

SOUTHERN CALIFORNIA PM SUPERSITE

Progress Report for Period December 1, 2001 - March 15, 2001

United States Environmental Protection Agency

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1. Introduction

The overall objective of the Southern California PM Supersite is to conduct research and monitoring 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 suspended particulate matter (PM) in the Los Angeles Basin (LAB).

This report addresses the period from December 1, 2001 through March 15, 2001. It is divided into 10 sections, each addressing a specific research area, including an update on our Data Management report. Furthermore, a major portion of the information included in this report has been either submitted or accepted for publication in peer-reviewed journals. Below is a list of manuscripts either submitted or accepted for publication which were produced through the Southern California Supersite funds and in which the EPA Supersite program has been acknowledged:

Publications

1. Misra, C., Geller, M., Sioutas, C and Solomon P. "Development and evaluation of a continuous coarse particle monitor". *Journal of Air and Waste Management Association*, 51:1309-1317, 2001
2. Geller, M.D., Kim, S. Misra, C., Sioutas, C., Olson, B.A and Marple, V.A. "Methodology for measuring size-dependent chemical composition of ultrafine particles" *Aerosol Science and Technology*, accepted for publication, October 2001
3. Misra, C., Kim S., Shen S. and Sioutas C. "Design and evaluation of a high-flow rate, very low pressure drop impactor for separation and collection of fine from ultrafine particles". *Journal of Aerosol Science*, accepted for publication, October 2001
4. Zhu, Y., Hinds, W.C., Kim, S and Sioutas, C. "Concentration and Size Distribution of Ultrafine Particles near a Major Highway". *Journal of Air and Waste Management Association*, accepted for publication, September, 2001

5. Singh, M., Jaques, P. and Sioutas, C. "Particle-bound metals in source and receptor sites of the Los Angeles Basin". Manuscript submitted to *Atmospheric Environment*, September, 2001.
6. Kim, S., Shi, S., Zhu, Y., Hinds, W.C., and Sioutas, C. "Size Distribution, Diurnal and Seasonal Trends of Ultrafine Particles in Source and Receptor Sites of the Los Angeles Basin". *Journal of Air and Waste Management Association*, 52:174-185, 2002
7. Eiguren, A, Miguel, A.H, Jaques, P. and Sioutas, C. "Evaluation of a Denuder-MOUDI-PUF Sampling System to Determine the Size Distribution of Semivolatile Polycyclic Aromatic Hydrocarbons in the Atmosphere". Manuscript submitted to *Aerosol Science and Technology*, January 2002.
8. Shen, S., Zhu, Y., Jaques PA and Sioutas C. "Evaluation of the SMPS-APS system as a Continuous Monitor for PM_{2.5} and PM₁₀". Submitted to *Atmospheric Environment*, February , 2002
9. Zhu, Y., Hinds, W.C., Kim, S., Shen, S. and Sioutas, C. "Study on Ultrafine Particles and other Vehicular Pollutants near a Busy Highway". *Atmospheric Environment*. Submitted, January 2001

2. PIU Sampling Location and Status

A key feature of our Supersite activities has been in the ability to conduct state-of-the-art measurements of the physicochemical characteristic of PM in different locations of the Los Angeles Basin (LAB). We originally proposed a 2.5-year repeating cycle of measurements at five locations. Each location is sampled during a period of intense photo-chemistry (defined approximately as May – October) and low photochemical activity (defined as the period between November – April). During this period, we deployed the Particle Instrumentation Unit (PIU) to Claremont, our fourth sampling site, on September 12, 2001. Sampling at Claremont commenced during the fourth week of September, and has continued through the winter of 2002. We have completed most of the chemical speciation analysis for integrated samples collected in that location through this February. We have continued to make size-segregated on-line measurements of particulate nitrate using the Integrated Collection and Vaporization System (ICVS) developed by Aerosol Dynamics Inc. (ADI), and have made measurements with the newer prototype ICVS Carbon monitor – of which the results will be presented in the next progress report.

Additionally, we have continued to make our mobile particle trailer available for co-located exposure studies at Claremont. The following health studies have been supported by the Supersite measurements:

1. In vitro studies undertaken by Drs. Andre Nel and Arthur Cho (UCLA) and Robert Devlin (US EPA) investigating the hypotheses that organic constituents associated with PM, including quinones, other organic compounds (PAHs, nitro-PAHs, and aldehydes/ketones) and metals, are capable of generating reactive oxygen species (ROS) and acting as electrophilic agents. These are ongoing studies.
2. Animal inhalation toxicology studies using Concentrated Ambient Particulates (CAP) investigating the hypotheses that atmospheric chemistry is important in the toxicity of PM and co-pollutants, airway injury and cardiovascular effects will be greater at receptor sites downwind of source sites along the mobile source trajectory in the Los Angeles basin. These studies are led by Drs. Harkema (University of Michigan), Kleinman (UC Irvine), Froines and Nel (UCLA). These co-located studies have taken place during the late summer season at Claremont, and during the Winter months of January and February 2002.

3. Time Integrated Size Fractioned Chemical Speciation for Rubidoux & Claremont

Introduction

Our current sampling scheme involves the use of three MOUDIs for 24-hour averages: size-fractionated measurements of ambient and concentrated PM mass and chemical composition. Sampling is conducted once a week, on a Tuesday, Wednesday or Thursday, in order to coincide with one of the sampling days of the AQMD speciation network (which takes place every 3rd day). However, this schedule is flexible to be adjusted for our “intensive” particulate characterization studies and/or for our support of co-located health effects exposure studies. Typically, ambient data are averaged over 24 hours (midnight to midnight), whereas for exposure or source contribution measurements, the time integrals may vary, depending on the requirements of the specific study.

In each run, consistent with our original Supersite proposal, we have used three collocated Micro-Orifice Uniform Deposit Impactors (MOUDI). In slight modification of the original protocol, an additional (0.56 um cut) impactor was included on December – largely to match the size fractionation of the ICVS Nitrate and Carbon monitors. The inclusion of this impactor adds a finer resolution to the size distribution, and results in six PM size ranges:

- <0.1 μm (ultrafine particles)
- 0.1- 0.32 μm (accumulation mode, “condensation” sub-mode)
- 0.32 – 0.56 μm (accumulation mode, “droplet” sub-mode)
- 0.56 – 1.0 μm (accumulation mode, “droplet” sub-mode)
- 1.0 – 2.5 (“intermediate” mode)
- 2.5-10 μm (coarse particles)

In addition to mass concentration, the following chemical components have been analyzed within these size groups:

- a. inorganic ions (i.e., sulfate, nitrate, ammonium), analyzed by ion chromatography (Dionex)
- b. trace elements and metals, analyzed by XRF
- c. elemental and organic carbon (EC/OC) content, analyzed by thermal optical
- d. concentrations of polycyclic aromatic hydrocarbons (PAH)

One of the major objectives of the Supersite is to investigate the physiochemical differences between PM source and receptor locations within the Los Angeles basin. Normally, “condensation” particle growth occurs rapidly, and Downey, which is immediately downwind of the 710 Freeway, has the greatest heavy engine diesel truck traffic density in Los Angeles (about 30 to 40% of total vehicles, at any time of day), while the Riverside and Rubidoux sites do not, and are 40-50 miles downwind of downtown LA. Under these conditions, it may be expected that ultrafine particles emitted at the freeway source grow to the condensation sub-mode, measured at Downey, while the larger particles (droplet sub-mode, and coarse mode) at Riverside and Rubidoux are from different sources. Claremont is along the “Vehicle Trajectory”, but about 3-5 miles north into the San Gabriel Mountain foothills, where the predominant winds may blow into from the West-South-West. The Vehicle Trajectory is a mobile source particulate plume, in contrast to the Long Beach–Rubidoux Nitrate trajectory. The Nitrate trajectory travels predominantly Northeast from Long Beach, carrying NO_x emissions that mix with ammonia gas generated by the Mira Loma dairy farms. NH₄NO₃-associated particles are generated during photochemistry, and carried to, first, Rubidoux, and further downwind to Riverside. Rubidoux has historically had the highest measurements of nitrate particulate in the south coast basin, and is nearest (about 3-5 miles north) to the NH₃ source.

Results

Size-segregated PM₁₀ mass and chemical composition data from MOUDI and Partisol measurements are presented. Included are results from Downey, Riverside, and Rubidoux (i.e., previously presented in the August-November 2001 Supersite Quarterly Report) to compare trends with the presently reported status of Claremont. Filter samples are mass and chemically speciated, in part, to: determine the source receptor trajectory profile, and to provide information for other Supersite related health studies within the SCPCS and for the NARSTO archives. Figures 1 to 3 present MOUDI collected mass concentrations, by chemical group, for the four sites. On average, much higher levels of PM₁₀ OC have been measured in Downey (about 17 $\mu\text{g}/\text{m}^3$), compared to about 9 $\mu\text{g}/\text{m}^3$ in Riverside and Rubidoux, and 8 $\mu\text{g}/\text{m}^3$ in Claremont. In

contrast, PM₁₀ NH₄NO₃ levels are predominantly greater in Rubidoux (14 ug/m³), lesser in Riverside (9 ug/m³) and Claremont (8 ug/m³), and least in Downey (5 ug/m³). This is expected, as Rubidoux is immediately downwind of a dairy farm, while Riverside is also, but further east by about 5-7 miles. The results also show that OC dominates all other chemical species in the PM 1 fraction in Downey, while NH₄NO₃ dominates the droplet sub-mode at Riverside and Rubidoux.

The size distribution for total chemical mass is bimodal for all sites, with the condensation sub-mode predominating in Downey, where in Riverside, Rubidoux, and Claremont, the droplet sub-mode is the most predominant. Within the Fine PM fraction: 1) at Downey, OC dominates other species in its contribution to the condensation mode; 2) at Riverside and Claremont, NH₄NO₃ and OC similarly contribute to the droplet mode; and 3) at Rubidoux, NH₄NO₃ is the primary contributor to the droplet mode. All 4 sites also have a coarse mode, dominated by metal oxides, but in much greater concentrations in Riverside (7 ug/m³) and Rubidoux (14 ug/m³). The metals at Downey (~5 ug/m³) are primarily from locally re-suspended road dust, and those at Riverside and Rubidoux are mostly alkali (*see previous report*), and are from locally suspended soil. Since Riverside and Rubidoux are in the desert environment, it is expected that they may be higher. In addition, Rubidoux is much greater than Riverside, very likely, because these measurements took place while the PIU was located at Riverside in the late winter and spring, while it was at Rubidoux throughout the dry summer months.

The [presence of a substantial amount of nitrate in the 1-2.5 μm mode may be due in part to some agglomerated aged NH₄NO₃-associated particles, but also to sodium nitrate particles that represent a tail of the sodium nitrate-rich coarse PM mode (see Figure 3). In addition, OC increases in predominance from more than 50% of all chemical groups in the condensation mode to about 70% in the ultrafine fraction. Metals predominate in the coarse mode, attributing about 40% of all groups. As presented in Figure 4, the most (if not all) metals are found in the supermicrometer range except of Ni, Sn and Ba that have 30-35% of their mass in the submicron mode. Figure 2b presents the chemical size separated mass balance for Claremont. The sum of all chemical groups is 95% of the total measured mass for PM 2.5, and 98%, 82%, and 84% for the intermediate, droplet, and condensation modes, respectively. However, the coarse mode is underestimated at 41% and the ultrafine mode is overestimated at 240%. For the coarse mode, metals may be present in their oxide form, which is not what is measured by XRF, thus uncertainties associated with this conversion may explain some of the discordance between mass and chemical speciation balances. For ultrafine PM, we believe that adsorption of gas-phase organic vapors on the MOUDI after-filter explains the higher OC concentrations hence higher mass determined by summing all chemical species. Figure 5 presents a scatter plot of the Partisol versus the MOUDI measurements of PM 2.5 mass in Claremont. The two instruments were highly correlated (R-Sq = 0.910), and nearly 1 to 1 (m = 1.15), with the MOUDI 15% greater than the Partisol – on average. For PM_{2.5}, this suggests that the 2 instruments may be used interchangeably, and also suggests a relatively high level of accuracy in the Fine mass measurements.

