

D.1. PROJECT DESCRIPTION: SOUTHERN CALIFORNIA PARTICULATE MATTER SUPERSITE (SCPMS)

D.1.1 Overall Objectives

The overall objective of the Southern California **Particulate** Matter Supersite (SCPMS) is to conduct monitoring and research that contributes to a better understanding of the measurement, sources, size distribution chemical composition and physical state, spatial and temporal variability and health effects of airborne particulate matter (PM) in the Los Angeles Basin (LAB). The SCPMS objectives are:

1. To integrate the activities of the SCPMS with the multidisciplinary research in exposure assessment, toxicology, and epidemiology of the EPA supported Southern California Center for Airborne Particulate Matter (SCCAPM) to investigate PM and to better ensure public health protection.
2. To interact with the California Air Resources Board (ARB) and the South Coast Air Quality Management District (AQMD) to maximize the use and value of the data collected by the SCPMS and the State and Local Agencies on PM.
3. To link the research and monitoring of the SCPMS, the SCCAPM, the State and local agency with research being conducted using a mobile PM concentrator facility to investigate health effects associated with exposure to ultrafine, fine and coarse particles.

D.1.2 Research Objectives

The research objectives of the Southern California Particulate Matter Supersite are:

1. To make detailed, state of the art measurements of the ambient concentrations of PM in the LAB and to describe the spatial and seasonal variations of the PM constituents in at least five discrete areas.
2. To study the “within” community variability through the use of satellite stations deployed in communities.
3. To characterize PM, its constituents and precursors, to better understand sources and transport affecting human exposure and to support development of State Implementation Plans (SIPs).
4. To assess the relevance of mobile source contributions to PM concentrations in the LAB and to link this information with health related studies being conducted in the context of the SCCAPM.
5. To obtain atmospheric measurements to support health studies designed to address causal factors, etiologic pathways and mechanisms of PM related morbidity and mortality with particular emphasis on PM source-receptor-exposure-effects pathways
6. To conduct methods testing that will enable comparisons and evaluation of different technologies for characterizing PM including evaluation of new instrumentation, sampling methods and federal reference methods.

D.1.3 Background

The LAB is home to more than 15 million individuals and it has been described as the most polluted airshed in the nation, with a complex, persistent and unique airborne particulate matter. Despite considerable improvements in air quality over the past two decades, Los Angeles continues to exhibit the most severe ozone and PM air quality problem in the U.S. The LAB covers approximately 12,000 square miles and this region has experienced faster population growth than the rest of the nation since

World War II. Growth is expected to increase significantly towards the end of the century and through 2020. The population is expected to increase 1.5 times by the year 2020 from 1990 levels (SQAAMD, 1998). By 2020 the south coast air basin is expected to have a population of 19,000,000 as compared to 4,800,000 in 1950.

The topography and climate of the LAB are some of the reasons for the areas having high air pollution potential. Light winds limit ventilation during the summer and the marine layer inhibits pollutants from dispersion. Afternoon sunlight and the persistence of fog and low clouds trigger both homogeneous and heterogeneous reactions forming secondary particles in the basin (SQAAMD, 1998). Dry hot summers are responsible for fugitive dust emissions. Offshore winds provide another source of PM during winter months in the basin.

PM is both directly and indirectly emitted from numerous emission sources in the basin. The SQAAMD reported 412 tons per day of PM₁₀ were emitted in the basin including 38 tons from mobile sources, 333 tons of fugitive dust from geological sources, and point sources accounted for 10%. The region has millions of motor vehicles, tens of thousands of factories, hundreds of thousands of business and millions of residences all putting primary particles and reactive gases that act as particle precursors into the atmosphere.

The LAB has also been the site of many air pollution studies. It has some of the nation's most extensive gas and particulate matter data. The majority of the air quality studies on PM in Los Angeles, however, have focused on generating time-integrated data on PM₁₀ or PM_{2.5} mass concentrations in different locations and over different seasons to determine compliance, without providing detailed information on the size and chemical composition of PM. Moreover, the time-integrated PM₁₀ and PM_{2.5} concentrations, measured by means of the Federal Register Methods (FRM), were very likely underestimated due to sampling errors. These artifacts are related to the loss of volatile constituents, such as ammonium nitrate and organics, during sampling (Solomon et al, 1988; Hering and Blumenthal, 1989; Lawson, 1990; Hering and Cass, 1999). The high fraction of these labile constituents in PM₁₀ and PM_{2.5} is one of the unique aspects of the LAB particulate matter. A limited number of studies, such as the Southern California Air Quality Study (SCAQS), produced size-resolved chemical composition data of PM₁₀. Nevertheless, these studies were intensive, short in duration, e.g., less than a month, and over specific seasons, normally associated with anticipated pollution episodes.

Saxena and Cass (1998) have proposed a conceptual theme for a program of atmospheric measurements designed to support determination of source/receptor relationships and they argue the purpose of such an effort would include construction of data sets confirm source-oriented air quality models are working appropriately. They cite the Southern California Air Quality Study as an example of a starting point for developing the atmospheric measurements. These authors suggest that Los Angeles should be studied as a region by itself because it "epitomizes a noticeable and yet distinct fine particle air quality problem in terms of particle composition, source mix, and meteorology." The PM in Southern California is characterized by nitrate and carbon with a much smaller contribution from sulfate in contrast to the eastern seaboard. Southern California is therefore a unique environment in terms of the problem of PM, the potential health issues that may arise from continued population growth, and the opportunity to make use of existing data sources collected from earlier studies and anticipated by the EPA PM Center and local air district activities. These factors represent important considerations for Supersite location and they indicate that southern California is a particularly important environment and opportunity for additional study.

Additional activities in southern California relevant to the siting of a Supersite in this region include:

- The Southern California Center for Airborne Particulate Matter (SCCAPM)
- The Southern California Center for Children's Environmental Health and Disease Prevention
- The Southern California Environmental Health Sciences Center (SCCEHS)
- The Mobile Concentrator Exposure Facility (MCEF)
- The Children's Health Study (University of Southern California)

A more detailed description of these studies as well as their interaction with the proposed SCPMS is given in Section 5 (Collaborations) of this proposal. The SCCAPM and the MCEF programs will supply virtually all of the instrumentation that will be used to support the monitoring activities of the SCPMS. Given the budgetary constraints associated with the number of projects and investigators participating in both the SCCAPM and MCEF, the PM monitoring activities of these programs are limited in scope and depth. A central objective of the SCPMS is to provide PM data whose quality, depth and detail will go beyond the resources of each individual program listed above.

D.2 APPROACH

The SCPMS projects described in this section will follow the three major objectives detailed by U.S. EPA in the Supersite RFP. The instrumentation and timetable for sampling for the SCPMS is listed in section D.2.4. Acronyms for the instrumentation are listed. The reader may want to review that section before proceeding with the specific research and monitoring projects.

D.2.1 Characterization of PM: to obtain atmospheric measurements to characterize PM, its constituents, precursors, co-pollutants, atmospheric transport and source categories that affect PM in the LAB

Specific objectives

1. To comprehensively characterize Particulate Matter in the LAB and obtain correlations between particle size distribution, chemical composition and gaseous co-pollutants.
2. To determine the occurrence, frequency and prevalence of PM_{2.5} sub-modes in different locations of the LAB.
3. To systematically evaluate sampling artifacts of the Federal Register Method (FRM) in measuring PM_{2.5}, PM₁₀ and Coarse PM concentrations.
4. To determine the seasonal and spatial variation of Ultrafine, Accumulation and Coarse PM in the LAB and their relation to sources. These studies will be conducted in collaboration with AQMD and ARB.

Site selection for the projects defined here is described in Section D.3 below. Instrumentation for PM characterization is described in Section D.2.4 below. All instruments for particulate and gaseous pollutant measurement will be placed inside a mobile Particle Instrumentation Unit (PIU), which is also described in section D.2.4

D.2.1.1 Comprehensive Characterization of Particulate Matter in LAB: Correlations between Particle Size Distribution, Chemical Composition and Gaseous Pollutants

Research projects proposed in this section will aim at characterizing PM and its precursors and will provide the information that is needed to understand the relationship between PM sources and

receptors, as well as providing insight into the factors that affect the spatial and temporal variability of PM characteristics. The relationships between PM components, including their gaseous precursors, are important for the apportionment of PM sources, which permits the development of effective control strategies. The SCPMS measurements will provide a comprehensive database for the PM₁₀ State Implementation Plan (SIP) and for the Air Quality Management Plan (AQMP).

We propose to conduct a series of statistical modeling studies using the Supersite particle and gas data to relate aerosol composition and particle size characteristics to possible sources. The data generated by the Supersite and affiliated facilities will also be used for regional dispersion and exposure modeling studies, which are conducted independently by the SCCAPM. These studies will use the data generated through the Supersite to develop and calibrate advanced computational tools in order to link sources of particulate matter with individual and collective regional exposure, and support the development of comprehensive models that simulate the microphysical and chemical processes that affect the evolution of aerosol properties.

In each intensive SCPMS sampling location, the continuous data generated will first be integrated into the following periods: a) three 4-hour sampling periods during the day, beginning at 6:00 am, and; b) one 12-hour overnight period.

The size-segregated PM volume, nitrate, sulfate and elemental carbon (EC) concentrations measured by the Continuous Nitrate, Sulfate and Carbon Monitor (CNSCM, [Aerosol Dynamics Inc.](#)) and by the Micro-Orifice Uniform Deposit Impactor (MOUDI, [Marple et al, 1991](#)) (every 6th day) will be grouped into the following size ranges:

- 0.01-0.15 μm (ultrafine particles)
- 0.15-0.4 μm (accumulation mode, “condensation” sub-mode)
- 0.4-1.0 μm (accumulation mode, “droplet” sub-mode)
- 1.0-2.5 μm (“intermediate” mode)
- 2.5-10 μm (coarse particles)

These are the same size classifications used by John et al (1990) during the Southern California Air Quality Study (SCAQS) of 1987. For each Supersite sampling location, Pearson correlation coefficients will be determined between particle concentrations of selected particle size groups and chemical composition, and the concentrations of gaseous precursors. These correlations seek to elucidate the relationship between PM and its precursors. T-tests will be conducted to test the null hypothesis (H_0) that there is no linear relationship between any two data sets. Over the 5-year period, more than 1200 field data sets will be generated. This number yields a critical correlation coefficient value at the 99% level of significance of about 0.25 ([Fuller 1987](#)). Of particular focus will be significant correlations between the following parameters:

1. Particle concentrations of any size or chemical composition sub-group and the concentrations of NO_x and CO, which would indicate that a significant source of that specific sub-range is automotive emissions.
2. Correlation between nitrate concentrations in any of the five PM₁₀ sub-groups and concentrations of ammonia or NO_x will provide insight into whether ammonia or nitric acid is the limiting species in the formation of ammonium nitrate. It is generally believed that there is no ammonia limitation ([Chow et al, 1997](#)) in the LAB, hence nitrogen oxides are the limiting species for the production of ammonium nitrate.

3. We will evaluate the relationship between the number concentration of 0.01-0.15 μm particles and the mass, sulfate, nitrate or carbon concentrations of the 5 different PM_{10} sub-groups at a given SCPMS location. A positive correlation (i.e. subgroup concentration increases with ultrafine number concentration) will indicate common sources. A lack of correlation will indicate that ultrafine PM has entirely different sources, whereas a negative correlation between the number concentration of ultrafine PM and the rest of the sub-groups may indicate that these particles grow out of ultrafine PM.
4. We will study the relationship between ozone, NO_x and gas-phase VOC concentrations with nitrate and mass concentrations of the different PM sub-groups. Ozone and PM are chemically coupled through a series of atmospheric reactions (Meng et al, 1997) and control strategies will have to account for this intricate coupling. By modeling gas-particle chemical interactions, Meng and Seinfeld (1997) showed that in general control of gas-phase organics and NO_x does not necessarily lead to proportionate reductions of PM. We will perform multiple regressions between the nitrate and mass concentrations and those of ozone and VOC concentrations in order to investigate whether, and to what extent, reductions in either VOC or ozone concentrations are associated with reductions in coarse and fine PM. These results will also be compared to the models derived by Meng and Seinfeld (1997). They will provide insight into the effectiveness of reducing PM concentrations by controlling emissions of various gaseous pollutants.
5. We will evaluate interactions of mass and nitrate, sulfate or EC concentrations of the different sub-groups will indicate whether these groups have common sources. *A priori* we expect to find no correlation between coarse and fine PM and coarse and ultrafine PM. However, the relationship between ultrafine PM and particles in the “condensation” and “droplet” sub-modes in the LAB has not been previously investigated and will be evaluated in this study.

