

# SOUTHERN CALIFORNIA PARTICLE SUPERSITE

**Progress Report for Period April 1, 2002 – June 30, 2003**

**United States Environmental Protection Agency**

**Principal Investigator:** John R. Froines, Ph.D., UCLA School of Public Health

**Co-Principal Investigator:** Constantinos Sioutas, Sc.D., USC School of Engineering

## 1. Introduction

The overall objective of the Southern California Particle 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 April 1, 2002 to June 30, 2003. It is divided into 12 sections, each addressing a specific research area. 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.

## 2. Publications

The Southern California Particle Supersite has been acknowledged so far in the following 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*, 36(6): 748-763, 2002
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*, 33(5): 735-752, 2002
4. Li, N., Kim, S., Wang, M., Froines, J.R., Sioutas, C. and Nel, A. “Use of a Stratified Oxidative Stress Model to Study the Biological Effects of Ambient Concentrated and Diesel Exhaust Particulate Matter”. *Inhalation Toxicology*, 14(5): 459-486, 2002

5. 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*, 52:1032-1042, 2002
6. Singh, M., Jaques, P. and Sioutas, C. "Particle-bound metals in source and receptor sites of the Los Angeles Basin". *Atmospheric Environment*, 36(10): 1675-168, 2002
7. 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
8. Misra, C., Singh, M., Hall, P. and Sioutas, C. "Development and evaluation of a personal cascade impactor sampler (PCIS)". *Journal of Aerosol Science*, 33(7), 1027-1047, 2002
9. Eiguren-Fernandez 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". *Aerosol Science and Technology*, 37: 201-209, 2003
10. Fine, P.M., Hering, S.V., Jaques P.A. and Sioutas, C. "Performance Evaluation and Field Use of a Continuous Monitor for Measuring Size-Segregated PM<sub>2.5</sub> Particulate Nitrate". *Aerosol Science and Technology*, 37: 342-354, 2003
11. Singh, M., Misra, C., and Sioutas, C. "Field Evaluation of a Particle Monitor for Size-Dependent Measurement of Mass and Chemical Composition of Individual Exposures to PM". Manuscript submitted to *Aerosol Science and Technology*, June 2002.
12. Shen, S., Zhu, Y., Jaques PA and Sioutas C. "Evaluation of the SMPS-APS system as a Continuous Monitor for PM<sub>2.5</sub> and PM<sub>10</sub>". *Atmospheric Environment*, 36, 3939-3950, 2002
13. 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*. 36, 4375-4383, 2002
14. Misra, C., Geller, M.D., Solomon, P.A. and Sioutas, C. "Development of a PM<sub>10</sub> Inertial Impactor for Coarse Particle Measurement and Speciation." *Aerosol Science and Technology*, 37:271-282, 2003
15. Zhu, Y., Hinds, W.C., Kim, S., Shen, S. and Sioutas, C. "Seasonal Trends of Concentration and Size Distributions of Ultrafine Particles Near Major Freeways in Los Angeles". *Aerosol Science and Technology*, in press, April 2003
16. Misra, C., Geller, M., Fine, P.M.. and Sioutas, C. "Development and Evaluation of an Ultrafine Particle Concentrator Facility for Human Exposures". Submitted to *Aerosol Science and Technology*, September 2002.

17. Gong, H.Jr, Linn, W.S., Sioutas, C., Terrell S.L., Clark, K.W., Anderson K.R and Terrell, L . "Controlled Exposures of Healthy and Asthmatic Volunteers to Concentrated Ambient Fine Particles in Los Angeles". *Inhalation Toxicology*, 15(4), 305-325.
18. Li, N., Sioutas, C , Froines, J.R., Cho, A., Misra, C and Nel, A., "Ultrafine Particulate Pollutants Induce Oxidative Stress and Mitochondrial Damage" *Environmental Health Perspectives*, in press, December 2002
19. Chakrabarti, B., Singh, M and Sioutas C. "Development of a Continuous Monitor For Measuring the Mass Concentration of Ultrafine PM." *Aerosol Science and Technology*, in press, January 2003
20. Jaques, P.A., Ambs, J.L. and Sioutas, C. "Field Evaluation Of The Differential TEOM® Monitor For Continuous PM<sub>2.5</sub> Mass Concentrations ". Submitted to *Aerosol Science and Technology*, September 2002
21. Zhu, Y., Hinds, W.C. and Sioutas, C. "Vertical Profile of Ultrafine Particles in the Vicinity of a Major Highway". Submitted to *Atmospheric Environment*, December 2002
22. Fine, P.M., Si, S., Geller, M.G., and Sioutas, C. "Diurnal and Seasonal Characteristics and Size of Ultrafine PM in Receptor Areas of the Los Angeles Basin". *Aerosol Science and Technology*, in press, 2003
23. Chakrabarti, B., Fine, P.M, Delfino R.J. and Sioutas C. "Performance Evaluation of an active personal DataRAM PM<sub>2.5</sub> mass monitor (Thermo Anderson pDR-1200) designed for continuous personal exposure measurements" Submitted to *Atmospheric Environment*, February 2003
24. Yu, R.C., Teh, H.W., Sioutas, C. and Froines, J.R. "Quality Control of Semi-Continuous Mobility Size-Fractionated Particle Number Concentration Data". Submitted to *Atmospheric Environment*, February 2003
25. Miguel, A.H., Eiguren-Fernandez, A., Jaques, P.A., Mayo, P.R. and Sioutas, C. "Seasonal variation of the particle size distribution of polycyclic aromatic hydrocarbons and of major aerosol species in Claremont, California" Submitted to *Atmospheric Environment*, February 2003
26. Sardar, S.B., Fine, P.M., Jaques, P.A., Sioutas, C. "Seasonal and Spatial Variability of the Size-Resolved Chemical Composition of PM<sub>2.5</sub> in the Los Angeles Basin." Submitted to *Atmospheric Environment*, June 2003
27. Geller, M.D., Fine, P.M., Sioutas, C. "The Relationship between Both Real-time and Time-integrated Coarse (2.5 – 10 µm), Intermediate (1 – 2.5 µm), and Fine (0 – 2.5 µm) Particulate Matter in the Los Angeles Basin." Submitted to *Journal of the Air and Waste Management Association*, June 2003.

28. Eiguren-Fernandez, A., Miguel, A.H., Froines, J.R., Thurairatnam, S., Avol, E. "Seasonal and Spatial Variation of Polycyclic Aromatic Hydrocarbons in Vapor-Phase and PM<sub>2.5</sub> in Southern California Urban and Rural Communities" Submitted to *Atmospheric Environment*, June 2003.
29. Reisen, F., Wheeler, S. and Arey, J. "Methyl- and Dimethyl-/Ethyl- Nitronaphthalenes Measured in Ambient Air in Southern California" accepted by *Atmospheric Environment*, June 2003.

### 3. 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 physiochemical characteristics 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 has been scheduled to sample during a period of intense photochemistry (defined approximately as May-October) and low photochemical activity (defined as the period between November-April). During the period of this progress report, we've continued PM sampling with the Particle Instrumentation Unit (PIU) at the University of Southern California (USC), the fifth Southern California Supersite location, beginning September 2002. The site is located about one mile directly south of downtown Los Angeles and the 10 Freeway, which runs east to west, and is about 100 meters directly east of the 110 Freeway. The site is embellished with typical urban sources: centralized within a major congested urban center; adjacent to several 2 – 7 story buildings; adjacent to pedestrian and local traffic as well as central arteries; and near building and road construction projects. Since the site is about 15 miles directly east north east of the ocean, prevailing winds are primarily from the west and southwest during most of the daytime when mobile and stationary emission sources may be expected to predominate. However, the nearby relatively large buildings can also disturb the winds, affecting urban canyon and wake properties. These factors consist of turbulent winds and updrafts that may confound local measurements of regional wind trajectories, and increase the delivery of local sources (e.g., construction debris, and larger settled particles from road related vehicle wear-and-tear) in addition to the close-by 110 Freeway. Several studies are being conducted as we enter the 3<sup>rd</sup> quarter at the USC site to investigate local source contributions in addition to the regional transported emissions that may generally come from the west freeways.

We have completed all Metal/Element speciation, Ion, and EC/OC analysis for integrated samples, through most of early May. As of early June, we have finalized size integrated on-line measurements of particulate nitrate and carbon using the Integrated Collection and Vaporization System (ICVS) developed by Aerosol Dynamics Inc. Additionally, paired semi-continuous PM<sub>2.5</sub> measurements using a prototype Differential TEOM, designed to measure "non-artifact" laden mass, has been completed. Two continuous BAM monitors continue to operate: one, with the standard PM<sub>2.5</sub> inlet, the second with an ultrafine concentrator inlet (designed at our USC lab). Coupled with our USC-TEOM coarse monitor, time-integrated mass measurements are being compared to those by our SMPS-APS and Differential ESP TEOM for short term periods,

and to MOUDI, Partisol, and other filter mass samplers for longer sample integrals, overall, resulting in paired integrated semi-continuous, diurnal, and 24-hour mass measurements of coarse, fine, and ultrafine PM.

We have continued to make our mobile particle trailer available for co-located exposure studies. The following health studies have been supported by the Supersite measurements: In vitro studies undertaken by Drs. Andre Nel and Arthur Cho (UCLA) investigating the hypotheses that organic constituents associated with PM, including quinines, 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. 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. Led by Drs. Harkema (University of Michigan), Kleinman (UC Irvine), Froines, and Nel (UCLA), these co-located studies have commenced during our first month at the USC site.

#### 4. Time integrated, size fractionated mass and chemical speciation for five sites in the Los Angeles Basin.

Introduction:

Sampling has been conducted at five locations in the Los Angeles Basin over a period of more than two years. The sites and the periods of sampling are given in Table 1. Three MOUDI samplers were deployed and collected 24-hour samples for size-fractionated ambient PM mass and chemical composition. The MOUDI samples were analyzed for sulfate, nitrate, EC, OC and individual metals. The PM size ranges measured are  $<0.1 \mu\text{m}$  (ultrafine),  $0.1- 0.32 \mu\text{m}$ ,  $0.32 - 1.0 \mu\text{m}$  and  $1.0 - 2.5$ , (these three sizes comprising the accumulation mode) and  $2.5-10 \mu\text{m}$  (coarse mode). A Partisol sampler was also used to in some cases to measure coarse PM properties. The inorganic ions, sulfate and nitrate are analyzed by ion chromatography (Dionex), trace elements and metals by XRF and the elemental and organic carbon (EC and OC) by thermal evolution/optical transmission analysis.

**Table 1**

Site	Period of Sampling
Downey	Oct 2000 – Feb 2001
Riverside	Feb 2001 – June 2001
Rubidoux	June 2001 – Sept 2001
Claremont	Sept 2001 – Aug 2002
USC	Oct 2001 – Ongoing

#### Results and discussion:

Figure 1 shows the monthly average mass distribution in the three modes (coarse, accumulation and ultrafine) for all five sites. The highest PM levels are observed at one source site, Downey, and two receptor sites, Rubidoux and Riverside. Ultrafine concentrations were observed to be highest in Downey. As a source site, influenced by nearby high traffic density and industrial areas, fresh primary emissions contribute to the high observed ultrafine concentrations in Downey. The accumulation mode concentration increases in summer and decreases in winter across all sites, especially at the receptor sites (Riverside, Rubidoux and Claremont). This trend may be due to increased advection with higher wind speeds in the summer and/or increased secondary PM formation with higher photochemical activity. The coarse mode PM mass is also seen to generally increase in the summer, presumably due to higher contributions from wind-blown dust.

Figures 2, 3 and 4 present the monthly average PM chemistry in the coarse, accumulation and ultrafine modes respectively. The major chemical species of PM are shown, namely  $\text{NH}_4\text{NO}_3$ ,  $(\text{NH}_4)_2\text{SO}_4$ , elemental carbon (EC), organic compounds and the sum of the metals and trace elements. In the coarse mode (Figure 2) metals and nitrate dominate, and the overall emission levels are observed to be generally lower in winter than in summer due to the increased summertime onshore wind speeds leading to resuspension of road and soil dust. The high observed metal content affirms that crustal materials are one of the major sources of coarse PM. Coarse PM nitrate levels are also higher in the summer when there is both increased

photochemical formation of nitrates and increased inland advection. In the accumulation mode (Figure 3) nitrate and organics dominate. The particulate nitrate concentration is generally higher at the receptor sites, especially Riverside and Rubidoux. These two sites are downwind of the intense ammonia sources at the Chino area dairy farms. Claremont, another receptor site, also has higher nitrate concentrations than source sites, with the associated ammonia coming from vehicular and other urban sources. The source sites (Downey and USC) have higher organic concentrations, which are explained by primary emissions from nearby vehicle sources. High sulfate concentrations are observed at the receptor sites, especially during summer due to photochemical formation and/or increased advection of background aerosol. Organic compounds dominate the ultrafine mode (Figure 4) across all sites and seasons ranging from 54% of the total mass in April 2001 at Riverside to 95% in February 2003 at USC. Increased wintertime organic concentrations at source sites are possibly due to condensable organics from vehicular emissions. Higher summertime organic compounds at receptor sites are a result of secondary organic aerosol formation and new ultrafine particles formed via nucleation. Higher concentrations of EC at source sites are also observed suggesting primary emissions from diesel engines. Finally, overall sulfate concentrations was observed to be low in ultrafine mode, but the concentration is higher in summer compared to winter due to its photochemical origin.

Figure 5 and 6 show the monthly average Organic Carbon (OC) and EC distribution across the three different particle size modes. From Figure 5, it can be seen that OC concentrations are high in the accumulation and ultrafine modes at source sites. At the receptor sites, higher summertime OC concentrations are observed for the ultrafine and accumulation modes, possibly due to increased photochemistry and advection. The monthly average EC distribution in the three modes is shown in Figure 6. It was observed that the elemental carbon concentration in the ultrafine mode is higher at the source sites due to fresh emissions from diesel vehicles. At the receptor sites, higher elemental carbon concentrations occur during the summer in the ultrafine and accumulation modes. Particulate elemental carbon can only come from primary sources, so high concentrations of elemental carbon at receptor sites is most likely due to advection of PM from the upwind source areas. It appears that increased summer wind speeds and the subsequent advection of polluted air masses overwhelms any dilution effect due to the higher mixing height in the summer months.

The ratio of organic carbon to elemental carbon has been previously utilized to distinguish between the primary and secondary organic carbon content of PM. Table 2 shows the average ratio of OC to EC at all the sites for PM<sub>2.5</sub> (the sum of the ultrafine and accumulation modes). The weekly EC and OC data are averaged to calculate the overall average for each site. The source sites have a lower OC/EC ratio and, particularly at Downey, higher degrees of correlation, both of which are indicative of primary emissions from vehicular sources. The receptor sites have a generally higher organic to elemental carbon ratio above the primary emissions ratios of the source sites. The formation of secondary organic compounds in the atmosphere can cause the higher OC content relative to EC. The higher organic to elemental carbon ratios observed in Claremont may also be driven by a lack of concentrated diesel sources upwind.

Table 2 . Averaged OC/EC ratios and correlation coefficients at source and receptor sites

<b>Source site</b>	<b>Average and Std Dev</b>	<b>Range</b>	<b>R<sup>2</sup></b>
Downey	5.08 ± 2.3	2.7 – 9.57	0.81
USC	5.35 ± 1.98	2.86 – 7.7	0.59
<b>Receptor site</b>	<b>Average and Std Dev</b>	<b>Range</b>	<b>R<sup>2</sup></b>
Rubidoux	7.78 ± 1.76	6.6 – 8.9	0.57
Riverside	6.05 ± 3.55	3.6 – 15.2	0.64
Claremont	14.84 ± 8.2	4.4 – 35.7	0.38

The correlation coefficients between measured metal concentrations in the coarse and fine (accumulation plus ultrafine) modes at receptor and source sites are given in Table 3. Only the more significant correlations are included ( $r^2 > 0.6$ ). In the coarse mode at the source sites, high correlations are observed for many of the elements. The highest correlations suggest a common source of Al and Si, and a related source of Fe, Ti, Mn, Zn, and Cu. The major source of coarse particles is soil and road dust, and these elements can all be of crustal origin. In the fine mode and at the source sites, the degree of correlation among elements drops significantly. Fine particles have more varied sources than coarse particles, and thus inter-element correlations are reduced by varying contributions of multiple sources of the same element. The results show moderately high correlations among some metals (Fe, Si, Mn, Zn), which may originate from crustal, vehicular, or industrial sources. Additional high correlation coefficients were observed in the coarse mode at the receptor sites between Al and Si and some other crustal metals indicating a soil/road dust source. Unlike the coarse mode, no significant correlations were observed in the fine mode at the receptor sites. In general, less correlation is expected at the downwind receptor sites due to the potential influence of a greater variety of sources upwind.

Table 3 Significant ( $R^2 > 0.6$ ) Correlation between 24-h averaged mass concentrations of selected metals at source and receptor sites

**Source Sites (Downey/USC)**

<b><u>Coarse mode</u></b>			<b><u>Fine mode</u></b>		
<b>Metal vs.</b>	<b>Metal</b>	<b>R<sup>2</sup></b>	<b>Metal vs.</b>	<b>Metal</b>	<b>R<sup>2</sup></b>
Al	Si	0.98	Si	Fe	0.81
Al	Fe	0.83	Si	Mn	0.69
Al	Ti	0.72	Si	Zn	0.72
Al	Mn	0.81	Fe	Ti	0.81
Al	Zn	0.66	Fe	Mn	0.67
Si	Fe	0.81	Fe	Cu	0.67
Si	Ti	0.71	Fe	Zn	0.72
Si	Mn	0.79	Mn	Zn	0.81
Si	Zn	0.66			
Fe	Ti	0.96			
Fe	V	0.79			
Fe	Mn	0.96			
Fe	Cu	0.90			
Fe	Zn	0.92			
Ti	V	0.86			
Ti	Mn	0.96			
Ti	Cu	0.94			
Ti	Zn	0.92			
V	Mn	0.85			
V	Cu	0.88			
V	Zn	0.81			

**Receptor Site (Claremont/Riverside/Rubidoux)**

<b><u>Coarse mode</u></b>		
<b>Metal vs.</b>	<b>Metal</b>	<b>R<sup>2</sup></b>
Al	Si	0.92
Al	Fe	0.64
Al	Mn	0.81
Al	Cu	0.66
Mn	Cu	0.71

Figure 1.

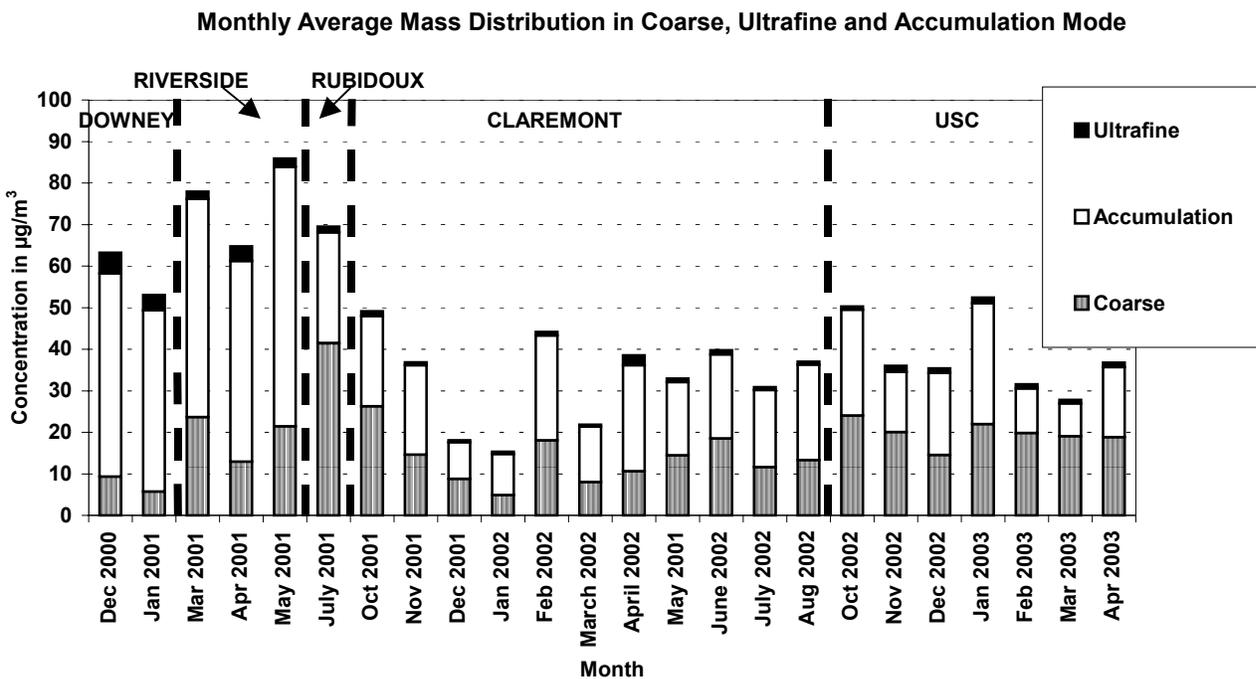


Figure 2.

