

The following document was submitted “for the record” to the Intermodal Container Transfer Facility (ICTF) Joint Powers Authority (JPA) during the Notice of Preparation/Initial Study (NOP/IS) comment period for the ICTF Modernization and Expansion Project.

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# **Results from the Research of the Southern California Particle Center and Supersite (SCPCS)**

## **Part I: Atmospheric Measurements and Development of Instrumentation**

**Constantinos Sioutas**

**Associate Professor**

**USC School of Engineering**

**Civil and Environmental Engineering**

**Deputy Director of Southern California Particle Center  
and Supersite**

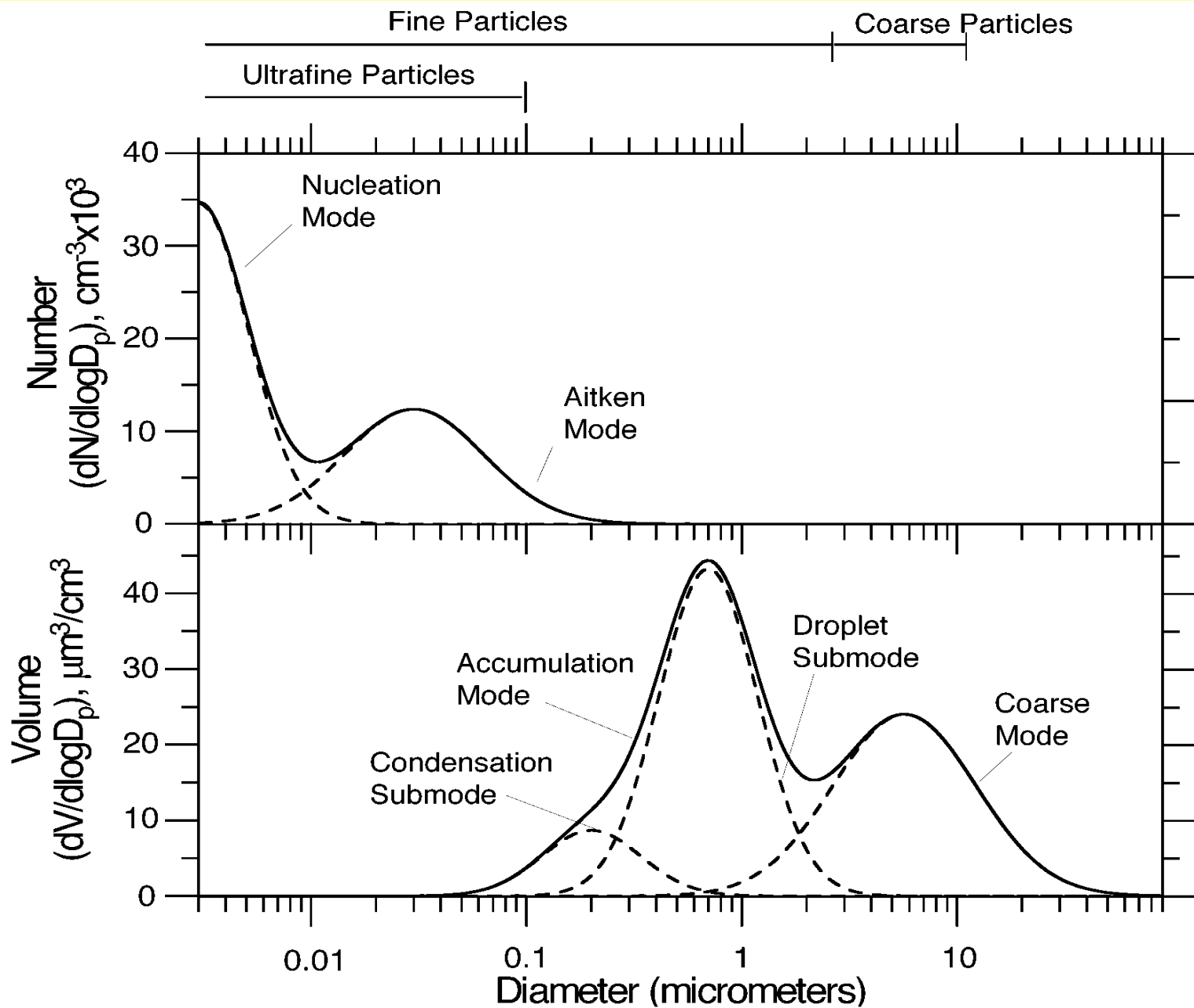
**Presented to the California Air Resources Board**

**Wednesday, June 18**

## Summary:

- **Why Are We Interested in Ultrafine PM**
- **What do we know about their toxicological properties**
- **What do we know (or do not) about their sources, formation mechanisms**
- **What do we know about their diurnal, seasonal and spatial characteristics**
- **Technologies developed by the Aerosol Laboratory at USC by funds through the SCPCS to measure physical, chemical and toxicological properties of ultrafine PM**

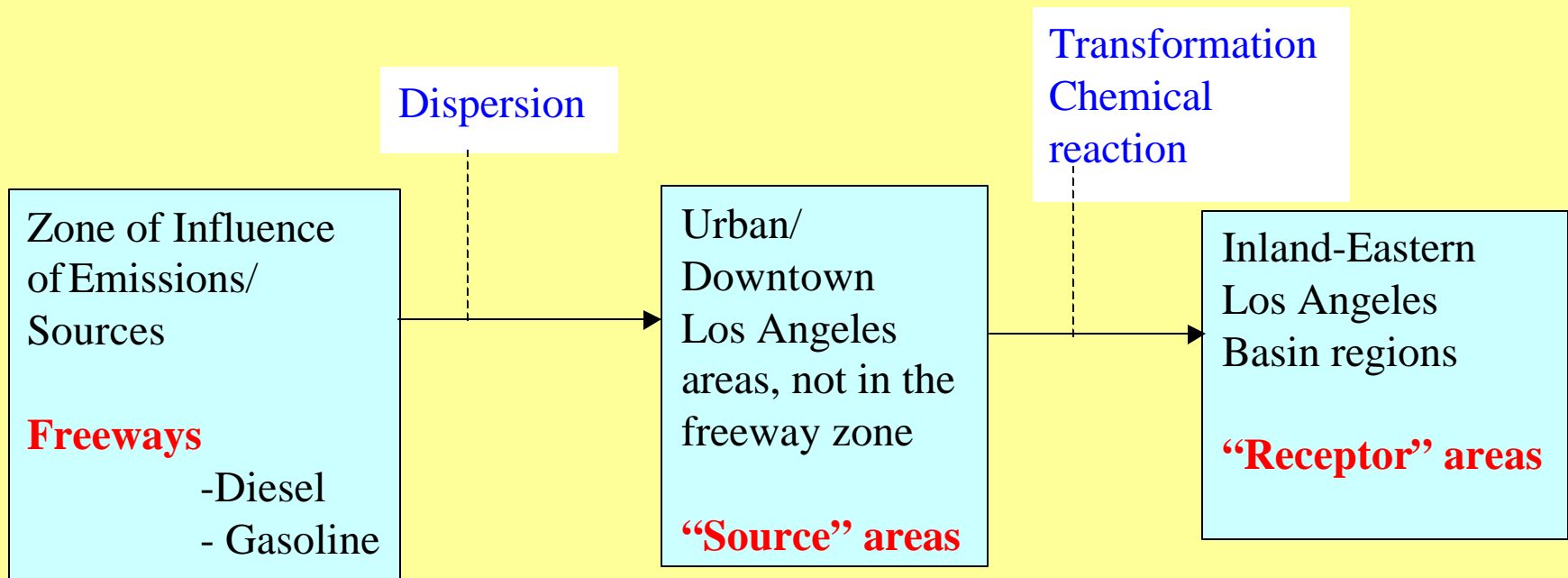
# Ambient Aerosol Size Distribution



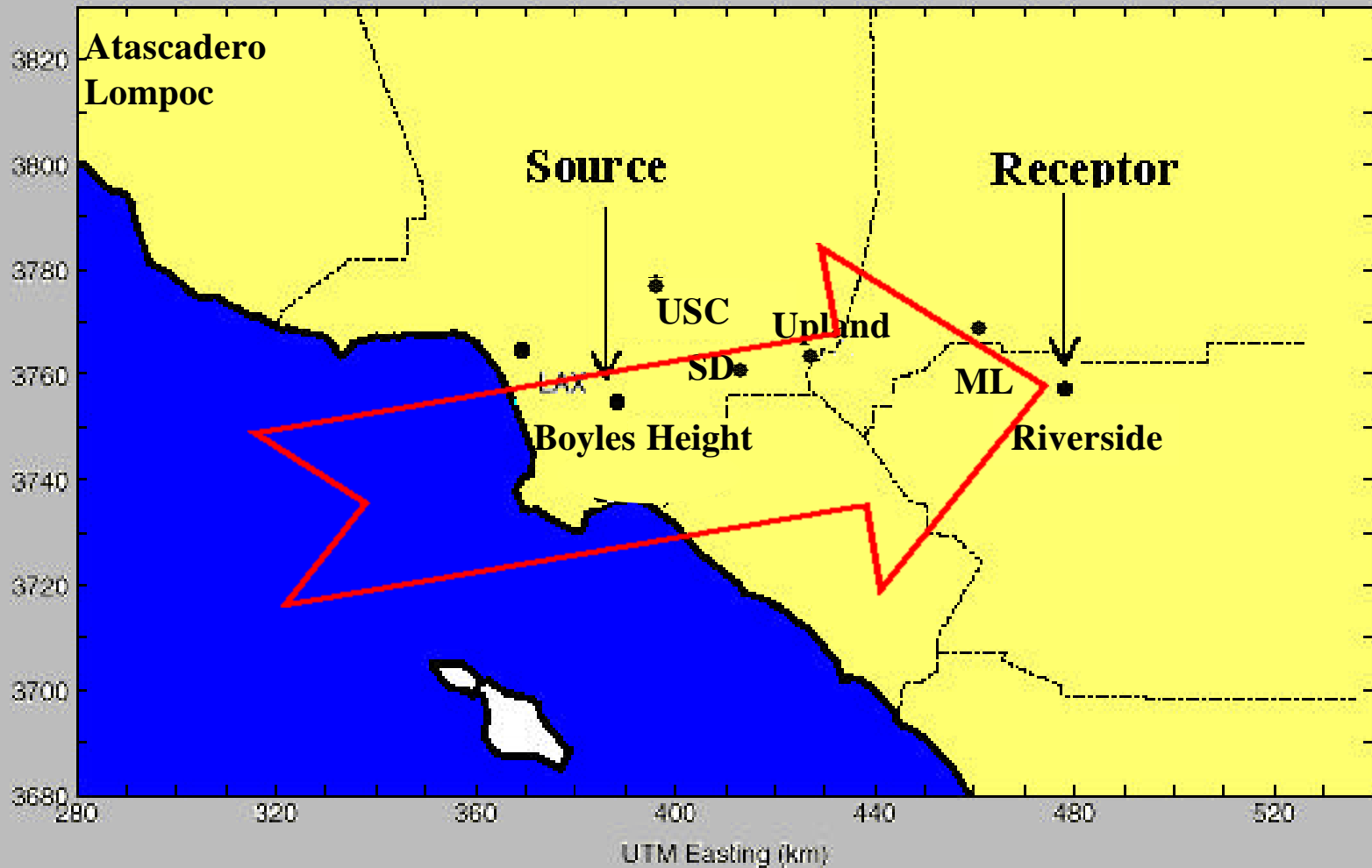
# Los Angeles is a Very Unique Air Basin

- Distinct areas of different meteorological conditions result in **spatial variation of PM<sub>2.5</sub>**
- **Predictable, well-defined and consistent** meteorology; suitable for “controlled”, **laboratory-style** experiments using **real-life air pollutants** as test aerosols.
- The **distinct sources** affecting **specific areas** of the LAB provide an ideal testing ground for **hypotheses driven** health studies.

# Three Different PM Exposure (or Air Pollution) Regimes in the Los Angeles Basin



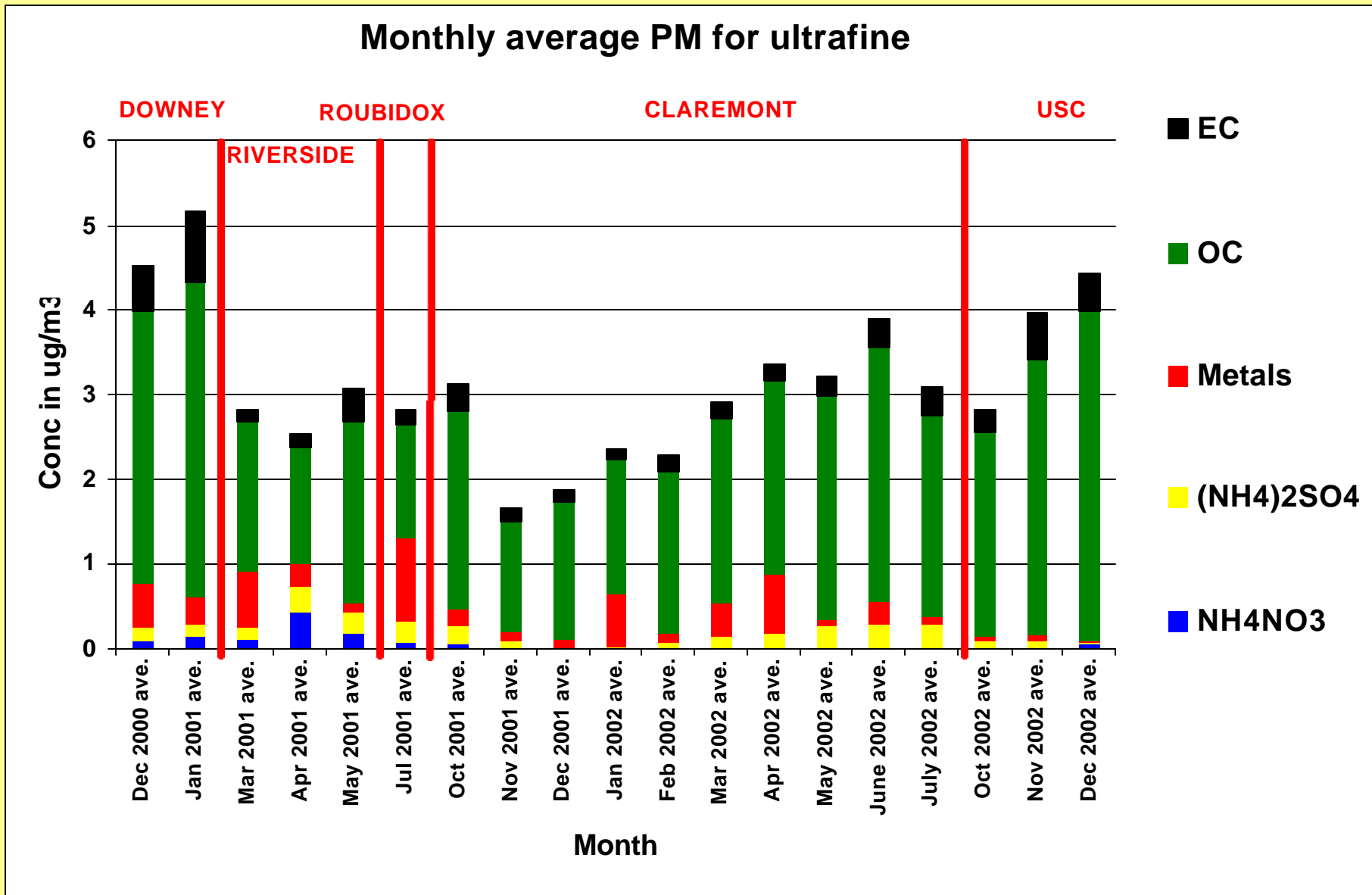
# Source and Receptor Areas in the Los Angeles Basin



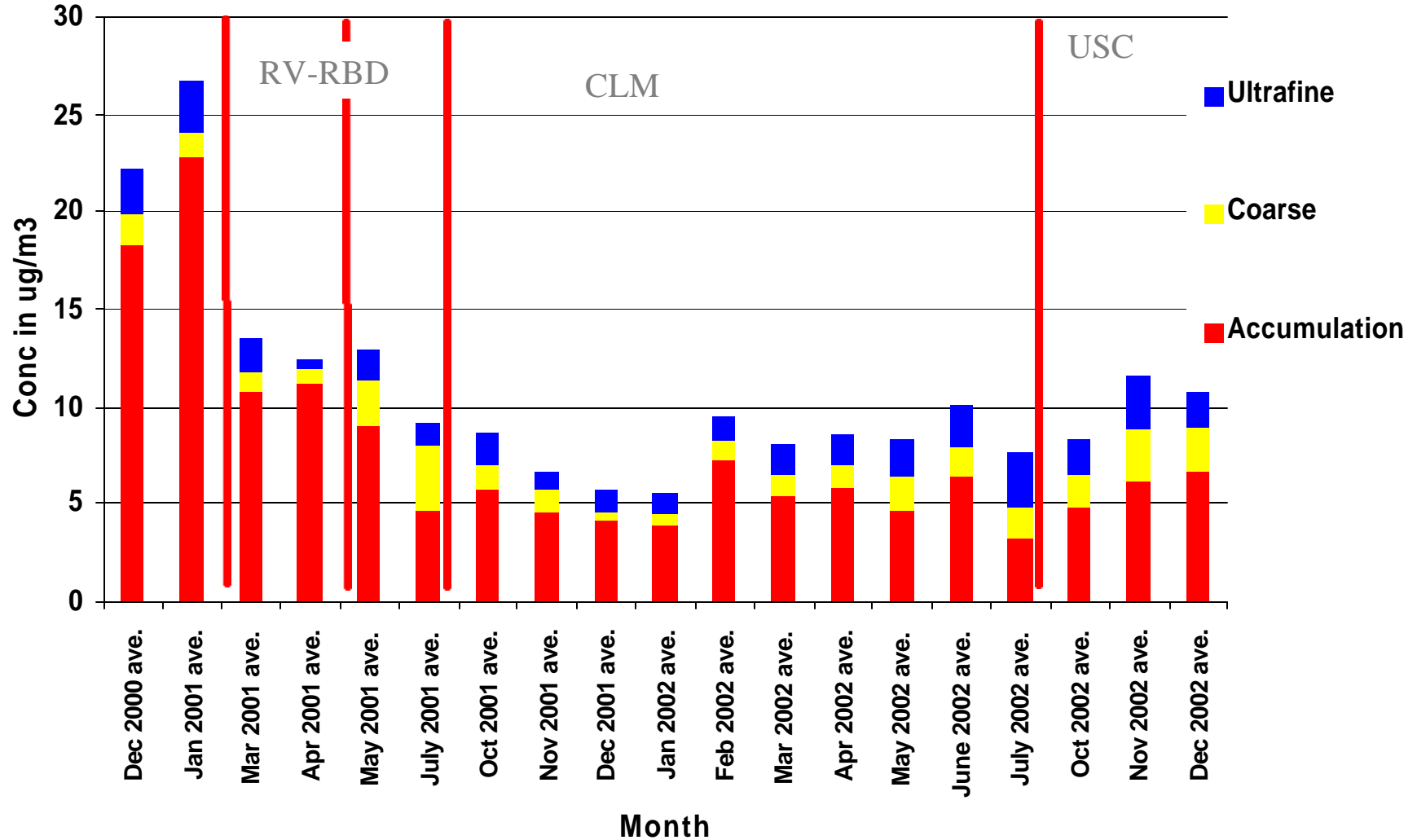
## Sampling was Conducted in :

- **Downey (source) September 2000-  
January 2001**
- **Riverside (receptor) February – June  
2001**
- **Rubidoux (receptor) June – September  
2001**
- **Claremont (receptor) September 2001-  
August 2002**
- **USC (source) September 2002 - present**
- **Concurrently with in vivo and in vitro  
studies to concentrated air particulates  
(CAPS)**

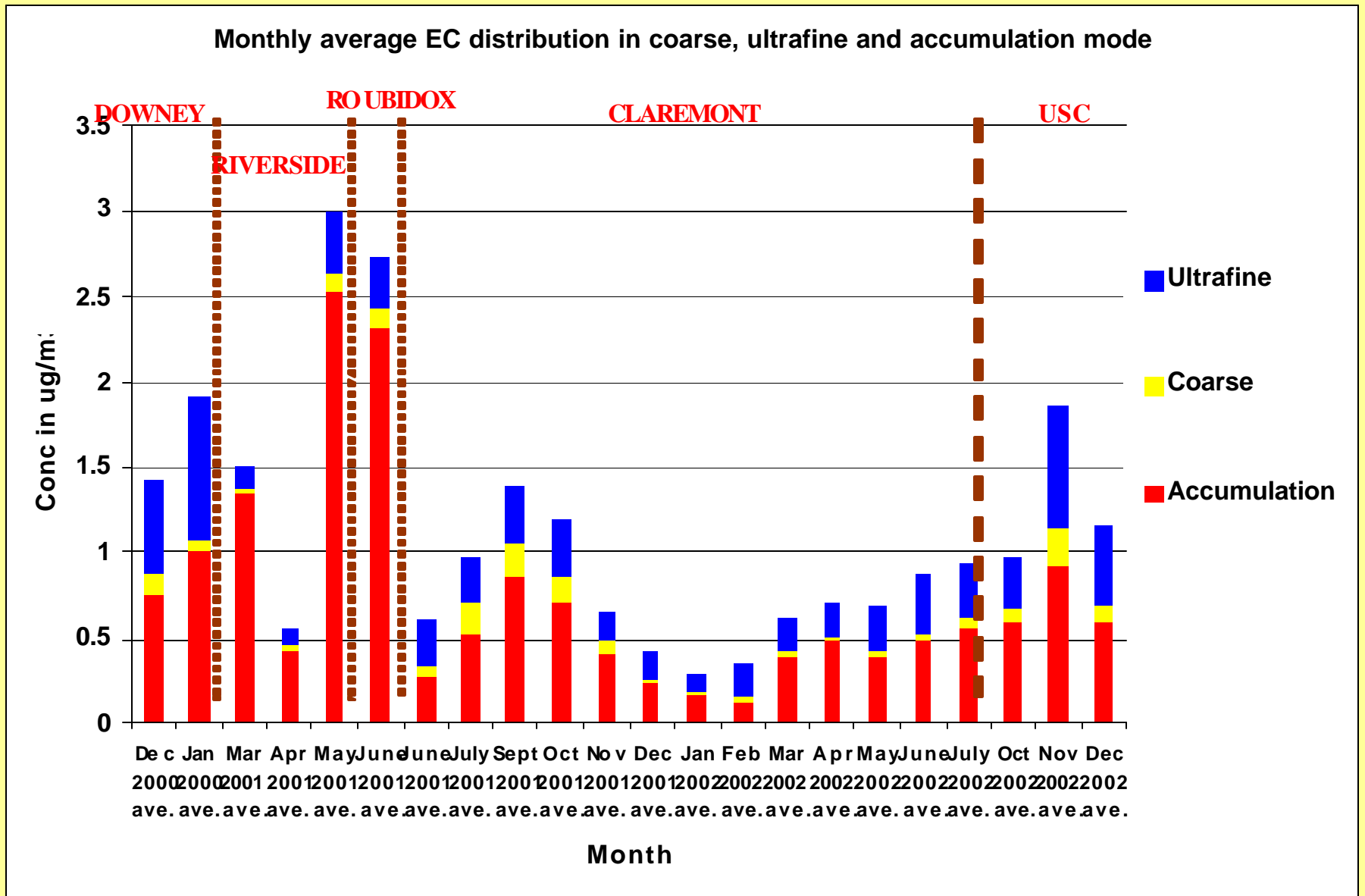




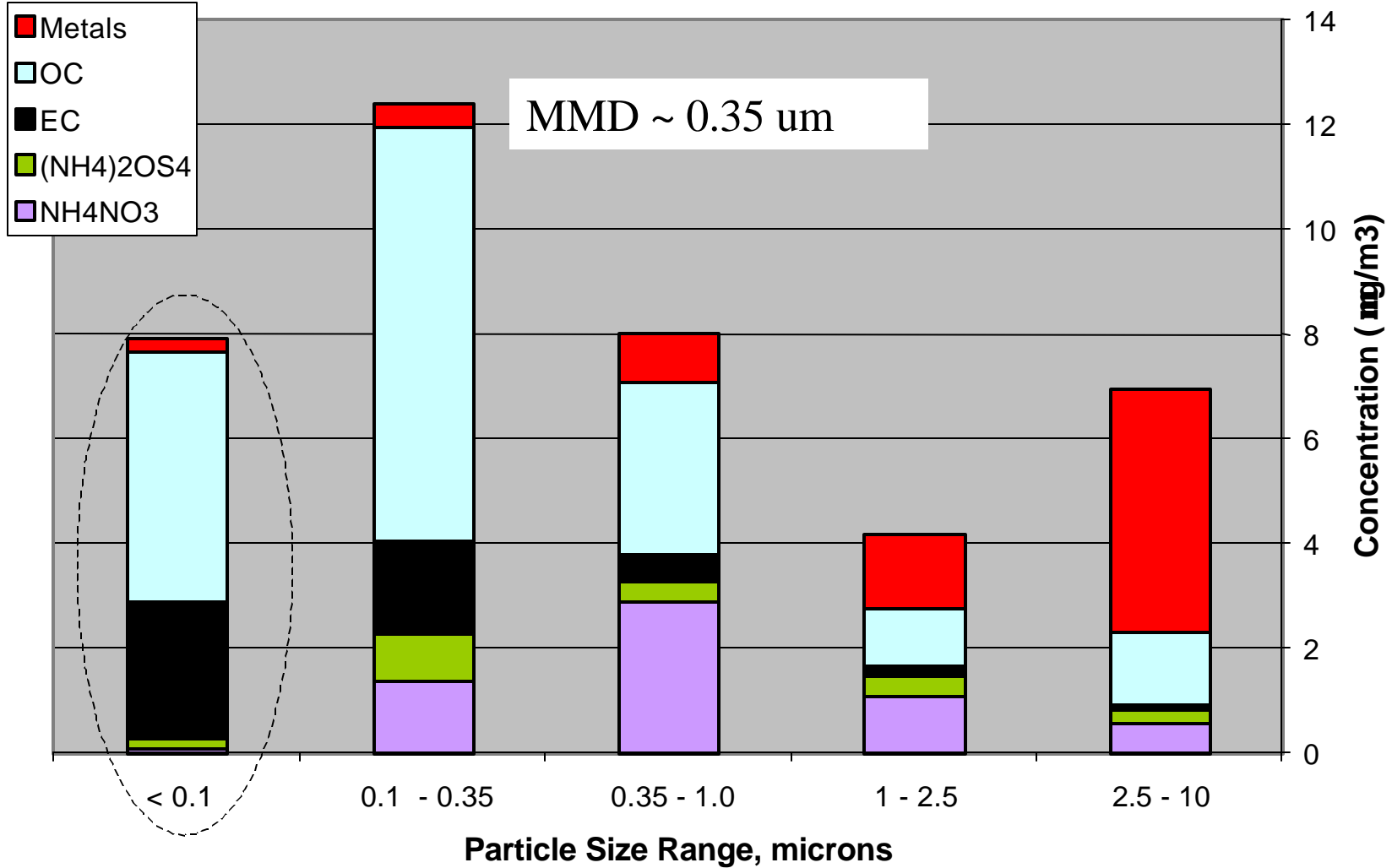
Monthly average OC distribution in coarse, ultrafine and accumulation mode



