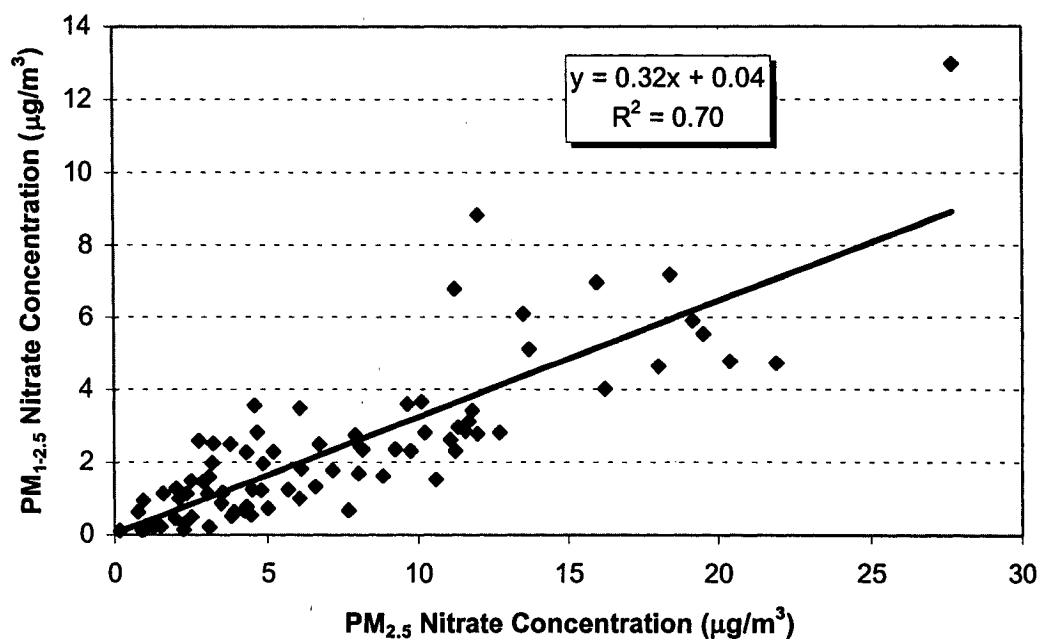


Figure 6.8b. PM_{1-2.5} Versus PM_{2.5} Nitrate Concentrations at All Sites

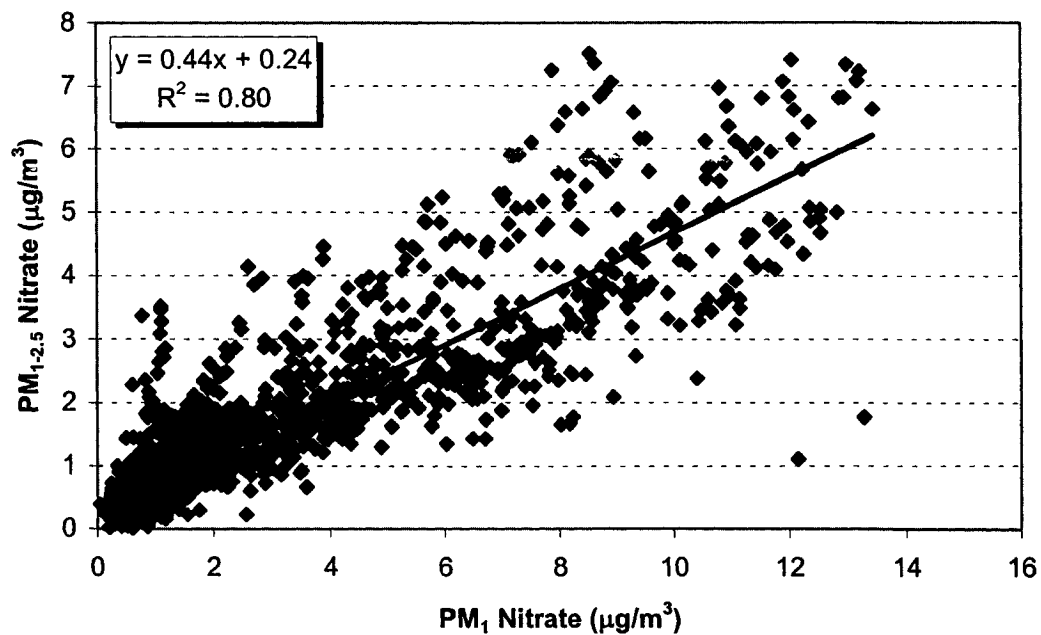


Figure 6.9. Continuous PM_{1-2.5} Versus PM₁ Nitrate at Claremont, CA in September 2001