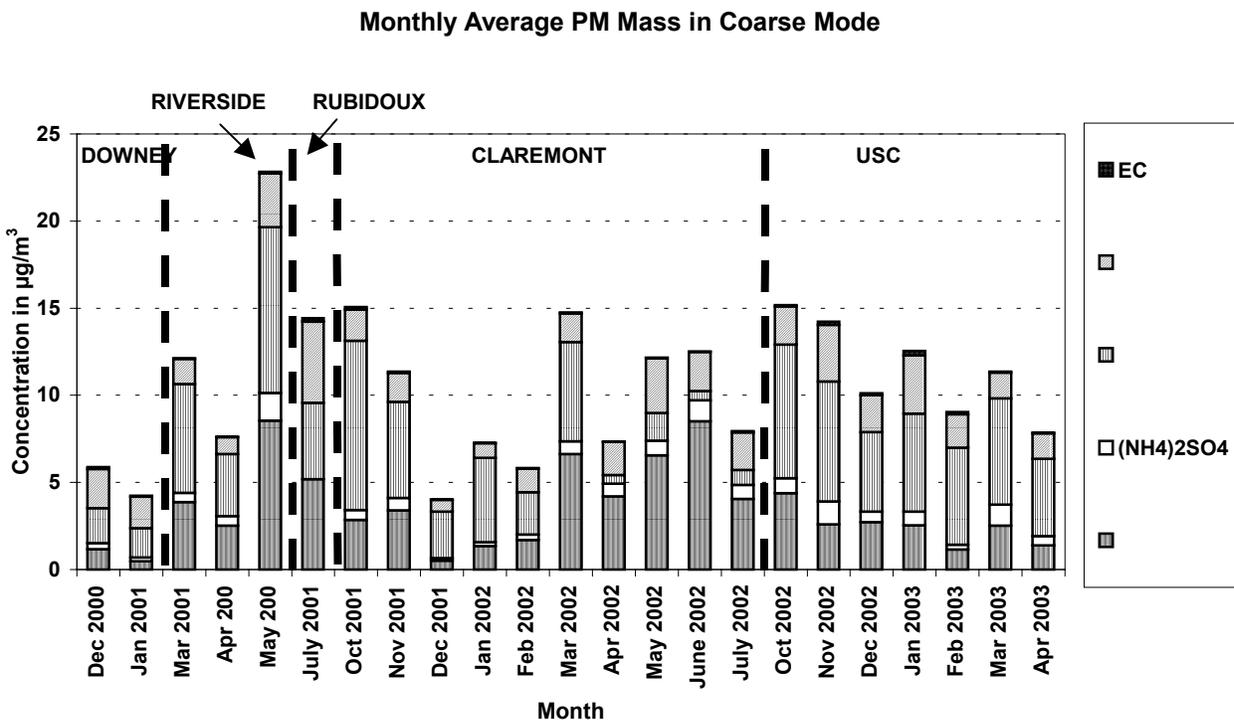


Figure 3.

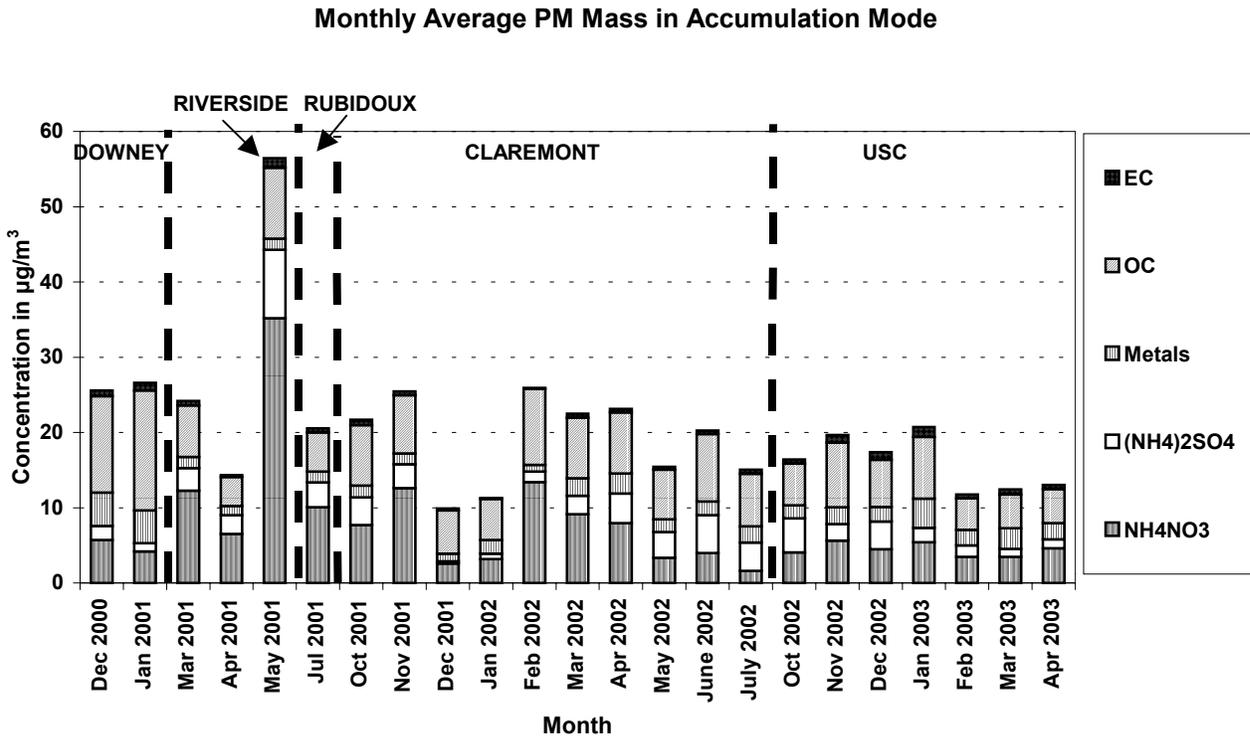


Figure 4.

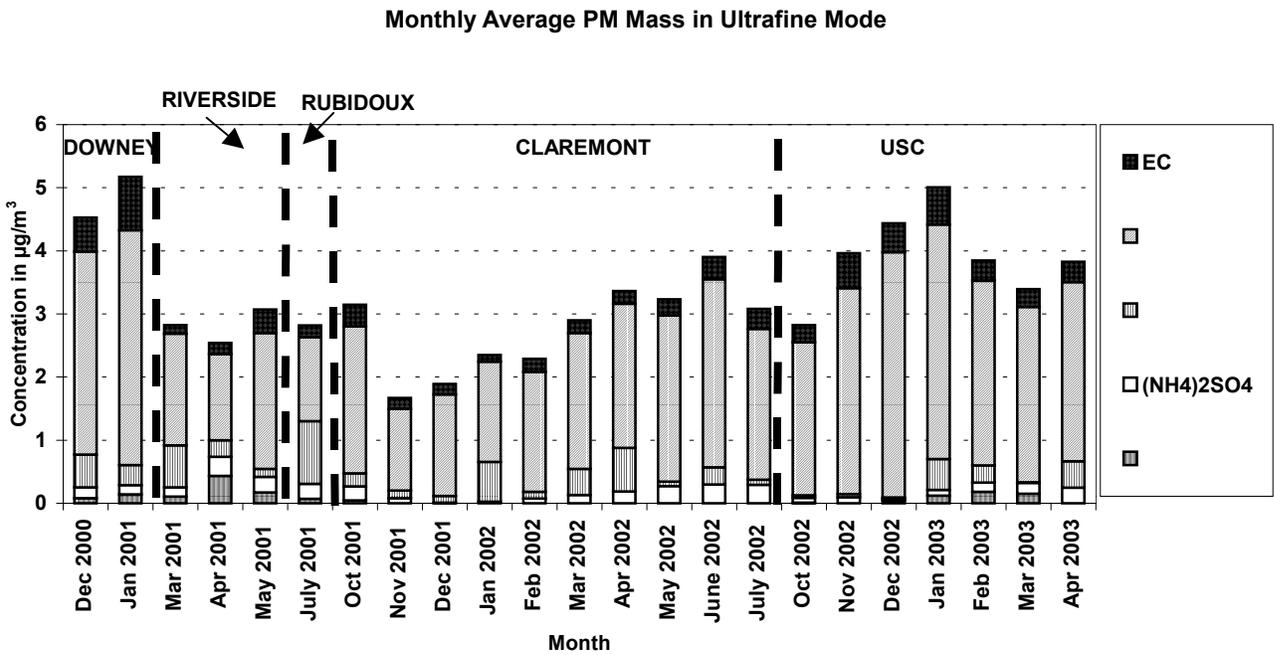


Figure 5.

Monthly Average OC Distribution in Coarse, Ultrafine and Accumulation Mode

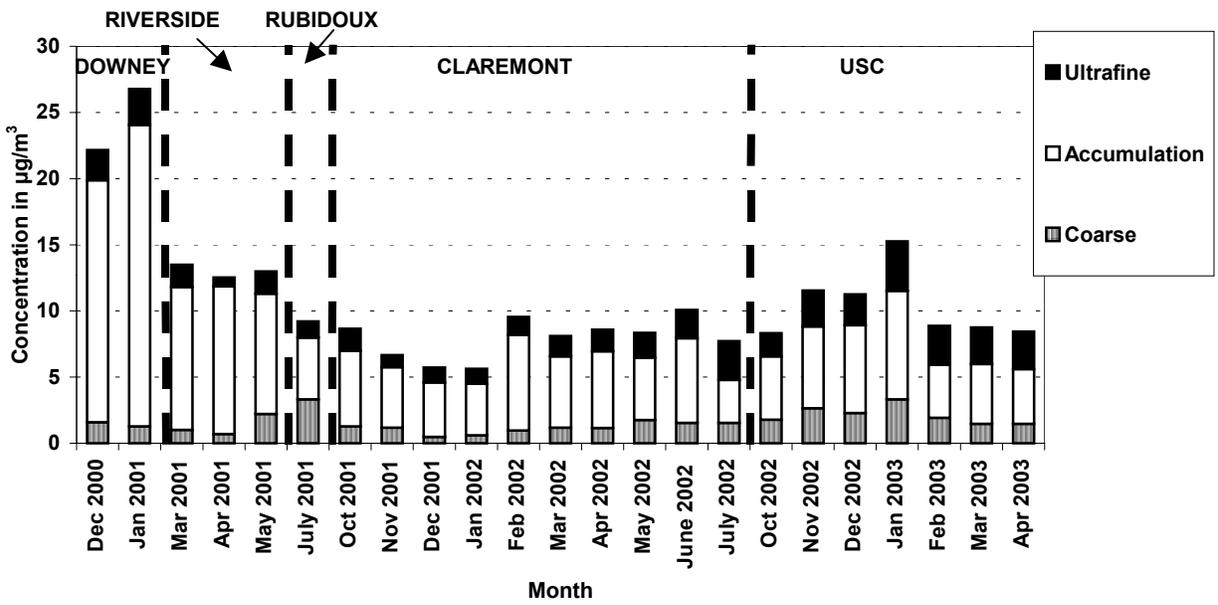
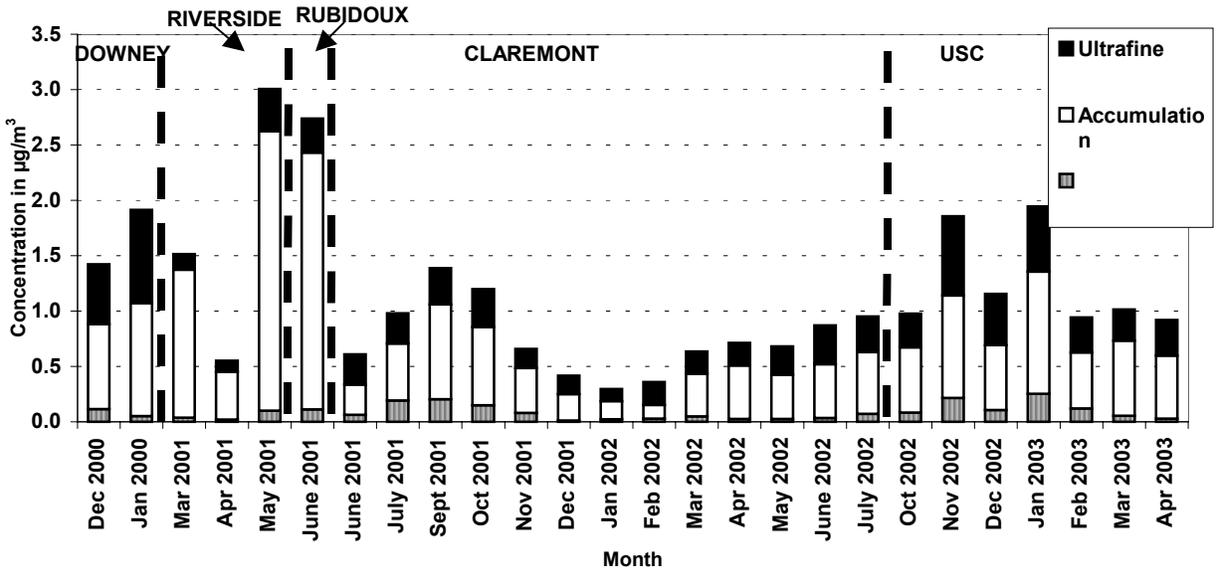


Figure 6.

Monthly Average EC Distribution in Coarse, Ultrafine and Accumulation Mode



## 5. Seasonal and Spatial Variation of Polycyclic Aromatic Hydrocarbons in Vapor-Phase and PM<sub>2.5</sub> in Southern California Urban and Rural Communities

This report summarizes the results and conclusions of a field study that has been written up and submitted for publication in a special issue of *Atmospheric Environment*

**Authors:** Arantzazu Eiguren-Fernandez, Antonio H. Miguel\*, John R. Froines, Suresh Thurairatnam, Ed Avol

### Summary

Priority polycyclic aromatic hydrocarbons (PAHs) were measured in two rural communities (Atascadero and Lompoc) located several hundred Km northwest of Los Angeles and in four urban communities 40-100Km downwind of Los Angeles (San Dimas, Riverside, Upland and Mira Loma), during all seasons, from May 2001 to July 2002. The community locations are shown in Figure 1. PAHs in PM<sub>2.5</sub> and in the vapor-phase were collected, respectively, on pre-baked quartz fiber filters, and PUF-XAD-4 resin, at 113 LPM, during 24-hr periods, every 8<sup>th</sup> day. PAHs were quantified by HPLC-Fluorescence. Annual means measured in all sites are shown in Figure 2. In all sites, vapor-phase PAHs contained >99.9% of the mass, and were dominated by naphthalene (NAP), which varied from about 60 ng m<sup>-3</sup> in Lompoc, a community with light traffic, to ~ 580 ng m<sup>-3</sup> in Riverside, a community criss-crossed by ~200,000 vehicles day<sup>-1</sup>. During summer pollution episodes in urban sites, NAP concentrations reached 7-30 times annual average concentrations. Except for summer episodes, concentrations of low MW PAHs showed small seasonal variations (~2 times higher in winter) as shown in Figure 3. Similar concentrations of particle-phase PAHs were observed in all sites (except for Lompoc). Benzo[ghi]perylene (BGP), a marker of gasoline exhaust emissions, showed the highest concentration among particle-phase PAHs, varying from 23.3 pg m<sup>-3</sup> in Lompoc to 193 pg m<sup>-3</sup> in Mira Loma (Figure 2). Benzo[a]pyrene and indeno[1,2,3-cd]pyrene, found exclusively in the particle-phase, were much higher in urban sites (~ 40-100 pg m<sup>-3</sup>), than in Lompoc (~12 pg m<sup>-3</sup>). Winter particle-phase PAHs were, on average, about sevenfold higher than summer levels (Figure 4). Particle-phase PAHs were negatively correlated with mean air temperature in urban sites (r = -0.50 to -0.75). The data suggest that in Southern California, vehicular exhaust emissions are a major contributor to particle-phase PAHs.

### Conclusions

Ambient PAH concentrations were measured over a one-year sampling period for six Southern California communities, including both rural upwind and metropolitan downwind sites from central Los Angeles. Observed vapor- and fine-particle phase PAHs showed significant seasonal differences, both in the rural and the urban communities studied. The highest seasonal difference was observed for particle-phase PAHs, which increased with decreasing ambient temperature. Rural site PAHs, EC and OC levels were significantly lower than observed at communities located downwind from Los Angeles. In all the sites, PAH mass was dominated by the vapor-phase (with more than 99.9% of the target PAH mass). Total PAH levels were dominated by naphthalene, which was typically 1000s of times higher in concentration than other measured PAHs. Occasional episodic events were captured with elevated PAH levels, but the explanation

for these elevated occurrences will require further investigation. PAH concentrations correlated well with their sub-cooled liquid vapor pressure. We conclude that exhaust emissions from motor vehicles play an important role in observed PAH levels, and that human exposure to particulate PAHs is considerably higher in the winter.



Figure 1. Sampling locations in Southern California. Lompoc: LOM; Atascadero: ATS; San Dimas: SDS; Upland: UPL; Mira Loma: MRL; Riverside: RIV

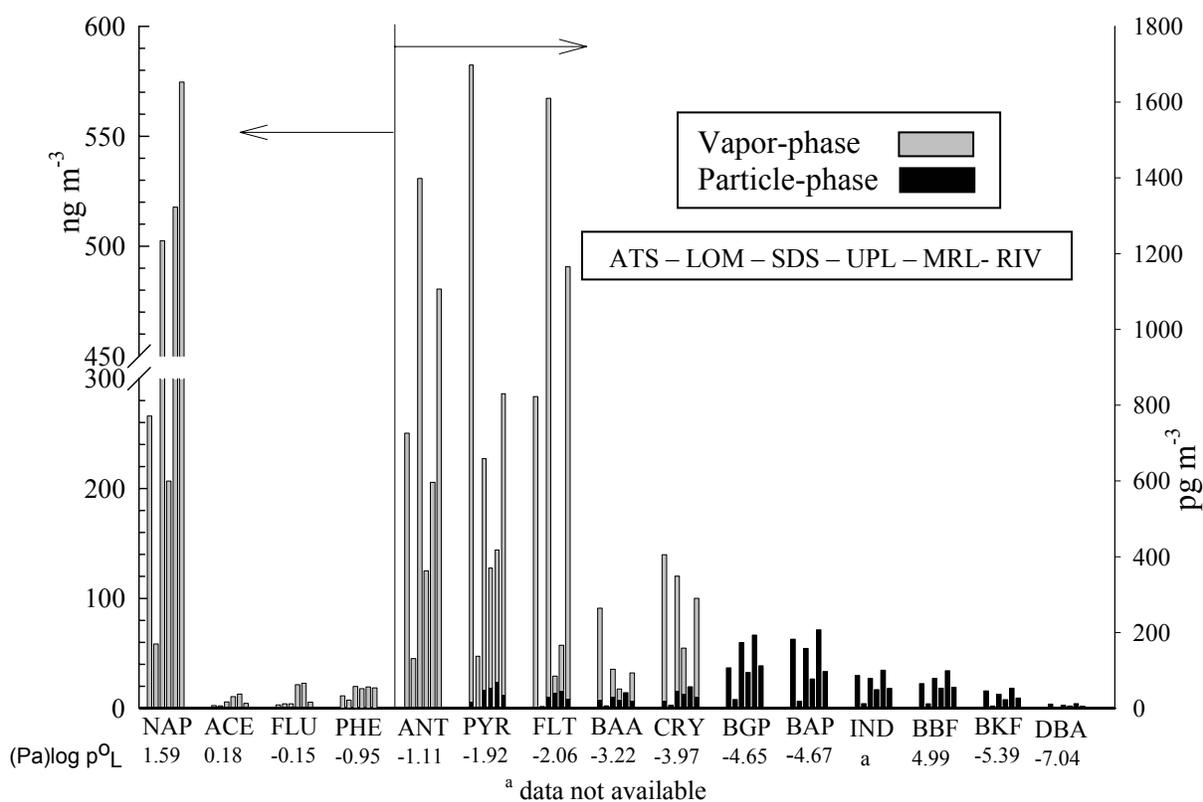


Figure 2. Annual averages of total PAH concentrations (vapor+particle) and log sub-cooled liquid vapor pressure (Pa) for individual species.