D.2.1.2 Studies of the Occurrence, Frequency and Prevalence of $\text{PM}_{2.5}$ Sub-modes in PM Formation and Growth Mechanisms in Different Locations of the LAB.

Several studies over the past 10 years in Southern California (Hering and Friedlander, 1982; John et al, 1990) have indicated that the accumulation mode may consist of two sub-modes, one peaking at around 0.25-0.3 μm and the other at about 0.6-0.7 μm . The first mode is created by gas-to-particle conversion, whereas the second mode results from growth of hygroscopic sulfate and nitrates. These preliminary studies suggest that $\text{PM}_{2.5}$ in the LAB does not follow the classic Whitby distribution of a single accumulation mode (Whitby and Svendrup, 1980).

The occurrence, frequency and prevalence of these modes as well as their chemical composition have been based on a rather limited number of field tests. The Supersite program offers an opportunity to expand on these studies to improve our understanding on particle formation mechanisms in the LAB and their dependence on climatological parameters and geographical conditions within the LAB.

The size-fractionated data generated daily in each SCPMS location will be integrated into the following periods: a) three 4-hour sampling periods during the day, beginning at 6:00 AM, and b) one 12-hour overnight period (6 PM -6 AM). In addition to these data, the mass, sulfate, nitrate, EC and OC concentrations will also be grouped in similar time periods. Two MOUDIs will be used in Year 1, one for mass and inorganic ions, and one for the EC/OC concentrations. The size-fractionated PM inorganic ion concentrations for Years 2-5 will be determined using the CNSCM. Based on the above sampling scheme, about 1200 mass, nitrate, sulfate and carbon size distributions and about 240 EC/OC

MOUDI size distributions will be generated in each sampling location. The measured size distributions for each species will be fitted by means of a modified Twomey non-linear iterative algorithm (Dzubay and Hassan, 1990). John et al (1990) gives details of this algorithm. Each size distribution mode is fitted by a lognormal distribution by least squares. The fitting program begins with the largest mode and adds other modes in decreasing order, stopping when any remaining mode contains less than 5% of the total mass. Each mode for each chemical species is then characterized by the following parameters: mode diameter, geometric standard deviation and concentration. For each PM species and each sampling location, the relative mode concentration will be plotted as a function of mode diameter. We will thus determine whether the points cluster into discrete modes or whether the data are scattered over the entire size diameter range.

In each SCPMS location, we will determine how the prevalence, concentration and composition of the observed sub-modes depend on RH, temperature, season and time of the day. The relative fractions of bimodal and tri-modal size distributions will be determined. The percent chemical composition of its mode in terms of its nitrate, sulfate, EC and OC contents will also be determined and plotted. We expect the droplet mode to be dominated by nitrate contributions whereas the condensation mode by organic and elemental carbon. Sulfate and nitrate concentrations in coastal areas are expected to have a more pronounced coarse mode due to increased RH. Coarse nitrate could also be produced by the reactions on coarse sea salt particles, producing sodium nitrate. To test this hypothesis further, we will correlate the sulfate and nitrate concentrations of the coarse mode sodium concentrations measured in all of the five SCPMS locations over the 5-year period.

D.2.1.3 Evaluation of Sampling Artifacts of the FRM in Measuring the True PM_{2.5}, PM₁₀ and Coarse (2.5-10 μm) Concentrations

The research hypothesis to be tested here is whether the true 24-hour average PM_{2.5}, PM₁₀ and Coarse (2.5-10 μm) concentrations and those determined gravimetrically with a FRM are the same. In each intensive sampling site, the 24-hour average true actual mass concentrations for PM₁₀, PM_{2.5} and coarse particles will be compared to those obtained with the FRM to determine how the differences depend on season, temperature, relative humidity, PM mass concentration and chemical composition.

We will estimate the sampling bias of the FRM for both nitrate and organic carbon. This will be expressed as the percentage of the sampling error for different locations and seasons as a function of parameters such as temperature, RH, particle mass concentration, sampling duration, and Total Particle Surface (TPS) area. TPS will be determined from 24-hour averaged data from the SMPS and the APS by converting the number-based particle concentrations to surface concentrations. The experimentally determined artifact data will be compared to the theoretical models of evaporative losses of adsorbed and absorbed species, developed by Pankow and Bidleman (1992) and Zhang and McMurry (1991) and will thus provide an opportunity to validate these models.

Previous theoretical studies have shown that enrichment in the concentration of the particulate phase of a compound partitioned in both particulate and gas phases may result in a substantial reduction of evaporative losses. In our recent evaluation of the concentrator at Rancho Los Amigos, we found that losses of ammonium nitrate from impactor and filter samplers can be virtually eliminated when these devices sample concentrated as opposed to ambient aerosols (Chang et al, 1999, Atmos. Environ. *in press*). Results from this study are summarized in Appendices 1 and 2.

Elimination of losses of ammonium nitrate from filter and impactor substrates using fine particle concentrators is possible only because the majority of ammonium nitrate is typically associated with 0.15-2.5 μm particles (Wang and John, 1988; Chang et al, 1999). Nevertheless, other volatile and semi-volatile constituents of ambient PM, including PAH, PCB and other organic compounds, are known to have a considerable mass fraction in the ultrafine mode. We will use our recently developed fine plus ultrafine concentrators described in detail by Sioutas et al (1999) and Kim et al (1999), and expand these studies to include semi-volatile organic compounds which are assumed to be associated mostly with ultrafine PM. We will test the hypothesis of whether the use of these concentrators can actually eliminate sampling errors from filter and impactor samplers. Teflon filter and MOUDI will be placed downstream of the fine plus ultrafine particle concentrator to sample concentrated $\text{PM}_{2.5}$ including the ultrafine fraction. The nitrate, OC and selected PAH concentrations measured by these samplers will then be compared to the artifact-free nitrate concentrations determined using the Honeycomb Denuder Sampler (HDS) and the artifact-free OC and selected PAH concentrations measured by the Multi-channel Denuder Sampler (MDS, Eatough et al., 1993).

D.2.1.4 Measurement of the Spatial and Seasonal Variation of Ultrafine, Accumulation and Coarse PM in the LAB and their Relation to Sources

The purpose of this research is to determine whether coarse, accumulation and ultrafine particle concentrations are affected mainly by local sources rather than having a uniform spatial distribution. Data obtained in the eastern coast of the US have indicated that particles of the accumulation mode are homogeneously distributed in urban areas (Spengler and Thurston, 1983; Sexton et al, 1984). This may not be the case in the LAB. The majority of epidemiological studies have been based on associations between health effects and mass concentrations.

As part of this research, the correlation between ultrafine number concentrations, coarse mass concentrations, PM_{10} and $\text{PM}_{2.5}$ mass concentrations in each location and within intensive and boundary locations will be determined. This information is very important in determining whether the observed epidemiological associations can be attributed to ultrafine or coarse particles.

Starting in late summer of 1999, the ARB 12 Condensation Particle Counters (TSI CPC, 3022) in each of the USC Children's Health Study sites (see collaborations). These sites include Long Beach, Fontana, Lake Elsinore, Upland, and Rubidoux Mira Loma, Glendora and the University of California Riverside campus (Figure 1).

The 24-hour averaged ultrafine number concentrations measured in each site will be correlated to those concurrently measured in the USC Children's Health Study sites. Of particular note will be the degree of correlation obtained between ultrafine counts in sites relatively close to each other that will confirm that importance of local sources on ultrafine PM concentrations. Multiple regression will be performed between the 24-hour average number concentrations and distance from sampling site to a freeway. We anticipate that a strong negative correlation exists between ultrafine PM concentrations and distance to freeways. The 24-hour average coarse PM concentrations will be compared to all of the existing monitoring sites operated by AQMD, shown in Figure 1. Linear regression and correlation between the coarse mass sulfate and nitrate and those of the four AQMD speciation sites will be made. The degree of correlation will be also examined as a function of distance between two sites to determine the effect (if any) of local sources. Linear regression and correlations will also be made between the 24-hour average PM_{10} and $\text{PM}_{2.5}$ mass, sulfate and nitrate concentrations measured by the FRMs of a

given Supersite location and those measured in the four AQMD speciation sites. Analysis of the relationship between the coarse mass sulfate and nitrate and those of the four SCAQMD speciation sites will be made. The correlation will be also examined as a function of distance between two sites to determine the effect of local sources. The studies outlined below will be conducted in collaboration with the AQMD and the ARB.

D.2.2 Support of Health Effects and Exposure Research

Specific objectives

1. To provide detailed physico-chemical characterization of concentrated PM used in ongoing toxicity studies currently under way in the LAB.
2. To provide within-community particle data for improved dispersion models describing personal exposure indices based on traffic-based emissions for use in ongoing epidemiological investigations of chronic respiratory health effects of ambient particle matter in children.
3. To measure the size distribution as well as the spatial and seasonal variation of particle bound PAH, oxy-PAH, nitro-PAH, quinones and other polar PAHs in the LAB.
4. To characterize PAH Derivatives in Ultrafine and Accumulation Mode at a Source Site Impacted by Vehicle Emissions and a Downwind Receptor Site
5. To determine the contribution of volatile and semi-volatile species to Total Suspended PM_{2.5} mass and assess any resulting bias in interpreting epidemiological results.
6. To provide data on aerosol oxidant partitioning in the ultrafine, accumulation and coarse PM modes.

D.2.2.1 Physico-chemical characterization of concentrated PM used in ongoing toxicity studies currently under way in the LAB.

The research objectives of this Supersite category will be targeted atmospheric monitoring to address specific hypothesis-driven studies developed by the SCCAPM. These studies will make use of the MCEF, which will be transported to the SCPMS intensive sites. Exposures to animals or human subjects will be conducted to concentrated ultrafine, fine and coarse PM while detailed physico-chemical characterization of the ambient and concentrated aerosols will be conducted. Human and animal inhalation exposure studies using the MCEF will focus on identifying relationships between health outcomes observed in human and/or animals and the concentrations of the above species. Of particular note will also be PM components such as PAH and redox-active quinones in PM (see below) and their effects on allergic inflammation as well as the reactive oxidant content of coarse, accumulation and ultrafine PM.

The health studies currently under way in LAB will examine the following toxicological and physiological mechanisms that have been proposed to explain the epidemiological associations (Mauderly et al, 1998, Lippmann, 1992; McClellan and Henderson, 1995; NRC, 1998; Samet and Spengler, 1991; Phalen and Lee, 1998; Phalen and McClellan, 1995; Wolff, 1996):

- PM mass concentration
- Particle size and surface area
- Ultrafine PM
- Organic compounds
- Metals
- Allergens and other biogenic particles
- Acids
- Peroxides
- Nitrate and sulfate salts
- Soot

An important theme of the SCPMS is the role of mobile sources in the health effects associated with particulate matter. This emphasis derives from ongoing toxicologic and epidemiologic studies currently underway in southern California, the significant contribution of particulate from mobile sources in the LAB, and the public health concerns for exposure to diesel emissions in the State. Research that addresses the role of ultrafine PM is particularly important. Active research currently underway at UCLA (Nel et al, 1998) indicating exposure to PAHs and diesel particulate has an important role in the enhancement of asthma emphasizes the importance of this theme.