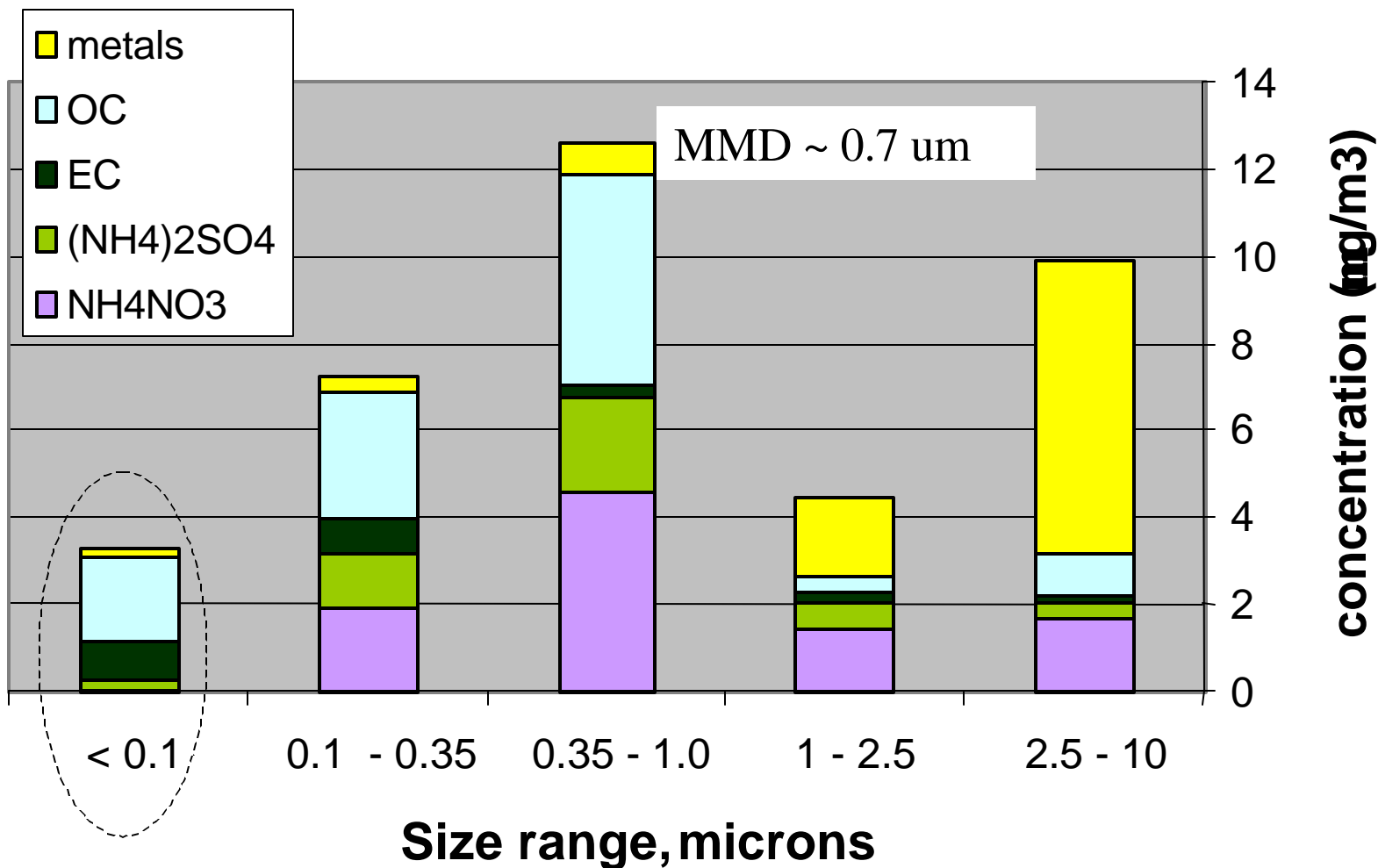
# Sardar et al., Atmos. Environ, 2003



## 24-h Average PM10 Mass and Chemical Composition in Downey

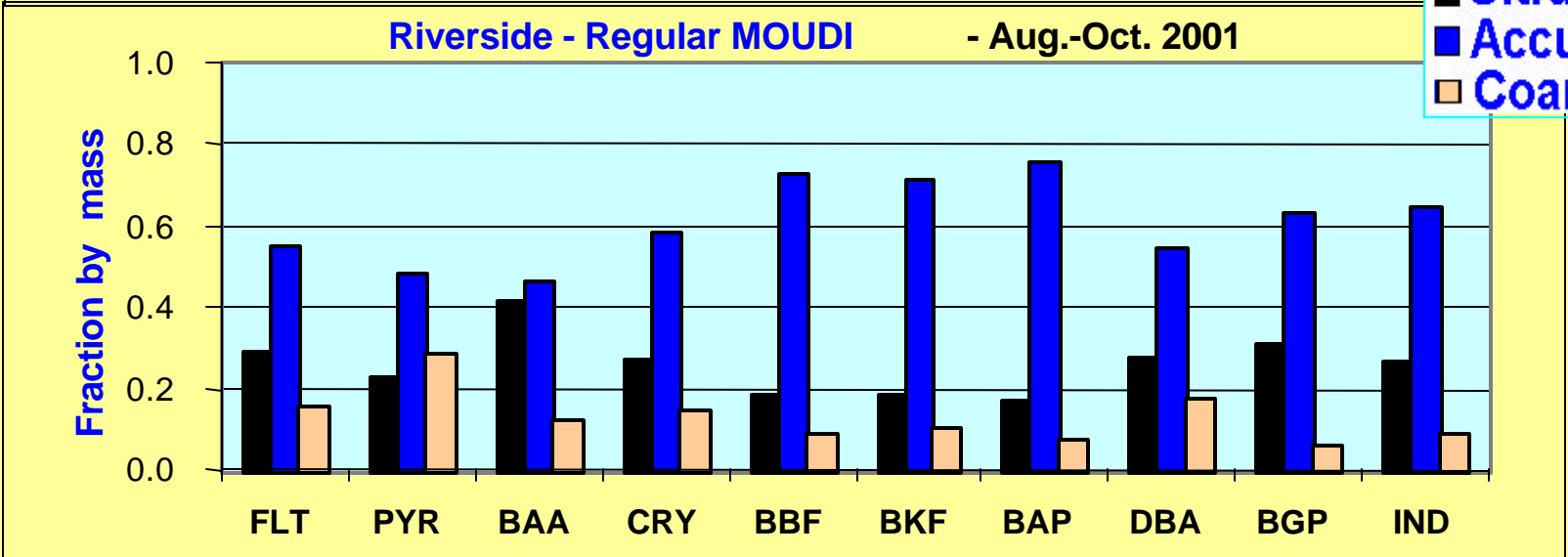
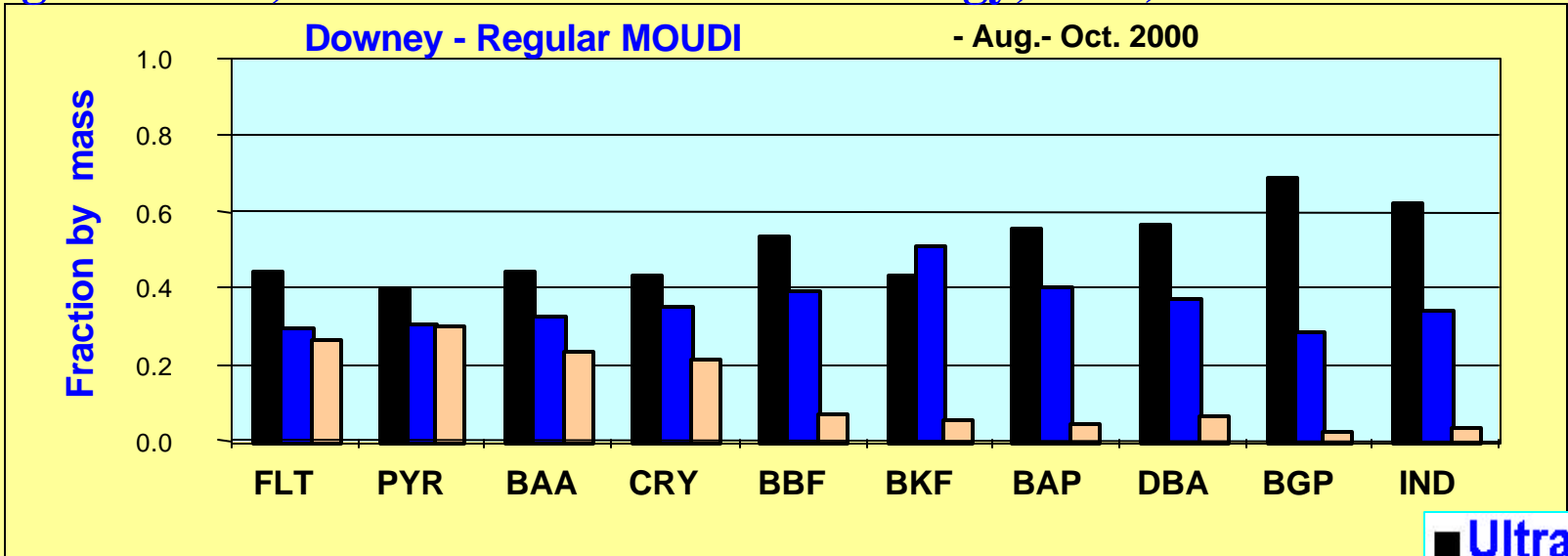


## 24-h Average PM10 Mass and Chemical Composition in Riverside



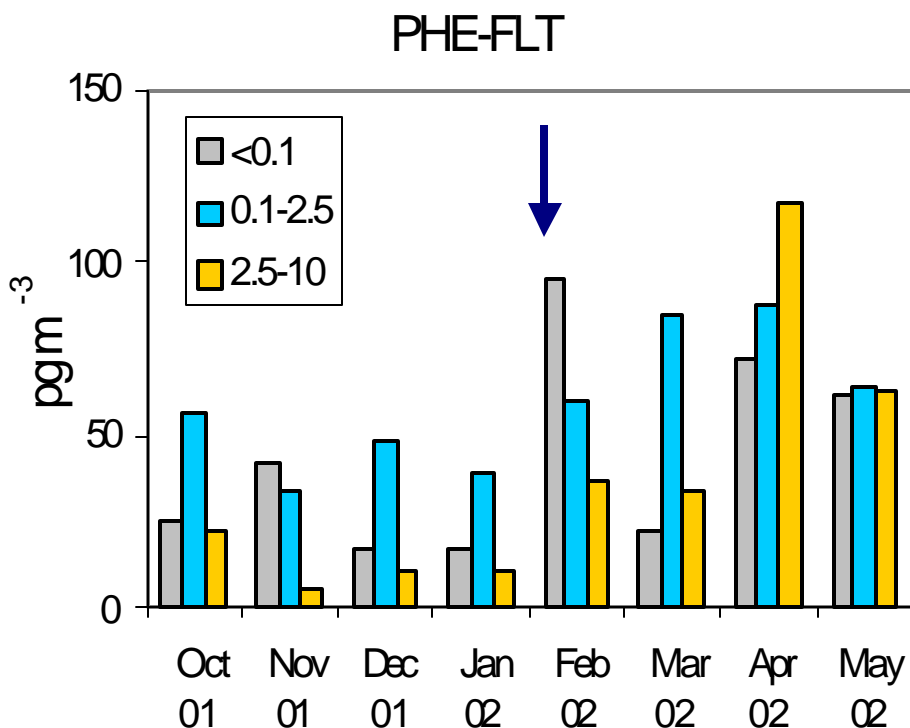
# Effect of transport on PAH size distribution

(Eiguren et al., Aerosol Science and Technology, 2003)

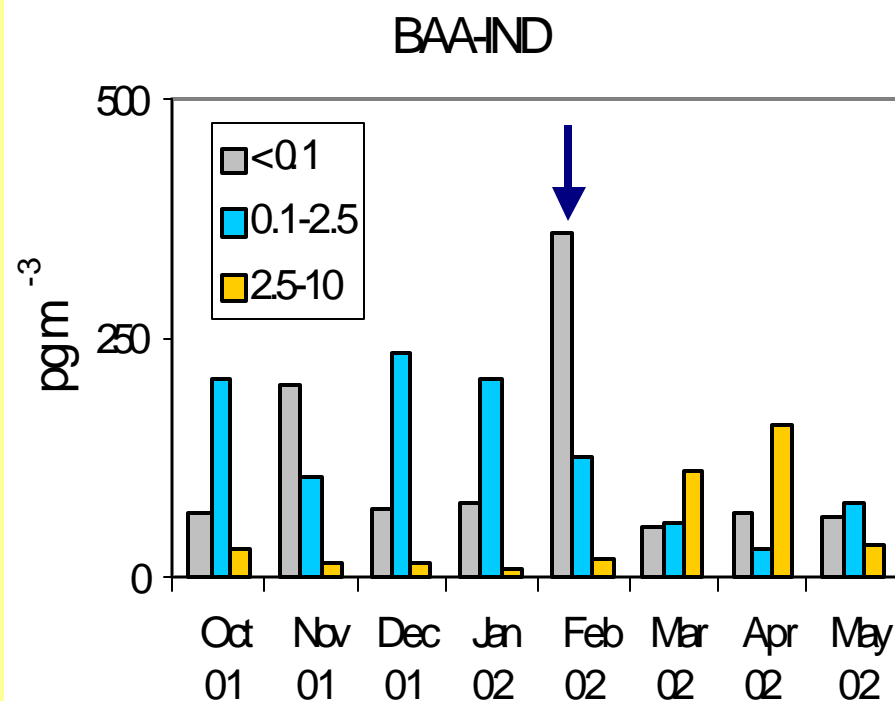


■ Ultrafine  
■ Accumulation  
■ Coarse

## Higher Volatility PAH



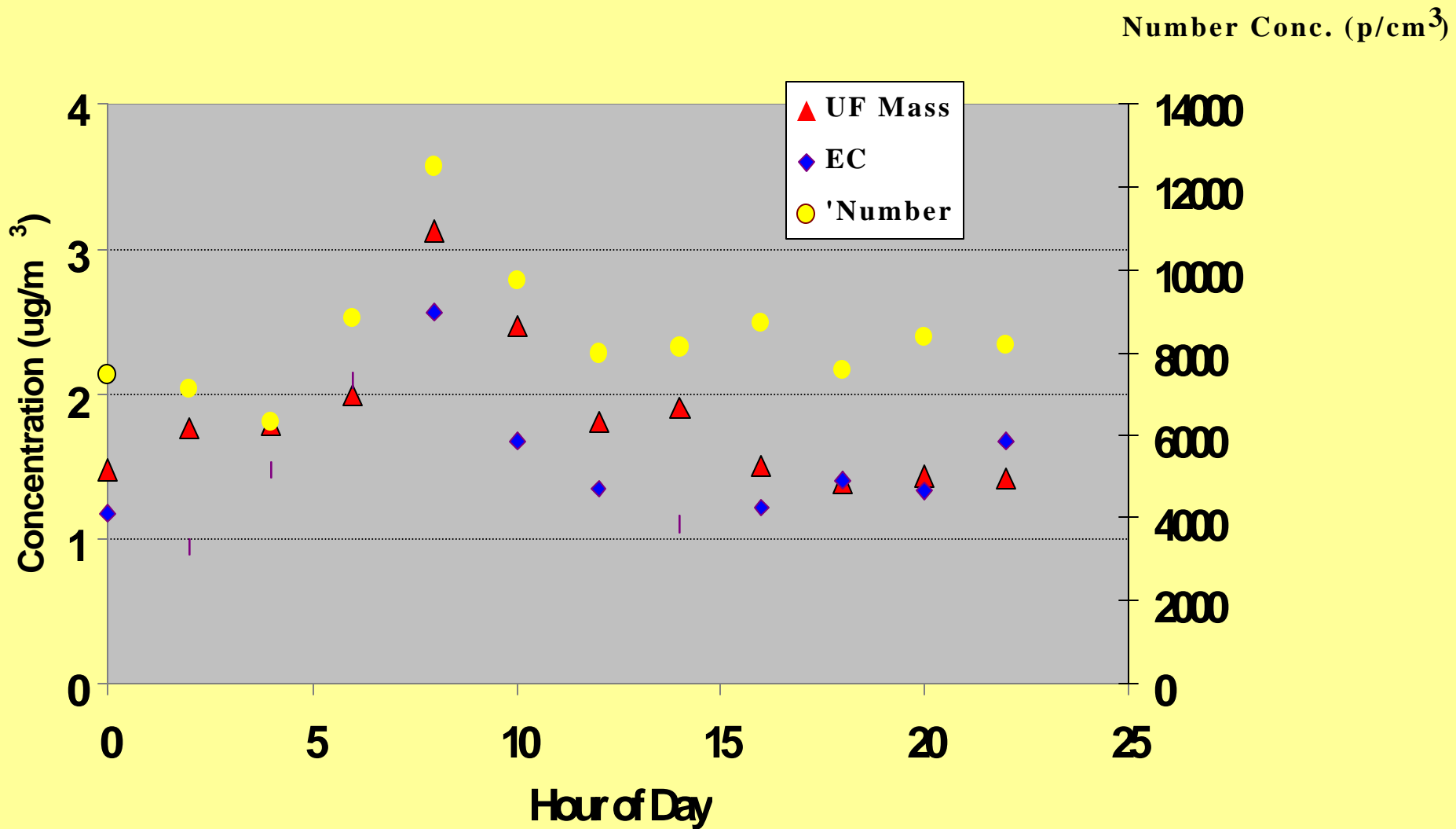
## Lower Volatility PAH



**Total mass concentrations of PAH from October, 2001 to May, 2002 in Claremont, CA.** Data obtained from monthly composites (Miguel et al., 2003).

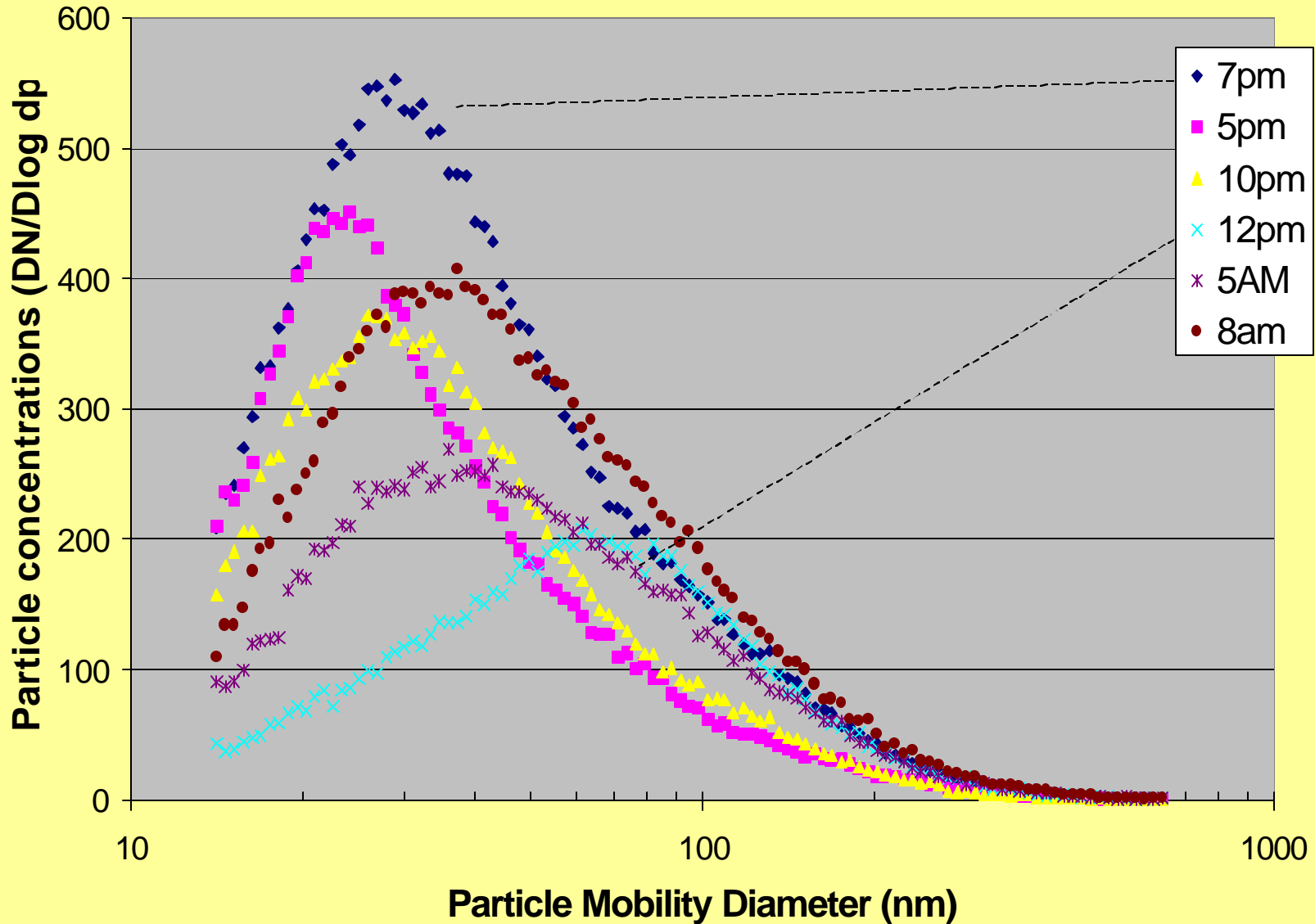
- coarse PAH increase with Temperature
- most PAH in accumulation mode except February 2002 (Santa Ana conditions)
- PM<sub>2.5</sub> concentrations of PHE-FLT increase from winter > summer
- PM<sub>2.5</sub> concentrations of BAA-IND decrease from winter > summer

