ULTRAFINE PARTICLES

MEASUREMENT METHODOLOGIES AND ATMOSPHERIC DATA

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AQMD Meeting:

ULTRAFINE PARTICLES

The Science, Technology, and Policy Issues,

April 30, 2006

Summary:

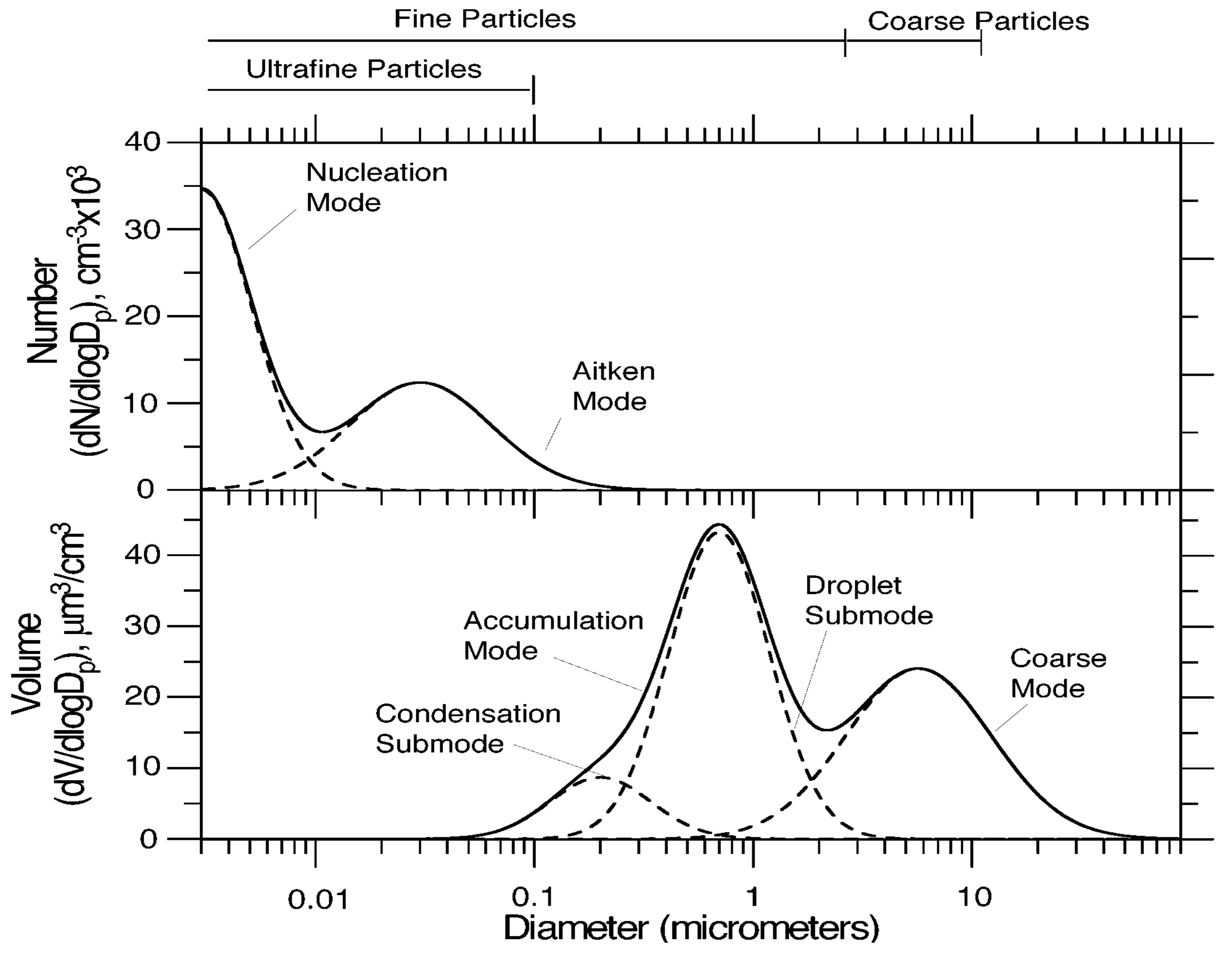
-Why Are We Interested in Ultrafine PM

-Technologies for measuring their physical , chemical and toxicological properties

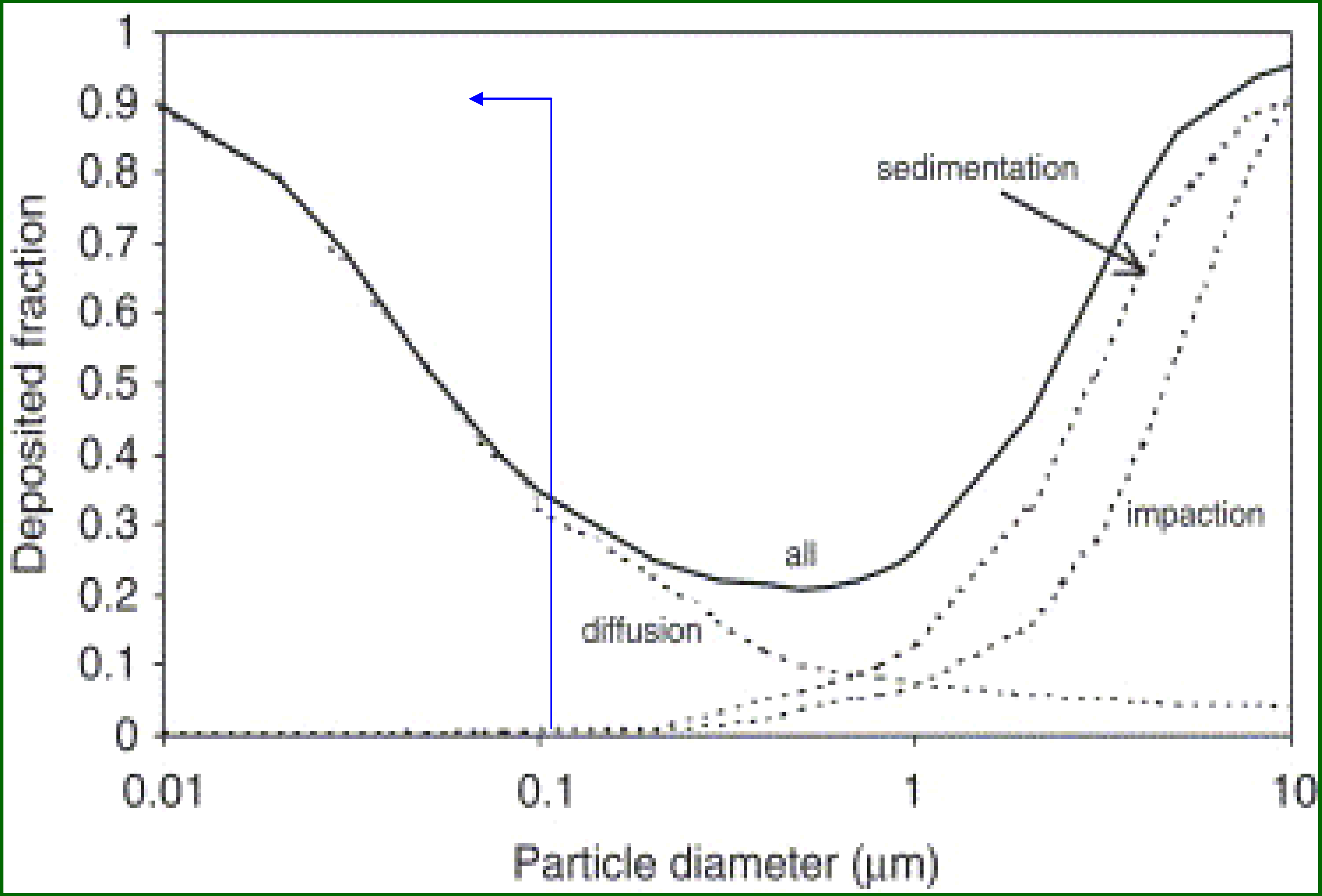
- What do we know (or do not) about their sources, and formation mechanisms in urban areas

-What do we know about the impact of new technologies in improving air quality

Why Are We Interested in Atmospheric Ultrafine PM



Ultrafine particle have a much higher deposition fraction in the lower lung than accumulation mode PM.



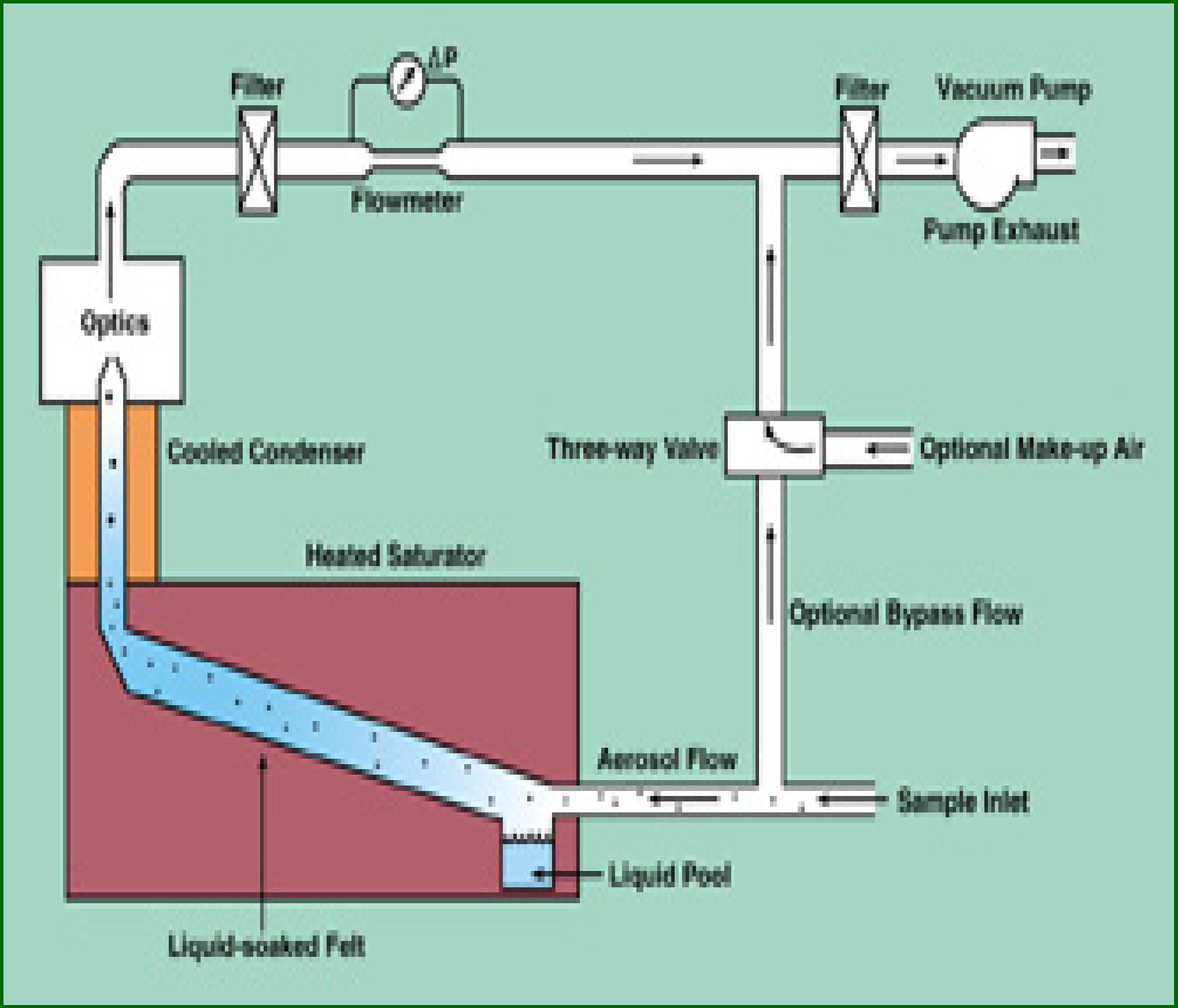
Overview of our Work
Air Pollution, Particulate Matter and Health Effects

