

# SOUTHERN CALIFORNIA PARTICLE SUPERSITE

**Progress Report for Period January 1, 2004 – March 31, 2004**

**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 January 1, - March 31, 2004. It is divided into 11 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 was 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 PM2.5 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". Atmospheric Environment, 37(34), 4781-4793, 2003.
12. Shen, S., Zhu, Y., Jaques PA and Sioutas C. "Evaluation of the SMPS-APS system as a Continuous Monitor for PM2.5 and PM10". 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 PM10 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". Aerosol Science and Technology, 38, 27-35, 2004.
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, 111 (4), 455-460, 2003

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 " .Aerosol Science and Technology, in press, January 2004
21. 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
22. 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" Accepted in Atmospheric Environment, February 2003
23. Yu, R.C., Teh, H.W., Sioutas, C. and Froines, J.R. "Quality Control of Semi-Continuous Mobility Size-Fractionated Particle Number Concentration Data". Accepted in Atmospheric Environment, February 2003
24. 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" Accepted in Atmospheric Environment, February 2003
25. Geller, M.D., Fine, P.M. and Sioutas\* C. " The Relationship Between Real-Time and Time-Integrated Fine and Coarse Particle Concentrations at an Urban Site in Los Angeles, CA". Journal of Air and Waste Management Association, in press, November 2003
26. 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" Accepted in Atmospheric Environment, June 2003.
27. 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.
28. Sardar, S.B., Fine P.M., Jaques, P.A and 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 Journal of Geophysical Research, December 2003
29. Jaques, P.A., Ambs, J.L., Hering, S.V., Fine, P.M. and Sioutas\* , C. " Field Assessment of the Dynamics of Particulate Nitrate Vaporization Using Differential TEOM® and Automated Nitrate Monitors ". Atmospheric Environment, in press, October 2003
30. Fine, P.M., Chakrabarti, B, Krudysz M., Schauer J.J. and Sioutas\* , C. "Seasonal, Spatial, and Diurnal Variations of Individual Organic Compound Constituents of

Ultrafine and Accumulation Mode PM in the Los Angeles Basin”.  
*Environmental Science and Technology*, 1296 – 1304, 2004

31. Sardar, S.B., Fine P.M., and Sioutas\* . C. “The Relationship Between Particle Number and Co-pollutant Concentrations in the Los Angeles Basin” Accepted in *Journal of Air and Waste Management Association*, October 2003
32. Zhang, K.M., Wexler, A.S., Zhu, Y., Hinds, W.C. and Sioutas, C. “Evolution of Particle Number Distributions Near Roadways. Part II: The “Road-to-Ambient Process”. Submitted to *Atmospheric Environment*, December 2003.
33. Miguel, A.H., Cho A.K., Sioutas C., Schmitz, D.A., Kumagai Y., Misra C., Singh M., and Froines, J.R. “DTT Activity Assay for Measurement of the Oxidative Stress Inducing Capacity of Polycyclic Aromatic Compounds in the Atmosphere”. Submitted to *Polycyclic Aromatic Compounds*, November 2003.
34. Zhao, Y., Bein, K.J., Wexler, A.S., Misra, C., Fine, P.M. and C. Sioutas\* , C. “Using a Particle Concentrator to Increase the Hit Rates of Single Particle Mass Spectrometers”. Submitted to *Journal of Geophysical Research*, December 2003.
35. Sardar, S., Fine, M., Mayo, P.R. and Sioutas\* , C. “Size Fractionated Chemical Speciation Measurements of Ultrafine Particles in Los Angeles Using the NanoMOUDI”. Submitted to *Journal of Geophysical Research*, January 2004
36. Phuleria, H., Fine, P.M., Zhu, Y. and Sioutas\* , C. “Characterization of Particulate Matter and co-Pollutants During the Fall 2003 Southern California Fires”. Submitted to *Journal of Geophysical Research*, January 2004
37. Cho A.K., Sioutas C., Schmitz, D.A., Kumagai Y., Singh M., Miguel A.H and Froines, J.R. “Redox activity of airborne particulate matter (PM) at different sites in the Los Angeles Basin” Submitted to *Environmental Science and Technology*, February 2004
38. Khlystov, A., Zhang, Q., Jimenez, J.L., Stanier, C.O., Pandis, S., Wornop, D.R., Misra, C., Fine, P.M. and Sioutas, C. “On Concentrating Semi-volatile Aerosols Using Water-Based Condensation Technology” Submitted to *Journal of Geophysical Research*, February, 2004.

### 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 third 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 to the end of February. In early June 2003, we 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 inlet (designed at the USC lab). Coupled with our USC-TEOM coarse monitor, time-integrated mass measurements are being compared to those by our SMPS-APS, 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 and have continued periodically to the present. A demonstrative-level cooperative project of the California Air Resources Board and the Supersite was initiated during the winter of 2003 to evaluate the nature of PM and gaseous pollutants in various microenvironments of Southern California, especially those impacted by vehicular traffic. Gaseous pollutants evaluated included carbon monoxide, carbon dioxide, and oxides of nitrogen using advanced monitoring equipment including ultrafine PM counters and sizers as well as carbon, PM 2.5, and PAH monitors placed in an electrically powered Toyota RAV4. Data reporting resolution was one minute or less with operations of the study closely linked to the Supersite, its instrumentation and staff. In conjunction with this study, the South Coast Air Quality Management District (SCAQMD) has provided instruments to monitor oxides of nitrogen, ozone and carbon monoxide. These instruments continue to operate at the site.

#### **4. Associations Between Particle Number and Gaseous Co-Pollutant Concentrations in the Los Angeles Basin**

##### **Introduction**

Ultrafine particles, which dominate the particle number concentration of ambient aerosols, have recently been the focus of several health studies. It has been traditionally hypothesized that these particles originate from vehicular emissions, thus the concentrations of gases such as CO, NO or NO<sub>2</sub> that also originate from traffic sources can be used as a surrogate measures of ultrafine PM. The current study attempts to explore the relationship between particle number concentrations and those of various co-pollutants, at five sites in the Los Angeles basin for the entire 2002 calendar year.

##### ***Sites***

Measurements of particle number, CO, O<sub>3</sub>, PM<sub>10</sub>, NO and NO<sub>x</sub> were conducted as part of the routine sampling protocol of the South Coast Air Quality Management District. The five sites selected for the current analysis are Long Beach, Glendora, Mira Loma, Upland and Riverside.

Of the five sites, Long Beach is considered a “source” site while the other sites; Riverside, Upland, Glendora and Mira Loma are designated “receptor” sites. It is important to note that; the proximity of Upland to a freeway alters some of the characteristics typical of a receptor site, adding the influence of local traffic to the regional effects.

##### **Results and Discussion**

The Pearson correlation coefficient ( $r$ ), between the hourly and 24-hr average PN concentration data and the co-pollutant concentrations (CO, NO, O<sub>3</sub>, NO<sub>2</sub> and PM<sub>10</sub>) are shown in Tables 1 and 2, respectively for the calendar year 2002. The values shown in Table 1 and Table 2 indicate generally low to moderate (i.e.,  $r < 0.5$ ) levels of association between PN and co-pollutants, and in only few cases, moderate to high ( $r$  between 0.5 to 0.68) levels of correlation on both an hourly and 24-hr basis. Based on these results, which were highly variable among sites, using

any of these co-pollutants as a surrogate for ultrafine particles over a prolonged time period, in Los Angeles is likely to introduce a high level of error in PN predictions.

It is possible that seasonal differences might affect different pollutants differently, and could account for the lack of correlation over an entire year. Thus, the data were separated by season to determine whether the associations among co-pollutants improved. Table 3 shows the Pearson correlation coefficients between PN and the other co-pollutant (both hourly and 24-hr average) concentrations for the five sites and the four seasons. The lowest levels of correlation ( $r < 0.59$ ) between PN and co-pollutants, for any season and for both averaging times, were observed in Glendora. The apparent lack of correlation with NO and CO may be due to the minimal traffic influence at that site, which is located in a residential area and away from major roadways. However, at the Upland site, which is located only 6 km to the east, the hourly correlation between PN and the other primary vehicular emissions (CO and NO) showed higher correlations, particularly in the winter and fall. The PN correlations with CO and NO were almost always lower for the 24-hr average data than the hourly averages. The high hourly correlations for vehicular pollutants suggest a local traffic sources at Upland. Furthermore, the association is higher in the winter when stagnant conditions and lower inversion layers trap pollutants near the ground and enhance the influence of local sources.

The lower correlations between PN and both CO and NO in the spring and summer is most likely due to the different meteorological conditions, which favor increased advection of pollutants from urban Los Angeles areas located upwind of that site. Another factor may be photochemical secondary formation of particles in the atmosphere, which would increase particle numbers while not affecting CO or NO levels. Other sites that showed moderate to relatively high levels of correlation among hourly measurements of vehicular pollutants, and thus are thought to be influenced by local traffic, were Mira Loma and Riverside in the spring and summer.

While high correlations between hourly measurements of vehicular co-pollutants indicate a local traffic source, high correlations of 24-hr average co-pollutant concentrations may signify a different influence. Table 3 shows that the 24-hr correlation coefficients are often higher than their hourly counterparts, especially in the receptor sites, with the exception of Glendora. This trend is more pronounced in the summer season, and applies to non-vehicular and secondary co-pollutants as well. The summer season showed high ( $r > 0.70$ ) degrees of correlation of 24-hr PN with CO, NO and NO<sub>2</sub> at Riverside, and moderately high correlations between PN and CO, NO and NO<sub>2</sub> at Upland ( $r$  0.49 to 0.55) and Mira Loma ( $r$  0.56 to 0.78). In all these cases, the daily average data was more correlated than the hourly data. Thus, while the hourly levels of certain co-pollutants may not peak, dip or vary in similar diurnal patterns, the 24-hr average levels of all pollutants might show higher correlations during a day of generally poor air quality. The summer period in Los Angeles is characterized by increased on-shore flow and thus, enhanced advection of air masses inland. Pollutant concentrations, especially at inland sites, are therefore influenced by upwind sources and aged air parcels, as opposed to the influence of more local sources during the stagnant conditions in the winter. This may provide an explanation for the higher 24-hr correlations between PN and the more secondary (formed during transport and aging) co-pollutants during the warmer seasons. The scatter plots for PN vs. CO, NO and NO<sub>2</sub> during the summer at Riverside are shown in Figures 1a-f. As already discussed, the correlation is higher in all cases for the 24-hr data than for the hourly data, reaching as high as  $r = 0.87$  for NO. Although advection on generally polluted days is causing these high associations, the

influence of local sources is not absent. The hourly data (Figures 1b, d, and f) demonstrate that the relatively high hourly correlations given in Table 3 are driven by the high levels during the morning commute hours.

### Summary and Conclusions

The results presented in this study indicate that there are overall weak to moderate associations for both hourly and 24-hr average concentrations between PN and other co-pollutants when considered for the whole calendar year of 2002. Our results suggest that at least in Los Angeles, gaseous co-pollutants cannot be used as surrogates of PN to assess human exposure.

**Table 1.** Hourly Pearson Correlation Coefficient,  $r$ , of PN vs. Co-pollutant concentrations for the entire calendar year 2002, all sites

	Glendora	Long Beach	Mira Loma	Riverside	Upland
CO	0.13	0.46	0.47	0.52	0.66
NO	0.06	0.44	0.60	0.59	0.65
NO <sub>2</sub>	0.21	0.50	0.24	0.32	0.17
PM <sub>10</sub>	0.18	0.27	0.00	-0.16	0.14
O <sub>3</sub>	0.30	-0.22	-0.34	-0.04	-0.26

**Table 2.** 24-hr Average Pearson Correlation Coefficient,  $r$ , of PN vs. Co-pollutant concentrations for the entire calendar year 2002, all sites

	Glendora	Long Beach	Mira Loma	Riverside	Upland
CO	0.00	0.50	0.44	0.39	0.63
NO	0.30	0.48	0.34	0.32	0.66
NO <sub>2</sub>	0.07	0.68	0.11	0.23	0.08
PM <sub>10</sub>	-0.18	0.10	-0.17	-0.32	-0.19
O <sub>3</sub>	-0.31	-0.63	-0.33	-0.26	-0.54

**Table 3. Hourly and 24-hr average Pearson Correlation Coefficient (r) of PN vs. co-pollutant concentrations on a seasonal basis**

Winter	Glendora		Long Beach		Mira Loma		Riverside		Upland	
	24-hr Average	Hourly								
CO	0.20	0.19	0.33	0.47	0.17	0.43	0.33	0.43	0.55	0.74
NO	0.35	0.42	0.58	0.48	0.55	0.67	0.41	0.53	0.54	0.72
NO <sub>2</sub>	0.37	0.33	0.64	0.58	0.34	0.29	0.38	0.33	0.20	0.35
PM <sub>10</sub>	0.03	0.30	0.19	0.54	0.51	0.53	0.06	0.01	0.17	0.41
O <sub>3</sub>	-0.64	-0.37	-0.42	-0.28	-0.48	-0.65	-0.02	-0.14	-0.38	-0.25

Spring	Glendora		Long Beach		Mira Loma		Riverside		Upland	
	24-hr Average	Hourly								
CO	0.04	0.14	0.27	0.28	0.46	0.59	0.38	0.61	0.50	0.57
NO	0.49	0.00	0.39	0.41	0.36	0.70	0.38	0.66	0.63	0.59
NO <sub>2</sub>	0.16	0.29	0.52	0.34	0.46	0.46	0.30	0.48	0.34	0.30
PM <sub>10</sub>	0.13	0.37	0.10	0.18	0.14	0.25	-0.11	-0.05	0.06	0.26
O <sub>3</sub>	-0.24	-0.40	-0.54	-0.15	-0.23	-0.03	-0.18	-0.04	-0.21	-0.16