The period between April and July in the Los Angeles basin is characterized by frequent fog-like conditions with high relative humidities in the overnight and early morning hours. Particles emitted mostly to the west travel by advection eastwards towards the inland valleys of the basin, such as Claremont. While in transit, these particles experience condensational growth and participate in photochemical reactions. Some particles remain in the sub-micron range after growth, while others become intermodal particles. This process takes place over multi-hour time spans, whereby PM₁ particles may grow into PM_{1-2.5} following several hours of advection and stagnation. Growth of sub-micrometer nitrate into the super-micrometer range is also supported by previous studies showing very similar

chemical composition between PM_1 and $PM_{1-2.5}$ (Hughes et al., 1999; Kleeman et al., 1999; Hughes et al., 2000). The data plotted in Figure 6.10 further support the argument that intermodal nitrate originates from fine and not coarse PM. While wind speed peaks at 3 PM, the ratio of intermodal to PM_1 nitrate peaks at 6 PM. The Claremont site is surrounded by many large unpaved areas and gravel pits. If the wind were creating resuspension of local coarse particles that were in turn affecting intermodal PM concentrations, wind speed would peak concurrently with mass concentration. Advection, however, would be represented by the time lag seen here. After wind speed peaks, intermodal PM nitrate particles, that have been undergoing photochemistry and growth, blow toward Claremont and peak shortly thereafter.

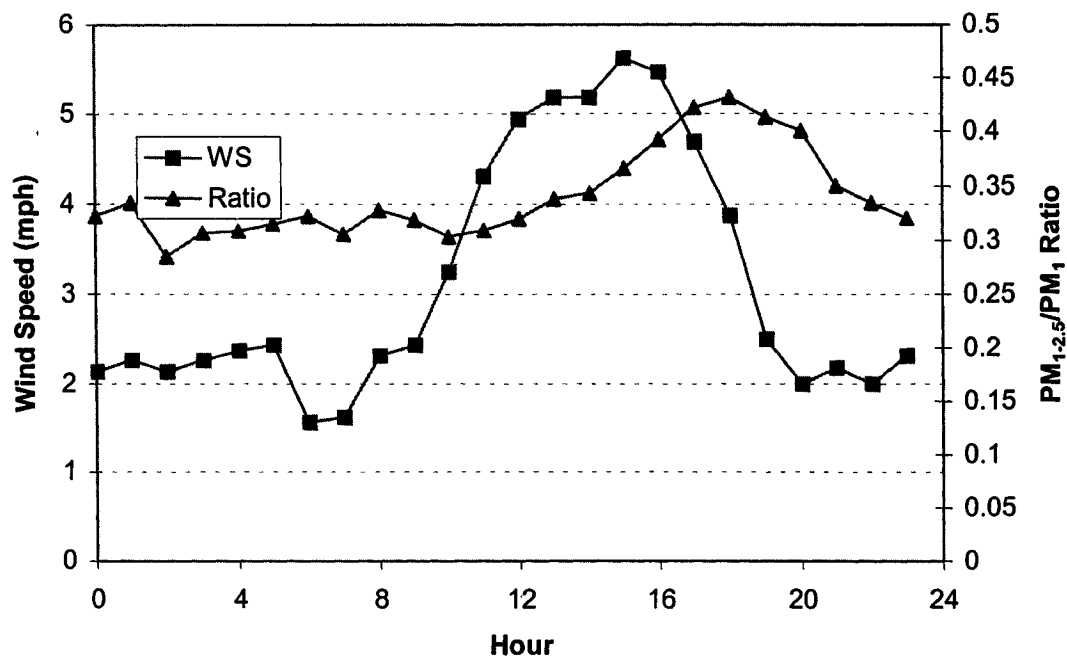


Figure 6.10. Daily Wind Speed and $PM_{1-2.5}/PM_{2.5}$ Nitrate at Claremont, CA in September 2001

Figure 6.11 also illustrates the photochemical growth and advection of intermodal PM in the Los Angeles basin. The mass concentration ratio of intermodal to fine mode PM in all sites (based on time integrated data) increases during the summer months due to increased solar radiation and enhanced advection.