# Average EC, UF Mass and Total PM Number at USC Nov. 2002 - February 2003

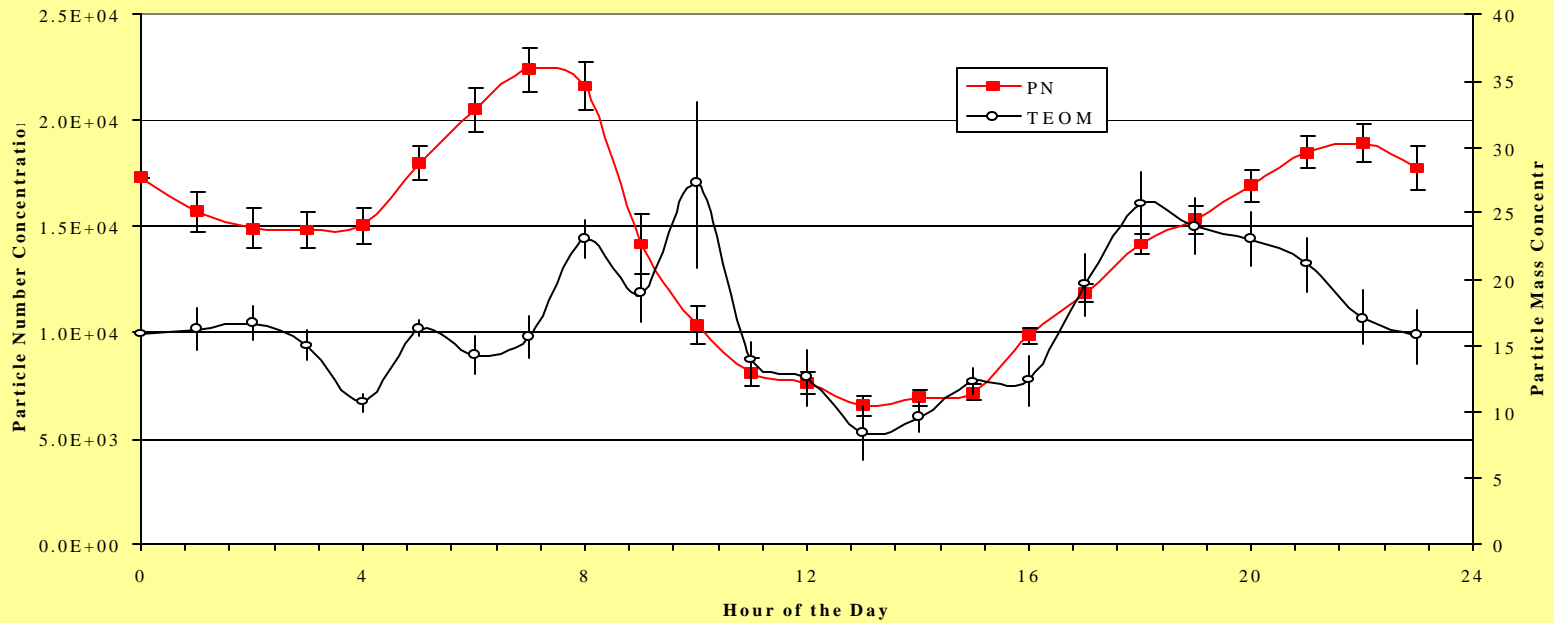




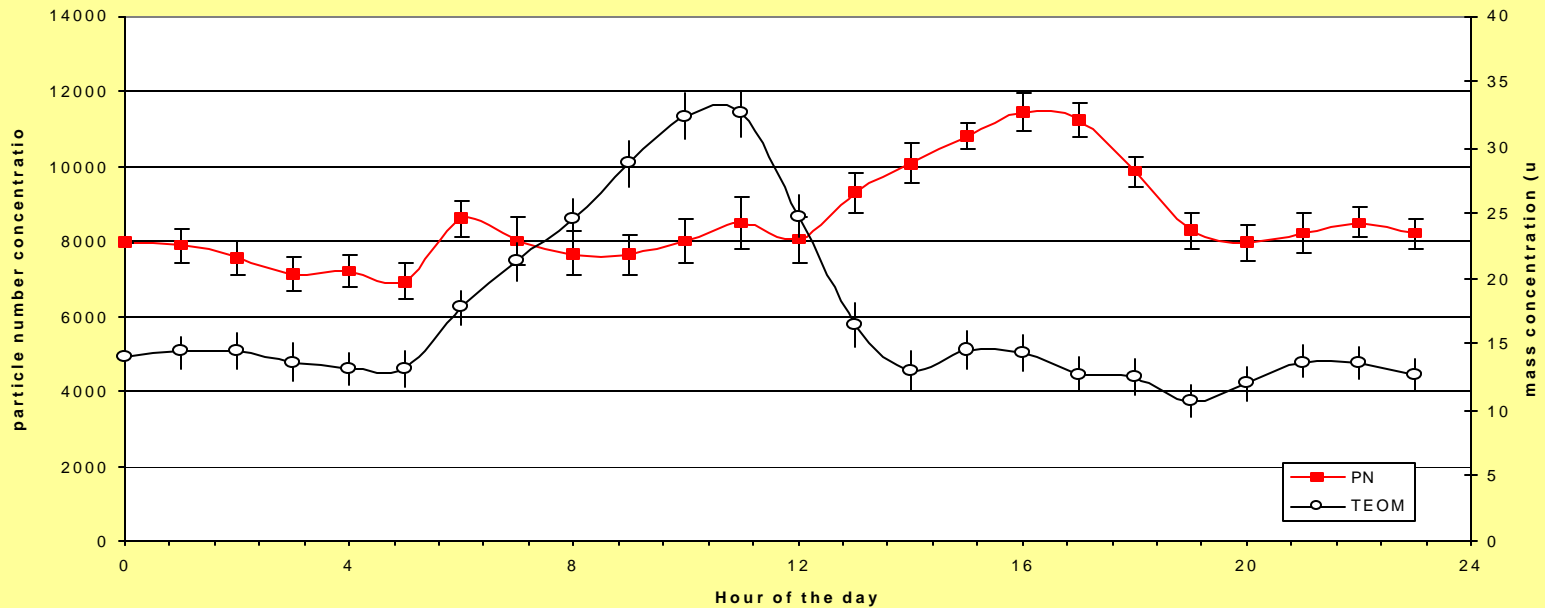
# Typical Size Distributions at USC December 2002



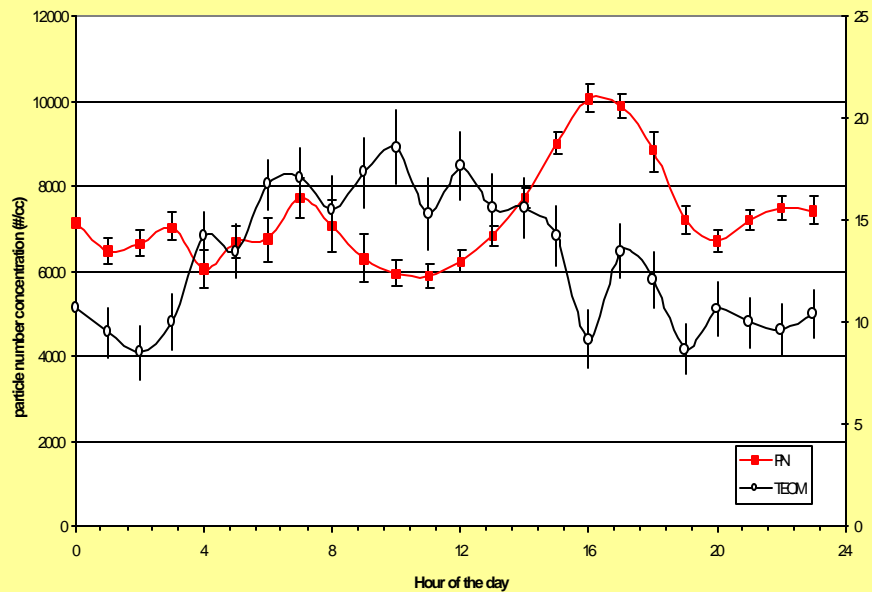
## Hourly averaged PM2.5 and PN Concentrations at UCR- January 2002



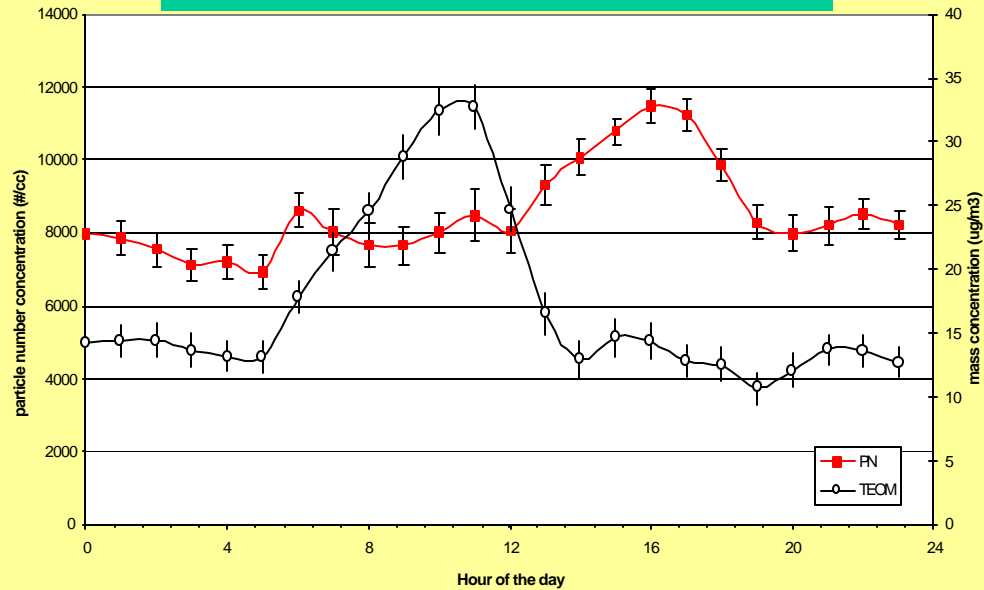
## Hourly averaged PM2.5 and PN Concentrations at UCR- July 2002



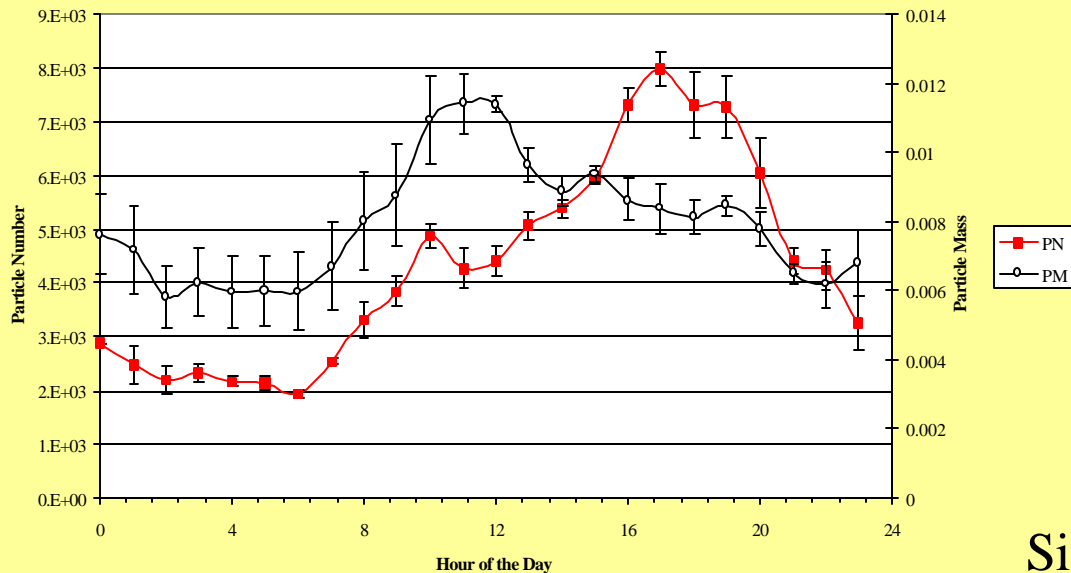
# Claremont



# Riverside



# Glendora



**Regional Nature of  
Ultrafine PM due to  
Secondary Formation**

**3 Receptor Sites**

**July 2002**

# Advection of UFP from source to receptor sites is important in warmer period (Fine et al., 2002, AS&T)

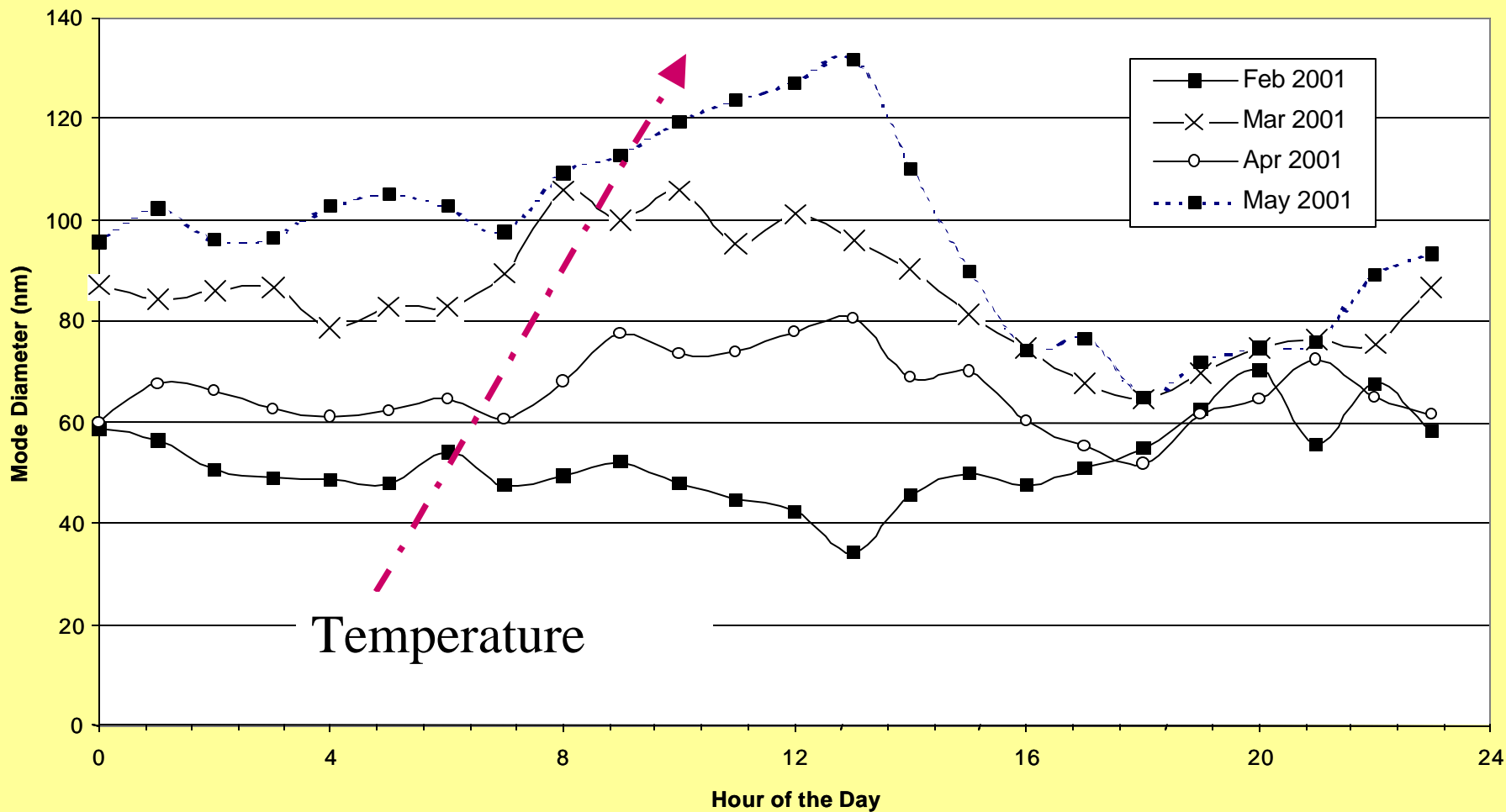


Figure 4. Monthly averaged mode diameter in Riverside, California

# Effect of photochemistry on ultrafine PM production

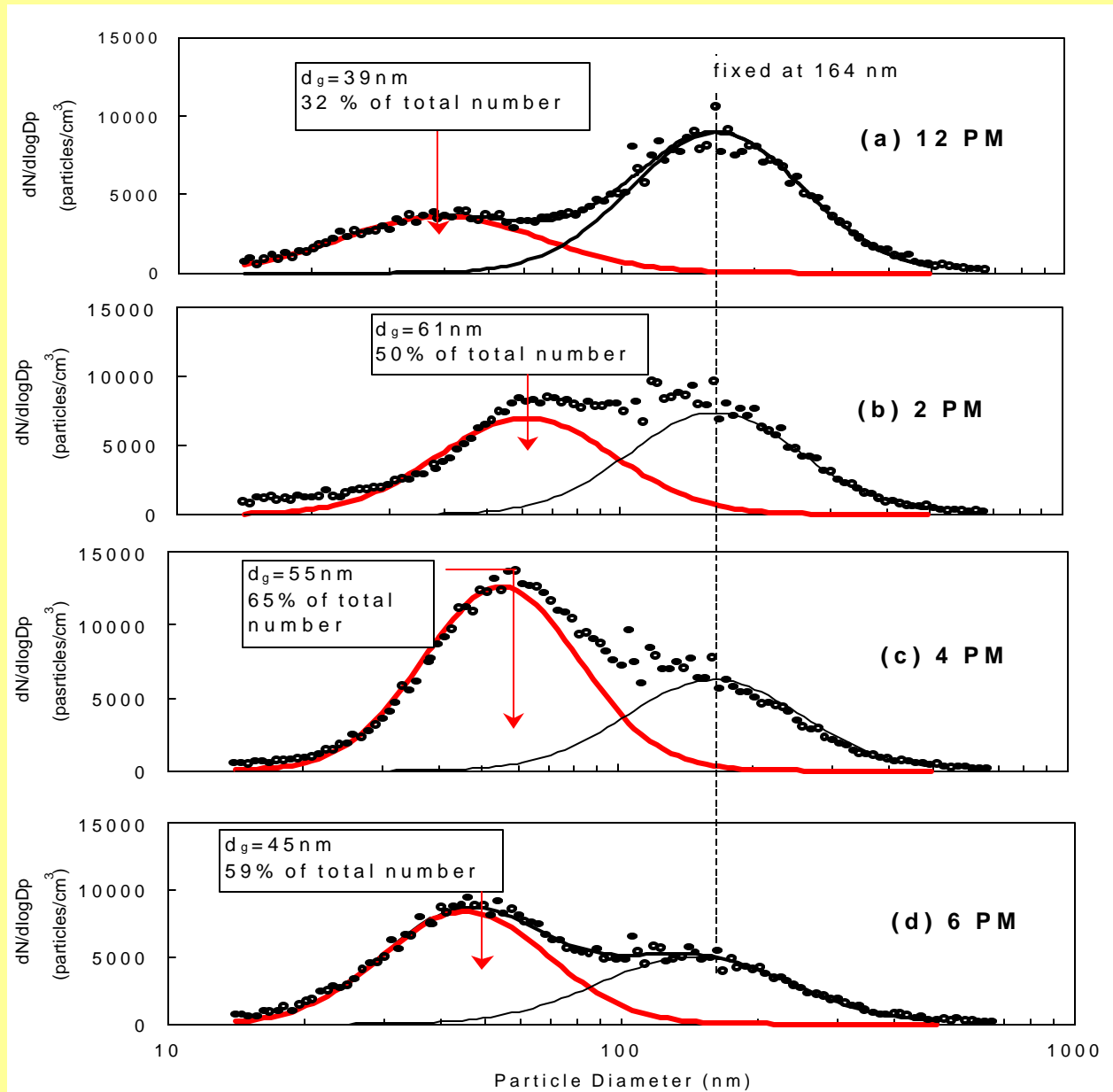


Figure 12. Simulated sub-modes of particles in the afternoon: Riverside, 5/16/2001.

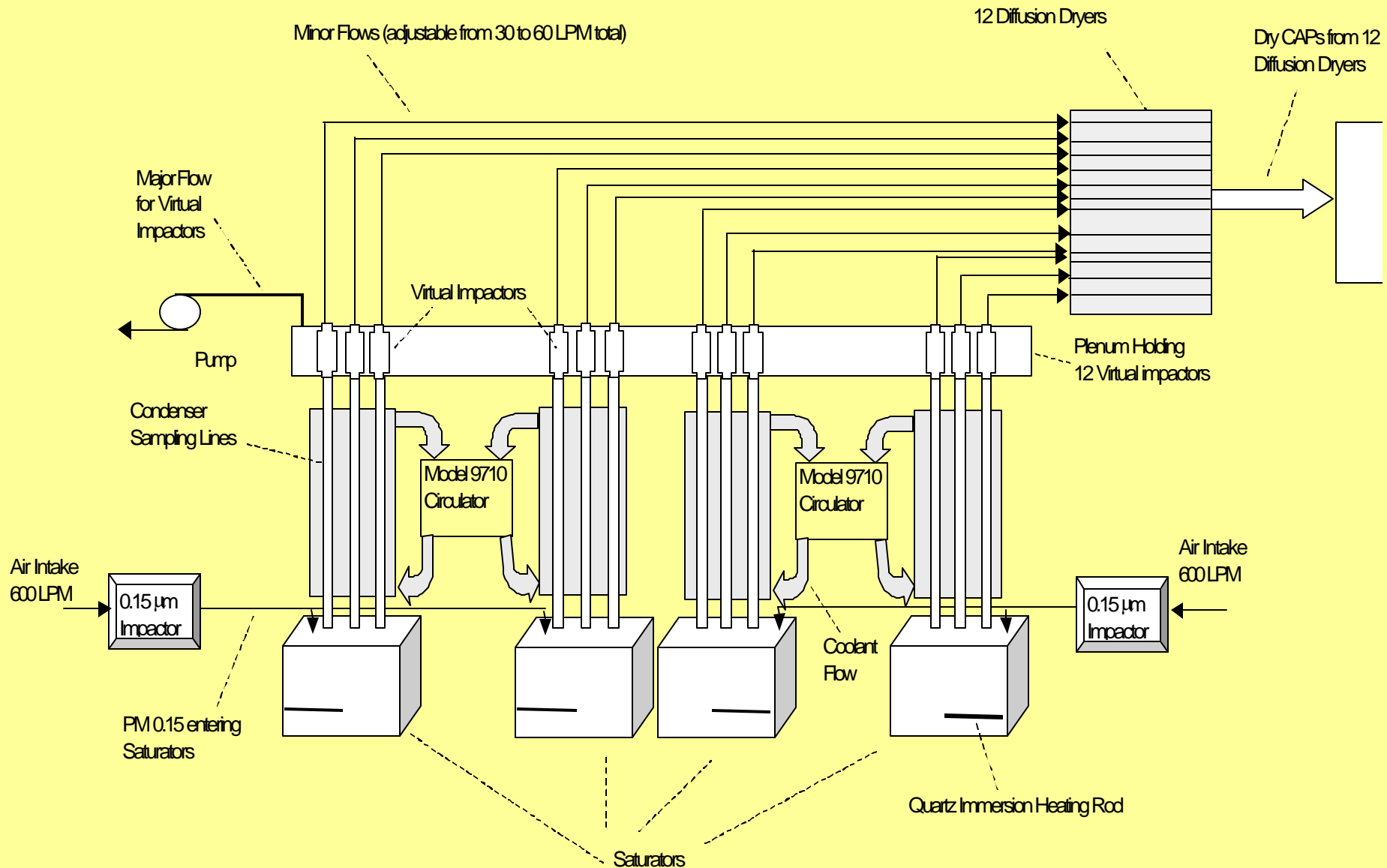


Figure 1. Schematic of the Ultrafine Particle Concentrator (UFPC) for Human Exposure