- 9 million drivers daily
- 500,000 diesel trucks
- 5th busiest airport in world
- biggest US harbor

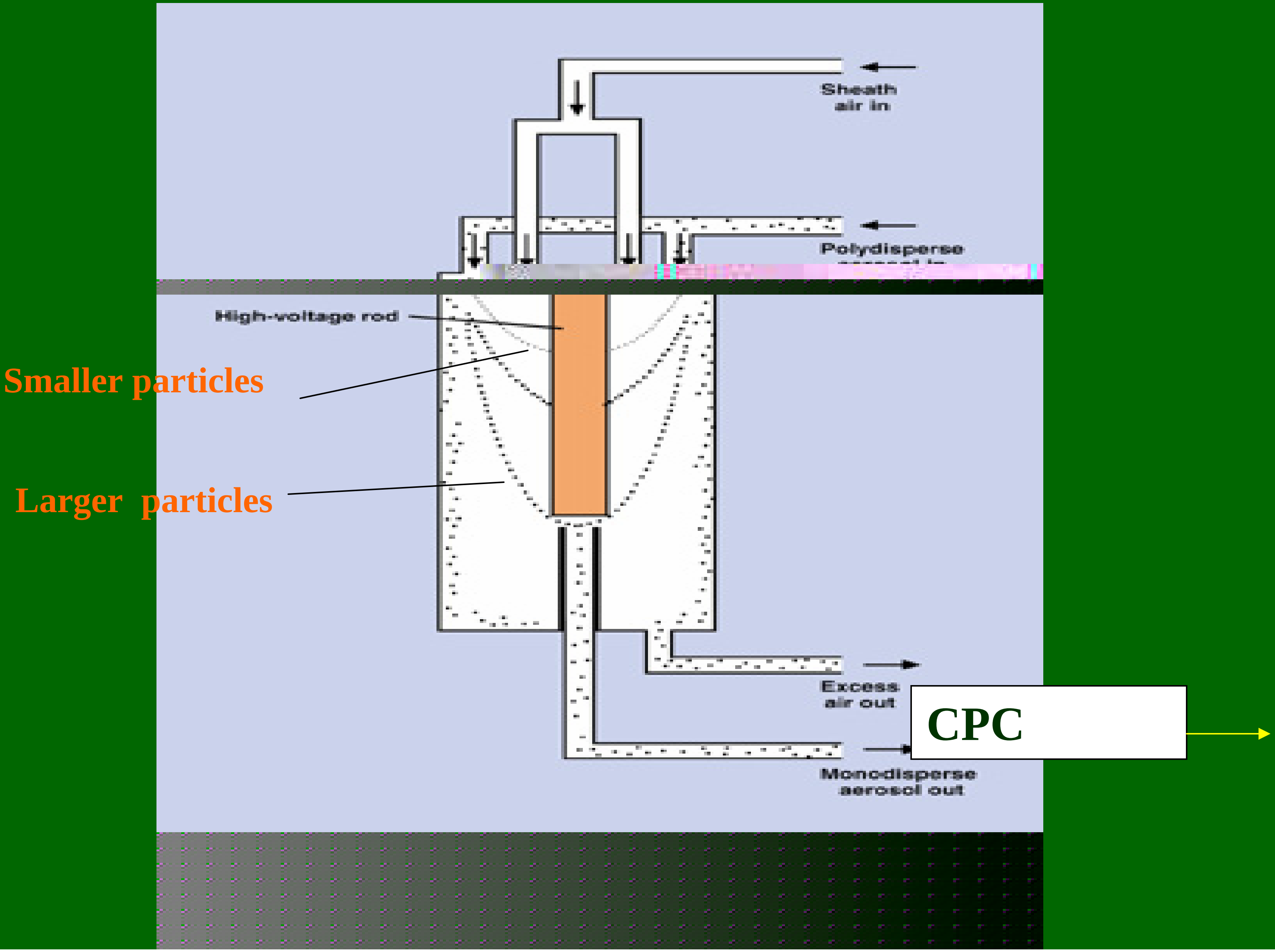
- Continuous Monitors for:
  - Particle Size Distribution
  - Mass and Surface Area
  - Chemical Composition
- Time Integrated Monitors for:
  - Size Distribution
  - Mass
  - Chemical Composition
- Particle Concentrator Technologies for High Volume Collection for Toxicological In Vitro and In Vivo Studies
- Personal Ultrafine Particle Samplers

Condensation Particle Counter (TSI 3022)

Number Concentration Measurements



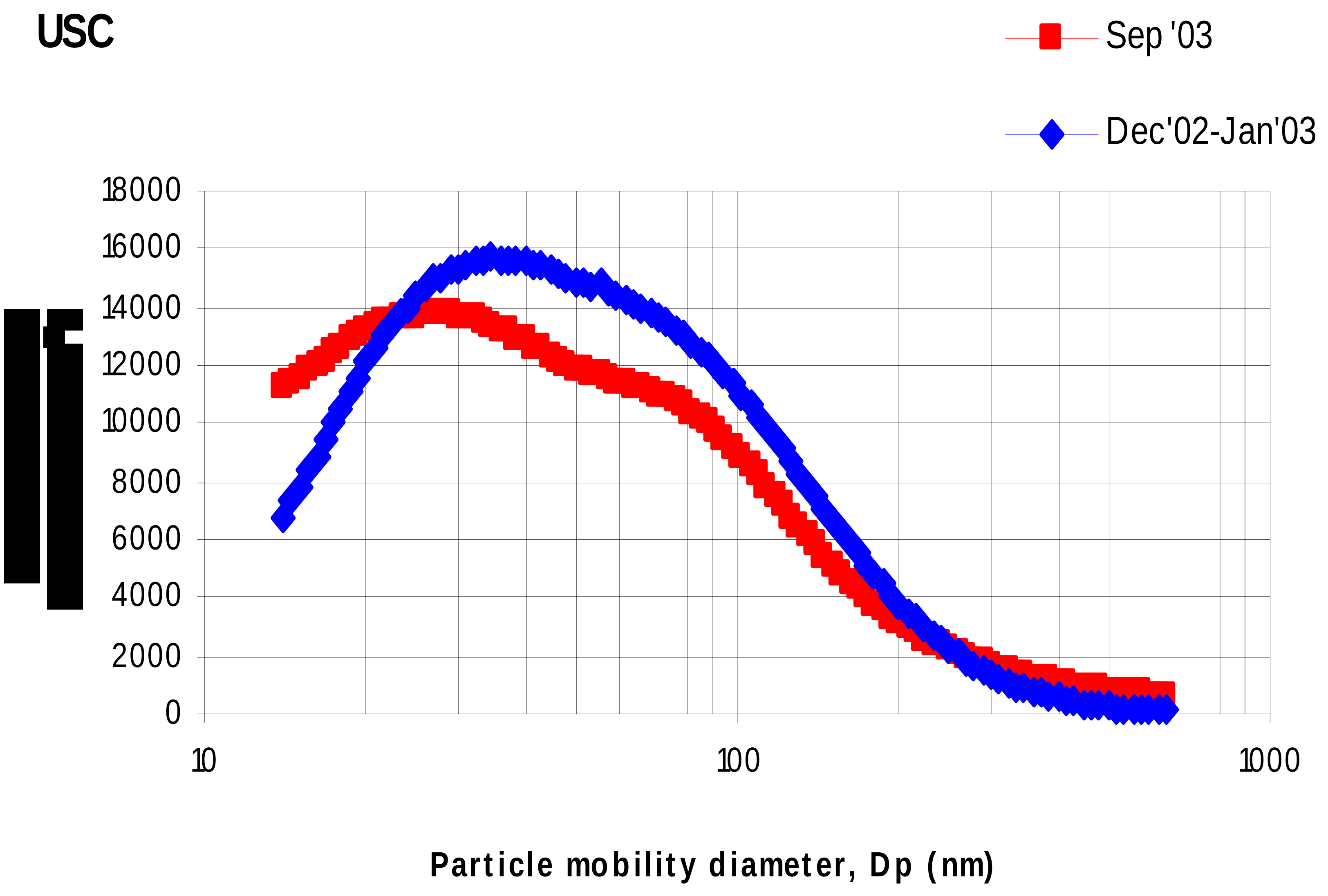
Scanning Mobility Particle Sizer (TSI 3936)



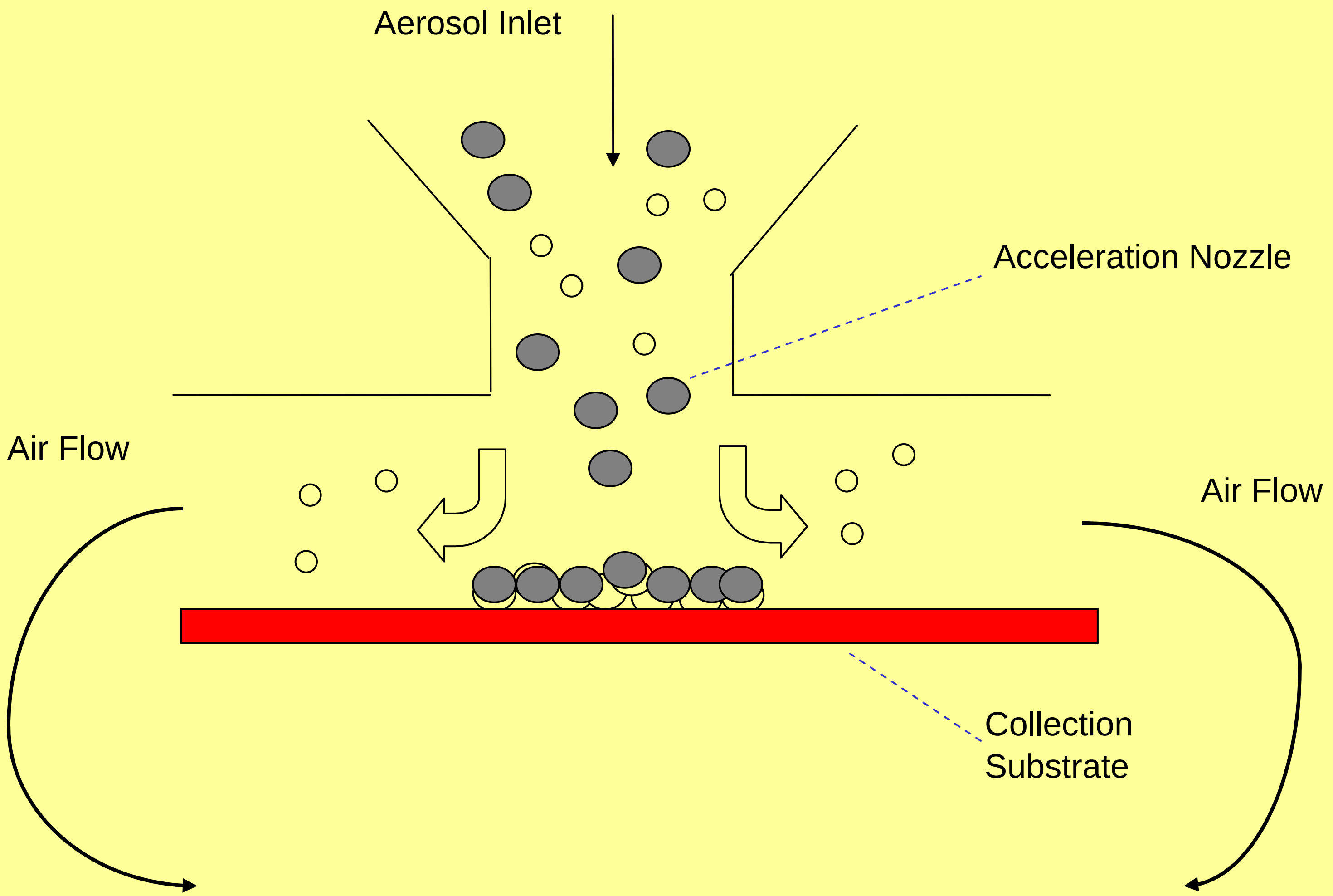
Smaller particles

Larger particles

CPC


USC
Sep '03
Dec'02-Jan'03
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
10
100
1000
Particle mobility diameter, Dp (nm)