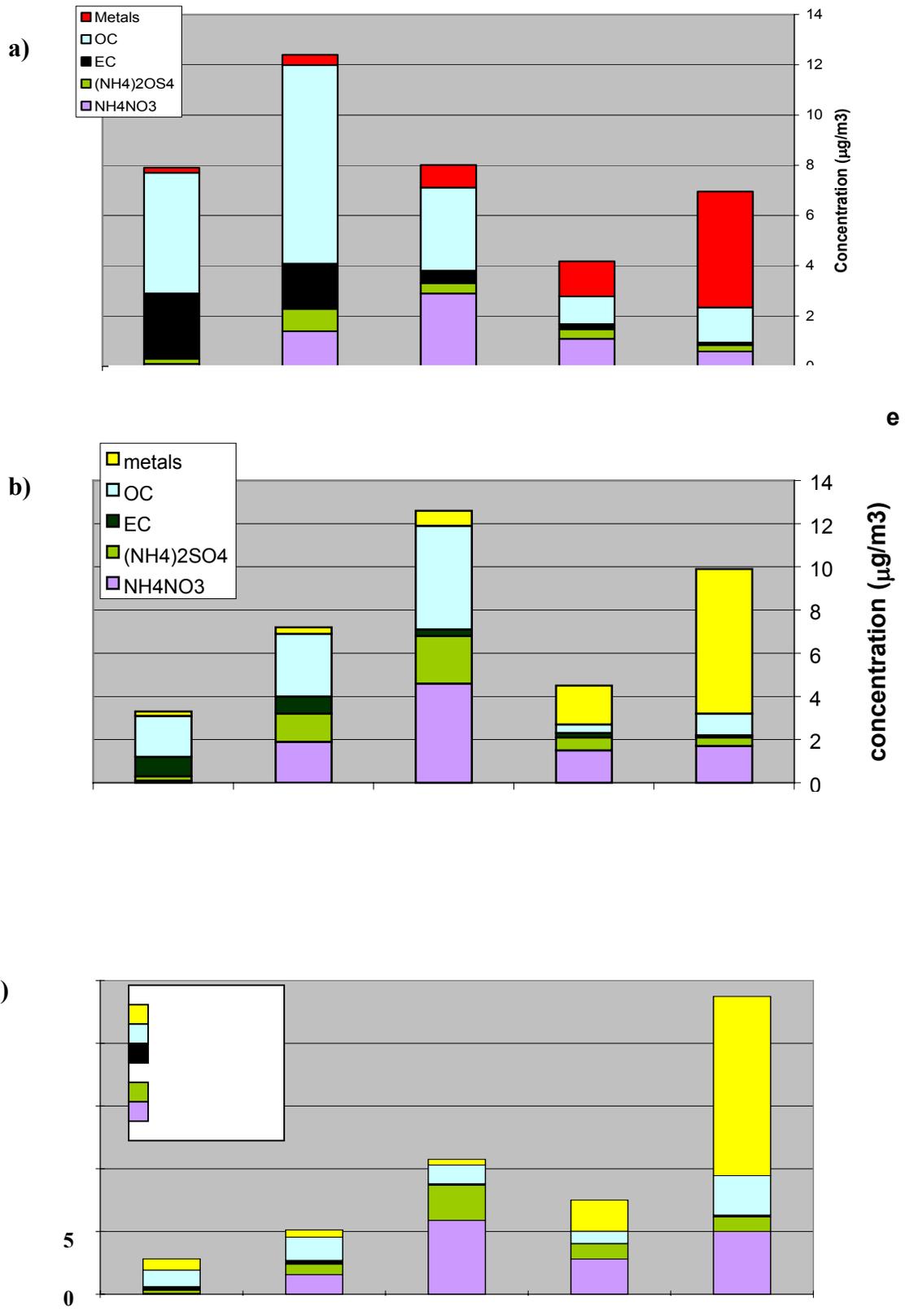


Figure 1. Geometric means of 24-hour averaged size distributions of size speciated chemical mass, measured by the MOUDI at: a) Downey; b) Riverside; and c) Rubidoux.

MOUDI Size Fractionated Mass, Claremont (Sept 2001 - Feb 2002)

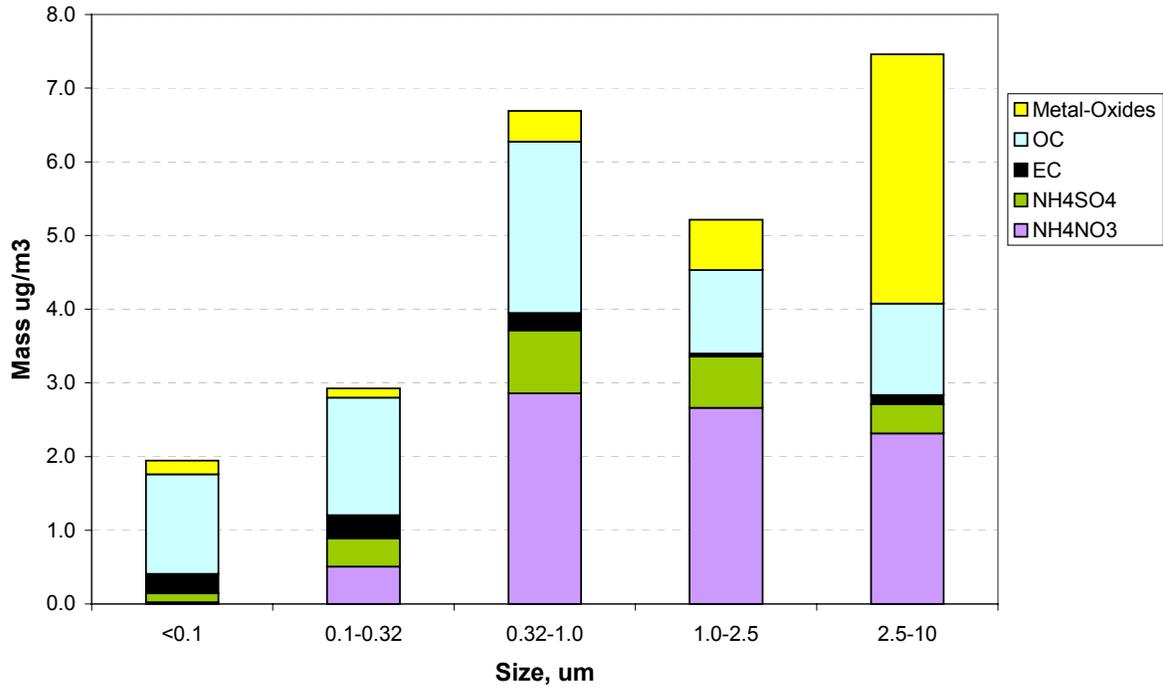


Figure 2. Chemical and mass size segregated concentrations for Claremont by MOUDI and coarse PM mass by Partisol (September 2001 to February 2002).

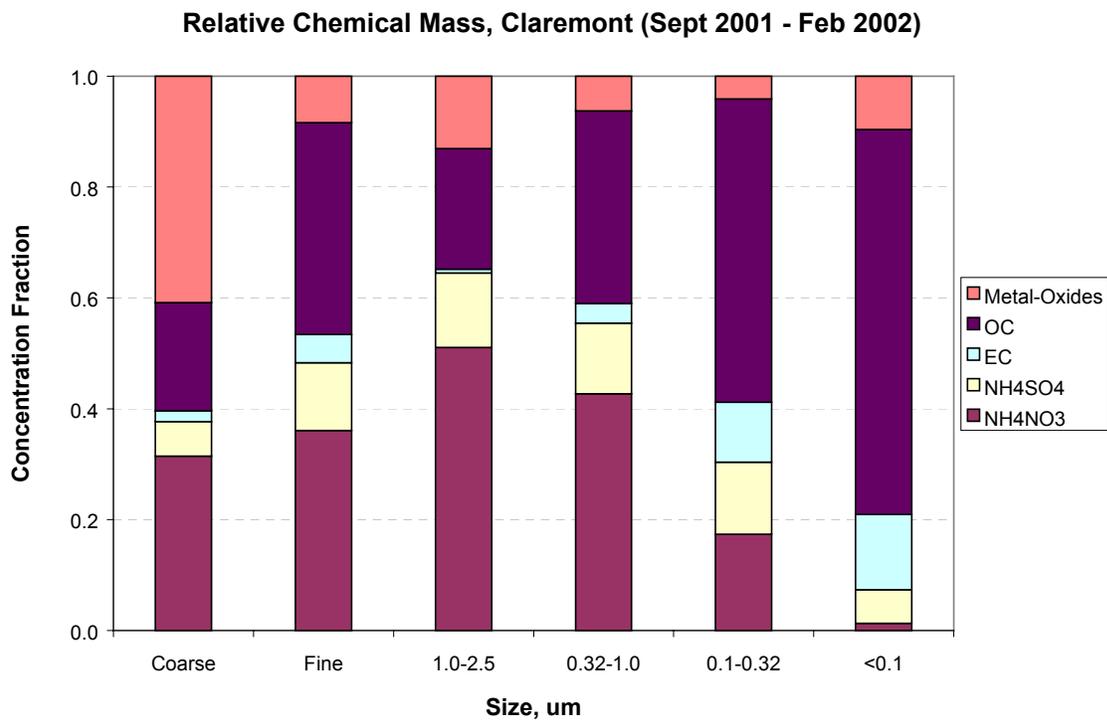


Figure 3. Relative Chemical and Mass Size Segregated concentrations for Claremont by MOUDI and Coarse PM mass by Partisol (September 2001 to February 2002).

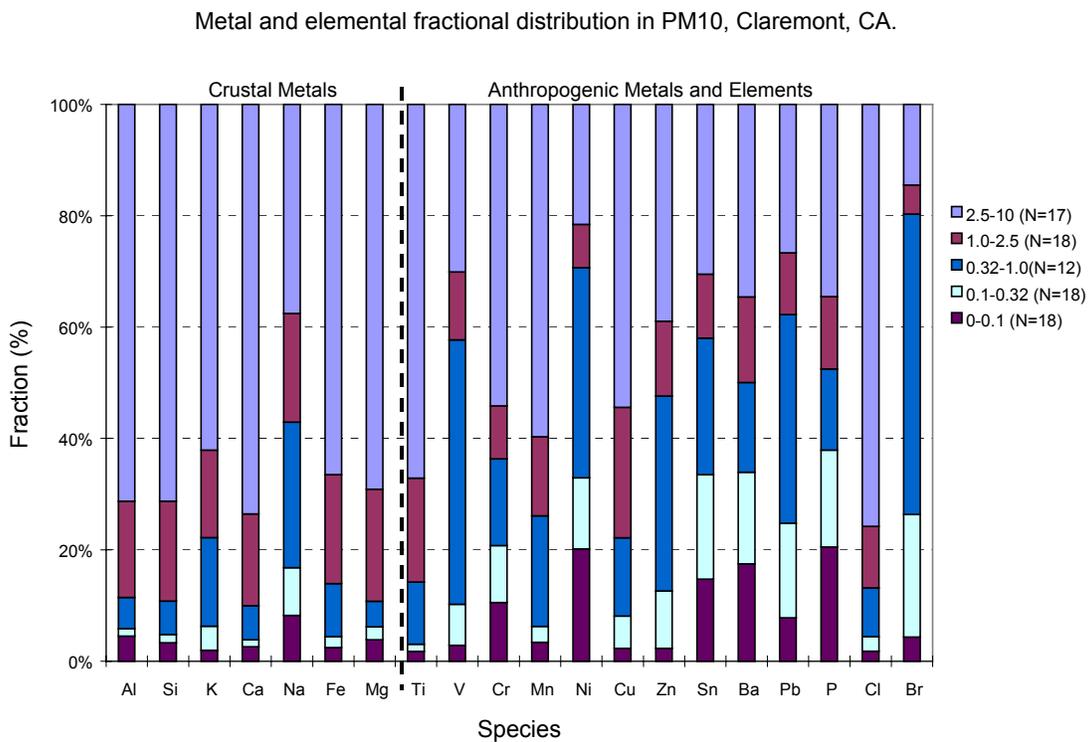


Figure 4. Metals species: a) Crustal; and b) Anthropogenic.

Fine Particulate Mass by MOUDI and Partisol at Clarmemont, 9/01 - 2/02

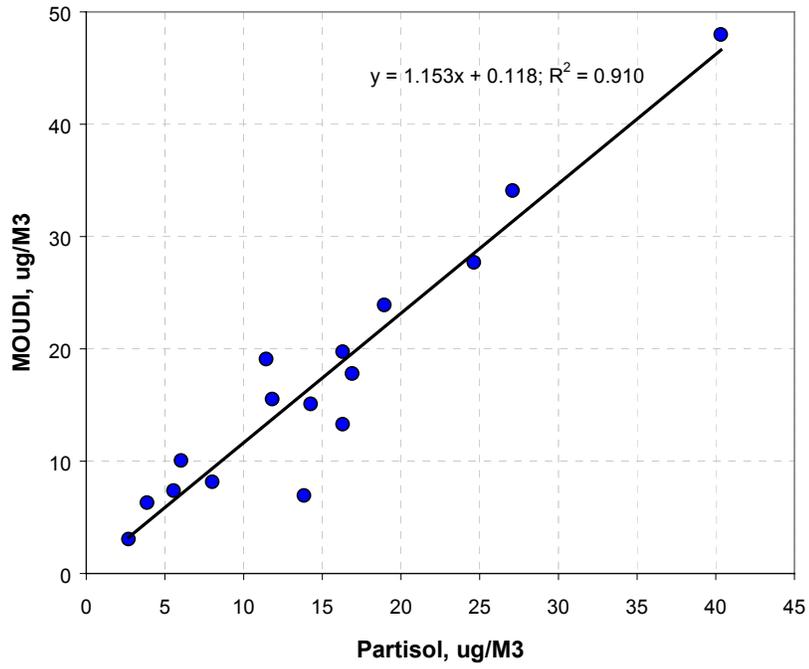


Figure 5. Partisol and MOUDI paired measurements for PM2.5 at Claremont (N=16).