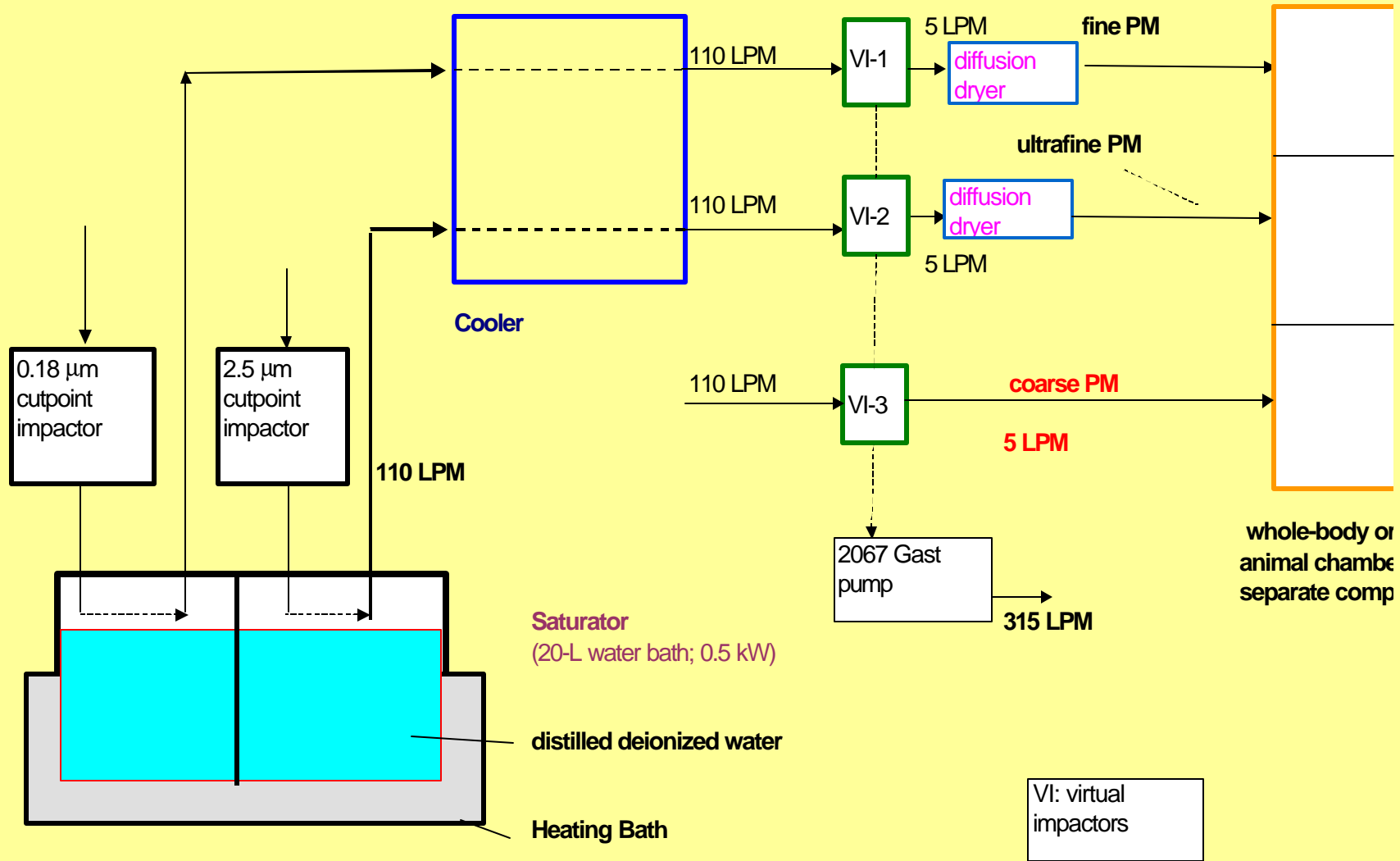
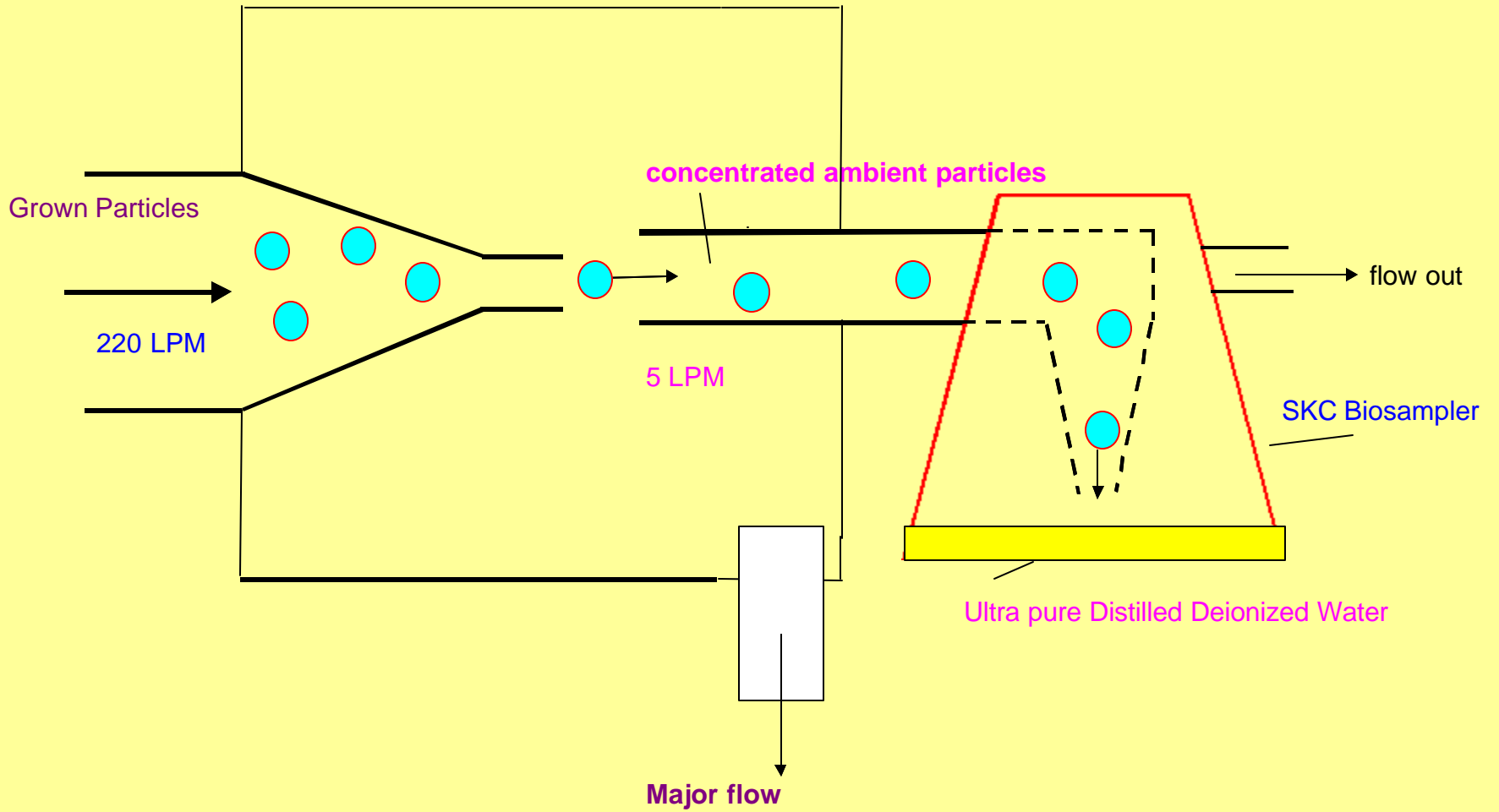


Figure 1a. Versatile Aerosol Concentration Enrichment System (VACES) for concurrent in vivo studies to coarse, fine and ultrafine PM

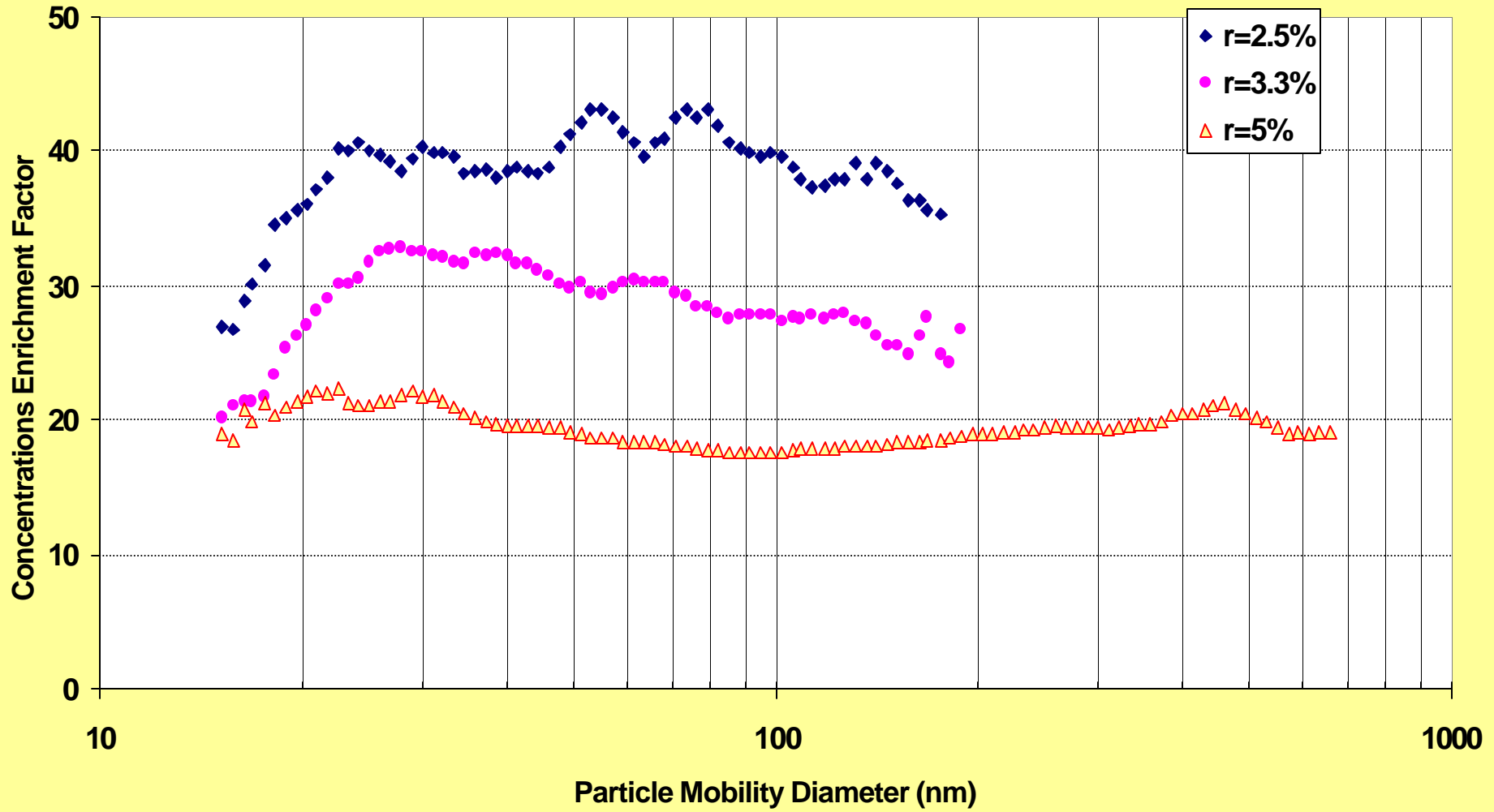
Kim et al., J Aerosol Sci, 2001



**Particle Concentrator for Collection of Particles  
for in vitro tests**

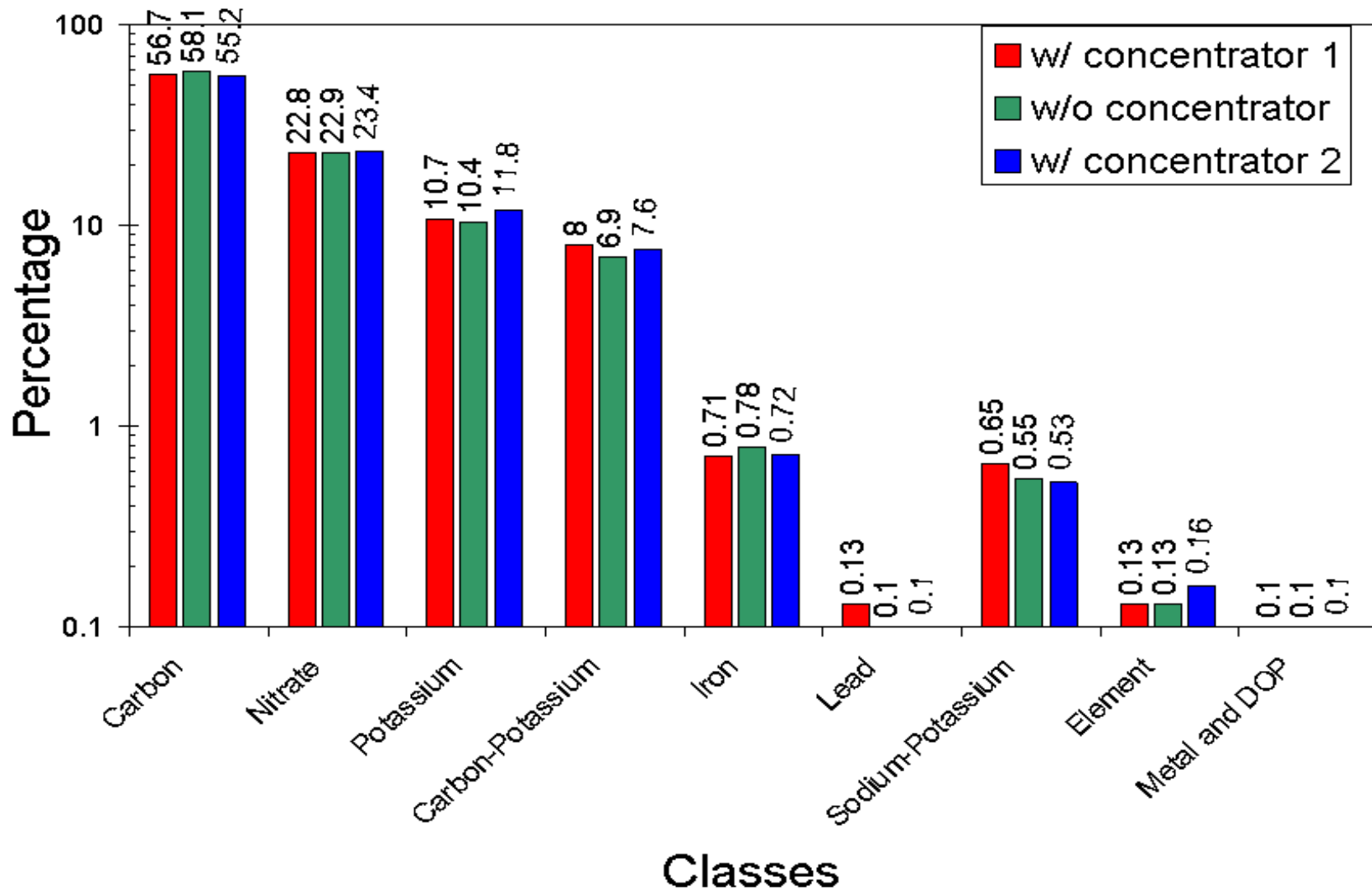


# Concentration Enrichment as a Function of Particle Diameter for Three Minor to Total Flow Ratios (r). Intake Flow = 1200 LPM



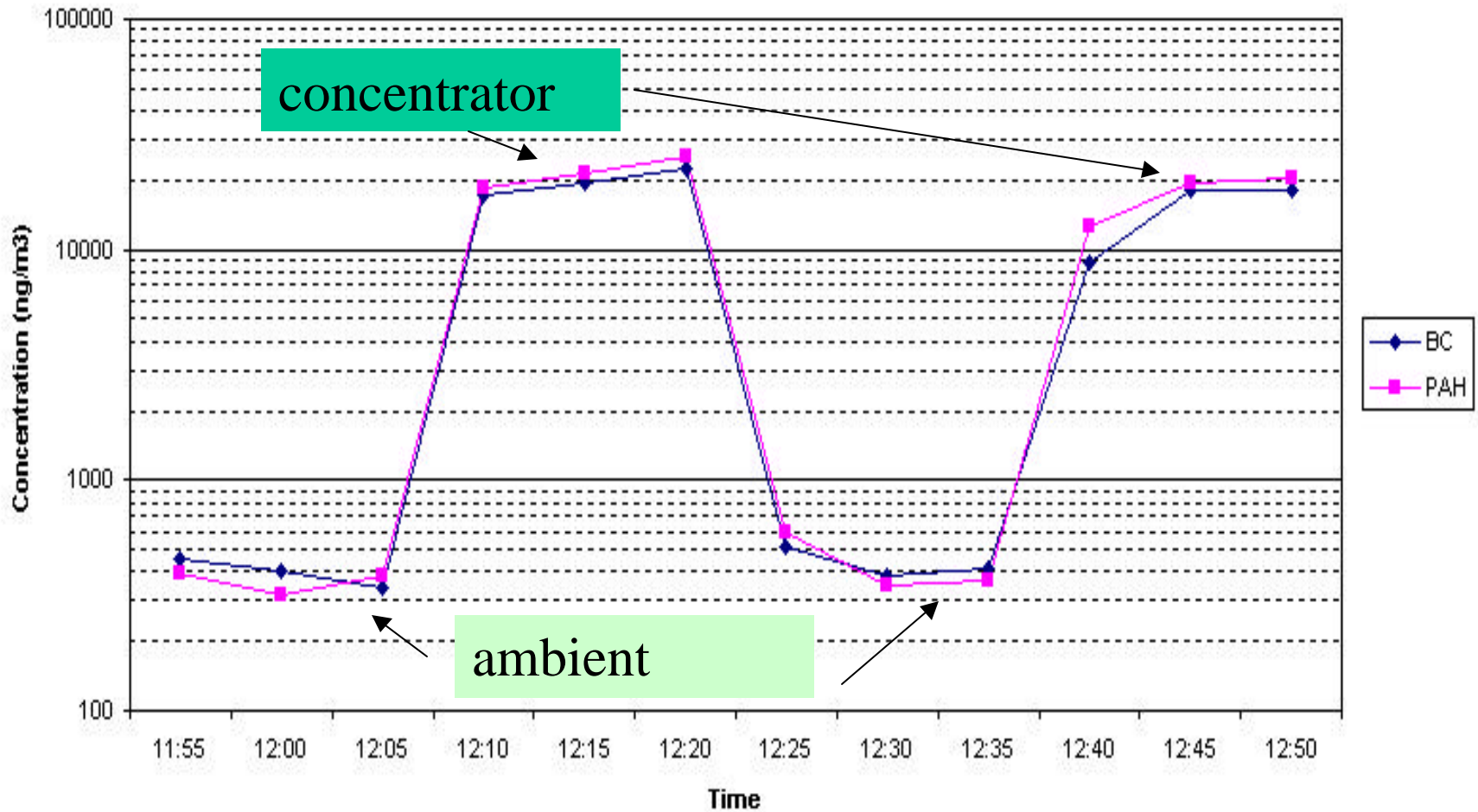
Misra et al., AS&T,  
2003

# Preservation of Chemical Composition of Ambient PM After Concentration based on Single Particle Analysis (Zhao et al., AS&T, 2003)





Concentration of EC and PAHs vs Time (Minor Flow=20 LPM)



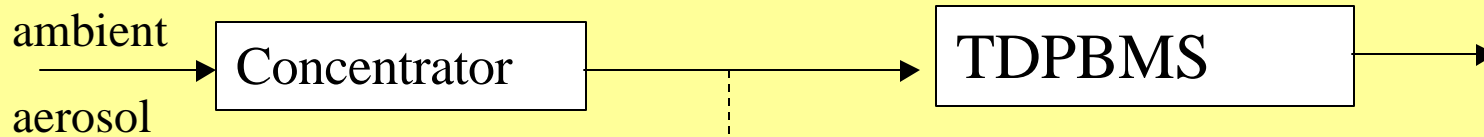
Misra et al., AS&T,  
2003

Max. Concentration Enrichment of 50 in a  
single-stage virtual impactor

## Use of the F+UF Concentrators to Increase the Signal of Other Instruments :

- NanoMOUDI (Geller et al., AS&T, 2002)
- Pittsburgh Supersite Nucleation Experiments (Steiner et al., 2002)
- Wexler Rapid Single-Particle Mass Spectrometer (RSMS-3)
- P. Ziemann (UCR) Thermal Desorption Mass Spectrometer

# Thermal Desorption Mass Spectrometer tests with Concentrators



Concentr.  
Factor x 50

## Goals :

- **rapid organic speciation** analysis of PM in accumulation and ultrafine modes
- identification of **source tracers**
- in source (**USC**) and receptor (**UC Riverside**) sites
- during **winter** and **summer** periods

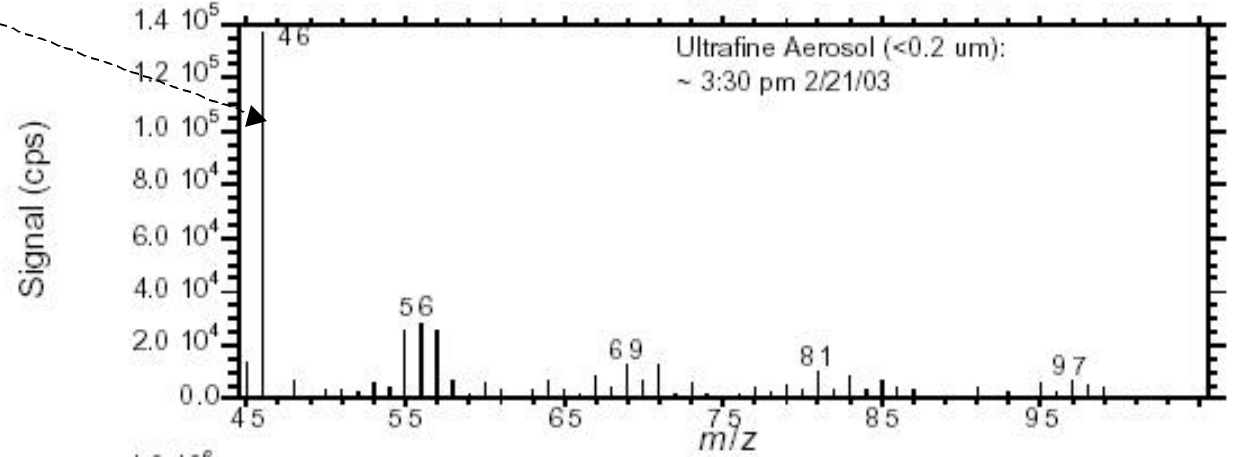
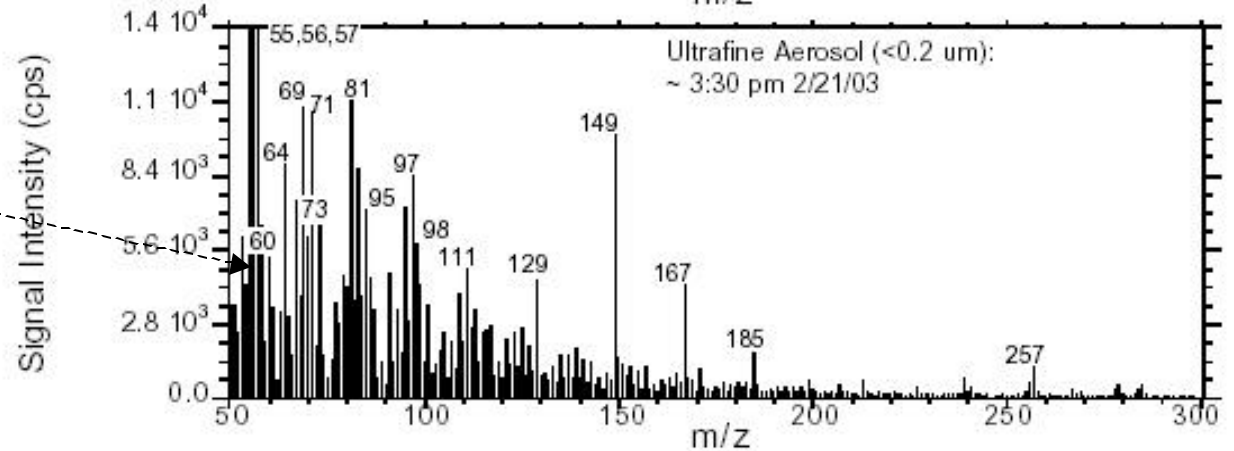
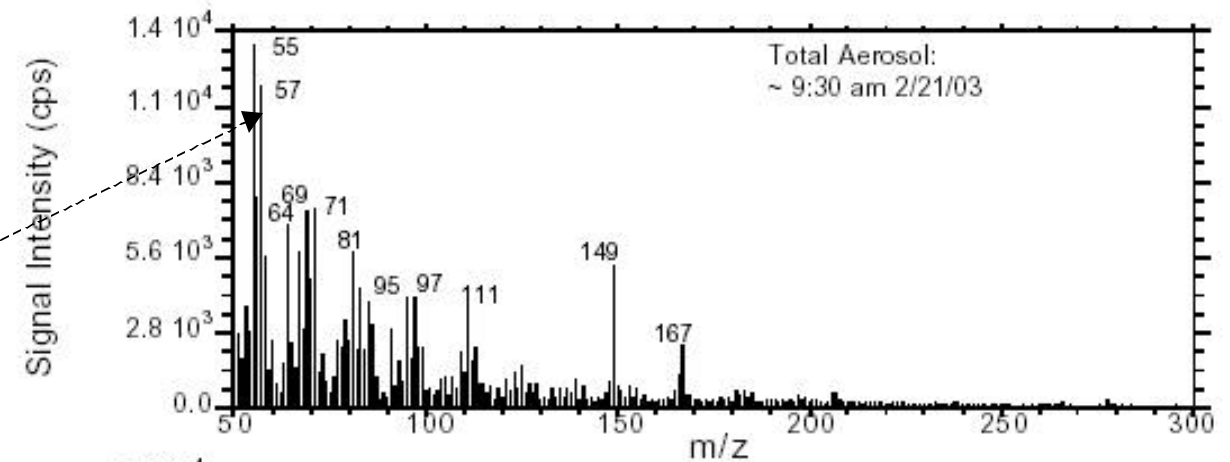
# UCR samples in February 2003