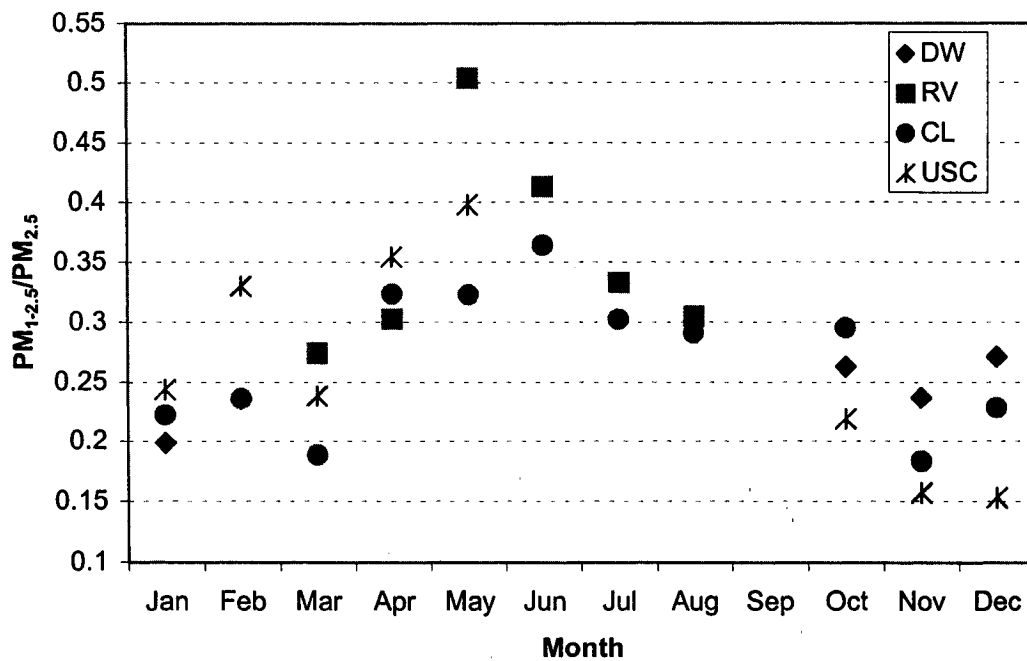


Figure 6.11. Monthly Average of the Ratio of Intermodal PM to Total $PM_{2.5}$

Figures 6.12a and b show the OC and sulfate concentrations vs. nitrate concentrations for the 1 – 2.5 μm PM range in source and receptors sites, respectively. Nitrate and sulfate are correlated for this size range in source sites ($R^2 = 0.63$) whereas the OC concentrations are poorly correlated with nitrate concentrations ($R^2 = 0.14$). This suggest that even in the source sites, nitrate and sulfate in the intermodal PM range share a common origin, i.e., secondary formation and growth by condensation into the super-micrometer range, whereas OC in that