A central component of this Supersite will be near real-time measurement of particle size distribution that will cover the size range from approximately 0.006 to 20 μm at the 5 selected sites. A complete size distribution will be obtained every 15 minutes. This activity will provide essential data for the hypothesis that particles depositing in the lung airways or alveolar region trigger or exacerbate asthma attacks. The near real-time measurements are necessary because peak concentrations are believed to play a role in asthma episodes as well as in the morbidity and mortality associated with PM_{10} . Data will be analyzed to yield a consistent size distribution over the entire size range. From these results a wide range of particle size-selective metrics will be calculated, including PM_{10} , $\text{PM}_{2.5}$, $\text{PM}_{1.0}$, inhalable fraction, thoracic fraction, respirable fraction. This information will be used for initial dosimetry modeling by application of the ICRP LUDEP 1.1 code to calculate the deposition in five regions of the respiratory tract. The system will thus provide an estimate of number, surface area, and mass deposition in each region of the respiratory system for adults and children every ten minutes.

D.2.2.2 Understanding Within-Community PM Variability to Link Neighborhood-Scale PM Data to Personal Health Exposure Responses

Recent investigations of the respiratory health of Southern California school children have established that small but measurable differences in lung function performance are observable across several communities characterized by differing levels of gaseous and particulate air pollution (Peters et al, 1999). Careful examination of the annual lung function growth rates among these children has demonstrated that children living in communities with higher levels of particles and traffic-related emissions have lower rates of lung function growth (Gauderman et al, submitted manuscript, 1999). However, the relative importance of particles *per se*, or of some characteristic of particles (such as mass concentration, number count, chemical speciation, or physical size, in relation to health outcomes has been difficult to specify, in a variety of health investigations (Peters et al, Six Cities, AHSMOG, CORD). Furthermore, local variation of particle concentrations within a given community is poorly understood, making it difficult to link exposure with health. Information about the within-community PM variability would enable researchers to build and validate improved dispersion models to describe personal exposure indices based on traffic-based emissions. Use of this data would potentially allow CHS investigators to disentangle the "respirable particles/primary gaseous pollutants" package of pollutants associated with longitudinal lung function growth rate differences across communities of differing pollution profiles and levels. Ultimately, this information could be generalized across a number of communities, with a variety of traffic densities, highway configurations, and street usage patterns.

The movable Supersite facility will be located at a central location in a given community. A limited number of "satellite" stations will be deployed to schools and homes in the surrounding area, to assess the maximum and minimum concentrations of particles from community highways, roads, and neighborhood streets across the areas where residents actually spend their time and typically receive

their daily pattern of exposure. The exact number of satellite stations will depend on the number of CHS participating schools in the community typically two or three elementary schools, one or two middle schools, and one or two senior high schools as well as their location with respect to freeways and busy thoroughfares. Approximately 10-50 homes depending on local topography and related sampling considerations will be chosen from CHS subject homes across the community of study interest.

Efforts will be made to create about 12-15 satellite stations in each Supersite location, situated as diversely as possible from community highways, roads, and neighborhood streets. In each satellite site single-stage size-fractionated 37 mm filter samplers will be deployed for automated timer operation in these intra-community locations for discrete 12-hour sampling periods to exploit diurnal wind flow patterns, and these samples will be related to those measurements made concurrently at the main Supersite facility.

At least 20 12-hour sampling runs, conducted every 6th day in concert with the time-integrated Supersite measurements will be conducted in each community sampling location to assess consistency of observations. A similar sampling study will be performed in two other communities of CHS interest, and a model will be developed that describes both intra-community variation with regard to pollutant dispersion as a function of traffic density and distance from busy thoroughfares, and inter-community variability, with regard to other ecological factors. Performance of this study will therefore facilitate the collection of previously unavailable information, which will be readily linkable to ongoing health studies and of direct use in assessing the association between respiratory health and ambient particle exposure.

D.2.2.3 Size Distribution and Spatial Seasonal Variation of PAHs, Polar PAHs including Nitro Compounds, Ketones, and Quinones in the LAB

Of the known organic compounds present in the atmosphere, combustion-generated aerosols containing polycyclic aromatic hydrocarbons (PAH) are of particular concern due to their capacity to cause adverse health effects (Atkinson and Arey, 1994; Tokiwa and Ohnishi, 1986; King, 1988, Miguel et al., 1990). Particle- and gas-phase PAH may react in the atmosphere to form toxic derivatives (Atkinson and Arey, 1994, Ciccioli et al., 1996). Studies on the characterization of PAH derivatives are described in a separate section of this proposal (Arey and Atkinson) for a site impacted by vehicle emissions and a downwind receptor site.

Recent research indicates that diesel exhaust enhances allergic airway inflammation, airway hyperresponsiveness, acts as mucosal adjuvants at the molecular and cellular level and results in increased expression of respiratory allergic disease including asthma (Nel et al, 1998, Diaz-Sanchez, 1997, Ichinose et al., 1998a, and Ichinose et al, 1998b). The key etiologic agents responsible for these effects have not been identified but there is particular interest in the role of PAHs, both non-polar and polar PAHs. For example, diesel exhaust is known to contain PAH quinones (Schuetzle, 1983) which may bind to thiol groups in proteins and act as haptens; the redox cycling of quinones may create oxidative stress through redox cycling and production of superoxide anion radical and hydroxyl radical (Monks et al., 1992, O'Brien, 1991. Current research being conducted at UCLA and elsewhere (Penning et al., 1999) indicates that biotransformation of PAHs may result in PAH ortho-quinones capable of binding with nucleic acids and proteins thereby representing a risk of carcinogenesis and allergic airway disorders. The bioactivation of PAHs also results in redox cycling with the production of reactive oxygen species (ROS) capable of toxicity. Exposure to metals may enhance this process.

Diesel particles also enhance formation of nitric oxide, which may exert toxicity itself, or through formation of peroxyxynitrite. Sun et al (1984) reported lung retention of BaP when associated with ultrafine, insoluble particles derived from diesel particulate and they noted that approximately 20% of the retained BaP was in the form of BaP ortho-quinone one day after nose-only inhalation. In the tissue environment or within the cell these compounds can be toxic by their ability to act as antigens, cause biochemical lesions directly or through increases in reactive oxygen species. A number of toxicological studies using the Particle Concentrator Facility in the SCCAPM focus on evaluations of toxic effects of compounds such as PAHs, polar PAHs including quinones and ketones and nitro-PAHs in ambient PM₁₀ and PM_{2.5}.

Recent studies (Miguel et al., 1998, Marr et al., 1999) carried out in the Caldecott tunnel (located on State Highway 24 in Berkeley) showed that diesel trucks constitute the major source of automotive exhaust emissions of lighter PAH, contrasting with light-duty gasoline vehicles that emit higher molecular weight PAH. Detailed size-resolved measurements showed that a significant fraction of diesel-derived PAH is present in both the ultra-fine (<0.12 µm) and the accumulation mode (0.12-2 µm). In contrast, gasoline-engine particulate PAH were found almost entirely in the ultrafine mode (Miguel et al., 1998, Marr et al., 1999). While studies conducted in California indicated that ambient particulate PAH have size distributions that are similar to motor exhaust emissions (Miguel and Friedlander, 1978; Venkataraman et al., 1994a, Venkataraman et al., 1994b), experiments conducted in Massachusetts reported that the size distribution of PAH in urban areas is qualitatively different from rural sites (Allen et al, 1996). The authors attributed this difference to mass transfer operating during the partitioning process. The purpose of this portion of the supersite proposal is to measure detailed size-resolved PAH in all of the five proposed Los Angeles basin sites. Because the sites are located near sources and downwind from major sources, they provide an opportunity to determine whether partitioning also occurs during transport across the Los Angeles Basin. Partitioning would effectively alter the size distribution of the PAH and result in changes in their atmospheric transport and deposition in the human respiratory system. Our research (Miguel and Pereira, 1989, Miguel et al., 1998, Marr, 1999) and that of others (Daisey et al., 1986, Venkataraman et al., 1994a) showed that certain PAH may be used as markers in source apportionment using receptor based models.

Size-resolved aerosols particles will be collected every 7th day during two-week intensive campaigns for 12-hr daytime and 12-hr nighttime periods at all five supersite locations, comprising 140 samples during the summer and 140 samples during the winter sampling campaigns. The timing of the sampling period using a cyclone-denuder-MOUDI-PUF system will coincide with the period in which PAH derivatives will be sampled. Particulate PAH will be collected at 30 LPM using a 7-stage MOUDI impactor with size cuts from 0.056 to 1.8 µm aerodynamic diameter (dp). Samples will be withdrawn through an AIHL-design cyclone separator (John and Reischl 1980) at 30 lpm allowing particles with dp 1.8 µm and smaller to pass through it together with the gas-phase. A XAD-4 coated annular denuder placed downstream of the cyclone separator will trap semi-volatile organics while allowing transmission of particles equal to or smaller than 1.8 µm which then flow into the MOUDI impactor. Blow off from the impactor's backup filter will be trapped with two polyurethane foam plugs (PUF) placed in series behind it. With this configuration, collection artifacts, if present, are eliminated or greatly minimized.

XAD-4 resin, filter, PUFs and impactor samples will be stored in pre-baked amber glass containers and placed in a freezer immediately after each sampling period. All samples will be handled under room

light shielded with a yellow filter to avoid photooxidation of the PAH. All samples will be extracted with dichloromethane and analyzed by GC-MS and, if needed for higher molecular weight PAH, by HPLC-fluorescence. These techniques have been demonstrated previously for PAH in Caltech and UC Berkeley research supported by the California Air Resources Board (Miguel et al., 1998; Marr et al., 1999, Schauer et al, 1996, Schauer et al, 1998, Schauer, 1998). The size distribution data obtained at all five SCPMS locations will be used to calculate the deposition of toxic PAH in the upper, lower, and alveolar regions of the human respiratory system. In addition, together with PAH source signature data available in the literature (Miguel., et al., 1998, Marr et al., 1999, Venkataraman and Friedlander, 1994), the ambient PAH concentration data obtained in each of the SCPMS locations after correction for chemical reactivity (Friedlander et al., 1996, Miguel et al., 1986), will be used to separately apportion black carbon and associated toxic components to gasoline- and diesel-fueled vehicles using the US EPA Chemical Mass Balance receptor model.

D.2.2.4 Characterization of PAH Derivatives in Ultrafine and Accumulation Mode at a Source Site Impacted by Vehicle Emissions and a Downwind Receptor Site

Gas-phase two- to four-ring polycyclic aromatic hydrocarbons (PAH) will react with hydroxyl (OH) radicals during the daytime and, if they are present, with nitrate (NO₃) radicals during the nighttime (photolysis of NO₃, formed from reaction of NO₂ with O₃, prevents its build-up during the daytime). These radical-initiated atmospheric reactions will produce PAH derivatives more polar and less volatile than the parent PAH which may then condense onto particles. Particle-associated PAH may be photolyzed and may react with ozone. Thus, polar particle-associated PAH derivatives may be expected to increase at sites receiving aged air masses in comparison with sites close to emission sources (Arey, 1998). This is significant because certain of these polar PAH-derivatives have been shown to be highly mutagenic in bacterial and human cell assay systems and carcinogenic in animal studies (Arey, 1998 and references therein).

Naphthalene and methylnaphthalenes are abundant in emission sources such as diesel exhaust. These gas-phase PAH react with OH radicals (with lifetimes <1 day) and with NO₃ radicals to produce polar products, including nitro-derivatives. The isomer profile of the 14 methylnitronaphthalenes (MNNs) formed from the OH radical-initiated reaction of the methylnaphthalenes is distinct from the profile of MNNs formed by NO₃ radical-initiated reaction. Thus, ambient measurements of MNNs may be used as a signature to identify the atmospheric chemistry that has occurred in an air mass, whether OH radical-initiated reactions, NO₃ radical-initiated reactions or a combination of both. We have previously observed MNN isomer profiles in Glendora, CA (where abundant NO emissions from vehicles would prevent the build-up at night of NO₃ radicals) that strongly resembled those observed from laboratory chamber reactions of methylnaphthalenes simulating daytime OH radical-initiated reactions (Zielinska et al., 1989). In contrast, downwind from Los Angeles in Redlands, CA, especially during nighttime samples, we have observed MNN isomer profiles that correspond with those obtained in laboratory methylnaphthalene reactions with the NO₃ radical (Gupta et al., 1996).