m/z: 55, 57, 69,  
71, 95, 97

Hydrocarbons

m/z: 60, 73:  
organic acids

m/z 30, 46:  
ammonium nitrate



# Near **Continuous Ultrafine Mass Concentration Monitor** (Chakrabarti et al., *Aerosol Science and Technology*, 2002)

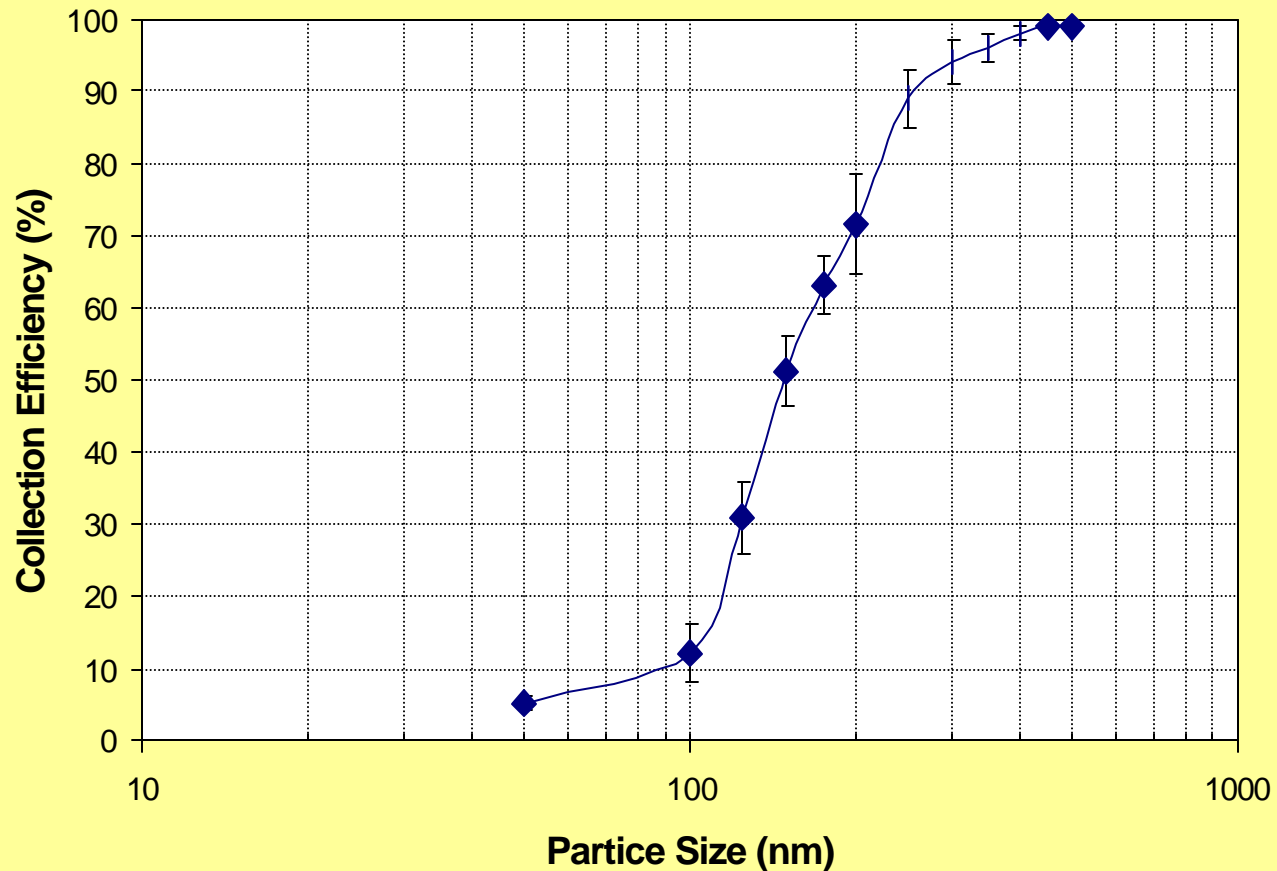
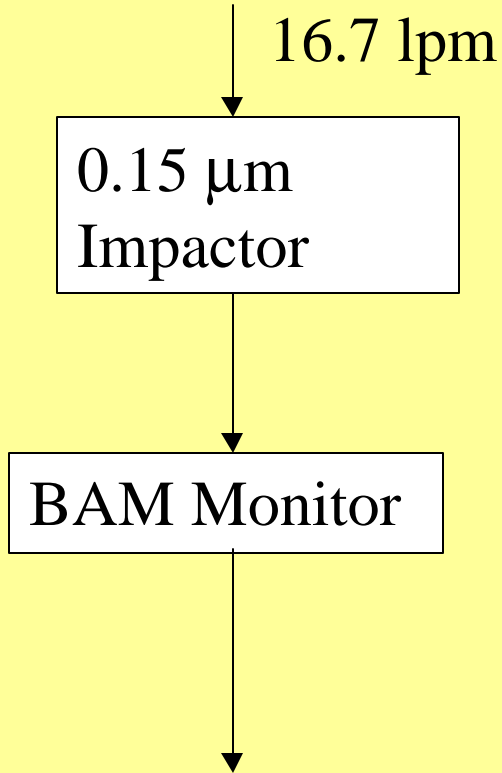
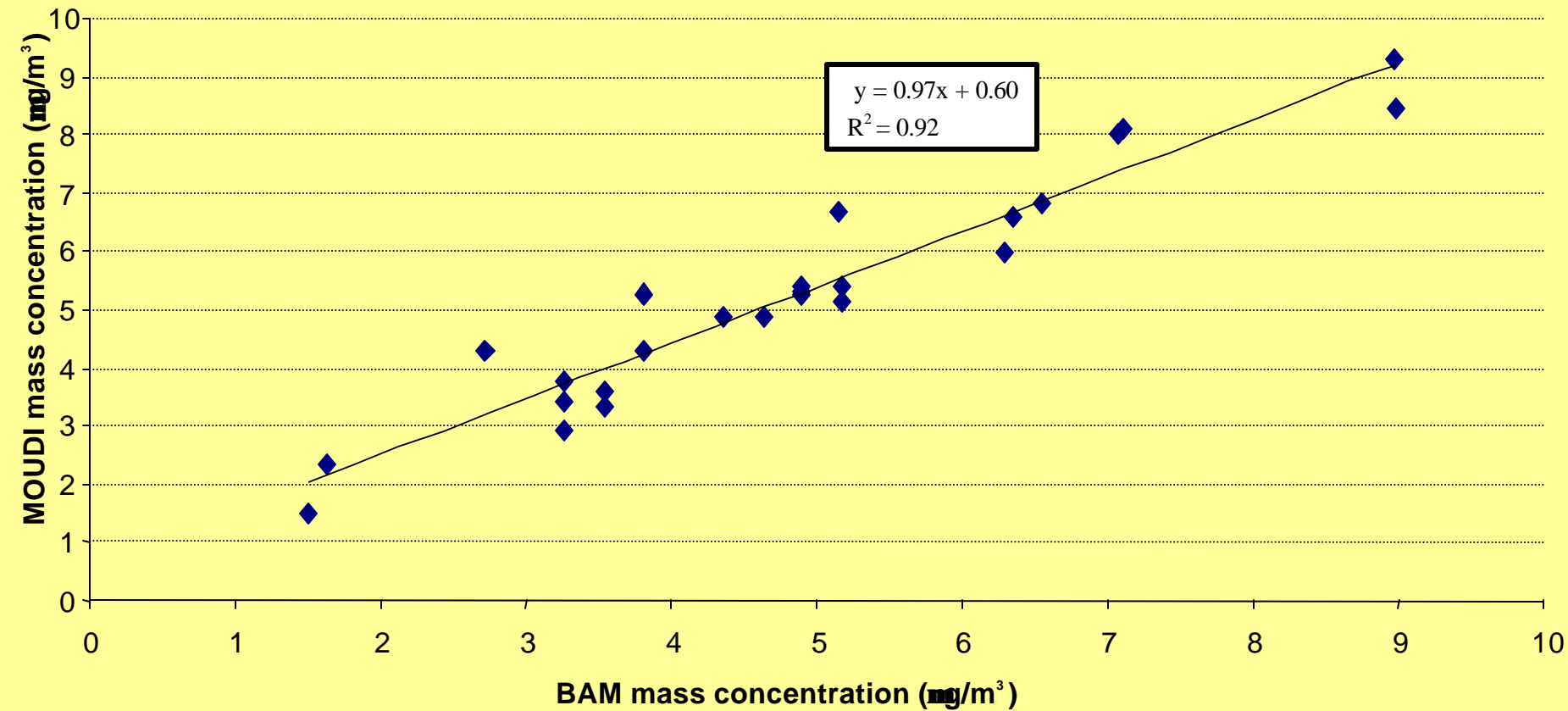


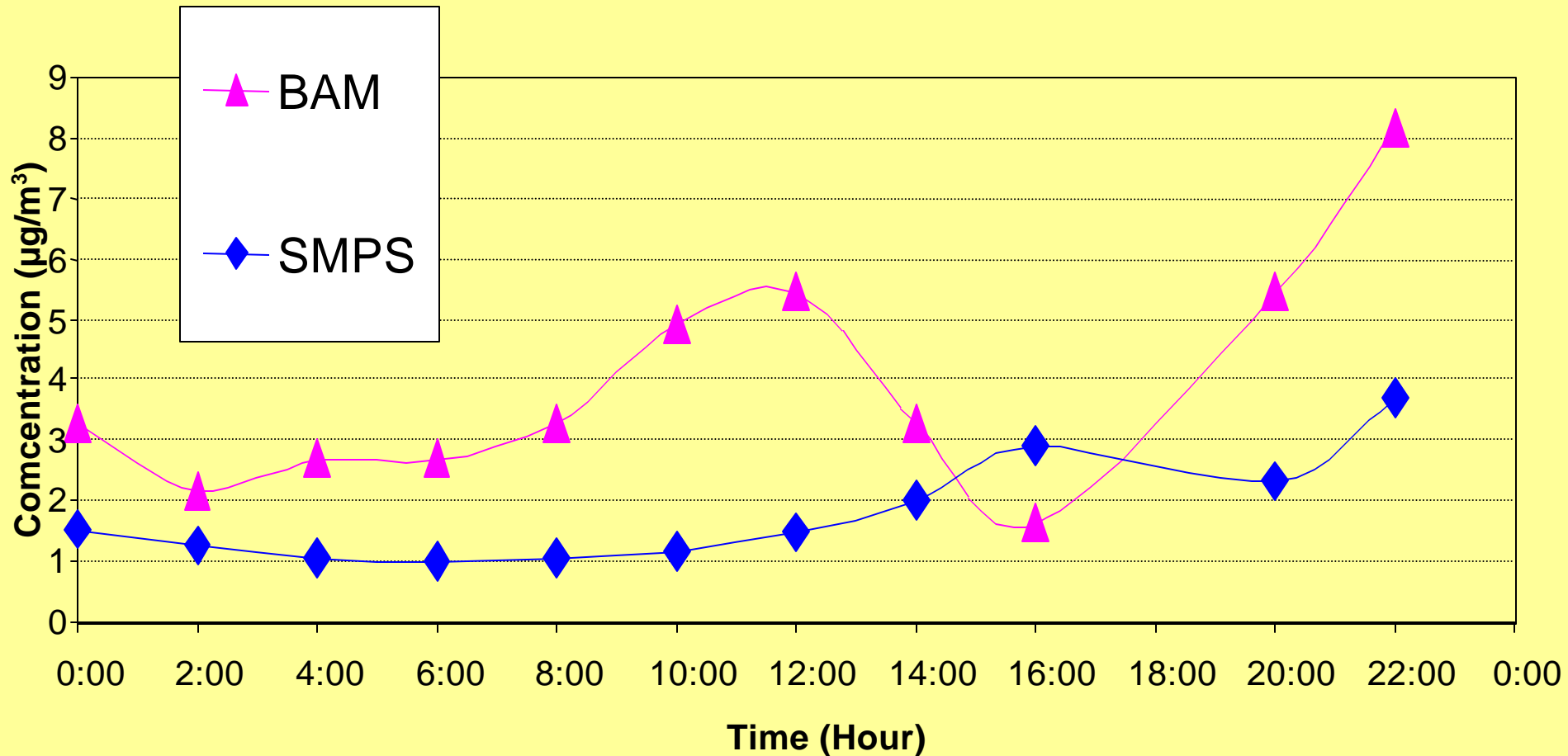


Figure 2. BAM vs. MOUDI Ultrafine PM concentration



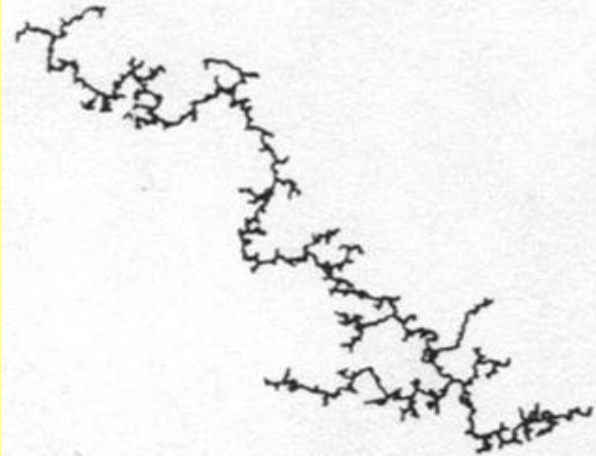
The SMPS cannot measure ultrafine PM mass concentrations.  
Events of July 4, 2002 (fractal-like PM produced by combustion)

Figure 4c. BAM and SMPS Ultrafine Mass Concentrations on July 4, 2002





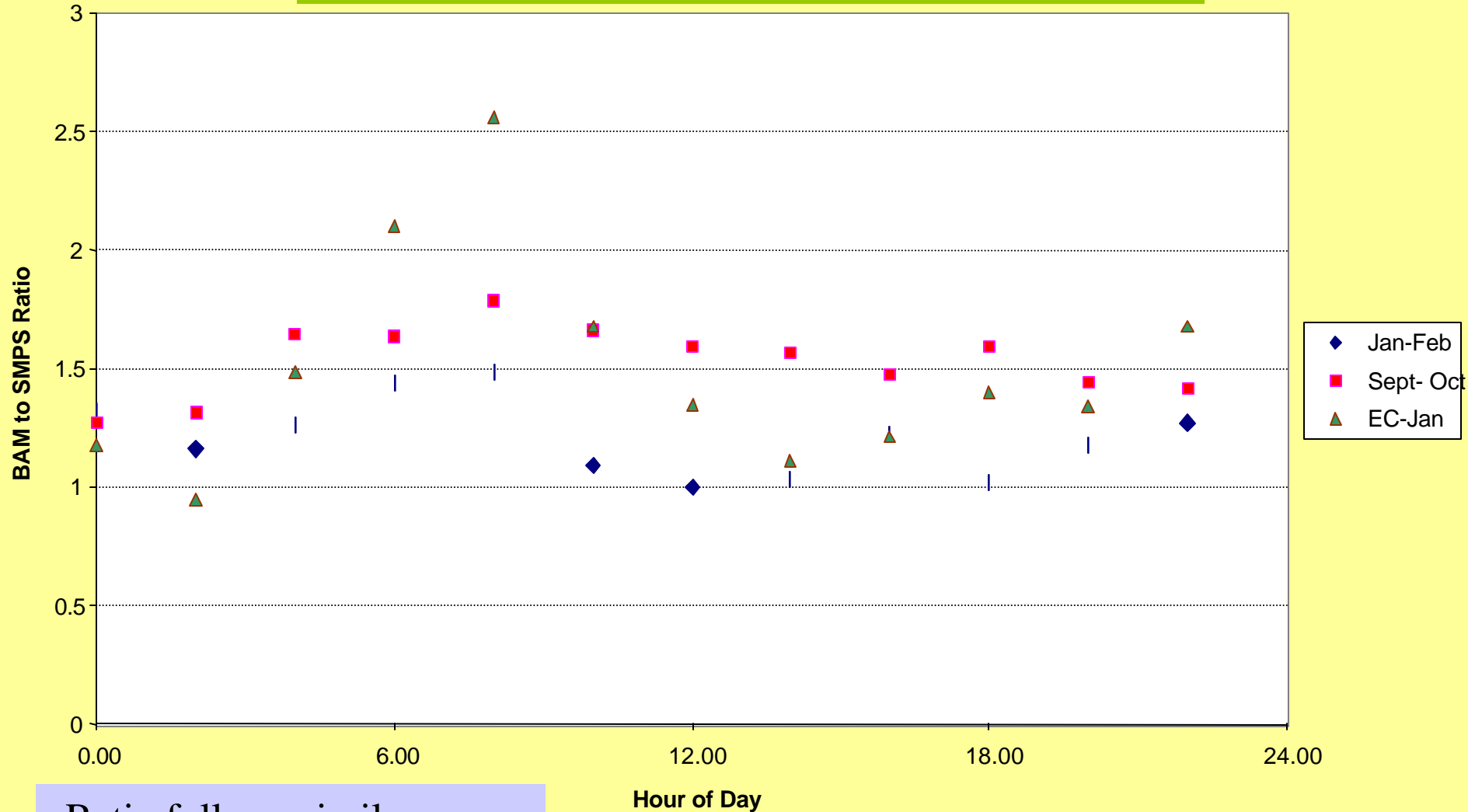
$$D_f = 2.50$$



$$D_f = 1.80$$

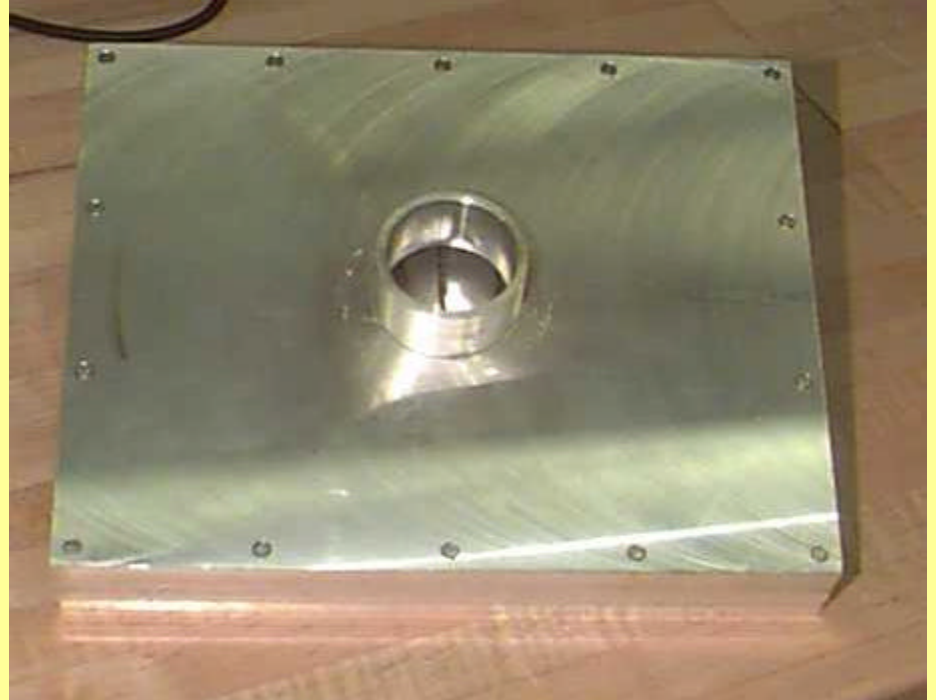
Fractal-like combustion particles have a **high surface area**, hence electrical mobility, but a **low density**

# BAM-to -SMPS Ultrafine Mass Concentration Ratio as a Function of Time of Day



-Ratio follows similar diurnal trend with EC

-Evidence for increased fractal content?



**High-Volume, Very Low  
Pressure Drop Impactor  
for Separation of Coarse-  
Fine-Ultrafine PM**

Misra et al *Journal of  
Aerosol Science*, 33(5): 735-  
752, 2002

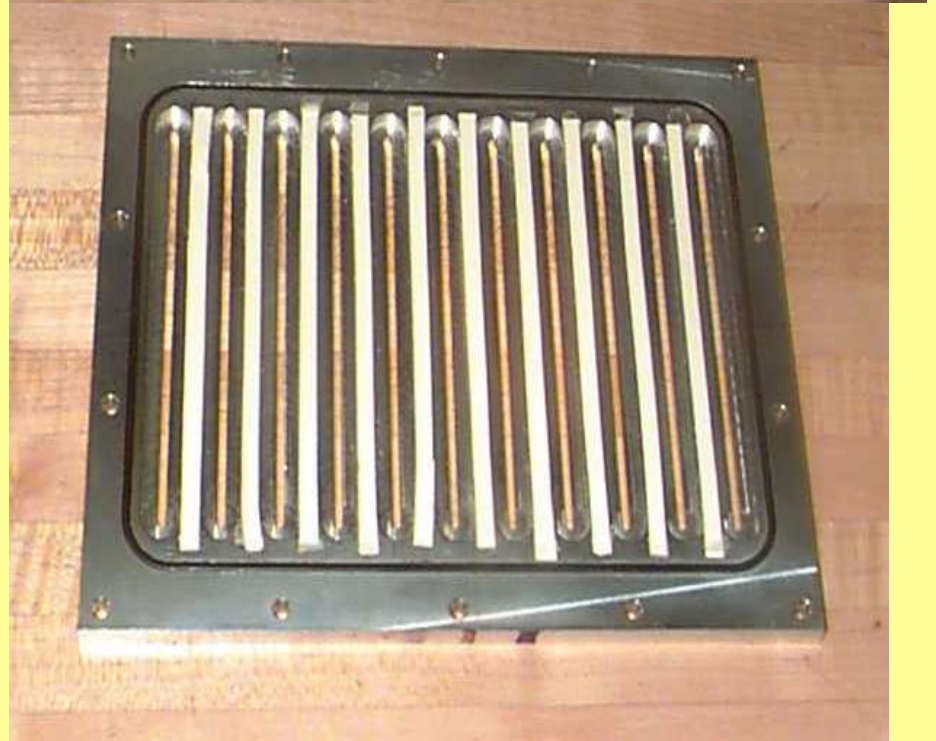
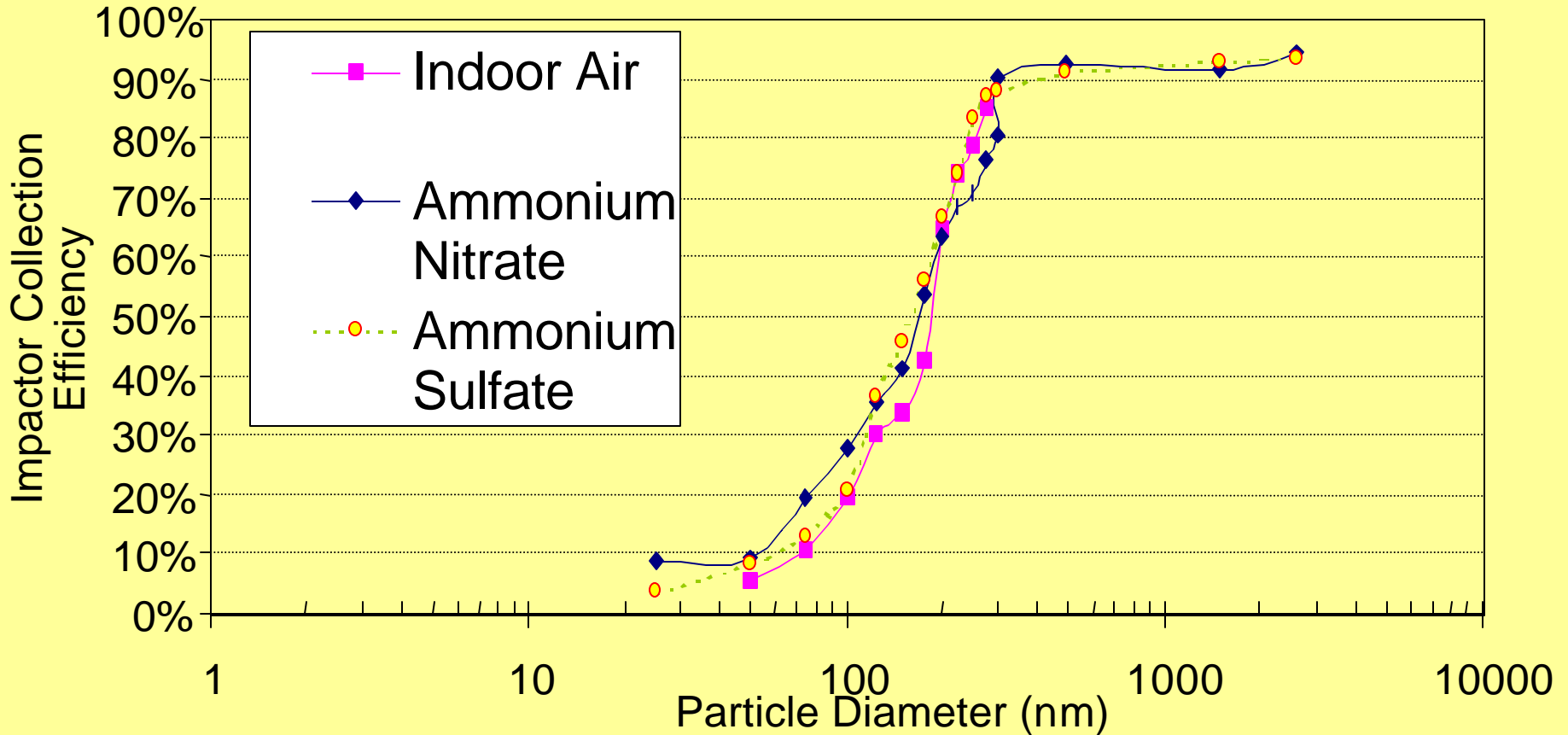


Figure 4. Evaluation of the USC High Volume Low Cutpoint Impactor with an Uncoated Quartz Substrate and Different Types of Test Aerosols



# Use of Source Tracers in Exposure and Toxicology Research

Using individual organic compounds as tracers of primary emissions sources, how do source contributions vary from:

- site to site,
- over the course of the day
- between size fractions?