Schematic of an Impactor

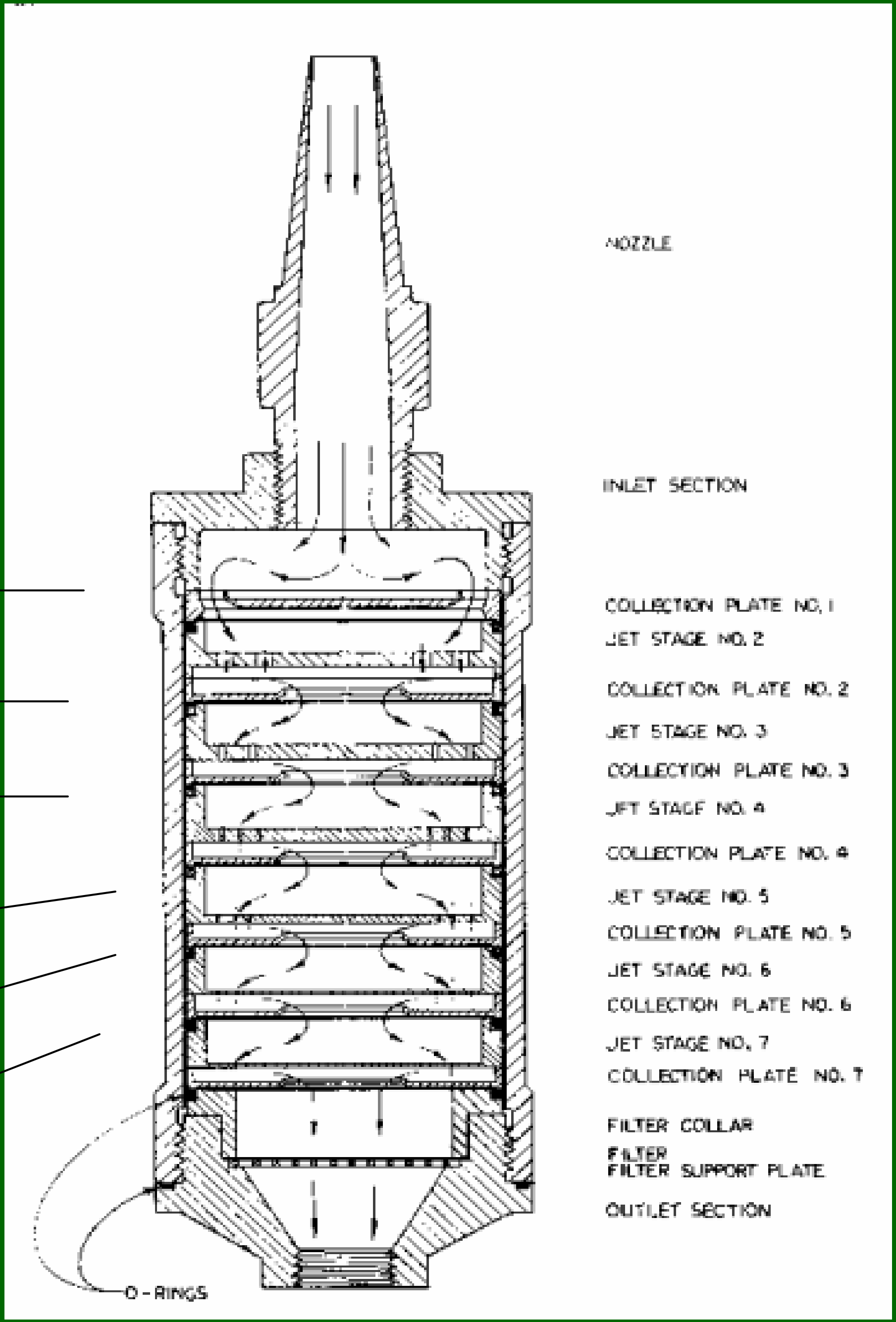


NanoMOUDI Cascade Impactor (MSP Corp.,

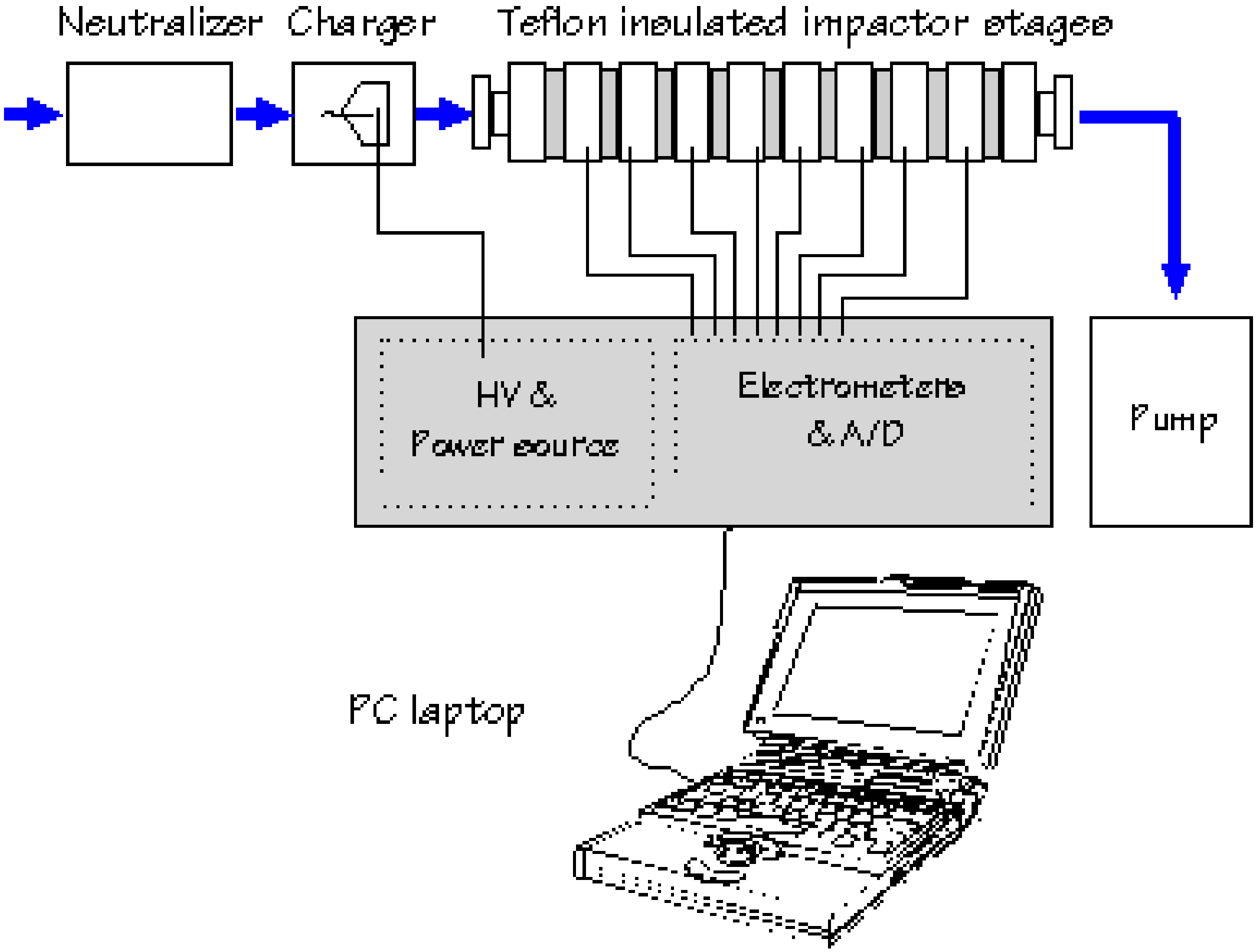
Geller, et al. *Aerosol Science and Technology*, 36(6): 748-763, 2002

Cutpoint

Stage 2	0.18 µm
Stage 3	0.10 µm
Stage 4	0.056µm
Stage 5	0.032 µm
Stage 6	0.018 µm
Stage 7	0.010 µm



Electrical Low Pressure Impactor (Dekati Instruments)



UC Davis Real Time Mass Spectrometer

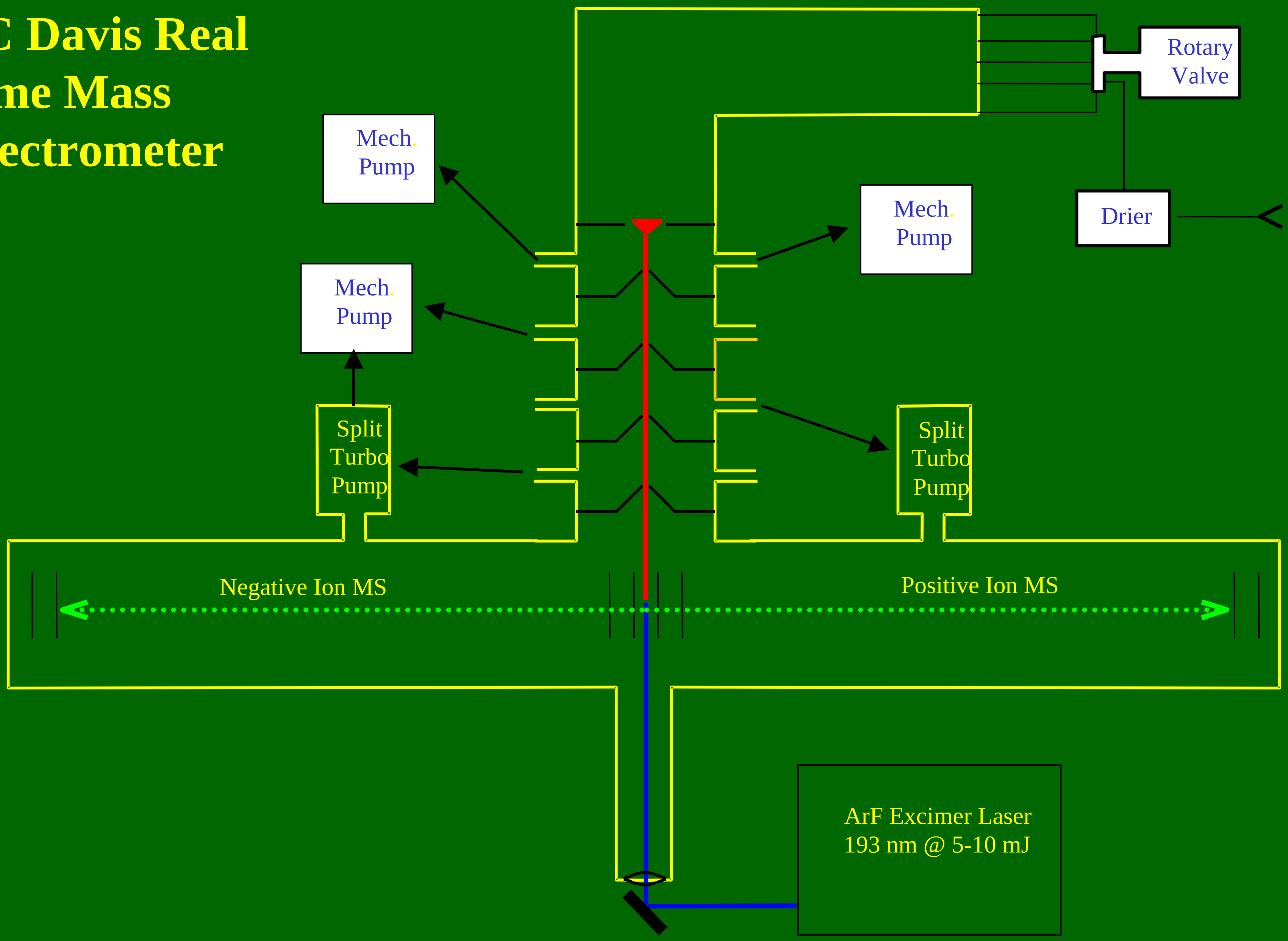


Figure 1. RSMSIII design for the Pittsburgh and Baltimore Supersites.