4. Intensive Inter-lab Comparison Summer Study at Rubidoux

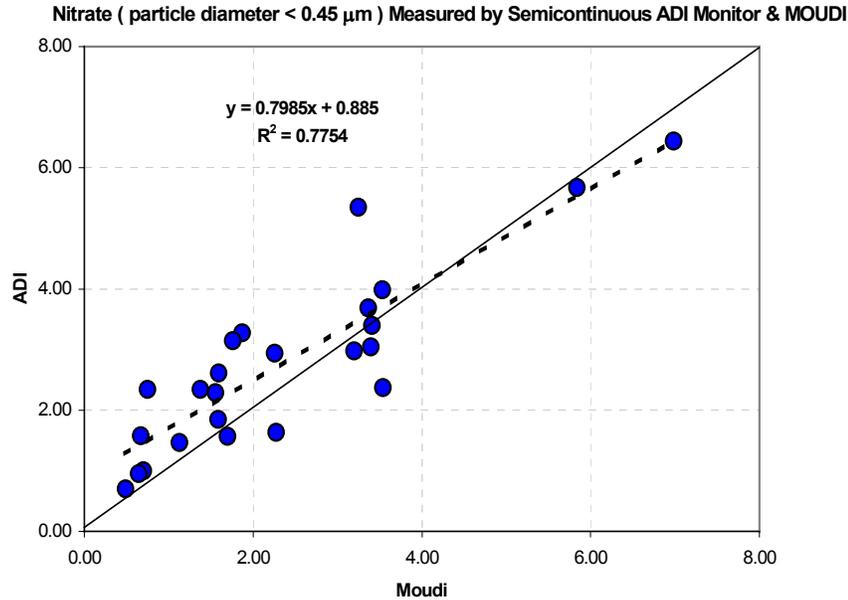
Over a three-week period in August and September of 2001, several continuous, semi-continuous, and time-integrated fine particle samplers were deployed. The L.A. Supersite collected time-integrated data from a Partisol FRM sampler, a single stage MOUDI impactor and a HEADS sampler, and continuous data from a tandem SMPS-APS system and an Integrated Collection and Vaporization System (ICVS) Size-Fractionated Continuous Fine Particle Nitrate Monitor. The New York Supersite team collected data from a Continuous Aerosol Mass Monitor (CAMM), a Real-time Ambient Mass Sampler (RAMS), two nephelometers (one with a dryer and one without), a 30°C TEOM, and a semi-continuous EC/OC carbon analyzer. R and P Inc. measured semi-continuous mass using two pairs of prototype TEOMS that are designed to measure non-artifact mass.

Data from the continuous and semi-continuous instruments were averaged over four daily time-integrated periods corresponding to the bulk time-integrated measurements. Comparisons between instrument measurements were made for fine particle mass, nitrate, and elemental, organic and total carbon. The data collected by the L.A. Supersite has been provided to Dr. Philip Hopke (Clarkson University), and Jeff Ambs of R and P to undertake the second phase of data analysis and evaluate the instrument performance.

5. ADI-ICVS Size-Fractionated Continuous Fine Particle Nitrate Monitor

Results for size-fractionated fine particle nitrate concentrations measured by the ADI-ICVS continuous monitor were compared to the size-fractionated nitrate results from MOUDI samples and PM_{2.5} nitrate measured on HEADS filters. Several time-integrated 4 to 10 hour MOUDI and HEADS samples were collected in late July and early August of 2001 in Rubidoux. ADI data was averaged across these time periods and compared to the MOUDI data for each size fraction. The sum of nitrate concentrations measured by the three ADI size bins was used for comparison to the HEADS data. In addition to these sub-daily time-integrated samples, 24-hour MOUDI and HEADS samples from Claremont collected from late September 2001 through late January 2002 were also included in the comparisons to the ADI monitor.

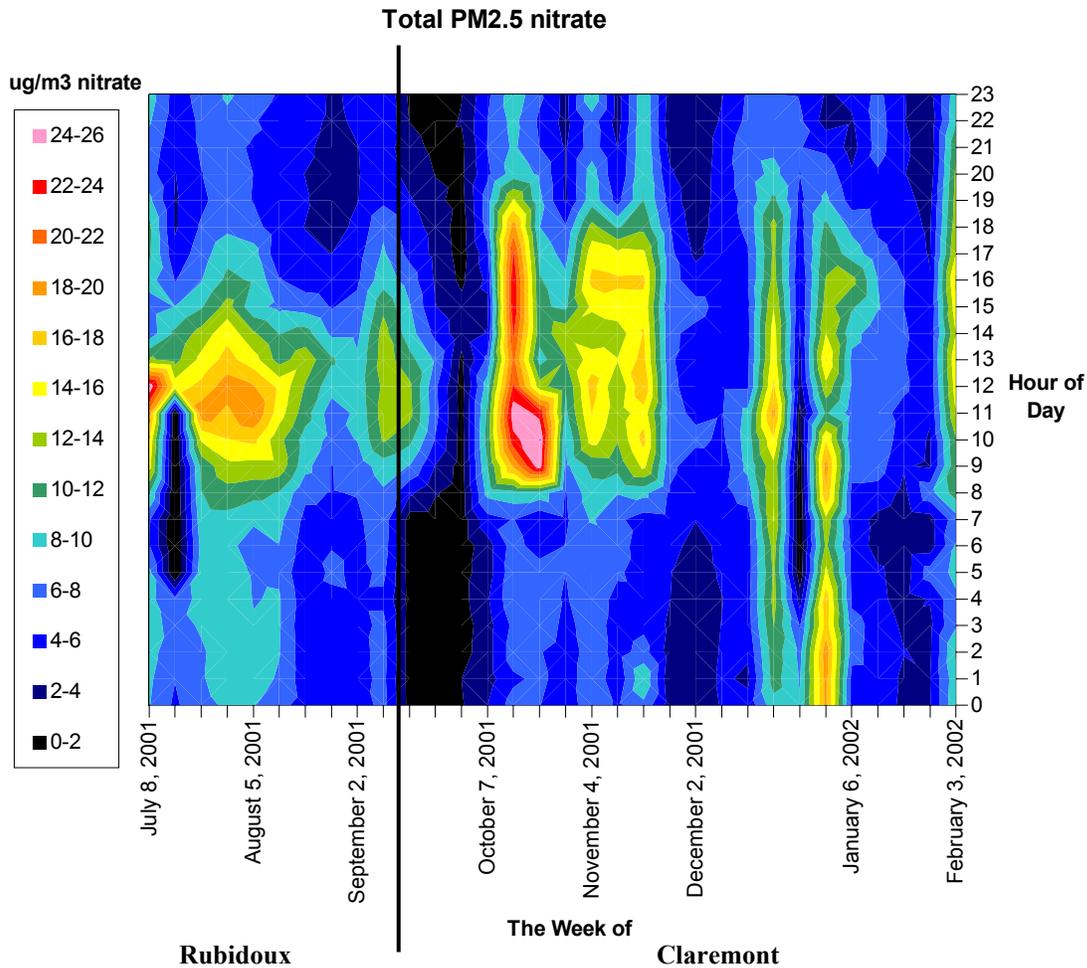
The following chart shows an example of the correlation found between the MOUDI and the ADI monitor for particle with diameters less than 0.45 μm . Good agreement was found with an R^2 of 0.78.



The other two size ranges (0.45 - 1.0 μm and 1.0 – 2.5 μm) also showed reasonable agreement between ADI and MOUDI results. The following table summarizes the results of the intercomparison by providing the geometric mean of the ratios between nitrate measurements from the different methods.

Instruments Compared	Particle Size Range (μm)	Geometric Mean (± SD)	p-value
ADI vs HEADS	PM_{2.5}	0.92 (± 0.29)	0.17
MOUDI vs HEADS	PM_{2.5}	0.59 (± 0.19)	<0.001
ADI vs MOUDI	1-2.5	1.04 (±0.18)	0.37
ADI vs MOUDI	0.45 – 1.0	1.44 (± 0.88)	0.03
ADI vs MOUDI	0.1 – 0.45	1.28 (± 0.25)	0.01

The continuous size-segregated nitrate data provided by the ADI monitor also shows the potential of the instrument in identifying atmospheric phenomenon relating to particulate nitrate. The following chart displays the weekly-averaged diurnal cycles of PM_{2.5} nitrate concentrations in Rubidoux and Claremont. Ten-minute ADI data was averaged hourly and then averaged by hour of the day across each week.



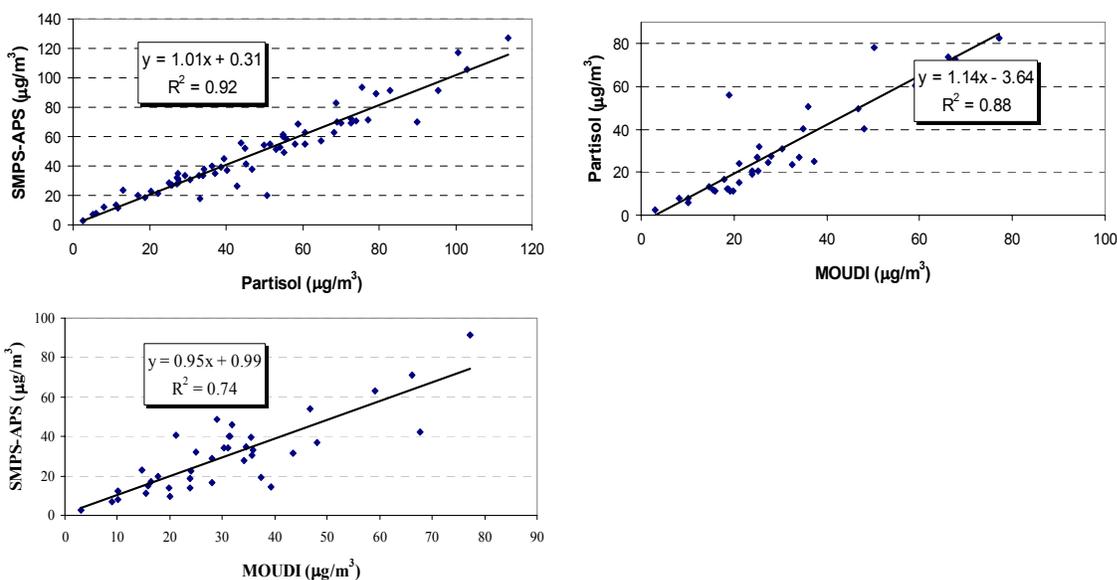
Daily midday nitrate peaks are seen in Rubidoux and a second afternoon nitrate peak appears for several of the weeks in Claremont. During the colder winter months, the nitrate peaks are less sharp and particulate nitrate is spread out more evenly throughout the day. Size-fractionated data from the ADI monitor reveals the contribution to the overall particulate nitrate from particles of different sizes. For example, coarser particles (1.0-2.5 μm) were less important for the nitrate peaks observed in Rubidoux than for the Claremont nitrate peaks in October. The midday peak in October at Claremont has more of a contribution of finer particles ($< 0.45 \mu\text{m}$) than the afternoon peak of the same week. The accumulation mode aerosol nitrate (0.45 – 1.0 μm) shows much sharper daily maxima than the finer size nitrate, which tends to be more spread out throughout the day. Such differences between nitrate concentrations among different particle sizes will help to identify the atmospheric conditions, primary sources, and secondary reactions which lead to particulate nitrate formation over the course of the day and the year.

6. SMPS-APS Comparison with Mass Monitors.

The purpose of this work is to compare the Scanning Mobility Particle Sizer and the Aerodynamic Particle Sizer tandem (SMPS-APS) to other continuous PM measurement devices. This system has the advantage over other continuous mass monitors of generating mass concentrations at discrete size intervals near-continuously. The instruments used for comparison in this study include DataRAM nephelometer, Micro-Orifice Uniform Deposit Impactor (MOUDI), and Partisol Dichotomous Sampler.

During the period of this study, measurements were conducted at four sites for about four to five months each, across separate seasons. From October 2000 – February 2001, sampling was done in Downey, a typical urban site in south central Los Angeles impacted mostly by primary vehicular emissions. From mid-February through June 2001, sampling was conducted in Riverside, from July to August 2001 in Rubidoux, and from September through December 2001 in Claremont. Riverside, Rubidoux and Claremont are receptor areas of the eastern inland valleys of the basin, in which the aerosol plume generated by the millions of vehicles, mostly west of downtown Los Angeles, is advected by the predominant westerly winds after aging for several hours to a day. Rubidoux and Riverside (unlike Claremont) also lie downwind of significant ammonia emissions from nearby farming and livestock, which results in high concentrations of ammonium nitrate.

The time-integrated fine particle mass concentrations determined with the semi-continuous SMPS-APS system are compared to those measured gravimetrically by the MOUDI and Partisol are shown in Figure 1.



The geometric average $\text{PM}_{2.5}$ ratios of SMPS-APS to Partisol and MOUDI are $1.04 (\pm 0.11)$ and $0.93 (\pm 0.33)$, respectively. The SMPS-APS concentrations are also highly correlated with both Partisol and MOUDI data: the R^2 for the SMPS-APS vs. the Partisol is 0.92; for the SMPS-APS vs. the MOUDI is 0.74 [The MOUDI-Partisol concentrations are also highly correlated, with $R^2 = 0.88$].

Hourly PM_{2.5} mass concentration measured by the SMPS-APS against those measured by the DataRAM is plotted in figure 2. Overall, there is high correlation between the two instruments ($R^2=0.88$). However, the DataRAM overestimates the SMPS-APS PM_{2.5} mass by a factor of 2.2 (± 0.34). There are several reasons which could attribute to the observation. First, the concentration readings of DataRAM increase when the relative humidity of the ambient environment increases due to the condensational growth of hygroscopic PM components as well as additional light scattering by water vapor. DataRAM's performance also depends strongly on the mass median diameter (MMD) of the ambient particle distribution. As evident from the data plotted in figure 3, the DataRAM-to-Partisol ratio increases with particle size, reaches a maximum in the 0.7 to 0.85 μm range, and subsequently decreases with further increase in MMD.