We propose to measure gas-phase PAH (using Tenax and polyurethane foam (PUF) adsorbents), MNNs (using PUF) and particle-associated PAH and PAH derivatives in PM-2.5 at Downey (a source site in the Alameda corridor) and San Dimas (a receptor site), in summer and during winter and segregate the samples into daytime and nighttime samples. We hope to identify episodes in which NO₃ radicals were important reactive species and compare the PAH derivatives from fresh emissions with

those in air masses “processed” by OH radical-initiated chemistry (i.e., the daytime samples collected at the receptor site) and air masses in which NO₃ radical-initiated reactions occurred (i.e., downwind nighttime samples).

The samples will be collected over a two-week time period, with gas-phase PAH samples on Tenax collected for 12-hr daytime and 12-hr nighttime periods. Based on the results of the gas-phase PAH analysis, the PUF samples will be pooled into composite daytime and nighttime samples and analyzed for MNNs. If the occurrence of atmospheric reactions is indicated by differences in the MNN isomer profiles between the source and receptor sites and by increases in the ratios of MNNs to the parent methylnaphthalenes at the downwind site, pooled daytime and nighttime composite samples of ambient ultrafine and fine PM 2.5 will be analyzed for PAH, nitro-PAH and oxy-PAH and other derivatives such as nitro-PAH lactones and ketones (Helmig et al., 1992; Sasaki et al., 1995).

The ultrafine and fine PM 2.5 particles will be collected with the Ambient Fine and ultrafine Particle Concentrators (Sioutas et al., 1997; Sioutas et al., 1999). These systems small at 1000 and 300 LPM, respectively, and concentrate particles to a flow of 10 LPM. Concentrated ultrafine and accumulation mode PM will be collected on 47-mm Teflon filters (2 μm pore, Gelman Science, Ann Arbor, MI). Filter samples will be Soxhlet-extracted with dichloromethane, fractionated by high performance liquid chromatography and analyzed by gas chromatography/mass spectrometry as described previously (Helmig et al., 1992).

D.2.2.5 Detailed Functional Group Analysis of PAH samples

The detailed chemical analysis of the airborne particles will be based on functional groups, since the functionalized PAHs are the most likely to be involved in particle toxicity. The analytical procedure is based on derivatizing aliquots of the particle extracts and characterizing compounds containing the function by GC/MS with selected ion monitoring. Initial work will develop a reproducible protocol for the systematic derivatization of each airborne particle fraction.

For example, the aromatic nitro compounds could be derivatized with p-bromophenacyl bromide by first reducing the aliquot with zinc and HCl, extracting the alkalized mixture (removes phenolics also) and derivatizing the reduced nitro-compounds. The alkylated amine functions will be readily detected by GC/MS with ion selection for the fragment corresponding to derivatizing agent. The other functions of interest would be simpler in that they could be directly derivatized. For example, phenols could be acylated, ketones converted to hydrazones and quinones treated with thiols containing appropriately detectable aromatic structures. This method of analysis, coupled with a cellular toxicity assay for each fraction will provide the basis for the fractions and functional groups to be used in mechanistic studies.

The toxicity of organic air pollutants is commonly associated with the functionalized compounds such as the diol, the quinone and the nitro derivatives of polyaromatic hydrocarbons. The functional groups can react with tissue macromolecules to form covalent bonds and initiate genetic mutations through reaction with DNA, antigenic responses through protein modification and generation of reduced oxygen species through NADPH mediated quinone reactions. The object of this study is to determine the functional groups present in different size fractions of airborne particles. This data, together with a toxicological screening of different fractions, will be used to determine the active toxins associated with each fraction according to functional group.

In the procedure, each particle fraction will be extracted with a sequence of organic solvents of increasing polarity, in the order: hexane, ethyl acetate, methanol by covering the particles with the solvent (500 L) and sonicating for 30 minutes, centrifuged and the residue suspended in the next solvent. The extracts will be evaporated under a stream of nitrogen at room temperature and the residue reconstituted in acetonitrile. Aliquots of the acetonitrile solutions will then be analyzed for the different functional groups by the following procedures:

- Aromatic nitro compounds. The extract will be reduced by addition of 2N HCl, followed by addition of zinc. The reduced mixture will be alkalized and the neutral compounds removed by extraction with dichloromethane. The dichloromethane will be evaporated and the residue again reconstituted in acetonitrile, and the generated aromatic amines will be derivatized with a halobenzyl bromide. The resulting mixture will be scanned by GC/MS in the selected ion monitoring (SIM) mode for fragments containing the halo tropylium ion fragment characteristic of benzyl groups. The number of peaks in the mass chromatogram and their intensity will indicate the number of such compounds and their relative amounts. Subsequent mass spectral analysis of the positive peaks will be used to tentatively identify each peak.
- Phenols. Another aliquot of the extract will be derivatized with an acyl chloride of an aromatic compound with a characteristic ArCO fragment that will be used in GC/MS – SIM in the same manner as the tropylium ion in section 1.
- Ketones. This function will be trapped with an aromatic hydrazine and detected by GC/MS – SIM.
- Quinones. This function readily undergoes a 1,4 addition reaction and this property will be used with a thioalkyl benzene derivative so that the tropylium ion fragment can be used in GC/MS – SIM.

D.2.2.6 Measurement of the Aerosol Oxidant Partitioning in the Ultrafine, Accumulation and Coarse PM Modes

The laboratory of Dr. S. K. Friedlander has initiated a research project involving a novel combination of methods for characterizing aerosols morphologically and chemically. The new methods of aerosol characterization will prove useful in testing hypotheses for agents present in the aerosol responsible for adverse health effects, and in theoretical studies of atmospheric aerosol dynamics. We propose to apply these methods to supplement the methods currently planned for use in characterizing the ambient and concentrated aerosols to be used in the studies using the ARB Concentrator facility.

The principal objectives of this project are to determine certain characteristics of the modes as they relate to active agent hypotheses for health effects including fractal properties for the ultrafine particle range and aerosol oxidant concentrations in the accumulation mode. In this project, the presence of aerosol oxidants in the aqueous component of the ultrafine, accumulation and coarse modes will be determined, including peroxides from the gas phase and products of reactions involving transition metal ions dissolved in the solution. These data will be valuable in the interpretation of the outcomes of the toxicology studies proposed under the SCCAPM.

The Hering Low-Pressure Impactor (Hering and Friedlander, 1978) will be used to collect ultrafine (0-0.1 m); accumulation mode (e.g., 0.15-2.5 m) and coarse (e.g., 2.5-10 m) droplets by impaction on cover slips coated with fused KI. The presence of iodine in the region of the deposited particles will be investigated by optical microscopy. The relative fractions of aerosol oxidants in the ultrafine, accumulation and coarse mode will be investigated in each SCPMS site.

The morphology of concentrated and ambient ultrafine PM will be determined using the radius of gyration technique and a program written in Visual Basic scripts under Corel Draw. Over the same time period, a differential mobility analyzer followed by a condensation particle counter will be used to detect the particle count in each electrical mobility diameter range. By combining the two methods, the fraction of particles having fractal-like morphology can be estimated.

D.2.2.7 Measurement of Protein, Allergens and Other Biological Constituents of Urban Airborne Particulate Matter

Biological molecules present in urban ambient particulate matter have the capacity to cause adverse health effects (Dockery et al, 1993; Dockery and Pope, 1994). The substances found in airborne particles include allergenic proteins that can generate allergic reactions ranging in severity from hay fever and asthma to anaphylaxis followed by death (Swanson et al, 1994; Slater JE, 1989). Endotoxins, lipopolysaccharides from bacterial cell walls, also are present that can lead to airway inflammation and reduced pulmonary function (Jacobs, 1989; Haglind and Rylander, 1984).

Recent work at the California Institute of Technology (Cass group laboratory) shows that proteins and allergens are present in airborne particulate matter and in paved road dust that becomes airborne as traffic passes over city streets (Miguel et al, 1996; Miguel et al, 1998). In a companion research program recently selected for funding by the USEPA, experiments will be conducted at Caltech to quantify the presence of allergenic proteins in the emissions from additional man-caused air pollution sources that process biological materials (e.g. wood smoke). The purpose of this portion of the Supersite proposal is to seek to measure these allergens in ambient particulate matter samples and to conduct a formal comparison of sources vs. ambient samples. In the course of this work we shall study the seasonal and spatial variation of protein and allergenic material present in airborne particulate matter in Southern California.

Airborne PM₁₀ samples will be collected on quartz fiber filters by high volume samplers (Graseby – Anderson) at the Mira Loma Supersite, every 6th day during a one-year period. Mira Loma is one of the communities where allergic and asthmatic children are under study as part of the USC Children's Health Study and quantification of allergen identity and concentration there will aid interpretation of the cause of allergic respiratory disease. Two additional satellite air monitoring stations will be established in other communities where asthmatic children are under study as part of the Children's Health Study, thereby allowing a study of contrasting conditions across communities with higher and lower allergy and asthma incidence.

Protein will be extracted from these samples and the concentration determined by the bicinchoninic acid method (Stoscheck, 1990). Extracts will be screened for the presence of relative allergenicity using slot-immunoblots, for the detection of IgE-binding allergens (Miguel et al, submitted). The slot-blot data will be used to study the seasonal variation of the allergenicity of the aerosol. *In vitro* ELISA (enzyme-linked immunoassay) – inhibition assays (AlaSTAT, Diagnostic Products Co.) will be applied to annual composites of the filter samples collected to measure the presence of allergens originating from specific source materials (e.g. trees or smoke from burning tree parts). These techniques for allergen detection in ambient samples have been demonstrated previously in Caltech research supported by the California Air Resources Board and the South Coast Air Quality Management District (Miguel et al, 1998). Endotoxin will be extracted from the particulate matter and measured by the endpoint chromogenic *Limulus* amebocyte lysate assay (Thorne et al, 1997). The resulting data will be useful in

defining spatial and temporal changes in airborne particulate matter properties that can directly cause respiratory diseases such as allergies and asthma in a way that will assist interpretation of the differences in health status seen between communities in the USC Children's Health Study. By comparison of ambient samples to source samples taken during the separately funded source test program, it may be possible to detect and assess the importance of any man-caused sources of allergenic bioaerosols that could be modified through application of environmental controls.

D.2.3 Development of New Technologies and Methods for Characterizing PM

Specific objectives:

1. To compare the true 24-hour averaged PM₁₀ and PM_{2.5} concentrations with those determined using continuous PM mass monitors, including the Scanning Mobility Particle Sizer (SMPS), Aerodynamic Particle Sizer (APS), Tapered Element Oscillating Microbalance (TEOM), Continuous Ambient Mass Monitor (CAMM) and the Real-Time Ambient Monitor (RAM).
2. To develop and evaluate a semi-continuous monitor for size-dependent nitrate, carbon and sulfate measurement.
3. To test and compare new and emerging measurement methods for single-particle analysis

The research activities and projects described in this section will compare emerging sampling methods to routine monitoring PM techniques and federal register methods. New and improved state-of-the-art PM measurement technologies will be developed and evaluated in field studies proposed under this section. Upon successful evaluation of their performance characteristics, these new technologies will be used in other research activities and projects to be undertaken as part of this Supersite application as well as the SCCAPM.

D.2.3.1 Comparison between the True PM₁₀ and PM_{2.5} Concentrations and those Determined using Continuous PM Mass Monitors (SMPS, APS, TEOM, CAMM, DataRAM) and Estimation of Sampling Bias

Measurement of both PM₁₀ and PM_{2.5} mass concentrations using the Federal Reference Method (FRM) is based on the gravimetric analysis of particle filters collected over a period of twenty-four hours. In operation, a time-integrated sample is collected on a filter, which is later equilibrated at designated temperature and RH conditions in a laboratory, and then weighed to determine the mass of the deposited particulate matter. Although the proposed FRM is simple and relatively inexpensive, it presents the following drawbacks: a) it requires a sequential sampling unit to collect two to seven daily samples per week; b) it requires both a weighing room and labor to weigh the filters and; c) it does not provide short term measurements, and; d) in places like Los Angeles, FRM suffer from serious losses of volatile PM components, such as ammonium nitrate and volatile organic compounds. Therefore, the capital investment and labor costs can be significant for the implementation for a particle mass standard, while very little will be known about the temporal variability of fine particle concentrations. The values of key atmospheric metrics influencing ambient particle concentration, 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 12-24 hours. Thus, a 24-hour average measurement may not be indicative of human exposure.