Concentration Enrichment To Increase Sampling Efficiency of Ultrafine PM Samplers

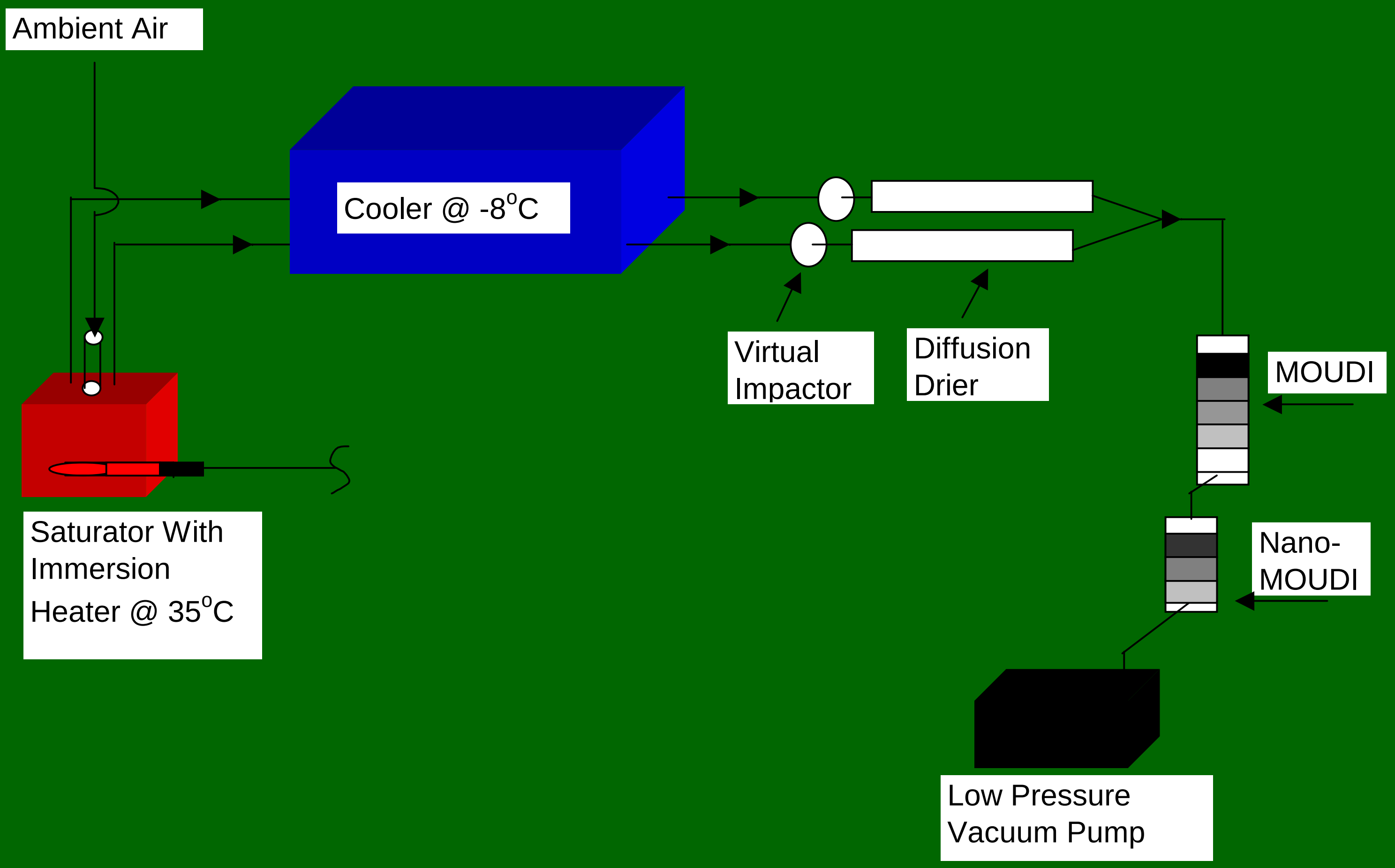


Figure 1. USC Ultrafine Concentrator/Nano-MOUDI System

Ambient Air

Cooler @ -8°C

Virtual Impactor

Diffusion Drier

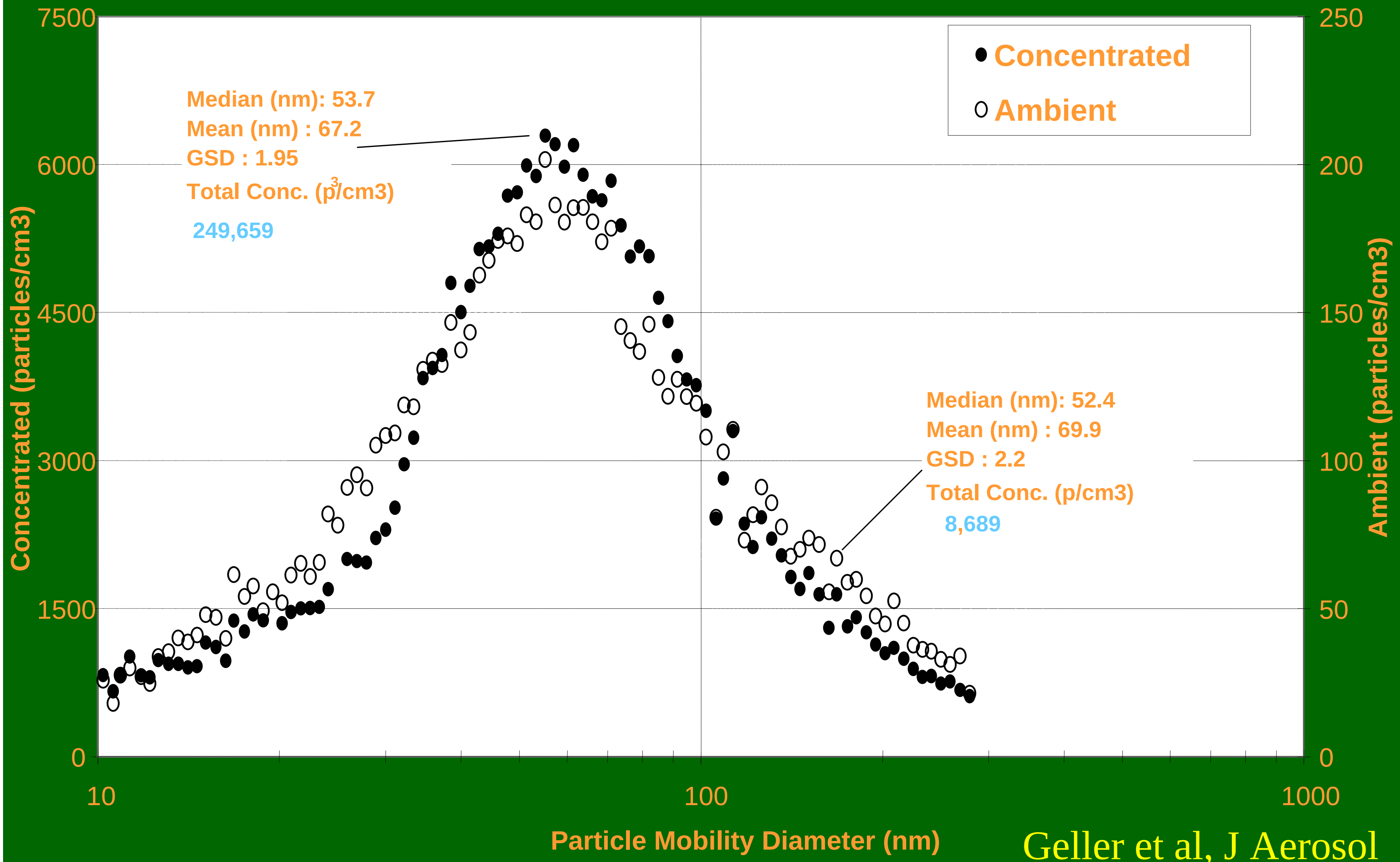
MOUDI

Nano-MOUDI

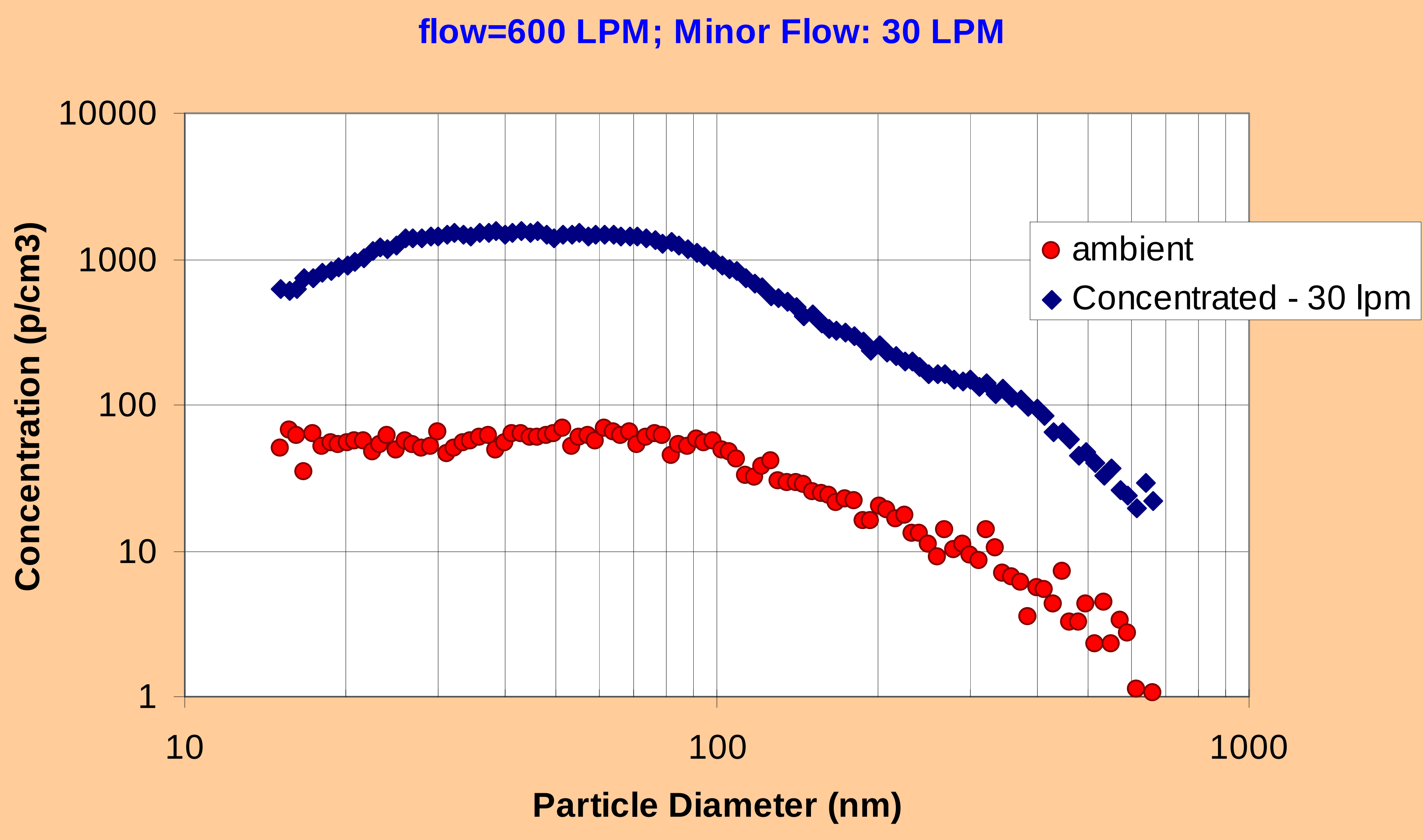
Saturator With Immersion Heater @ 35°C

Low Pressure Vacuum Pump

Averaged ambient and concentrated outdoor aerosol size distributions at USC.
major flow = 30 lpm, minor flow: 1 lpm)

