Sources, Composition, Variability and Toxicological Characteristics of Coarse (PM10-2.5) Particles in Southern California

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Study Objectives:

- The objective of this study is to provide the much-needed information on the relationships between coarse particulate matter (PM) sources, spatial and seasonal characteristics, and toxicity in Southern California.

- The proposed multidisciplinary research in exposure assessment and toxicology activities will be integrated with other major efforts currently under way in Southern California.

- These include :

  - the EPA-supported Southern California Particle Center (SCPC)

  - the Multi-Ethnic Study of Atherosclerosis Air Pollution (MESA Air)

The goals of the MESA Air are to prospectively examine the relation between long-term ambient air pollution exposures (including PM2.5 and gaseous co-pollutants) and the progression of subclinical cardiovascular disease in a multi-city, multi-ethnic cohort

Research Questions:

a. What are the spatial, daily and seasonal differences in coarse PM mass and chemical composition found in rural and in urban areas of the Los Angeles Basin?

b. How do the physico-chemical and toxicological characteristics of coarse PM measured near schools with minority populations compare to those of other urban and rural areas?

c. What is the fraction of chemically speciated PM that penetrates indoors in the above classrooms and how does indoor and outdoor coarse PM differ toxicologically?

d. How do the chemical characteristics of coarse PM collected in each of the above environments and over different seasons determine their toxicity?

e. How does coarse PM toxicity differ from that of fine and ultrafine PM, measured in studies undertaken by the PIs, and sponsored separately by the recently renewed SCPC?
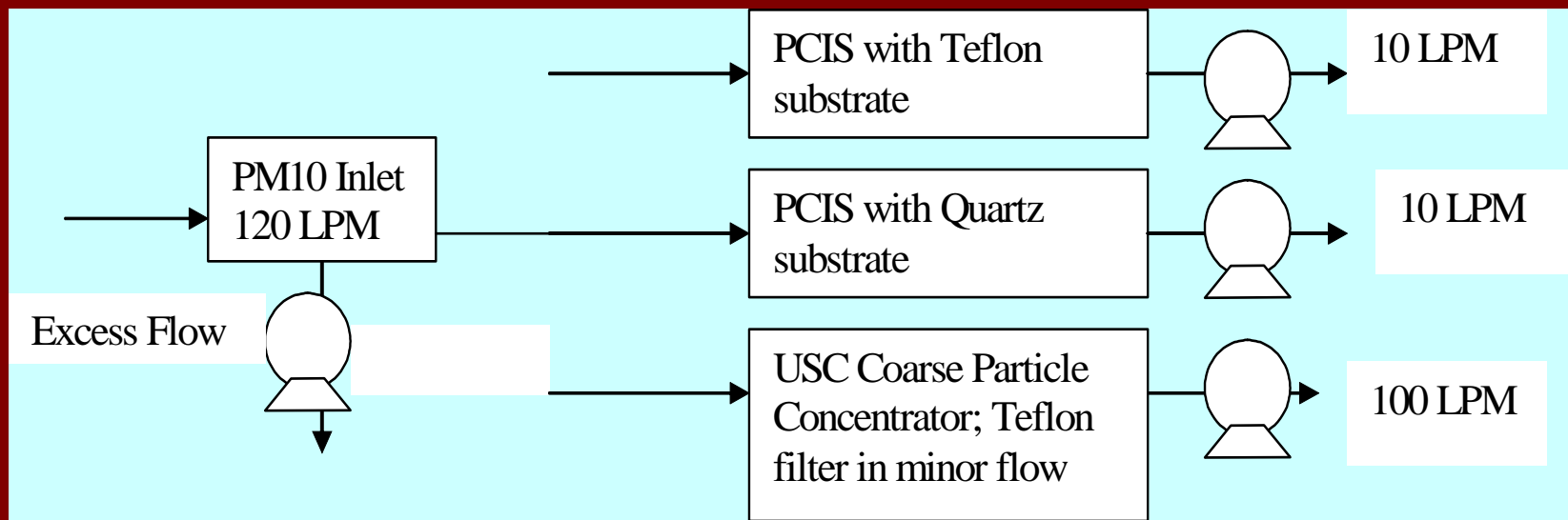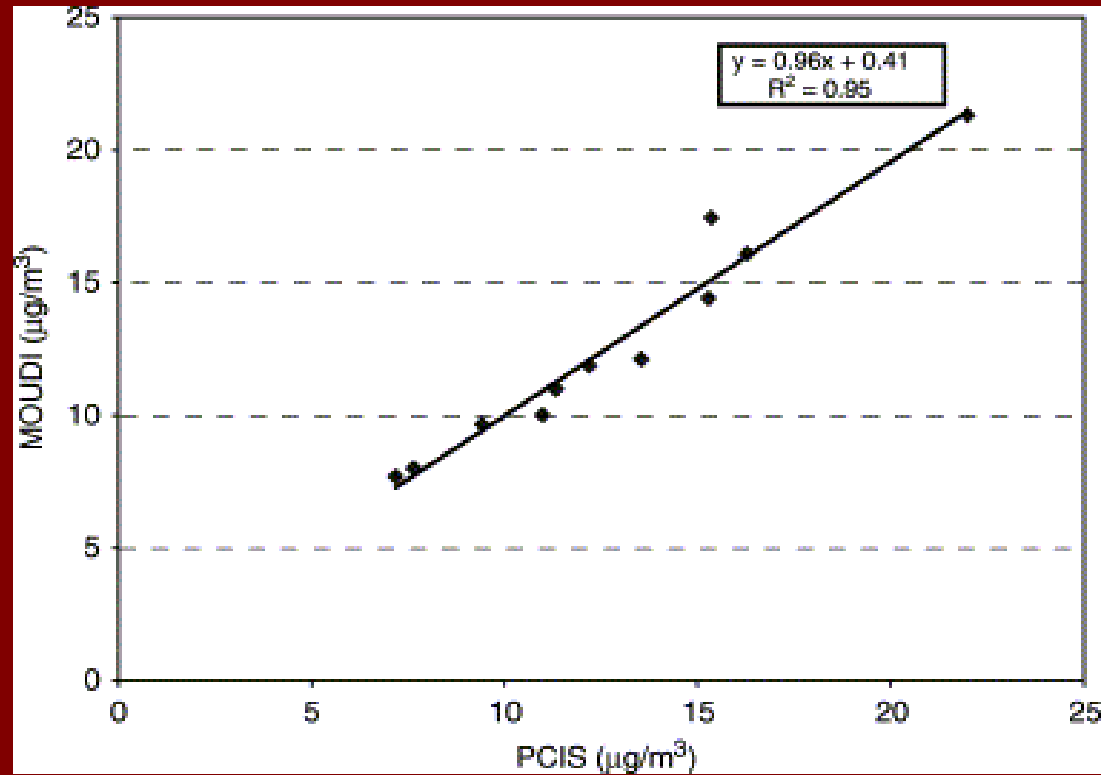
Sampling Sites