Hot season (22.7° C)
  Warm season (20.9° C)
  Cold season (13.7° C)

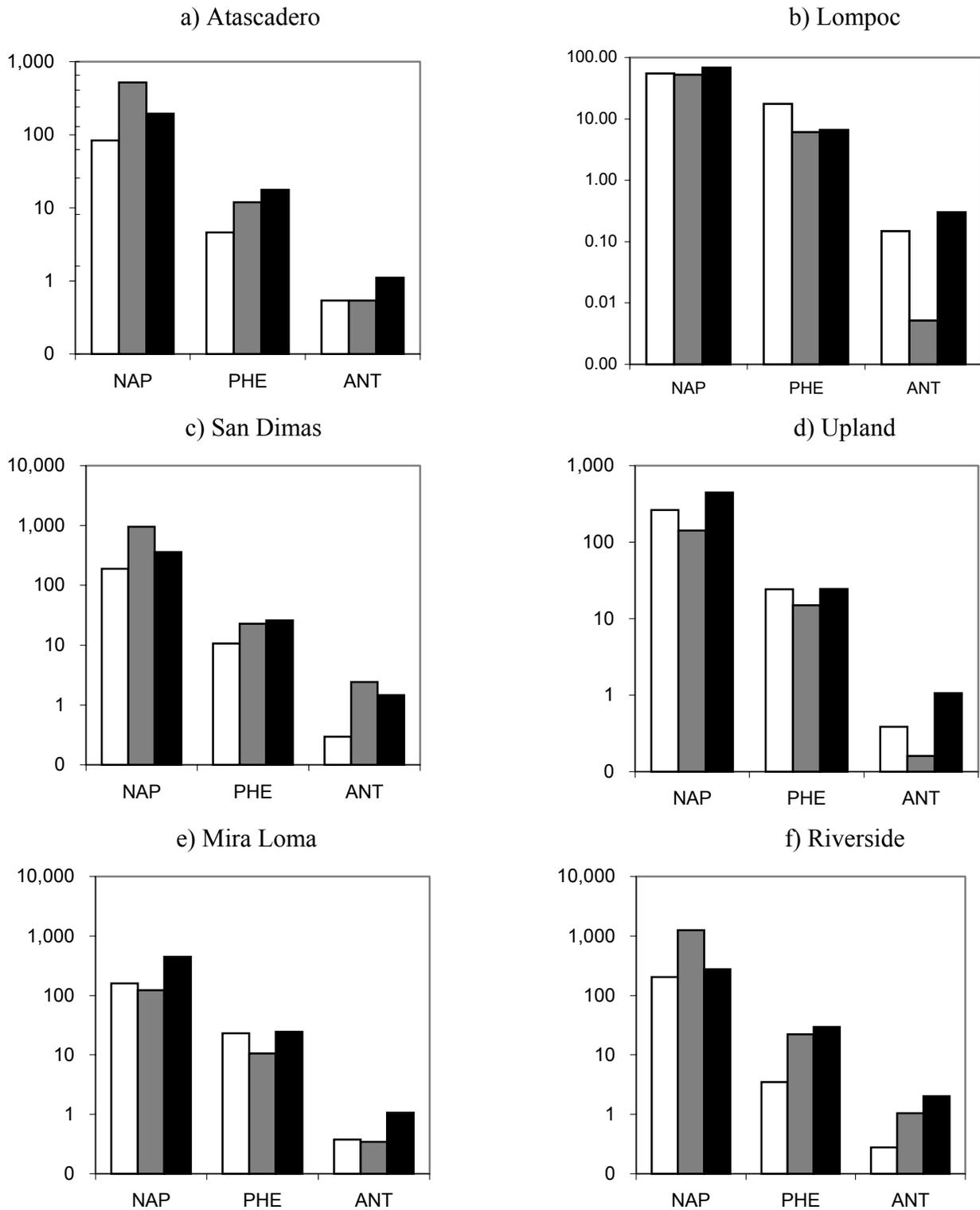


Figure 3. Seasonal concentration averages (ng m<sup>-3</sup>) observed for vapor-phase PAHs at the six community sites.

Hot season (22.7° C)
  Warm season (20.9° C)
  Cold season (13.7° C)

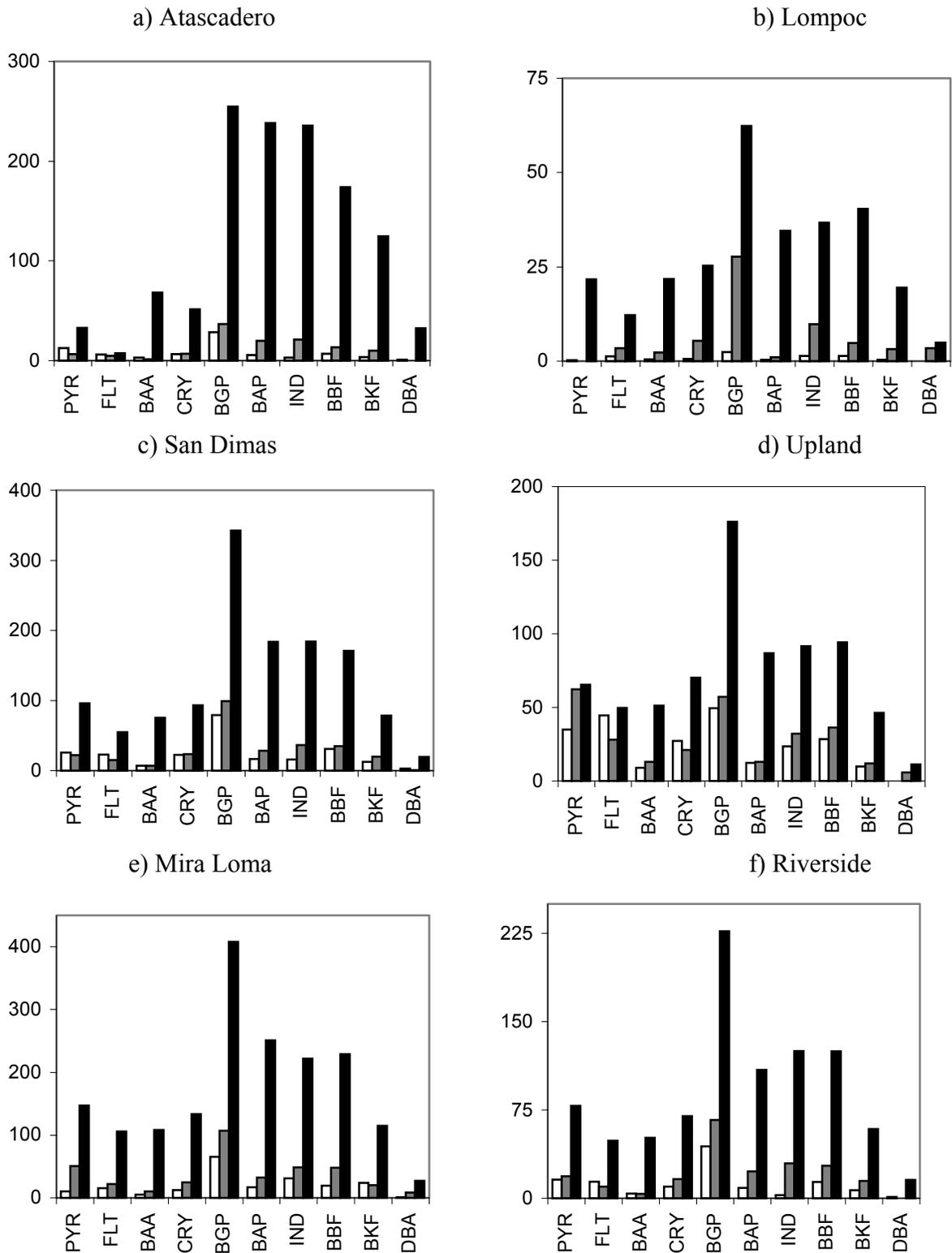


Figure 4. Seasonal concentration averages ( $\text{pg m}^{-3}$ ) observed for particle-phase PAHs at the six community sites.

## 6. Characterization of PAH and PAH-Derivatives

Janet Arey and Fabienne Reisen  
Air Pollution Research Center  
University of California, Riverside

### Introduction

The goal of our work 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. Of particular interest are nitro-PAHs and nitro-polycyclic aromatic compounds (nitro-PACs) since these compounds are potent mutagens and have been observed as products of gas-phase atmospheric reactions of PAHs. Four time intervals per day were sampled during one week in the summer at Los Angeles (August 12-16, 2002) and Riverside (August 26-30, 2002) and one week in the winter at Los Angeles (January 13-17, 2003) and Riverside (January 27-31, 2003). The daytime samples were 3.5 hours (morning 7 am-10:30 am, midday 11 am-2:30 pm and evening 3 pm-6:30 pm) and the nighttime sample was 11.5 hours (7 pm-6:30 pm). The sampling sites were equipped with the following instrumentation: a Tenax solid adsorbent sampler, operating at  $200 \text{ cm}^3 \text{ min}^{-1}$  for the daytime samples and at  $100 \text{ cm}^3 \text{ min}^{-1}$  for the nighttime samples; two high-volume sampler with 2 polyurethane foam plugs (PUFs) located in series beneath a Teflon-impregnated glass fiber (TIGF) filter ( $20 \text{ cm} \times 25 \text{ cm}$ ) operated at  $\sim 0.6 \text{ m}^3 \text{ min}^{-1}$ .

Since the last progress report we have completed analyses of the semi-volatile and particle-associated PAHs and nitro-PAHs.

### Results

The Tenax samples for the volatile PAHs were analyzed as soon as possible after the actual sampling and the results from the summer sampling were reported in the December, 2002 report and from the winter sampling in the March, 2003 report. The results of the semi-volatile nitro-PAHs collected on PUFs were reported for the summer sampling in the December, 2002 report and are given here for the winter sampling. The results of the semi-volatile PAHs collected on PUFs and filters are reported here, as are the results of the particle-associated nitro-PAHs. The preliminary data tables are given below and these show some very interesting differences between the summer and winter samples. Data analysis and interpretation continues and will be reported on in our next quarterly progress report.

A manuscript entitled "Methyl- and Dimethyl-/Ethyl- Nitronaphthalenes Measured in Ambient Air in Southern California" by Fabienne Reisen, Stephanie Wheeler and Janet Arey has been accepted for publication in *ATMOSPHERIC ENVIRONMENT*. Our ambient nitro-PAH data from the summer sampling at USC and UCR are described in this manuscript. The manuscript reports on environmental chamber reactions simulating ambient photooxidation of volatilized diesel fuel PAHs and demonstrates for the first time that dimethylnitronaphthalenes (DMNNs) and/or ethylnitronaphthalenes (ENNs) identified as formed from the OH radical-

initiated reactions of alkyl-PAHs present in diesel fuel are also present in ambient air samples collected in Southern California.

USC Average Ambient Concentrations of Nitro-PAHs for January 13-17, 2003

	0700-1030 hr pg/m <sup>3</sup>	1100-1430 hr pg/m <sup>3</sup>	1500-1830 hr pg/m <sup>3</sup>	1900-0630 hr pg/m <sup>3</sup>
1-NN	111	132	153	100
2-NN	151	144	130	76
3-NBph	138	138	48	26
2M1NN	37	7	18	24
1M8NN	3	2	3	3
2M8NN	16	9	13	12
2M4NN	10	8	10	9
1M2NN+2M5NN	15	12	16	12
1M5NN	24	52	63	27
1M6NN+1M4NN	35	48	56	30
2M7NN	15	14	15	9
2M6NN	9	7	7	4
1M7NN	4	3	4	2
1M3NN	10	11	9	6
SUM MNNs	178	174	214	139
SUM DMNNs	152	115	130	120

UCR Average Ambient Concentrations of Nitro-PAHs for January 27-31, 2003

	0700-1030 hr pg/m <sup>3</sup>	1100-1430 hr pg/m <sup>3</sup>	1500-1830 hr pg/m <sup>3</sup>	1900-0630 hr pg/m <sup>3</sup>
1-NN	106	41	178	201
2-NN	131	53	163	142
3-NBph	80	62	86	49
2M1NN	21	2	10	26
1M8NN	3	1	2	5
2M8NN	12	3	11	16
2M4NN	15	3	10	23
1M2NN+2M5NN	13	5	16	20
1M5NN	28	25	63	48
1M6NN+1M4NN	30	19	56	45
2M7NN	13	6	14	11
2M6NN	7	3	6	5
1M7NN	3	1	3	3
1M3NN	12	7	10	8
SUM MNNs	156	76	201	209
SUM DMNNs	107	34	91	130

**KEY:** NN = nitronaphthalenes; NBph = nitrobiphenyl; xMyNN = x-methyl-y-nitronaphthalene; DMNN = dimethylnitronaphthalenes (also includes ethylnitronaphthalenes)

**USC Average Ambient Concentrations of PAHs for August 12-16, 2002**

	0700-1030 hr ng/m <sup>3</sup>	1100-1430 hr ng/m <sup>3</sup>	1500-1830 hr ng/m <sup>3</sup>	1900-0630 hr ng/m <sup>3</sup>
<b>Phenanthrene</b>	<b>14.9</b>	<b>11.6</b>	<b>8.2</b>	<b>5.7</b>
Anthracene	0.5	0.3	0.3	0.03
Methylphenanthrenes	7.2	7.1	5.7	2.6
Fluoranthene	2.8	2.2	1.5	1.5
Pyrene	3.3	2.0	1.8	1.6

**UCR Average Ambient Concentrations of PAHs for August 26-30, 2002**

	0700-1030 hr ng/m <sup>3</sup>	1100-1430 hr ng/m <sup>3</sup>	1500-1830 hr ng/m <sup>3</sup>	1900-0630 hr ng/m <sup>3</sup>
<b>Phenanthrene</b>	<b>10.5</b>	<b>8.2</b>	<b>7.7</b>	<b>5.3</b>
Anthracene	0.3	0.1	0.1	0.1
Methylphenanthrenes	4.9	4.3	4.8	1.6
Fluoranthene	1.4	1.3	1.0	1.1
Pyrene	1.3	0.8	0.6	0.7

**USC Average Ambient Concentrations of PAHs for January 13-17, 2003**

	0700-1030 hr ng/m <sup>3</sup>	1100-1430 hr ng/m <sup>3</sup>	1500-1830 hr ng/m <sup>3</sup>	1900-0630 hr ng/m <sup>3</sup>
<b>Phenanthrene</b>	<b>17.3</b>	<b>15.1</b>	<b>18.0</b>	<b>15.4</b>
Anthracene	1.6	0.5	1.2	1.3
Methylphenanthrenes	8.8	8.5	10.2	7.6
Fluoranthene	6.0	3.4	4.1	3.1
Pyrene	6.9	3.3	4.9	3.7

**UCR Average Ambient Concentrations of PAHs for January 27-31, 2003**

	0700-1030 hr ng/m <sup>3</sup>	1100-1430 hr ng/m <sup>3</sup>	1500-1830 hr ng/m <sup>3</sup>	1900-0630 hr ng/m <sup>3</sup>
<b>Phenanthrene</b>	<b>13.5</b>	<b>7.2</b>	<b>12.8</b>	<b>10.5</b>
Anthracene	0.7	0.1	0.3	0.6
Methylphenanthrenes	7.2	4.5	6.3	4.4
Fluoranthene	2.4	1.3	2.0	1.7
Pyrene	2.7	0.9	1.6	1.5

USC Average Ambient Concentrations of Particle-Associated Nitro-PAHs for August 12-16, 2002

	0700-1030 hr pg/m <sup>3</sup>	1100-1430 hr pg/m <sup>3</sup>	1500-1830 hr pg/m <sup>3</sup>	1900-0630 hr pg/m <sup>3</sup>
<b>9-NA</b>	<b>64</b>	<b>18</b>	<b>11</b>	<b>36</b>
<b>NPhe</b>	<b>72</b>	<b>46</b>	<b>26</b>	<b>13</b>
2-NFL	<b>135</b>	<b>71</b>	<b>18</b>	<b>50</b>
1-NP	<b>13</b>	<b>9</b>	<b>3</b>	<b>4</b>
2-NP	<b>1</b>			

UCR Average Ambient Concentrations of Particle-Associated Nitro-PAHs for August 26-30, 2002

	0700-1030 hr pg/m <sup>3</sup>	1100-1430 hr pg/m <sup>3</sup>	1500-1830 hr pg/m <sup>3</sup>	1900-0630 hr pg/m <sup>3</sup>
<b>9-NA</b>	<b>31</b>	<b>17</b>	<b>34</b>	<b>26</b>
<b>NPhe</b>	<b>60</b>	<b>45</b>	<b>54</b>	<b>19</b>
2-NFL	<b>229</b>	<b>78</b>	<b>36</b>	<b>273</b>
1-NP	<b>14</b>	<b>5</b>	<b>3</b>	<b>4</b>
2-NP	<b>2</b>			

USC Average Ambient Concentrations of Particle-Associated Nitro-PAHs for January 13-17, 2003

	0700-1030 hr pg/m <sup>3</sup>	1100-1430 hr pg/m <sup>3</sup>	1500-1830 hr pg/m <sup>3</sup>	1900-0630 hr pg/m <sup>3</sup>
<b>9-NA</b>	<b>12</b>	<b>13</b>	<b>44</b>	<b>20</b>
<b>NPhe</b>	<b>20</b>	<b>44</b>	<b>52</b>	<b>10</b>
2-NFL	<b>117</b>	<b>96</b>	<b>57</b>	<b>36</b>
1-NP	<b>47</b>	<b>14</b>	<b>13</b>	<b>23</b>
2-NP	<b>7</b>	<b>2</b>	<b>1</b>	<b>3</b>

UCR Average Ambient Concentrations of Particle-Associated Nitro-PAHs for January 27-31, 2003

	0700-1030 hr pg/m <sup>3</sup>	1100-1430 hr pg/m <sup>3</sup>	1500-1830 hr pg/m <sup>3</sup>	1900-0630 hr pg/m <sup>3</sup>
<b>9-NA</b>	<b>11</b>	<b>9</b>	<b>50</b>	<b>21</b>
<b>NPhe</b>	<b>16</b>	<b>27</b>	<b>65</b>	<b>15</b>
2-NFL	<b>78</b>	<b>45</b>	<b>60</b>	<b>127</b>
1-NP	<b>19</b>	<b>8</b>	<b>10</b>	<b>12</b>
2-NP	<b>3</b>	<b>1</b>	<b>1</b>	<b>2</b>

**KEY:** NA = nitroanthracene; NPhe = nitrophenanthrenes; NFL = nitrofluoranthene;  
NP = nitropyrene

## 7. Coarse, Intermodal (PM<sub>1-2.5</sub>), and Fine PM Measurement

### Introduction

During this quarter, data has been collected from various instruments and sites. All data has been compiled and sorted in this quarter, and the paper has been submitted to the Journal of the Air and Waste Management Association. The following data has been included in the final paper: time-integrated mass measurements, time-integrated chemical species data, continuous mass and nitrate measurements. Plots of mass concentrations versus time and versus other size mode mass concentrations have been presented in totality (if not presented in prior reports).

