

Final Technical Report

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Center Name: Southern California Particle Center and Supersite (SCPCS)

Center Director: John R. Froines

Title: Physical and Chemical Characteristics of PM in the LAB (Source Receptor Study)

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Project Period: June 1, 1999–May 31, 2005 (no-cost extension to May 31, 2006)

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RFA: Airborne Particulate Matter (PM) Centers (1999)

Research Category: Particulate Matter

Topic C: Studies of the Effects of Varying Spatial and Temporal Patterns of Ambient Particulate Matter (PM) and Co-pollutants and Resulting Health Effects with Emphasis on the Role of Atmospheric Chemistry

Objective(s) of the Research Project: This final report covers the activities undertaken by the Aerosol Laboratory of the University of Southern California (USC), which is part of the Southern California Particle Center and Supersite (SCPCS). The SCPCS was associated with a U.S. Environmental Protection Agency (EPA) Supersite during the years 1999-2004 and many projects benefited from joint support. The activities performed by the Aerosol Laboratory were originally proposed in three project sub areas:

1. Characterization of the airborne concentrations, size distribution and other chemical/physical elements of ambient air particulate within the Los Angeles Basin (LAB) in relation to health studies. PM characterization in the Exposure Core at the Aerosol Laboratory supported a wide range of health studies. The findings of these health studies are reported elsewhere in other SCPCS Final Reports, including:
 - a. The aged rat pilot study (in collaboration with Drs. Froines, Kleinman, and Cho, reported as Project 5, R827352C005).
 - b. Acute cardiopulmonary responses to concentrated coarse particulate matter in human volunteers (directed by Dr. Henry Gong, USC Keck School of Medicine, reported as Project 12, R827352C012).
 - c. Animal inhalation studies using concentrated ultrafine (UF), fine (F), and coarse (C) PM in source and receptor sites of the LAB (Dr. Kleinman, UC-Irvine, reported as Project 4, R827352C004, with detailed report available at <http://www.arb.ca.gov/research/abstracts/98-316a.htm>; Dr. Harkema, Michigan State University, final report on source receptor study at

http://cfpub.epa.gov/ncer_abstracts/index.cfm/fuseaction/display.abstractDetail/abstract/1762/report/0)

- d. *In vitro* studies of PM chemical and cellular toxicology (Dr. Andre Nel, UCLA, reported as project 2; Drs. Arthur Cho and John Froines, UCLA, reported as Project 1, R827352C001)
2. Development of concentrators for UF, F, and C in support of animal inhalation studies, conducted at air pollution source and receptor sites of the LAB (collaborations and other relevant reports listed in a, c, d above)
3. Development of concentrators and support of studies of human exposure to concentrated PM (in collaboration with Dr. Henry Gong, USC School of Medicine, Project 12, R827352C012).

Summary of Findings: Over the course of six years of the SCPC, extensive studies by the Aerosol Laboratory have characterized PM size distribution and chemical composition at many locations around the LAB, both in the context of Center health studies and independently. Sites identified as primarily source or receptor influenced, freeway sampling sites, indoor locations, and specific locations associated with ongoing health studies have been studied. Taken together, the many findings establish that the physical and chemical properties of ambient PM depend greatly on locations and season. In general, UF concentrations are highest at sites heavily impacted by sources such as fresh vehicular combustion emissions. More detailed findings on the size distribution of UF at various locations are reported below. Mass concentrations in the accumulation mode and C mode showed pronounced seasonal dependence. Concentrations of these larger modes tend to be lower in winter than in summer, especially at the receptor sites.

There has been some debate as to whether a 1.0 μm or a 2.5 μm cut-point provides good separation between accumulation mode particles (combustion emissions and photochemical formation and processing) and C, mechanically-generated particles (such as soil and road dust). Although previous research does suggest a relationship between C and intermodal (1–2.5 μm) PM, the sites in which these studies were conducted are not representative of all locations. Similar data for C, intermodal, and F were collected across four sites in the LAB. While some similarities exist between these results and those of comparable studies, our Supersite studies showed that intermodal PM consists of a significant portion of particles that are similar in chemical composition to PM_{10} particles that are thought to cause the greatest health effects. This study was performed to shed light on the origin and chemical composition of intermodal particles between the C and F in Los Angeles, a unique city where crustal, oceanic, and anthropogenic primary and secondary sources are responsible for the high observed PM levels. Our results indicate that a PM_{10} standard would not constitute an unambiguous separation of C and F in this urban air shed. (Geller, et al., 2004).