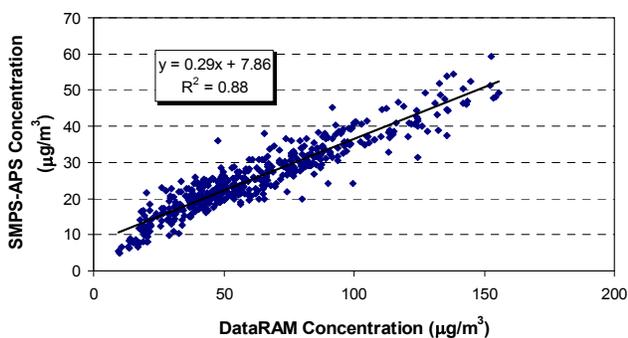


Fig 2. SMPS-APS concentration vs. DataRAM concentration for PM_{2.5}.

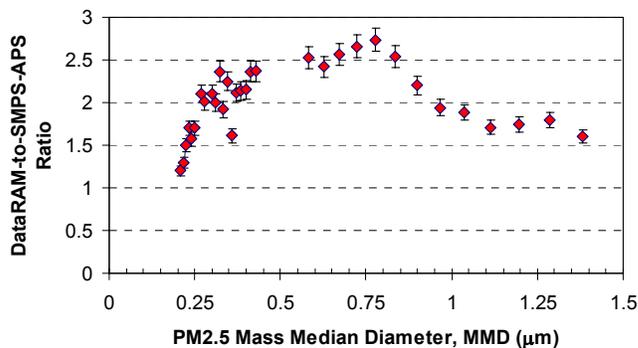


Fig 3. PM_{2.5} DataRAM-to-SMPS-APS ratio as a function of the mass median diameter estimated using SMPS-APS measurements.

The SMPS-APS PM₁₀ mass concentrations are compared to those of the Partisol in figure 4. The agreement between the two instruments is still very good but not as consistent as that observed for the PM_{2.5} concentrations. The geometric average ratio of the SMPS-APS to Partisol concentration was 0.96 (± 0.21). However, the degree of correlation (R^2) decreases from 0.92 to 0.80. This is primarily due to the influence of the coarse PM (PM_{2.5-10}) measurements of the APS.

Figure 5 presents a comparison between coarse (PM_{2.5-10}) particle mass concentration measured by the APS and the Partisol. A weak correlation was found between the instruments ($R^2 = 0.28$). Although the average ratio of APS to Partisol concentrations was 0.92 (± 0.64), both the relatively large standard deviation of this ratio as well as the weak correlation between the data indicate that there is considerable scatter in the overall agreement between APS and gravimetrically determined concentrations. Further analysis of our data was conducted to investigate whether the APS to gravimetric ratio is dependent on particle size. Coarse PM measured by the APS was divided into 16 size intervals of equal logarithmic length. Results from this analysis are shown in Figure 6, in which the APS-to-Partisol mass concentrations ratio is plotted against the mass median diameter (MMD) of the coarse PM mode. This ratio increases as the MMD increases from about 4 to 5.5 μm and reaches a maximum of about 1.6 for

a mass median diameter between 5 to 5.5 μm . The APS to Partisol ratio subsequently decreases sharply to levels below 1 as the MMD exceeds 6 μm .

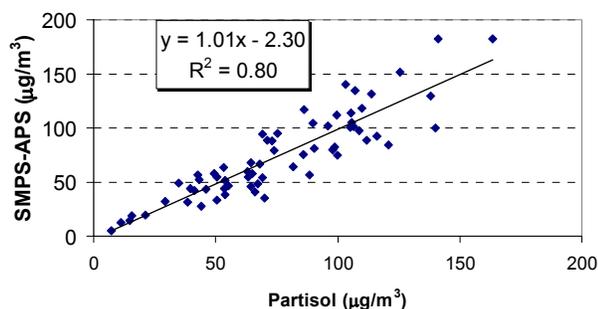


Fig 4. PM_{10} mass concentration comparison between SMPS-APS and Partisol.

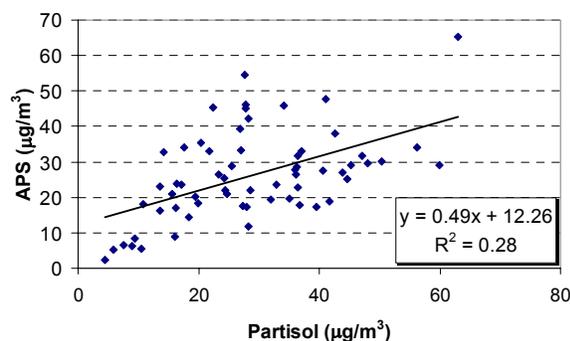


Fig 5. Partisol vs. APS coarse particle mass concentration comparison.

There are several possible explanations for the observed trend. Previous studies have found that artificial particle counts creates distortion of the APS size distribution for particles larger than approximately $5\mu\text{m}$. This causes overestimations of the true mass concentration by the APS. It was also observed in previous studies that the counting efficiency of the APS 3320 decreases from losses of larger particles, particles larger than $5\mu\text{m}$, inside the APS due to settling and impaction. For particles larger than $6\mu\text{m}$, internal APS particle losses apparently are high enough to compensate for the added mass associated with the artificial particle counts as indicated by Figure 6.

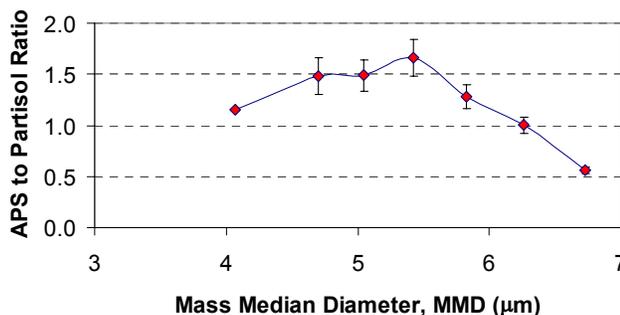


Fig 6. Partisol to APS ratio for coarse particles ($\text{PM}_{2.5-10}$) as a function of mass median diameter.

Figure 7 shows a size-fractionated comparison between the SMPS-APS and the MOUDI mass concentrations. With the exception of ultrafine particles (i.e., below $0.1\mu\text{m}$) the data appear well-correlated, with R^2 varying from 0.62 to 0.65. Very good overall agreement between the SMPS-APS and MOUDI was obtained for the concentration of particles in the ranges of 0.32-1.0 and 1.0-2.5 μm , with the average SMPS-APS to MOUDI concentration ratio being $0.95 (\pm 0.24)$ and $0.94 (\pm 0.22)$, respectively. The relative scatter in the data is probably due to variations in the chemical composition of each sub-mode and in each sampling location, which would affect the validity of the assumption that particle density is 1.6 g cm^{-3} across all size ranges and all sampling sites. The overall agreement between SMPS-APS and MOUDI is excellent considering the assumptions made. Paired t-tests between the SMPS-APS and MOUDI

concentrations for the size ranges of 1 – 2.5 and 0.32 – 1.0 μm indicate that these concentrations are not significantly different ($p=0.46$ and $p=0.48$, respectively).

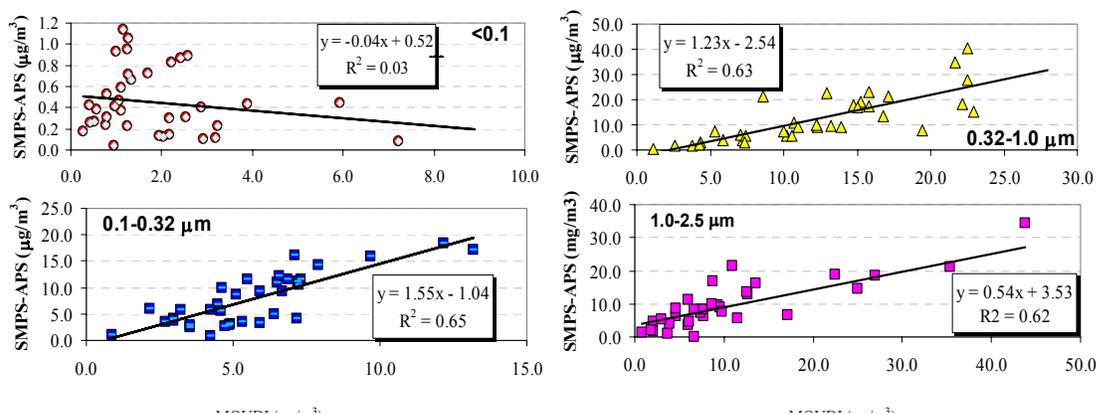


Fig 7. Size fractionated mass concentration comparison of SMPS-APS and MOUDI

Statistically significant differences, however, were observed between the concentrations of SMPS and MOUDI for the 0.1 – 0.32 and $<0.1 \mu\text{m}$ ranges ($p < 0.001$ for both ranges). SMPS concentrations are on average 1.37 (± 0.35) times higher than those of the MOUDI for the 0.1-0.32 μm range, whereas the SMPS concentrations are lower than those of the MOUDI for the ultrafine PM mode, 0.39 (± 0.18). The differences between SMPS and MOUDI for smaller particles may be due to the effect of shape and density of local vehicular emissions on the measurement of particle mobility by the SMPS, resulting in its underestimation of ultrafine PM mass relative to the MOUDI. Additionally, particle bounce may occur at the lower stages of the MOUDI, and thus explain the MOUDI mass concentration being lower than the SMPS in the accumulation mode but higher in the ultrafine mode.

While the coarse particle concentration measured by the APS may be biased due to sampling errors, our experiments showed that as a continuous $\text{PM}_{2.5}$ size selective mass monitor, the SMPS-APS is reliable and also offers several advantages over other continuous and time-integrated monitors. Notably, it is not subject to the potentially wide range of sampling, handling, and analysis errors to which filter-based mass measurements of PM are prone. Also, other semi-continuous mass monitors do not have the ability to simultaneously measure particle mass at selected sizes. Thus, the SMPS-APS system may be useful and convenient for source apportionment and health-based studies.

7. Evaluation of a Denuder-MOUDI-PUF Sampling System to Determine the Size Distribution of Semivolatile Polycyclic Aromatic Hydrocarbons in the Atmosphere

Summary of the results and conclusions of a field study that was submitted for publication to *Aerosol Science and Technology*, Jan 2002 (Fernandez A.E., Miguel A. H., Jaques P.A., and Sioutas C.)

Summary

The study describes a field comparison conducted between two methods employing different MOUDI impactor configurations to evaluate their performance in sampling and measurement of the size distribution of fifteen US EPA “priority pollutant” polycyclic aromatic hydrocarbons (PAH). A series of field experiments were conducted in two of the Southern California Particle Center and Supersite (SCPCS) sampling sites located in the Los Angeles basin: Downey, near Central Los Angeles, and Rubidoux, in the inland eastern valleys of the basin, located about 60 km downwind of Central Los Angeles. Samples were collected during 24-hr periods approximately every 7th day, beginning at 8:00 AM, in two different sites of the Los Angeles Basin. One site was near Central Los Angeles in an area impacted by high vehicular traffic, whereas the other site was located about 60 km downwind of central Los Angeles (receptor site). Particle samples from about 42 m³ of air were collected using collocated MOUDI impactors and classified in three aerodynamic diameter size intervals: 0-0.18 µm (ultrafine mode I), 0.18-2.5 µm (accumulation mode II), and 2.5-10 µm (coarse mode III). One MOUDI operated in the conventional mode; the other with a vapor trapping system that included an XAD-4 coated annular denuder placed upstream of the impactor, and a polyurethane foam plug (PUF) placed in series behind the impactor. PAH were separated and quantified by HPLC with fluorescence detection optimized for the highest sensitivity. The results showed that, for both sites, the size distribution obtained using either system are similar for the less volatile PAH ($\log [p^{\circ}L] < -3$), but different for the semivolatile species. Mean total particle-phase PAH mass concentrations collected with the regular MOUDI were 16 to 20% higher. The Junge-Pankow PAH gas-particle partitioning model fitted best when the vapor phase fraction was considered as the sum of PAH collected with the denuder plus the PUF, and the particle-phase the fraction collected on the impactor substrates. In the central Los Angeles site, the largest PAH fraction was found in the 0-0.18 µm (mode I) size range, typical of primary emissions. At the downwind location, the largest fraction was in the 0.18-2.5 µm (mode II) size range, consistent with an “aged” aerosol.

Conclusions

We have examined the effects of a denuder placed upstream of a MOUDI impactor on the size distributions of 15 priority pollutant PAH, including both semivolatile and particle-bound species, collected near Central LA and at a downwind location. Consistent with literature data, the percentage of PAHs found in the particle-phase increases with decreasing vapor pressure. Particle-bound fractions found in the Downey and the Rubidoux samples agree reasonably well with the values predicted by the Junge-Pankow model. The use of a denuder upstream of a MOUDI does not significantly affect the size distribution shape and form of the less volatile PAH ($\log [p^{\circ}L] < -3$). The fraction of PAH mass in the coarse mode increased with increasing PAH vapor pressure. The strongest effect of the denuder on the size distribution was seen for the

more volatile PAH collected at the downwind site. PAH size distributions measured with the regular MOUDI configuration peaked in the 0-0.18 μm size range (mode I) in samples collected in central Los Angeles, and in the 0.18-2.5 μm size range (mode II) at the downwind receptor site. PAH with $\log[p_L^\circ]$ values >-2.1 (NAP, ACE, FLU, PHE, ANT, PYR, and FLT) were $>90\%$ associated with the vapor phase. Finally, the ΣPAH concentrations found in the 3-stages using the regular MOUDI were, on average, 16 to 20% higher compared with the denuder configuration. We believe that this difference is due to a negative artifact with the denuded MOUDI configuration. In either case, the total PAH mass differences are relatively small when considering chemical analysis and sampling errors.