Sampling Site Details

	Site Name	Location	AQMD site	MESA site	Site Description	Other relevant site information
1	Downtown AQMD	Downtown LA	Yes	Yes	Central site	Typical urban site in downtown LA
2	Fremont School	Alhambra, central LA		Yes	Central site. Near Freeway	< 50 m downwind of I-10
3	St. Cecilia School	South Central LA		Yes	Central site	~ 500 m upwind of I-10
4	St Gerard School	West LA		Yes	Coastal urban site	~300 m upwind of I-405
5	LDS Church	West LA		Yes	Near Freeway	~ 100 m upwind of I-10
6	Granite Hill School	Riverside		Yes	Rural Receptor site- community	Semi-rural receptor site in the inland valleys of LAB
7	Van Buren AQMD	Rubidoux-Mira Loma	Yes	Yes	Rural Receptor Site- Near Freeway	Semi-rural receptor site ~ 150 m downwind of CA-60
8	Lancaster	Mojave Desert	Yes		Desert Site	Typical desert site away from traffic sources
9	Hollenbeck Middle School	Eastern LA			Inner City central site; near freeway	Site ~ 25 m from I-10. Mostly Hispanic student High School
10	Hudson Elementary School	Long Beach	Yes		Coastal urban site	Located in the Port of LA area; Mostly Hispanic student elementary school

Time Integrated Coarse PM Measurements

PCIS Schematic

Singh et al, Atmos. Env. 2003)

y = 0.96x + 0.41
R² = 0.95

MOUDI (µg/m³) vs PCIS (µg/m³)

	PCIS with Teflon substrate	10 LPM
PM10 Inlet 120 LPM	PCIS with Quartz substrate	10 LPM
Excess Flow	USC Coarse Particle Concentrator; Teflon filter in minor flow	100 LPM

Sampling Strategy:

- One of the PCIS will be used with Teflon substrates for measurement of mass, trace elements and inorganic ions

- The other PCIS will be used with quartz filters as impaction- collection substrates for measurement of EC-OC and speciated organics.

- A Teflon filter (47 mm, PTFE, 2μm pore) will be placed in the minor flow of the virtual impactor for coarse PM collections that will be used for redox activity and oxidative potential measurements in the *in vitro* studies described below.