Composition studies of ambient PM were a major focus of our work. Generally, C was composed mostly of nitrate and crustal elements (iron, calcium, potassium, silicon, and aluminum). Consistent relative levels of these elements indicate a common source of soil and/or road dust. In the accumulation mode, nitrate and organic carbon were the predominant species.

Higher nitrate levels were found in accumulation mode PM from receptor sites. The UF consisted of mostly carbon, especially organic carbon (OC). At source sites, levels of OC in UFs were higher in the wintertime, attributable to increased organic vapor condensation from vehicles at the lower wintertime temperatures. Conversely, at receptor sites, organic carbon levels in the UF mode peak in the summertime for two reasons: secondary organic aerosol formation by photochemical reactions is enhanced in the summer, and increased advection of polluted air masses from upwind occurs (Sardar, et al., 2005a).

Measurement of metals in daily size-fractionated ambient PM₁₀ samples was conducted at source (Downey) and receptor (Riverside) sites within the LAB. The main source of crustal metals, e.g., Al, Si, K, Ca, Fe and Ti, can be attributed to the re-suspension of dust at both source and receptor sites. All the crustals were predominantly present in super micron particles. At the source site, potentially toxic metals, e.g., Pb, Sn, Ni, Cr, V, and Ba, are predominantly partitioned (70–85%, by mass) in the sub micron particles. The receptor site exhibited C distributions for almost all particle-bound metals. Fine PM metal concentrations in that site seem to be a combination of few local emissions and those transported from urban Los Angeles. The majority of metals associated with fine particles are in much lower concentrations in the receptor compared to the source site. Coarse PM metal concentration trends are governed by variations in the wind speeds in each location, whereas the diurnal trends in the fine PM metal concentrations are found to be a function both of the prevailing meteorological conditions and their upwind sources (Singh, et al., 2002).

UF dominate the number concentrations of ambient aerosols and have been implicated in numerous studies of the health and toxicological effects of PM exposure. For this reason, UF have been a particular focus of our work. We have conducted several detailed studies of size distribution of UF (number and mass concentrations) at various sampling sites, including indoor locations, and explored the effect of season on size and composition of particles in the UF mode. This work was complemented by in vitro studies in other SCPCS labs on the chemical and cellular toxicology of our ambient UF collections. Key UF studies are summarized in the following paragraphs.

Studies conducted in Southern California showed that the size distribution of UF in source sites was generally unimodal with a mode diameter of 30–40 nm and without significant monthly variations. In contrast, the number-based particle size distributions obtained in receptor sites were bimodal, with a significant increase in accumulation mode as the season progressed from winter to summer. Afternoon periods in the warmer months are characterized by high number counts while mass and elemental carbon (EC) remain low, suggesting the formation of new particles by photochemistry. Particle mode diameters range from 30 nm up to above 100 nm, a result not seen in most other studies of particle size distributions in other urban or rural areas where mode diameters are generally less than 50 nm. Although vehicular emissions have been assumed to dominate the observed UF concentrations and size distributions our study presents evidence that day to day UF levels are also influenced by long range advection and photochemical processes. (Fine, et al., 2004b).

The very small mass of UF has posed a great challenge in determining their size-dependent chemical composition using conventional aerosol sampling technologies. Implementing two

technologies in series (the USC Ultrafine Concentrator described by Kim, et al., 2001b, and the MSP NanoMOUDI) has made it possible to overcome these two problems. UF were measured in source and receptor sites during three consecutive 3-hour time intervals, i.e., morning, midday and afternoon. The results indicate a distinct mode of UF mass in the 32–56 nm size range that is most pronounced in the morning and decreases throughout the day. While the mass concentrations at the source site decrease with time, the levels measured at Riverside, CA (a “receptor” site) are highest in the afternoon with a minimum at midday. In that site, UF EC and OC concentrations were highly correlated only during the morning period, whereas these correlations collapsed later in the day. These results indicate that in this area, UF is generated by primary emissions during the morning hours, whereas secondary aerosol formation processes become more important as the day progresses (Geller, et al, 2002). Another study with the Nano-MOUDI explored the UF chemical composition at urban source sites (USC and Long Beach) and inland receptor sites (Riverside and Upland) in the LAB over three different seasons. Two week composite samples showed a distinct OC mode was observed between 18 and 56 nm in the summer, likely due to photochemical secondary organic aerosol formation. Collocated continuous measurements of particle size distributions and gaseous pollutants helped to differentiate UF sources at each site (Sardar, et al., 2005b).