Over the past decade, a number of continuous mass monitors have been developed and used in laboratory and field studies (TEOM, DataRAM, CAMM, SMPS and APS), all of which are described

in section D.2.4. Some of these monitors have been evaluated in limited field studies, but no systematic evaluation of the monitors has even been conducted. It is therefore unclear to what degree these monitors can be used to yield real-time continuous or near continuous data on PM₁₀ and PM_{2.5} concentrations. Due to its large fraction of volatile and semi-volatile constituents, the Los Angeles PM presents an ideal test aerosol for these continuous monitors.

We will compare the 3-hr, 6-hr and 24-hr average mass concentrations measured with the Tapered Element Oscillation Microbalance (TEOM), the Continuous Ambient Mass Monitor (CAMM), the Real-Ambient Monitor (DataRAM) and the combined SMPS/APS monitors to the true actual mass concentration for PM_{2.5} and PM₁₀ (e.g., including its volatile components).

The time-integrated, actual particle mass concentration for each size group will be determined as follows:

$$PM_{true} = PM_{FRM} + AN_{HDS} - AN_{FRM} + OC_{DEN} - OC_{FRM} \quad (1)$$

where PM_{FRM} is the mass concentration measured by the FRM, AN_{HDS} and AN_{HMI} are the ammonium nitrate concentrations measured by the HDS and FRM, respectively, and OC_{DEN} and OC_{FRM} are the organic carbon concentrations determined by Denuder Sampler and FRM, respectively. As PM_{true} in equation (1) refers only to PM without its aqueous component, diffusion dryers will be placed at the inlet of the TEOM, DataRAM, CAMM, APS and SPMS monitors. We will determine the conditions under which each of these monitors provides accurate, real-time PM concentrations. For the SMPS and APS concentrations, the PM_{2.5} and PM₁₀ mass concentrations will be determined by converting the size-resolved particle number to particle mass concentrations using reasonable assumptions about particle shape and density.

For the DataRAM monitor, PM_{2.5} and PM₁₀ mass concentrations are estimated from light extinction. For each intensive sampling location and over different seasons, the ratio of the 24-hour averaged true PM_{2.5} to that measured by means of the DataRAM will be analyzed by the following parameters: 1) particle mass median diameter; 2) sulfate, nitrate and carbon mass median diameters. The aerosol size distribution and chemical composition data will also be used to compare the measured RAM light scattering coefficient values to those determined by the Mie theory (Eldering et al, 1994, Cass, 1979). For the CAMM monitor, PM_{2.5} and PM₁₀ mass concentrations will be determined from the pressure drop increase with loading across a filter based on reasonable assumptions about particle shape, density, index of refraction, size distribution, and liquid water uptake.

The 1-hr, 3-hr and 24-hr average mass concentrations of each continuous monitor will be compared and to those concentrations measured by the 24-hour averaged FRM. Data will be stratified by SCPMS sampling site and season. Linear regression and correlation between the mass concentrations will be performed. Table 1 shows the different mass concentrations to be correlated and the time-scales over which these comparison will be conducted.

Table 1. Continuous and Time-Integrated Mass Concentrations to be Correlated

Method	Time-Scale		
	1-hr	3-hr	24-hr
PM _{2.5} DataRAM	v ^a	v	v
PM _{2.5} CAMM	V	v	v

PM ₁₀ and PM _{2.5} TEOM	V	v	v
PM ₁₀ SMPS/APS	V	v	v
PM ₁₀ FRM			v
PM ₁₀ (actual, equation 1)			v
PM _{2.5} actual (equation 1)			v

^aThe (v) sign indicates the parameters in each column to be correlated

We will also examine how these methods can be implemented to measure near-continuously particle-bound bound water. We will select the most reliable monitor whose PM levels are closer to the actual PM_{2.5} and PM₁₀. We will use two of these monitors, one with water. Furthermore, we will investigate the possibility of modifying these methods to develop real-time, size-dependent particle mass monitors. The difference in the mass concentrations between the two monitors will provide a measure of the particle-bound water. The feasibility of developing such monitors will be determined from the results of the first stages of this research.

D.2.3.2 Automated, Semi-Continuous Measurement of Nitrate, Sulfate and Carbon Aerosol Size Distribution

We propose a system for the automated, size-resolved measurement of fine particle nitrate, sulfate and carbon with a time resolution of 15-20 minutes. The size-fractionated Continuous Nitrate, Sulfate and Carbon Monitor (CNSCM) will be based on an already developed automated particle nitrate monitor (Hering and Stolzenburg, 1998). With this technique, particles are collected in an integrated collection and vaporization cell (ICVC) and are analyzed in place at the nanogram level by flash vaporization and quantitation of the evolved vapors. Prior to collection, the aerosol sample stream is denuded to remove interfering vapors such as vapor organics, and then humidified to enhance particle collection. The denuded, humidified particles are collected by impaction onto a metal substrate. At the end of collection the cell is filled with a carrier gas, the substrate is heated resistively, and the particles thermally decompose to vapors that are quantitated using a commercial gas phase analyzer. A unique flow system eliminates the need for valves on the aerosol transport line.

For the nitrate monitor the substrate is heated in a nitrogen stream, with quantitation of the evolved nitrogen oxides by chemiluminescence. For sulfate and carbon analysis we have used a separate collection cell with analysis by heating the substrate to a higher temperature, using a scrubbed air carrier gas, and analyzing the evolved sulfur dioxide and carbon dioxide. Field tests with the nitrate system show comparable results to denuder-filter systems for nitrate in several air quality studies. The carbon and sulfate systems have only recently been validated in the field, and filter comparison data are not yet available.

We propose to adapt a system to provide collection and analysis of five size fractions through the use of cascaded ICVC cells. These fractions are: <0.1, 0.1-0.4, 0.4-1, 1-2.5 and 2.5-10 μm . This will provide a division between ultrafine, condensation, droplet, intermediate mode and coarse aerosols. As our technique does not require valving-off the sample line for analysis, individual impaction stages can be analyzed without pneumatic isolation from the other stages. Thus we feel it can be readily adapted to provide size-resolved chemistry through the use of cascaded collection and vaporization cells. Samples from each stage will be analyzed in place, and then the next sample collected.

For analysis, carrier gas will be bled into the cells or lines immediately above and below the target cell, and the majority of the carrier gas will be introduced into the cross flow of the target cell, which will be opened to the analyzer. Isolation between the cells will be done without the use of valves, quite analogous to the valveless isolation from the sample line used with the current system. In addition, some care will be taken to limit the degree of humidification to the range between 70% and 85%, so as not to unduly influence particle size. Based on experience with our current system, we expect to collect sufficient sample in 13-18 minutes, and to be able to analyze all size fractions within 120 s. This will provide 15-20 minute time resolution for particle nitrate, sulfate and carbon in five size fractions.

The size-resolved automated particle chemistry system will be tested in the laboratory and in the field. Particle collection and sizing is tested in the laboratory using monodisperse particles of known size generated with a high-flow differential mobility analyzer. Evaluation of the analysis step is done using liquid standards applied directly to the collection substrate. Tests for gaseous interferences are done by measuring the response to filtered, ambient air. The complete system is evaluated in the laboratory using monodisperse aerosols of known composition with parallel concentration measurements by optical counter and condensation nucleus counter. Evaluation in the field is done by comparison to more traditional filter-based methods, and to real-time indicators of particle mass concentration, such as can be obtained by size distribution or light scattering.

D.2.3.3 Testing of New and Emerging Measurement Methods for Single-Particle Analysis

The Supersite will serve as a venue or platform for testing new and emerging aerosol instrumentation methods. Many new methodologies are currently under development. This phase of the project will stress on-line measurements of size-segregated chemical characteristics and the size distribution and properties of ultrafine and fine particles. It is widely recognized that existing methods of chemically characterizing atmospheric aerosols may cause major changes in their composition from the time of collection to the time of measurement. Once the particles are removed from the gas and combined on a filter or on an impaction plate, particles may react with each other or exchange components with the new air parcels. Components of deposited particles may also evaporate or trap other chemical species. This may lead to irreversible changes especially in the reactive components of the aerosol that are of most biochemical concern. Such changes are especially likely to occur when periods of hours, days or even weeks pass between the time of sampling and the time of analysis.

In response to these concerns, the development of aerosol instrumentation is moving in the direction of on-line measurements or single particle studies that minimize or even eliminate the need to remove the particles from the gas. This includes both chemical and physical measurements. Several instruments of this type are under development. Examples of emerging aerosol instruments include: [delete names from whom letters have not been received](#)

- Single particle chemical analysis by mass spectrometry (Prather, UC Riverside; Reents, AT&T Bell Labs; Marijnissen, Delft)
- Thermal desorption particle beam mass spectrometry (chemical analysis of clouds of particles) (Ziemann, UC Riverside).
- Photon correlation spectroscopy for ultrafine particle size measurement (Hinds; Marijnissen, Delft)
- Raman spectroscopy for measuring the chemical composition of aerosol streams (Friedlander; Stowers/Marijnissen, Delft)

- Single particle oxidant detector (Friedlander)

As an example of a collaborative effort involving these investigators, the thermal desorption particle beam apparatus under development at UCR by Professor P. Ziemann has been used in the measurement of aerosol phase peroxides. This system could be tested with the single particle peroxide analyzer currently under development by Professor Friedlander at UCLA. Another example is photon correlation spectroscopy. Professors Friedlander, Hinds and Marijnissen recently collaborated in such measurements. We have been in communication with these investigators and letters indicating their interest in participating are included in the Appendix to this proposal. The site for the Methods Testing Laboratory will be co-located with the fixed station calibration and maintenance station for the transportable laboratory located at UCLA. There will also be opportunities for such measurements at the transportable laboratory at the various sites where it is located.

The Supersite project will not directly support the development of these instruments since the resources available will not be sufficient. The Supersite Laboratory will provide a platform where investigators working on such instruments can make their measurements along with other scientists working on advanced instruments. We expect that the investigators will be able to find support for their research from other sources. Working on the UCLA platform with other scientists similarly engaged will help them in leveraging funding and will provide an incentive for them to want to come to the UCLA Supersite.

D.2.4 Mobile Particle Instrumentation Unit (PIU)

Intensive aerosol measurements that go beyond the traditional PM_{2.5} mass, sulfate and nitrate concentrations will be conducted at the Supersite locations. A mobile Particle Instrumentation Unit (PIU), funded by the SCCAPM will be deployed to these locations, along with a new MCEF to conduct shorter-term human and animal exposure studies to coarse, fine and ultrafine ambient particles, enriched in concentration.

All of the particle and gas monitors described below will be placed inside a light-duty trailer truck. Ambient air will be drawn through a manifold on top of the trailer truck, and distributed to specific samplers by means of sampling ports connected to a central manifold. Depending on the sampling mission, all or a part of the instrumentation may be operational at a given site.

The following particulate and gas instrumentation will be included in the PIU facility.