- In each of 10 sites, we will collect one 24-hr set of sample per week for a period of approximately 18 months

- We will also conduct winter and summer intensive campaigns in 3 of our 10 sites. (6:00 a.m. to 10:00 a.m), midday (10:30 a.m. to 2:30 p.m), afternoon (3:00 p.m. to 7:00 p.m.), and overnight (7:30 p.m. to 5:30 a.m.).

- These will be the AQMD sites in downtown LA, in Rubidoux and in Lancaster. Each of them represents a distinctly different region of LA (urban, rural- receptor and desert, respectively

- We will collect a smaller number (~32) of indoor coarse PM samples in two locations inside the classrooms of the proposed schools in Long Beach and east LA.

Summary of Coarse PM measurements, number of samples to be collected, sampling frequency and expected mass (in mg) assuming average coarse PM concentrations of 10 µg/m3

Sample Type	Sampling duration (hrs)	No. of samples x no. of sites	Estimated no. of total samples	Total coarse PM mass per sample (in mg)
Outdoor mass and chemical speciation	24 hrs	50 x 10	~ 500	0.15
Indoor mass and chemical speciation	24 hrs	16 x 2	~ 32	0.15
Intensive study – mass and chemical speciation	4 hrs (12 hrs for overnight sample)	32 x 3	~ 96	0.20 - 0.60
Redox – (DTT, DHBA) Assays	Bi-monthly composites	9 x 10	~ 90	6.50
In Vitro assays – (Nel group) and organic speciation (Schauer group)	Seasonal (3- month) Composites	4 x 10	~ 40	8.62

Note; collected samples can be <u>shared with other investigators</u> for health studies

Continuous Coarse PM Measurements
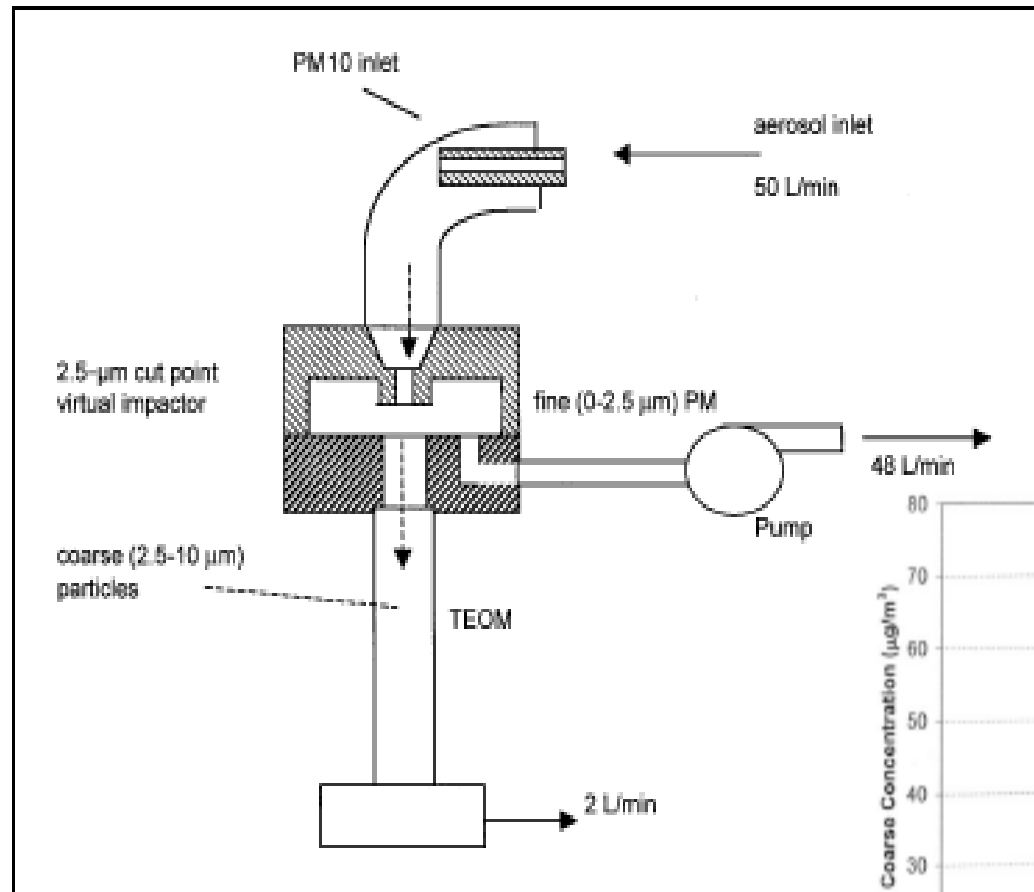
Continuous Coarse PM Monitor developed by our Supersite program
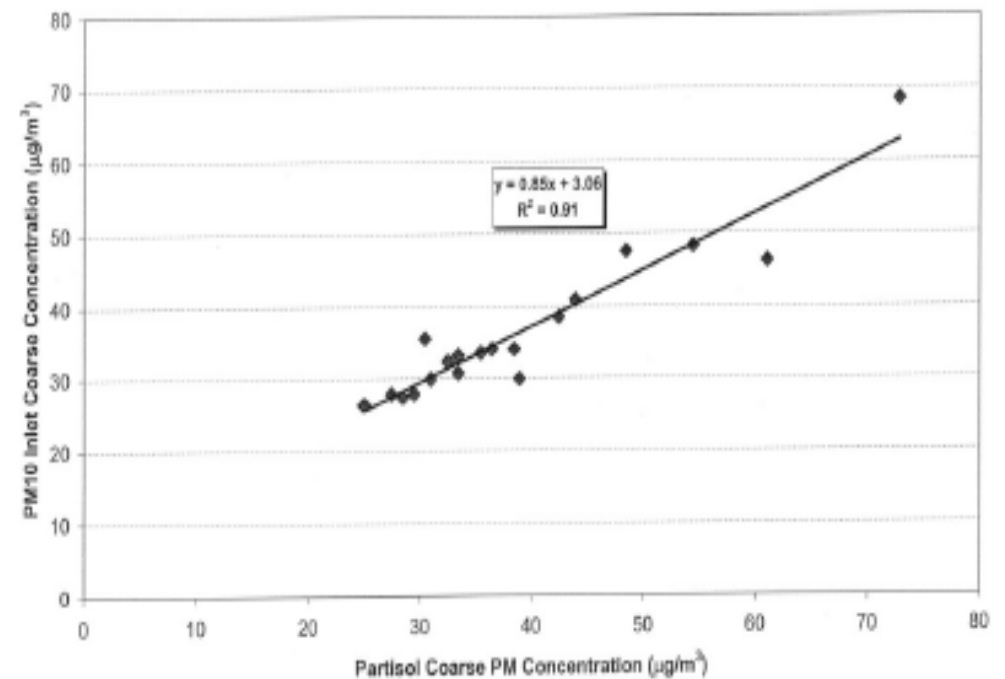
Misra et al JAWMA 2001