It has been hypothesized that UFs originate primarily from vehicular emissions; thus, the concentrations of gases such as CO, NO, or NO₂ that also originate from traffic sources could be used as surrogate measures of UF. The advantage of this approach is that concentrations of these gases are monitored routinely in compliance networks and on personal levels by means of relatively simple and easy-to use monitors. The validity of the assumption that gases can be used as surrogate measures of UF was tested in five sites of the LAB over the course of one calendar year. Our studies indicate an overall lack of significant associations between hourly and 24-hr UF particle number and gaseous co-pollutant concentrations. The findings can be attributed to the differences in the sources and formation mechanisms that are responsible for generating these pollutants in various locations of the LAB. These findings also imply that potential confounding effects of co-pollutants will not affect epidemiologic analysis seeking to link UF to health effects because of the weak to moderate associations between PM and co-pollutant concentrations. (Sardar, et al., 2004).

In collaboration with the California Air Resources Board (CARB), we developed a mobile platform designed to characterize UF and associated pollutants inside vehicles. The equipment was applied during commutes in Los Angeles freeways and residential streets. Freeway exposure concentrations were frequently an order of magnitude higher than on residential streets for UF, NO_x, BC, and CO, with higher NO_x and black carbon (BC) values observed in diesel traffic freeways than those with mostly light duty vehicle traffic (Westerdahl, et al., 2005).

We conducted a study to evaluate contributions of vehicle generated UF to indoor environments in close proximity to freeways in the absence of known indoor aerosol sources. Indoor/outdoor (I/O) ratios of particle number concentration showed a strong dependence on particle size and were influenced by different ventilation mechanisms. Among different size ranges of UF, the highest I/O ratios (0.6–0.9) were generally observed for larger ultrafine particles (70–100 nm), while the lowest I/O ratios (0.1–0.4) occurred typically around 10–20 nm. The size distributions of indoor aerosols showed less variability than those of outdoor freeway aerosols. The

penetration factors and deposition rates also varied significantly depending on particle size and agree with literature data and theories for particles greater than 20 nm. For particles less than 20 nm, I/O ratios, penetration factors, and deposition rates did not conform to theoretically predicted values. UF from freeways are unique particles with a high semi-volatile content. The sub-50 nm particles are especially high in semi volatiles and thus shrink to a smaller size (or evaporate completely) as they infiltrate indoors (Zhu, et al., 2005). These results were further supported by a study in which we examined volatility of penetrating ultrafine outdoor particles, predominantly from freeway emissions, into indoor environments using a tandem differential mobility analyzer (TDMA).

Evaluation of outdoor particle volatility as a function of distance to the freeway revealed that aerosol volatility decreases with increasing distance from the source (Kuhn, et al., 2005b). Physical and chemical characteristics, including volatility of PM in the proximity of a Light-Duty Vehicle (LDV) freeway were also measured and analyzed. The volatile component ranged from about 65% volume of 120 nm particles heated to 110°C, to 95% volume of 20 nm particles (Kuhn et al., 2005a). Our freeway PM measurements were compared to those performed in two bores of the Caldecott Tunnel in Northern California. One bore (Bore 1) is open to both heavy- and light-duty vehicles (HDV–LDV) while heavy-duty vehicles are prohibited from entering the second bore (Bore 2). A strong association between particle number and normalized vehicle speed ($R^2 = 0.69$) was observed, and heavy-duty diesel vehicles showed higher particle number emissions than light-duty vehicles. Compared to previous studies at the Caldecott Tunnel, less particle mass but more particle numbers (by factors of 2–4 fold) are emitted by vehicles than was the case 7 years ago. As the emissions of carbonaceous PM of newer engines decreases, the formation of nucleation mode particles is favored due to the reduction of the available surface for adsorption of the semi-volatile material. The resulting supersaturation of the mostly organic vapor increases the production of nano-particles by nucleation (Geller, et al., 2005).