8. Characterization of PAH and PAH-Derivatives

The goal of our sampling is to characterize the polycyclic aromatic hydrocarbons (PAHs) and PAH-derivatives present at sites chosen to represent source sites or downwind receptor sites and to investigate the atmospheric chemistry occurring at these sites during different seasons. As part of the goal of sampling and characterizing the PAH-derivatives, such as nitro-PAHs, which are the result of atmospheric chemical reactions of the parent PAHs, we analyzed samples from the source site of Downey, CA and nighttime samples from Riverside, CA. Two types of samples were collected to span the range of volatility of the nitro-PAH: polyurethane foam (PUF) samples for gas-phase nitro-PAH and filter samples for particle-associated nitro-PAH such as 1-nitropyrene and 2-nitrofluoranthene. The samples at the downwind, receptor site at Riverside were collected on nights following days of elevated afternoon ozone in an attempt to isolate nitro-PAHs formed from nighttime NO_3 radical chemistry.

In the last progress report, we reported on the particle-adsorbed nitro-PAH of molecular weight 247, i.e., the nitrofluoranthenes and nitropyrenes. 2-Nitrofluoranthene was the most abundant of the four-ring nitro-PAH at both sites and the concentrations measured were comparable. Notable at Riverside was the lack of detectable nitropyrenes. The nondetectable 1-nitropyrene is consistent with dilution occurring at this downwind site, while the lack of 2-nitropyrene suggests that the observed 2-nitrofluoranthene was formed from NO_3 radical-initiated chemistry. We report here on the analysis of the semi-volatile nitro-PAH, in particular the methylnitronaphthalenes, which can be used as a "marker" to distinguish the occurrence of NO_3 radical-initiated chemistry from the more commonly occurring OH radical-initiated nitro-PAH formation.

Listed in the table below are the concentrations (pg/m^3) of the gas-phase nitro-PAH measured in the PUF plug samples: 1-nitronaphthalene (1-NN), 2-nitronaphthalene (2-NN), 2-methyl-1-nitronaphthalene (2M1NN), 2-methyl-4-nitronaphthalene (2M4NN) and 1-methyl-6-nitronaphthalene (1M6NN). Also shown for comparison are the previously reported concentrations of 2-nitrofluoranthene (2-NF) measured from filter samples.

Gas-phase nitro-PAH concentrations (pg/m^3) and 2-nitrofluoranthene.

Downey	1-NN	2-NN	2M1NN	2M4NN	1M6NN	Ratio ^a	2-NF
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Day composite	72	555	1	14	36	0.4	90
Night composite	77	965	n.d.	14	23	0.6	72
Riverside							
8/18/01 night	92	199	5	22	20	1.4	52
8/25/01 night	190	191	13	51	33	1.9	50
8/26/01 night	315	368	16	58	34	2.2	79

^aRatio calculated: $(2M1NN + 2M4NN)/1M6NN$

Downstream of the main PUF plug sample, a thinner PUF wafer was placed to check for breakthrough. Breakthrough of the nitronaphthalenes clearly occurred at both Downey and Riverside, and the nitronaphthalenes concentrations should not be regarded as quantitative. No breakthrough of the methylnitronaphthalenes was observed.

As noted in our previous report, the directly-emitted nitro-PAH 1-nitropyrene was observed at Downey, but not at Riverside. Our experience with diesel emissions, which are a major source at Downey, was that twice as much 2-NN as 1-NN was emitted and no methylnitronaphthalenes were detected (Final Report to California Air Resources Board Contract No. 94-312, June, 1998). Therefore, the very high 2-NN relative to 1-NN measured at Downey is puzzling and this result should be confirmed by additional analyses.

Since methylnitronaphthalenes are not expected from diesel emissions and the methylnitronaphthalene profile formed as a result of OH radical-initiated reactions of 1- and 2-methylnaphthalene is distinct from that formed from NO₃ radical-initiated reaction of the methylnaphthalenes, certain methylnitronaphthalene ratios can be used as markers of the chemistry forming them. In particular, 2M1NN and 2M4NN are formed in higher abundance in the NO₃ radical reaction, while 1M6NN is a dominant product in the OH radical-initiated reactions. Therefore, the "Ratio" shown in the table of $(2M1NN + 2M4NN)/1M6NN$ will be higher for air masses having undergone nighttime NO₃ radical chemistry. This ratio is clearly higher for the Riverside samples in comparison with the Downey samples. The ratio is highest for the night of 8/26/01 at Riverside, consistent with the higher 2-nitrofluoranthene on this night relative to other Riverside nights.

2-Nitrofluoranthene is formed in high yield from the NO₃ radical-initiated reaction of fluoranthene and the detection of 2-NF, but not 2-nitropyrene at Riverside, was previously interpreted as indicating NO₃ radical formation of the 2-NF. Thus the occurrence of nighttime NO₃ radical chemistry at Riverside is supported from data on the gas-phase methylnitronaphthalenes, as well as data on the particle-associated 2-NF measured at Riverside.

Future Work

Under other funding, we have started to investigate the formation of dimethylnitronaphthalenes from the NO₃ radical-initiated reactions of dimethylnaphthalenes and of volatilized diesel-fuel PAHs. Preliminary results suggest that the nitro-PAH formed (m.w. 201) from reaction of the volatilized diesel fuel-derived PAH are also present in ambient samples where nighttime NO₃ chemistry occurred. As these nitro-PAH are identified from environmental chamber reactions, their presence in the Riverside ambient air samples will be investigated.

9. Ultrafine Particles near 710 Freeway

It is now well established that increases in the concentration of fine particulate matter in urban areas are associated with increases in morbidity and mortality. It is not known what properties of fine particulate matter cause these effects, but one candidate is ultrafine particles. These are particles less than 100 nm or 0.1 μm in size and are found near combustion sources, such as motor vehicles. Previously we conducted a systematic ultrafine particle study near one of the busiest freeways in the Los Angeles basin, Interstate 405. Traffic on that freeway was dominated by gasoline-powered cars and light trucks, with less than 5% of vehicles being heavy-duty diesel trucks. In the U.S., spark ignition vehicles usually account for most of the vehicles operating on highways. However, since diesel vehicles emit more particulate matter on a fleet average, gram-per-vehicle mile mass basis (Kittelson et al., 2001), and that diesel engine exhaust has been proposed as carcinogen in animals and probably carcinogenic for humans (IARC, 1989), it is necessary and timely to conduct a comprehensive study of ultrafine particles in the vicinity of a diesel vehicle dominated freeway. Thus, the aim of the present research is to systematically evaluate ultrafine particles in the vicinity of the 710 freeway in the Los Angeles basin, a freeway where more than 25% of vehicles are heavy-duty diesel trucks. The results from the current study are compared to these by Zhu et al., (2002) which were obtained near the 405 freeway.

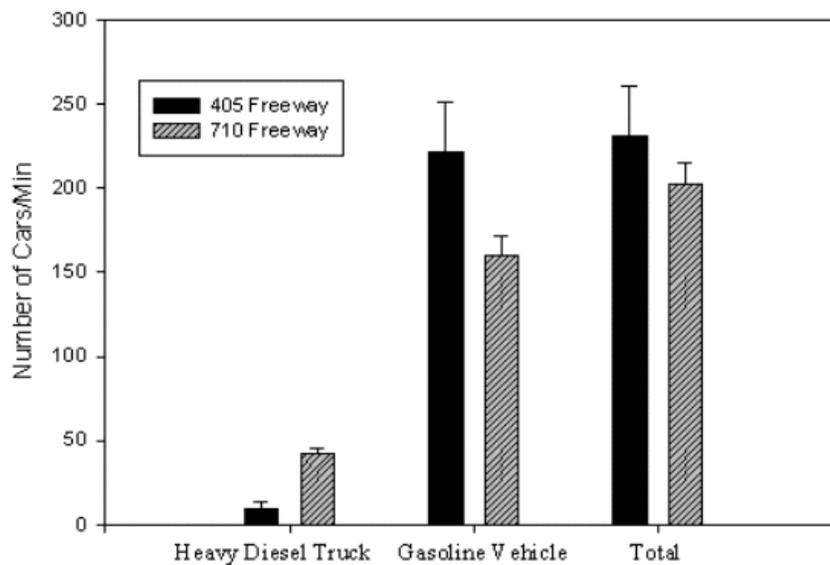


Figure 1. Traffic Volume Comparison for Different Locations near the 710 freeway.

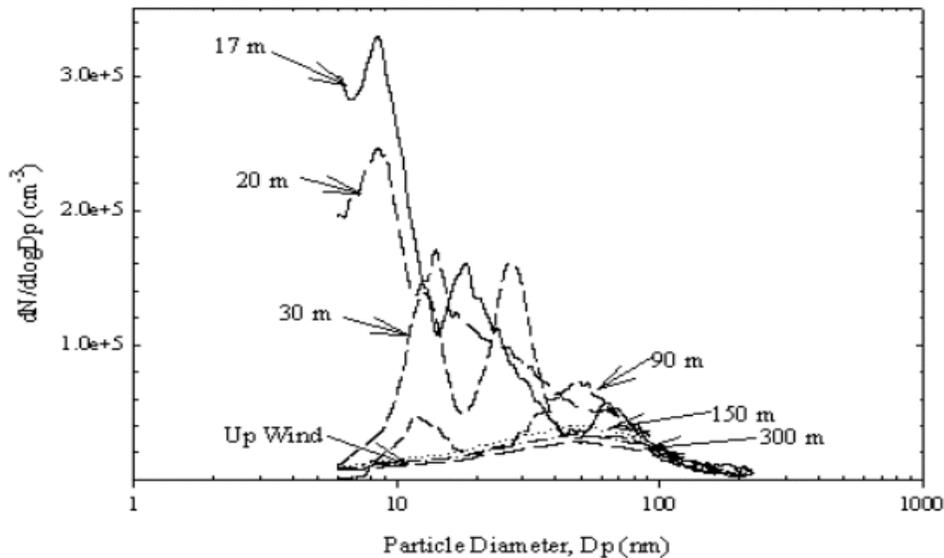


Figure 2. Ultrafine Particle Size Distribution at 405 and 710 freeways.

Figure 1 compares the traffic volume on both the 405 and the 710 freeways. Error bars represent one standard deviation. It is seen that the 710 freeway has about 7 times as many diesel vehicles and 70% of gasoline vehicles as the 405 freeway. The total vehicle numbers on both freeways are quite similar 12180 versus 13900/hour for the 405 freeway.

Particle number concentration and size distribution in the size range from 6 nm to 220 nm were measured by a condensation particle counter (CPC) and a scanning mobility particle spectrometer (SMPS). Measurements were taken at 17 m, 20 m, 30 m, 90 m, 150 m, 300 m downwind and 200 m upwind from Interstate highway 710. At each sampling point, the concentration of carbon monoxide, and black carbon were also measured by a Dasibi CO monitor, and an Aethalometer, respectively.

As shown in Figure 2, ultrafine particle size distribution changed markedly and its number concentration dropped dramatically with increasing distance. At the nearest sampling location, 17 m downwind from the center of the freeway, the dominant mode was around 10 nm with a modal concentration of more than $3.2 \times 10^5 / \text{cm}^3$. This mode remained at 10 nm for the second sampling location, 20 m downwind from the freeway, but its concentration dropped to $2.4 \times 10^5 / \text{cm}^3$. It shifted to larger size range and its concentration kept decreasing for farther sampling locations. This mode was not observed at distance greater than 150 m downwind from the freeway. The dramatic decrease of particle number concentration in the size range around 10 nm was likely due to atmospheric dilution and several atmospheric aerosol particle loss mechanisms that favor small particles, diffusion to surfaces, evaporation, and coagulation. The smaller the particle, the greater its diffusion coefficient and its Brownian motion. Particles of 10 nm diffuse about 80 times faster than particles of 100 nm (Hinds, 1999). As particle size gets smaller, the Kelvin effect becomes more important, making it easier for molecules to leave the particle's surface by evaporation. In addition, when two small particles collide due to their Brownian motion (coagulate), they form a bigger particle. Thus, coagulation reduces number concentrations and shifts the size distribution to larger sizes.