Summer	Glendora		Long Beach		Mira Loma		Riverside		Upland	
	24-hr Average	Hourly								
CO	0.27	0.14	0.46	0.40	0.56	0.49	0.71	0.54	0.52	0.48
NO	0.36	0.10	0.61	0.49	0.67	0.65	0.87	0.65	0.49	0.38
NO <sub>2</sub>	0.37	0.28	0.68	0.53	0.78	0.50	0.79	0.70	0.55	0.33
PM <sub>10</sub>	0.45	0.46	0.31	0.44	0.57	0.26	0.52	0.30	0.16	0.21
O <sub>3</sub>	0.07	0.59	-0.17	0.23	0.30	0.11	0.56	0.17	0.05	0.19

Fall	Glendora		Long Beach		Mira Loma		Riverside		Upland	
	24-hr Average	Hourly								
CO	0.25	0.31	0.88	0.56	0.32	0.47	0.41	0.41	0.53	0.64
NO	0.53	0.19	0.79	0.60	0.11	0.69	0.33	0.25	0.60	0.64
NO <sub>2</sub>	0.38	0.35	0.94	0.66	0.20	0.45	0.49	0.33	0.29	0.32
PM <sub>10</sub>	0.06	0.23	0.71	0.49	0.05	0.33	0.41	0.25	0.27	0.34
O <sub>3</sub>	0.04	0.28	-0.10	-0.05	0.13	-0.23	0.52	0.10	-0.13	-0.25

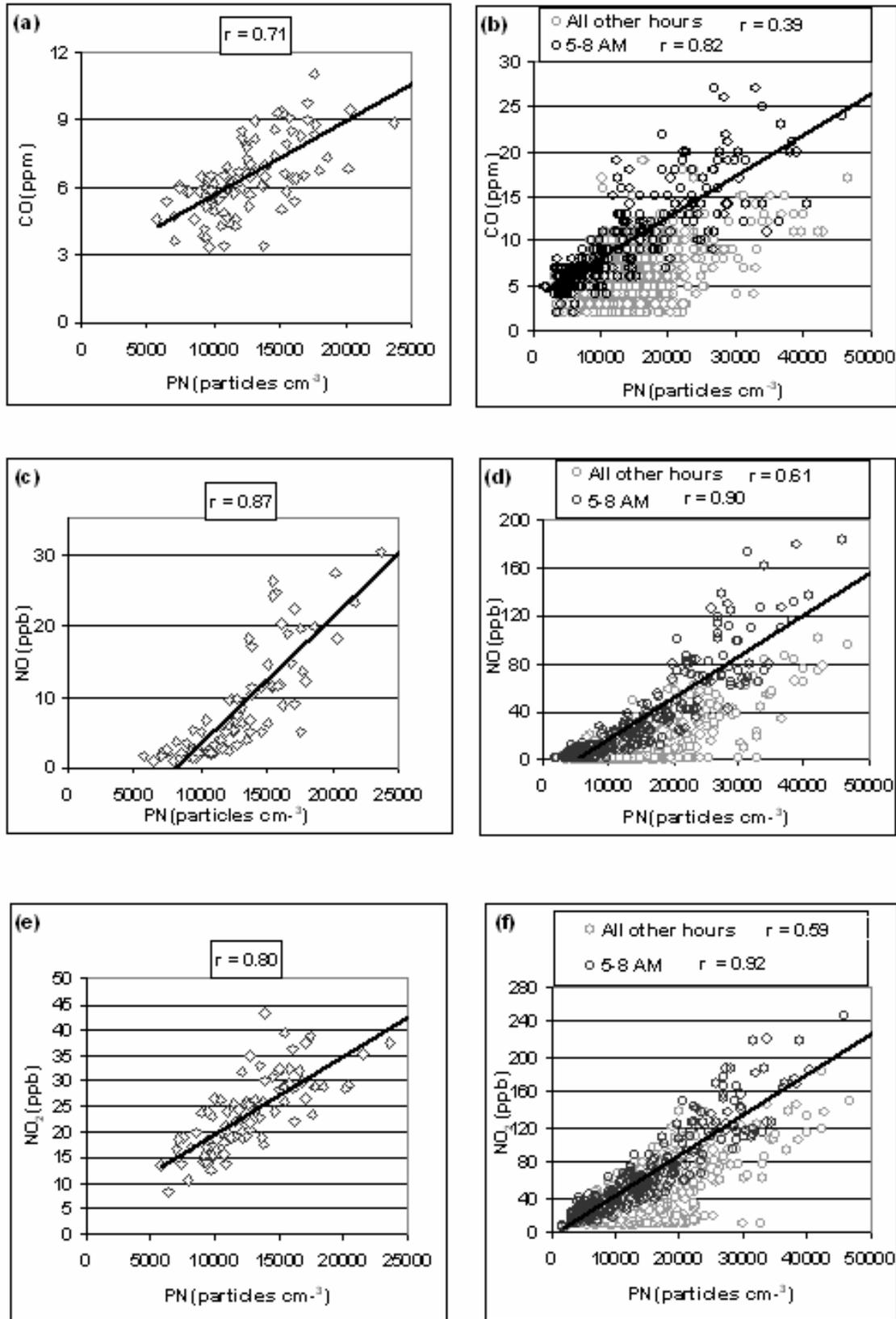


Figure 1

## **5. The Size Distributions of Polycyclic Aromatic Hydrocarbons in the Aitken (10-32nm), Ultrafine (32-180nm) and Accumulation Mode (180-2500 nm): Diurnal and Nocturnal Measurements in the Los Angeles Basin**

### **Background**

Ultrafine particles --formally defined as having diameter smaller than 100nm-- found in urban air contain chemical species that may contribute to the reported increases in mortality and morbidity with increasing particulate matter concentrations. Among the hundreds of organic and inorganic species found in ambient particulate matter (PM), polycyclic aromatic hydrocarbons (PAHs) are a candidate component class of particular interest with respect to acute and chronic toxicity because a large fraction of their mass is associated with ultrafine particles. For this reason, a great deal of recent health research interest has focused on this class of compounds.

Particle size distributions of toxic species present in ambient air are needed to estimate their deposition in the human respiratory system, their atmospheric residence time, and, more importantly, their capacity to be transported across cell wall membranes. Our recent studies in the Los Angeles basin have shown that PAHs measured near vehicular emission sources are found mostly in the ultrafine mode (operationally defined in our study as particles of diameter  $<0.18 \mu\text{m}$ ), while tens of km downwind of emission sources, a large fraction of the mass is found in the accumulation mode ( $0.18\text{--}2.5 \mu\text{m dp}$ ; Eiguren-Fernandez et al. 2003; Miguel et al. 2004). Similar results have been previously observed by other investigators, in other cities in the US (Friendlander's group, 1994), in Rio de Janeiro (Miguel's group, 1989), and the UK (Harisson's group). Recent studies conducted in our Center have shown that heme oxygenase-1 (HO-1) expression, a sensitive marker for oxidative stress, and dithiothreitol (DTT) activity, a quantitative measure of in vitro reactive oxygen species formation, are directly correlated with the PAH and the organic carbon content of ultrafine particles (Li et al. 2000, 2003). More specifically, high correlations have been observed between DTT activity and benzo[ghi]perylene, elemental carbon, and organic carbon contained in PM collected in several sites in the Los Angeles basin (Froines-Cho group, 2003).

While particles with diameters in the 3-10nm have been measured in urban Atlanta, as well as in remote locations ranging from the North Pole to Mauna Loa and Tasmania in the south pole (McMurry et al., 2000) and in the 10~40nm range in tunnel-diluted diesel exhaust, and in motorway measurements (Collins and Graskow, 2000), we report here what appears to be the first set of measurements of PAH size distributions in the 10-32nm dp (Aitken size range), i.e., what constitutes a 4th PAH mode, in addition to the three typical ultrafine, accumulation, and coarse modes commonly observed by several investigators in ambient air over the last three decades.

The health significance of this finding is important because the deposition efficiency of particles in the 10-32nm diameter range peaks (~50%) in the alveolar region of the human respiratory tract, according to models that assume spherical particles of unit density (ICRP 1994). Aerosol dynamics considerations of the behavior of particles in this size range suggest that the use of denuders, commonly used to remove vapor-phase species that might promote sampling artifacts, could lead to significant errors in PAH size distribution measurements.

## Experimental

The sampling system consisted of a nano-MOUDI impactor ( $10 \text{ nm} < dp < 180 \text{ nm}$ ) behind a MOUDI impactor ( $180 \text{ nm} < dp < 2.5 \text{ }\mu\text{m}$ ). Twenty-four hour samples (7am-6:30am) were collected for two weeks (Fall 2002, Winter and Summer 2003) in Long Beach, at USC, and downwind in Upland, and Riverside (Figure 1). Twelve-hour composite samples (7 am-6:30 pm) were collected for four days each, during August 2002, at USC and in Riverside. Twelve EPA priority PAHs were quantified by HPLC-Fluorescence as described in detail previously. We report here PAH size distribution measurements in the Aitken, ultrafine and accumulation size modes.

## Summary of Results and Discussion

**12-hr PAH data:** Our 12-hr  $\Sigma$ PAH mass size distribution measurements taken during the summer 2002 show a larger PAH mode in the 10-32 nm diameter range (Aitken size range) during the night-time, compared with day-time, at both USC and Riverside (figures 2 a,b). Also significant is the observed shift, toward smaller size, of the night-time measurements in Riverside.

In terms of  $\Sigma$ PAH mass in each of the three size bins analyzed, particles in the Aitken mode range observed during night-time at USC and Riverside, is, respectively, about 3 and 2 times higher, compared with daytime (figures 3a,b). The ultrafine particle mode, defined for the purpose of this report as particles with  $dp$  in the 32-180nm range, is significantly higher during night-time at USC, compared with day-time, and  $\sim$  equal in Riverside (figures 3a,b). The accumulation mode, the largest of the three, is a little higher during daytime at USC, compared with Riverside (3a,b). A comparison of the two sites in terms of day-time and night-time measurements of  $\Sigma$ PAH mass by size bin (figures 4a,b) shows that both the day-time and night-time Aitken mode is higher in Riverside. The night-time ultrafine and accumulation modes measured at both sites are  $\sim$  equal (figure 4b).

Since this is, to our knowledge, the first report of measurements of PAHs down to 10nm using an impactor, the question that immediately comes to mind is if they are real! A literature search shows that, during winter in Atlanta, Woo et al. (*Aerosol Sci. Technol.*, 34:75-87, 2001) observed several significantly elevated particle concentrations in the 10-35nm diameter range, in early morning and late afternoon, and sometimes during late evening hours (11 °C average temperature). Average night-time ( $\sim 19$  °C) and day-time ( $\sim 23$  &  $25$  °C) temperatures at our two sites differed by  $\sim 4$  &  $6$  °C with Riverside being a little warmer during the day. While our findings appear consistent with their observations, a study reported two years later by Park et al. (*Environ. Sci. Technol.* 37:577-583, 2003) compared mass distributions measured with the SMPS and the MOUDI and hypothesized that nanoparticles observed in the MOUDI may have resulted from particle bounce from upper stages of the impactor, or artifact formation in the low-pressure stages. While the sources of the nanoparticles observed with the SMPS by the Minneapolis group are not yet known, they suggested that the prevailing ambient temperature may play an important role in their formation, and that they originate from combustion processes.

**24-hr PAH data:** At USC, Upland, and Riverside, our 24-hr fall  $\Sigma$ PAH data show significant nucleation modes (32-180nm) for the semivolatile PAHs (figures 5b-d), and for the higher MW

PAHs at Upland (figures 6c). At Long Beach, USC, and Upland, our winter 24-hr size distribution measurements (figures 7a-c) show a significant nucleation mode for the semivolatile PAHs, and a large one in Long Beach, for the higher MW PAHs (figure 8a).

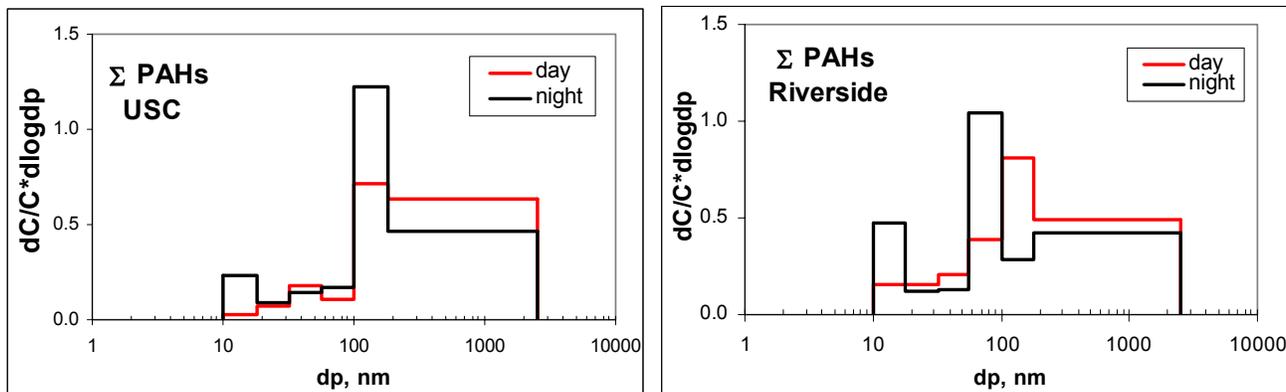
**Individual PAH data:** Figure 9 shows the 12-hr size distributions for twelve individual PAHs measured in Riverside, during nighttime periods in the summer 2002. As the figure shows, a significant fraction of PAH mass is found in the Aitken size range (10-32nm) for all twelve target PAHs, regardless of MW or vapor pressure! PAHs in the Aitken size range may be result from rapid cooling (self-nucleation) of the hot vapors when they exit the exhaust system into ambient air, or, as hypothesized by McMurry (personal communication) by partitioning, from the vapor into the particle-phase of oily droplets originated from self-nucleated lube oil. Since PAHs have been reported to accumulate in the lube oil, it is plausible that they self-nucleate together with the oil upon rapid cooling as they exit the exhaust system. A non-MOUDI sampling system and a higher sensitivity analytical method considered by McMurry and Miguel to try and validate these measurements.