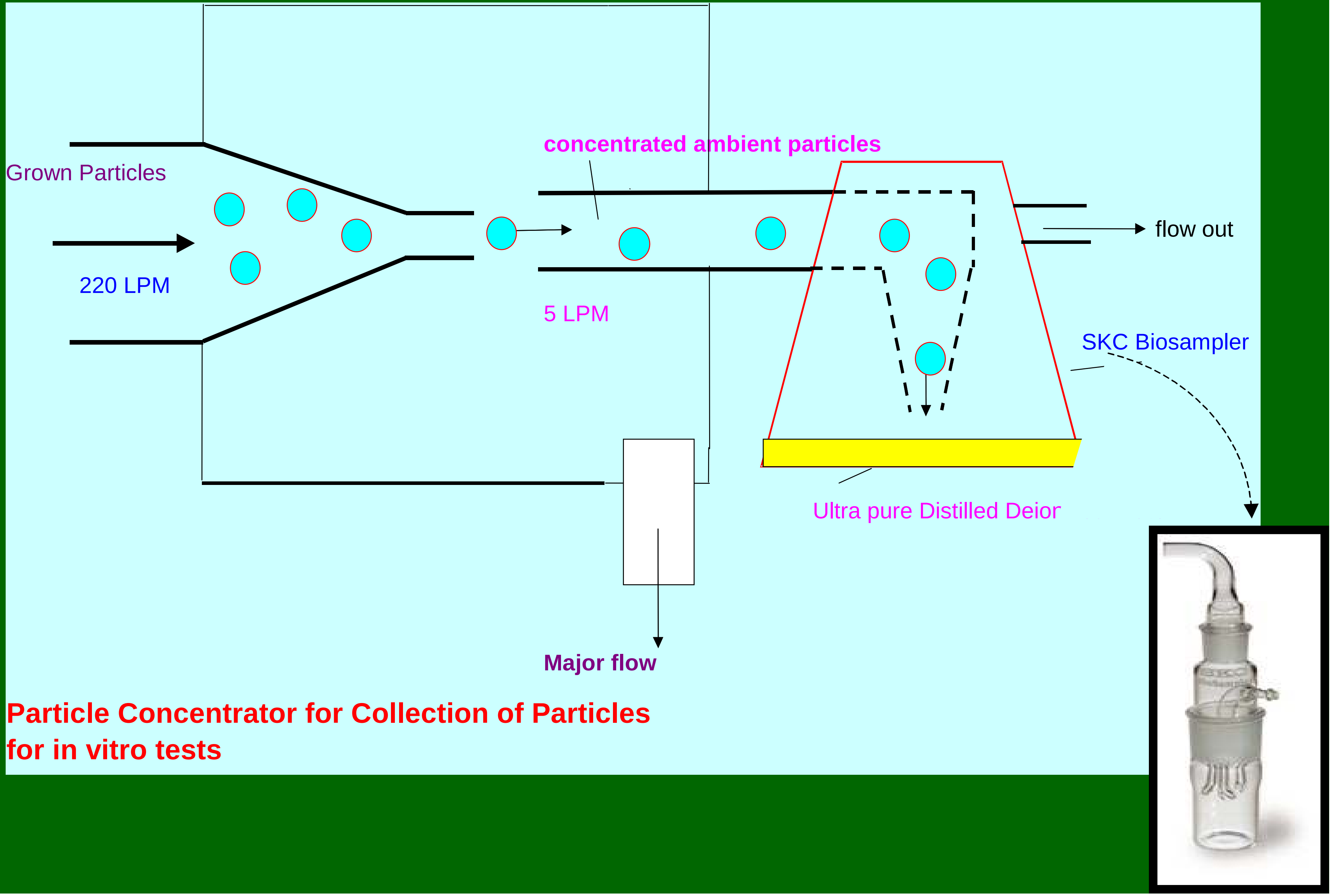


Geller et al, J Aerosol Science, 2005



Misra et al *Aerosol Science and Technology*, 2002.