In Figure 2, the second mode at 17 m downwind from the freeway was around 20 nm with a concentration of $1.5 \times 10^5 / \text{cm}^3$. This mode remained at similar size range and concentration for the next sampling location, 20 m, but shifted to 30 nm at 30 m downwind from the freeway. It is of particular note that, while the concentration for the primary mode, 10 nm mode, decreased about 60% of its maximum value from 17 to 30 m with a slight shift in its mode, the 20 nm mode concentration did not change significantly but the modal size shifted noticeably. This second mode continued to shift to larger sizes with increasing distance from the freeway. In general number concentrations for smaller particles, $d_p < 50 \text{ nm}$, dropped significantly with increasing distances from the freeway, but for larger ones, $d_p > 100 \text{ nm}$, number concentrations decreased only slightly. These results are in excellent agreement with what Zhu et al., (2002) reported for freeways impacted mostly by gasoline vehicles, which suggests that coagulation is more important than atmospheric dilution for the smallest ultrafine particles and vice versa for large particles. Ultrafine particle concentrations measured at 150 and 300 m downwind of the 710 freeway were statistically within the variation of the 300 m upwind background concentration. The maximum number concentration that was observed next to the freeway was about 30 times greater than that for the background location. This suggests that people who live or work within 100 m downwind of major traffic sources, or spend a substantial amount of time commuting on such highways, will have a much higher ultrafine particle exposure than those who do not. This result can be used in epidemiological studies to estimate exposure to ultrafine particles.

The range of average concentration of CO, black carbon and total particle number concentration at 17 m was 1.9 to 2.6 ppm, 20.3 to 24.8 $\mu\text{g}/\text{m}^3$, 1.8×10^5 to $3.5 \times 10^5 / \text{cm}^3$, respectively

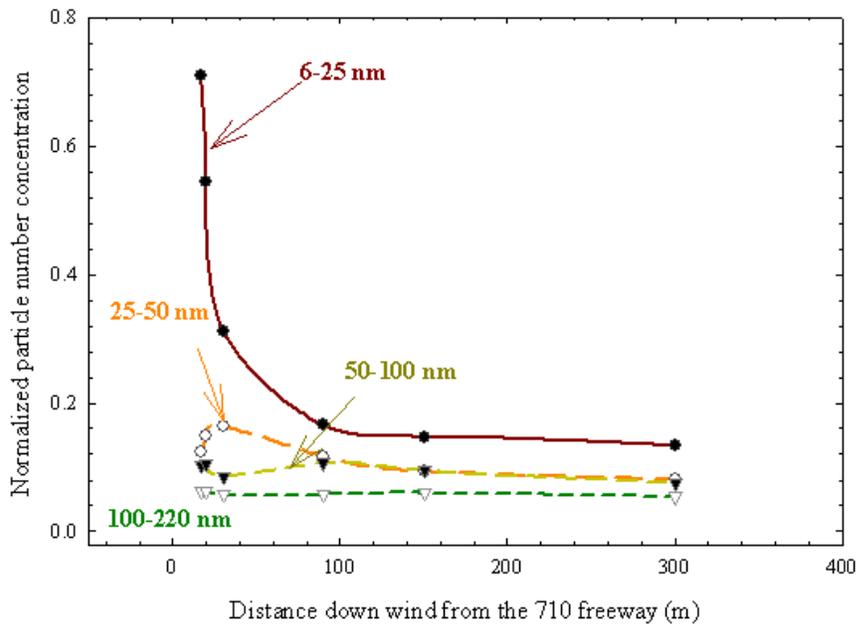


Figure 3. Ultrafine Particle number concentration in Difference Size Ranges

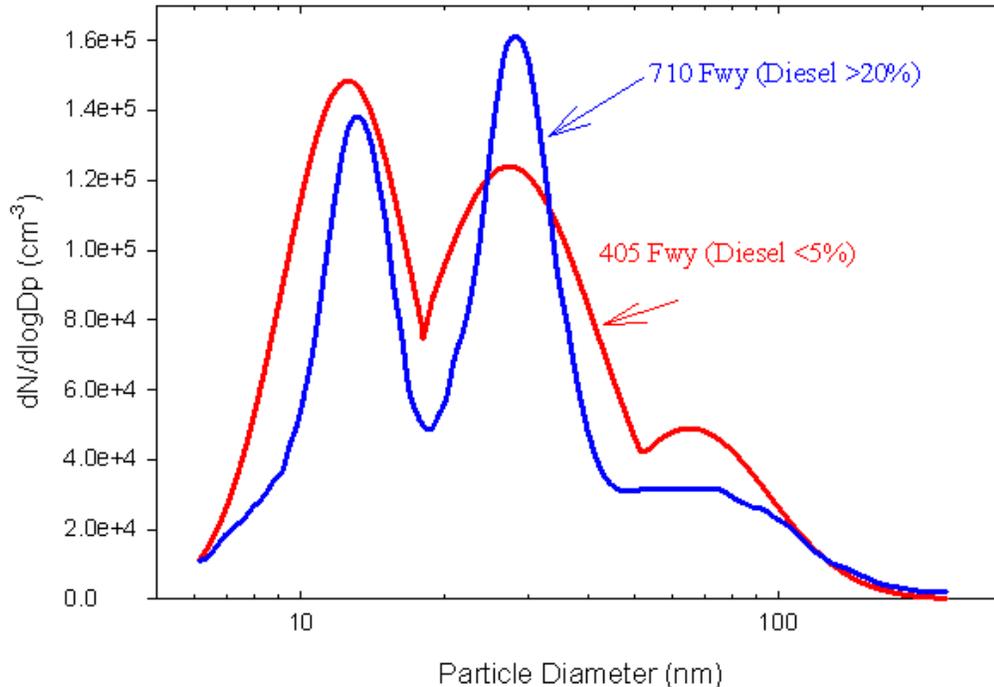
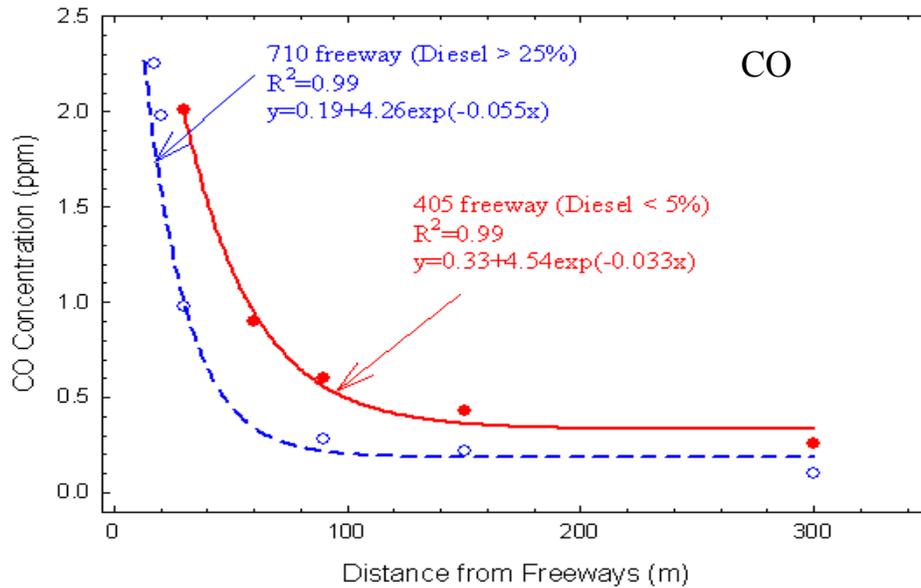


Figure 4. Comparison of Ultrafine Particle Size Distribution at 30 m downwind Locations.

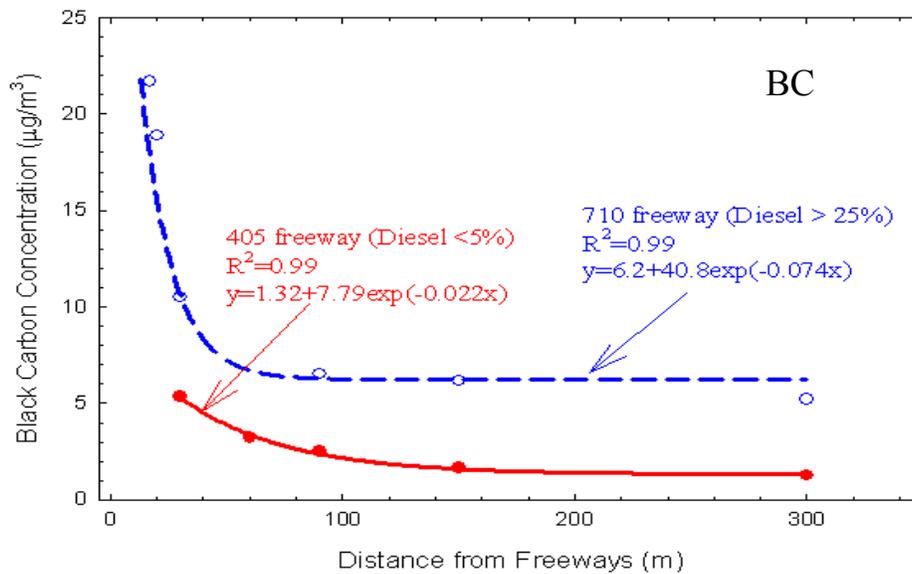
Based on Figure 2, it is clear that vehicle-emitted ultrafine particles of different size ranges behave quite differently in the atmosphere. Zhu et al., (2002) showed the decay of ultrafine particle number concentrations in four size ranges, 6-25 nm, 25-50 nm, 50-100 nm and 100-220 nm. They found coagulation played a significant role in modifying the particle size distribution of vehicle-emitted ultrafine particle downwind of a freeway. Figure 3 was prepared in the same ways as Zhu et al., (2002). The measured particle number concentrations in each SMPS size bin were combined in the corresponding size range, and the result was normalized to averaged wind speed. The general trends of sub-grouped ultrafine particle decay curves are quite comparable to those given by Zhu et al., (2002), Figures 7a-b. Total particle number concentration in the size range of 6 to 25 nm accounted for about 70% of total ultrafine particle number concentration and dropped sharply, by about 80%, at 100 m, and leveled off after 150 m. Overall, it decayed exponentially through out the whole measured distance. Number concentrations in the next two size ranges, 25-50 nm and 50-100 nm, all experienced a shoulder between 17 m and 150 m. These results are in excellent agreement with what Zhu et al., (2002) observed and can be explained by particles, in smaller size ranges, coagulating with these particles to increase their size.

Figure 4 compares the ultrafine particle size distributions at 30 m downwind from the 710 and the 405 freeways. In Figure 4, both size distributions have three distinct modes. The

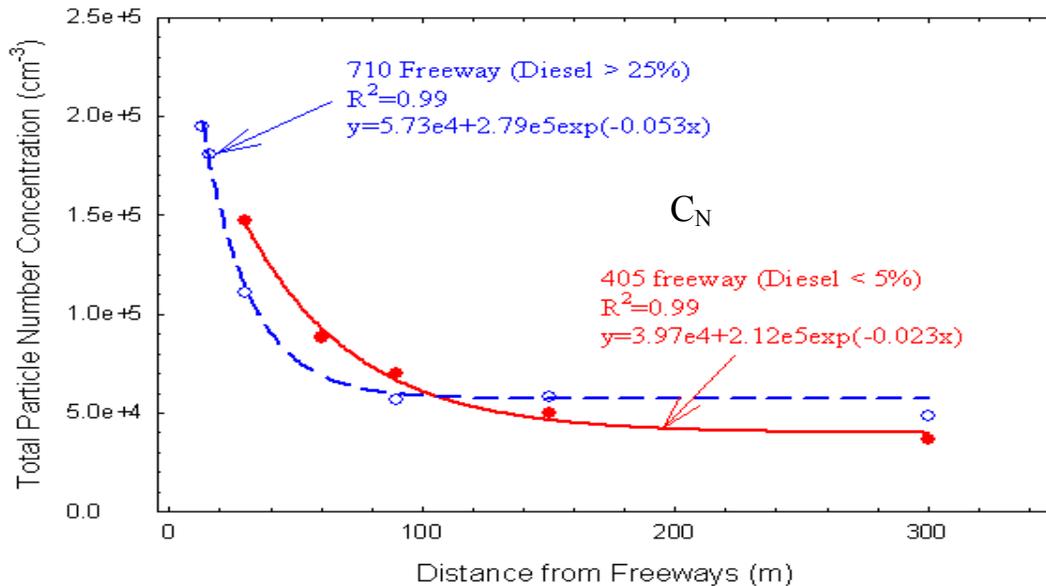
concentration for the first mode, in between 10 to 20 nm, is slightly higher near the 405 freeway. This mode is similar to that previously reported for direct laboratory measurement of gasoline vehicle emissions. The concentration for the second mode, around 30 nm, is about 30% higher near the 710 freeway than that near the 405 freeway. This is likely due to the much higher diesel emissions on the 710 freeway. The last mode, around 70 nm, represents an insignificant contribution to number concentrations for these two freeways and in both cases are comparable to the background concentrations.



a. CO Concentration



b. Black Carbon Concentration



c. Particle Number Concentration

Figure 5. Decay curves of (a) CO (b) Black Carbon and (c) Particle number concentration near the 405 and 710 freeway.