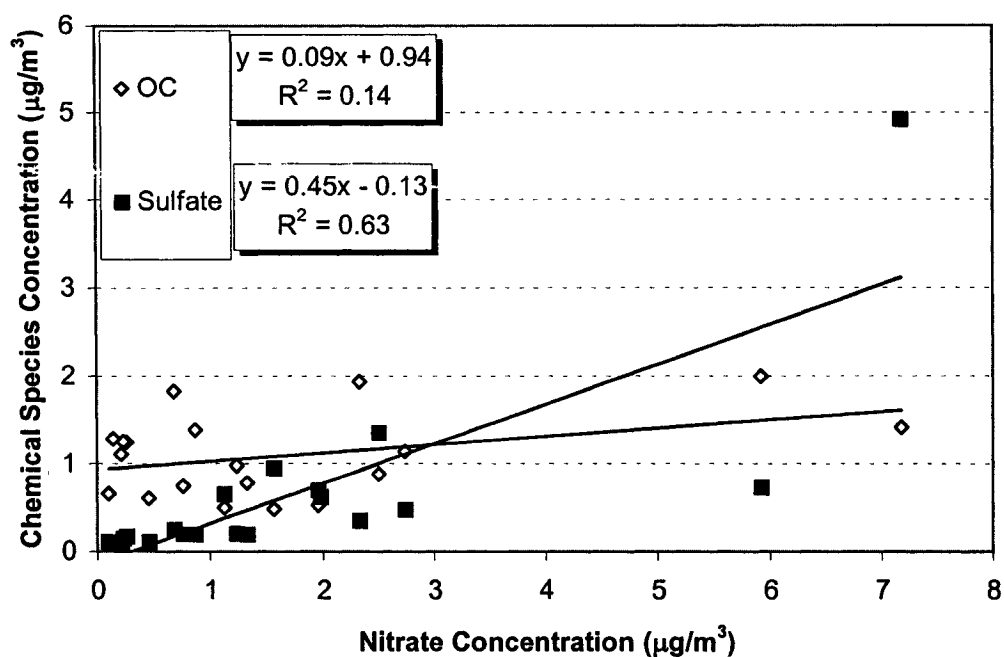


Figure 6.12a. OC and Sulfate Versus Nitrate Concentration in the 1 - 2.5 μm Range at Source Sites

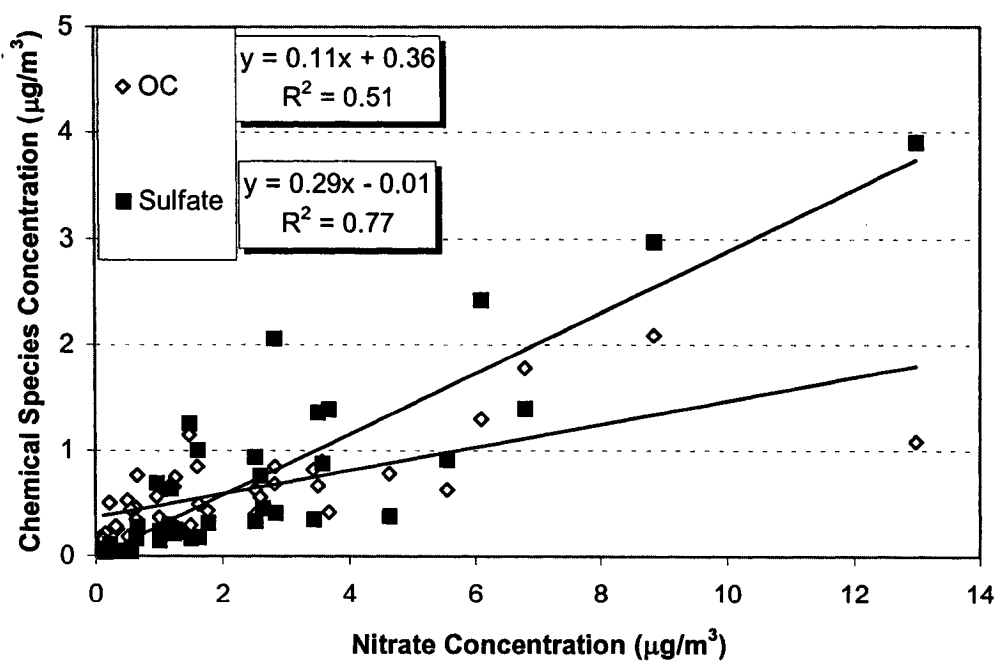


Figure 6.12b. OC and Sulfate Versus Nitrate Concentration in the 1-2.5 μm Range at Receptor Sites

range originates most likely from traffic road dust (the correlation between OC concentrations in the 1 – 2.5 μm and 2.5 – 10 μm size ranges yielded a $R^2 = 0.61$. A similar correlation between these two OC modes in receptor sites yielded a $R^2 = 0.21$ suggesting that the presence of OC in that range is not due to road dust in receptor areas). The sulfate and nitrate concentrations of the 1 – 2.5 μm range in receptor sites are very well correlated ($R^2 = 0.77$) while moderate correlations ($R^2 = 0.51$) were also observed between the nitrate and OC concentrations. These results are consistent with the findings of John et al. (1990) that nitrate and sulfate are uniformly mixed in the so-called “droplet” mode, defined as one containing accumulation mode PM exceeding about 0.5-0.7 μm in diameter. Whether organics are externally or internally mixed is not clear from our data. However, Pandis et al. (Pandis et al., 1993) showed that organics in the larger size range of the accumulation mode can result only if there exist sufficient primary particles in the $> 0.5 \mu\text{m}$ range and/or if the condensable organic species have a strong affinity for that size range. The former condition is consistent with our field data of several years in the Los Angeles Basin, showing that the aerosol size distribution in receptor areas of this basin contains a much larger number of particles in the larger size range of the accumulation mode compared to source sites (Kim et al., 2002; Fine et al., 2003), as result of aerosol aging in the atmosphere due to advection and long-range transport. The existence of a pronounced inorganic “droplet” mode, which possibly extends beyond the 1 μm range, will likely influence the presence of organics in that range

through condensation, given that at least some portion of OC is soluble (Meng et al., 1994).