Figure 5. Coarse PM concentrations determined by the 50 l/min PM₁₀ inlet and the R&P Partisol.

Continuous Measurements:

• 3 AQMD sites where we will conduct intensive sampling campaigns (i.e., downtown LA, Lancaster, Rubidoux).

• Coarse PM concentrations will be obtained concurrently in all 3 sites for 18 months.

• Collocated measurements in these stations: hourly PM2.5, CO, NOx, O3 as well as meteorological parameters such as wind speed and direction, temperature and relative humidity

• The real time coarse PM mass concentrations will be analyzed for trends that correlate with time of day, day of week, wind direction, wind speed, and regulatory pollutants

• First step to identify the impact of specific sources, such as a point source (wind direction and criteria pollutants), mobile sources (time of day and day of week and criteria pollutants), resuspension of off-road soil.

• Correlation coefficients will be determined between coarse particle concentrations and the concentrations of gaseous precursors, PM2.5, wind speed and direction.

Continuous Data.

• We will also investigate whether an inverse correlation of coarse PM concentration and ambient relative humidity (RH) exists, with higher coarse PM concentrations during daytime corresponding to lower RH.

• This is of particular note in the Los Angeles Basin, since the period between April-June is characterized by regular occurrence of marine layers and associated low cloud and fog formations with high RH in the overnight and early morning hours.

• Finally, the chemical composition of very high coarse particle events will be examined to potentially identify large local sources of coarse PM.

• We will also evaluate the relationship between coarse PM and PM2.5 using the hourly data in each site to determine whether these PM ranges share common sources. A priori, we expect to find no correlation between coarse and fine PM.

Redox Assays :

Non- Cellular (Cho group):

• Dithiothreitol (DTT) assay.

• Ascorbate-salicylate based assay for metal based redox activity

Cellular stimulation (Nel group).

(a) Cellular stimulation- Cultured cells will be exposed to the coarse PM suspensions in the concentration range of 1-50 µg/ml for 6-16 hrs
(b) Measurement of the cellular GSH/GSSG ratio
(c) Assessment of Tier 1 oxidative stress Phase II enzyme expression will be assessed at protein level. Protein expression will be determined by immunoblotting, e.g. for heme oxygenase 1 (HO-1).
(d) Assessment of Tier 2 oxidative stress responses: Pro-inflammatory cytokines and chemokines (e.g. IL-8, IL-6, TNF-a, MCP-1, and IP-10) will be analyzed by ELISA.
(e) Assessment of Tier 3 oxidative stress responses: This will involve the assessment of mitochondrial function at the cellular level.