### Results

PM<sub>1-2.5</sub> and PM<sub>2.5</sub> mass concentrations are very highly correlated for all sites (Figure 1). Another positive correlation exists between the chemical species in these two size fractions. The chemical characteristics of intermodal PM are displayed by site in Figure 2. These results are similar to those discovered by Hughes et al. (2000), in which they determined the chemical composition of the fine PM mode at four locations in Southern California. In contrast, the coarse size mode does not demonstrate as high of a positive correlation with intermodal PM. Intermodal PM tracks much better with PM<sub>1</sub> than the coarse mode in receptor sites while the correlations between coarse and intermediate and PM<sub>1</sub> and intermediate become closer in source sites.

### Comparison of Ionic Species

The correlation between coarse and intermodal nitrate is very weak ( $R^2 = 0.13$ ), which demonstrates the divergence of the sources of these particles (Figure 3a). Coarse mode nitrate is thought to be dominated by sodium nitrate while nitrate in the fine mode is mostly ammonium nitrate. Sodium nitrate originates from seaspray that aerosolizes upon hitting rocks while ammonium nitrate is formed via a detailed set photochemical reactions of NO<sub>x</sub> and NH<sub>3</sub> gases in the atmosphere (Harrison and Pio, 1983). Figure 3b shows that intermodal nitrate agrees with PM<sub>2.5</sub> nitrate with  $R^2 = 0.70$ . This agreement may be due in part to two causes. First, PM<sub>1-2.5</sub> is a significant portion of PM<sub>2.5</sub>, and it drives the mass in the fine mode; and second, the PM<sub>1</sub> particles are growing via condensation into the 1-2.5 μm size range. It has already been established that large amounts of ammonium nitrate are produced in Riverside in the submicron range (Allen et al., 2000). Koutrakis et al. (1989) have demonstrated that the aerodynamic diameter of atmospheric sulfate particles can exceed 1 μm for relative humidities greater than ninety percent, and Los Angeles frequently experiences similar relative humidities in the overnight and early morning hours. Another argument for the similarities between intermodal PM and total fine PM has already been mentioned above but is worth repeating here. The chemical compositions of PM<sub>1</sub> and PM<sub>1-2.5</sub> have been found to be very similar by previous studies as well as this one (Hughes et al., 1999; Hughes et al., 2000; Kleeman et al., 1999).

In order to investigate this further, an intensive study using the ADI Continuous Nitrate Monitor was conducted during the month of September 2001. Figure 4 demonstrates the high correlation between continuously measured intermodal nitrate and PM<sub>1</sub> nitrate ( $R^2 = 0.80$ ). A possible theory to account for this phenomenon is that particles emitted to the west are traveling by advection to Claremont. While in transit, these particles experience condensational growth and participate in photochemical reactions. Some particles remain in the submicron range after growth while others become intermodal particles. Because the process takes place over multi-hour time spans, the hourly average of relative humidity does not correlate well with the ratio of these two modes. In other words, PM<sub>1</sub> particles do not instantaneously grow into PM<sub>1-2.5</sub> particles because the process takes many hours of advection and stagnation. Figure 5 further elucidates this point. While wind speed peaks at 3 PM, the ratio of intermodal to fine PM peaks at 6 PM. If the wind were creating resuspension of coarse particles that were in turn affecting intermodal PM concentrations, wind speed would peak with mass concentration. Advection, however, would be represented by the time lag seen here. After wind speed peaks, intermodal PM nitrate particles, that have been undergoing photochemistry and growth, blow toward Claremont and peak shortly thereafter. Figure 6 also illustrates the photochemical growth and advection of intermodal PM in the Los Angeles basin. The ratio of intermodal to fine mode PM increases during the summer months due to increased solar radiation and enhanced advection.

Since the majority of PM<sub>2.5</sub> mass can be explained by organic carbon, ammonium sulfate, and ammonium nitrate (Christoforou et al., 2000), the correlation of only nitrate between PM<sub>1</sub> and intermodal PM does not completely illustrate the point. Due to lack of instrumentation, continuous monitors were not available to measure organic carbon and sulfate. Time-integrated data for these chemical species were measured, however. Table 1 shows the Pearson correlation coefficients between various parameters that include size and chemical composition of PM. Included in this table are R-values for the correlation between intermodal organic carbon, sulfate, and nitrate mass concentrations. The correlations between all three species are high with R-values from 0.68 to 0.86. These high correlations support the idea that OC, NO<sub>3</sub>, and SO<sub>4</sub> share similar sources in intermodal PM. Since PM<sub>1-2.5</sub> nitrate and sulfate correlate well with PM<sub>1</sub> nitrate and sulfate, and sulfate is found almost exclusively in the fine mode, we can conclude that PM<sub>1</sub> and PM<sub>1-2.5</sub> are closely related.

### **Crustal Metal Analysis**

Figure 7 displays the relationship between coarse and intermodal crustal metal concentrations. The crustal metal concentrations were obtained by analyzing MOUDI Teflon substrates via x-ray fluorescence (XRF) and utilizing the following formula (Malm et al., 1994):

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

Table 1. Correlations between MOUDI mass and chemical species measurements.

	Coarse NO <sub>3</sub> (CN)	PM <sub>1-2.5</sub> NO <sub>3</sub> (IN)	PM <sub>1</sub> NO <sub>3</sub> (PM1N)	Coarse SO <sub>4</sub> (CS)	PM <sub>1-2.5</sub> SO <sub>4</sub> (IS)	PM <sub>1</sub> SO <sub>4</sub> (PM1S)	Coarse OC (CO)	PM <sub>1-2.5</sub> OC (IO)	PM <sub>1</sub> OC (PM1O)
<b>CN</b>	<b>1.00</b>								
<b>IN</b>	0.55	<b>1.00</b>							
<b>PM1N</b>	<b>0.16</b>	0.66	<b>1.00</b>						
<b>CS</b>	0.80	0.45	<b>0.05</b>	<b>1.00</b>					
<b>IS</b>	0.50	0.82	0.41	0.59	<b>1.00</b>				
<b>PM1S</b>	0.68	0.46	<b>0.12</b>	0.67	0.65	<b>1.00</b>			
<b>CO</b>	<b>0.26</b>	<b>0.22</b>	<b>0.18</b>	0.39	<b>0.28</b>	0.34	<b>1.00</b>		
<b>IO</b>	<b>0.01</b>	0.47	0.37	<b>0.19</b>	0.53	<b>0.19</b>	0.61	<b>1.00</b>	
<b>PM1O</b>	<b>-0.08</b>	<b>0.06</b>	<b>0.18</b>	<b>-0.02</b>	<b>0.01</b>	<b>0.02</b>	0.61	0.56	<b>1.00</b>

Numbers in bold denote that the value is statistically significant with  $p < 0.01$

The moderate correlation between intermediate and coarse crustal metals is expected because the tail of the coarse mode crustals infiltrates PM<sub>2.5</sub> to a limited extent, which is indicated by the very low concentrations of crustal metals found in intermodal PM. Intermodal PM's relationship to its soil (crustal) component is shown in Figure 8. As evidenced by the slope of 3.42, the soil component of PM<sub>1-2.5</sub> is less than 25% of the total mass and has a moderate correlation with total mass ( $R^2 = 0.54$ ). The previous result differs from the Kegler et al. paper in that they found a similar correlation between intermodal mass and soil concentration but a much higher slope. The crustal component in Spokane, WA is closer to 50% of the total intermodal mass, which is to be expected in a city that is surrounded by rural areas.

Finally, Figure 9 displays the lack of correlation between the most prominent chemical species that comprise intermodal PM and the crustal metals found in that mode. While OC, nitrate, and sulfate correlate well with one another, none correlate with the crustal component. Since the crustal component comes from the coarse mode and does track with intermodal mass, the two are moderately correlated. The majority of the mass, however, does not correlate with the crustal component and likely shares more properties with particles in the PM<sub>1</sub> region.

Figure 1. PM<sub>1-2.5</sub> Versus PM<sub>2.5</sub> at All Sites

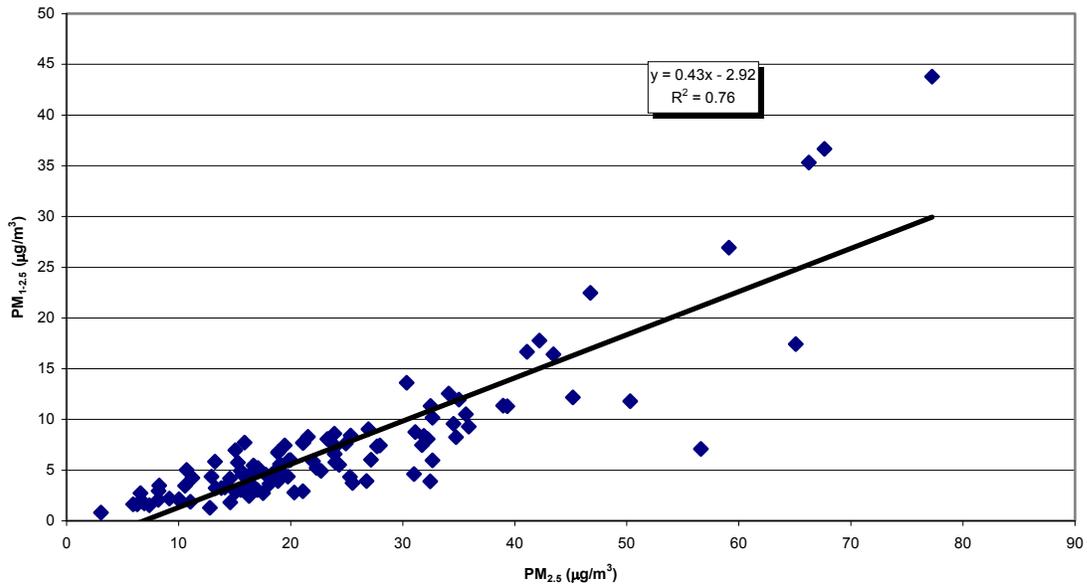


Figure 2. Chemical Composition of the Intermediate Mode Averaged By Location

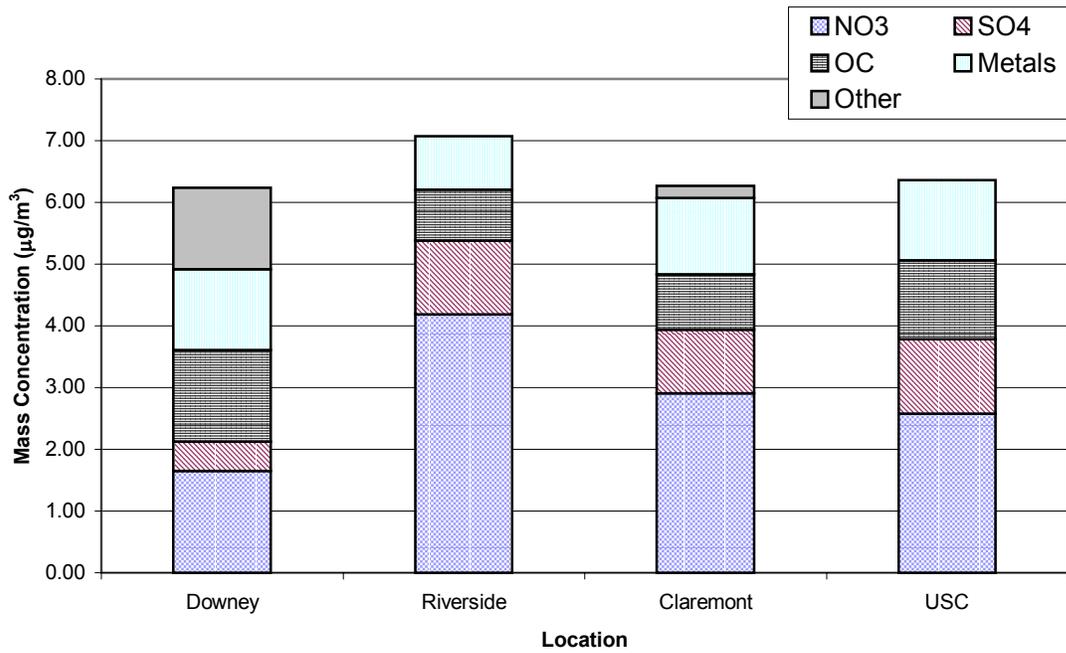


Figure 3a. PM<sub>2.5-10</sub> Vs. PM<sub>1.0-2.5</sub> Nitrate Mass Concentrations for Claremont, CA

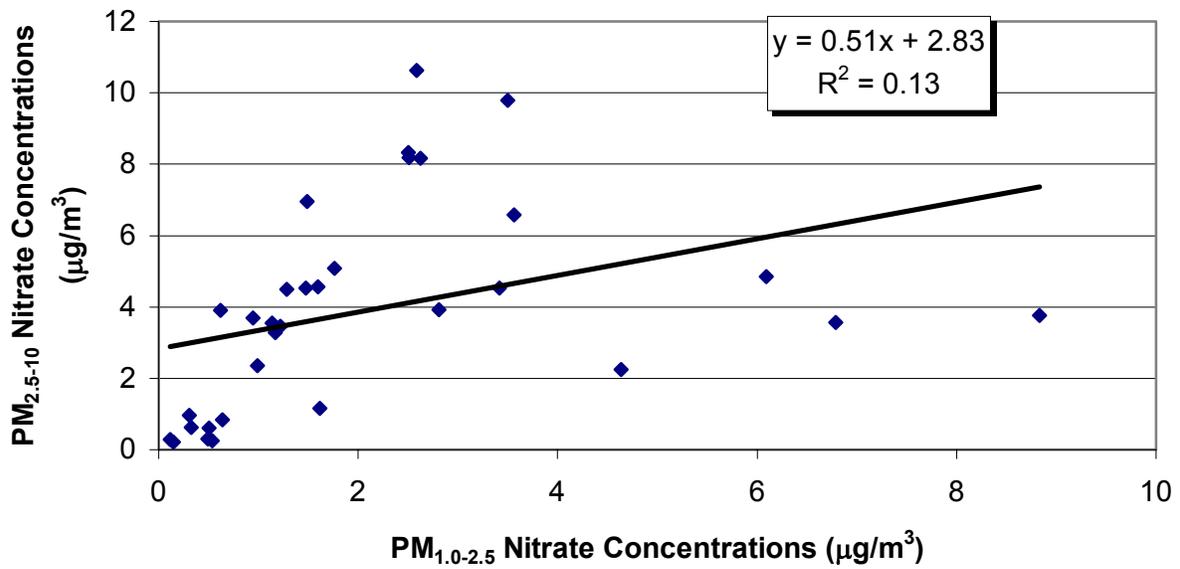


Figure 3b. PM<sub>1-2.5</sub> Versus PM<sub>2.5</sub> Nitrate Concentrations at All Sites

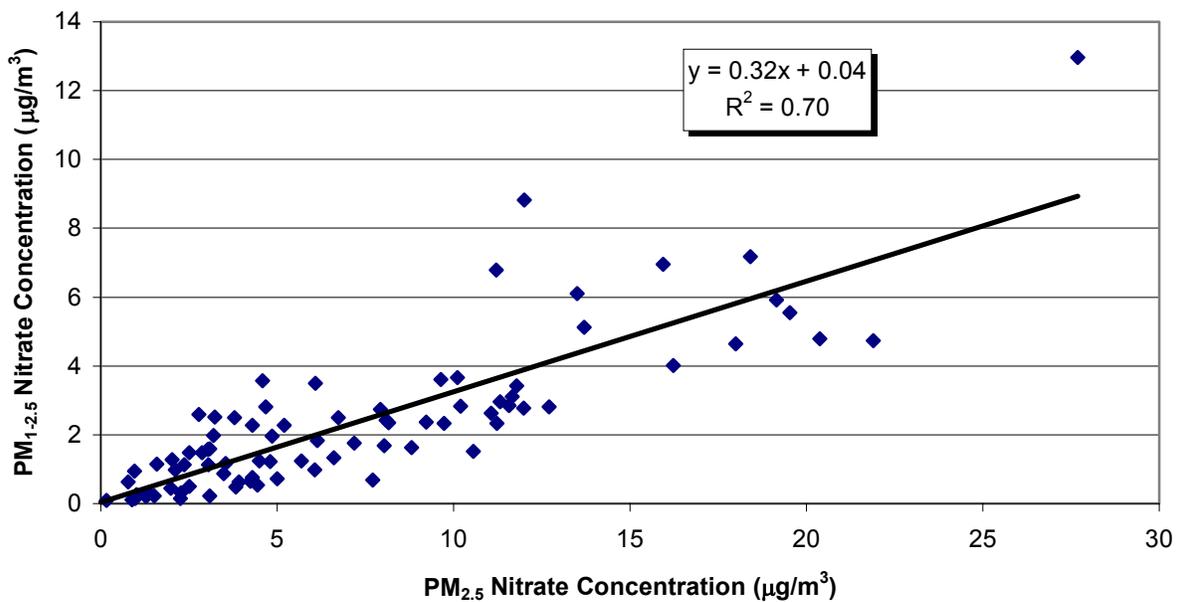


Figure 4. Continuous PM1-2.5 Versus PM1 Nitrate at Claremont, CA in September 2001