Figure 6.13 displays the relationship between coarse and intermodal crustal metal concentrations. The crustal metal concentrations were obtained by analyzing MOUDI Teflon substrates via x-ray fluorescence (XRF) and utilizing the following formula (Malm et al., 1994):

$$PM_{soil} = 2.2 * Al + 2.49 * Si + 1.63 * Ca + 2.42 * Fe + 1.94 * Ti$$

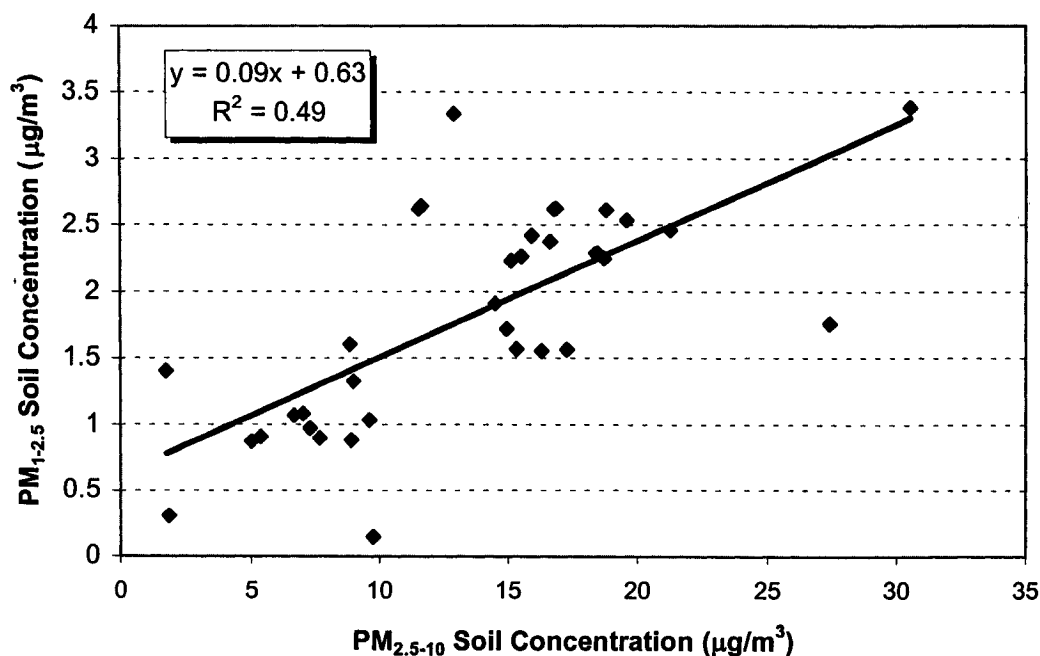


Figure 6.13. Intermodal Versus Coarse PM Crustal Elements for Claremont, CA

The moderate correlation ($R^2 = 0.49$) between intermodal and coarse crustal metals is expected because the tail of the coarse mode crustals infiltrates PM_{2.5} to a limited extent, which is indicated by the rather low concentrations of crustal metals found in

intermodal PM. The relationship between intermodal PM mass to its soil (crustal) component is shown in Figure 6.14. As evident by the slope of 3.42, the soil component of $PM_{1-2.5}$ is less than 25% of the total mass and has a moderate correlation with total mass ($R^2 = 0.54$). This result differs from the Kegler et al. (2001) study in that they found a similar correlation between intermodal mass and soil concentrations, but with a much higher slope. The crustal component in Spokane, WA is closer to 50% of the total intermodal mass, which is to be expected in a city that is surrounded by rural areas. Although the contribution of crustal metals to the intermodal PM mass is not negligible, it is far lower than that of nitrate, as illustrated in Figure 6.2. This may also explain the overall low correlation between the intermodal and coarse PM concentrations obtained in our study.