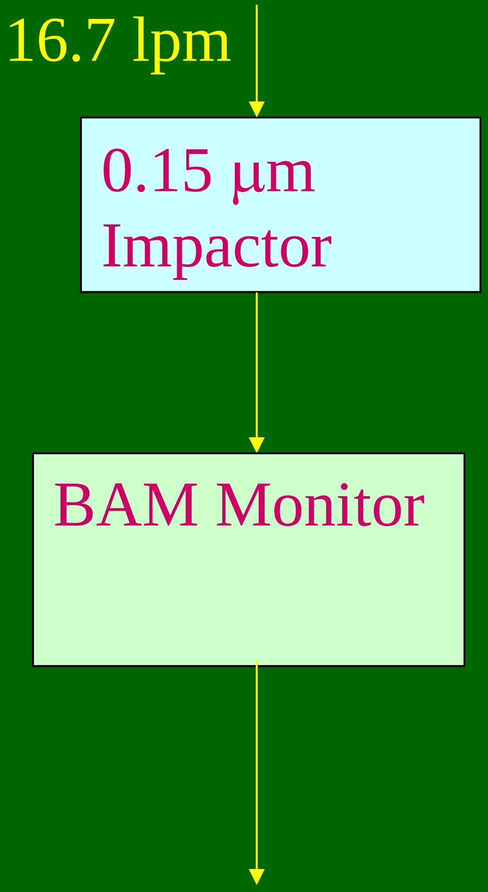
Concentrator – BioSampler Tandem



Particle Concentrator for Collection of Particles for in vitro tests

Near Continuous Ultrafine Mass Concentration Monitor

(Chakrabarti et al., *Aerosol Science and Technology*, 2002



16.7 lpm

0.15 µm Impactor

BAM Monitor

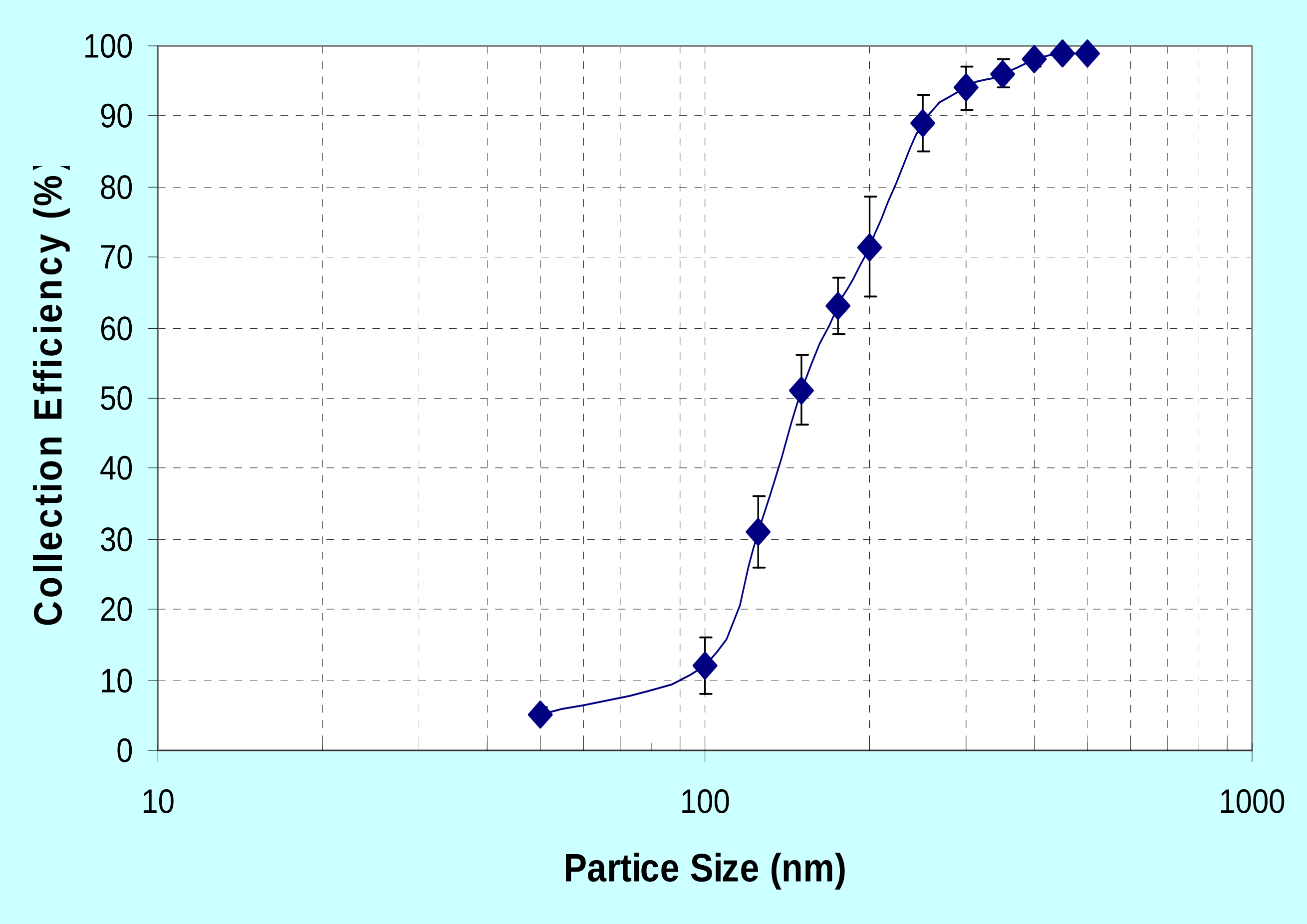
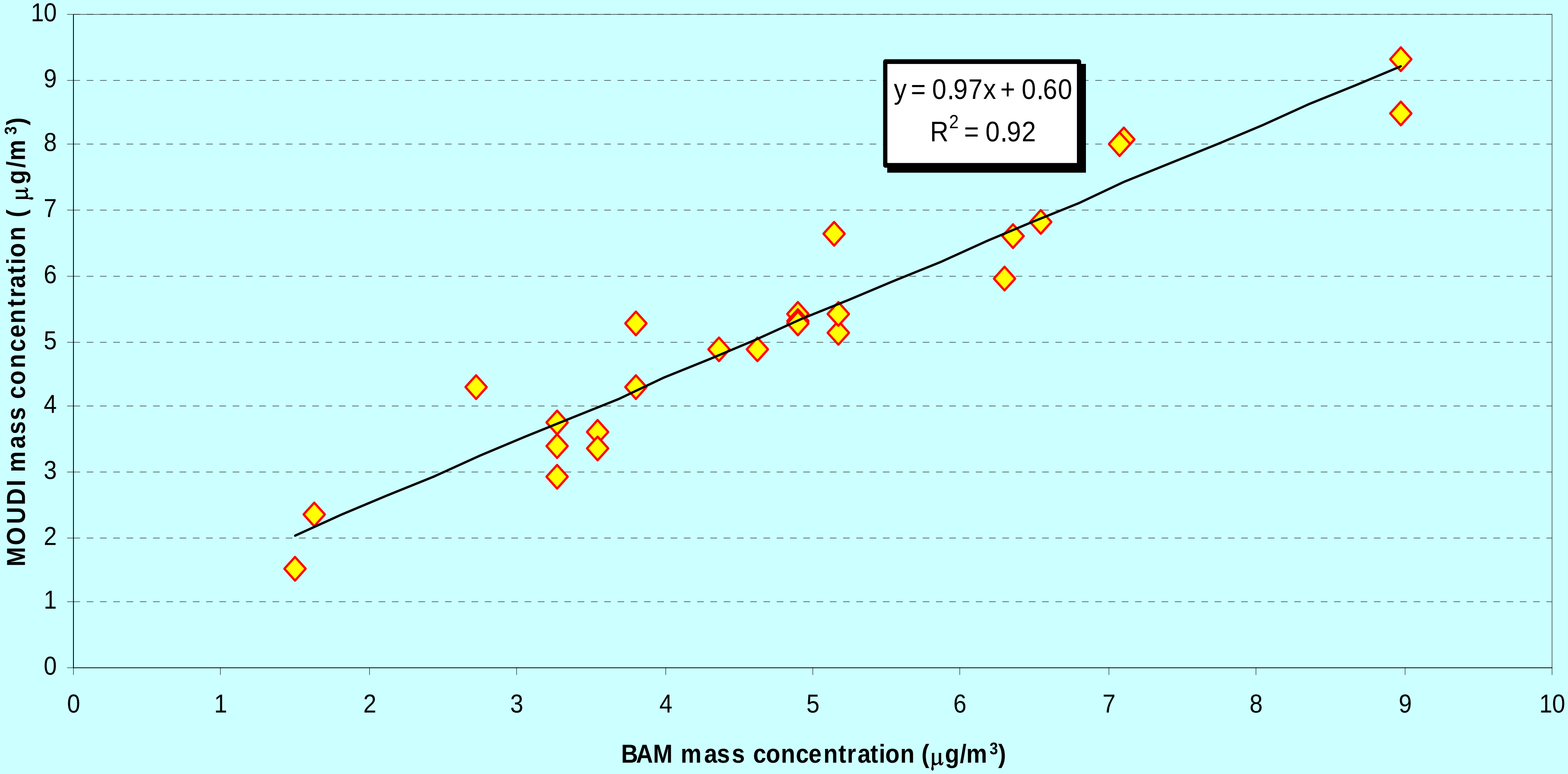
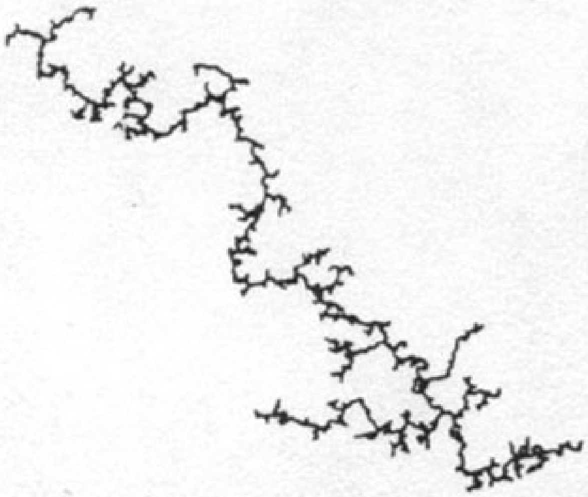


Figure 2. BAM vs. MOUDI Ultrafine PM concentration



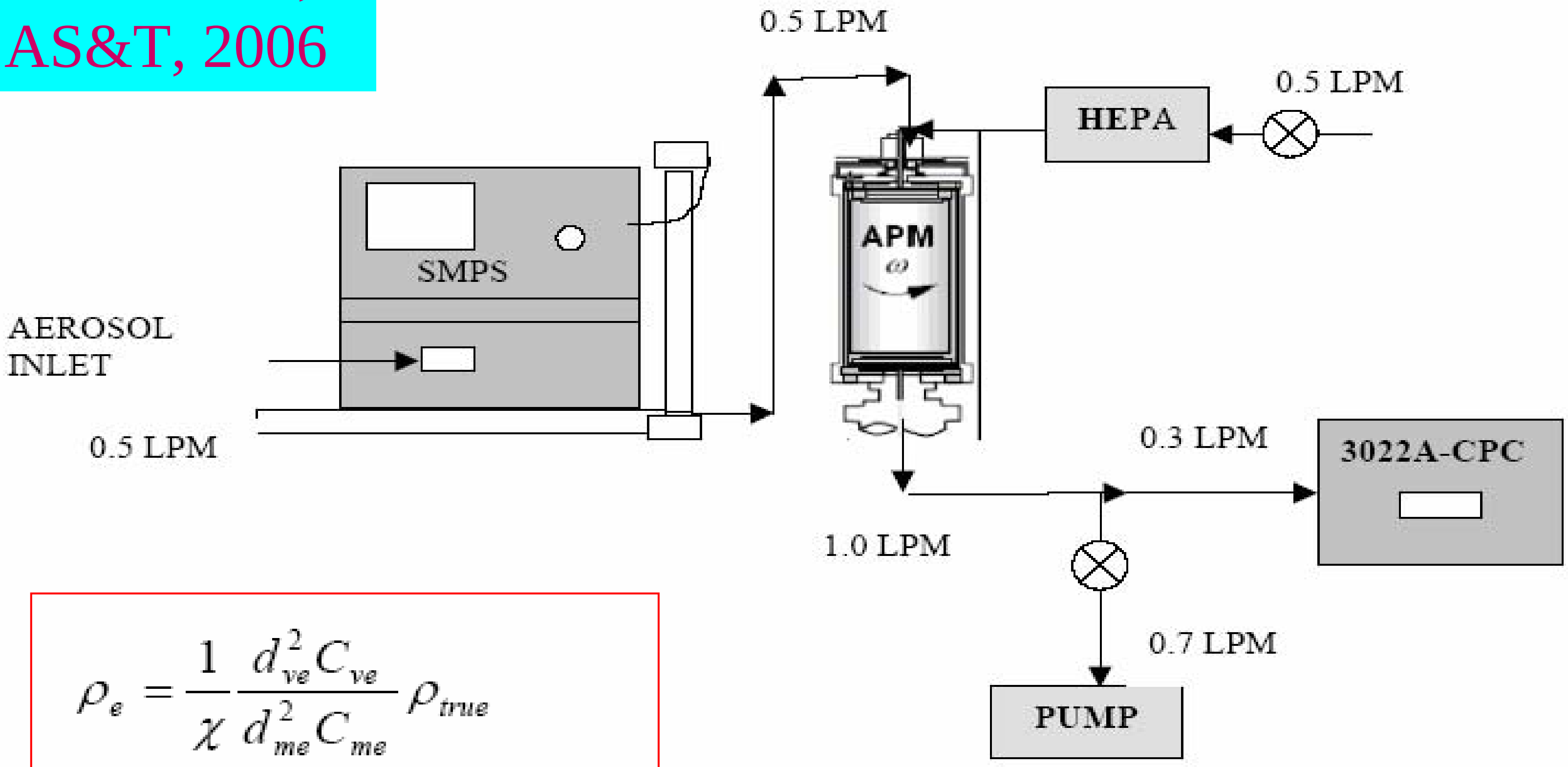
$D_f = 2.50$



$D_f = 1.80$

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

Geller et al., AS&T, 2006



$$\rho_e = \frac{1}{\chi}\frac{d_{ve}^2 C_{ve}}{d_{me}^2 C_{me}}\rho_{true}$$

FIGURE 1. Schematic diagram of DMA-APM set-up

where ρ_e is the effective density, X is dynamic shape factor, d_{ve} is the volume equivalent diameter, d_{me} is the mobility equivalent diameter, C is the Cunningham correction factor, and ρ_{true} is the bulk density of the material (McMurry et al., 2002).

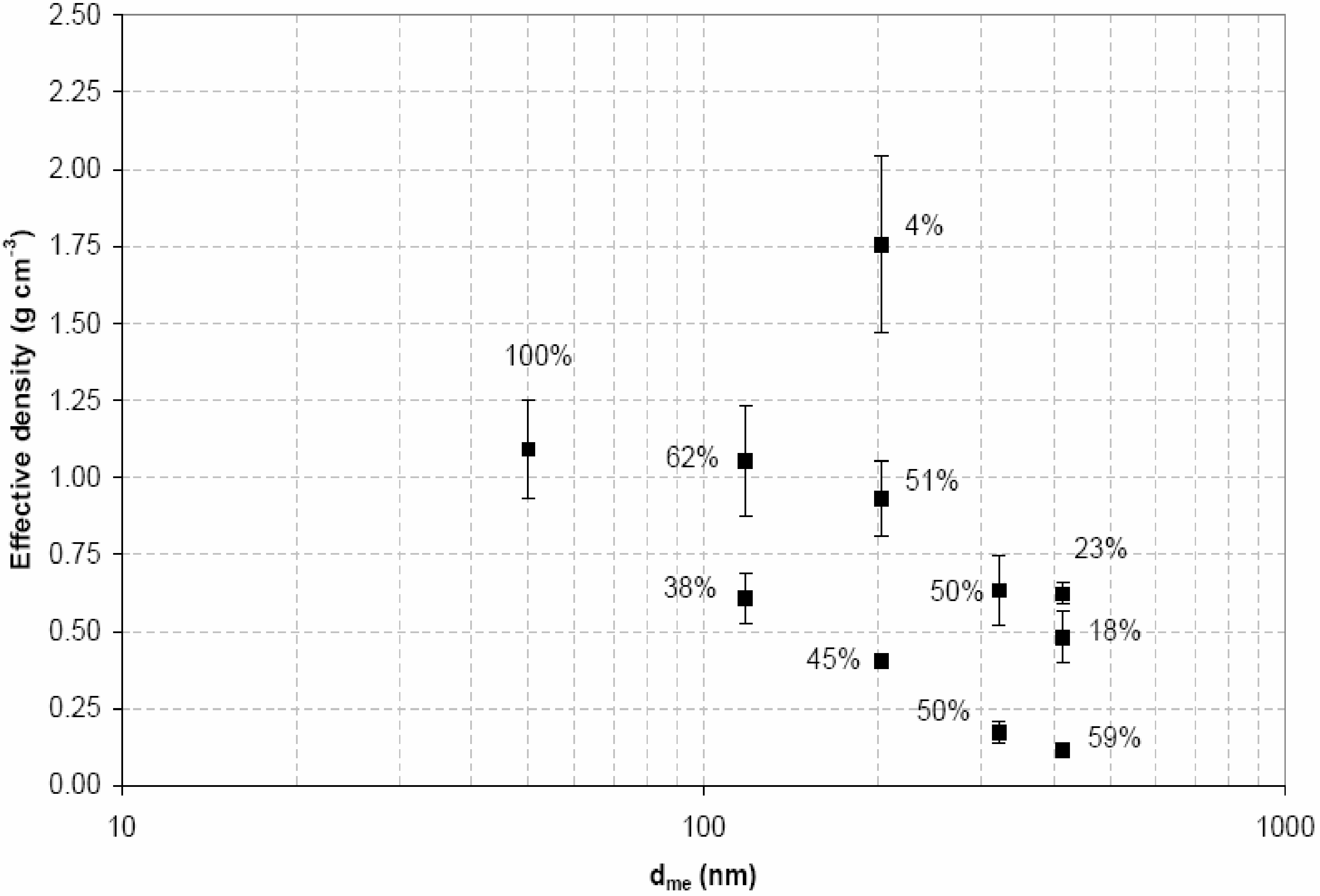


Figure 7. Effective density variation with respect to particle mobility diameter at I-710. Data labels indicate percentage of number concentration measured for each particle size with respective effective density.