Figures 5 a to c were prepared by comparing the decay characteristic of CO, black carbon and particle number concentrations near the 405, gasoline vehicle dominated, and the 710, diesel vehicle dominated, freeways. Exponential decay was found to be a good estimator for predicting total particle number concentrations at different locations (Zhu et al., 2002). Each data point in the figure represents an averaged value for all measurements with similar wind directions. The solid line was the best fitting exponential decay curve, determined using SigmaPlot 2000 nonlinear curve fitting procedure. The best fitting exponential decay equations and R-square values are also given in the figure. It can be seen, in general, all three pollutants decay at a similar rate near both freeways. This implies that atmospheric dilution plays a comparable role in both studies. As discussed previously, the average wind speed for these two studies are all close to 1.5 m/s. The discrepancies of the curves were mainly due to the different traffic fleet compositions on these two freeways. The 710 freeway has more than 25% heavy diesel trucks while the 405 freeway has less than 5%. It is well known that diesel engines emit less carbon monoxide and more black carbon comparing to spark ignition engines (Kittelson 2001). Figure 5 a shows that the concentration of CO near the 710 freeway is generally half of that near the 405 freeway. By comparison, Figure 5 b shows the black carbon concentration near a diesel vehicle dominated freeway is more than three times greater than that near a gasoline vehicle dominated freeway. As shown in Figure 5 c, the total particle number concentration close to the 405 freeway is somewhat higher than that near the 710 freeway, but drops faster with downwind distance. Since the rate of coagulation increases with decreasing particle size down to 20 nm

(Hinds 1999), the observed result is consistent with gasoline vehicles emitting more of the smallest ultrafine particles, mostly in nano-size range. It should be also noted that the exponential decay characteristic appears to extend to about 3 m downwind from the edge of the freeway for all three pollutants. Based on our results we conclude that atmospheric dilution is so rapid that pollutant's concentration decays continuously after leaving the tailpipe.

10. A High Flow Rate, Very Low Pressure Drop Impactor For Inertial Separation Of Ultrafine From Accumulation Mode Particles

Through the development of new instrumentation activities funded by the Southern California Superiste, we designed and evaluated a high-volume, low pressure drop separator-collector of accumulation and ultrafine mode particles. The USC ultrafine PM impactor has been developed primarily as a separator of ultrafine from accumulation mode particles for use in human exposure studies to concentrated ambient ultrafine aerosols, by removing the accumulation PM from the ambient air sample prior to concentration enrichment. Ultrafine particles penetrating the impactor can either be directly supplied to exposure chambers, or collected on standard, commercially available, 20 x 25.4 cm quartz or Teflon filters. High-volume collection of size-fractionated PM accomplished by this impactor further enables investigators in the field of environmental health to conduct toxicological studies using ambient accumulation and ultrafine mode particles *in vitro* as well as by means of intratracheal instillation. It also allows chemical speciation of ultrafine PM in time intervals of few hours or less in order to better understand their sources and formation mechanism.

The ultrafine PM separator is a multiple rectangular (slit) geometry jet conventional impactor that can be used to separate ultrafine from accumulation mode particles at high flow rates (550 LPM) and under a very low-pressure drop (i.e., 8 inches of H₂O or 0.020 kPa). These two features are extremely important in making human exposures to concentrated atmospheric ultrafine aerosols possible, as these exposures require that the concentrated aerosol is supplied to the exposure chamber at a much higher flow than the typical human breathing rate (12-30 l min⁻¹) and at near-atmospheric pressure. The key feature of this technique is the utilization of a multiple slit nozzle conventional impactor with a small 50% cutpoint (0.15 μm) to sample atmospheric particulate pollutants at high flow rates. Particles larger than 0.15 μm in diameter are collected on narrow strips (12.5 cm x 0.254 cm), which serve as the impaction substrate.

The ultrafine high-volume, low cutpoint impactor, shown in Figures 1 a-c, is a very compact and light weight (2.3 kg) conventional impactor made of aluminum. Its outside dimensions are 17 cm x 17 cm x 2.54 cm. Because of its very low pressure drop (0.020 kPa) the impactor can be operated using a relatively small pump (GAST 2067, 0.75 kW, Gast Corp., Benton Harbor, MI) operating at 110 V, single phase, thus does not require a large blower or a three-phase circuit. If removal of the coarse PM mode (i.e., 2.5 – 10 μm) is desired prior to separation of the accumulation from the ultrafine modes, the impactor's inlet has been made such that it can be connected directly to a commercially available high-volume virtual impactor (HVVI Model 340, MSP Corp., Minneapolis, MN) developed by Marple *et al.* (1990). The impactor consists of four different parts as shown in Figure 1. The inlet block (Figure 1a) has a circular opening, 5.08 cm in inside diameter. After entering through the inlet, the aerosol stream is accelerated by passing

through the 10 parallel slit nozzles, each 12.5 cm long by 0.0125 cm wide. The average jet velocity in each rectangular jet is approximately 5800 cm s^{-1} . Following acceleration, particles larger than approximately $0.15 \text{ }\mu\text{m}$ impact upon the collection substrates on the collecting blocks, while the aerosol fraction smaller than $0.15 \text{ }\mu\text{m}$ penetrates through the outlet of the impactor.

Particle collection efficiency on uncoated substrate surfaces was investigated using three different substrates, viz., a double-sided tape (3M Corp, St. Paul, MN), a quartz filter substrate (Tissuquartz, Pall Gelman, Ann Arbor, MI), and the original uncoated aluminum surface of the impactor. Laboratory generated ammonium sulfate aerosols and polystyrene latex particles (PSL, Bangs Laboratories Inc., Fisher, IN) were used for characterization of these substrates.

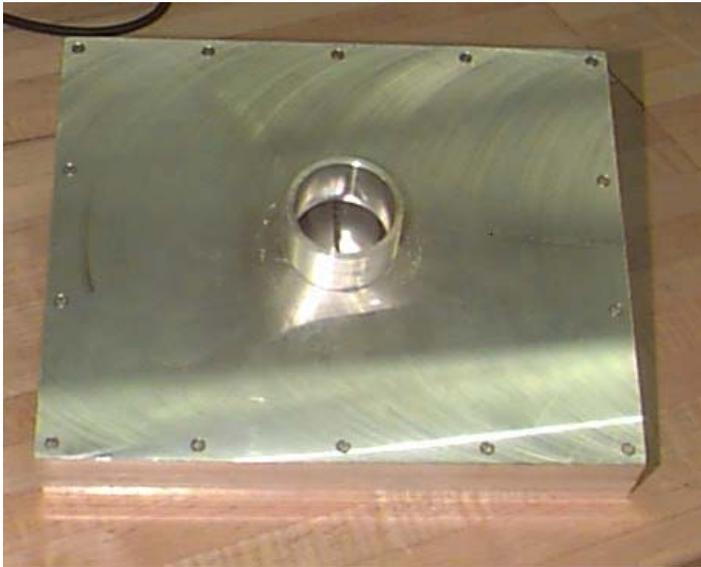


Figure 1 a: Inlet



Figure 1 b: Rectangular slits acceleration block



Figure 1c : Collection block

The data plotted in Figure 2 clearly illustrate the superiority of the quartz substrate used as the impaction surface. The increased collection efficiency observed for smaller particles could be attributed to partial entrainment of the impinging air streamlines into the upper layers of the quartz substrate fibers, which would tend to cause capture of particles somewhat smaller than the impactor's actual cutpoint. For particles larger than about $0.2 \mu\text{m}$, the very high collection efficiency observed for the quartz substrates is clearly due to the elimination of particle bounce. The experimental data plotted in Figure 2 show that the 50% cutpoint of the USC ultrafine impactor is approximately at $0.15 \mu\text{m}$, corresponding to a $\sqrt{\text{St}}$ of 0.42. Figure 3 shows a plot of the particle collection efficiency as a function of particle size using different types of test aerosols and the uncoated quartz filter strips as the impaction substrate. The data plotted in Figure 3 indicate that the particle collection efficiency obtained for ammonium nitrate particles is practically identical to that observed for non-volatile ammonium sulfate and the real-life indoor air particles, which comprise mostly of hydrophobic compounds such as organic and elemental carbon. These results suggest that particle properties such as hygroscopicity and volatility do not seem to affect the degree to which these particles would be captured by the impactor.

Figure 2. Evaluation of the USC High Volume Low Cutpoint Impactor With Different Surfaces as Impaction Substrates

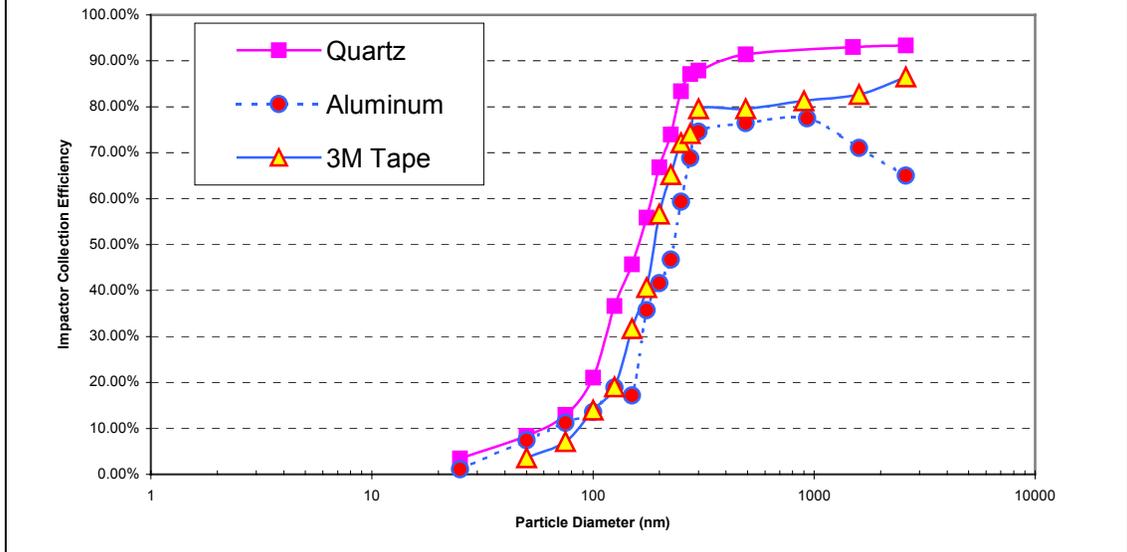
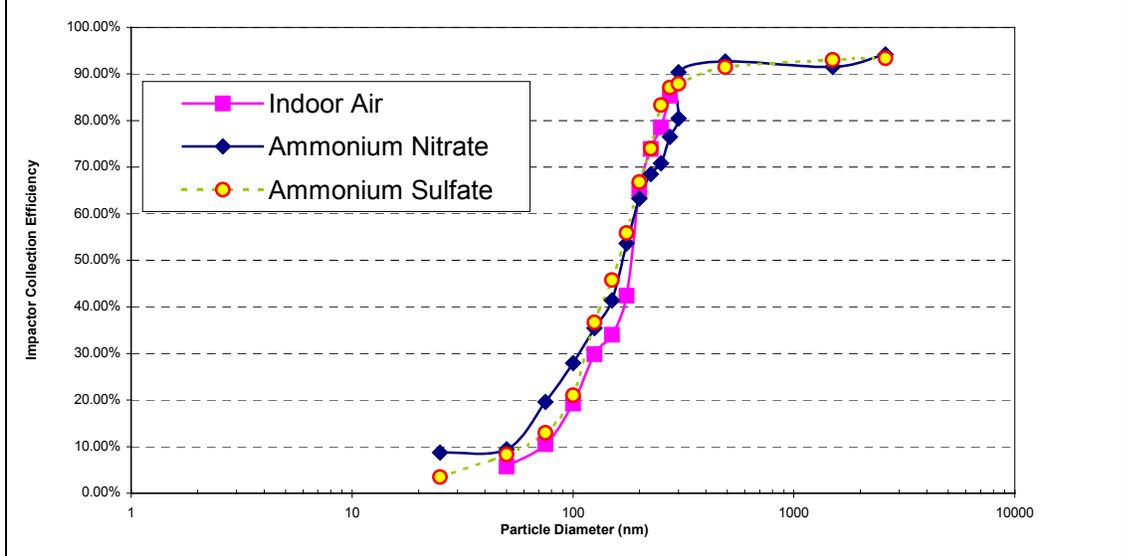
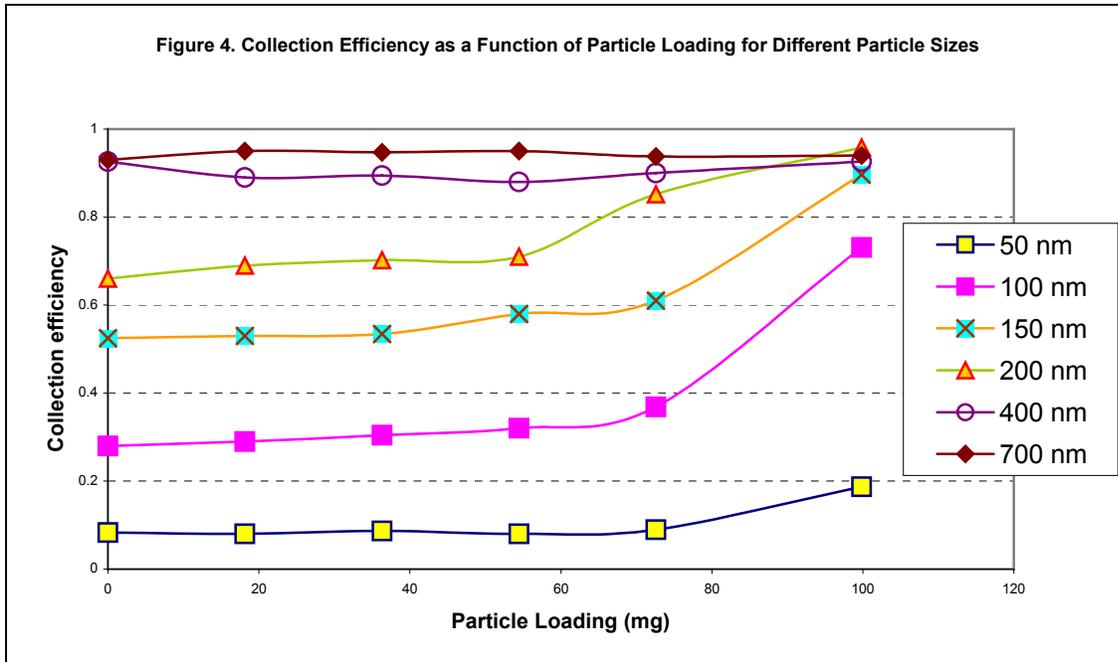


Figure 3. Evaluation of the USC High Volume Low Cutpoint Impactor with an Uncoated Quartz Substrate and Different Types of Test Aerosols



The effect of particle loading on the performance of the USC ultrafine separator was investigated by generating polydisperse ammonium sulfate aerosol. In a 1 h experiment, the mass concentration of the generated ammonium sulfate test aerosol was 3.3 mg m^{-3} resulting in a total impactor loading of approximately 108 mg. Results from the loading tests are shown in Figure 4. The data plotted in Figure 4 clearly demonstrate that particle bounce and reentrainment, which would have been manifested by a detectable decrease in the collection efficiency measured for any size, do not occur for loadings at least as high as 60-70 mg. In fact, the data of Figure 4 indicate that the impactor's efficiency increases with loading.