## Conclusions

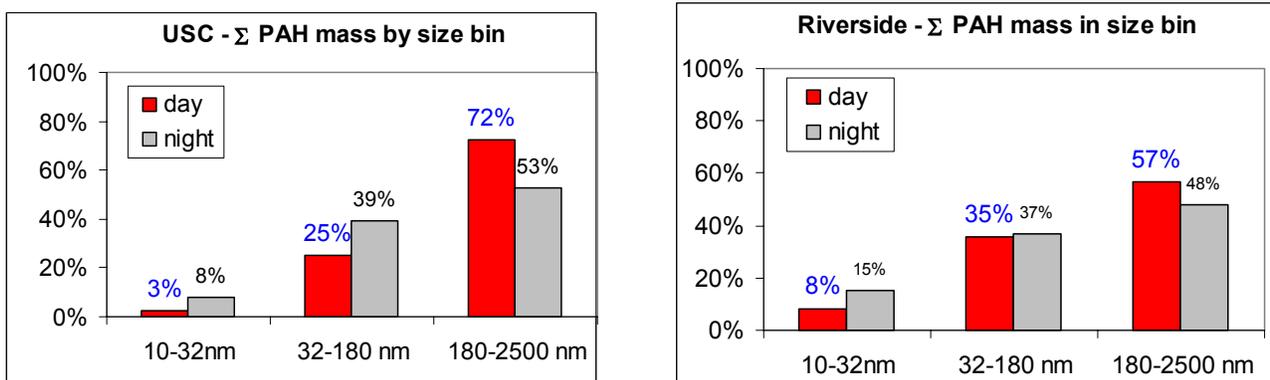
Although it needs further confirmation, it appears that PAH in the Aitken mode may be present in the air of the four sites studied to date. The health significance of this finding is important because the deposition efficiency of particles in the 10-32nm diameter range peaks (~50%) in the alveolar region of the human respiratory tract. Aerosol dynamics considerations of the behavior of particles in this size range suggest that the use of denuders, commonly used to remove vapor-phase species that might promote sampling artifacts, could lead to significant assignment errors in PAH size distribution measurements. A schematic showing the mechanism of formation of the four modes observed for PAHs derived from combustion emissions and roadways is shown in Fig 10.



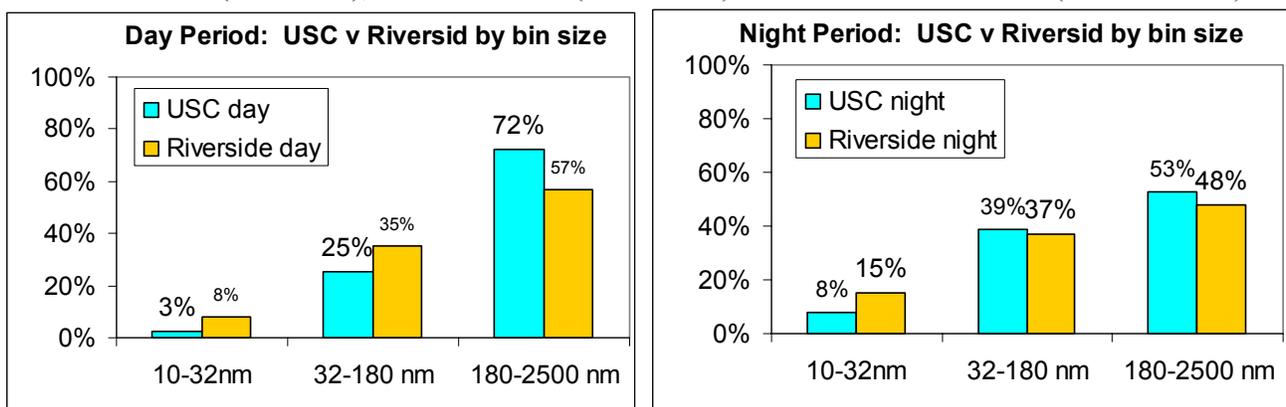
**Figure 1.** Location of the Long Beach, USC, Upland and Riverside sampling sites in the Los Angeles Air Basin.



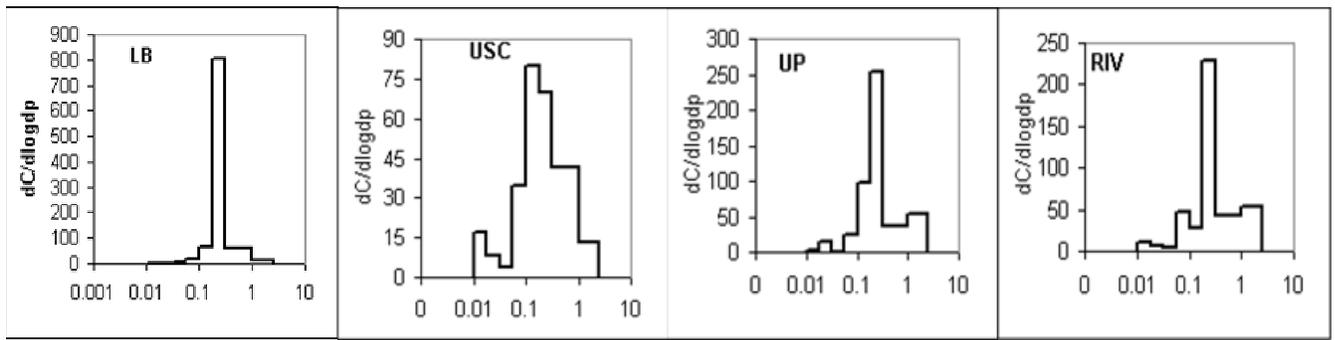
**Figure 2a,b.** Day and night size distributions for the  $\Sigma$ PAHs at USC (a) and Riverside (b). Samples are 12 hr composites taken in Aug 12-16, 2002 (a) and Aug 26-30, 2002 (b). Ave temp. ( $^{\circ}$ C) were: USC: 22.8 (day) and 18.7 (night), a 4.1  $^{\circ}$ C difference; Riverside: 25.4 (day) and 19.3 (night), a 6.1 $^{\circ}$ C difference.



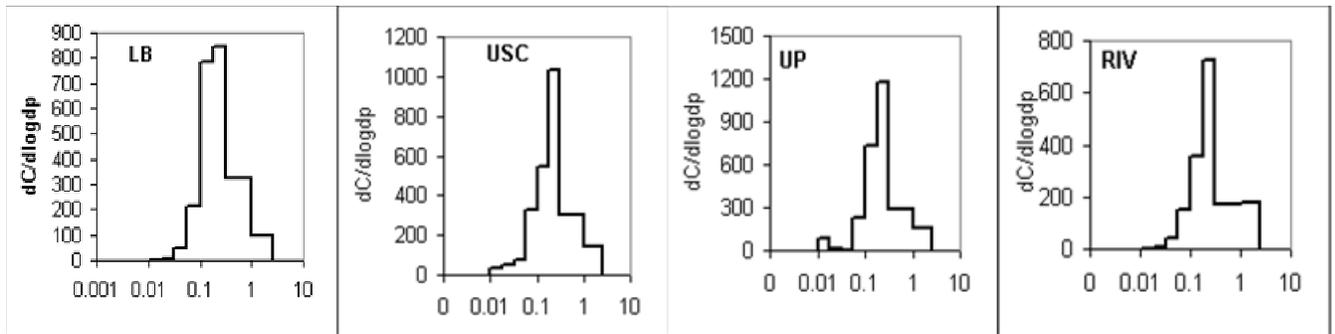
**Figure 3a,b.** Daytime vs. nighttime for the  $\Sigma$ PAHs measured at USC (a) and Riverside (b) in the nucleation mode (10-32 nm), ultrafine mode (32-180 nm) and accumulation mode (180-2500 nm).



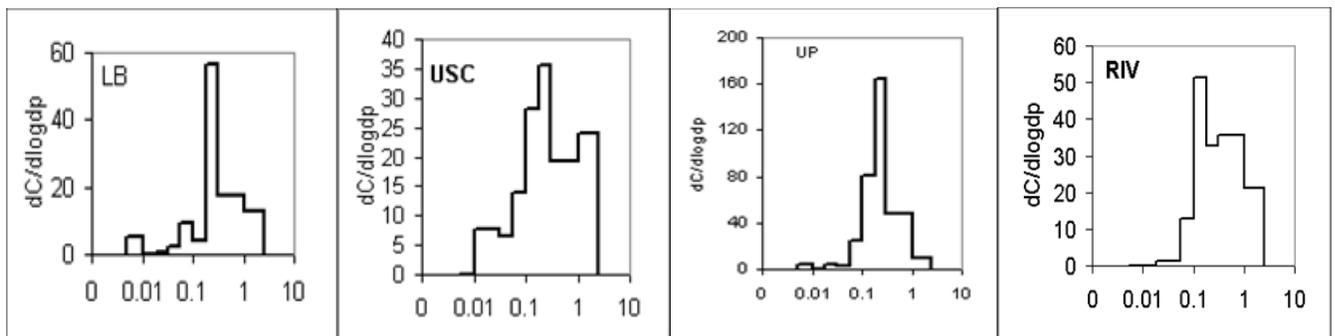
**Figure 4a,b.** USC vs. Riverside for the measured  $\Sigma$ PAHs during the daytime (a) and nighttime (b).



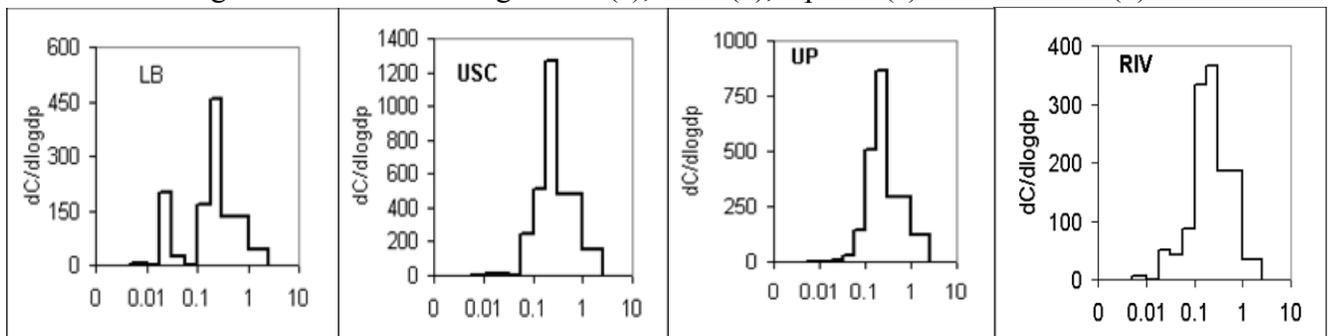
**Figure 5a-d.** Size distribution for the ΣPAHs in the semivolatile group (PHE, ANT, FLT, PYR) during the FALL of 2002 at Long Beach (a), USC (b), Upland (c) and Riverside (d).



**Figure 6a-d.** Size distribution for the ΣPAHs with higher MW (BAA,CRY,BBF, BKF,BAP, DBA, BGP, IND) measured in the during the FALL at Beach (a), USC (b), Upland (c) and Riverside (d).Long



**Figure 7a-d.** Size distribution for the ΣPAHs in the semivolatile group (PHE, ANT, FLT, PYR) measured during the WINTER at Long Beach (a), USC (b), Upland (c) and Riverside (d).



**Figure 8a-d.** Size distribution for the ΣPAHs with higher MW (BAA,CRY,BBF, BKF,BAP, DBA, BGP, IND) measured during the during the WINTER, 2003 at Long Beach (a), USC (b), Upland (c) and Riverside (d).