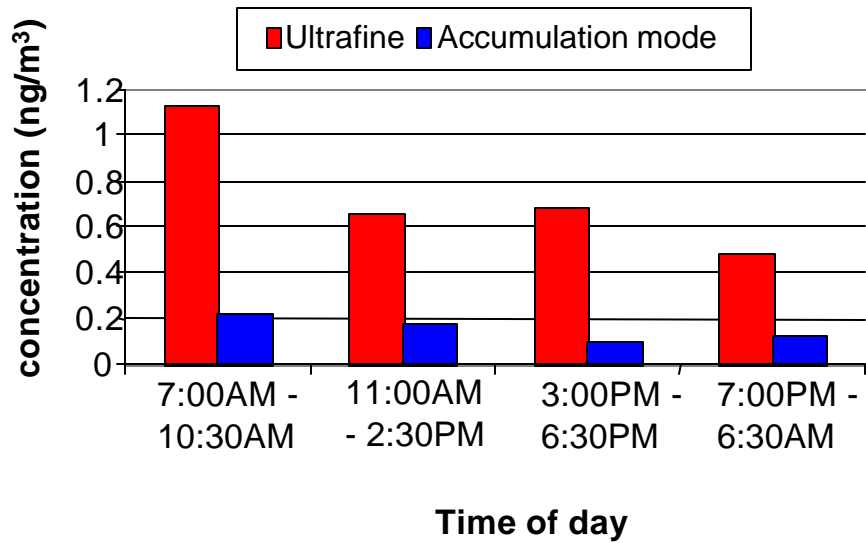
Size Distribution and Concentrations of :

- hopanes (vehicles)
- cholesterol (cooking)
- levoglucosan (wood smoke)
- 1,2 benzenedicarboxylic acid (photochemistry)

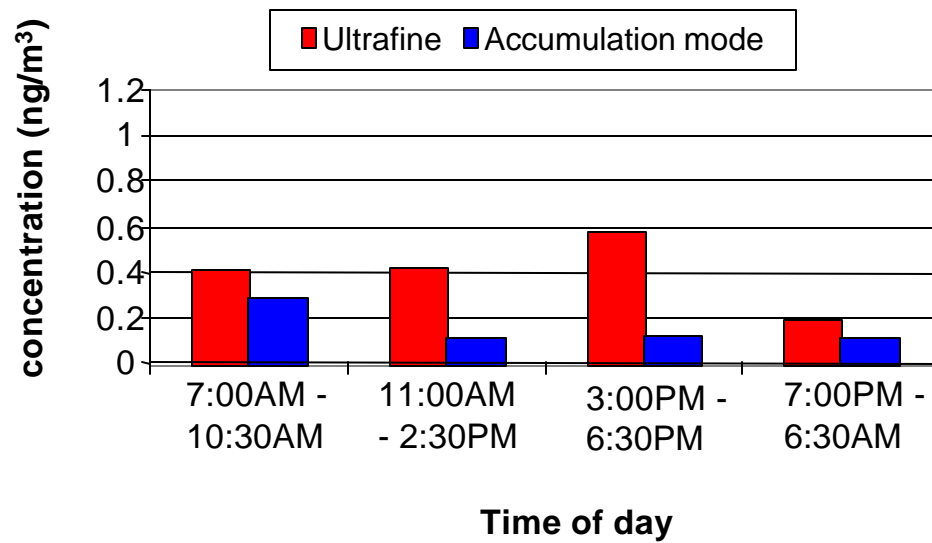
At UCR (receptor) and USC (source)

(Fine et al., Atmos. Environ., 2003)

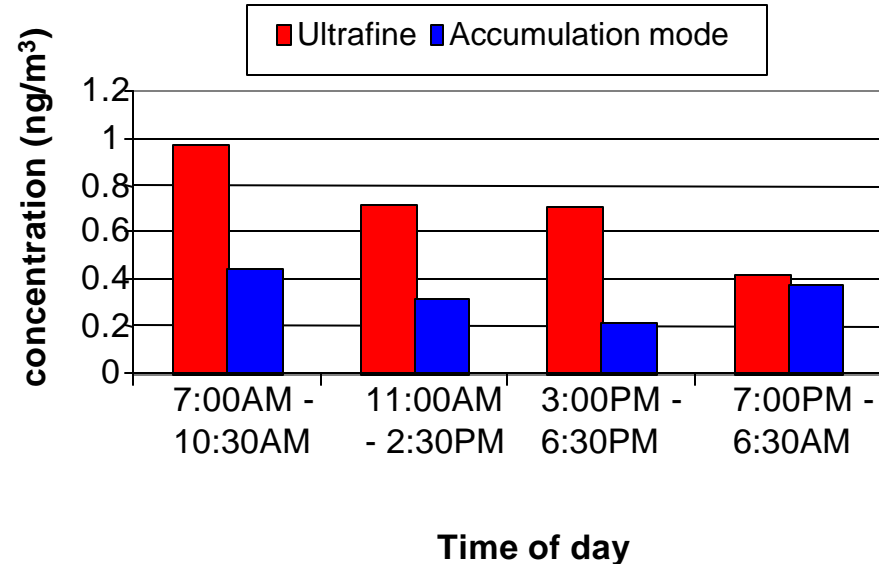
### Sum of Hopanes - USC Summer



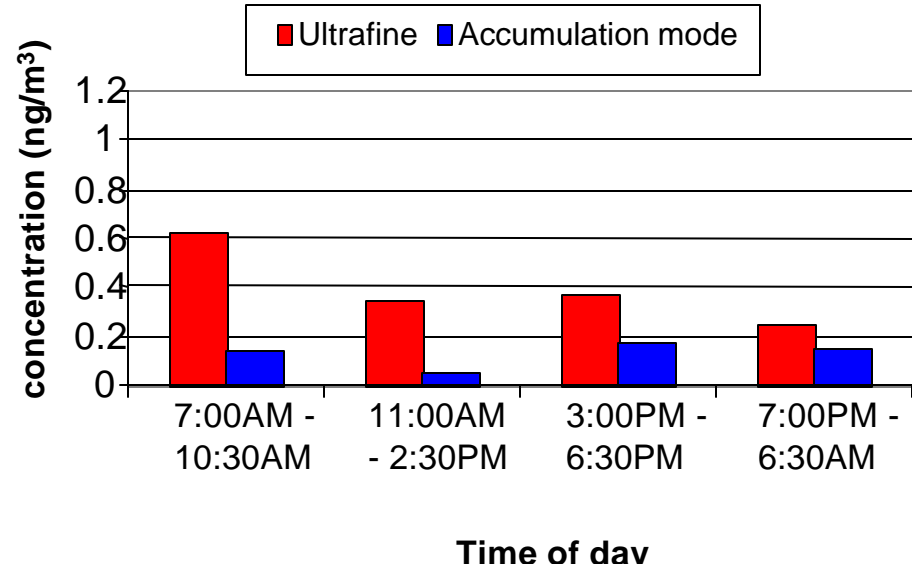
### Sum of Hopanes - Riverside Summer



### Sum of Hopanes - USC Winter

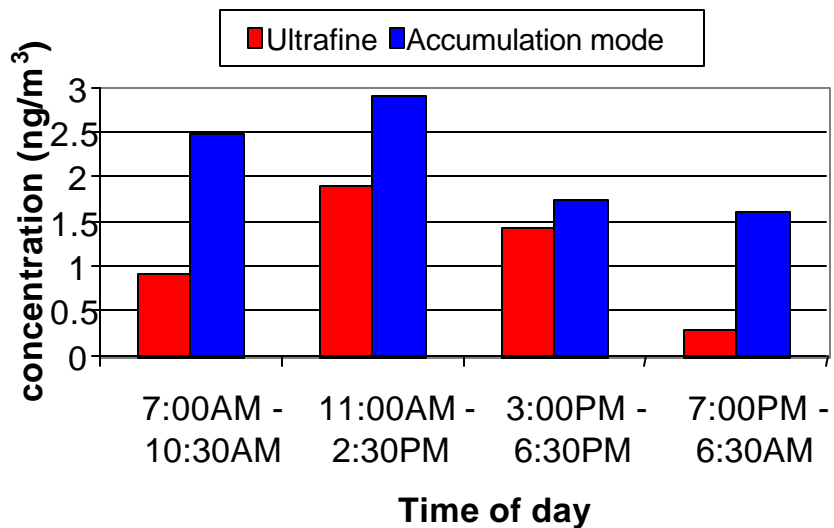


### Sum of Hopanes - Riverside Winter

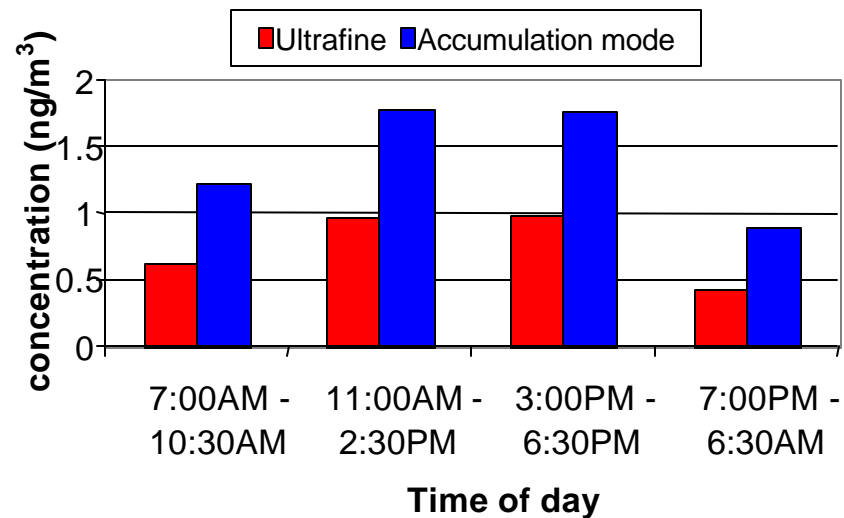




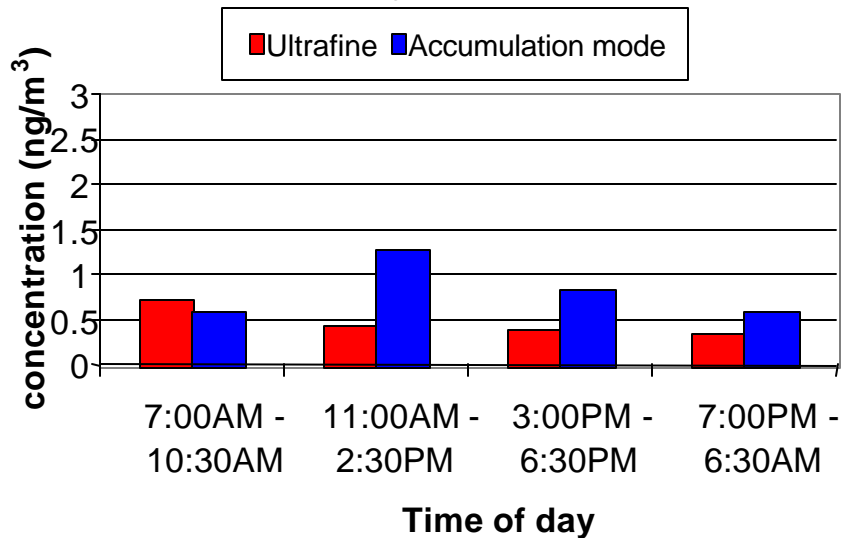
### 1,2 benzenedicarboxylic acid- USC Summer



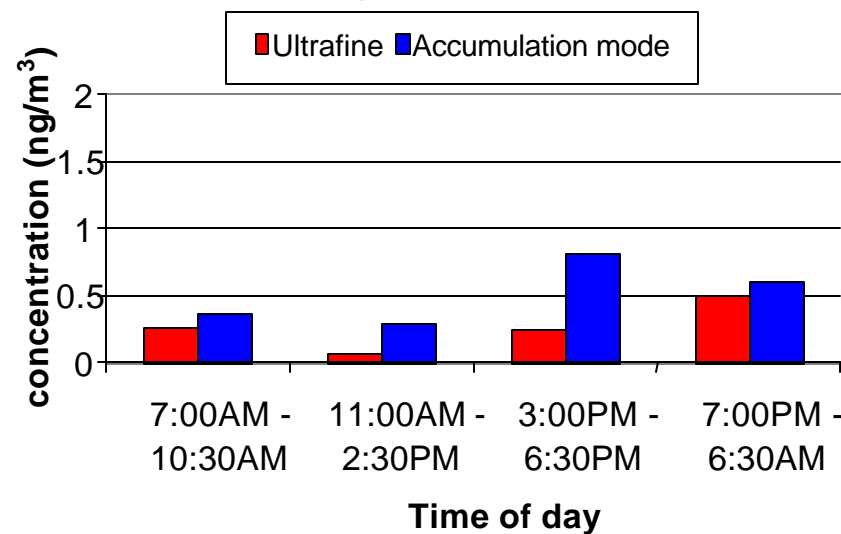
### 1,2 benzenedicarboxylic acid - Riverside Summer

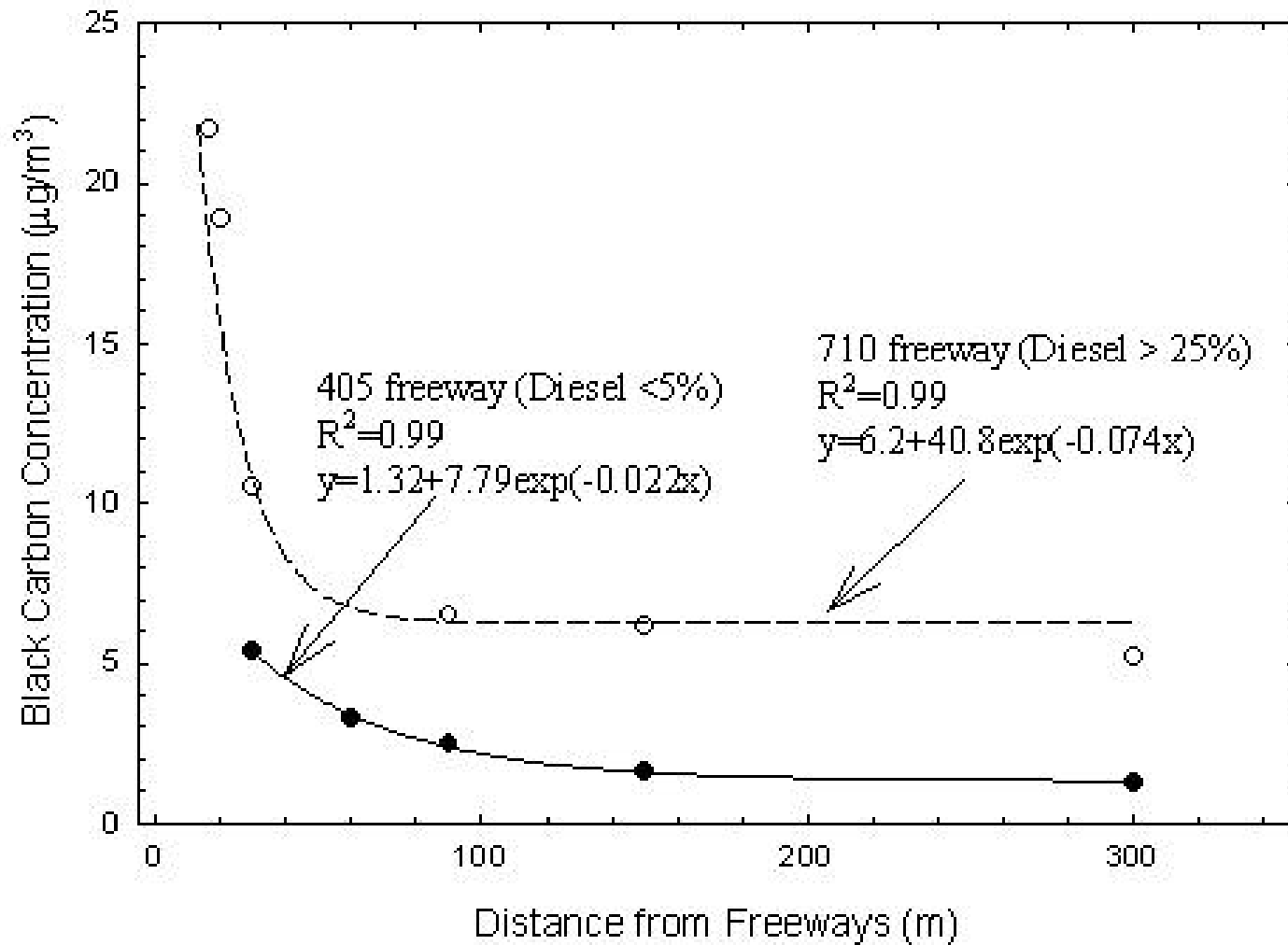


### 1,2 benzenedicarboxylic acid - USC Winter

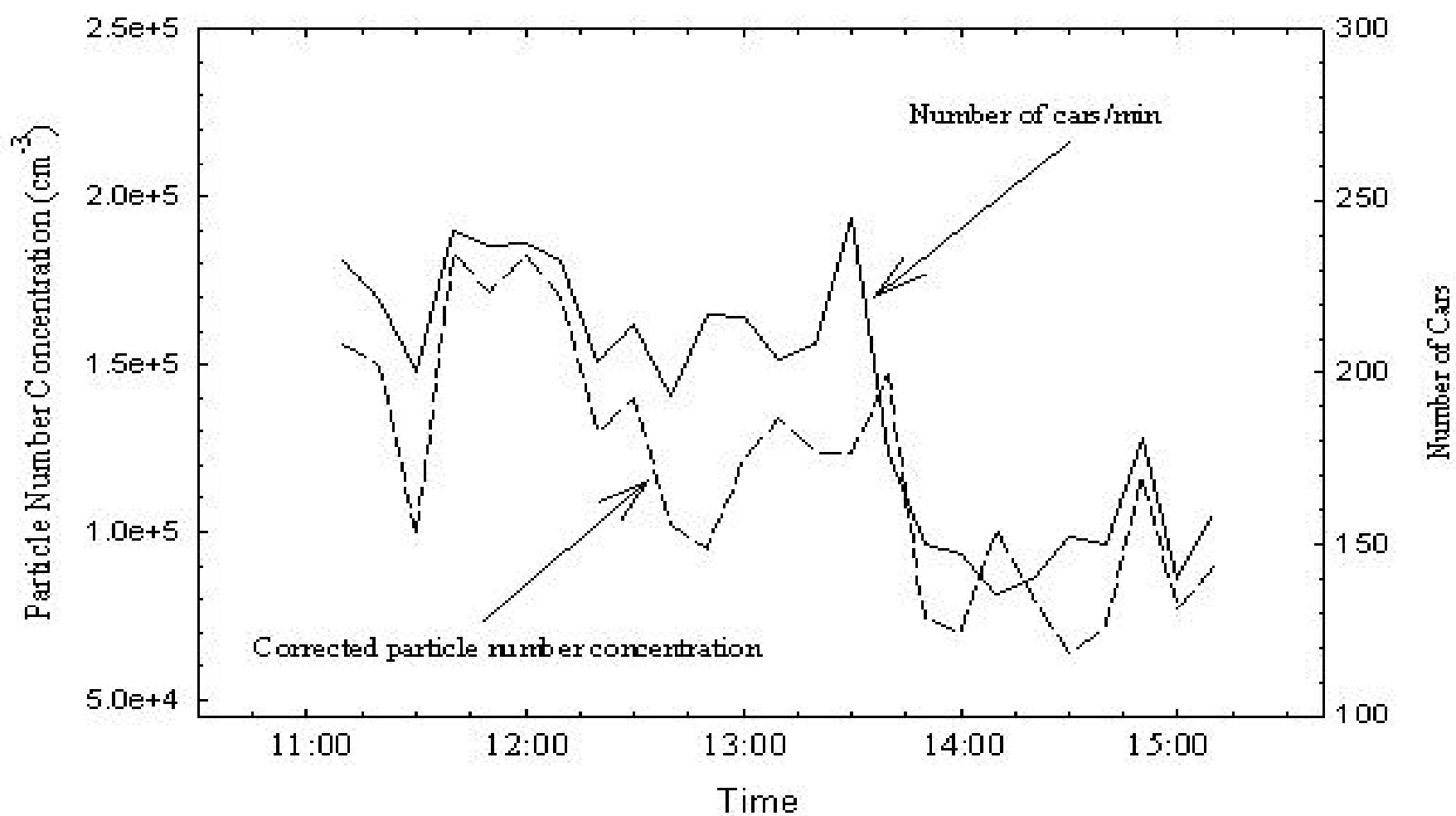


### 1,2 benzenedicarboxylic acid - Riverside Winter





**EC Diesel vs Gasoline Freeways** (Zhu et al.,  
*Atmospheric Environment*. 36, 4375-4383, 2002)  
 (b)

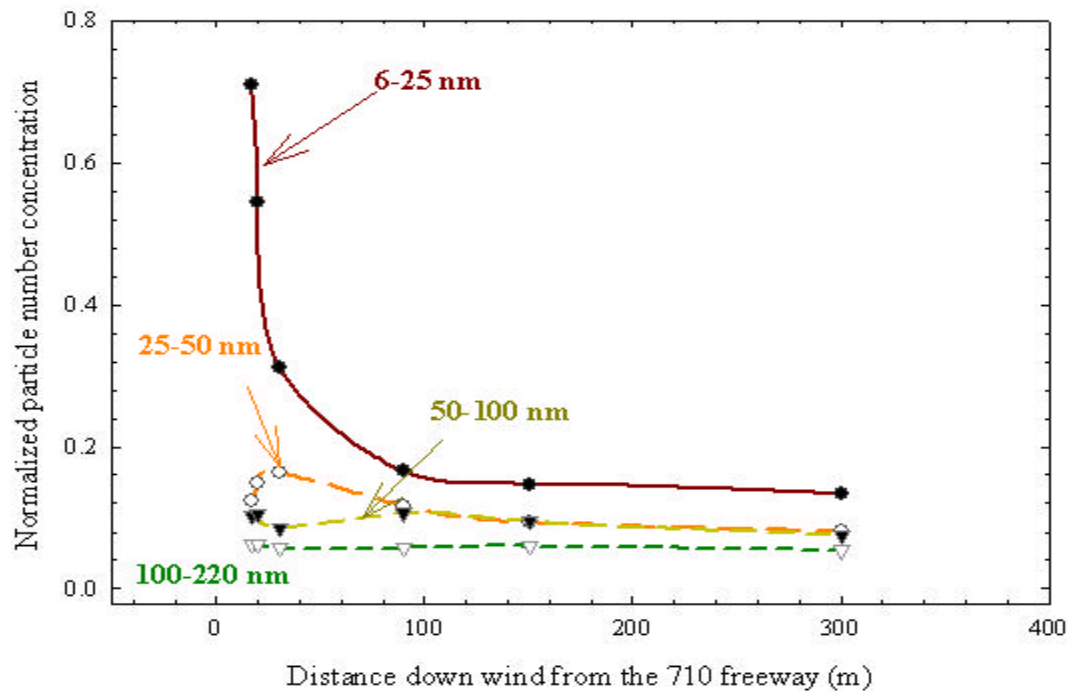


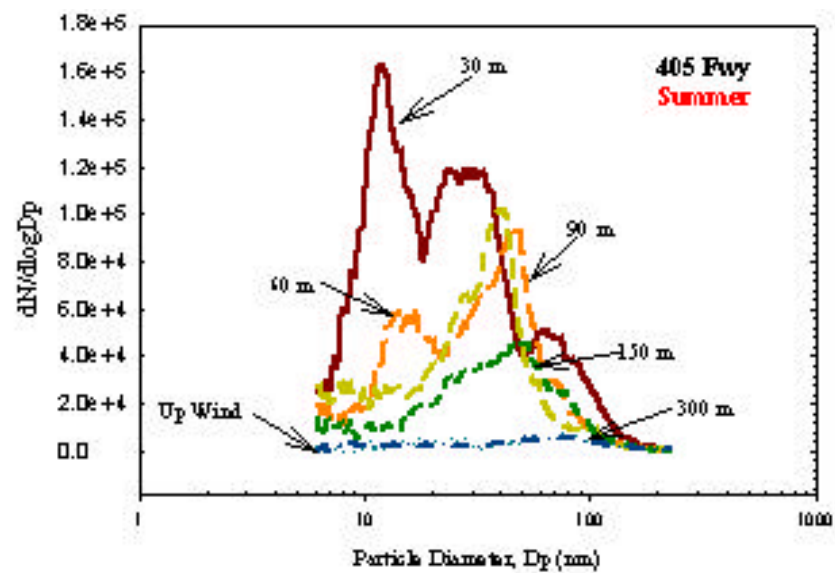
**Figure 3.** Correlation between traffic density and measured total particle number concentration, corrected for wind velocity at 30 m downwind from the freeway.