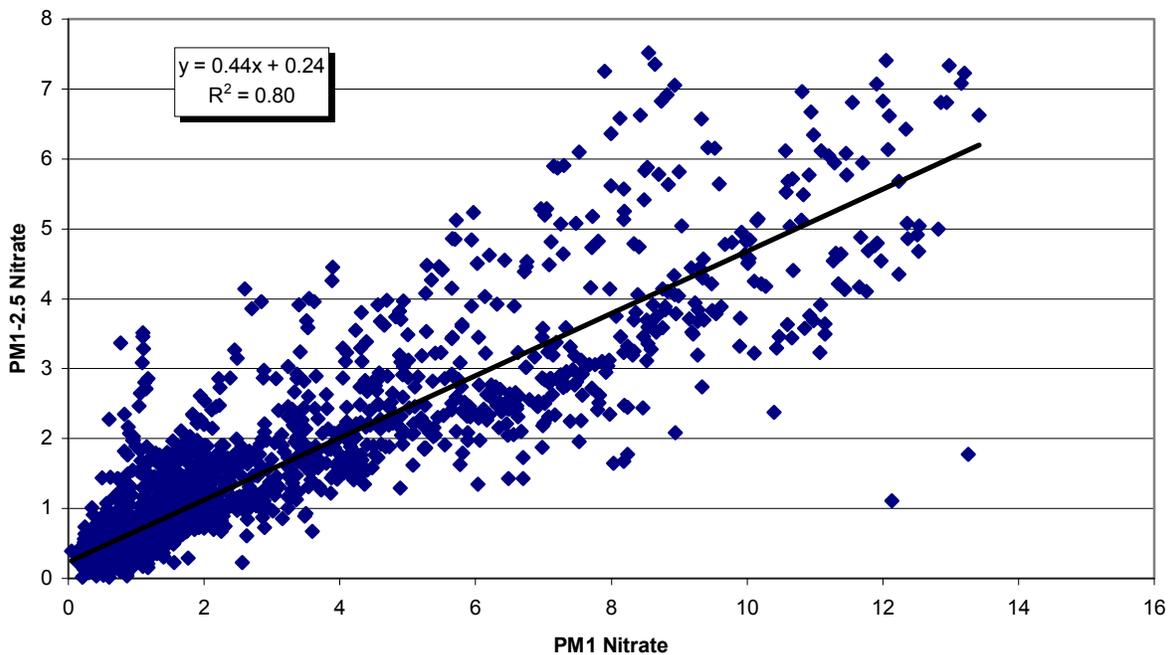
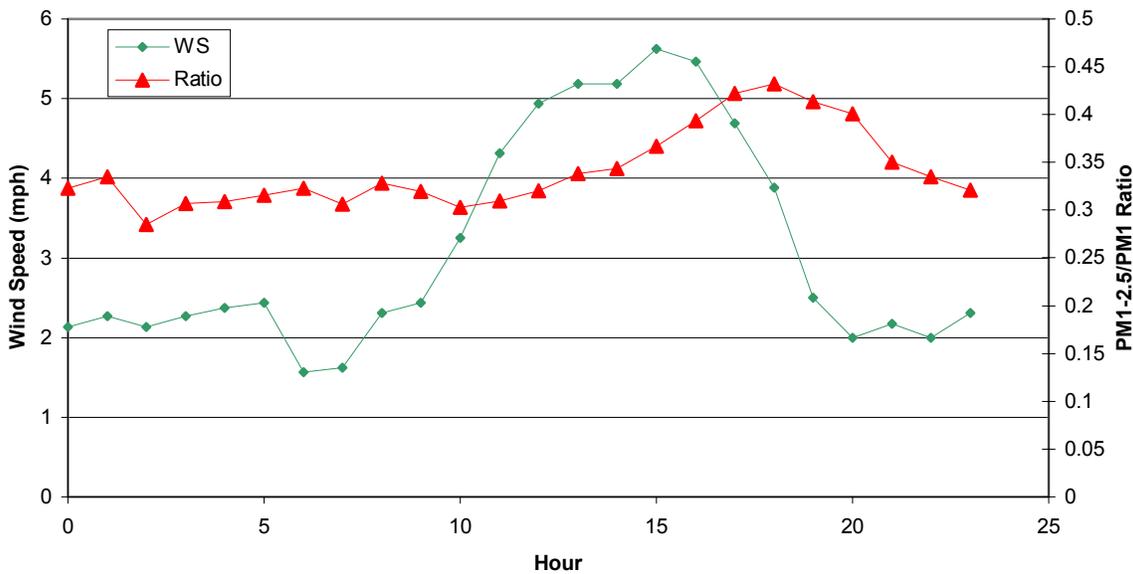
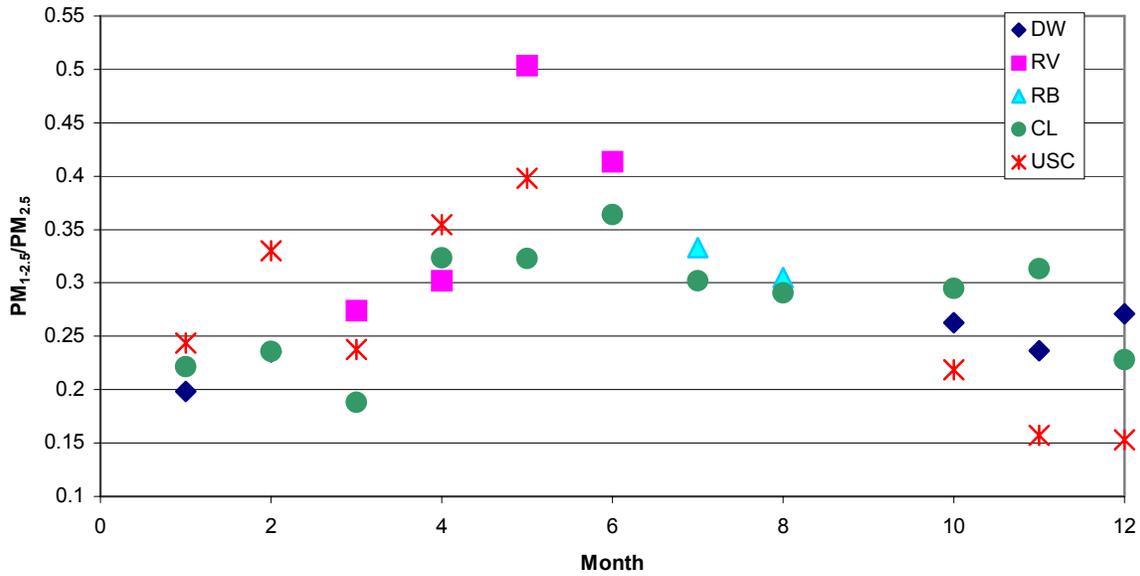


Figure 5. Daily Wind Speed and PM1-2.5/PM2.5 Nitrate at Claremont, CA in September 2001



**Figure 6. Monthly Average of the Ratio of Intermediate Mode PM to Total PM<sub>2.5</sub>**



**Figure 7. OC, Nitrate and Sulfate Concentrations Versus Soil Concentration in the Intermediate Mode**

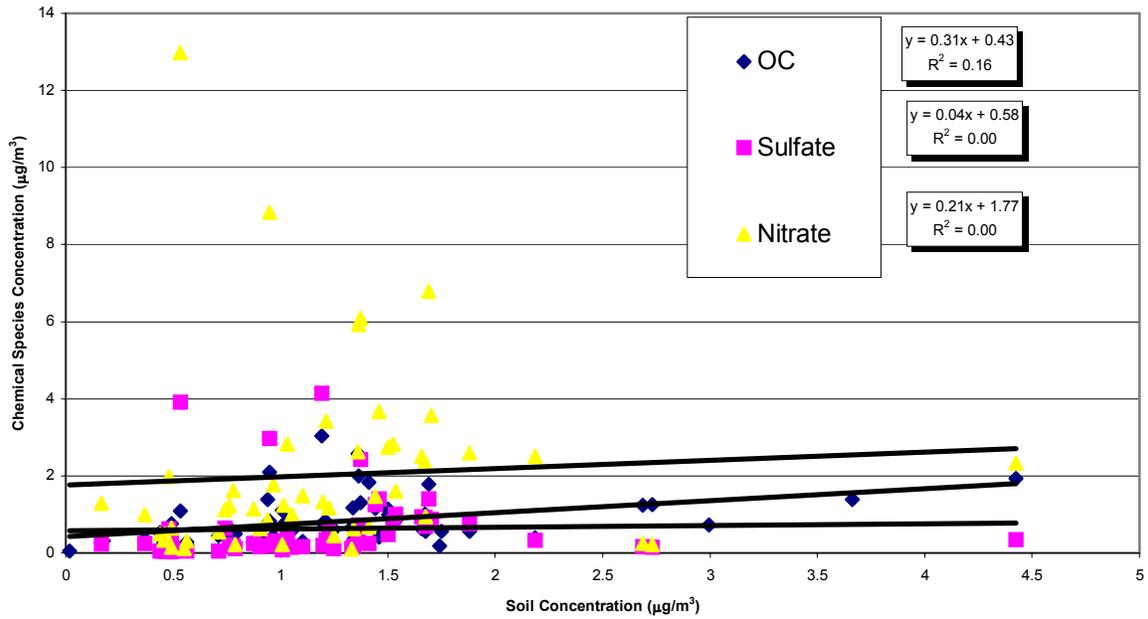


Figure 8. Intermediate Versus Coarse Mode Crustal Elements for Claremont, CA

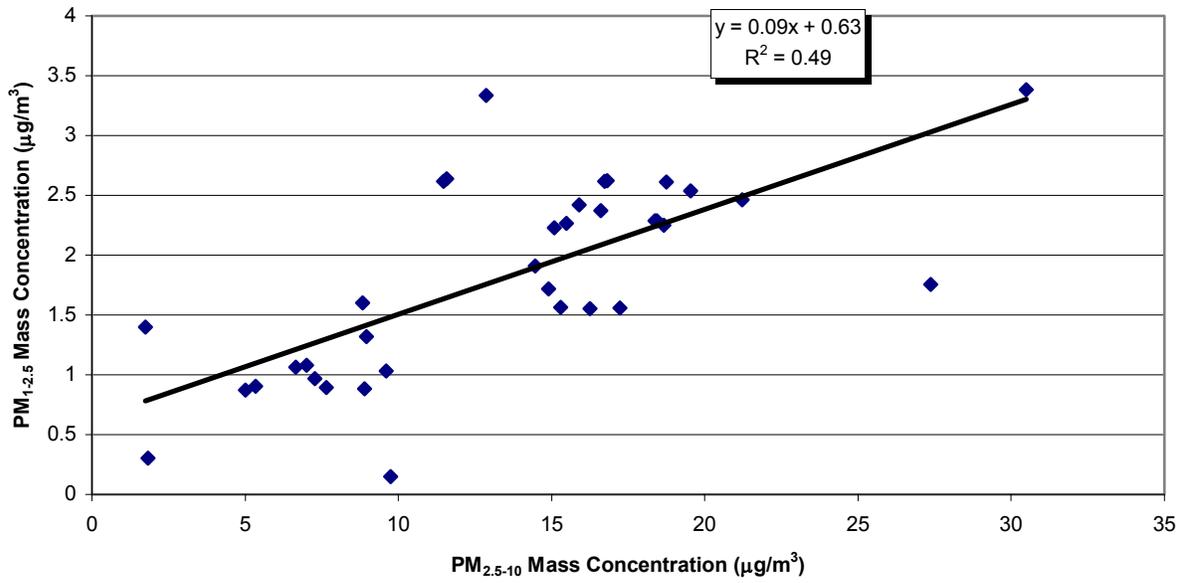
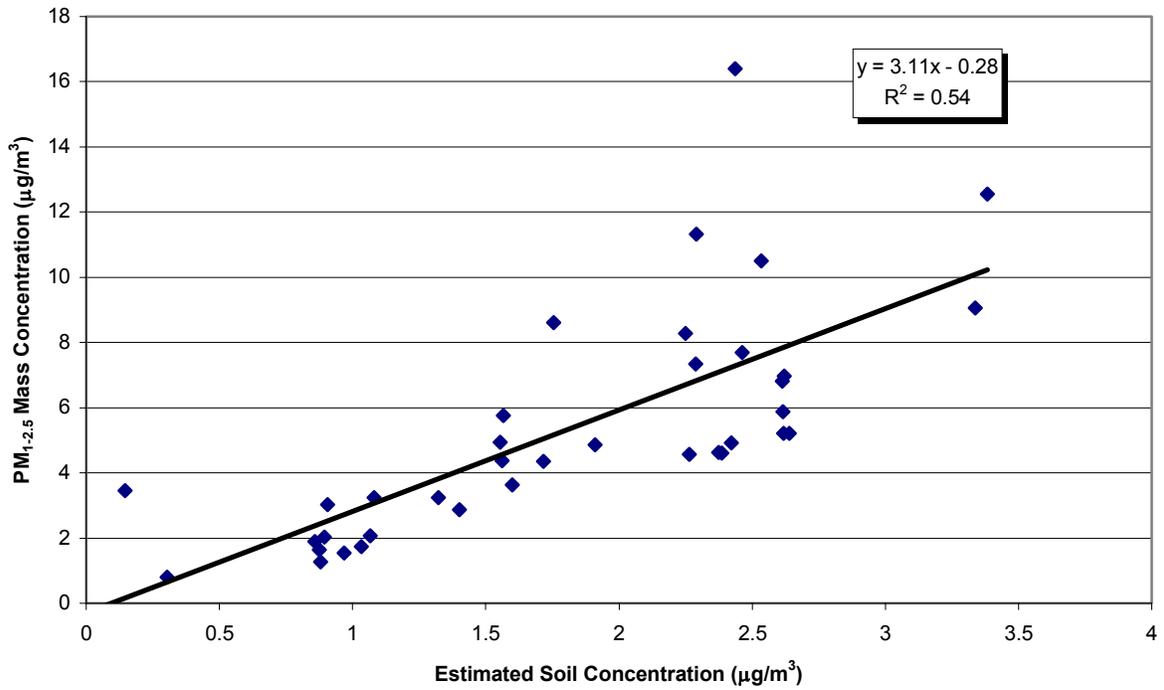


Figure 9. PM<sub>1-2.5</sub> Versus Estimated PM<sub>1-2.5</sub> Soil Concentration



## 8. Predicting Ultrafine Particles near Major Freeways

Recent toxicology studies have demonstrated that atmospheric ultrafine particles are responsible for some of the adverse health effects. Motor vehicle emissions usually constitute the most significant source of ultrafine particles (diameter < 100 nm) in an urban environment, yet, little is known about the concentration and size distribution of ultrafine particles in the vicinity of major highways.

The present research focuses on developing a model to determine ultrafine particle behavior after emissions, as they are transported away from the emission source --- a freeway. A major goal of this physical model is to characterize the atmospheric behavior of ultrafine particles by describing mathematically the spatial and temporal size distribution and relative concentration of ultrafine particles released from freeways into the atmosphere. Previously we observed rapid decrease in ultrafine particle number concentration and change in particle size distribution with increasing distance from freeways (Zhu et al. 2002a; Zhu et al. 2002b). Based on these experimental data, four sub-models, namely an atmospheric dispersion model, a coagulation model, a condensation-evaporation model and an adsorption model have been developed individually.

Figures 1a-c show measured and model predicted ultrafine particle size distributions at different sampling locations near the 405 freeway. The ultrafine particle size distribution at 30 m downwind from the 405 freeway which was reported by Zhu et al., (2002a) was used as the model input. Ultrafine particle size distribution at 60 m, 90 m, 150 m, and 300 m downwind distances were predicted using the model described above. Figure 1a is the measured ultrafine particle size distributions near the 405 freeway (Zhu et al. 2002a). Atmospheric dispersion model was the only model used in Figure 1b. Both atmospheric dispersion and coagulation model were used in Figure 1c. Figure 1a differs from Figures 1b-c in that significant mode growth was observed. It is also noted that Figures 1b and 1c are extremely similar indicating that coagulation process has been diminished by rapid atmospheric dilution.

To compare model predictions with experimental data, Table 1a was prepared to summarize ultrafine particle number concentrations in different size ranges at different locations near the 405 freeway as shown in Figure 1a. The ratios summarized in Tables 1b and 1c are predicted ultrafine particle concentration to measured ultrafine particle concentration. Table 1b is ultrafine particle number concentrations predicted by atmospheric dispersion model. Table 1c is those predicted by both atmospheric dispersion and coagulation model in each category. It is seen in Table 1b, the atmospheric dispersion model predicts total particle number concentration in the size range of 6 to 200 nm very well but it significantly over estimates particle number concentrations in the size range of 6 to 25 nm and under estimates particle number concentrations in the size range of 50 to 200 nm. With the coagulation model, the over estimates of 6-25 nm particles are reduced by a few percent but no improvement was found for the under estimates of 50-200 nm particles. Using the 60 m data as an example, the coagulation model helps to reduce the ratio of particle number concentration in the 6-25 nm size range by model prediction to experimental data from 1.30 to 1.25. The 5% reduction in the smallest particles should end up in the larger size ranges shown in the Table. However, that is not the case as

shown in Table 1c. This is because these particles become larger than 200 nm by coagulation and were not included in the table. Overall, the atmospheric dispersion model with the coagulation model over estimate particles in 6-25 nm size range up to 84% and under estimates particles in 50-200 nm up to 78% at 60 m downwind from the freeway 405.

There are two possible factors that may enhance coagulation to make the model better fit in experimental data. The first one lies in the fact only particles larger than 6 nm were measured (Zhu et al. 2002a). There may be significant numbers of particles smaller than 6 nm that could potentially coagulate with particles in 6-25 nm to reduce particle number concentrations in this size range while increasing particle number concentrations in the larger size ranges. The other is incomplete mixing that could be particularly important for the near field situation. When air parcels are carried away from the freeway by the wind, particle number concentrations are likely to be non-uniform between the air parcels. Some of the parcels may have higher number concentrations; some may have lower number concentrations. Since coagulation rate is directly proportional to the square of particle number concentrations, particles in the high number concentration region will have a greater coagulation rate than others. The overall effect is to enhance average coagulation rate.

Although discrepancies exist between the predicted and measured particle size distributions, the model predicts the total particle number concentration very accurate by atmospheric dispersion model alone. This implies that atmospheric dispersion is by far the most important mechanisms in determining particle number concentration near freeways. Other aerosol or chemical processes may have an effect on the particle size distribution but not on total particle number concentrations. Thus, the model developed in this study provides epidemiologists and toxicologists a simple tool to estimate ultrafine particle number concentrations near freeways for health related studies.

## REFERENCES:

Zhu, Y., Hinds, W. C., Kim, S. and Sioutas, C. (2002a). Concentration and Size Distribution of Ultrafine Particles near a Major Highway, *Journal of Air and Waste Management Assoc.* 52:174-185.

Zhu, Y., Hinds, W. C., Kim, S., Shen, S. and Sioutas, C. (2002b). Study of Ultrafine Particles near a Major Highway with Heavy-duty Diesel Traffic, *Atmospheric Environment.* 36:4323-4335.

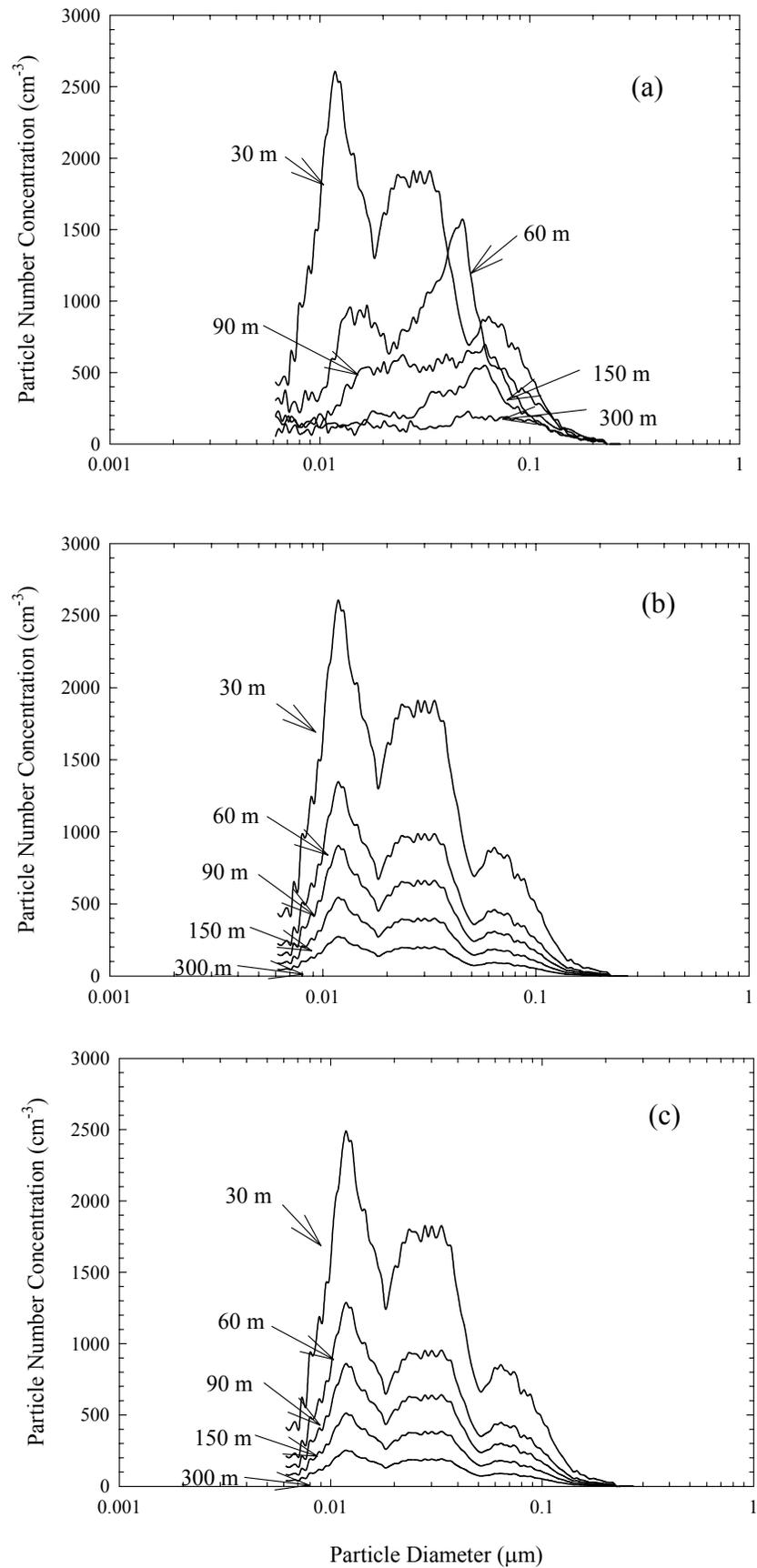


Figure 1. Measured and model prediction of ultrafine particle size distributions near the 405 freeway. (a) experimental data (b) atmospheric dispersion model only (c) atmospheric dispersion with coagulation model.