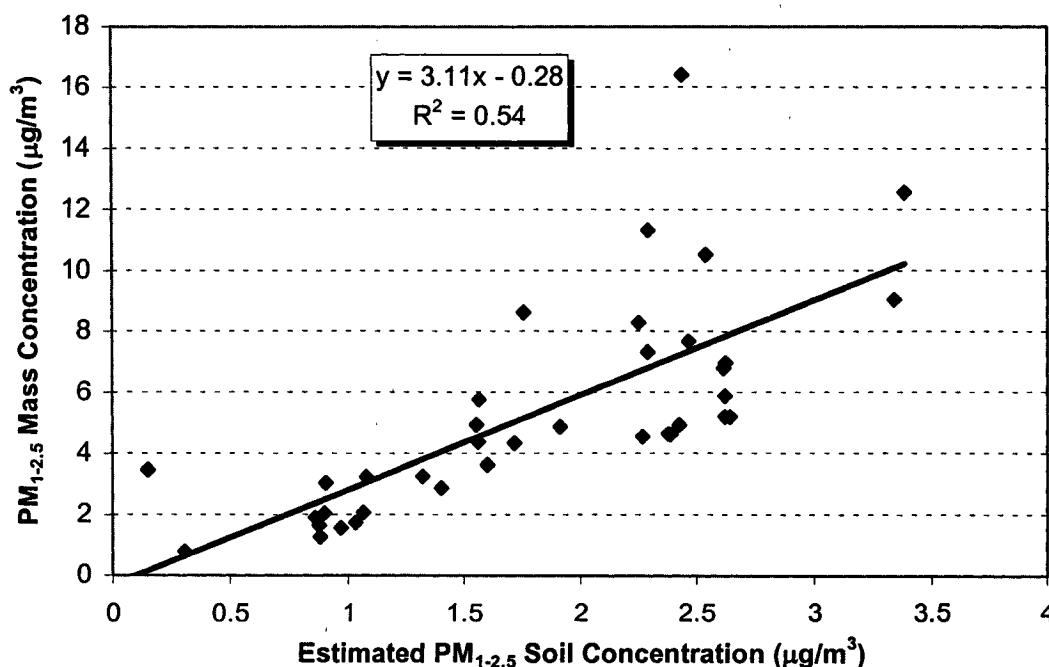


Figure 6.14. $PM_{1-2.5}$ Versus Estimated $PM_{1-2.5}$ Soil Concentration

Figure 6.15 displays the lack of correlation between the most prominent chemical species that comprise intermodal PM and the crustal metals found in that mode. While nitrate, sulfate and (at least in receptor sites) OC correlate well with one another, none correlate with the crustal component. While the crustal component of intermodal PM is moderately correlated with the intermodal mass (Figure 6.14) the majority of the mass, consisting of nitrate, sulfate, and OC, does not correlate with the crustal component and is chemically more similar to particles in the PM₁ range.