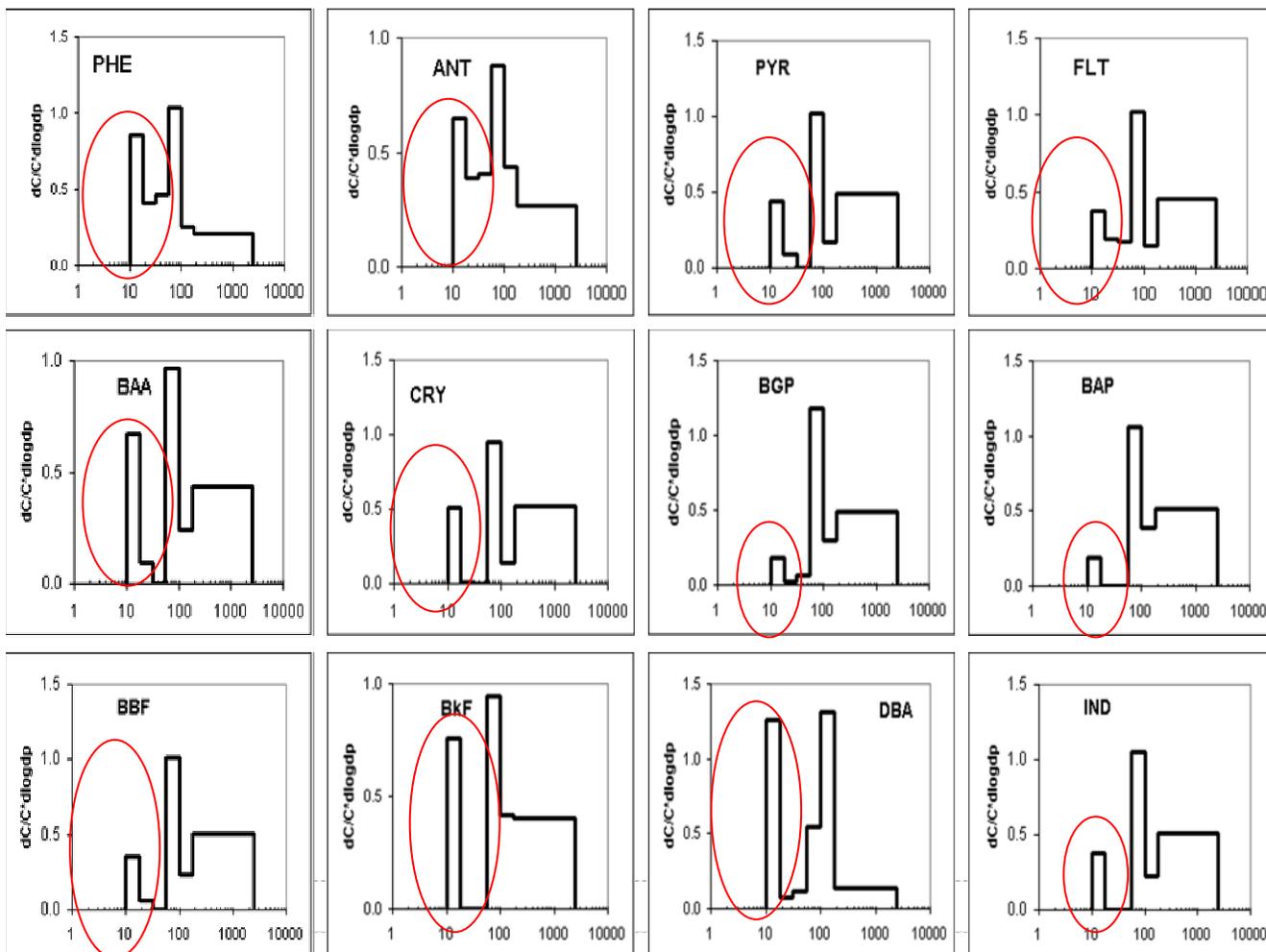
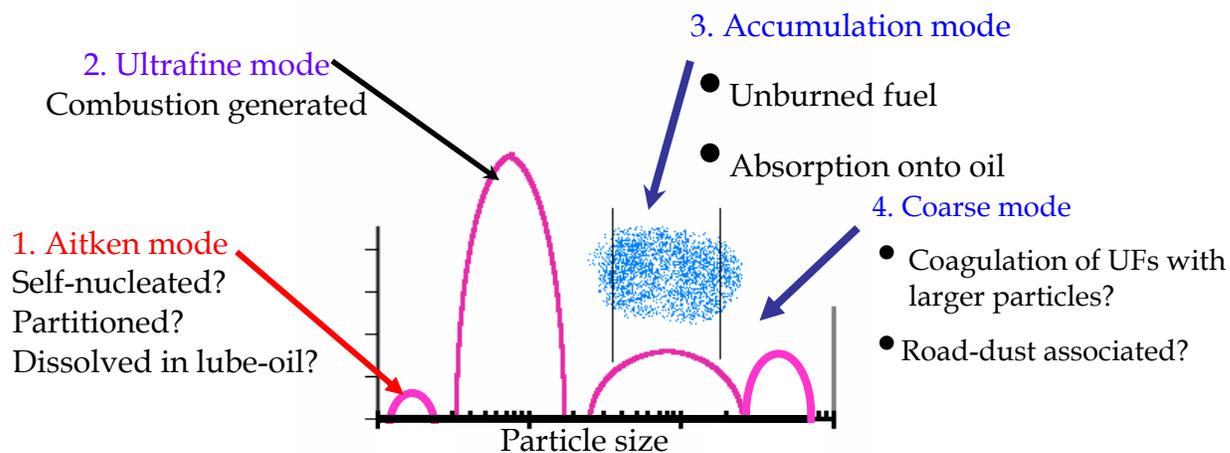


Figure 9. 12-hr size distributions for twelve individual PAHs measured in Riverside, during nighttime periods in the summer 2002. Red circles refer to particles in the Aitken size range.

## Mechanism of Formation of Four PAH Modes



**Figure 10.** Mechanism of formation of the four modes observed for PAHs derived from combustion emissions and roadways.

### Cited Literature

- A. Eiguren-Fernandez, Antonio H. Miguel, Peter A. Jaques, and Constantinos Sioutas (2003) - Evaluation of a Denuder-MOUDI-PUF Sampling System to Measure the Size Distribution of Semi-Volatile Polycyclic Aromatic Hydrocarbons in the Atmosphere. *Aerosol Science and Technology* 37:201–209.
- A. Eiguren-Fernandez and Antonio H. Miguel (2003) – Determination of Semi-Volatile and Particulate Polycyclic Aromatic Hydrocarbons in SRM 1649a and PM<sub>2.5</sub> Samples by HPLC-Fluorescence. *Polycyclic Aromatic Compounds*, 23:193-205.
- A. Eiguren-Fernandez, Antonio H. Miguel, John R. Froines, Suresh Thurairatnam, and Ed L. Avol - Seasonal and Spatial Variation of Polycyclic Aromatic Hydrocarbons in Vapor-Phase and PM<sub>2.5</sub> in Southern California Urban and Rural Communities *Aerosol Science and Technology*, 38:1–9, 2004.
- A. H. Miguel, Arantzazu Eiguren-Fernandez, Peter A. Jaques, John R. Froines, Bill L. Grant, Paul R. Mayo and Constantinos Sioutas (2004) - Seasonal variation of the particle size distribution of polycyclic aromatic hydrocarbons and of major aerosol species in Claremont, California. In press *Atmospheric Environment*.
- A.H.Miguel and P.A.P.Pereira (1989) - Benzo(k)Fluoranthene, Benzo(ghi) Perylene and Indeno(1,2,3-cd)Pyrene: New Tracers of Automotive Emissions in Receptor Modeling, *Aerosol Sci. & Technol.*, 10:292-295.
- A.H.Miguel and S.K.Friedlander (1978) - Distribution of Benzo(a)pyrene and Coronene with Respect to Particle Size in Pasadena Aerosols in the Submicron Range, *Atmos. Environ.* 12, 2407-2413.
- A.H.Miguel, T. W. Kirchstetter, R. A. Harley, and S. V. Hering (1998) – On-road Emissions of Polycyclic Aromatic Hydrocarbons from Gasoline and Diesel Vehicles. *Environ. Sci. Technol.*, 32, 450.

- Collins and Graskow, Chap 4, in *Ultrafine Particles in the Atmosphere*, The Royal Society, Imperial College Press, 2000.
- ICRP 1994. *Annals of the ICRP, human respiratory tract model for radiological protection*. ICRP Publication 66. Oxford: Pergamon, 1994.
- L.C. Marr, T.W. Kirchstetter, R.A. Harley, A.H. Miguel, S.V. Hering, and S. Katharine Hammond (1999) - Characterization of Polycyclic Aromatic Hydrocarbons in Motor Vehicle Fuels and Exhaust Emissions. *Environ. Sci. Technol.*, 33, 3091–3099.
- McMurry et al., Chap 5. *In Ultrafine Particles in the Atmosphere*, The Royal Society, Imperial College Press, 2000.
- N.Li, I. Venkatesan, A. H. Miguel, R. Kaplan, C. Gujuluva, J. Alam, and A. Nel (2000) – Induction of heme-oxygenase-1 expression in macrophages by diesel exhaust particle chemicals and quinones via the antioxidant-responsive element. *J. Immunology*, 3393-3401.
- Ning Li, Jawed Alam, M. Indira Venkatesan, Arantza Eiguren-Fernandez, Debra Schmitz, Emma Di Stefano, Ndaisha Slaughter, Erin Killeen Xiaorong Wang, Aaron Huang, Meiying Wang, Antonio H. Miguel, Arthur Cho, Constantinos Sioutas, Andre E. Nel (2004) - Nrf2 is a Key Transcription Factor that Regulates Antioxidant Defense in Macrophages and Epithelial Cells: Protecting Against the Pro-inflammatory and Oxidizing Effects of Diesel Exhaust Chemicals. Submitted *J. of Immunology*.
- P. A. Pereira, J. B. de Andrade, and A. H. Miguel (2001) – Determination of 16 priority polycyclic aromatic hydrocarbons (PAH) in particulate matter by HRGC-MS after extraction by sonication. *Anal. Sci.* 17, 1229-1231.
- Park et al. *Environ. Sci. Technol.* 37:577-583, 2003.
- S.V.Hering, A.H.Miguel and R.L.Dod (1984) - Tunnel Measurements of the PAH, Carbon Thermogram and Elemental Source Signature of Vehicular Exhaust Emissions, *The Sci. of the Total Environ.*, 36, 39-45.
- Woo et al. *Aerosol Sci. Technol.*, 34:75-87, 2001.

## 6. Characterization of PAH and PAH-Derivatives

### Work Conducted in the Last Quarter

In August, 2002 and January, 2003 joint field sampling was conducted by researchers from UCR (Reisen and Arey, 2004, submitted for publication; see also last quarterly progress report) and USC (Fine et al., *Environ. Sci. Technol.*, Vol. 38, pp. 1296-1304, 2004) with samples collected at two sites (USC and UCR) and during two seasons. Figures 1 and 2 show correlations of our gas-phase PAH and nitro-PAH analyses with the particle-associated dicarboxylic acid data of Fine and co-workers.

Fine and co-workers have suggested that phthalic acid (1,2-benzene-dicarboxylic acid) and 4-methylphthalic acid (4-methyl-1,2-benzene-dicarboxylic acid) can be used as markers of secondary aerosol formation, while other dicarboxylic acids are directly emitted, for example, in vehicle exhaust. Shown in the top two panels of Figure 1 are the average naphthalene concentrations ( $\text{ng}/\text{m}^3$ ) and the naphthalene concentrations normalized to the CO concentration. As expected, the differences between the winter and summer values are less when the naphthalene concentration is normalized to CO, reflecting the tighter wintertime inversions in the South Coast air basin. As seen in the third panel, in contrast with the naphthalene concentrations, the nitronaphthalenes concentrations,  $(1\text{NN}+2\text{NN})/\text{CO}$ , are higher in the summer and at the downwind UCR site reflecting their photochemical formation. The phthalic acid/CO ratio (4<sup>th</sup> panel) shows a very similar trend to the nitronaphthalene/CO ratio, consistent with

phthalic acid being a secondary organic aerosol component. The higher (1NN+2NN)/CO ratio in the UCR summer nighttime sample, relative to the phthalic acid/CO ratio may be attributed to nighttime NO<sub>3</sub> radical formation of the nitronaphthalenes. These profiles suggests that phthalic acid may be a product from OH radical-initiated reaction of naphthalene.

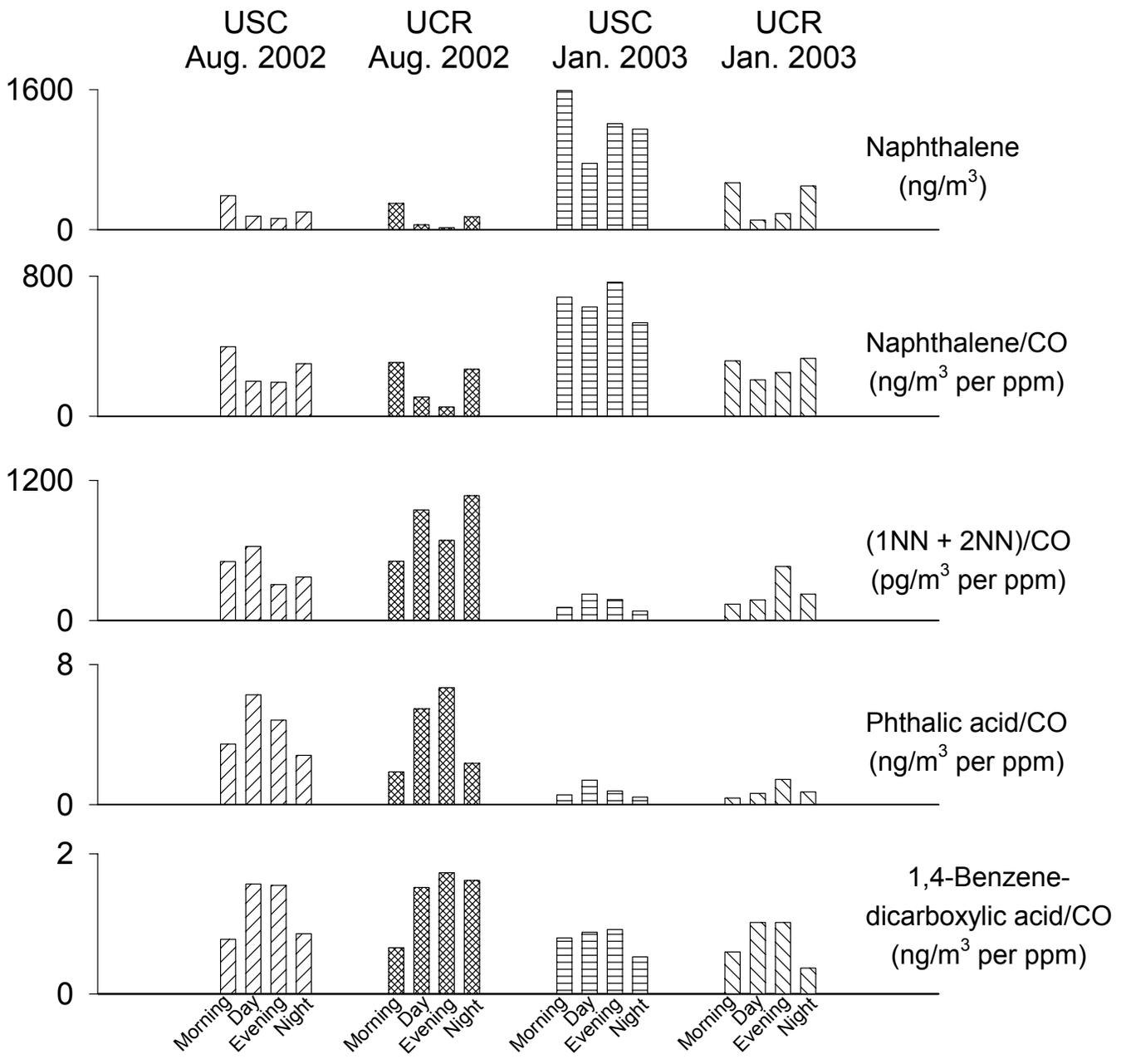
The final panel in Figure 1 shows 1,4-benzene-dicarboxylic acid/CO which shows little difference between the summer and winter samples, consistent with this dicarboxylic acid being directly emitted.