Table 2. Equipment for Particle Instrumentation Unit

Monitor	PM Property	Averaging Time	Sampling Frequency
PM Measurements			
Scanning Mobility Particle Sizer (SMPS 3934, TSI Inc.)	Particle number, surface and volume distribution (size range: 0.01–0.7 μm).	15-min	Daily
Aerodynamic Particle Sizer (APS 3310, TSI Inc.)	Particle number, surface and volume size distribution (size range: 0.5–20 μm).	15-min	Daily
PM ₁₀ and PM _{2.5} Tapered Element Oscillating Microbalance (TEOM Model 1400, R&P, Inc.)	Continuous measurement of the <i>non-volatile</i> component of ambient PM _{2.5} and PM ₁₀ .	1-hr	Daily

PM _{2.5} Continuous Ambient Mass Monitor (CAMM; Babich et al, 1999)	continuous PM ₁₀ and PM _{2.5} particulate mass concentrations from the pressure drop across porous membrane filters	1-hr	Daily
Continuous nitrate, sulfate and carbon monitor (ADI/R&P)	Size-segregated measurement of PM ₁₀ carbon, nitrate and sulfate content	1-hr	Daily
Real-Time Ambient Mass (RAM) Monitor (DataRAM, Mie Inc.)	Near-continuous mass concentrations of PM ₁₀ and PM _{2.5} .	1-hr	Daily
Micro-Orifice Uniform Deposit Impactor (MOUDI, MSP Corp.)	Size-fractionated PM ₁₀ mass, sulfate, nitrate	4-to-8 hr	6 th day
MOUDI	Size-fractionated PM ₁₀ metals and elements	4-to-8 hr	6 th day
MOUDI	Size-fractionated PM ₁₀ PAH, nitro-PAH	24-to-72 hr	6 th day
MOUDI	Size-fractionated PM ₁₀ EC/OC	24-hour	6 th day
High-Volume Particle Size Classifier (HVPSC)	Size-fractionated PM ₁₀ PAH, nitro-PAH	24-hour	6 th day
PM ₁₀ and PM _{2.5} FRM (Andersen Samplers)	PM ₁₀ and PM _{2.5} mass, nitrate, sulfate concentrations	24-hour	6 th day
PM ₁₀ and PM _{2.5} FRM	PM ₁₀ and PM _{2.5} EC and OC concentrations	24-hour	6 th day
PM ₁₀ and PM _{2.5} Honeycomb Denuders Samplers (HDS)	PM ₁₀ and PM _{2.5} nitrate concentration	24-hour	6 th day
PM ₁₀ and PM _{2.5} Multi-channel Denuder Sampler (MDS, Eatough et al, 1993)	PM ₁₀ and PM _{2.5} artifact-free EC/OC concentrations	24-hour	6 th day
PM ₁₀ Time-of-Flight Mass Spectrometer	PM ₁₀ individual particle chemical composition	15 min, 1, 4, 12 and 24 hr	Daily on episodes, Riverside only
Hering Low-Pressure Impactor (LPI, Hering and Friedlander, 1978)	Size distribution of particle-bound reactive oxidants and PM surface analysis	15 min, 1, 4, 12 and 24 hr	Selected sampling days
<i>Gaseous Pollutant Monitors</i>			
Continuous Chemiluminescence Analyzer (Monitor Labs Model 8840)	Nitrogen Dioxide	15 min, 1, 4, 12 and 24 hr	Daily
Thermo Environmental Inc. Model 48C trace level	Carbon Monoxide	15 min, 1, 4, 12 and 24 hr	Daily
UV photometer (Dasibi Model 1003 AH)	Ozone	15 min, 1, 4, 12 and 24 hr	Daily
Continuous Ammonia Monitor (Thermo Env Inc. model 17C)	Ammonia	15 min, 1, 4, 12 and 24 hr	Daily
NMHC Thermo Environmental Inc., Model 55	Non-methane Hydrocarbons	hourly	Daily
<i>Meteorology</i>			
Vaisala Model MP113Y	Temperature and Relative Humidity	15 min, 1, 4, 12 and 24 hr	Daily
Met One High-Sensitivity Wind vane	Wind direction	15 min, 1, 4, 12 and 24 hr	Daily

Met One High Sensitivity Anemometer	Wind velocity	15 min, 1, 4, 12 and 24 hr	Daily
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We will use an automated data acquisition system to collect and store data for all the continuous measurements (Commonwealth Environmental Inc.).

Sampling Frequency. The time-integrated data will be generated every 6th sampling day for the 5-year period except for episodes, during which they will be generated daily. These measurements will also be coordinated with the time-integrated speciation measurements conducted by the SCAQMD, which are also every 6th day. Thus, all of the proposed SCPMS measurements to be generated every 6th day will be conducted during the same day at which the SCAQMD samples are collected. This will make it easier to directly compare the results of the SCPMS to those of AQMD.

Continuous or Near-Continuous Measurements - (daily for the entire 5-year period)

- Particle number, surface and volume distribution (SMPS and APS)
- PM_{2.5} and PM₁₀ non-volatile mass concentrations (TEOM)
- PM_{2.5} and PM₁₀ mass concentrations including the volatile species (CAMM and Data RAM)
- Size-fractionated PM₁₀ nitrate, sulfate and elemental carbon concentrations
- Aerosol oxidants, especially peroxides
- Ultrafine fractal agglomerate structure analysis
- CO, ozone, sulfur dioxide, ammonia and nitrogen oxide concentrations
- Surface meteorology

4-12 hour Measurements (every 6th day)

- MOUDI and HVPSC samples will be collected over three 4-hour sampling periods during the day, beginning at 6:00 AM, and over one 12-hour overnight period (6 PM-6 AM). These data will be generated every 6th sampling day except for periods of pollution episodes, during which these data will be generated daily.

24-Hour Averaged Measurements (every 6th or 12th day)

- PM₁₀ and PM_{2.5} mass, sulfate and nitrate concentrations obtained with the FRM (6th day)
- Trace elements and metals, such as Si, Al, Fe, Mn, Pb, Ni, K, V, Cu, and Br (6th day). These will be grouped in the coarse (2.5-10), fine (0.15-2.5) and ultrafine (<0.15 m) ranges with the MOUDI. Eventually, higher size resolutions will be obtained with the HVPSC.
- Size-segregated analysis for PAH, polar PAH and nitro-PAH using the MOUDI (and eventually HVPSC), every 12th day. These size groups will be 0-0.1; 0.1-0.4; 0.4-1.0; 1.0-2.5 and 2.5-10 μm.

D.2.5 Analytic Chemistry within the SCPMS

Extensive analytical chemistry will be required in the SCPMS because of the need for analysis of PAHs, polar PAHs, nitro-PAHs, metals, and other organic compounds. See section D.5, Collaboration for a discussion of the analytical chemistry resources.

D.3 SITE SELECTION

D.3.1 Introduction

The LAB suffers the most serious photochemical smog impacts in the nation including the highest ambient air concentrations of ozone and particulate matter. Within the LAB it is important to carefully select the specific monitoring locations as well as the duration of operation at each location. The major goals of the site selection are to optimize the scope, importance and magnitude of the information to be obtained, and to facilitate the use of the data for health effects research being conducted under the SCCAPM.

After decades of research, it is now well understood that patterns of air pollutant emissions, transport and transformations, and related human in the LAB are highly complex, and subject to both geographical and temporal influences. In selecting specific locations for the principal Supersite facility over a five-year period, it is important to account for these geographical, seasonal and long-term air quality patterns. Similarly, attention must be paid to the need for “representative” sampling of the full spectrum of air pollution phenomena in the region with particular attention to the production, transport and impact of PM. This need is especially acute in the development and validation of models capable of forecasting and analyzing regional particulate pollution for policy or regulatory applications.

A key issue in site selection is the existence of the USC Children’s Health Study, a 10-year, 12-community study supported by the ARB and HEI. About 4000 school children living in 12 communities with differing levels and types of pollution have been under study since 1993. Monitoring stations are established in the 12 communities. We currently measure hourly O₃ and NO₂, continuous PM₁₀ and have PM_{2.5} assessment based on 2-week samples, which are analyzed for acid vapor (primarily HNO₃), and SO₄, NO₃ and Cl. The monitoring network can serve as the basis for more detailed assessments of particle size and speciation proposed in other sections of the application.

D.3.2 Siting Considerations

Geographical. During the past twenty years, growth in both the population and the density of emission sources has been greatest in the central and eastern portions of the LAB. Nevertheless, primary emissions of VOC, NO_x and PM are still dominated by the western, or coastal, portion of the region, which contains the greatest concentration of both mobile and stationary emission sources. Overall the highest ambient occur in the coastal areas for primary pollutants such as CO and NO₂, and in downwind inland valleys for secondary pollutants such as ozone and fine particulate. Thus, it remains appropriate to view the western/coastal portion of the LAB as a source region and the inland valleys of the central and eastern basin as receptor areas. This distinction is weakening and will likely have methodological implications over time.

Seasonal Air Quality Variations. The winter period in the LAB is characterized by surface temperature inversions in the coastal region and generally weak on-shore flow. Hence the highest ambient levels of primary pollutants such as CO and NO₂ are generally observed in the coastal region during the winter months. In contrast, the “summer” period is characterized by strong temperature inversions aloft, and by strong onshore flow and interior-mountain up-slope flow, which together produce rapid transport of primary pollutants from the coastal region to the interior valleys. Combined with high actinic radiation in the summer, these conditions produce elevated concentrations of a wide spectrum of secondary air pollutants, including ozone and fine PM, in the central and eastern areas of the Basin in the summer. In addition, during winter months, at any time of the year, offshore flow under Santa Ana conditions can trap large quantities of pollution over the coastal regions of the LAB.

Long-term Air Quality Trends. Since the proposed operation of the Supersite will span at least five years, it is important to consider long-term secular trends in air quality in the region. These trends are of two kinds: the results of those related to long-term emission control programs in the Basin; and those related to the influence of major meteorological phenomena characteristic of Southern California. The latter includes the so-called El Niño cycle, which approximately every fifteen few years can produces one or more unusually “clean” years with respect to air quality. Moreover, normal interannual variations in overall regional meteorology also guarantee that no individual will be representative of the average state of air quality. These factors must be considered along with the general long-term decline in emissions and ambient levels of ozone precursors in deciding whether to reconsider the location of instrumentation at particular monitoring sites over the planned five-year cycle.

Particulate Air Quality Modeling. The proposed will provide invaluable data for the construction, application and confirmation of regional models of aerosols and their health impacts. The selection of monitoring sites based on the criteria noted above also satisfies the needs of air quality and exposure assessment modelers. Important adjunct information would include simultaneous data collection at several sites and regional scale information on chemical/aerosol tracers and meteorology. The latter meteorology data are already available through the National Weather Service and the SCAQMD.