Table 1. Ultrafine particle number concentrations in different size ranges at different sampling locations near the 405 freeway.

(a) Experimental Data

Particle Diameter Range (nm)	Downwind Distance from Center of Freeway				
	30 m	60 m	90 m	150 m	300 m
6-25	6.16e4	2.37e4	1.35e4	6.40e3	4.77e3
25-50	2.91e4	2.21e4	1.07e4	6.00e3	2.60e3
50-100	1.41e4	1.09e4	1.02e4	7.19e3	3.44e3
100-200	3.37e3	1.65e3	3.02e3	2.08e3	1.60e3
Total*	1.08e5	5.84e4	3.74e4	2.17e4	1.24e4

\* 6-200 nm total

(b) Atmospheric dispersion model

Particle Diameter Range (nm)	Ratio predicted to measured particle number concentration				
	30 m	60 m	90 m	150 m	300 m
6-25	1.0	<b>1.30</b>	<b>1.53</b>	<b>1.95</b>	<b>1.31</b>
25-50	<b>1.0</b>	<b>0.72</b>	<b>1.00</b>	<b>1.08</b>	<b>1.25</b>
50-100	<b>1.0</b>	<b>0.67</b>	<b>0.48</b>	<b>0.41</b>	<b>0.43</b>
100-200	<b>1.0</b>	<b>1.04</b>	<b>0.38</b>	<b>0.33</b>	<b>0.22</b>
Total	<b>1.0</b>	<b>0.96</b>	<b>1.00</b>	<b>1.04</b>	<b>0.91</b>

(c) Atmospheric dispersion and coagulation model

Particle Diameter Range (nm)	Ratio predicted to measured particle number concentration				
	30 m	60 m	90 m	150 m	300 m
6-25	1.0	<b>1.25</b>	<b>1.46</b>	<b>1.84</b>	<b>1.22</b>
25-50	<b>1.0</b>	<b>0.70</b>	<b>0.97</b>	<b>1.04</b>	<b>1.20</b>
50-100	<b>1.0</b>	<b>0.65</b>	<b>0.47</b>	<b>0.40</b>	<b>0.42</b>
100-200	<b>1.0</b>	<b>1.03</b>	<b>0.38</b>	<b>0.34</b>	<b>0.22</b>
Total	<b>1.0</b>	<b>0.92</b>	<b>0.96</b>	<b>1.00</b>	<b>0.86</b>

9. Chemical Characterization of Ultrafine Particles in the LA Basin

The plan for this study is to conduct bi-weekly MOUDI/Nano-MOUDI sampling in the following sites\*:

**Table 1. \*Shaded dates indicate completed and/or in progress.**

<b>Date</b>	<b>USC</b>	<b>Long Beach</b>	<b>Riverside</b>	<b>Upland</b>
<b>Fall</b>	<b>Oct. 2-Oct. 16</b>	<b>Oct. 16-Oct. 30</b>	<b>Oct. 30-Nov.13</b>	<b>Nov. 13-Nov. 27</b>
<b>Winter</b>	<b>Feb. 27-Mar. 13</b>	<b>Mar. 13-Mar. 27</b>	<b>Jan. 27-Feb. 13</b>	<b>Feb. 13-Feb. 27</b>
<b>Spring</b>		<b>May. 20-June. 2</b>		
<b>Summer</b>	<b>July 15-July 28</b>	<b>July 29-Aug.11</b>	<b>Aug.12-Aug.25</b>	<b>Aug.26-Sept.8</b>

## **Introduction**

Fourteen-day composite size-fractionated PM<sub>2.5</sub> and UF impactor samples were collected and analyzed. The sampling is conducted over four seasons (autumn, winter, spring/marine layer, summer) and at four sites, including upwind source and downwind, inland receptor sites in the LAB as shown in the above table. Aluminum substrates were pre-baked and sealed prior to January 27, 2003. Six substrates per two-week period were used. The MOUDI/Nano-MOUDI combination was employed at each site listed above from January 27, 2003 to June 02, 2003. The summer sampling will start after the submission of this report. Sampling was non-stop for the listed periods with no change of substrates except between sites. Samples were collected on aluminum substrates and analyzed for gravimetric mass, sulfate and nitrate by ion chromatography, and elemental and organic carbon by thermal evolution/optical transmission analysis. Data on size-segregated PAHs was also obtained. Comparison of nano-MOUDI mass concentration with that of collocated SMPS was also performed. Upon completion of each site's sampling, the substrates were split into two pieces. Three-fourths were sent to Tony Miguel (UCLA) for organics analyses, and one-fourth was sent to Rancho Los Amigos for ion chromatography. The chemical analyses for the winter sampling period have been completed with results shown below.

## **Results**

Higher mass concentration levels (Table 2) at all sites are observed in the autumn than in the winter, possibly due to higher levels of photochemical activity. Of all four sites, Riverside, a receptor site, has the highest fall to winter mass concentration ratio, resulting from possibly increased advection as well as photochemistry. Average wintertime mass concentrations at the source sites are higher than the receptor sites. Higher concentrations of nitrate and sulfate were found in the larger particles and no observable levels of these compounds were detected in the 0-56 nm size range for any site at any season. Mass concentration ratios between SMPS and the nano-MOUDI showed lower values for smaller particles and higher values for larger particles, possibly due to the lower density of ultrafine agglomerates. Because of their low density, a

substantial fraction of these particles would be classified by an inertial separator (such as the nano-MOUDI) in smaller size bins than if measured by the SMPS, which would classify these irregularly shaped particles in larger size ranges due to their higher surface areas and aerodynamic drag. Table 3 shows size fractionated SMPS vs nano-MOUDI mass concentration ratios for fall and three sites. The following figures show the elemental carbon (EC) and organic carbon (OC) concentrations as a function of particle size. Figures 1-4 represent data obtained from USC, Long Beach, Riverside, and Upland, respectively. USC has the highest ultrafine elemental carbon concentrations followed by Long Beach. High EC levels are due to the high levels of diesel truck emissions in the vicinities of the USC and Long Beach sites. As might be expected, the total carbon concentration is highest at the urban location of USC. Upland has the second highest levels of carbon concentrations followed by Long Beach and Riverside. The winter levels of carbon are low compared to the fall season. The low photochemical activity during winter results in low secondary ultrafine particle production. Total carbon concentration (EC and OC) as a percentage of total mass concentration was determined for the ultrafine range (0 to 180 nm) and was found to vary from 70% and 35% for Long Beach and Riverside respectively. The highest percentages are noted for Long Beach considered a source site.

Table 2. Seasonal Mass Concentration

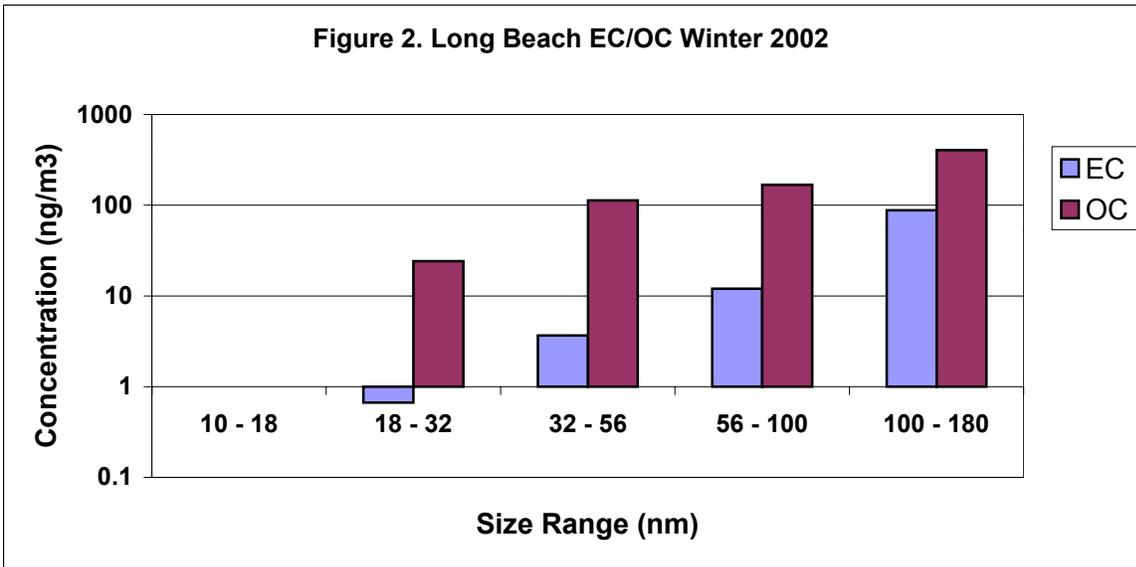
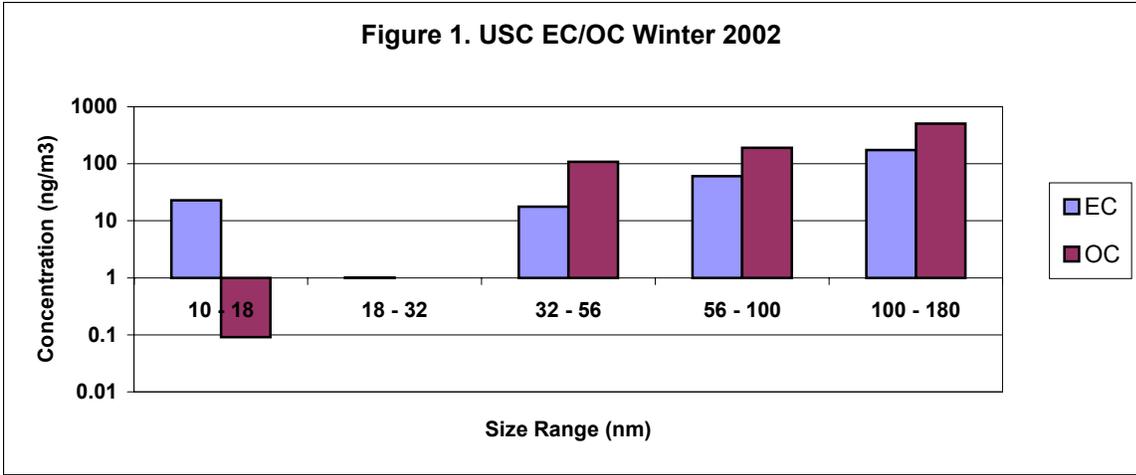
Site	Winter ( $\mu\text{g}/\text{m}^3$ )	Autumn ( $\mu\text{g}/\text{m}^3$ )
USC	19.04	29.72
Long Beach	13.06	21.43
Riverside	8.4	25.10
Upland	17.24	20.97

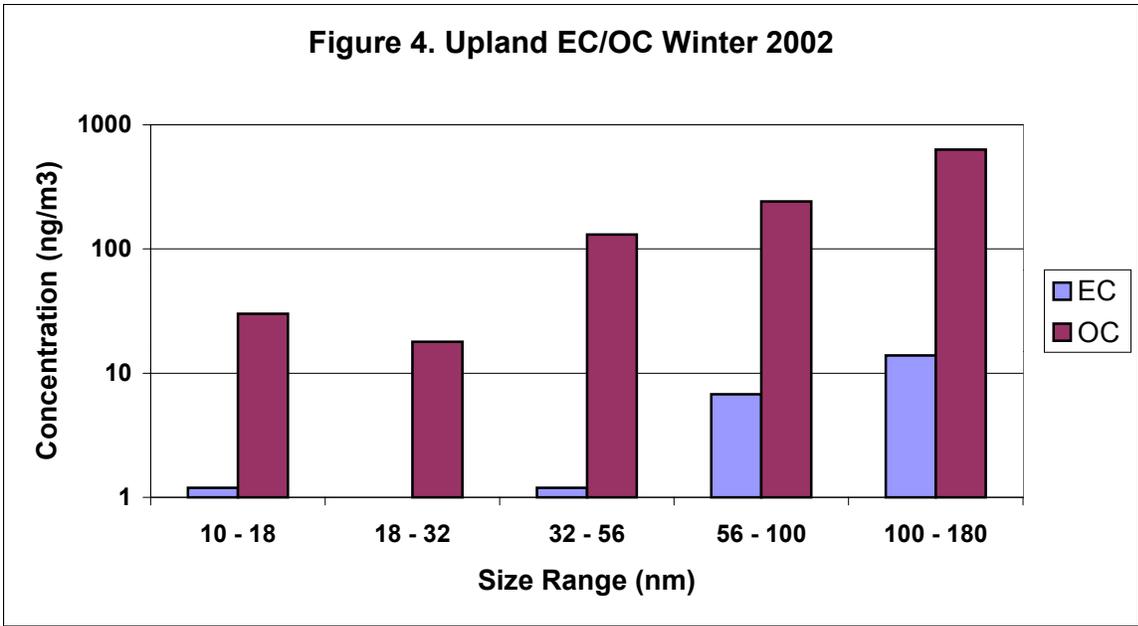
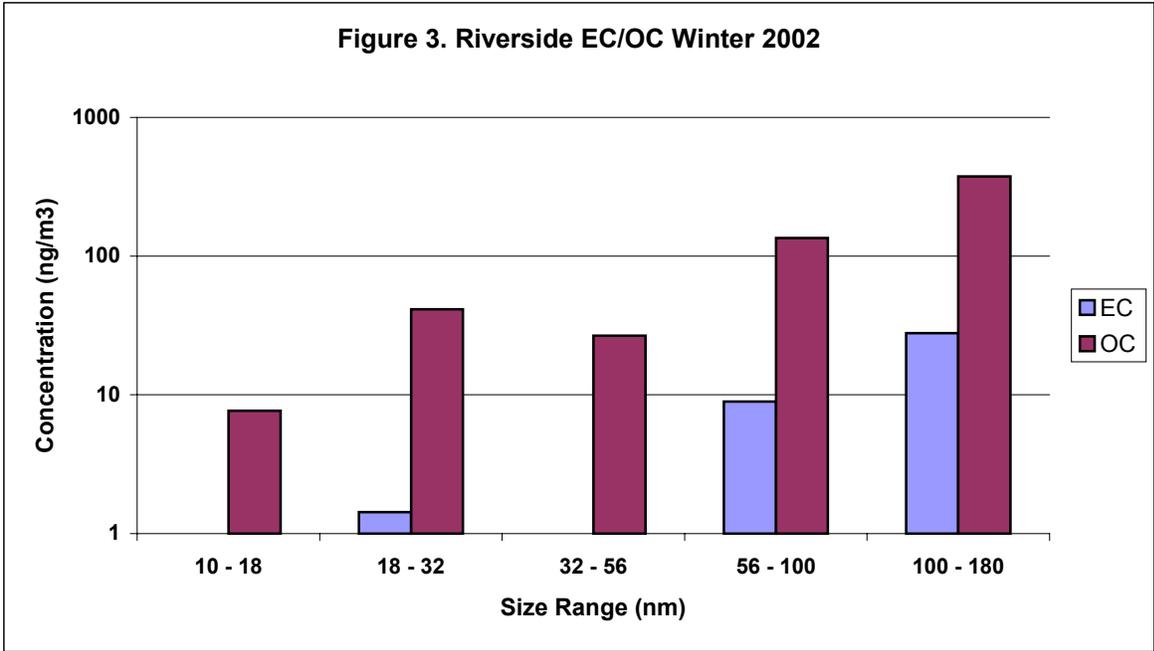
Table 3. Size fractionated SMPS vs NanoMOUDI mass concentration ratios for Fall 2002.

Aerodynamic Diameter (nm)	Long Beach	Riverside	USC
1000-320	3.18	2.33	1.94
320-180	2.00	2.06	2.303
180-100	0.94	1.89	0.63
100-56	0.62	1.11	0.36
56-32	0.08	0.35	0.28
32-10	0.001	0.12	0.15

### Next Quarter

The next phase of sampling will occur in what is the summer season in the LA basin. The same four sites will be visited from June to August.





## 10. Ultrafine Organic Speciation Study

Several studies have measured individual organic compounds in atmospheric particle samples by GC/MS or other analytical methods. Usually, only between 10 and 20% of the total organic compound mass (measured by thermal desorption methods) can be quantified as individual organic species. Some of these compounds can be used to trace primary particle emissions and be used in source apportionment studies. One of the major hurdles in the sampling of particles for organic speciation is collecting enough mass for the analysis. For this reason, sampling periods are very long (from 12 hours to several days) and they do not provide size-fractionated information on the organic particle concentrations. The one study that measured size-fractionated speciated organics only looked at PAH and oxy-PAH and sampled over 5 - 24 hour periods (J. Allen et al., 1996,1997, 1998).

A new particle slit impactor developed by Dr. Sioutas and his group (Misra et al., 2002) through funding by the Southern California Supersite enables the separation of particles with a cut point of 0.18  $\mu\text{m}$  and a very high flow rate of  $\sim 500$  lpm. Using a 2.5  $\mu\text{m}$  inlet, particles with diameters between 0.18  $\mu\text{m}$  and 2.5  $\mu\text{m}$  (fine) can be collected by impaction on this new impactor, and particles with diameters less than 0.18  $\mu\text{m}$  (ultrafine) can be collected on a high-volume filter downstream. The two size fractions roughly correspond to the accumulation mode and ultrafine modes of the urban aerosol size distribution. The high flow rate of the system allows for shorter collection periods, and thus diurnal (3 ½ - hour samples) and size-segregated sampling for organic speciation is now possible.

The sampling plan outlined below has been completed. Briefly, two sampling sites were selected: a typical urban site (USC); and a downwind receptor site (Riverside). For one week at each site (Mon. – Fri.), four time intervals per day were sampled (morning, midday, evening, and overnight). The daytime samples last 3 1/2 hours per day for each diurnal interval for five days. Nighttime sampling lasts for 11 1/2 hours per night for four nights. Filters and substrates are replaced in the sampler such that one set of accumulation mode quartz-fiber substrates and one ultrafine mode high-volume Teflon-coated glass fiber filter represent a weekly average for each diurnal interval. Parallel to the high volume sampler, a MOUDI was run at 30 lpm to collect particles on Teflon substrates for mass determination. The stages in the MOUDI will be chosen to correspond to the same cut-points as the high volume sampler. A second MOUDI with the same flow rates and size cuts collected aluminum foil substrates and a quartz fiber after filter for EC/OC analysis by the thermal desorption/optical transmission method used regularly by the Supersite. In addition, a 47mm filter train will consist of a PM2.5 cyclone inlet, a Teflon filter and a back-up quartz fiber filter. The flow rate will be chosen to create a face velocity on the quartz back-up filter equal to the face velocity on the MOUDI quartz after filter. This filter-based sampling helps to assess the degree of organic vapor adsorption onto the MOUDI quartz after filter.

An additional high volume sampling system, operated by Janet Arey's UCR group, consisted of a filter followed by a PUF and was used for analysis of both semi-volatile and particle-phase PAH, oxy-PAH and nitro-PAH, and results are presented in another section of this report.

The purpose of this project is several-fold. First, with the exception of the one study on PAH and oxy-PAH, the speciated organic composition of ultrafine particles has not been investigated. Several other classes of compounds, including alkanolic acids and diacids, aromatic carboxylic acids, resin acids, sugar derivatives and sterols have been found in atmospheric particles but their distribution among size fractions is unknown. Ultrafine particles consist of fresh particles emitted directly from sources, freshly condensed material on these primary particles, and freshly nucleated particles resulting from atmospheric reactions. It has also been shown that ultrafine particles consist of up to 80% - 90% organic carbon. Source profiles for many of the organic compounds of interest have been previously determined for the most important particle sources in Los Angeles (Schauer Thesis, 1998). Furthermore, smog chamber studies have identified many particle phase organic atmospheric reaction products that should also be found in the atmosphere.