Cellular assays for mitochondrial perturbation and apoptosis will utilize our established flow cytometric procedures for dual-color annexin V/PI (apoptosis) and dual-color DiOC6(3)/hydroethidine staining (mitochondrial membrane potential and superoxide generation).

Data Analysis

Spatial and Temporal Variability

- Time series plots for each site,

- Descriptive statistics for each site and PM species.

- Calculate for each site the monthly and seasonal average, geometric mean and standard deviations of coarse PM mass and each of the chemical species measured.

- The frequency distributions for each of these parameters will be plotted to determine the skewness of their values and obtain a better estimate of the degree of variability between sites and seasons.

- The spatial variability of coarse PM mass and each chemical species measured will be determined by means of two methodologies.

  a. The arithmetic average of the Spearman correlation coefficients (r) between all of the site pairs for coarse PM mass, EC-OC and trace elements measured.

  b. The coefficients of divergence (COD).

The COD provides information on the degree of uniformity between sampling sites and is defined as:

$$\text{COD}_{fn} = \sqrt{\frac{1}{n} \sum_{i=1}^{n} \left(\frac{x_{if} - x_{ih}}{x_{if} + x_{ih}} \right)^2}$$

where x_{if} is the ith concentration measured at site f, f and h are two different sites, and n is the number of observations

Crustal Enrichment Factors (CEF)

The concentration of the element in a sample to its concentration in the Upper Continental Crust (UCC),

$EF = (EI_{sample}/X_{sample})/(EIU_{CC}/XU_{CC})$

where EI is the concentration of the element under consideration, both in the sample and in the UCC and X is a reference element

Aluminum (Al) will be chosen as a reference element because we expect its PM mass fraction to be the most insensitive to transitions across the range of urban measurement sites

Tiers of statistical analysis and data presentation to link coarse PM species and sources to biological outcomes:

• First, statistical analysis of the mass and chemical speciation data will describe the mean values of each chemical species characterized by location and season, and the general correlation structure (over all locations and seasons) of the chemical species.

• To evaluate the complexity and variability of sources in each of the proposed sampling sites, we will employ two different techniques:

- chemical mass balance (CMB)

- principal component analysis (PCA).

• Source profiles for CMB will be obtained from the SCPS source sampling efforts

• PCA methods will be applied to sub-classified sets of the data to address potential differences in the composition of resuspended soil or other sources across the sampling sites.   (*note that there will be about 500 samples*).

Data Analysis:

• Using CMB and PCA analysis, estimates of daily source specific coarse PM concentrations will be obtained.

• We will determine for each site (including the indoor locations) and season the average coarse PM toxicity measured by the various biological endpoints expressed on a *per coarse PM mass* basis.

• Incremental differences in toxicity across sites and seasons will be correlated with incremental differences in the chemical composition of coarse PM to identify specific species or sources that may dominate toxicity of coarse particulate matter.

• Multivariate regression techniques will be used to understand the relationship between sources and toxicity

• At a minimum, we expect that the following sources will have a substantial, albeit variable, contribution to coarse PM in each site: crustal (soil) material, traffic (road dust, brake lining, etc), oil combustion, sea salt, and growth of fine PM into coarse PM, as demonstrated previously by our SCPC

Project schedule (start date January- February 2008)

Task	Year 1				Year 2				Year 3			
	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Instrument set up	■											
Sample collection		■	■		■	■		■	■			
Intensive campaign				■			■					
In vitro tests			■	■	■	■	■	■	■	■		
Data Analysis					■	■	■	■	■	■	■	
Progress Reports				■		■			■			■
Manuscript preparation					■	■	■	■	■	■	■	■