Geller et al., AS&T, in press, 2006

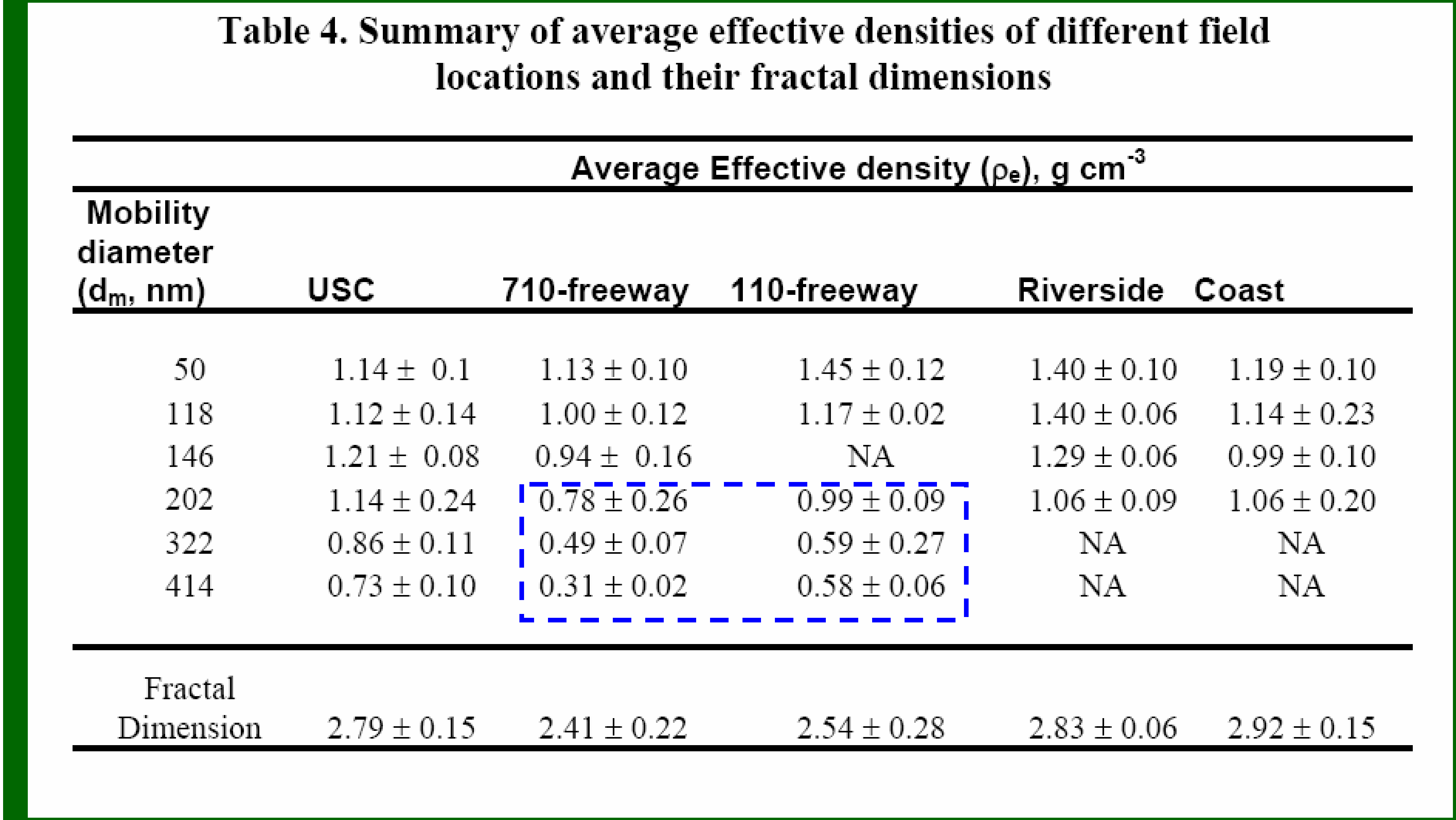


Table 4. Summary of average effective densities of different field locations and their fractal dimensions

	Average Effective density (ρ_e), g cm^{-3}				
Mobility diameter (d_m, nm)	**USC**	**710-freeway**	**110-freeway**	**Riverside**	**Coast**
50	1.14 ± 0.1	1.13 ± 0.10	1.45 ± 0.12	1.40 ± 0.10	1.19 ± 0.10
118	1.12 ± 0.14	1.00 ± 0.12	1.17 ± 0.02	1.40 ± 0.06	1.14 ± 0.23
146	1.21 ± 0.08	0.94 ± 0.16	NA	1.29 ± 0.06	0.99 ± 0.10
202	1.14 ± 0.24	0.78 ± 0.26	0.99 ± 0.09	1.06 ± 0.09	1.06 ± 0.20
322	0.86 ± 0.11	0.49 ± 0.07	0.59 ± 0.27	NA	NA
414	0.73 ± 0.10	0.31 ± 0.02	0.58 ± 0.06	NA	NA
Fractal Dimension	2.79 ± 0.15	2.41 ± 0.22	2.54 ± 0.28	2.83 ± 0.06	2.92 ± 0.15