12. Supersite Data Management Progress Report (NARSTO)

Two major progresses have been made during the past reporting period: submission of Aerodynamic Particle Sizer (APS) data to NARSTO and implementation of FTP server. First, as part of the Supersite program, we are required to submit all monitoring data sponsored by EPA to NARSTO, specifically to the Permanent Data Archive (PDA) at LaRC, Langley, Virginia, USA. In our knowledge, we are the first Phase II Supersites to submit monitoring data to the NARSTO PDA. At the end of this reporting period, we have submitted three data sets, all pertaining to APS data collected by our PIU at Downey (Los Angeles County), Riverside and Rubidoux (Riverside County), California. Second, we have constructed and implemented a FTP server, located at UCLA School of Public Health, to archive our Supersite data, including assembled data sets in Excel and SAS formats, which are directly extracted from APS software, data sets that were submitted to NARSTO, both in Excel and .csv formats. The purpose of this FTP site is to house all Supersite data sets in one central location, from where investigators will be able to retrieve these Supersite data.

1. Submission of APS Data to NARSTO

A. *NARSTO Data Exchange Template*

NARSTO data exchange template has been advanced substantially since the Data Management Working Group adopted it. We use the most updated version: NARSTO 2001/10/31 (2.213) (reference at http://cdiac.esd.ornl.gov/programs/NARSTO/NARSTO_template_atmospheric_measurements_20011031) to construct APS data sets. Upon extensive QA diagnoses (detailed later in C), these Excel data files were converted into .csv format, an ASCII or text format with comma delimited, the standard format required by NARSTO.

B. *APS Original Data and Processing*

Our PIU field staff used Model 3320 (TSI Inc. at <http://www.tsi.com/particle/products/partsize/3320.htm>) to collect APS data measuring size distributions at Downey (Los Angeles County), Riverside and Rubidoux (Riverside County), California. The instrument measured size distribution by count, surface area, and/or mass from 0.5 – 20 μm , divided by 52 size bins or channels, for every 15 minutes. A PIU computer that was connected to the instrument stored the size distribution data. These data were duplicated at several locations for security purposes, including Dr. Peter Jaques' computer at CHS 51-295, and two computers at SCPCS Data Management Office at CHS 21-297, UCLA School of Public Health. TSI-supplied APS programs (Aerosol Instrument manager Software, version 4.3) were used to convert the data into Excel format. Data collected over the entire time period of each sampling site were assembled to combine into one Excel data file. The sampling time periods cover from 12/08/2000 to 2/5/2001, from 02/14/2001 to 06/01/2001, and from 06/25/2001 to 08/26/2001 for Downey, Riverside, and Rubidoux, respectively. We reported only count size distribution (in number/cc).

C. *QA Diagnosis Tests*

The assembled Excel data file was gone through extensive QA diagnosis tests, including 1) visual examination on the size distribution plots generated by the TSI APS programs, 2) diagnosis test for extremely large or small observations by a in-house SAS program, 3) visual investigation of time series plots produced by a SAS program named “qa_plot_time_series_continuous.sas” that is an official NARSTO QA program developed by Bill Sukloff (Scientific Software Project Leader, Air Quality Research Branch, Environment Canada, 4905 Dufferin St., Toronto, Ont M3H 5T4), and 4) data file format check-up by a SAS program named “read_and_verify_des_files.sas,” the other NARSTO adopted program developed by Bill Sukloff.

We used the “read_and_verify_des_files.sas” program to check the format of the .csv file is consistent with that in the template of NARSTO. Any format errors detected by this diagnosis program were corrected before finalizing the Excel data files. Extremely large or small observations were set to be 5-fold standard deviations away from the sample means. These values were labeled for further examinations. The size distribution plots and time-series plots were used to investigate whether these extremely large values were actually unusual spikes (one or two observations occurred in this manner) or continuous developing patterns lasting for couple hours or ranging over many sizes. We invited the PIU Director, Dr. Peter Jaques to participate this diagnosis test. In the case of the former, these values were labeled as invalid and replaced with missing values, while in the later case, they were still considered as valid data, but a user note was attached in the Excel files.

After completing all QA diagnosis tests, we labeled the data having passed Level II validation and converted the Excel data files into .csv format, which were ready to be sent out.

D. *Sending APS .csv Data Files*

The .csv APS data files were sent to at a “1a” folder of the NARSTO FTP site at <ftp://narsto.esd.ornl.gov/>. NARSTO data management scientists helped to summarize the data sets in a “NARSTO DIST Metadata Report” shown in the attachment, in which the data sets were available at two locations, NARSTO QSSC Public Access FTP Site and Permanent Data Archive at LaRC, Langley, Virginia, USA.

E. Submission Progress and Tentative Schedule for Future Submission

Status of LA Supersite Data Submitted to NARSTO

Date: 2002/03/08

Sorted by: Submitted date and Instrument

<i>Type of Data</i>			<i>Data</i>	<i>Data</i>	<i>Data</i>
<i>Instrument</i>	<i>Location</i>	<i>Sampling Dates</i>	<i>Submitted to NARSTO*</i>	<i>Accepted by NARSTO</i>	<i>available to the Public</i>
APS	Downey	12/08/00-02/05/01	01/24/2002	Jan-02	Feb-02
APS	Riverside	02/14/01-06/05/01	03/08/2002	Mar-02	
APS	Rubidoux	06/25/01-08/26/01	03/08/2002	Mar-02	
Aethalometer	Riverside	02/21/01-06/05/01	1Q/2002		
Aethalometer	Rubidoux	06/25/01-09/08/01	1Q/2002		
SMPS	Downey	09/22/00-01/31/01	1Q/2002		
SMPS	Riverside	02/14/01-06/01/01	1Q/2002		
SMPS	Rubidoux	06/25/01-09/04/01	1Q/2002		
TEOM	Downey	11/28/00-02/05/01	2Q/2002		
TEOM	Riverside	04/03/01-05/22/01	2Q/2002		
Automet	Downey	12/08/00-02/05/01	2Q/2002		
Automet	Riverside	02/05/01-03/19/01	2Q/2002		
Automet	Rubidoux	06/19/01-09/08/01	2Q/2002		
DataRAM	Downey	09/15/00-10/13/00	2Q/2002		
DataRAM	Riverside	12/19/00-06/01/01	2Q/2002		
DataRAM	Rubidoux	06/26/01-09/08/01	3Q/2002		
MetOne	Rubidoux	06/19/01-09/08/01	3Q/2002		
MetOne	Riverside	03/21/01-06/05/01	3Q/2002		
Nitrate	Rubidoux	07/18/01-09/02/01	3Q/2002		
Partisol	Downey	11/15/00-02/02/01	3Q/2002		
Partisol	Riverside	02/05/01-05/25/01	3Q/2002		
Partisol	Rubidoux	06/27/01-08/29/01	3Q/2002		
Aethalometer	Claremont	10/08/01-12/07/01	4Q/2002		
APS	Claremont	09/17/01-11/22/01	4Q/2002		
Automet	Claremont	09/17/01-11/01/01	4Q/2002		
Carbon	Claremont	10/12/01-11/16/01	4Q/2002		
DataRAM	Claremont	10/08/01-12/07/01	4Q/2002		
MetOne	Claremont	10/17/01-12/07/01	4Q/2002		
Nitrate	Claremont	09/08/01-11/28/01	4Q/2002		
Partisol	Claremont	10/15/01-11/28/01	4Q/2002		
SMPS	Claremont	09/17/01-11/22/01	4Q/2002		

2. Implementation of FTP Site

A. *Purpose*

The FTP site is regarded as the Supersite data depository and exchange site, from which investigators and users are allowed to view databases, to download files, to upload files, and to back-up data.

B. *Location: at the Center of Health Sciences (CHS) of UCLA School of Public Health.*

C. *IP address: <ftp://128.97.116.65/>*

D. *Folder/Directory*

The folder or directory of Supersite data was at “c:\scpcs\PIU\” of the FTP site. Under the PIU, data were placed under different sampling sites: Downey, Riverside, Rubidoux, and Claremont.

E. *File Types Archived in the FTP site*

- 1) Excel original files – assembled data sets for original data converted from PIU instruments.
- 2) SAS data sets – SAS formatted data sets corresponding to the Excel original files.
- 3) NARSTO data exchange template files – information required in the NARSTO data exchange template was combined with the Excel original files. These files must have gone over QA diagnosis tests.
- 4) The .csv files that have been sent to NARSTO. These are the back-up files that we send to NARSTO PDA.

F. *Access*

The FTP site currently is only open to Supersite investigators, including SCPCS investigators. Before the site is made available to the public, interested individuals should submit their requests to the Center Director, Dr. Costas Sioutas at sioutas@usc.edu before gaining permissions from Data Management Office of the Supersite.

Attachment: NARSTO DIST Metadata Report



NARSTO DIST Metadata Report
[Help](#)



Title: **NARSTO EPA_SS_LOS_ANGELES Aerodynamic Particle Size Data**
Project: **EPA Supersites--Los Angeles**
Investigator(s): **Sioutas, Dr. Costas Email: sioutas@usc.edu
Jaques, Dr. Peter Email: pjaques@ucla.edu
Yu, Dr. Rong Chun Email: rcyu@ucla.edu**

Status: **Preliminary**
Access Restrictions: **Public**
Data Set Location: **NARSTO Permanent Data Archive at the Langley DAAC**

Data Center Contact: **Yu, Rong Chun Email: rcyu@ucla.edu Phone: 310-794-1408**
Data Center URL: **<http://eosweb.larc.nasa.gov/>**
Data Set Citation: **Sioutas, Costas, Peter Jaques, and Rong Chun Yu. 2002. NARSTO EPA_SS_LOS_ANGELES Aerodynamic Particle Size Data. Available on-line (http://eosweb.larc.nasa.gov/project/narsto/table_narsto.html) at the Langley DAAC, Hampton, Virginia, U.S.A.**

Download Data Set(s): **[NARSTO PDA: NARSTO EPA SS LOS ANGELES Aerodynamic Particle Size Data](#)**
Note: Permanent Data Archive, Table of all archived NARSTO data sets. Follow links to order data.

[QSSC FTP SITE: NARSTO EPA SS LOS ANGELES Aerodynamic Particle Size Data](#)
Note: NARSTO QSSC Public Access FTP Site. FTP to narsto.esd.ornl.gov and login as anonymous. Look in the pub/ directory for project subdirectories and data sets.

Parameter Description: Parameter
Sensor
Source
Term
Topic

Particle Size
APS - Aerodynamic Particle Sizer
GROUND STATION
AEROSOLS
ATMOSPHERE

Particle Count
APS - Aerodynamic Particle Sizer

**GROUND STATION
AEROSOLS
ATMOSPHERE**

Keyword(s):

**APS
particle count
Downey
LA Supersite**

Abstract:

**Southern California Particle Center and Supersite
The overall objective of the LA Supersite in the Southern California Particle Center and Supersite (SCPCS) 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 linkages to health effects of airborne particulate matter in the Los Angeles Basin. At several locations in Los Angeles County, California, a TSI Aerodynamic Particle Sizer (APS) was used in a mobile trailer to collect size characteristics of particles ranging from about 0.5 to 20 μm . Based on the time-of-flight principle, the APS measured particle count concentrations for 52 channels that cover sizes from 0.5 to 20 μm in every 15 minutes. Note that the first channel reports particle count concentrations for sizes < 0.523 μm .**

Site Information:

Bounding Coordinates

Site
N
S
E
W

**EPA SS Los Angeles
34.2
33.9
-117.3
-118.2**

Content Time Range:

Begin: 20001208 - End: 20010501

Metadata Author:

Hook, Les Email: hookla@ornl.gov Phone: 865-241-4846

Additional Documentation:

**[The Southern California Particulate Matter Supersite \(SCPMS\) Website](#)
[Los Angeles Supersite Quality Assurance Project Plan](#)
[PROJECT DESCRIPTION: SOUTHERN CALIFORNIA PARTICULATE MATTER](#)**