Figure 2 shows the corresponding data for 2-methylnaphthalene and its atmospheric reaction products, the methylnitronaphthalenes. The 4-methyl-1,2-benzene-dicarboxylic acid correlates well with the methylnitronaphthalenes, suggesting that its source may be the OH radical-initiated reaction of 2-methylnaphthalene. The higher relative  $\Sigma$  MNNs/CO for the UCR summer nighttime sample is again attributed to NO<sub>3</sub> chemistry.

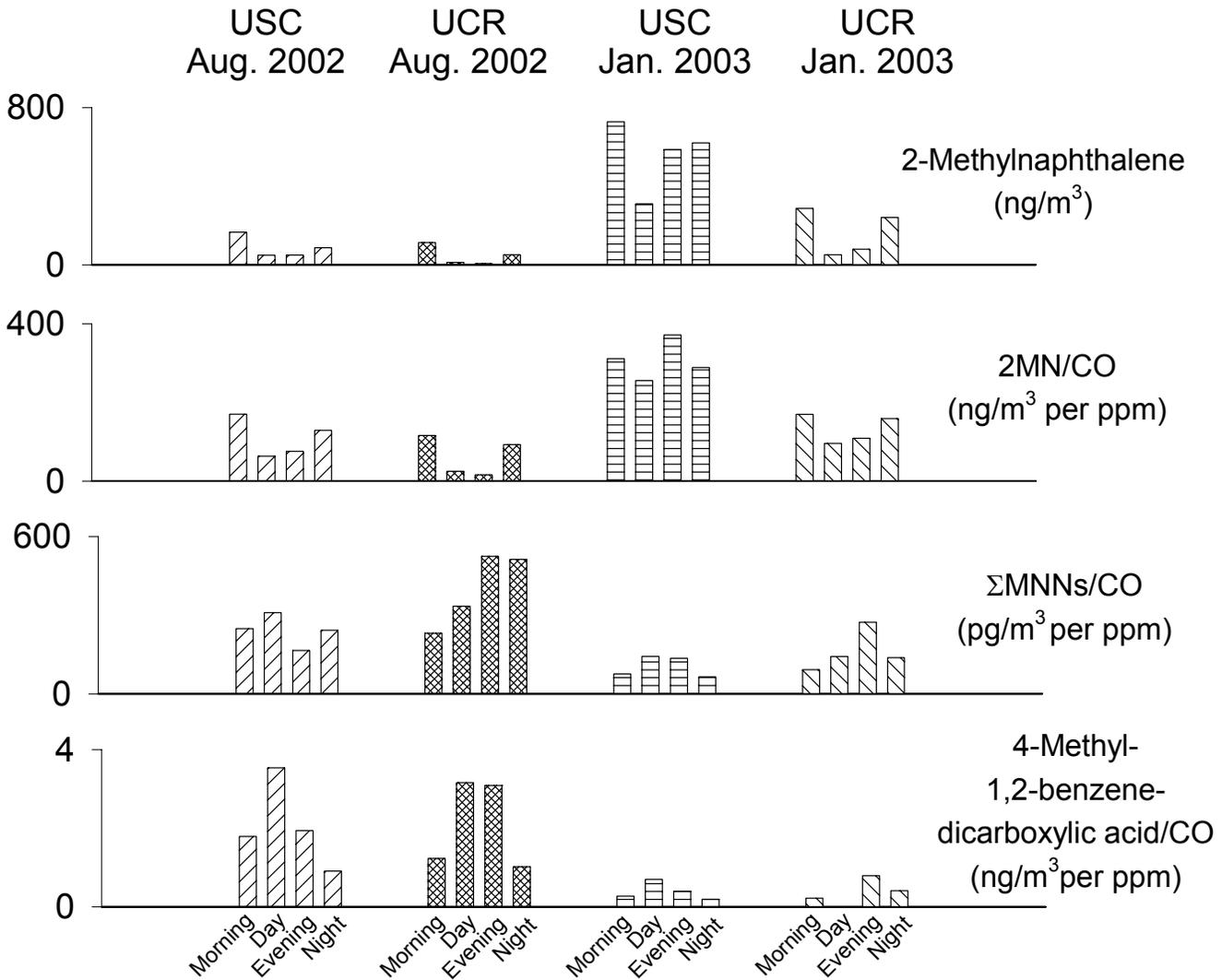
We have received from Drs. Fine and Sioutas the extracted, size-fractionated samples collected at USC and UCR in August, 2002 and January, 2003 [the same samples for which the phthalic acid concentrations are shown in Figure 1]. We have received approximately 50% of each accumulation (0.18 – 2.5  $\mu$ m) mode and ultrafine (diameters <0.18  $\mu$ m) mode particle sample. We have spiked the samples with deuterated 1-nitropyrene and benzo[b]fluoranthene and started fractionation by HPLC prior to GC/MS analysis by negative ion methane chemical ionization for the nitro-PAHs and positive ion methane chemical ionization (and/or electron impact ionization) for the PAHs. It will be interesting to determine if the distribution of 2-nitrofluoranthene, an atmospheric reaction product of radical-initiated atmospheric reactions of fluoranthene, between the accumulation mode and ultrafine particles is similar to the reported distribution (Fine et al., Environ. Sci. Technol., Vol. 38, pp. 1296-1304, 2004) of phthalic acid.

### **Future Work**

The 32 samples from USC and UCR will be analyzed for 2-nitrofluoranthene, 1-nitropyrene and 2-nitropyrene. PAH analyses will also be conducted on each sample to allow quantification of the fraction of the sample extracts delivered to UCR.



**Figure 1.** Atmospheric concentrations of naphthalene and atmospheric concentrations normalized by dividing by the CO concentration for: naphthalene, the sum of 1- and 2-nitronaphthalene (NN), phthalic acid and 1,4-benzene-dicarboxylic acid.



**Figure 2.** Atmospheric concentrations of 2-methylnaphthalene and atmospheric concentrations normalized by dividing by the CO concentration for: 2-methylnaphthalene, the sum of the methylnitronaphthalenes (MNNs), and 4-methyl-1,2-benzene-dicarboxylic acid.

## **7. Study of Indoor/Outdoor Ultrafine Particles near Busy Freeways**

### **Objective**

Because ultrafine particles in urban areas show high spatial variability near sources and because people spend more than 80% of their time indoors, it is necessary to study the levels of ambient ultrafine particles in the indoor environment at hot urban spots, i.e. near freeways. The overall objective of this project is to improve our knowledge of the indoor levels of ultrafine particles from outdoor origin, especially those from motor vehicles in the vicinity of freeways. The basic hypothesis is that the existing indoor/outdoor aerosol penetration models may not be appropriate to predict indoor ultrafine particles levels, because of the unique nature of vehicle emitted ultrafine particles.

### **Sampling Site**

Four two-bedroom apartments in the vicinity of the 405 Freeway in Los Angeles, CA were recruited for this study. Three of the four apartments are on the downwind side of the 405 freeway located from 20-50 m from the edge of the freeway. The remaining apartment is on the upwind side of the 405 Freeway. By arrangement with the tenants, no smoking, cooking, or cleaning activities took place during the sampling periods. The apartments have mechanical ventilation systems that can be turned off. Most sampling during the reporting period was conducted with the mechanical ventilation turned off. This study design provides a unique opportunity to monitor infiltration of particulate matter of outdoor origin into the indoor environment.

### **Instrumentation**

Measurements were made through a common manifold that was switched to alternately sample indoor or outdoor air every 9 min. The switching manifold consisted of a solenoid valve programmed to switch in synchrony with the sampling interval of the instruments. Indoor and outdoor particle size distributions in the size range from 6 nm to 220 nm were measured by a Scanning Mobility Particle Sizer (SMPS 3936, TSI Inc., St. Paul., MN). In each 9-minute sampling period three size distribution samples were taken in sequence with the SMPS. At the same time black carbon concentrations were measured by an Aethalometer and CO concentrations were measured by a TSI Q-trak. Average air exchange rates were measured by means of Harvard CATs samplers. Total particle number concentrations were measured by a TSI P-trak.

### **Tandem-DMA Volatility Measurements**

A Tandem-DMA (TDMA) system was used in two of the four apartments to measure the degree of volatility of fresh vehicular emissions as a function of particle size. Similar TDMA experiments have sampled ambient air (in the context of nucleation or in more or less polluted urban and rural sites) and vehicular emissions from dynamometer tests. However, ultrafine particle emissions from dynamometer tests have been shown to vary significantly with dilution temperatures, ratios, and residence times. This study will characterize fresh vehicular emissions under real-world conditions downwind of freeways. The results will be used to determine the volatility of fresh emissions, to validate near freeway particle physics models, and to guide future

studies on toxicity as a function of particle mixing characteristics of volatile and non-volatile components.

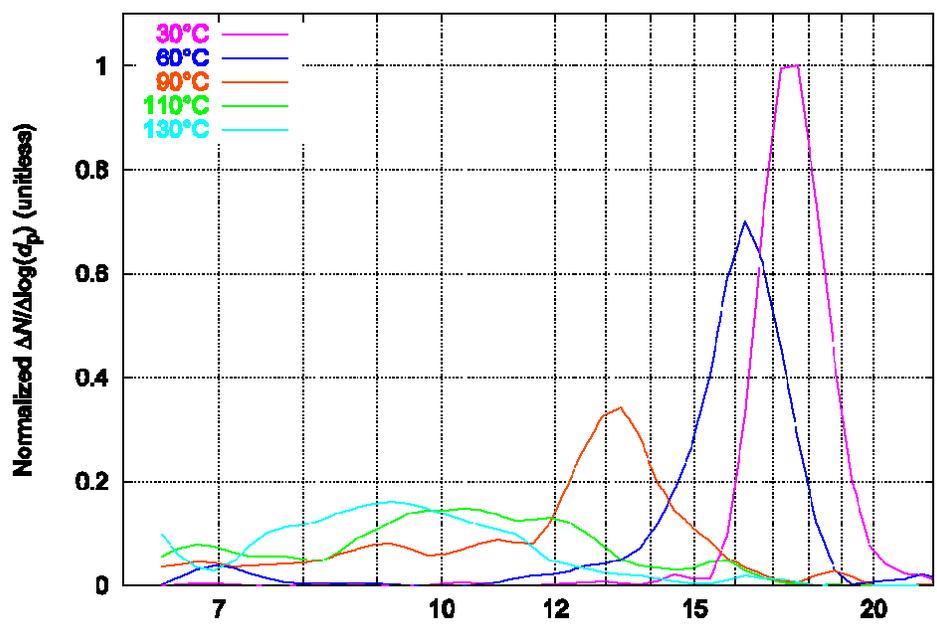
A particle size was selected with the first DMA, and the second DMA was used to observe the resulting particle size distribution. Input to the second DMA was alternated between heated, and ambient temperatures. Particle sizes were selected in the range from 15 nm to 100 nm

The tests included alternate sampling of indoor and outdoor aerosols. The data will help interpret the results from the Indoor/Outdoor Ultrafine Particles study conducted in the same apartments. As we measured in winter (December 2003 and January 2004), these data are more valuable in terms of PM volatility. More volatile PM is bound to be formed during winter from condensation of organic vapors found in vehicle exhaust than during summer.

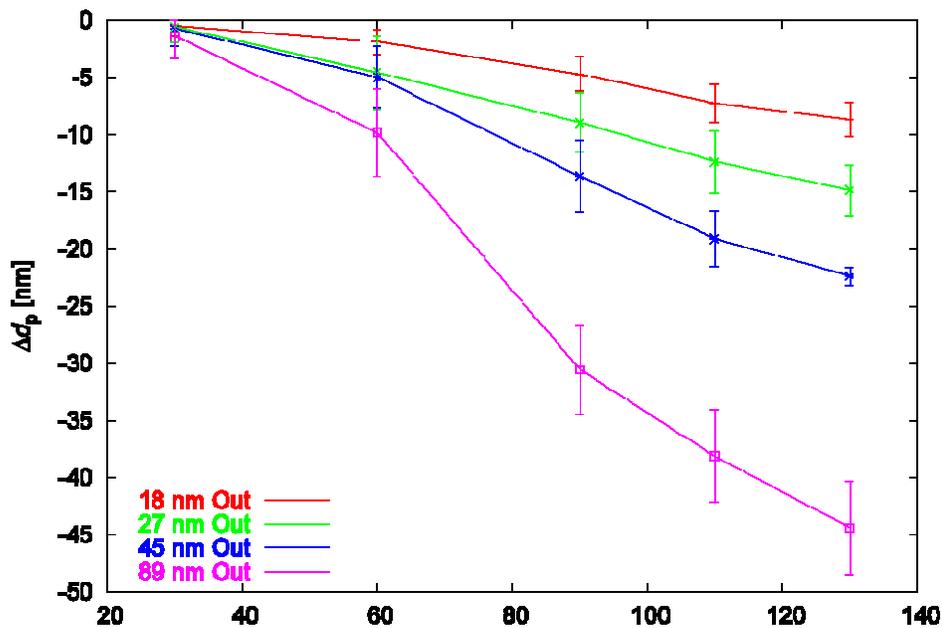
Results from measurements with 18 nm particles at various heater temperatures are shown in figure 1. The mode of the originally monodisperse aerosol shifts towards a smaller diameter with increasing heater temperature. For particles with diameter of 18 nm, 27 nm, 45 nm, and 89 nm the mode position was determined from measurements (like the measurements shown for 18 nm) at heater temperatures of 30 °C, 60 °C, 90 °C, 110 °C, and 130 °C. The results are shown in figure 2 as difference of the measured mode diameter to the selected particle diameter (“mode shift” as function of temperature).