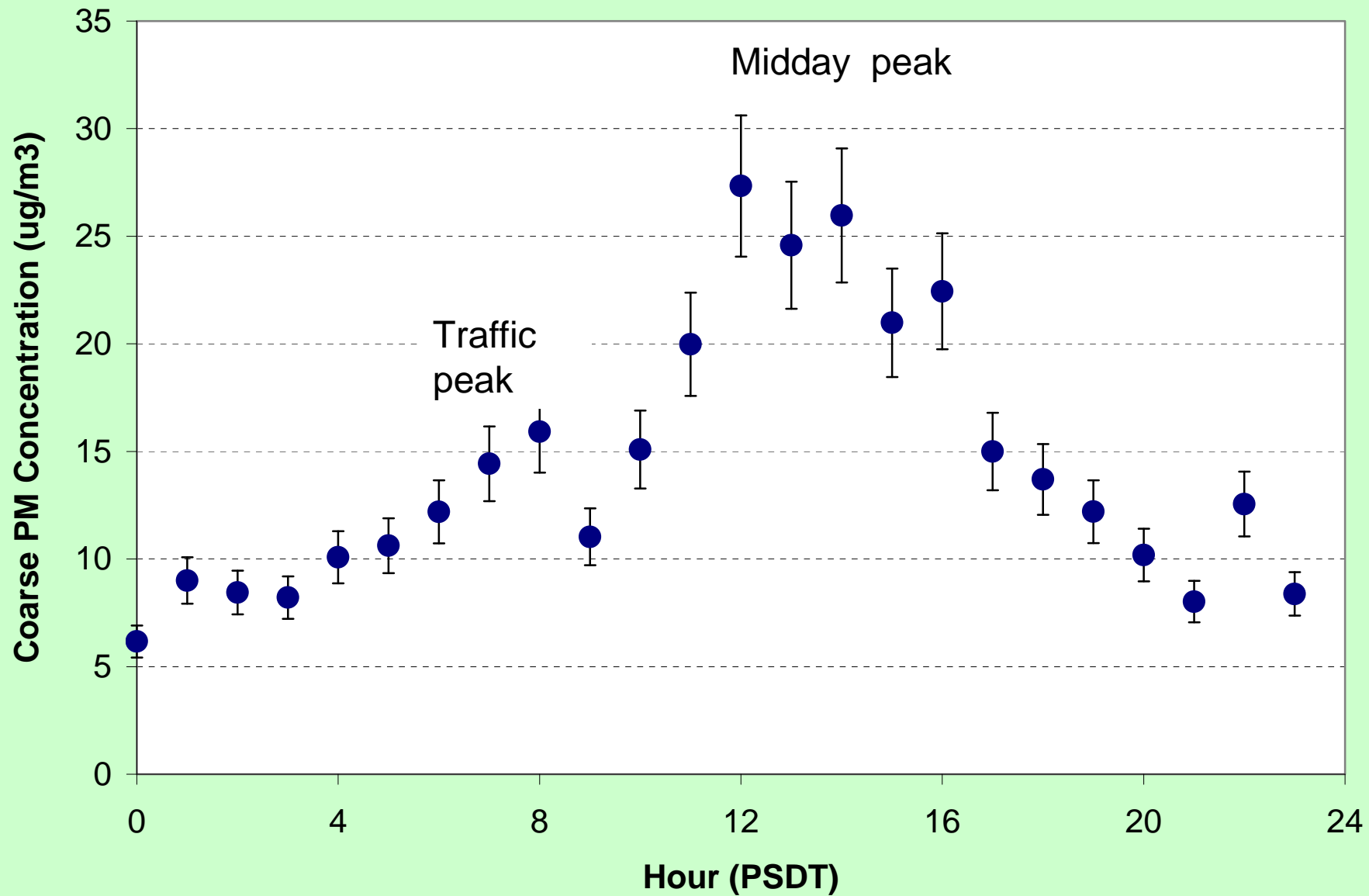# Characterization of our PM10 inlet; Collocated Field Tests with MOUDI
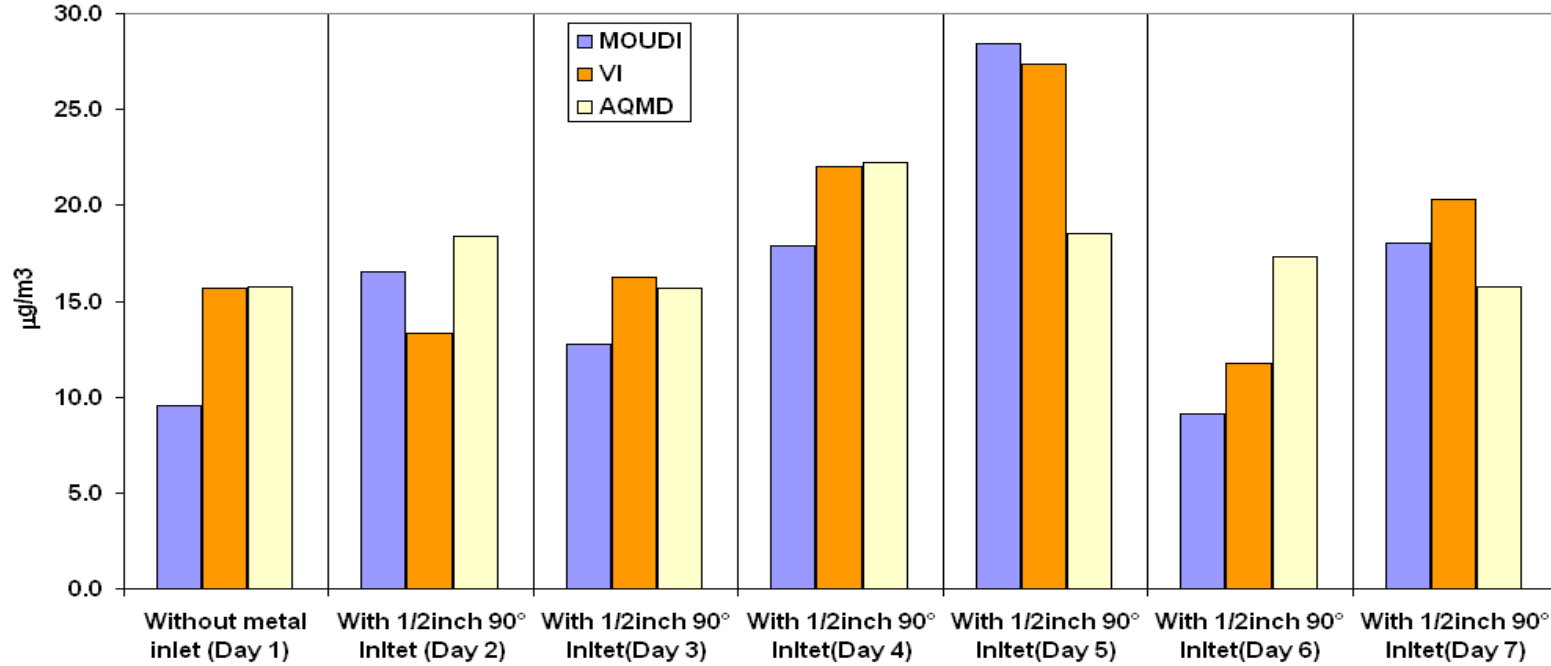
AQMD data are equal to the PM10-PM2.5 values at the nearest station