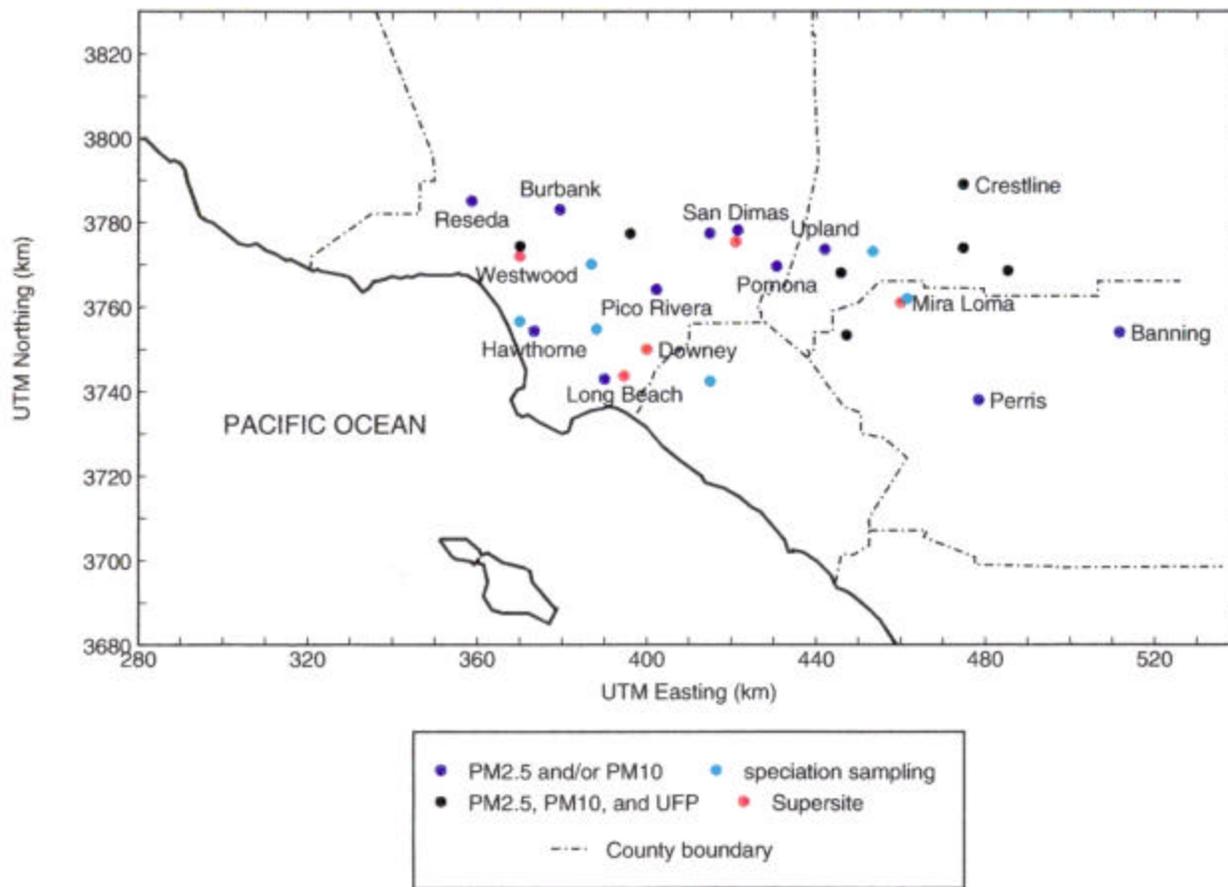
Selection of Specific Sites. In making our final proposed site selections we have also taken into account logistical and infrastructure considerations relevant to the implementation and support of the facility including the location of existing agency-sponsored air monitoring stations which offers the availability of secure sites. Finally, we have considered the scientific goals and hypotheses of the participating investigators and the needs of the collaborating health effects researchers affiliated with the EPA STAR PM Center based at UCLA. As described above, an important consideration in site selection was the location of the communities serving as sites in the Children’s Health Study. Additional linkages with that study will be developed over the course of the 5 years as health data emerges.

We propose a 2.5-year repeating cycle of measurements at five locations. Listed below are 6 locations that are candidates for the 5 sites. All 6 have high relevance, but budget constraints will likely limit us to 5 sites. Final site selection will be made in consultation with AQMD, ARB and EPA. These locations and the duration at each site are shown in Figure 1.

1. Long Beach (coastal site/winter/6 months)
2. Rubidoux (SCAQMD speciation site)/Mira Loma (eastern region/full year, Children’s Health Study)
3. Rancho Los Amigos Medical Center (Alameda Corridor) (West side/winter/6 months)
4. San Dimas/Azusa (SCAQMD PM monitoring site, Children’s Health Study) (central LAB region/summer/6 months)
5. UCLA (West side/winter/3 months)
6. Riverside (Children’s Health Study, eastern region, 6 months)

Measurements would be repeated at these sites on a 2.5-year cycle, with the possible replacement of UCLA by a site in Orange County for the first three six-month winter phases. This site would also be a speciation network site, operated by the SCAQMD.

Figure 1: Selected Supersite Sampling Locations



The selected Supersite sampling locations give a wide geographical coverage of the LAB and are located along the two primary air mass routes from the Los Angeles County and Orange county coastal areas toward the inland valleys. The sites at Long Beach, UCLA and Anaheim are would lie in residential-commercial areas with vehicular traffic influence. The facility at Rancho Los Amigos Medical Research Center in Downey would be situated in the middle of the Los Angeles “Alameda corridor.” Downey has some of the highest inhalable particle concentrations in the US often exceeding the National Ambient Air Quality Standard. The 20-mile long Alameda corridor is named after Alameda Street, joining the coastal area of Long Beach where a large number of industrial plants and oil distilleries are currently operating to downtown Los Angeles It is a main transportation artery for heavy-duty Diesel trucks. This site is expected to be enriched in diesel and organic PM emitted by mobile sources. San Dimas and Mira Loma are two “receptor” areas in the inland valleys of the central and eastern region of the LAB. They both have some of the highest inhalable particle concentrations in the US; they often exceed the National Ambient Air Quality Standard. Azusa is a light industrial region upstream of known ammonia sources, whereas Rubidoux is a semi-rural residential area downstream of ammonia sources (SCAQMD Report on *PM_{2.5} Monitoring Plan*, 1998). Riverside is a Children’s health study site with high PM levels and this PM would be considered to be “mature” or “aged” being on the far eastern end of the LAB. The nature of the PM in Riverside is different than that found in Mira Loma with the high

ammonia source in the latter area. San Dimas, Mira Loma, Riverside and Long Beach are sites of the Children's Health Study.

D.4 EXPECTED RESULTS AND BENEFITS

The research and monitoring activities proposed in the SCPMS will provide substantial benefits to air pollution researchers, regulators, and to the residents of the LAB. The proposed SCPMS activities will be integrated with the multidisciplinary research in exposure assessment, toxicology, and epidemiology of the recently funded by the EPA Southern California Center for Airborne Particulate Matter (SCCAPM). Furthermore, the SCPMS will interact with the California Air Resources Board (ARB) and the South Coast Air Quality Management District (SCAQMD) to maximize the use and value of the data collected by the SCPMS and the State and Local Agencies on PM.

The monitoring activities of the SCPMS will be linked with toxicology and epidemiology studies in the LAB to investigate health effects associated with exposures to ultrafine, fine and coarse particles. These studies are funded by the SCCAPM, the Health Effects Institute (HEI), the California ARB and the National Institute of Environmental Health Sciences (NIEHS). The SCPMS will become an invaluable resource to the ongoing and planned PM health and modeling studies in the LAB.

The detailed physico-chemical PM characterization, variation with time and season, and the frequency of brief periods of high concentration of particle size and chemical composition will also provide information for modeling the formation and physical and chemical changes that occur in the urban aerosol. The 2.5 year sampling cycles in each of the proposed SCPMS locations will provide long-term trend in PM concentration and composition and will make it possible to evaluate the effectiveness of the implementation of various control strategies. Local variation of particle concentrations within a given community will be determined. Information about the within-community PM variability will enable researchers to build and validate improved dispersion models to describe personal exposure indices based on traffic-based emissions. Use of this data will potentially allow investigators to disentangle the "respirable particles/primary gaseous pollutants" package of pollutants associated with longitudinal lung function growth rate differences across communities of differing pollution profiles and levels. Ultimately, this information could be generalized across a number of communities, with a variety of traffic densities, highway configurations, and street usage patterns.

The sophisticated suite of instrumentation and the detailed characterization of the ambient aerosol provided by the proposed Supersite will provide an opportunity for collaboration with other researchers by enabling them to co-locate instruments at the Supersite intensive monitoring sites. This will lead to the development of new instrumentation, new methods of sampling and analysis, and the validation of FRM methods. There will be a general benefit to the air pollution and aerosol research communities from the equipment development and validation that will occur as a result of the highly focused research proposed here.

D.5 COLLABORATION

Collaboration will occur with the following organizations or projects:

- Southern California Center for Airborne Particulate Matter (EPA funded STAR Center)
- Mobile Concentrator Exposure Facility (California Air Resources Board [ARB] funded research)

- USC Children's Health Study (ARB funded)
- Children's Environmental Health Center (NIEHS/EPA funded Center at USC/UCLA)
- Southern California Environmental Health Sciences Center (NIEHS funded Center at USC/UCLA/California Institute of Technology)
- California Air Resources Board
- South Coast Air Quality Management District (SCAQMD)
- Rancho Los Amigos Clinical Toxicology Project (HEI supported)

One of the most important objectives of the proposed SCPMS program is to support the research mission of the recently funded SCCAPM through environmental monitoring and analysis. SCCAPM is bringing together outstanding scientists from leading universities in Southern California to identify and conduct the highest priority research for airborne particulate matter to ensure protection of the public health.

Related research objectives of the SCCAPM include:

1. To make use of particle concentrators for exposure assessment and toxicological research.
2. To emphasize chemical and physical characterization of ambient PM (APM) especially size distribution in the study of the relationship of APM and associated morbidity and mortality.
3. To emphasize mechanistic toxicological research including in vitro, animal and human approaches for better understanding of the underlying bases for increased morbidity and mortality associated with exposure to APM.
4. To conduct toxicological research which reduces the uncertainties in the identification of causative APM constituents
5. To investigate the role of allergens and bioaerosols in the morbidity and mortality associated with APM exposure
6. To better characterize the relationship between mobile sources and airborne APM in the Southern California basin.
7. To investigate the relationship between outdoor, indoor and personal exposures to PM.

The SCPMS will enhance this research directly and indirectly. First, there are specific projects in SCCAPM, including the particle concentrator facility, which link directly with the SCPMS. These include research designed to investigate the role of PAHs, polar PAHs and nitro-PAHs in the health effects associated with particulate exposure. This requires characterization of particulate from mobile sources, its atmospheric chemistry, and spatial and temporal variability. Characterization of PM will enhance the use of the particle concentrator for conducting toxicological and clinical toxicological studies by identifying potential sites for PM concentration. The linkage with the Children's Health Study will permit augmentation of the particle characterization already underway and provide a basis for the expansion of the study to new areas or communities over the course of the SCPMS activity. The within community study will enhance provide a means to better understand community participant variability in terms of measured health outcomes. The SCPMS will make indirect contributions to ongoing health studies by providing atmospheric aerosol measurements to the ongoing health studies:

Some of the sampling locations of the SCPMS will be National Air Monitoring Sites (NAMS) operated by the SCAQMD. Letters of collaboration by SCAQMD are included in **Appendix xx**. The SCAQMD will operate several NAMS sites to collect similar air pollution data as those of the proposed Southern California Supersite. These satellite sites will provide a basis for comparison of pollutant concentrations within the LAB.

SCAQMD and ARB will collaborate on the planning and conduct of quality assurance/quality control audits at selected monitoring sites. We will coordinate annual audits of particulate and gaseous monitors, meteorological sensors, aerosol sampler flow rates, standards, and comparison methods for size- and chemical-specific continuous monitors and laboratory measurements with SCAQMD. We will also participate in inter-laboratory comparisons with the SCAQMD aerosol analysis laboratory. Details of these interactions are given in the Quality Assurance Narrative Statement.

The Southern California Supersite intends to establish relationships with other EPA Supersites. These will provide opportunities for comparison of PM characteristics in different airsheds across the U.S.

Analytic chemistry. There will be extensive analytic chemistry required in the SCPMS because of the requirement to characterize for PAHs, polar PAHs and nitro-PAHs, metals, peroxides, and other organic compounds. The SCPMS will use the Analytic Service Core of the SCEHSC to carry out analyses. This analytic unit will also be responsible for all analytic chemistry for the SCCAPM. This analytic unit will be enhanced by the additional participation of Dr. Antonio Miguel of UC Riverside and Professor Arthur Cho, Department of Pharmacology, UCLA. Both of these individuals have extensive analytic capability including GC/MS, HPLC and ICP/MS.

The NIEHS supported SCEHSC studies the effects of the environment on human health. One component of this Center is the Analytic Chemistry Service Core. Professor William Hinds is Director. The overall purpose of the Analytical Chemistry Services Core is the provision of high quality, state of the art, analytical chemistry services as well as field and laboratory exposure characterization capability to Center investigators. This Service Core unifies the analytical and field sampling resources on the UCLA campus into a well-defined and organized structure. This Core will be available to all SCPMS investigators.

Biostatistics. Biostatistical services will be required throughout the duration of the SCPMS. The Biostatistics Service Core of the SCCAPM will provide these services. The primary aims of this biostatistics core are to provide statistical support for research and Supersite projects being conducted by Center investigators. Members of the Biostatistics Core will assist in the development of study design, including calculations of power and sample size, and advise on the most appropriate statistical methods for use in data analysis. They will also provide an interface between Center investigators and statistical resources, for example by matching an investigator to a statistician with particular expertise in the area under investigation.