Freeway 710

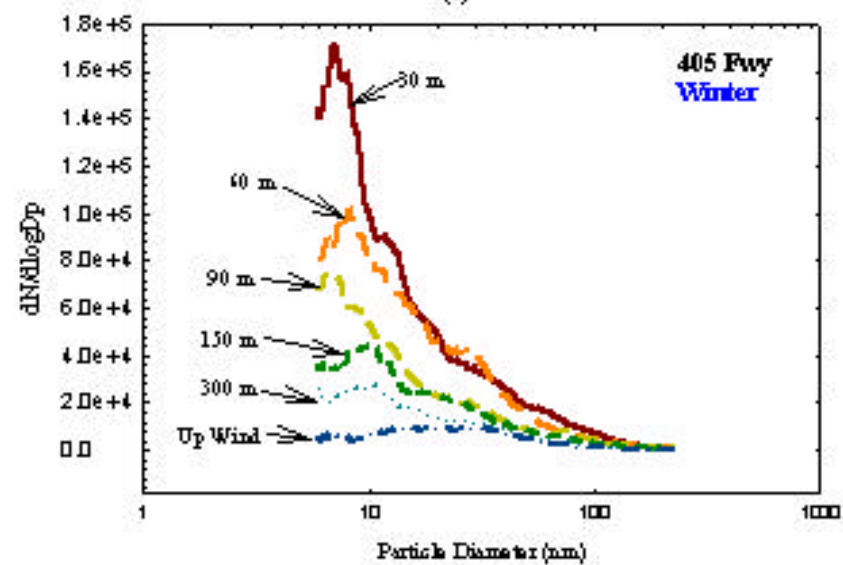
# RESULTS AND DISCUSSION

- ◆ **Number Concentration for Different Size Ranges Vs. Increasing Distance from Freeway 710.**

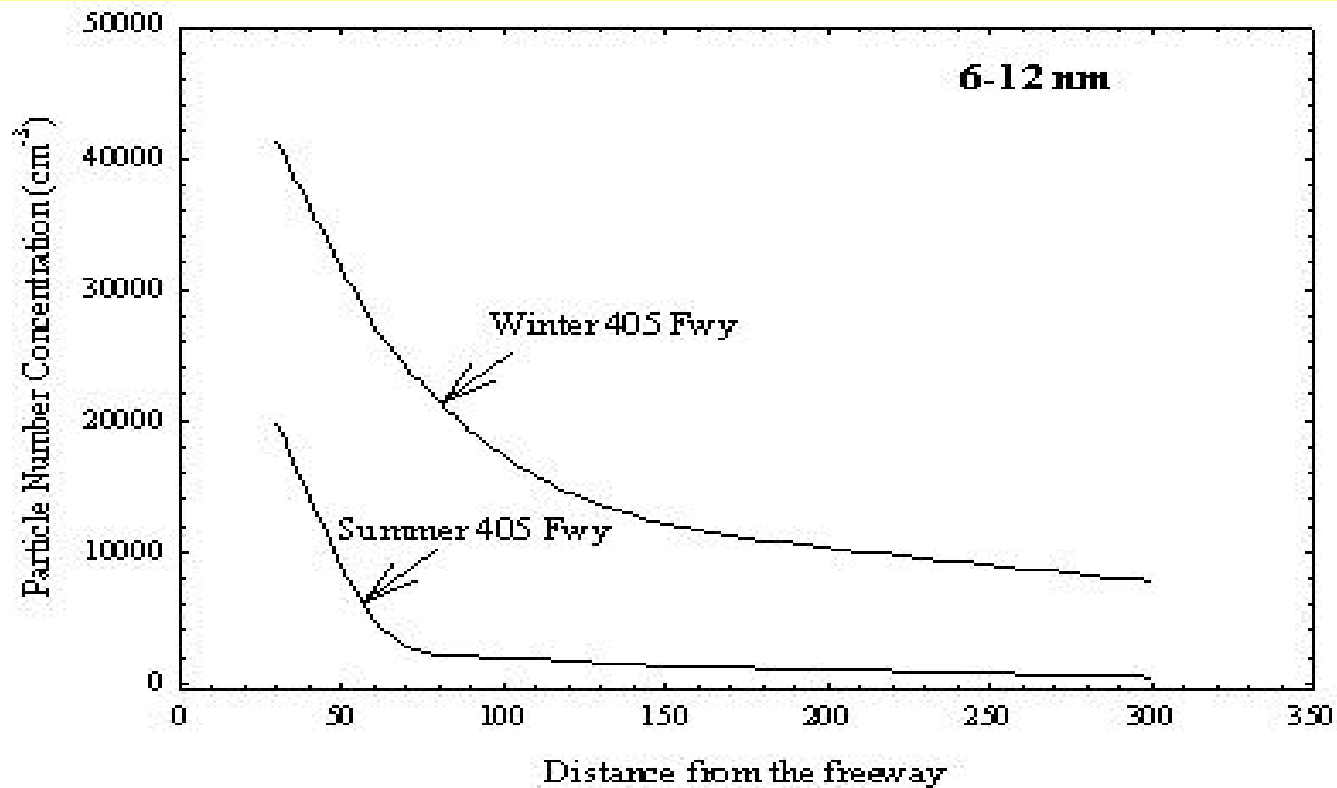




(a)

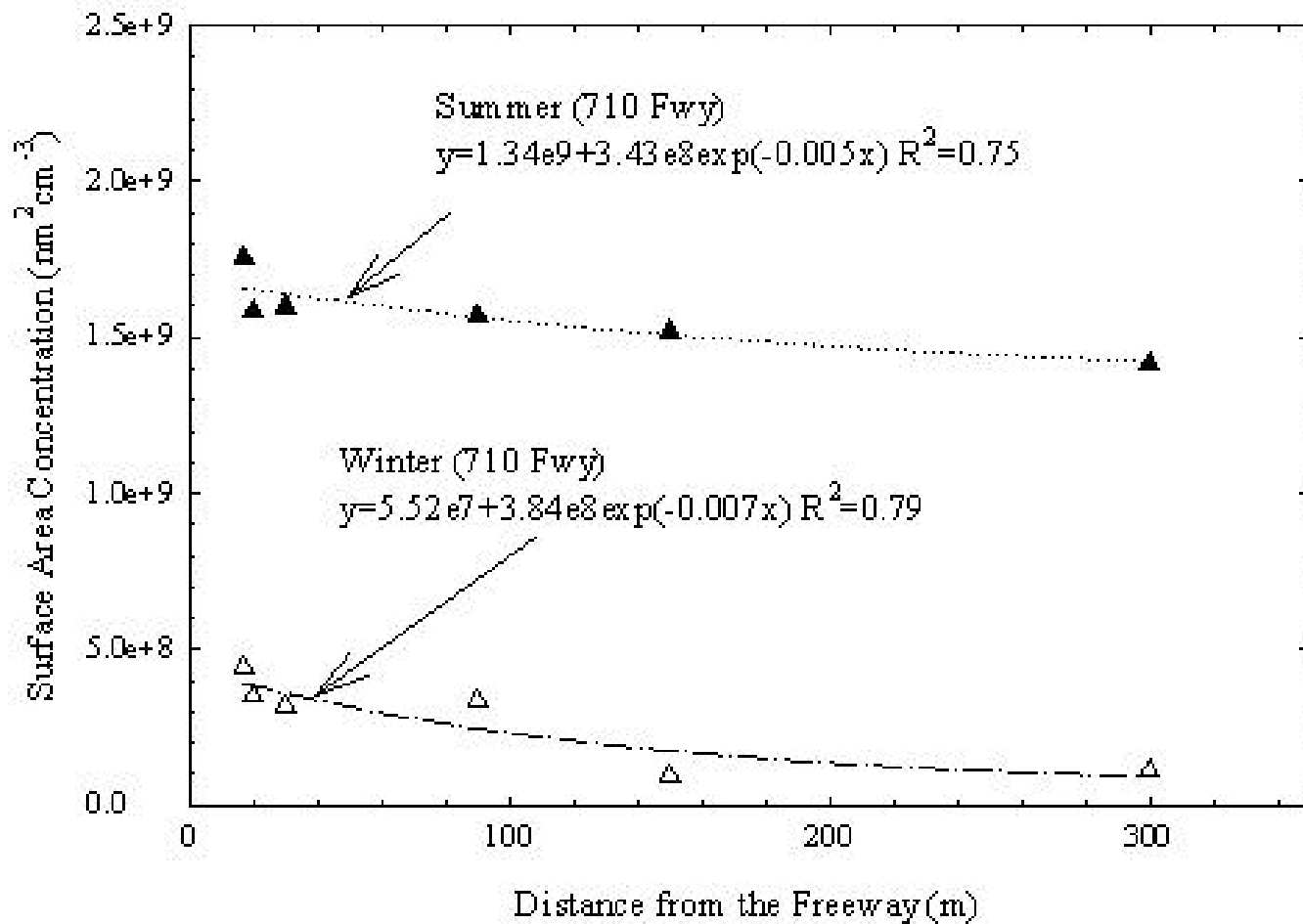


(b)



(a)

**Figure 4.** Comparison of decay of particle number concentrations in summer and winter in the size range of (a) 6-12 nm, (b) 12-25 nm, (c) 25-50 nm, (d) 50-100 nm, and (e) 100-200 nm near the 405 freeway.



**Increase of Particle Surface Area in Summer**

# Monitoring Particulate Matter in Community Air (Collaboration Between CARB and SCPCS)

## **CARB Staff:**

**Dane Westerdahl, Scott Fruin, Ken Bowers, and Steve Mara**

## **Overarching Concepts**

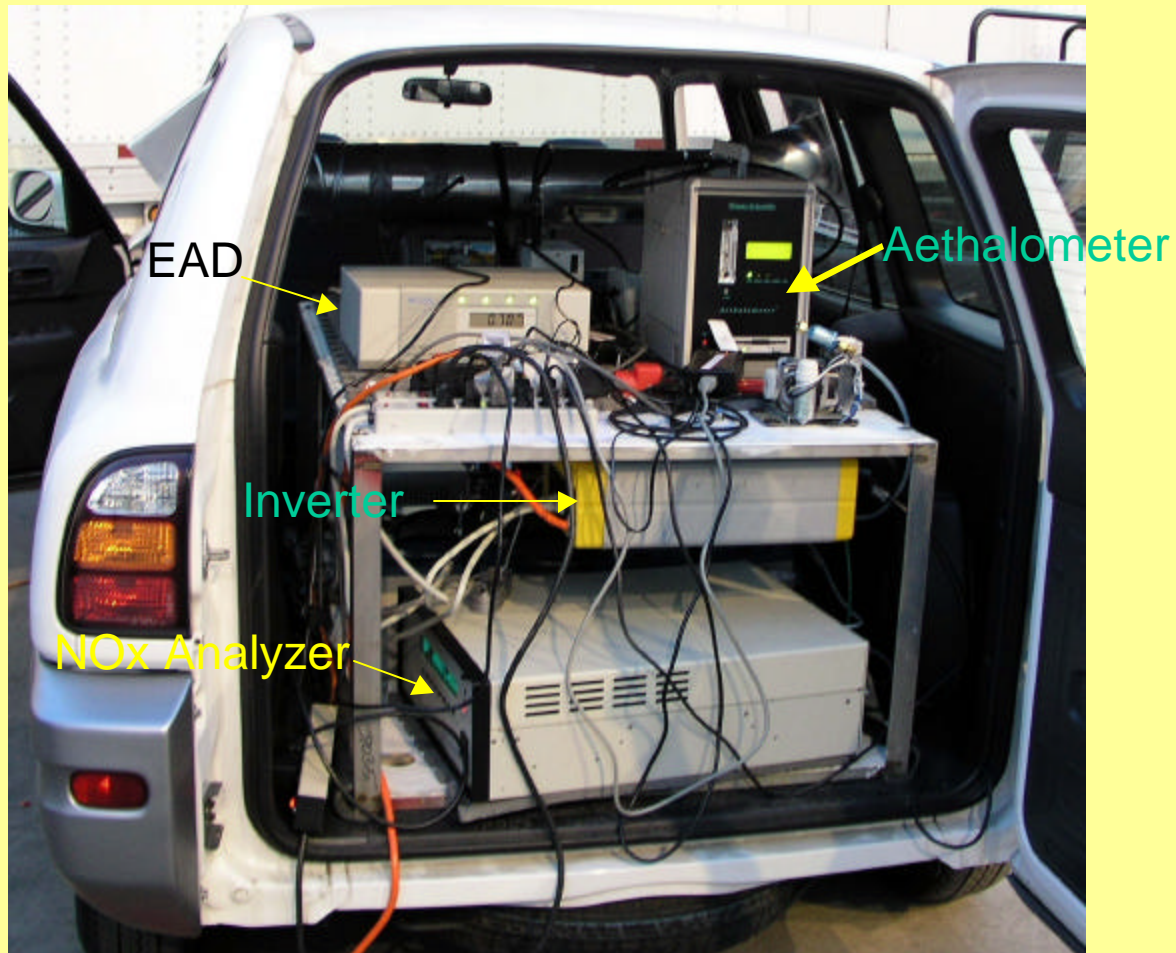
- People do not live at monitoring sites
- Fixed site monitors don't capture complexity of urban air pollution
- Fixed site monitoring does not measure many pollutants of concern

## **Objectives of Pilot Level Studies**

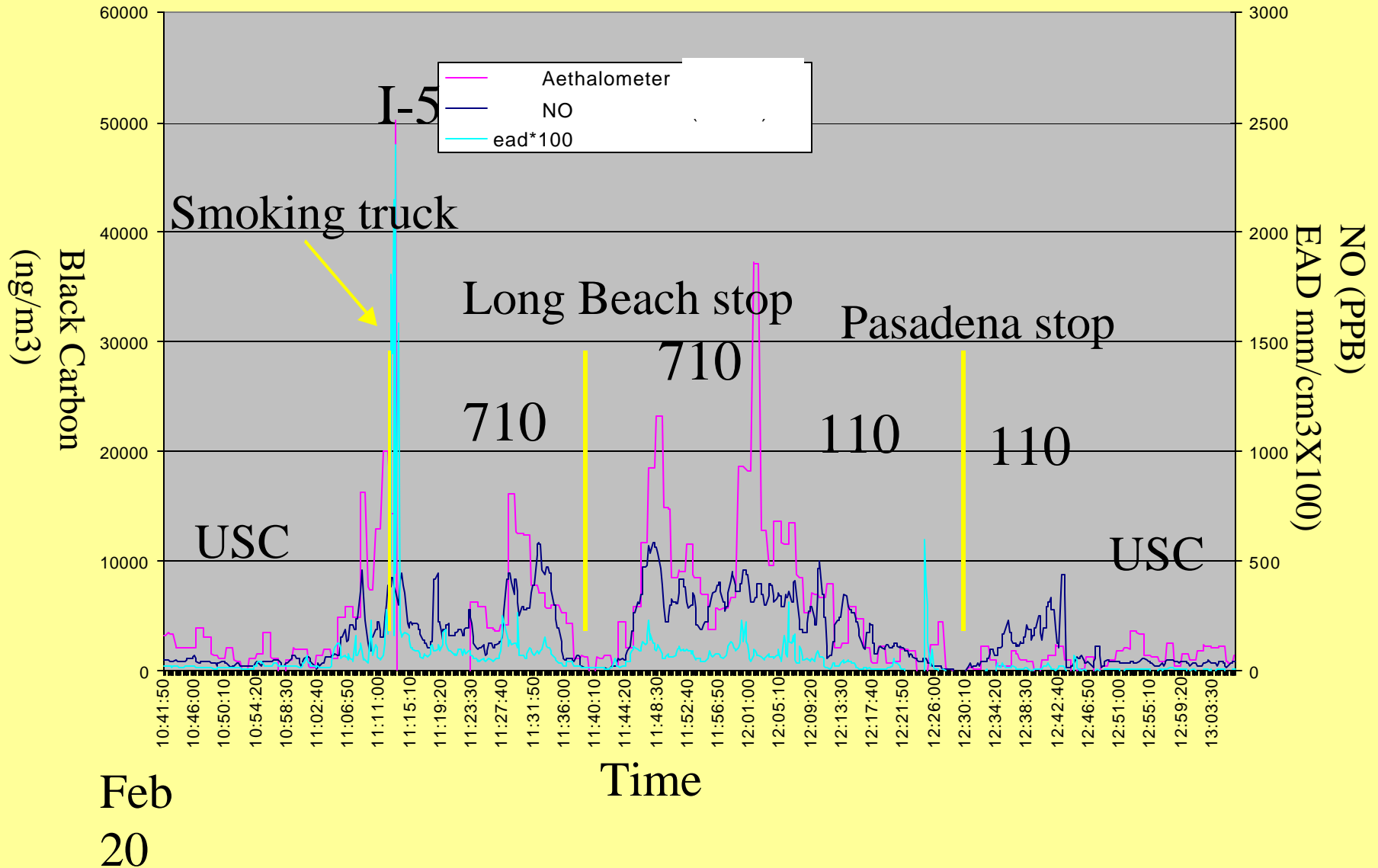
- Evaluate new methods to determine community exposures to fine and ultrafine PM and gases
- Compare observations with fixed site monitors
- Design future investigations



# Mobile Monitoring Project Electric RAV4 Instrumentation

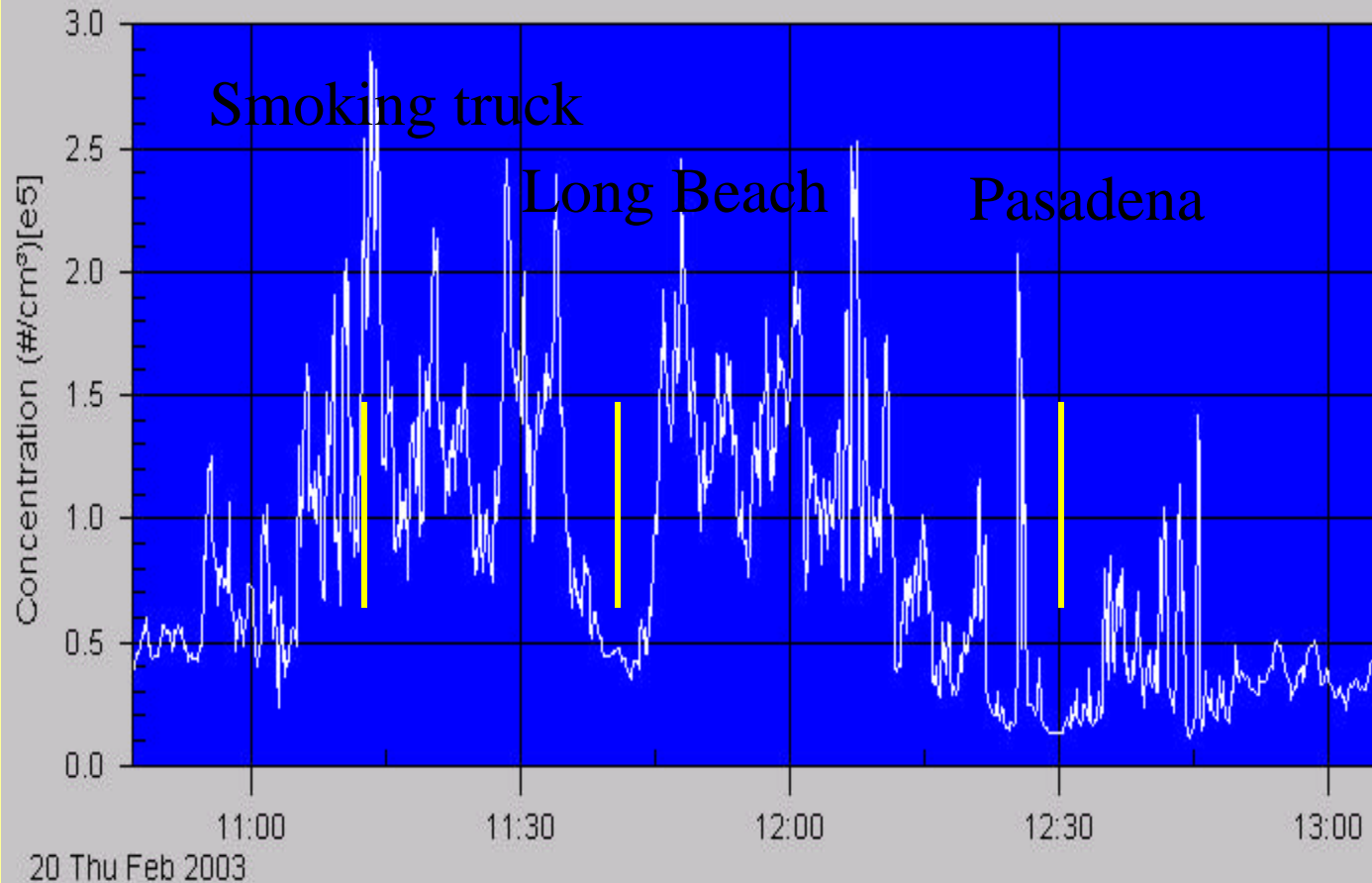


# Freeway Monitoring Aethalometer, NO, and EAD



# Freeway Monitoring

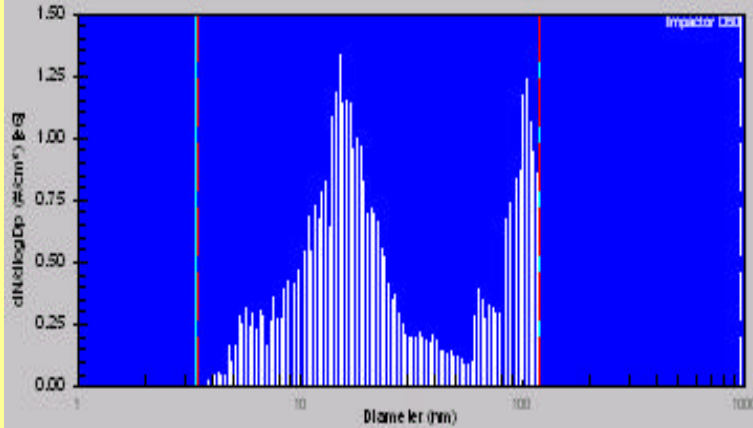
## Portable CPC 3007



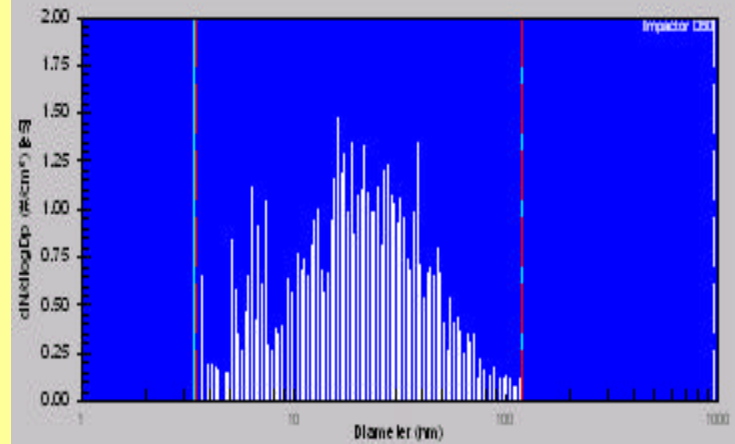
# Freeway and City Monitoring SMPS with Nano DMA