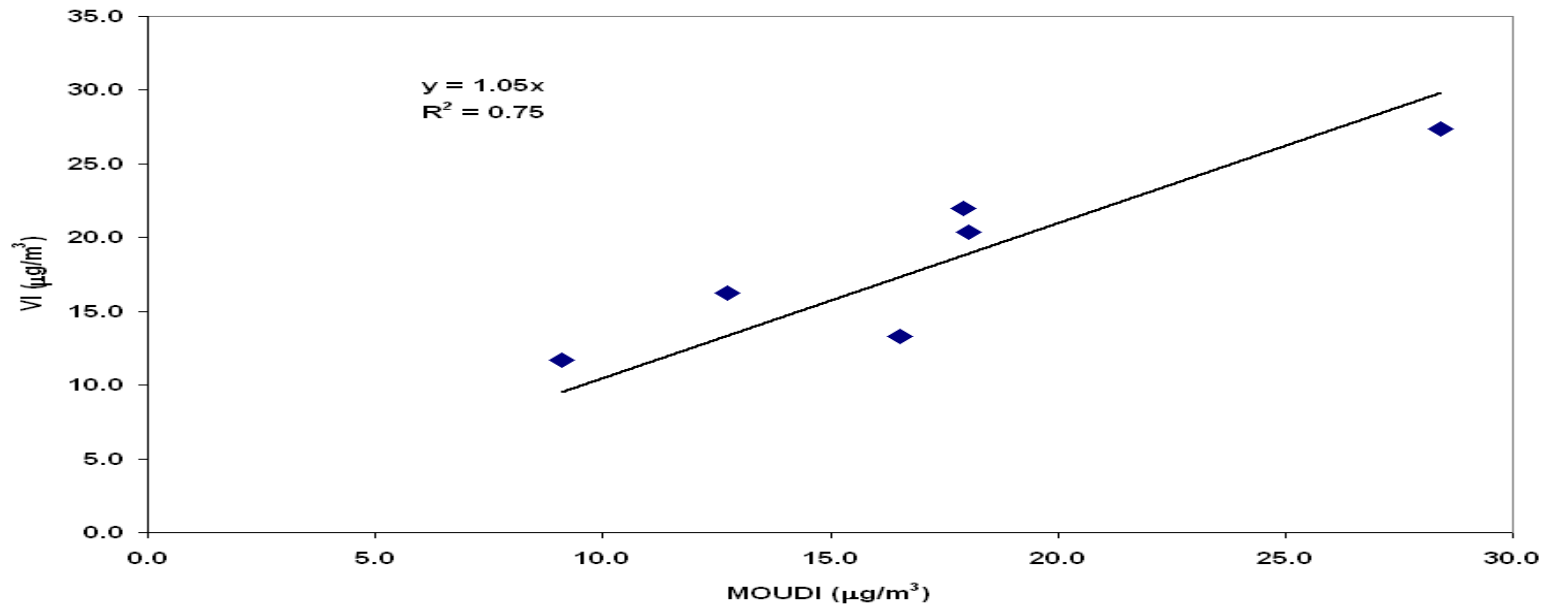
Evaluation of Collocated Coarse TEOMs
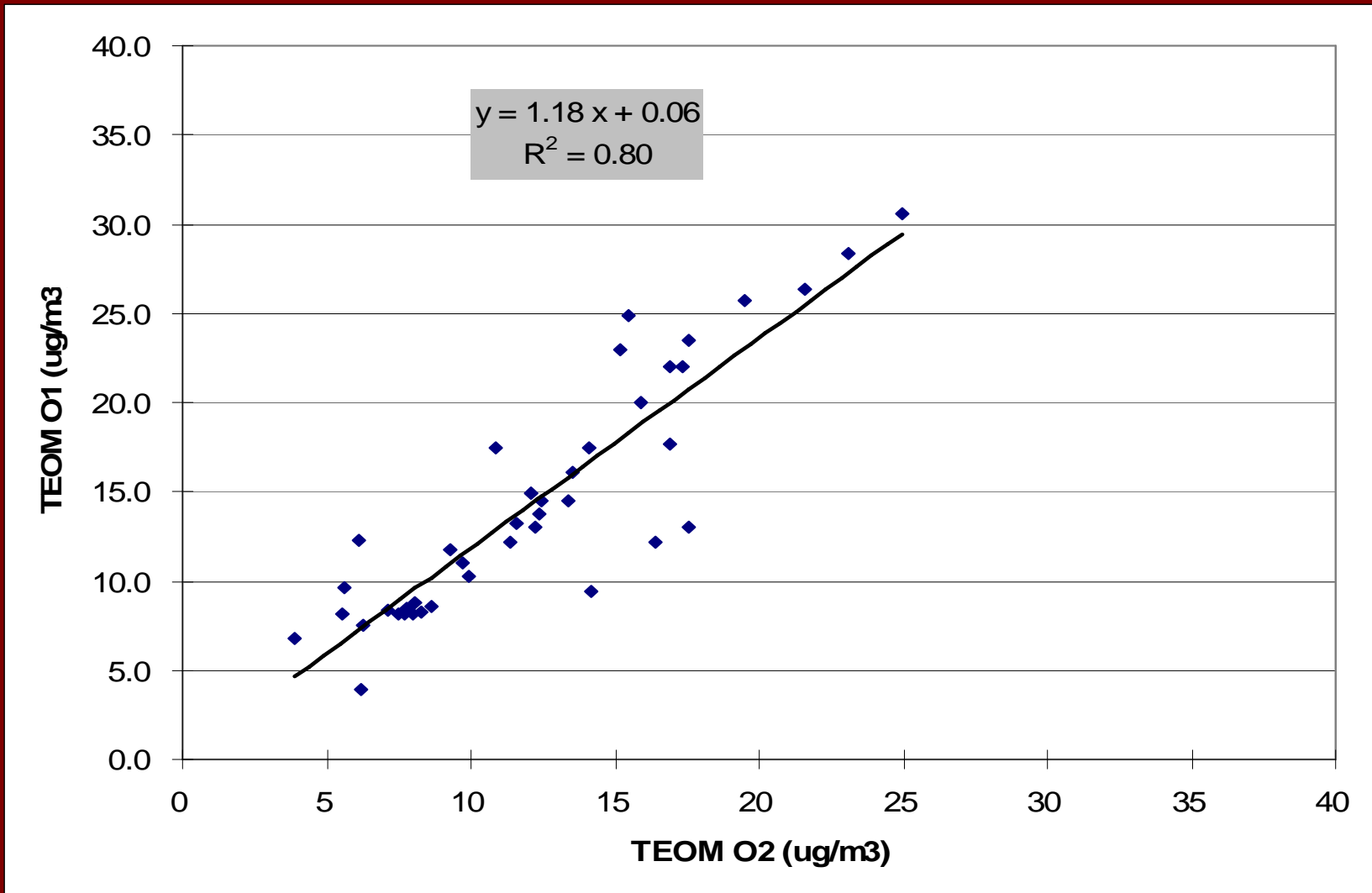
Diurnal Profile of Coarse PM at USC : April 7- 30, 2008

Current Activities:

- Secured all 10 sites , installed our PCIS and VIs

- Started sampling in mid April 2008 in all sites

- Installed 3 TEOMs in Lancaster, USC and Mira Loma in April 2008

- Ready for the summer indoor- outdoor school campaign; start some time in June 2008 – August 2008