In case of the 18 nm particles, they seem to be composed mostly of volatile material. The measurements have not shown a solid, non-volatile, core, but all particles shrink nearly uniformly as they are heated. This is different in case of larger particles, particularly the 89 nm particles for which measurements showed two modes when the particles are heated: a larger mode shrinking towards smaller diameters and a smaller mode that does not shrink with heating and has a mode diameter close to the original particle diameter. This indicates that a fraction of these particles is composed of non-volatile material.

Other preliminary results indicate a higher volatility of outdoor particles as compared to indoor particles; at the same heater temperature outdoor particles shrink more. The data also suggest that volatility of outdoor particles with diameter of 45 nm or smaller is decreasing between 20 m distance to the freeway and 50 m distance.



**Figure 1:** Measurements with 18 nm particles at heater temperatures of 30 °C, 60 °C, 90 °C, 110 °C, and 130 °C.



**Figure 2:** Evaporation profile (“mode shift” as function of temperature).

**Future Work**

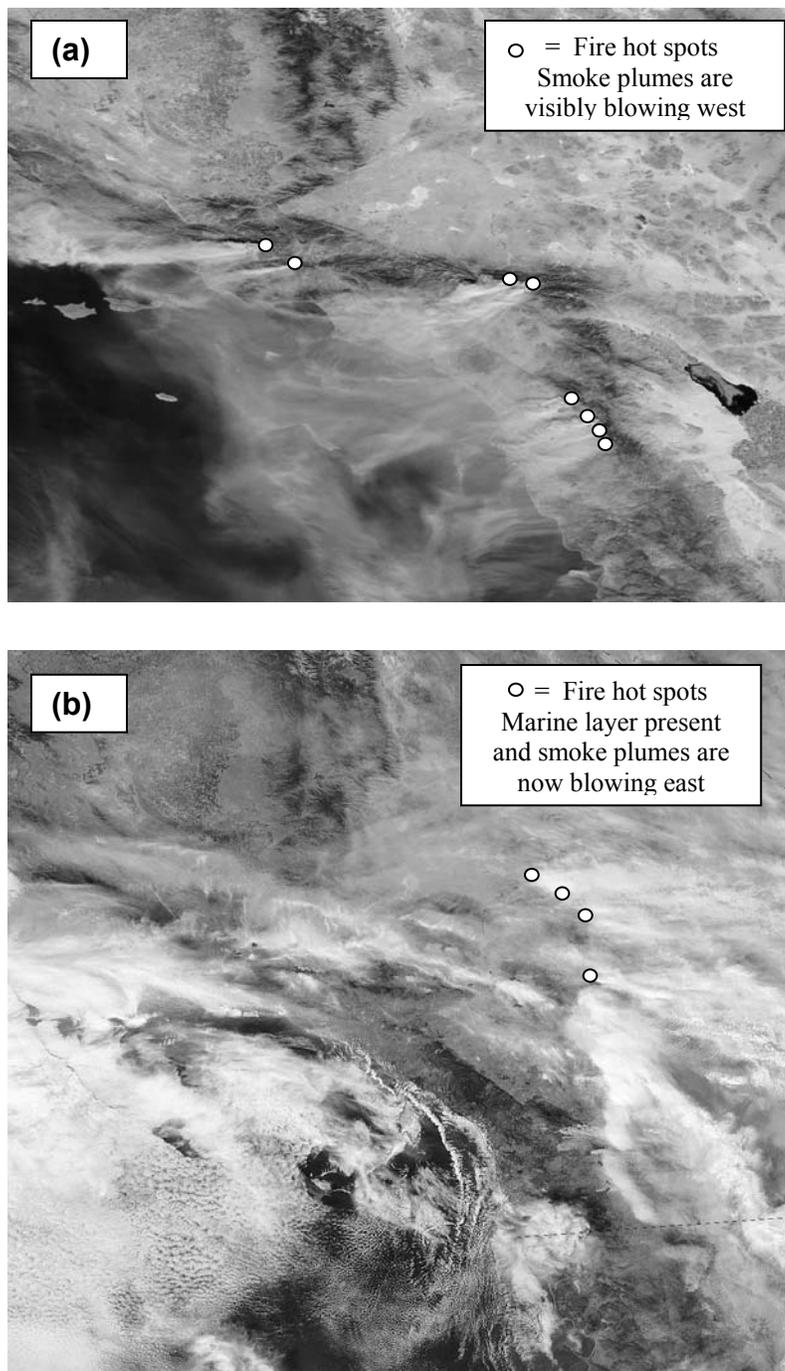
Results from these studies will be published. Ultrafine size distribution data measured in the four apartments concurrently and prior to the TDMA measurements are being analyzed and compared

to models. Results will help understand penetration characteristics of ultrafine particles better, especially in the case of mostly vehicle generated particles in the proximity of major highways.

## **8. October 2003 Fires in Southern California**

In Southern California, dry summers followed by hot and dry westerly wind conditions contribute to the region's autumn fire season. In late October of 2003, 13 large Southern California wildfires, ranging from Simi Valley in the North to San Diego 150 miles to the south, burned more than 750,000 acres of land, destroyed over 3,500 structures, including 2,700 homes, and displaced 100,000 people. Twenty human deaths were attributed to the wildfires. The cost of the damage was estimated to be US\$2 billion. The fires having the greatest effect on the air quality of the Los Angeles (LA) Basin included the Grand Prix and Old fires in San Bernardino County and the adjacent Padua fire in Los Angeles County. These fires were located to the northeast of central Los Angeles, with Santa Ana wind conditions, blowing towards the southwest, transporting emissions to the western portions of the Basin.

The fires started around October 23<sup>rd</sup> and had significant impacts on the air quality of the LA basin until October 29<sup>th</sup>, when the winds reversed direction and resumed their normal on-shore pattern (Figure 1). The fire episode was declared the deadliest and most devastating in more than a decade, and local media advised individuals to stay indoors to avoid exposure to excessive levels of PM, CO, VOCs, and ozone caused by the wildfires. This study examined the actual impact of these wildfires on air quality in urban Los Angeles using "opportunistic" data from Supersite or other air pollution studies being conducted at the time of the fires. Measurements of pollutant gases (CO, NO<sub>x</sub>, and ozone), particulate matter (PM), particle number concentrations (PN) and particle size distributions at several sampling locations in the LA basin before, during, and after the fire episode are presented.

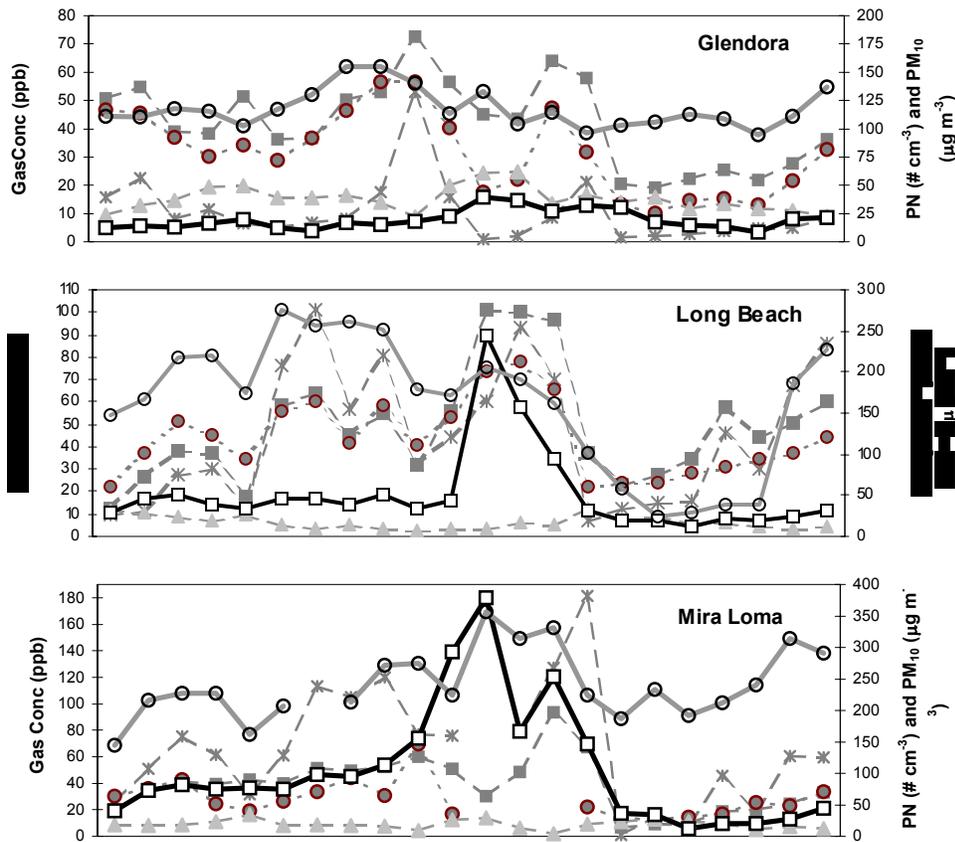


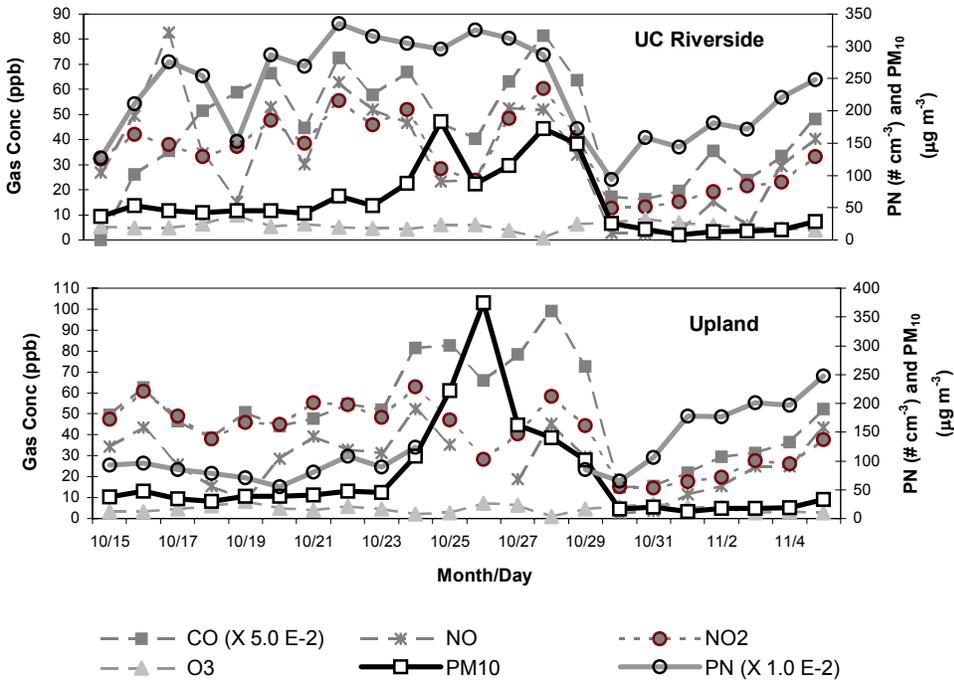
**Figure 1:** Satellite photos taken a) during the peak of the fires on October 28<sup>th</sup>, and b) after the winds shifted towards the east on October 29<sup>th</sup>

Continuous data were collected throughout the calendar year 2003, including the fire episode, and five sites within the LA Basin impacted by the wildfires were examined in this study: Long Beach, Glendora, Mira Loma, Upland and Riverside. The choice of these sampling sites was based on their location within the Los Angeles Basin, the availability of the data for the

desired period, and the observed impacts of the Grand Prix, Old and Padua fires. In addition to the data collected at the above sites, semi-continuous PM<sub>2.5</sub> (fine) and ultrafine PM mass concentrations were measured at the Southern California Supersite located near downtown Los Angeles at the University of Southern California (USC). Finally, in a concurrent Supersite study, particle size distributions were measured indoors and outdoors of a two-bedroom apartment in the Westwood Village area near the University of California, Los Angeles.

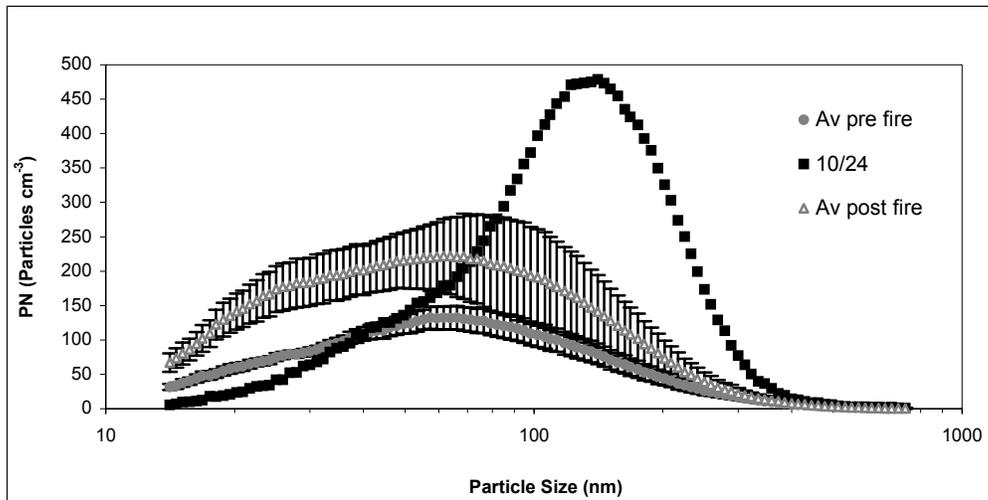
The greatest impact was observed on PM<sub>10</sub> concentrations, which increased by factors of three or four depending on location (Figure 2). CO and NO levels increased to a lesser extent (a factor of approximately two), most likely due to the different relative emission rates of these pollutants from wildfires compared to typical urban sources such as traffic.