Another focus of our work on particle characterization concerns the development of tracer species. Individual organic compounds can be used as tracers for primary sources of ambient PM in chemical mass balance receptor models. By examining the seasonal, temporal, geographical, size-fractionation, and inter-correlations of individual organic compounds, the sources and atmospheric fate of these tracers can be better understood and their utility as molecular markers can be assessed. Investigators in the SCPCS have used a high-flow rate, low pressure-drop UF separator to collect sufficient mass for organic speciation of UF and accumulation mode aerosol on a diurnal basis. Sampling was conducted at two sites (source and receptor) over two seasons (summer and winter). Hopanes, used as organic markers for vehicular emissions were found to exist primarily in the UF. Levoglucosan, an indicator of wood combustion, was quantified in both size ranges but more was present in the accumulation mode particles. An indicator of photochemical secondary organic aerosol formation, 1,2 benzenedicarboxylic acids, was found primarily in the accumulation mode and varied with site, season and time of day as one would expect for a photochemical product. These data will be used to assess the concentration of specific PM sources to personal exposure and ultimately health effects in upcoming epidemiological and toxicological studies in LAB (Fine et al., 2004a).

C, F, and UF concentrator technologies have been developed and evaluated by investigators of the SCPCS, as well as support from the ARB. These instruments are portable and have been

demonstrated to increase ambient particle levels by enrichment factors up to 40 without significantly affecting particle properties such as size (Misra, et al., 2004), bulk chemistry (Kim, et al., 2001a; Khlystov, et al., 2005) or single particle chemistry (Zhang, et al., 2004) and morphology (Kim, et al., 2001a). These concentrators have been applied in a range of studies to provide elevated ambient PM exposures to animal or human subjects, as well as to collect large quantities of PM material in aqueous solution suitable for subsequent toxicological assays. Highly concentrated liquid suspensions of these particle modes were obtained by connecting the concentrated output flow from each concentrator to a liquid impinger (BioSampler™, SKC West Inc., Fullerton, CA). Particles are injected into the BioSampler in a swirling flow pattern so that they can be collected by a combination of inertial and centrifugal forces. This inertia-based collection mechanism, coupled with the short residence time (i.e., on the order of 0.2 seconds) of particles and gases in the Biosampler precludes any inadvertent trapping of gaseous co-pollutants in the particulate layer. Two different particle mass spectrometers, the Aerodyne Aerosol Mass Spectrometer (AMS) and the UC-Davis Rapid Single-particle Mass Spectrometer (RSMS-3), were to evaluate the performance of the Versatile Aerosol Concentration Enrichment System (VACES) developed by USC. The RSMS-3 experiments were conducted as part of the U.S. EPA Supersite program in Pittsburgh during March 2002. RSMS-3 hit rate increases were measured and possible particle composition changes introduced by the VACES were examined in the single particle mass spectra. Both ambient and concentrated carbonaceous and ammonium nitrate composition distributions were indistinguishable with RSMS-3 suggesting that VACES introduces an insignificant artifact for those particles (Zhao, et al., 2005). The effect of concentrating semi-volatile aerosols using the VACES and the Aerodyne AMS during measurements of ambient aerosol in Pittsburgh, PA was also investigated. It was found that the shape of the sulfate mass-weighted size distribution was approximately preserved during passage through the concentrator for all the experiments performed, with a mass enhancement factor of about 10 to 20 depending on the experiment. The size distributions of organics, ammonium and nitrate were preserved on a relatively clean day (sulfate concentration around $7 \mu\text{g}/\text{m}^3$), while during more polluted conditions the concentration of these compounds, especially nitrate, was increased at small sizes after passage through the concentrator. The amount of the extra material, however, is rather small in these experiments: between 2.4% and 7.5% of the final concentrated PM mass is due to “artifact” condensation (Khlystov, et al., 2005).

Collection of ambient particles on filters and in the biosampler, using the VACES technology, was performed concurrently with our PM physico-chemical characterization studies. Collected particles were supplied to other SCPC laboratories for *in vitro* toxicological studies, and the findings of the toxicological studies could then be interpreted in light of the physicochemical analysis results. The toxicology findings that derived from these studies are summarized elsewhere in this report. Examples include assays for redox properties of PM and studies of cellular toxicity including mitochondrial effects, in which UF were generally found to possess greater toxic properties compared to F and C. *In vivo* studies using concentrated ambient particles (CAPs) in the vicinity of freeways were also supported in part by the SCPS. A series of studies found that CAPs exposure can exacerbate airway inflammation and allergic airway responses in a sensitized mouse model, with the responses being greater for UF, especially those in close proximity (within 50 m or less) of a freeway (Kleinman, et al., 2005; Campbell, et al., 2005). Neurological inflammation and cardiovascular effects were also observed in close proximity to freeways.

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Relevant Web Sites: <http://www.scpcs.ucla.edu>