Feb. 20

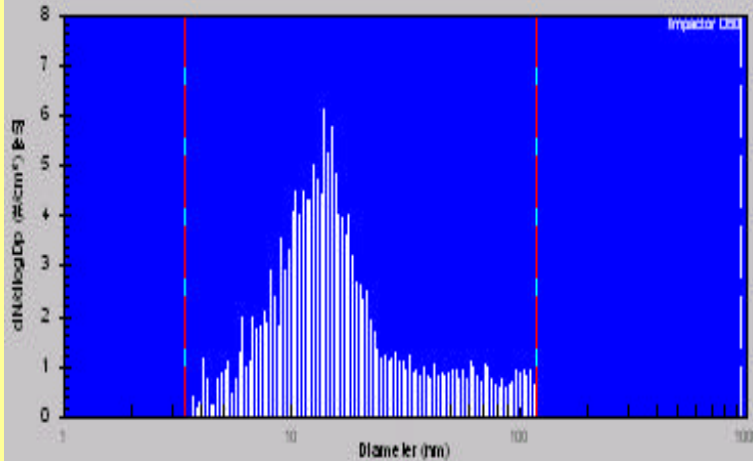
11:13 Smoking truck on 10



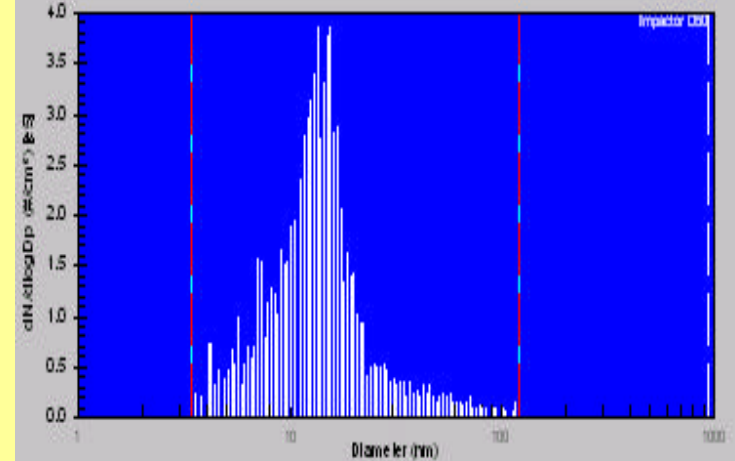
11:40 Long Beach Stop (urban)



12:02 710 Freeway (diesel)



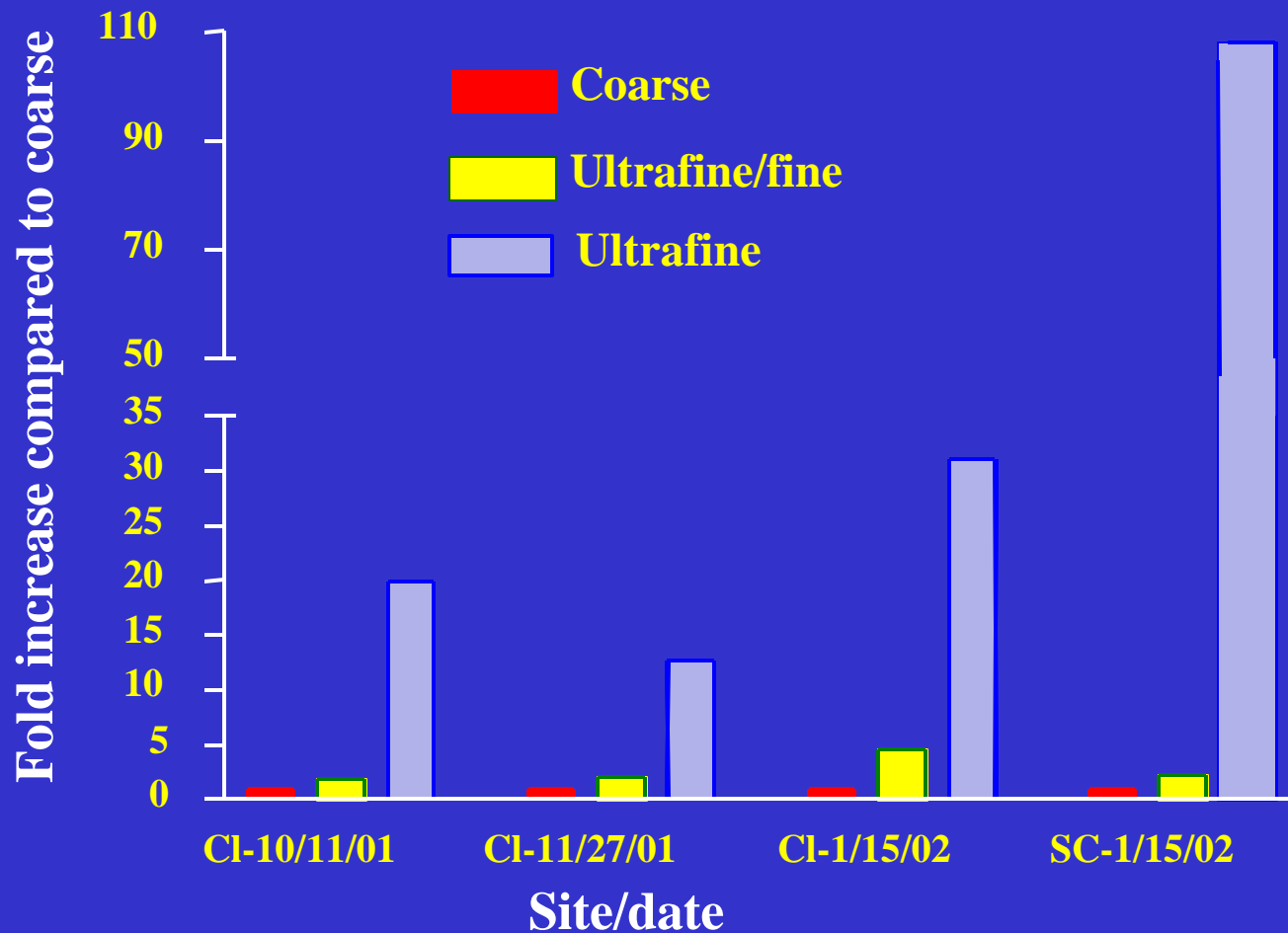
12:36 Pasadena 110 (gasoline only)



# Oxidative stress hypothesis

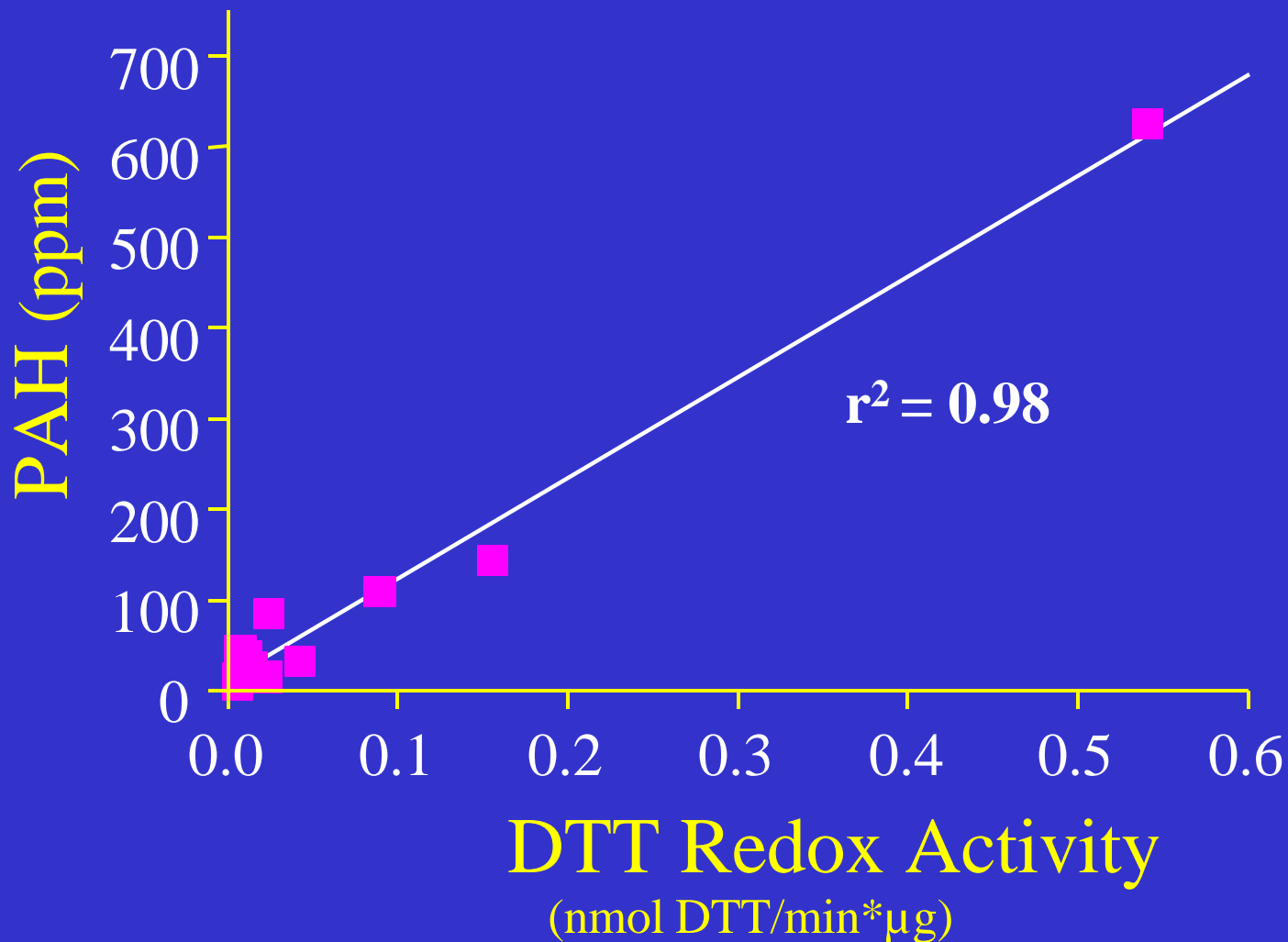
- Part of our SCPCS investigations focused on identifying PM components that induce **pulmonary inflammation** through the generation of **oxidative stress**
- We collected **coarse** (2.5-10  $\mu\text{m}$ ), **fine** (< 2.5  $\mu\text{m}$ ) and **ultrafine** (UFP) particles (< 0.15  $\mu\text{m}$ ) and examined their toxicity.
- **UFP were most potent** towards inducing cellular heme oxygenase 1 (HO-1) expression as an oxidative stress marker.
- This effect is directly correlated to the **high organic carbon and polycyclic aromatic hydrocarbon (PAH) content** of UFP.
- The PAH content of concentrated PM samples is a good surrogate for **redox cycling chemicals**, as demonstrated by electron transfer from **dithiothreitol (DTT)**.

# Redox Activity vs Fraction (Li et al., EHP, 2002)

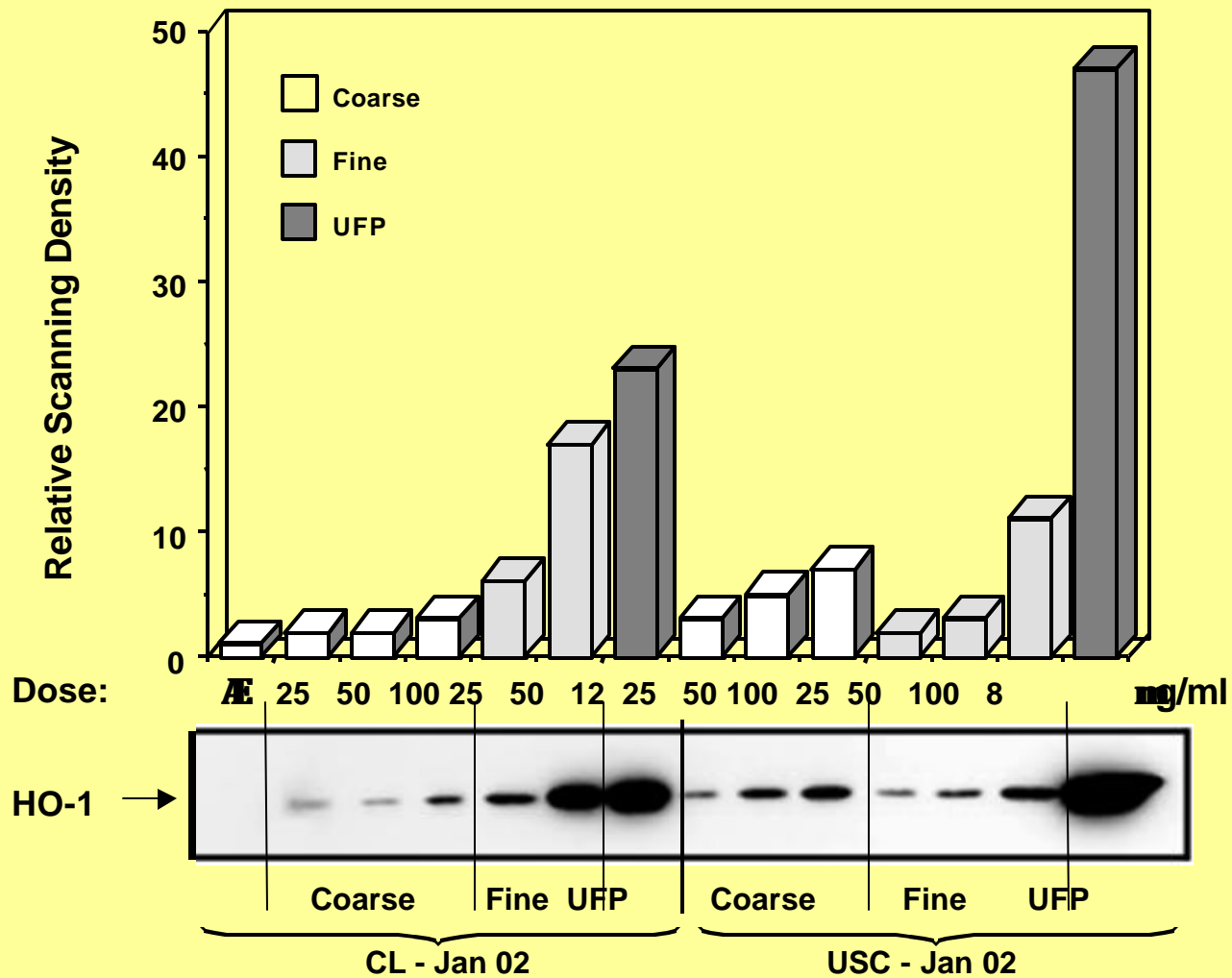


# Redox Activity vs Total PAH levels (Li et al., EHP, 2002)

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## UFP Induce Much Higher Oxidative Stress (Li et al., Env. Health Perspect., 2002)



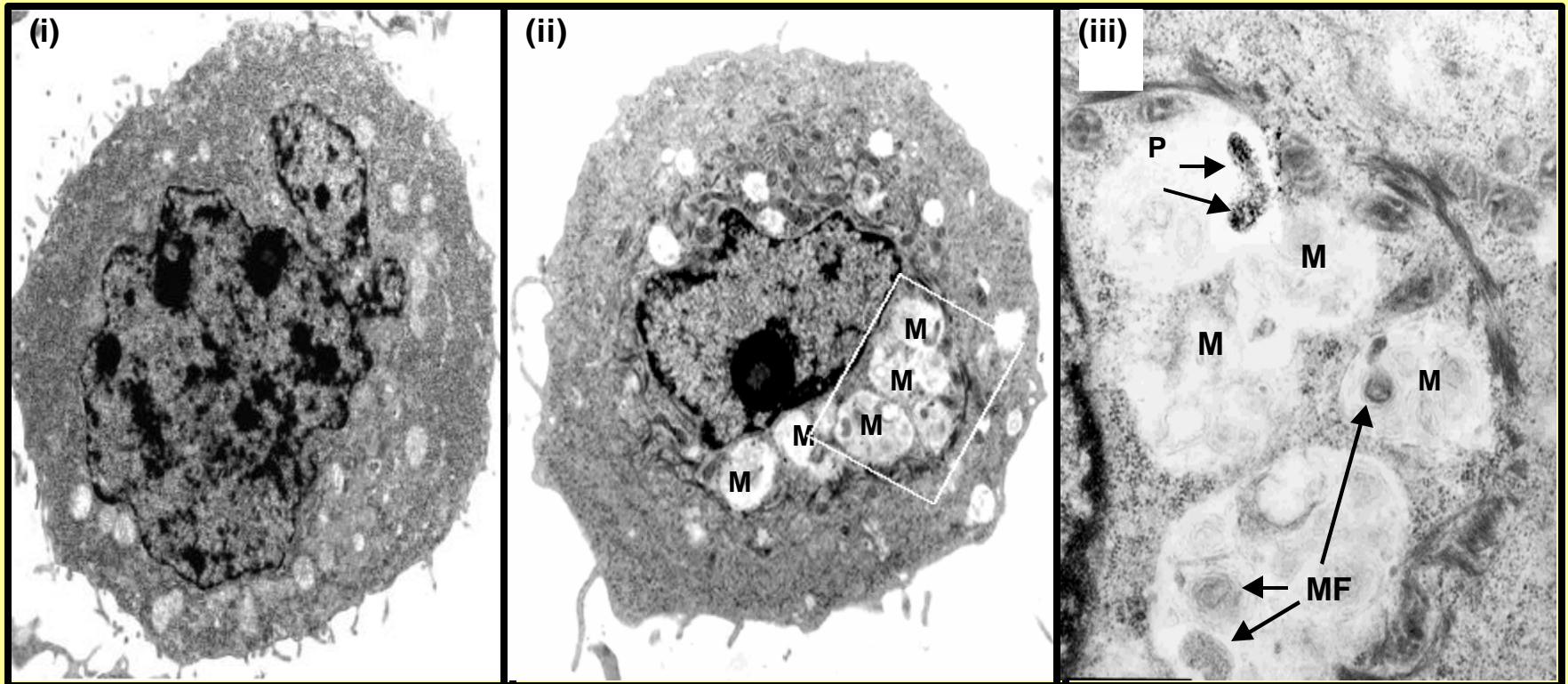


- **UFP localize in mitochondria** where they induce major structural damage.
- This contributes to **oxidative stress**.

Untreated Mag. x 8500

UFP Mag. x 8500

UFP Mag. x 85000



# Issues Related to the Diurnal, Spatial and Seasonal Characteristics of Individual Exposure to PM

Observations from our studies in LA which are (hopefully) applicable to other urban areas

$$PM_{\text{pers}} = PM_{\text{amb}} + PM_{\text{non amb}}$$

## Important Attributes of Ambient PM in Determining Where-When People Are Exposed

- **Local** (PM from specific sources)
- **Regional** (secondary PM; PM advected from source to receptor areas)
- **Volatile vs. Non – Volatile**
  - the concentrations of volatile PM of outdoor origin decrease substantially in indoor environments, especially in wintertime

- **Particle Decrease from freeway or busy road is a delicate balance between 2 mechanisms:**
  - **dilution** (affecting PM, CO and NO<sub>x</sub>)
  - **condensation-nucleation** (affecting PM only)
- **Summer:**
  - Dilution and mixing more pronounced in summertime
  - Concentrations **decrease more rapidly with distance from the road**
  - Particles grow faster to larger sizes by turbulent coagulation
- **Winter:**
  - Depressed mixing height preserves size distributions
  - Slower decay, **higher number concentrations (by a factor of 5 -10)**
  - Higher concentrations of **nuclei mode PM (3-10 nm)** even at distances ~ 150 away from road

### **Implication for Exposure Assessment- EPI studies**

- The concentrations of PM do not follow the same spatial, seasonal trends with CO and NO<sub>x</sub>
- **These gases cannot be used as surrogates of PM attributable to vehicular emissions**

# Effect of Season on PM Exposure from Our Studies in LA

## Cooler Season (Higher RH and Lower T)

- Increased Concentrations of PM from **Vehicles and Wood Smoke**
- Increased **Spatial Variability** in PM concentrations
- Much **higher particle number** concentrations
- High concentrations in **urban areas** and low concentrations in receptor sites
- **Finer PM** size – increased ultrafine fraction  
(indoor implications for dosimetry as well as outdoor- penetration)
- People spend **less time outdoors** and PM infiltration rates lower

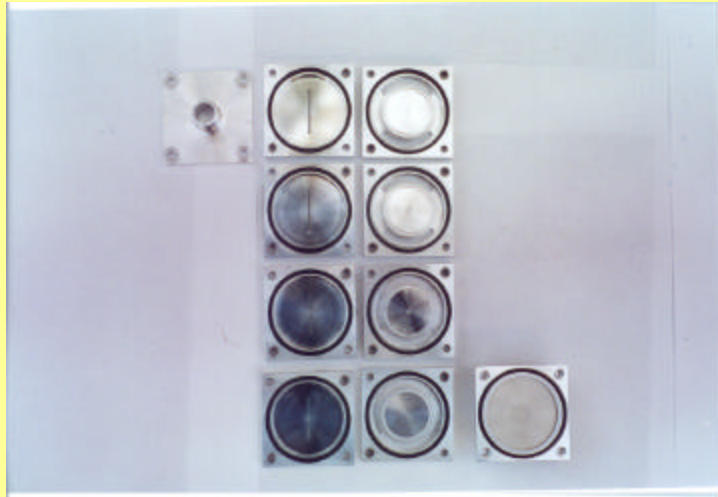
## Warmer Season

- Increased **secondary formation** of PM
- Increased **long-range transport** of PM from sources to receptors
  - More spatially homogenous distribution of PM
- Higher PM fraction in **accumulation** mode
- More time spent outdoors and (in the absence of A/C) more infiltration

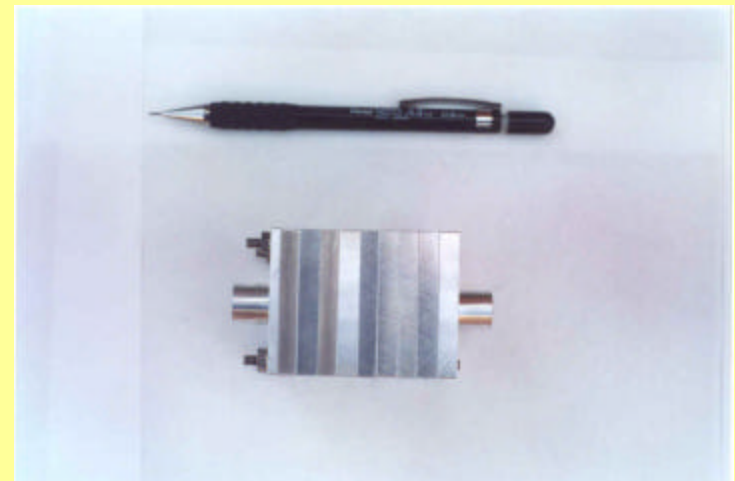
## Few concluding thoughts

- Rigorous Assessment of Contribution of **PM of Ambient Origin** to Personal Exposure is of Paramount Importance
- (Even more important) **assessment of PM from specific outdoor sources and formation mechanisms** to individual exposure
- Use of **Molecular Tracers-Signatures** of Specific Sources, Combined with **Advances in Personal PM Monitoring** to:
  - Understand the degree of the source contribution to personal exposure
  - Its dependence on season, proximity to source, home characteristics, individual activity patterns
  - (ideally) concurrent with panel studies as well as toxicological studies (CAP or other)
  - determine the effectiveness of reducing source emissions in protecting public health

Figure 4: Pictures of **Personal Cascade Impactor Sampler (PCIS)**



Misra et al., *Journal of Aerosol Science*, 33(7), 1027-1047, 2002



## USC Personal Cascade Impactor Sampler (PCIS)

- Classifies PM in 5 ranges at a flow of 10 LPM
  - 2.5 - 10; 1-2.5; 0.5 –1.0; 0.2 - 0.5; and ≤ 0.2  $\mu\text{m}$
- Used with a light, battery-operated personal pump
- 
- Combined with outdoor measurements and tracers of specific outdoor sources (i.e., vehicular emissions, photochemistry) allows us to determine the degree to which they contribute to personal exposures