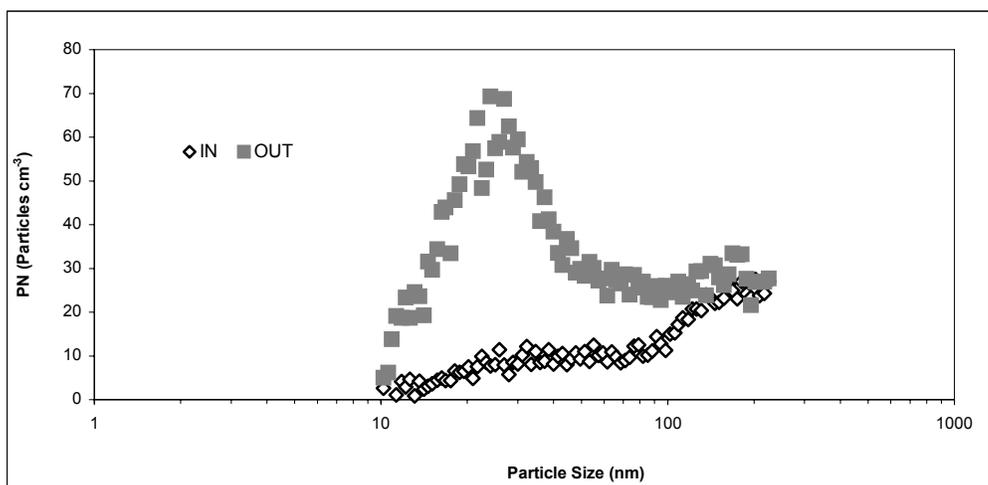


**Figure 2:** 24-hour averaged PM and gaseous pollutant concentrations during the study at a) Glendora, b) Long Beach, c) Mira Loma, d) UC Riverside and e) Upland. For comparison purposes, CO concentrations (in ppb) have been divided by 20, and PN concentrations (in # cm<sup>-3</sup>) have been divided by 100, as indicated in the legend.

Particle number concentrations and NO<sub>2</sub> were essentially unchanged, except at the sites nearest the fires where PN levels almost doubled. Ozone levels during the fires were observed to be lower during the fires at some sites, a possible result of light scattering by the smoke plume reducing photochemical activity levels (Figure 2). Particle number distributions downwind of the fires displayed number modes with diameters between 100 and 200 nm, larger than typical urban aerosol and explaining the larger increases in PM<sub>10</sub> and PM<sub>2.5</sub> mass concentrations than that for ultrafine particle mass and particle number (Figure 3). These particles were also shown to penetrate effectively indoors (Figure 4), calling into question the prevailing advice to the public to remain inside to avoid exposure to harmful wildfire emissions.



**Figure 3:** Particle size distributions at Upland a) at 10AM: before, 10/24/03, and after the fires.



**Figure 4:** Indoor/Outdoor particle size distributions at 6AM in Westwood Village on 10/27/03.

### 9. Redox Activity of Airborne Particulate Matter (PM) at different Sites in the Los Angeles Basin

There is extensive epidemiological evidence associating airborne particulate matter (PM) with adverse health effects in humans<sup>1-3</sup>. Many of these adverse effects have been attributed to cellular oxidative stress associated with the generation of reactive oxygen species (ROS) such as superoxide, hydrogen peroxide and hydroxyl radical by constituents of the PM or the PM itself<sup>4-7</sup>. High levels of ROS cause a change in the redox status of the cell<sup>8</sup>, thereby triggering a cascade of events associated with inflammation and, at higher concentrations, apoptosis<sup>9</sup>.

In this study, we have examined ambient PM from the Los Angeles Basin (LAB) for their DTT-based redox activity, together with chemical characterization assays, to assess the role of inorganic and organic species in this redox activity. Thus, PM samples of different sizes were collected in the LAB with a particle concentrator/virtual impactor<sup>19,20</sup> and their redox activity, levels of metals, organic (OC) and elemental carbon (EC), inorganic ions and polycyclic aromatic hydrocarbons (PAH) determined. The results, which are described in greater length and detail in a manuscript that we submitted to *Environmental Science and Technology* indicate that the DTT-based measure of redox activity correlates with PM content of organic and elemental carbon as well as with the levels of benzo(ghi)perylene (Bgp), a PAH originating mostly from vehicular emissions<sup>21,22</sup>.

### Sampling Locations

Since the objective of this study was to assess the different chemical properties and their relationship to PM redox activity, samples of mobile source PM as well as PM from the eastern side of the Los Angeles Basin that had undergone atmospheric chemical reactions were examined. The samples were size fractionated and collected with the Versatile Aerosol Concentration Enrichment System (VACES)<sup>19,20</sup> at three sites:

1. Boyle Heights (BH), an area just east of the Los Angeles downtown area. Particles were collected at two locations, 50 (BH1) and 150 (BH2) meters downwind of the confluence of two major freeways (I-60 and I-5) that include heavy diesel traffic.
2. The main campus of the University of Southern California (USC), which is about 2 km southwest of the downtown area. This site and Boyle Heights represent classic “source” sites in which aerosols are mostly generated from fresh vehicular emissions.
3. Claremont (CL), approximately 45 km east and downwind of downtown Los Angeles. This site represents a source as well as a “receptor site”, one in which ambient PM originating from emissions in urban Los Angeles have undergone secondary photochemical processes, including gas to particle processes

### DTT Assay

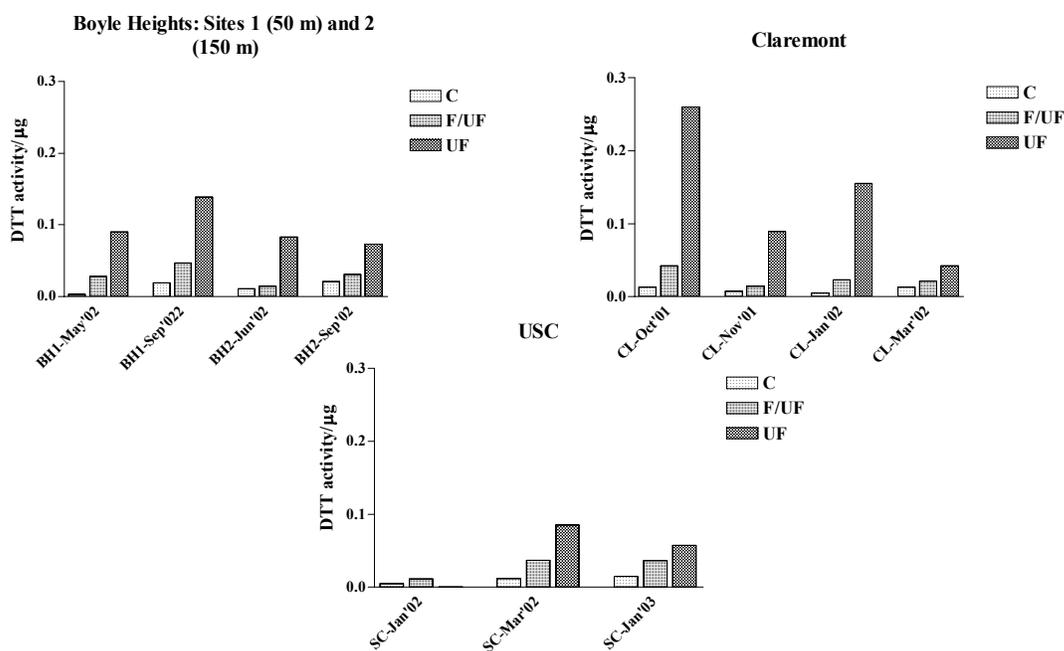
Kumagai et al<sup>17</sup> have shown that redox active compounds catalyze the reduction of oxygen to superoxide by DTT, which is oxidized to its disulfide. The remaining thiol is allowed to react with DTNB, generating the mixed disulfide and 5-mercapto-2-nitrobenzoic acid which is determined by its absorption at 412 nm. The PM dependent DTT consumption is measured under conditions such that the rate is linear, i.e., when less than 20% is depleted. Catalytic activity is expressed as the rate of DTT consumption per minute per microgram of sample less the activity observed in the absence of PM. A sample of a methanol extract of diesel exhaust particles,<sup>27</sup> is carried through the assay each time as a positive control to monitor the reaction.

In the assay, a Biosampler PM sample of known mass was incubated at 37°C with DTT (100 µM) in 0.1M potassium phosphate buffer at pH 7.4 (1 mL total volume) for times varying from 15 to 90 minutes. The PM samples used here were assayed at concentrations of 5-40 µg mL<sup>-1</sup>. At the designated times, 1 mL of 10% trichloroacetic acid was added to the incubation mixture and a 0.5 mL aliquot of the reaction mixture mixed with 1 mL of 0.4 M Tris HCl containing 20 mM EDTA and 25 µL of 10 mM DTNB. The concentration of the formed 5-mercapto-2-nitrobenzoic acid was measured by its optical density absorption at 412 nm.

## Results and Discussion

One of the major working hypotheses of the Southern California Particle Center and Supersite (SCPCS) has been that the health effects of PM are due to their chemical properties. These chemical properties relate to the intact particle as well as its constituents and inasmuch as PM exposure is to the particles in their entirety, characterization must reflect the entire particle. Accordingly, we are attempting to characterize the particles in terms of their overall activity instead of attempting to isolate compounds of known chemical and biological reactivity. In this context, we used the DTT based catalytic reduction of oxygen by PM as a measure of their redox activity which reflects their ability to induce a state of oxidative stress<sup>10</sup>.

The redox activity for PM samples collected at the three sites is shown in figure 1. All the PM collected, regardless of site, exhibited activity as measured by the DTT assay. The UF fraction exhibited the greatest redox activity on a per microgram basis, consistent with the greater toxicity associated with this fraction observed earlier<sup>7</sup> and suggestions by reports in the literature<sup>30,31</sup>. The potencies varied with location and with the collection day. The variability was such that it was difficult to establish differences in activity with site of collection. It is clear that assessment of changes in the chemistry of PM that may occur between a source and a receptor site, would require that the samples be collected simultaneously



**Figure 1**

### *Relationship between DTT activity and chemical composition*

The consumption of DTT is based on the ability of a given sample to accept electrons from DTT and transfer them to oxygen. A variety of chemical agents are capable of this reaction including transition metal ions such as those of iron and copper<sup>32,33</sup> as well as organic compounds such as quinones<sup>10</sup>. However, DTT activity did not correlate with any of the inorganic species, including metals (table 1). There was significant correlation, however, with OC ( $r^2 = 0.53$ ) and

EC ( $r^2 = 0.79$ ) as shown in figure 5A and Table 2. The greater localization of DTT activity in the UF fraction is consistent with this correlation, indicating that the activity in these samples is due to organic compounds, not metals or other inorganic species

**Table 1**

Coefficients of determination ( $r^2$ ) between the rate of DTT consumption and the PM content for selected inorganic species.

Species	$r^2$
EC	0.791
OC	0.530
SO4	0.004
NO3	0.254
Na	0.081
Mg	0.008
Al	0.010
Si	0.065
S	0.044
Cl	0.062
K	0.000
Ca	0.098
Ti	0.043
V	0.061
Mn	0.010
Fe	0.003
Ni	0.091
Cu	0.014
Zn	0.028
As	0.058

Table 2 shows the values for the coefficient of determination ( $r^2$ ) between the rate of DTT consumption and the concentration of selected PAH (expressed in picograms per microgram of PM mass, or PPM). The listed PAH were selected for this analysis because they were found in measurable amounts in all samples. The correlation of DTT activity with PAH overall was limited, indicative of the variability due to differing source sites. PAH themselves are not redox active in the DTT assay, but must be oxidized to quinones in order to be redox active. Quinones are generated by the combustion process<sup>27</sup> but can be generated in vivo by biotransformation<sup>35</sup>.

**Table 2.** Coefficients of determination ( $r^2$ ) between the rate of DTT consumption and the PAH content of PM samples.

Organic species	$r^2$
Total measured PAH	0.41
Benzo[g]perylene (BgP)	0.82
Phenanthrene	0.73
Fluoranthene	0.39

Pyrene	0.73
Benz[a]anthracene	0.43
Chrysene	0.60
Benzo[b]fluoranthene	0.56
Benzo[k]fluoranthene	0.32
Benzo[a]pyrene	0.42
Indeno[1,2,3-cd]pyrene	0.32

This study demonstrates that ambient PM samples collected at different sites in the Los Angeles Basin have an inherent capacity to transfer electrons from a source such as dithiothreitol to oxygen. The major source of this redox activity appears to be organic compounds, and not transition metals as the correlations with iron and copper were poor. The role of metals in PM redox activity requires further investigation. The active components of the PM studied here appear to be associated with gasoline vehicle and diesel emissions as determined by the correlation between DTT activity and OC, EC and BgP. The greatest DTT potency was seen in the UF fraction of PM consistent with earlier findings. The results reported here are indicative of the value of a quantitative assay for assessment of redox activity from airborne PM over a wide ranging geographical area. Further evaluation of the spatial and temporal characteristics of PM redox activity are underway. The DTT assay is a valuable tool in determining the relationship between the physical/chemical characteristics of PM, redox activity, and the underlying mechanisms of PM related health effects.