By comparing individual ultrafine organic species to known organic source profiles and expected atmospheric reaction products, the sources and formation mechanisms of these ultrafine particles can be determined. Recent data suggesting that ultrafine particles may be more toxicologically potent than larger particles add even more relevance to this study. Identifying the origin, the geographical distribution, and the diurnal and seasonal variations of these particles will help to model personal exposure to ultrafines and to formulate any future pollution control efforts. By also looking at the organics on the accumulation-mode filter sample, the contributions of primary particle sources and secondary organic aerosol to the two particle size fractions can be resolved over the course of the day, as air parcels move across the LA basin, and as atmospheric conditions change with season.

Finally, the warm weather and large number of pollution sources in the LA basin create ideal conditions for secondary organic aerosol (SOA) formation. A goal of this study is to identify individual components of SOA in order to provide a chemical signature that can estimate the degree of SOA contribution to ambient particle mass concentrations. The temporal and spatial aspects of this study will shed additional light on SOA formation mechanisms.

### **Experimental Matrix**

- Two sites: Urban (USC), and Receptor (UC Riverside)
- One week (five days) at each sampling site for each season
- Four time intervals each day: 7AM - 10:30AM, 11:00AM – 2:30PM, 3PM –6:30PM, and 7:00PM – 6:30AM
- Weather conditions and traffic patterns should remain constant throughout each week, and preferably, throughout the entire study.
- When: August, to maximize effect of photochemistry; and January, a low photochemical and cold weather sample

## **Progress**

The sampling phase of this study has been completed. From August 12 to August 16, 2002, sampling was conducted on the rooftop of a 3-story building at the University of Southern California campus (urban site). From August 26 to August 30, 2002, sampling took place at the University of California, Riverside Citrus Research Center and Agricultural Experiment Station (CRC-AES) adjacent to an existing SCAQMD air sampling facility (receptor site). Sampling at the same two locations was repeated to obtain wintertime samples. Winter USC sampling occurred from January 13-17, 2003 and Winter Riverside sampling took place from January 27-31, 2003.

In the summer, PM<sub>2.5</sub> mass peaked midday at USC and in the morning at Riverside. The winter samples showed the highest PM<sub>2.5</sub> and ultrafine concentrations at USC in the morning, which may be due to the wintertime inversion level that increases in altitude over the course of the day. Winter in Riverside was characterized by high PM<sub>2.5</sub> levels overnight. At both sites during the summer, ultrafine PM mass was higher in the midday and evening than the morning or overnight. This pattern was repeated in Riverside during the winter, however, USC in winter showed the highest ultrafine levels in the morning. Also note that ultrafine levels at USC were generally higher in the winter than in the summer. In both seasons, ultrafine mass concentrations were higher in Riverside than at USC, suggesting a photochemical origin above primary contributions from vehicular emissions.

Organic speciation by GC/MS has been completed. Results were presented in a poster presentation at the AAAR PM colloquium in Pittsburgh in April, 2003 and a manuscript is in progress for submission to the journal *Environmental Science and Technology*. Following is a summary of these new results.

Figure 1 shows the seasonal and diurnal variations of the sum of the three most abundant hopanes for both size fractions at both sites. Hopanes are a marker for vehicular emissions due to their presence in motor oil. These hopanes were well correlated with one another and were measured at ratios similar to previous studies (see Figure 2). The hopane concentrations were found to be higher at the urban USC location than inland Riverside. Hopanes were found to be enriched in the ultrafine mode relative to the accumulation mode, indicative of a primary (vehicular) source.

Figure 1

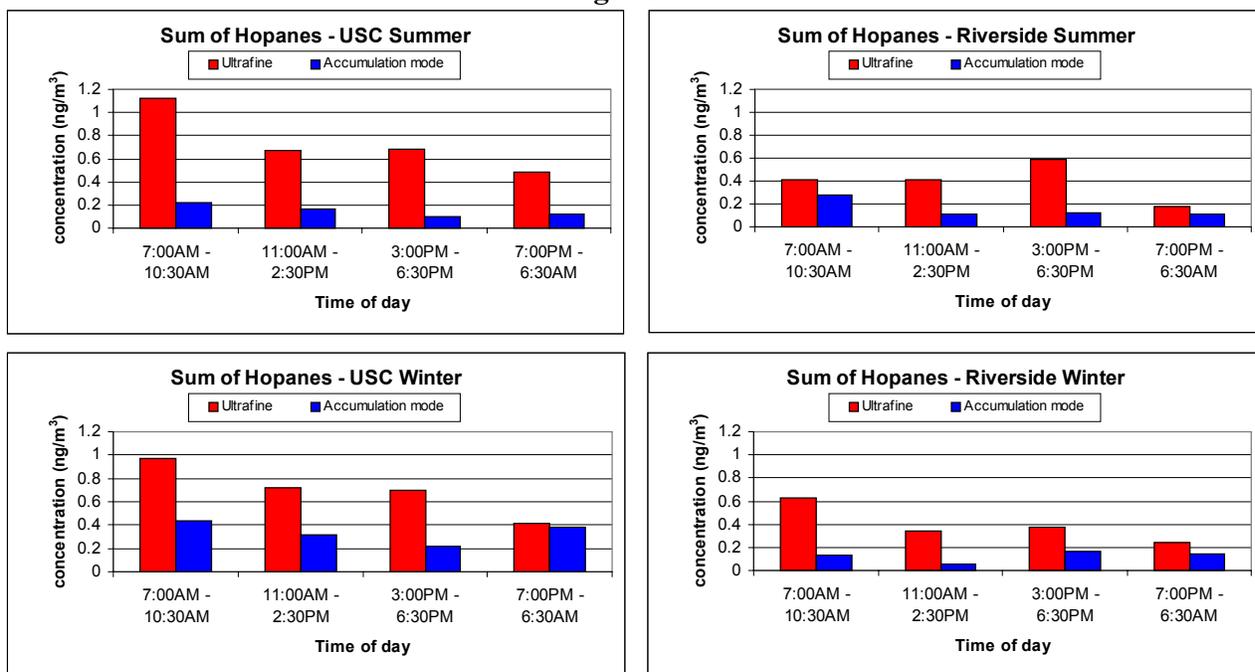
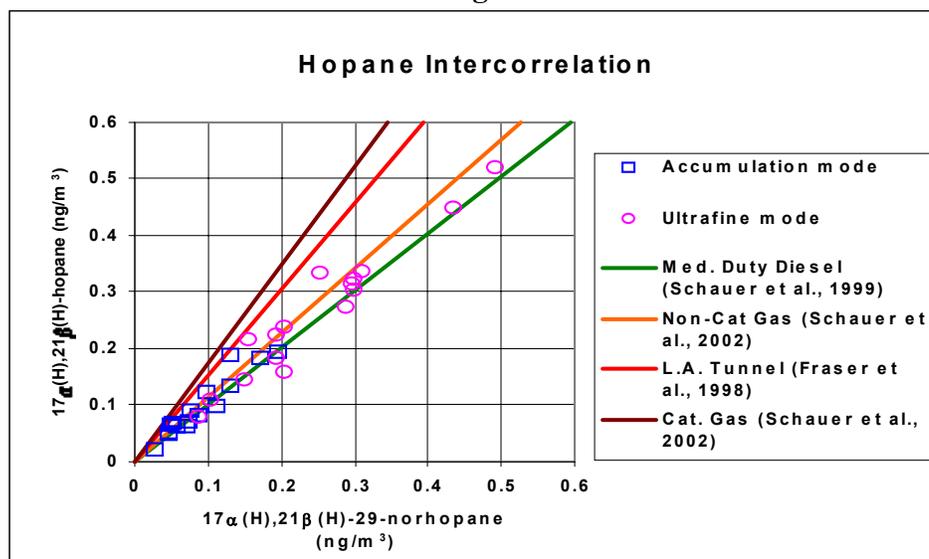


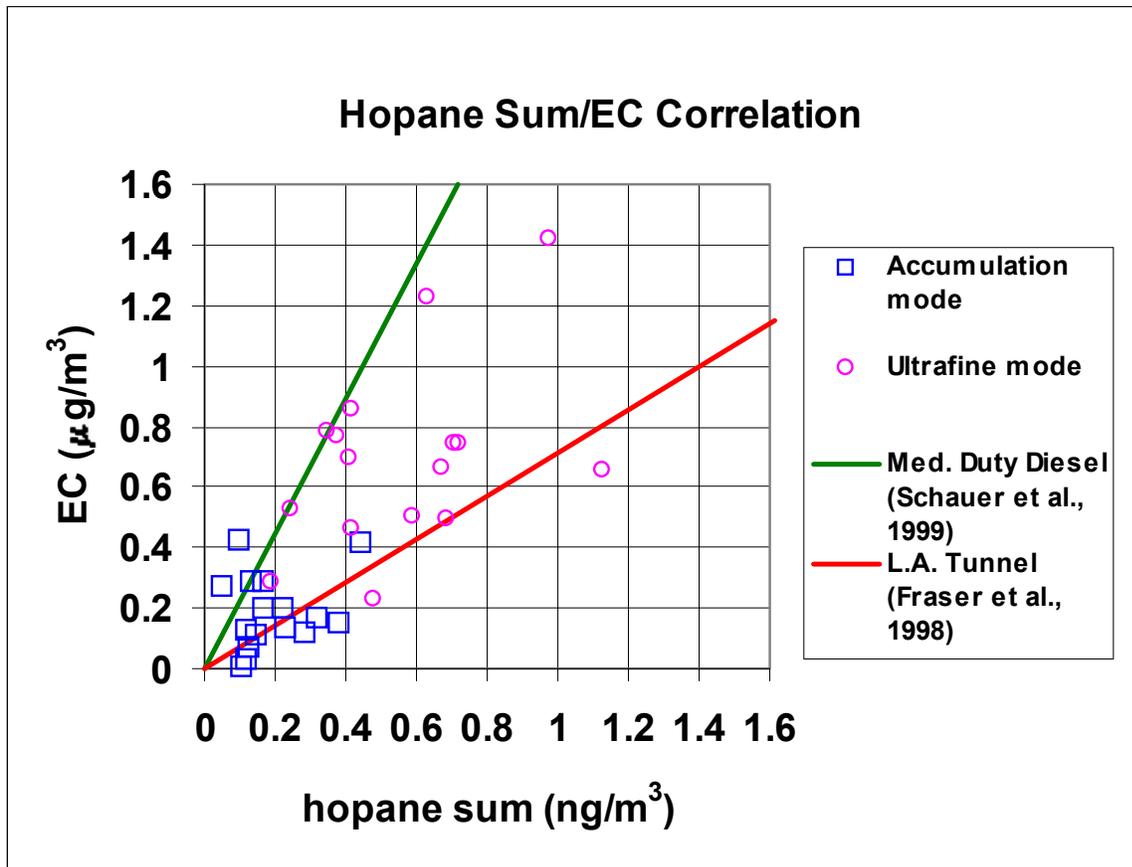
Figure 2



Since hopanes in airborne PM derive from motor oil, they do not provide sufficient source specificity to determine the relative contributions from diesel vs. gasoline powered vehicles. However, since elemental carbon (EC) is primarily emitted from diesel engines, EC levels can provide a rough gauge of the impact of diesels on an ambient sample. Figure 3 compares the hopane to EC ratio for our samples vs. previously conducted analyses of dynamometer and tunnel emissions. Our data fall generally in line with these two very different studies, and the proximity to the upper curve might provide an at least qualitative measure of the impact of

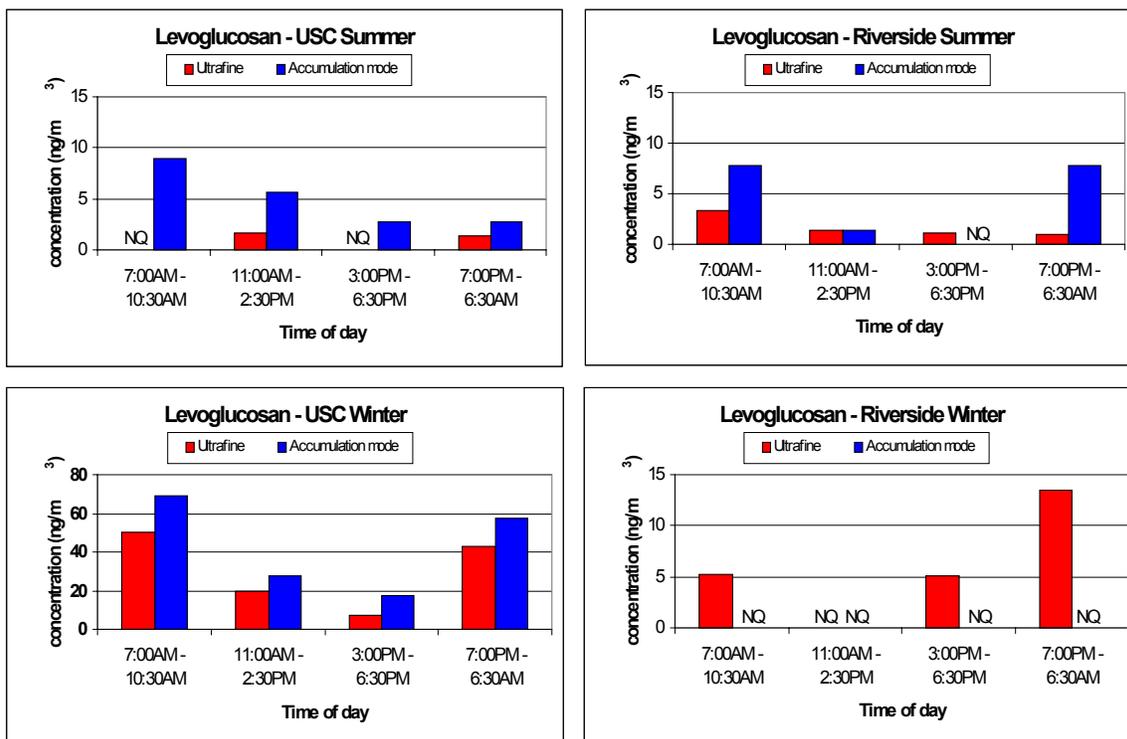
diesels on a particular sample. Also note how EC and hopanes are found at higher levels in the ultrafine mode.

Figure 3



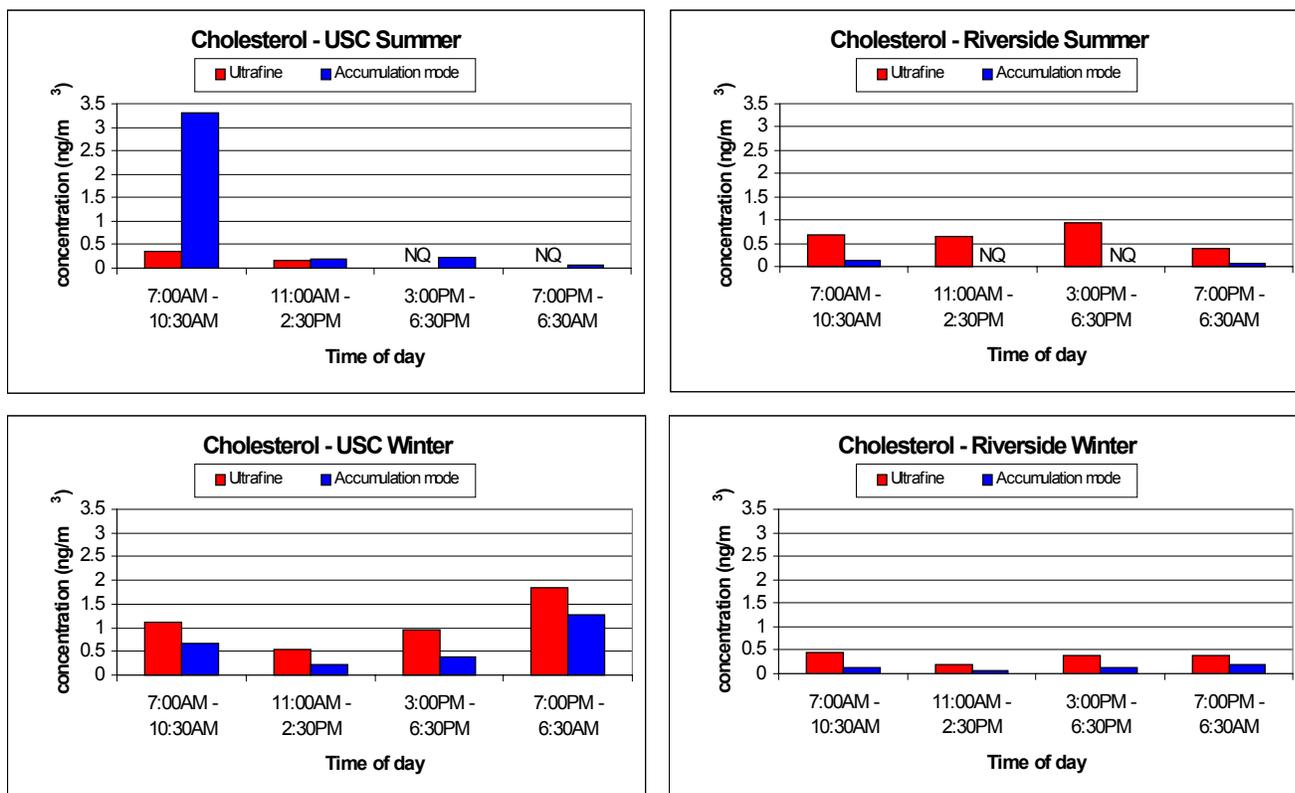
Other sources of ultrafine and accumulation mode PM were also examined. Figure 4 shows results for the measured concentrations of Levoglucosan, a pyrolysis product of cellulose that has been used as a marker for wood combustion. More levoglucosan is found in the accumulation mode than the ultrafine mode, and levels are generally higher in the winter as expected. Unexpectedly high levels were found at USC in the winter overnight and in the early morning. Missing data is due to a few samples with poor internal standard recovery during the extraction and injection process.