The director of the Biostatistics Core is Dr. James Gauderman, who will coordinate all the activities of the members of the Core and will be the primary contact person for Supersite investigators.

D.6 GENERAL PROJECT INFORMATION

D.6.1 Facilities

UCLA, USC, UC Riverside, California Institute of Technology and Rancho Los Amigos have extensive facilities for the study of air pollution in general and PM, in particular because of the presence of a critical mass of outstanding scientists and major commitment by their respective universities to address this major regional problem. Because of the page limits in this RFA we cannot detail those facilities. We have collected information on the facilities to each investigator and we can make those

descriptions available to reviewers. Dr. Froines has discussed the Supersite and STAR Centers with the Executive Vice Chancellor of UCLA and received a commitment to provide space for the two programs. UCLA administration has committed building space for the construction of the new concentrators. Computing capability at all the universities is world class in scope and sophistication.

UCLA has a collaborative agreement with SCAQMD to co-locate monitoring and research equipment at current and proposed monitoring sites.

D.6.2 Personnel

We have described the key personnel and their qualifications in detail in the budget justification section of the application. Page limits prevent us from describing the qualifications of the investigators in this section. The faculty from the four universities and Rancho Los Amigos represent some of the finest investigators in the U.S. in the area of air pollution.

D.6.3 Project Schedules

The proposed SCPMS activities will span at least a five-year period with an assumed start date of January 1, 2000. The milestones of this project are shown in the following table. The Particle Instrumentation Unit (PIU) will be developed and constructed by the end of 1999, as part of our SCCAPM activities. The first SCPMS site at which the PIU as well as the Particle Concentrator facility will be deployed will be UCLA for the first half of 2000. During that time, the HVPSC as well as the size-fractionated Continuous Nitrate, Sulfate and Carbon Monitor (CNSCM) will be developed and tested. The development of the HVPSC is part of the SCCAPM, whereas the development of the CNSCM will be part of the SCPMS. Once completed, the HVPSC and CNSCM will be installed into the PIU trailer, which will be deployed to the rest of the SCPMS locations. The locations, the seasons involved, and the duration at each site are described in section D.2.4 of this proposal.

Table 3. Proposed Timetable

Activity/Task	Year 1	Year 2	Year 3	Year 4	Year 5
Program Plan	---				
PIU installation at UCLA	--				
Development of new technologies instruments (HVPSC, CNSCM)	-----				
PIU installation and operation in Mira Loma/Rubidoux	-----		---	----	
PIU installation and operation at Downey			----		----
PIU installation and operation in San Dimas/Azusa		----		----	
PIU installation and operation in Long Beach/Anaheim		----			---
Chemical analysis	-----	-----	-----	-----	-----
Data validation and interpretation	----	-----	-----	-----	-----

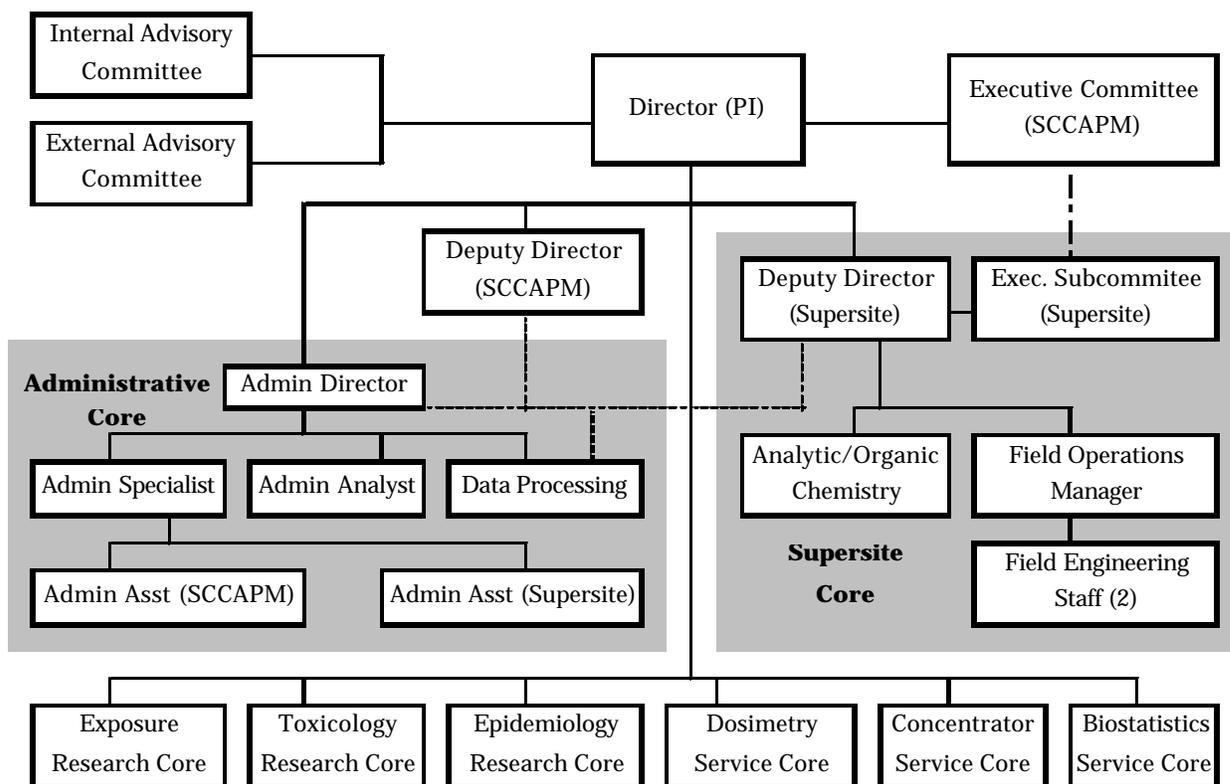
D.6.4 Proposed Management

The SCPMS will represent be one of three elements of the overall Southern California Consortium whose goal is the study of airborne PM. The three components are the Mobile Concentrator Exposure Facility, the SCCAPM and the SCPMS. The first two elements are beginning operation. The overall management structure is described in Figure 2. The overall title of the three components will be the

“Southern California Center for Airborne Particulate Matter and Supersite” (SCCAPMS). The Principal Investigator for the three elements will be Dr. John Froines, Professor in the School of Public Health. A Deputy Director of the SCCAPMS, Dr. Constantinos Sioutas of the University of Southern California, will head the SCPMS unit. An Executive Committee will be established to assist guidance of the Supersite. This Committee will be a subcommittee of the SCCAPM Executive Committee and will have different representation in order to include representatives from ARB and SCAQMD although there will also be overlapping membership to ensure integration of effort. The Deputy Director and the Executive Subcommittee will have the responsibility for planning, day to day operation of the facility, quality assurance/control, data management, and program evaluation in consultation with the P.I. and the relevant Center Committees. The Field Operations Manager will be responsible for daily operation of the Supersite and will have oversight over the Field Engineering Staff. The Analytic Chemist will report to the Deputy Director. The Center Director will also interact with the Analytical Chemist because of the need for oversight of the complex chemistry that will occur within the Center. A high priority for the management structure will be the integration of the research in SCCAPM with the monitoring and research in SCPMS. There will be a common administrative structure (Figure 2) under an Administrative Director who will oversee all 3 elements of the SCCAPMS. The Administrative Analyst will oversee all budgetary activities and there will be an Administrative Assistant who will address all administrative needs of the SCPMS. We believe maximum efficiency of operation will result from this integrated administrative structure.

The Internal Advisory Committee of the Center will be asked to evaluate and review the effectiveness of the interaction between the 3 elements of the Center, and the External Advisory Committee will also review the entire Center including the Supersite. The Deputy Director for the Supersite will sit on both the Executive Committee and the Executive Supersite Subcommittee. He will report to the oversight committees (Internal Advisory and External Advisory) at their meetings. The Deputy Director for Supersite will meet at least weekly with the Director and Center Deputy to assure integration of effort. The Executive Subcommittee will meet every two weeks at the outset and later on a monthly basis.

Figure 2: Proposed Organizational Structure



Data Management. Since the Supersite will generate considerable data it will be necessary to develop a data management plan as an element of the quality control/assurance plan. A data manager will coordinate data receipt, analysis, storage, and backup. Details of the data handling are described in the QA/QC section. Four levels of data are envisioned. Raw data, investigator data, refined data, and archival data. The raw data will be stored in the dedicated computer for the real-time instruments with automatic transfer to the data acquisition system and backup. Investigator data will include calibration adjustments, normalization, time period integration, and scaling. It will be available on a web site to all investigators. Refined data is investigator data that has been reviewed for accuracy, representativeness, and completeness. It will be available to the public on a web site. Archival data is refined data that has been evaluated and documented and put in proper form for the NARSTO permanent data archiving system. These data will also be generated every 6th sampling day for the 5-year period except for episodes, during which they will be generated daily.

D.6.5 Interactions with Other Institutions

The possible interactions with other institutions have been described under D.5, Collaboration. Interaction across institutions is a major priority for the SCPMS. The interaction with governmental agencies will be enhanced by the fact that Dr. Froines chairs the Scientific Review Panel of the California ARB and is responsible for all matters relating to toxic chemicals in the ambient environment and Dr. Froines and Dr. Colome, Deputy Director of the Center, serve on a key air toxics committee of the SCAQMD.

D.7 ATTACHMENTS

D.7.1 Appendix 1 - Sampling Efficiencies for Particulate Nitrate of the MOUDI, Denuded and Undenuded Filter Samplers for Ambient and Concentrated Air (Chang et al, 1999)

Sampler Type	Ambient Air	Concentrated Air
MOUDI	0.57 ((0.27)	0.99 ((0.17)
Denuded Filter	0.39 ((0.31)	0.81 ((0.19)
Undenuded Filter	0.41 ((0.32)	0.93 ((0.11)

D.7.2 Appendix 2 - Summary of the Statistical Paired Comparisons Between Total Particulate Nitrate and MOUDI, Denuded and Undenuded Filter Particulate Nitrate Concentrations

	Mean ((s.d.) Nitrate Concentration ((g/m ³))	p-value	Correlation Coefficient ^b
<i>Ambient Air</i>			
Total	11.5 ((10.7)		
MOUDI	9.2 ((11.1)	0.0013	0.97
Denuded Filter	7.2 ((10.3)	5 x 10 ⁻⁶	0.90
Undenuded Filter	8.9 ((10.8)	0.00013	0.97
<i>Concentrated Air</i>			
Total	97.6 ((68.3)		
MOUDI	93.4 ((64.1)	0.60	0.96
Denuded Filter	90.2 ((68.3)	0.14	0.99
Undenuded Filter	86.9 ((73.8)	0.03	0.99

^a p-value of paired t-test between nitrate concentrations measured by sampler and total nitrate concentration.

^b correlation coefficient between nitrate concentrations measured by sampler and total nitrate concentration.

D.7.3 Appendix 3 - Collaborating Faculty

- **UCLA:** Steven D. Colome, Sc.D., Adjunct Professor, Public Health, Annmarie Eldering, Ph.D., Adjunct Assistant Professor, Atmospheric Sciences, Suzanne E. Paulson, Ph.D., Assistant Professor, Atmospheric Sciences, Richard P. Turco, Ph.D., Professor, Atmospheric Sciences, Indira Venkatesan, Ph.D., Research Geochemist, Planetary Chemistry and Physics, Arthur M. Winer, Ph.D., Professor, Environmental Health Sciences.
- **Rancho Los Amigos Medical Center:** Henry Gong, Jr., M.D., Professor, Medicine and Preventive Medicine.
- **University of California, Riverside:** Roger Atkinson, Ph.D., Professor, Environmental Sciences and Chemistry, Paul Ziemann, Ph.D., Assistant Professor, Environmental Sciences.

- **University of Southern California:** Rob McConnell, MD, Associate Professor, John Peters, MD, ScD, Professor, Division of Occupational and Environmental Health
- **Delft University of Technology:** Johannes C. M. Marijnissen, Ph.D., Associate Professor, Aerosol Technology.