## REFERENCES

- (1) Schwartz, J.; Morris, R. *Am. J. Epidemiol.* **1995**, *142*, 23-35.
- (2) Schwartz, J.; Neas, L. M. *Epidemiology* **2000**, *11*, 6-10.
- (3) Dockery, D. W.; Pope, C. A., 3rd; Xu, X.; Spengler, J. D.; Ware, J. H.; Fay, M. E.; Ferris, B. G., Jr.; Speizer, F. E. *N. Engl. J. Med.* **1993**, *329*, 1753-1759.
- (4) Gurgueira, S. A.; Lawrence, J.; Coull, B.; Murthy, G. G.; Gonzalez-Flecha, B. *Environ. Health Perspect.* **2002**, *110*, 749-755.
- (5) Li, N.; Kim, S.; Wang, M.; Froines, J.; Sioutas, C.; Nel, A. *Inhal. Toxicol.* **2002**, *14*, 459-486.
- (6) Veronesi, B.; de Haar, C.; Roy, J.; Oortgiesen, M. *Inhal. Toxicol.* **2002**, *14*, 159-183.
- (7) Li, N.; Sioutas, C.; Cho, A.; Schmitz, D.; Misra, C.; Sempf, J.; Wang, M.; Oberley, T.; Froines, J.; Nel, A. *Environ. Health Perspect.* **2003**, *111*, 455-460.
- (8) Schafer, F. Q.; Buettner, G. R. *Free Radic. Biol. Med.* **2001**, *30*, 1191-1212.
- (9) Nel, A. E.; Diaz-Sanchez, D.; Li, N. *Curr. Opin. Pulm. Med.* **2001**, *7*, 20-26.
- (10) O'Brien, P. J. *Chem. Biol. Interact.* **1991**, *80*, 1-41.
- (11) Dellinger, B.; Pryor, W. A.; Cueto, R.; Squadrito, G. L.; Hegde, V.; Deutsch, W. A. *Chem. Res. Toxicol.* **2001**, *14*, 1371-1377.
- (12) Brunmark, A.; Cadenas, E. *Free Radic. Biol. Med.* **1989**, *7*, 435-477.
- (13) Squadrito, G. L.; Cueto, R.; Dellinger, B.; Pryor, W. A. *Free Radic. Biol. Med.* **2001**, *31*, 1132-1138.
- (14) Kumagai, Y.; Arimoto, T.; Shinyashiki, M.; Shimojo, N.; Nakai, Y.; Yoshikawa, T.; Sagai, M. *Free Radic. Biol. Med.* **1997**, *22*, 479-487.
- (15) Veronesi, B.; Oortgiesen, M.; Carter, J. D.; Devlin, R. B. *Toxicol. Appl. Pharmacol.* **1999**, *154*, 106-115.
- (16) Wu, W.; Graves, L. M.; Jaspers, I.; Devlin, R. B.; Reed, W.; Samet, J. M. *Am. J. Physiol.* **1999**, *277*, L924-931.
- (17) Kumagai, Y.; Koide, S.; Taguchi, K.; Endo, A.; Nakai, Y.; Yoshikawa, T.; Shimojo, N. *Chem. Res. Toxicol.* **2002**, *15*, 483-489.
- (18) Li, N.; Venkatesan, M. I.; Miguel, A.; Kaplan, R.; Gujuluva, C.; Alam, J.; Nel, A. *J. Immunol.* **2000**, *165*, 3393-3401.
- (19) Kim, S.; P, J.; MC, C.; Froines, J.; C., S. *J. of Aerosol Sci.* **2001**, *11*.
- (20) Kim, S.; Jaques, P.; Chang, M.; Sioutas, C. *J. Aerosol Sci.* **2001**, *11*, 1299-1314.
- (21) Marr, L.; Kirchstetter, T.; Harley, R.; Miguel, A. *Environ. Sci. Technol.* **1999**, *33*, 3091-3099.

## 10. Analysis of Size- and Time-Resolved Particulate Measurements

ADI presented results of our nitrate vaporization study at the Las Vegas Supersite PI meeting in February 2004. This study examined the mass vaporization rates from the TEOM filter, as indicated by the change in mass of the TEOM filter when sampling particle-free air, with comparison to the hourly-averaged ambient nitrate concentration as measured by the ADI automated nitrate system. The objective is to determine the conditions for which the time constant for evaporative losses is longer than the 5-min cycle time of the differential TEOM measurement, and assumption that is inherent to the its approach for particle mass determination.

The data show that:

- for most days, TEOM reference signal (for particle-free air) tracks ambient nitrate, but with a delay of 40-100 min.
- saturation downstream of filter  $< 1$ , indicating that loss never reaches the maximum evaporation rate.
- filter temperature is generally more important than filter pressure drop to evaporative loss rate.

The measured time constant for mass loss was compared to that predicted by theory of Zhang and McMurry, and Furuuchi et al.. This analysis showed that

- for the winter period, when the TEOM filter was held at 35C, the measured lag time for evaporation was 40 min, while theory yielded a characteristic time of 10-20 minutes.
- for the summer measurements, when the TEOM filter temperature was held at 30C, the characteristic evaporation time from measurements and from theory increased to 80-100 min, and 50-80min respectively.

An important result of these analyses is that theory and experiment show that evaporation times, at the same nitrate concentrations, are longer for lower filter temperature. The assumption of slow evaporation rate compared to the 5-min TEOM cycle time is better met by the 30C TEOM filter temperature than by the 35C filter temperature.

In the coming year we will be analyzing the size distribution data from the cascaded nitrate and carbon systems, with comparison to the physical size distributions. We identified periods of interest, and received input from UCLA on the integrated parameters from the physical size distributions (modal diameters and volumes). The variability in the physical size distributions will be compared to that seen in the size-resolved nitrate and carbon.

# Presentation from the February 2004 Supersite PI meeting

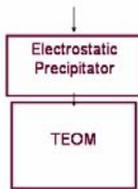
## Field Assessment of the Dynamics of Particulate Nitrate Vaporization Using Differential TEOM® and Automated Nitrate Monitors

Susanne Hering, Aerosol Dynamics Inc.  
 Philip M. Fine, Constantinos Sioutas, University of Southern California  
 Peter A. Jaques, UCLA (now Clarkson University)  
 Jeffrey L. Ambs, Rupperecht and Patashnick Company  
 Olga Hogrefe and Kenneth L. Demerjian, ASRC, SUNY Albany

## Background

- Filters often used for semi-continuous ambient particulate mass monitors.
- Federal standards specify standard environmental conditions for gravimetric mass determination
- How can the equilibration be handled for the semi-continuous instruments?
  - Traditional: heat filter
  - Problem: loss of semivolatiles, such as nitrate

## Differential Tapered Element Oscillating Microbalance (Differential TEOM)



- Precipitator cycles on and off
- Data set: alternate 5 minute periods of
  - Particle – laden air (particles plus artifact)
  - Particle – free air (reference signal, artifact alone)
- Particle Mass:
  - Difference between the two signals.

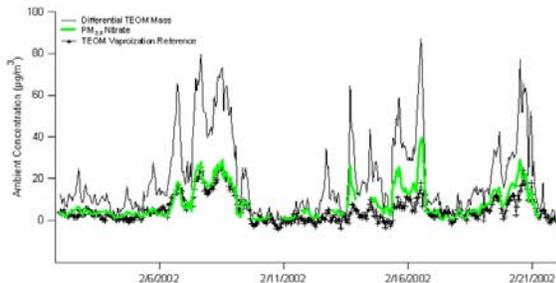
## Our primary hypothesis:

That the time scale for volatilization is longer than the five-minute cycle time for the system.

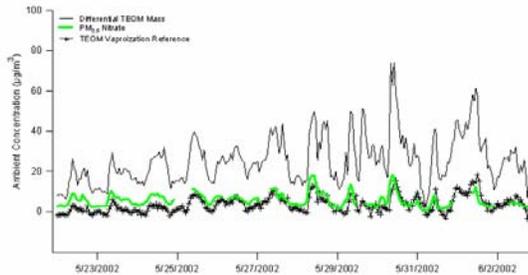
## Evaluation:

Through comparison to the 10-min particulate nitrate data in Claremont, CA

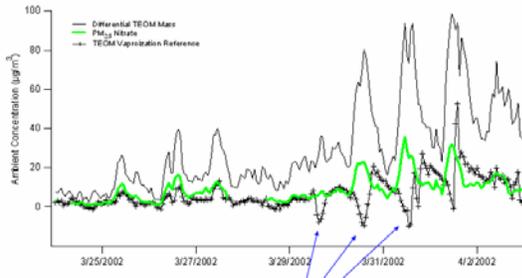
## Example Ambient Data



Vaporization Reference = (-1)( Mass change for particle-free air )

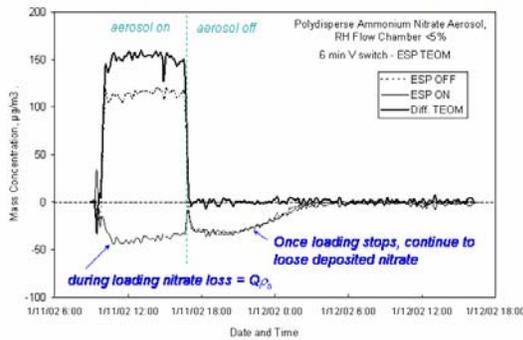


Further example of vaporization reference signal tracking nitrate concentration.

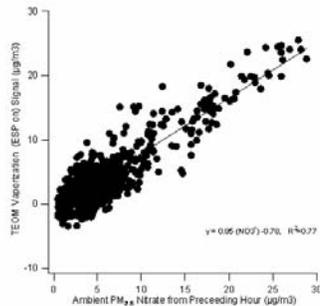


Example of a net adsorption of mass onto the TEOM filter during particle-free ambient air sampling

### Laboratory Data for Ammonium Nitrate (SUNY)



For ambient, best correlation between loss and nitrate is with one-hour time lag.



### Characteristic Time for Volatilization: Theory and Experiment

	Winter (Feb-March)	Summer (June-Aug)
TEOM Filter Temperature	35 C	30 C
Saturation at Filter Exit (mean)	0.15	0.52
Characteristic time (theory)	10 - 20 min	50 - 80 min
Lag time (ambient data)	40 min	80 -100 min

### Theoretical Considerations

Mass loss given by Mass Balance Relationship:

$$M_e = Q_2 \rho_2 - Q_0 \rho_0 \quad \text{Maximum loss when } \rho_2 = \rho_s$$

$$= Q_0 f \left[ (\rho_2 - \rho_0) + \left( \frac{f-1}{f} \right) \rho_0 \right]$$

large when filter temperature elevated.      arises from pressure drop across filter

where  $\rho_0, \rho_2$  = upstream and downstream vapor concentration  
 $Q_0$  = volumetric flow rate at inlet to filter  
 $Q_2 = f Q_0$  = volumetric flow downstream

### In ambient, how close is $\rho_2$ to saturation?

- Equilibrium vapor pressure of ammonium nitrate (equal molar volumes)
  - 10 C = 2 µg/m<sup>3</sup>
  - 25 C = 16
  - 30 C = 30 (TEOM Filter temperature)
  - 35 C = 52
- Rarely reach maximum evaporation rate
- For differential TEOM, require approach to max rate is slow compared to precipitator cycle time.

Time to reach maximum loss rate, when downstream vapor pressure to reach equilibrium at filter temperature ( $\rho_2 = \rho_s$ ), depends on dimensionless time  $\tau$ :

$$\frac{dS}{dx'} = \tau e^{-\gamma x'} (1-S) - \frac{dS}{dt'}$$

where

$$\tau = 2\pi D_p g DC_N \gamma t$$

(Zhang and McMurry, Furuuchi et al.)

### Conclusions

- For most days, TEOM reference signal (for particle-free air) tracks ambient nitrate, but with a delay of 40-100 min.
- Saturation downstream of filter < 1, indicating that loss never reaches the maximum evaporation rate.
- Filter temperature is generally more important than filter pressure drop to evaporative loss rate.
- Characteristic lag time for ambient data similar to characteristic evaporation time from theory.
- Both theory and experiment show evaporation times are longer for lower filter temperature (at same nitrate level).

## 11. Data Management

1. During this quarter, data were submitted to NARSTO and SIRD, as shown in the following table:

To NARSTO	To SIRD	To be sent in June to NARSTO
-----	-----	-----
• <b>HEADS</b>	• <b>HEADS</b>	• <b>HEADS</b>
Claremont: Mass	Claremont: IONS, Mass	Claremont: IONS
• <b>Partisol</b>	• <b>Partisol</b>	Riverside: IONS
Claremont: Metals/Elements, Mass	Claremont: IONS, Mass, Metals / Elements	USC: IONS
Downey: Metals/Elements, Mass	Rubidoux: IONS, Mass	• <b>Partisol</b>
Riverside: Metals/Elements, Mass	• <b>MOUDI</b>	Claremont: IONS
Rubidoux: Metal/Element, Mass	Claremont: ECOC, IONS, Mass, Metals/Elements	Riverside: IONS
USC: Metals/Elements, Mass	Rubidoux: ECOC, IONS, Mass, Metals/Elements	Rubidoux: IONS
• <b>MOUDI</b>	• <b>Aethalometer</b>	USC: IONS
Claremont: Metals/Elements, Mass	Claremont and Rubidoux	Claremont: IONS
Downey: Metals/Elements, Mass	• <b>Automet</b>	• <b>MOUDI</b>
Riverside: Metals/Elements, Mass	Rubidoux	Claremont: IONS, ECOC
Rubidoux: Metal/Element, Mass	• <b>APS</b>	Downey: IONS, ECOC
USC: Metals/Elements, Mass	Claremont and Rubidoux	Riverside: IONS, ECOC
• <b>SMPS</b>	• <b>SMPS</b>	Rubidoux: IONS, ECOC
USC	Claremont and Rubidoux	USC: IONS, ECOC
	• <b>TEOM</b>	
	Claremont and Rubidoux	
	• <b>Nitrate</b>	
	Claremont and Rubidoux	
	• <b>Carbon</b>	
	Claremont	

2. During the next quarter more data will be sent to NARSTO, as shown above.