Figure 4



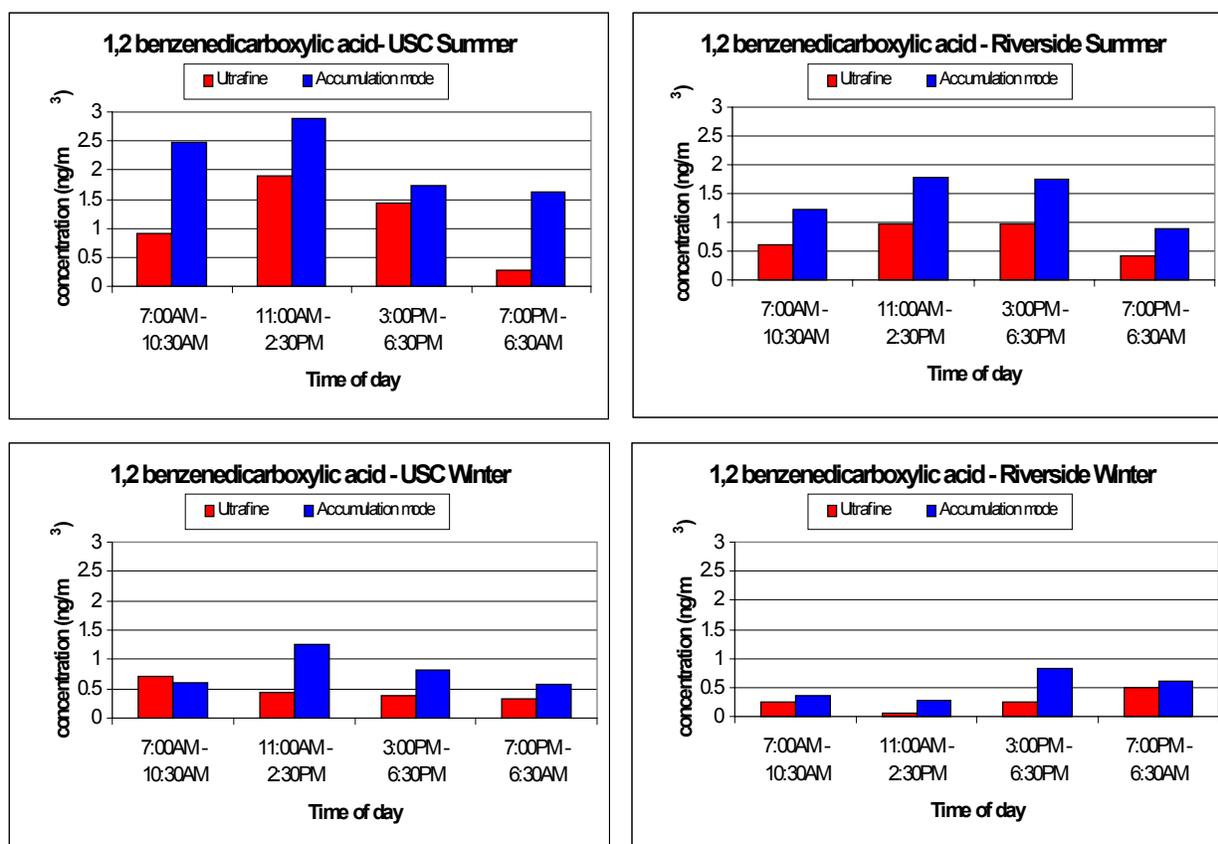
Cholesterol can be used as an indicator of meat cooking emissions and Figure 5 displays how this tracer varies with season, size, site, and time of day. While most sites and times show more cholesterol in the ultrafine mode, a singular morning source at USC in the summer of cholesterol in larger particles was discovered. This is an example of how organic tracer analysis such as this can identify unexpected sources of PM to a given ambient sample.

Figure 5



Finally, 1,2 benzenedicarboxylic acid has been proposed as a secondary organic aerosol product that might be used as a surrogate for the contribution of SOA to an ambient sample. Figure 6 shows that the abundance of compound follows some expected trends for SOA formation: 1) higher in summer than in winter, 2) higher in the day than at night, 3) higher in the accumulation mode than in the ultrafine mode (condensation on existing particles and aging), and 4) a delay in the peak concentrations inland (advection) which is more delayed in the winter (longer transport times). It is interesting that USC levels are higher than the Riverside levels since secondary formation is thought to be more important at inland sites.

Figure 6.



## 11. Automated, Size- and Time-Resolved Measurements of Particulate Carbon and Nitrate

Submitted by Aerosol Dynamics Inc.

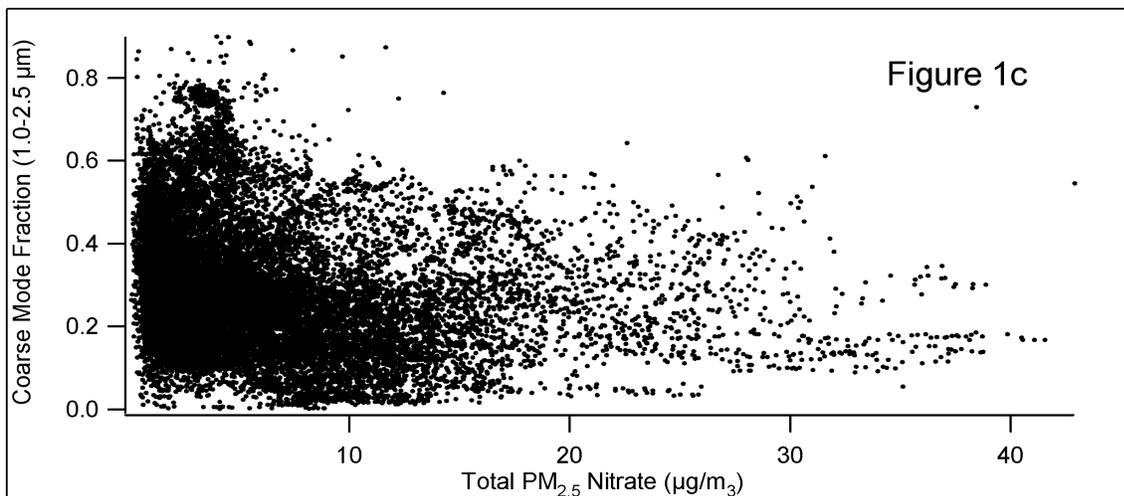
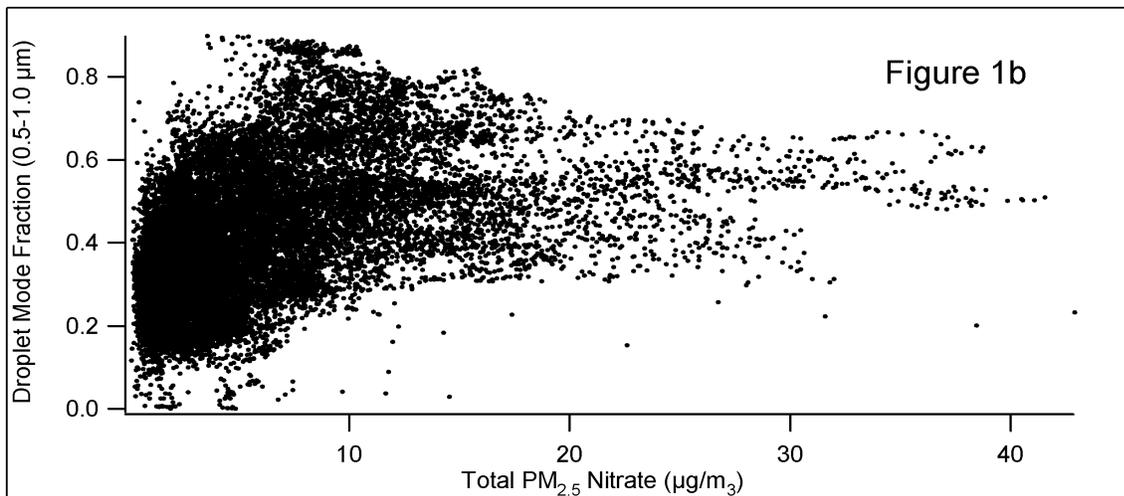
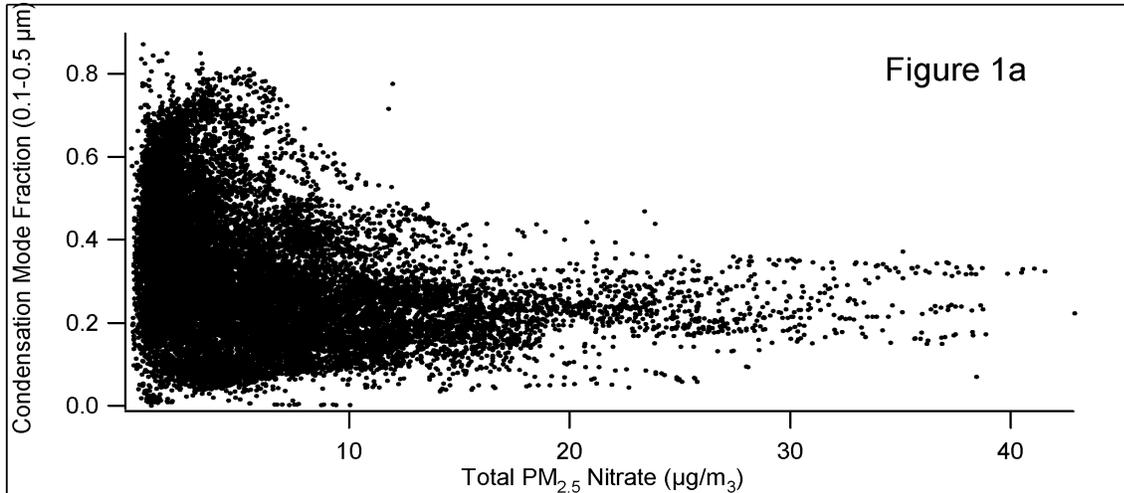
Data collection has ended at the USC site for both the Carbon and Nitrate ICVS's from Aerosol Dynamics Inc. Data have been validated and submitted for the period through May 6, 2003. The carbon system continues to run, though data after May 6, 2003 will not be validated at this time. The last valid nitrate data were on April 3, 2003 before a pump failure occurred. Both instruments will be removed and returned to Aerosol Dynamics in June.

Three size fractions were collected for both nitrate and carbon. 0.1 to 0.5  $\mu\text{m}$  is referred to as the condensation mode, 0.5-1.0  $\mu\text{m}$  as the droplet mode, and 1.0-2.5  $\mu\text{m}$  as the coarse mode. Analysis of the final nitrate data from the Claremont site yields interesting results with regard to the droplet mode. Figure 1b shows a scatter plot of the fraction of droplet mode  $\text{PM}_{2.5}$  nitrate versus total  $\text{PM}_{2.5}$  nitrate. Nitrate concentrations below approximately 10  $\mu\text{g}/\text{m}^3$  can have any range of droplet mode fraction. However, the highest nitrate periods correspond to droplet mode fractions of 0.5 on average, dominating the other two modes.

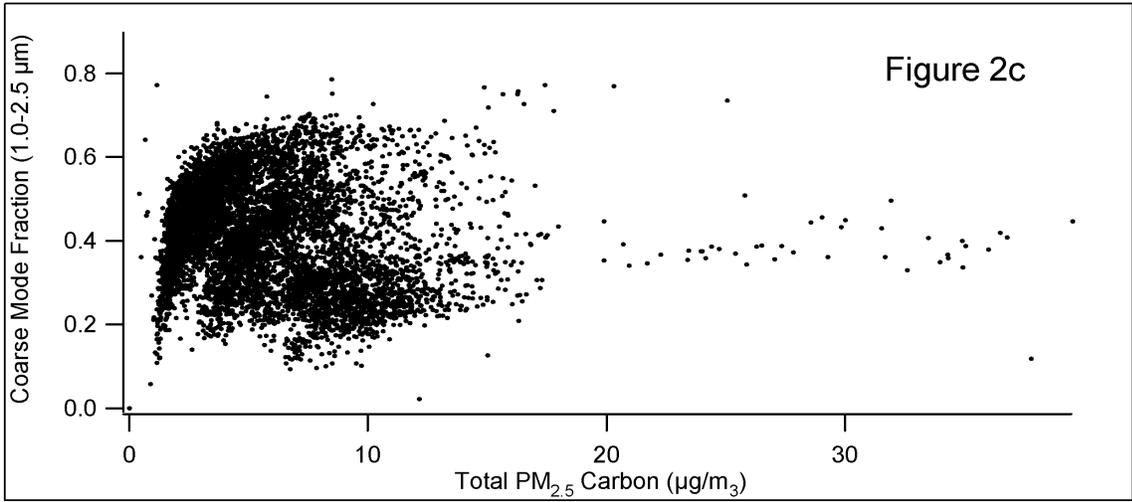
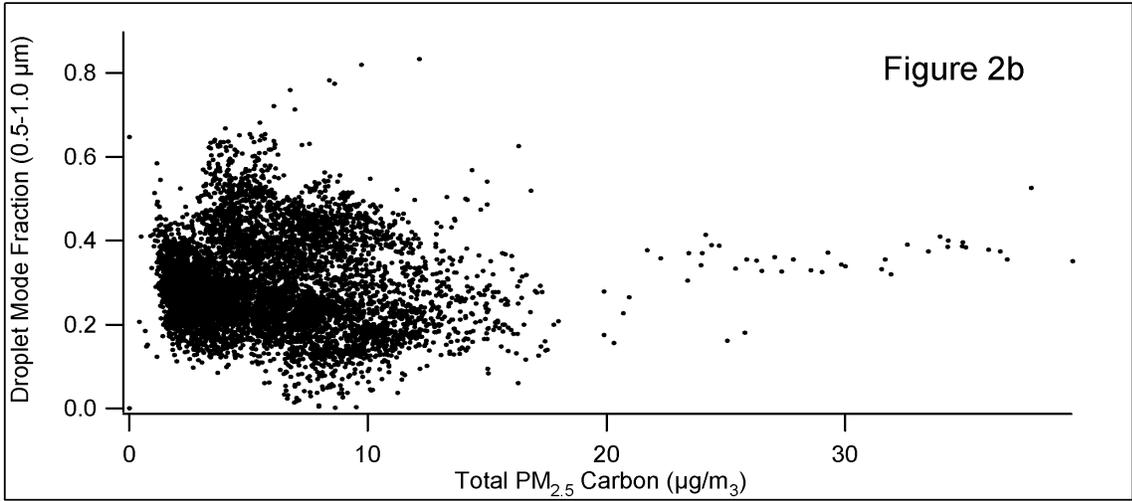
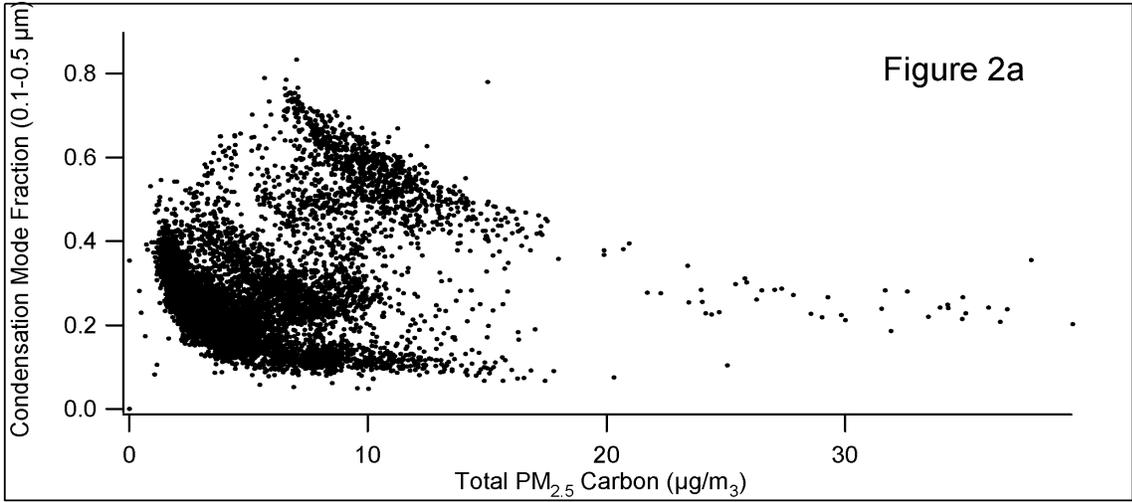
Nitrate one-hour averages were correlated with ambient RH meteorological data, as formation of droplet mode nitrate is highly dependant on relative humidity. A division was made based on the maximum humidity reached during the nighttime humidity peak. Droplet mode formation may be activated by peak humidity. There were no measured nitrate concentrations above 11  $\mu\text{g}/\text{m}^3$  when the humidity the previous night failed to reach 50%. 14% of the data fell into this category. Further analysis is necessary to explore droplet mode formation and its dependence on humidity.

Figure 2 is a similar plot for carbon data, shown for comparison. No major differences in mode fraction versus total concentration are evident. Carbonaceous particle sizes are clearly not correlated with total concentration. This is not surprising given that significant differences exist between the formation mechanisms of nitrate and carbonaceous particles.

Greater analysis and comparison of these data sets to other instruments will result in more novel observations of the size-specific properties of the nitrate and carbon aerosols in the Los Angeles basin. For example, differential TEOM data, relating to mass lost through volatilization from filters shows high correlation to nitrate concentrations. Work is in progress to make such comparisons.



**Figure 1. Scatter plots of condensation, droplet, and coarse mode fractions versus total PM<sub>2.5</sub> nitrate concentration at the Claremont site.**



**Figure 2. Scatter plots of condensation, droplet, and coarse mode fractions versus total PM<sub>2.5</sub> carbon concentration at the Claremont site.**

## **12. Quality Control of Semi-Continuous, Mobility Size-Fractionated Particle Number Concentration Data and 2<sup>nd</sup> Quarter Data Management**

By RC Yu

1. The manuscript “Quality Control of Semi-Continuous Mobility Size-Fractionated Particle Number Concentration Data” (Manuscript No. 03/107/SS/HS) submitted to *Atmospheric Environment* was in the process of reviewing, according to the editor: Dr. Hanwant B. Singh.
2. During this quarter, we submitted data of Aethalometer, Automet, (some) APS, and SMPS to NARSTO and SIRD. We also updated the metadata for Nitrate and Carbon so that NARSTO is ready for release of the data sets to the public.
3. The Data Management Office newly received the metal species data of Partisol and MOUDI, as well as USC data up to May 2003.
4. The update status of Supersite data submission follows:

Status of LA Supersite Data Submitted (Sumission Date) to NARSTO & SIRD												
		Claremont		Downey		Riverside		Rubidoux		USC		
		NARSTO	SIRD	NARSTO	SIRD	NARSTO	SIRD	NARSTO	SIRD	NARSTO	SIRD	
<b>Partisol</b>	<b>Ions</b>	ND	2002/11/04	ND	2002/11/04	ND	2002/11/04	ND	2002/11/04	ND	ND	
	<b>Mass</b>	ND	2002/11/04	ND	2002/11/04	ND	2002/11/04	ND	2002/11/04	ND	ND	
	<b>Metal_details</b>	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	
<b>MOUDI</b>	<b>ECOC</b>	ND	2002/11/04	ND	2002/11/04	ND	2002/11/04	ND	2002/11/04	ND	ND	
	<b>Ions</b>	ND	2002/11/04	ND	2002/11/04	ND	2002/11/04	ND	2002/11/04	ND	ND	
	<b>Mass</b>	ND	2002/11/04	ND	2002/11/04	ND	2002/11/04	ND	2002/11/04	ND	ND	
	<b>Metal_details</b>	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	
<b>Aethalometer</b>	2003/05/30	2002/10/25 - hourly 2003/05/30 - 5min	2003/05/30	2002/10/25 - hourly 2003/05/30 - 5min	2003/05/30	2002/10/25 - hourly 2003/05/30 - 5min	2003/05/30	2002/10/25 - hourly 2003/05/30 - 5min	2003/05/30	2002/10/25 - hourly 2003/05/30 - 5min	ND	ND
<b>Automet (MetOne)</b>	NA	NA	2003/06/06	2003/06/06	2003/06/06	2003/06/06	2003/06/06	2003/06/06	2003/06/06	2003/06/06	ND	ND
<b>APS</b>	2003/04/22	2002/04/27	2002/01/24	2002/09/10	2002/03/08	2002/09/10	2002/03/08	2002/09/10	2002/03/08	2002/09/10	ND	ND
<b>SMPS</b>	8/19/2002 (20010917_20020222)	10/25/2002 (20010917_20020222)	2002/07/22	2002/10/25	2002/08/19	2002/10/25	2002/08/19	2002/10/25	2002/08/19	2002/10/25	ND	ND
	4/13/2003 (20020326_20020910)	4/27/2002 (20020326_20020910)									ND	ND
<b>TEOM</b>	2003/01/30	2002/04/27	2003/01/30	2002/10/25	2003/01/30	2002/10/25	2003/01/30	2002/04/27	2003/01/30	2002/04/27	ND	ND
<b>Nitrate</b>	2002/12/10	2002/11/04	NA	NA	NA	NA	2002/12/10	2002/11/04	2002/12/10	2002/11/04	ND	ND
<b>Carbon</b>	2002/12/10	2002/11/04	NA	NA	NA	NA	NA	NA	NA	NA	ND	ND
<b>R&amp;P Carbon Monitor</b>	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	ND	ND
<b>BAM</b>	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	ND	ND
<b>Coarse TEOM</b>	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	ND	ND

Notes: 1. Data submitted to NARSTO and SIRD were in different formats. 2. SIRD - Supersite Integrated Relational Database  
3. Dataram data will not be submit to NARSTO and SIRD, a decision made by Costas and Peter in May 2003. 4. NA: Data were not available or were invalid