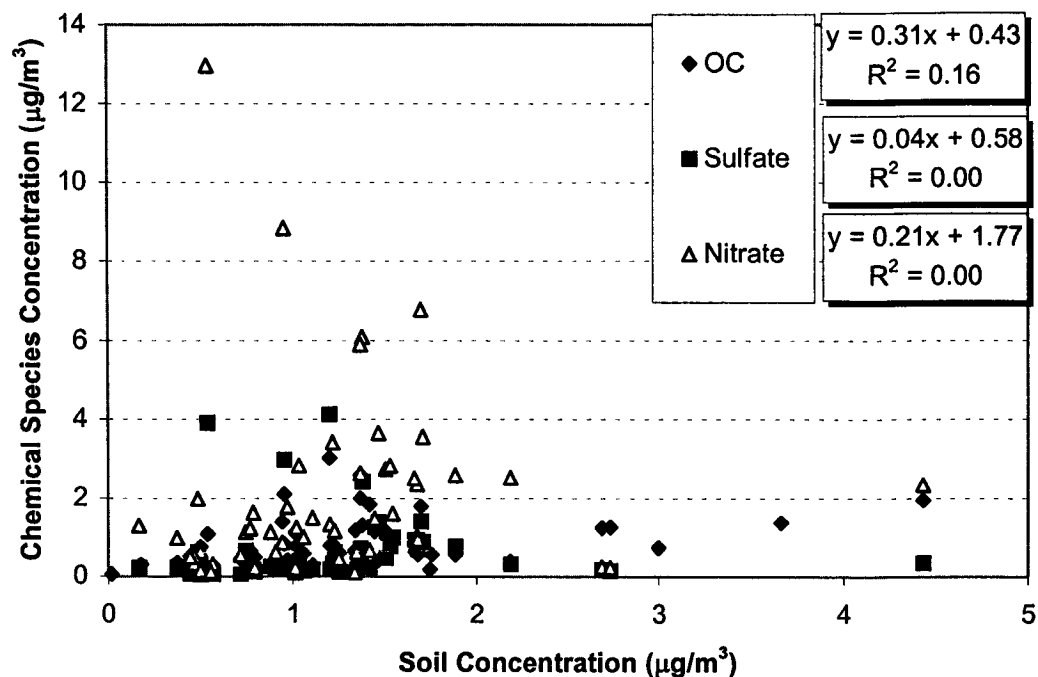


Figure 6.15. OC, Nitrate and Sulfate Concentrations Versus Soil Concentration in Intermodal PM

6.6 Summary and Conclusions

Although previous research does suggest a relationship between coarse mode and intermodal PM, the sites in which these studies were conducted are not representative of all locations. Similar data for coarse, intermodal, and fine PM were collected across four sites in the Los Angeles Basin. This study included a large database of time-integrated samples that spans nearly three years and complementary continuous measurements during intensive campaigns.

While some similarities exist between these results and those of comparable studies, the main finding established here is that intermodal PM consists of a significant portion of particles that are similar in chemical composition to smaller particles that are thought to cause the greatest health effects. In general, some fraction of intermodal PM originates from the lower-size range “tail” of the coarse PM size distribution. In Los Angeles, however, that correlation is not as strong as the one between PM_{10} and intermodal PM. Even the rural locations in this study demonstrated high correlations between PM_{10} and intermodal PM, which validates the strength of the $PM_{2.5}$ standard for locations that have both a crustal source and advected aerosol from an urban area upwind.

The receptor sites in this study showed a peak in the ratio between intermodal nitrate and fine nitrate in the early evening, which was three hours after the peak wind speed, indicating advection of particulate nitrate from upwind sources and growth into the intermodal size range. Overall, intermodal nitrate correlated very well with both PM_{10} and $PM_{2.5}$ nitrate, signifying its strong relationship to the fine

mode. Intermodal sulfate and nitrate demonstrated similar correlations and were also correlated with each other and OC in receptor sites. Intermodal crustal material did not correlate with any other chemical constituent.

This study was performed to shed light on the origin and chemical composition of intermodal particles between the coarse and fine PM modes in Los Angeles, a unique city where crustal, oceanic, anthropogenic primary, and secondary sources are responsible for the high observed PM levels. Our results indicate that a PM₁ standard would not constitute an unambiguous separation of coarse and fine mode PM in this urban air shed. Further studies at various locations are warranted, especially sites in areas of the eastern United States where air parcels are advected across much larger distances than those in Los Angeles, in order to determine the degree to which the promulgation of a PM₁ standard would be justifiable.

Acknowledgements

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Chapter 7

CONCLUSION

7.1 Summary

A study was conducted in the Coachella Valley in Southern California to determine the indoor penetration of coarse particles in a site heavily influenced by crustal sources during a time of maximum penetration indoors. The findings of this study were that outdoor coarse particles do not efficiently penetrate indoors, and thus indoor sources of these particles are more important for exposure assessment. Fine PM was found to dominate PM_{10} in indoor environments.

In order to study the relatively low ambient concentrations of coarse particles, a high volume coarse particle concentrator was developed and characterized. By concentrating the ambient coarse PM fraction, health researchers can conduct dose-response relationships, and aerosol scientists can measure these particles over shorter time intervals. The desired endpoint is reduction of measurement variability of this PM mode. The CPC can concentrate coarse PM levels in the 1-5 micrograms per cubic meter range, which can then be delivered to animal or human exposure chambers and/or collection devices.

While time-integrated samples have the advantage of yielding a sample with enough mass to perform many chemical and biological assays, they may mask the variations that occur over the course of the sample interval. Since this is especially true for coarse PM measurement, the Continuous Coarse Particle Monitor was developed.

This device measures real time coarse PM mass concentration by concentrating the coarse fraction of PM_{10} prior to delivery to a TEOM continuous mass monitor. This device has many relevant future applications in which the user must know the coarse concentration at a particular time, such as ambient monitoring and in vivo human exposure studies.

A PM_{10} inlet was developed in order to accurately separate particles larger than $10\ \mu m$ in aerodynamic diameter from the ambient aerosol prior to sampling with the CCPM. This was accomplished by modifying a currently available inlet for the flow rate requirement of the CCPM. The addition of this inlet to the CCPM greatly reduces the error incurred if no inlet is employed.

The coarse mode's intrusion into the fine PM mode was explored in Chapter 6. While coarse and intermodal PM did correlate with each other in some instances, intermodal PM correlated much better with total $PM_{2.5}$ and even PM_1 . If PM_1 is in fact a source of intermodal PM, then intermodal PM may be growing into coarse particles. This may explain some of the correlation that exists between these two size ranges. The main finding established here is that intermodal PM consists of a significant portion of particles that are similar in chemical composition to smaller particles that are thought to cause health effects. In general, some fraction of intermodal PM originates from the lower-size range "tail" of the coarse PM size distribution. In Los Angeles, however, that correlation is not as strong as the one between PM_1 and intermediate PM. Even the rural locations in this study demonstrated high correlations between PM_1 and intermodal PM, which validates the

strength of the $PM_{2.5}$ standard for locations that have both a crustal source and advected aerosol from an urban area upwind. Results indicate that a PM_1 standard would not constitute an unambiguous separation of coarse and fine mode PM in this urban air shed.

7.2 Conclusions

This thesis presented the idea that while the behavior of coarse particles has been studied for a very long time, the chemical composition and health effects of coarse particulate matter as a whole is variable depending upon time and location and must therefore be examined with different tools. The high degree of variability surrounding coarse PM results in increased uncertainty when trying to assess its health effects. Prior to this research, many have concluded that the coarse mode contains mostly benign materials due to its crustal component. The investigation presented here demonstrates that coarse PM found at certain locations in the Los Angeles Basin can contain significant amounts of nitrate, sulfate, and organic carbon, all of which have been attributed to health effects.

The aforementioned technologies aim at reducing the inconsistency in coarse PM measurements while increasing the body of knowledge surrounding this size mode of ambient particles. The coarse particle concentrator and continuous coarse monitor have already been employed in two “in vivo” health studies—one exposing animals and one exposing humans—and many in vitro assays. The preliminary results implicate coarse PM as a cause of adverse health effects in animals and humans.

The continuous coarse monitor has also been used to measure continuous coarse PM mass concentrations for intensive studies in the Los Angeles Basin and is now being considered for approval as an EPA reference method for monitoring this size range of particles.

7.3 Recommendations for Future Research

The studies that comprise this thesis demonstrate a small blueprint that can be expanded to a large-scale investigation. Obviously, some aspects of coarse particles are very well understood and need not be studied in further detail, such as physical characteristics and chemical composition at some locations. There is still insufficient evidence that resolves a person's exposure to coarse PM and describes the mechanism by which coarse particles harm humans. The only method of fixing these inadequacies is by performing many studies that target human exposure and health with respect to coarse PM.

Health effects researchers have already begun using particle concentrators in their studies, and the future will most likely see the role of concentrators increase in this research. Based on a coarse particle human exposure study of which I was a part, the delivery system and measurement of coarse particles are the two major components of the coarse particle concentration system that need improvement. Because coarse particles have very high losses due to impaction and settling, new particle delivery systems should consist of small, well-mixed chambers that can ideally fit over a subject's breathing zone (i.e. not full body exposures). Real-time

measurement instruments should sample from this well-mixed breathing zone chamber, which will yield the most accurate PM measurement.

The characterization of human exposure to coarse PM has been very difficult because studies usually utilize one of two sampling methods. In some cases an impactor or filter sampler is placed in a common area where the majority of the subject spends his time. While this allows for a larger sampler and thus higher flow rates, the sample is not representative of what the subject actually breathes because coarse particles are certainly not uniformly distributed in a room. The second method is a personal sampler that a subject wears and collects particles in his breathing zone. This sampler can only operate at low flows due to weight constraints of the pump that is worn by the subject. Low flow rates do not always isokinetically sample coarse particles. Thus, in both current exposure assessment methodologies, the accuracy can be questioned. Future research is necessary to correct this problem for it is a very difficult one to solve.

The use of continuous monitors for both exposure assessment and ambient monitoring will be the wave of the future. The change is already taking place, and the result has been an increase in the perception of coarse particle behavior and temporal variability. As these monitors become smaller, human exposure and health effect assessment will become simpler.

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