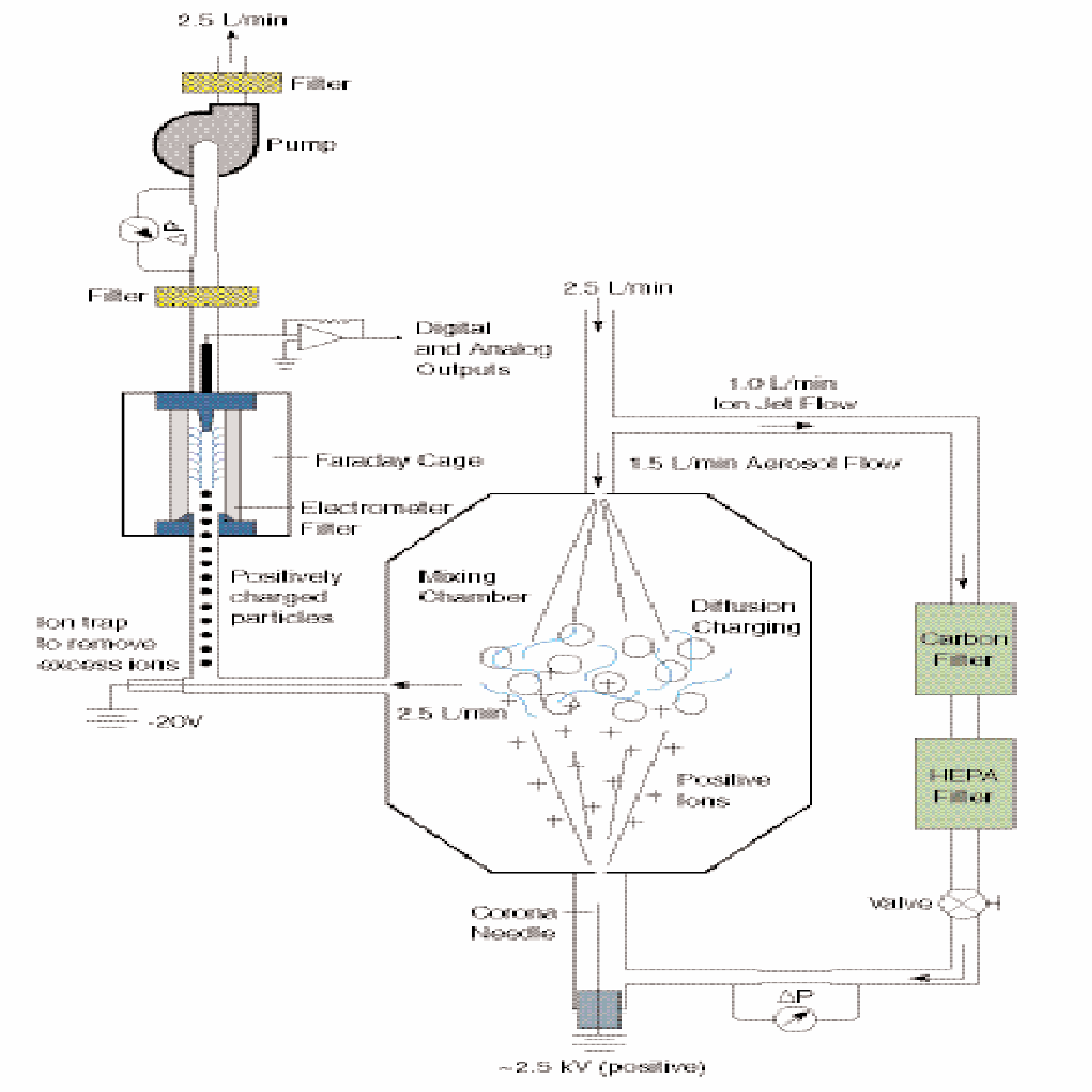
Geller et al., AS&T, in press, 2006

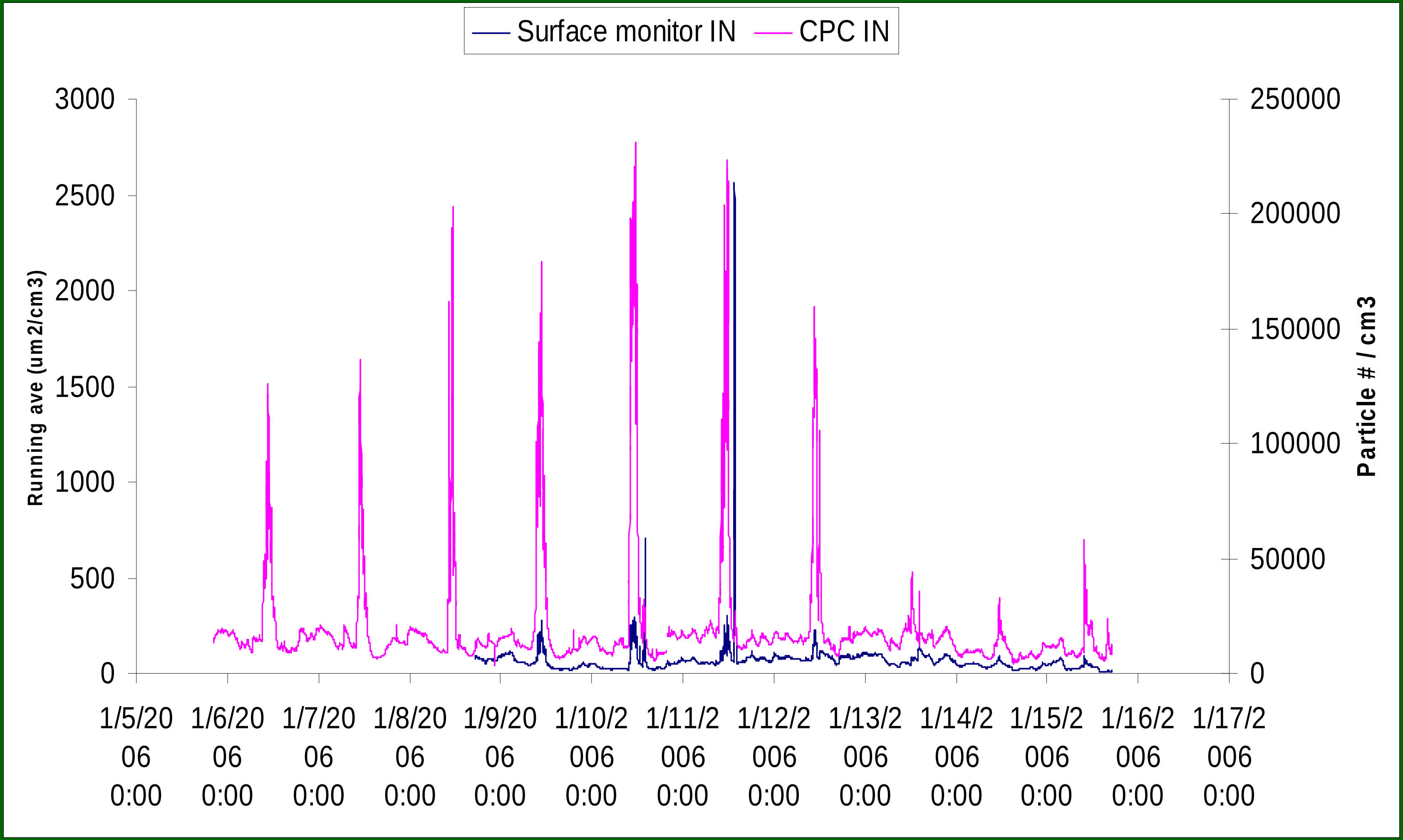
Measurement of Total Nanoparticle Surface Area Deposited in the Lung

TSI Diffusion Charger

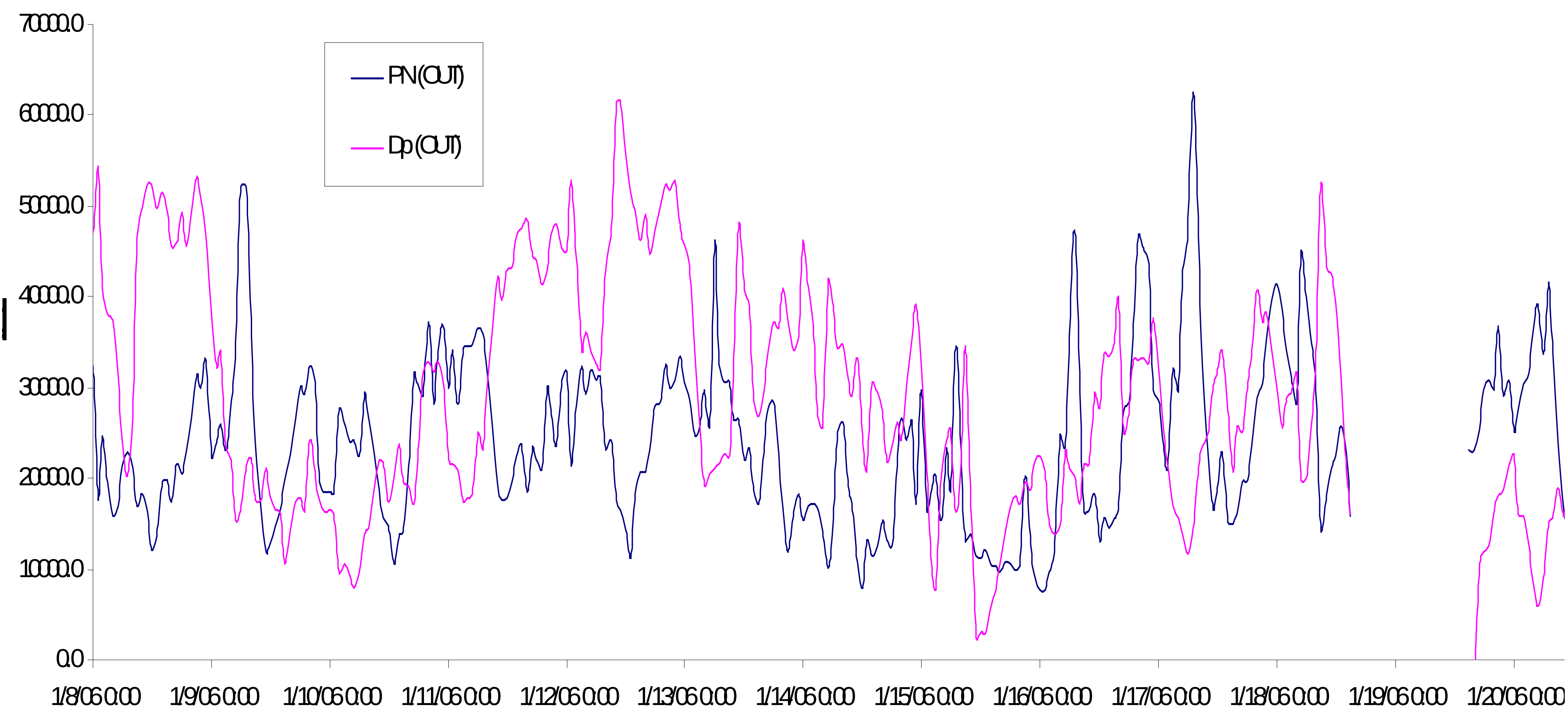
Number of Charges per particle:

$N \sim dp^{1.26}$





Indoor data indicating effect of cooking

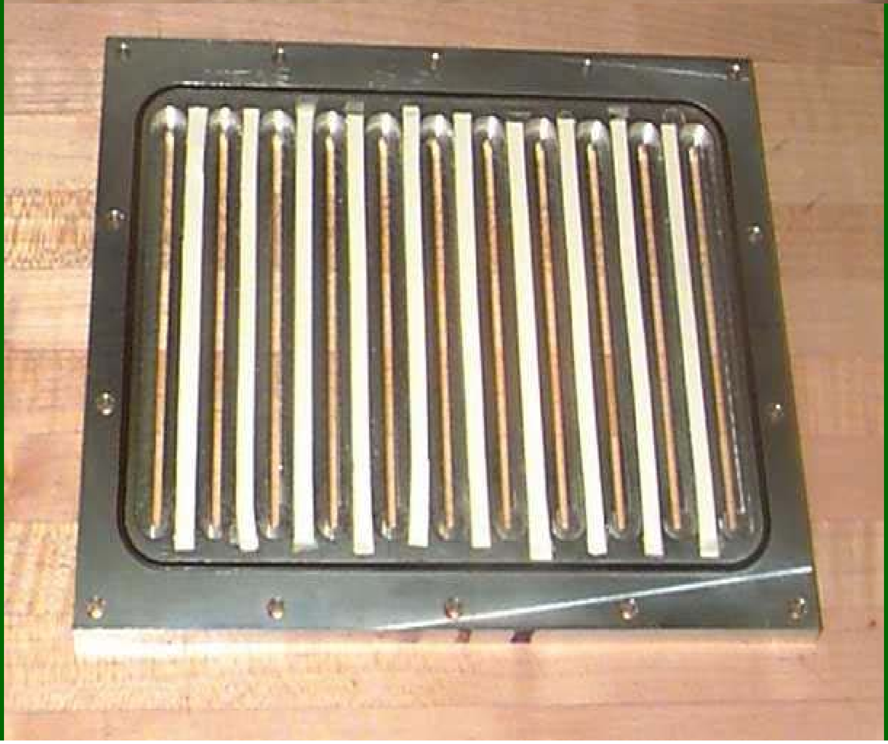


The ratio of the surface area monitor / total particle counts can also be used to provide very rapid estimate of the average particle size:

$$\mathbf{Dp \sim (NSAM\ /\ CPC)^{(1/1.26)}}$$

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



High Volume Low Pressure Drop PM Collector

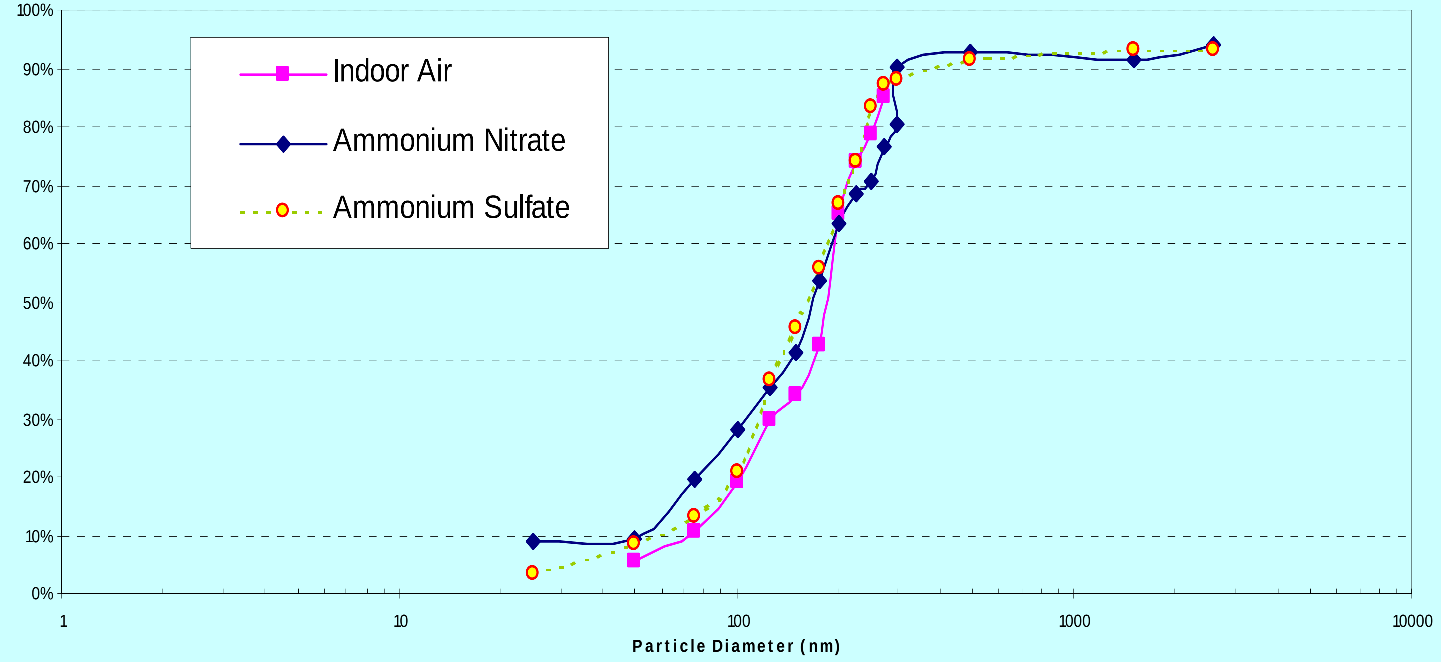
- Collects 500 LPM of Coarse, Fine and Ultrafine PM under a very low pressure drop

- Light weight, low powered and portable

- Allows high volume collection of size fractionated PM for chemical composition as well as in vitro toxicology studies

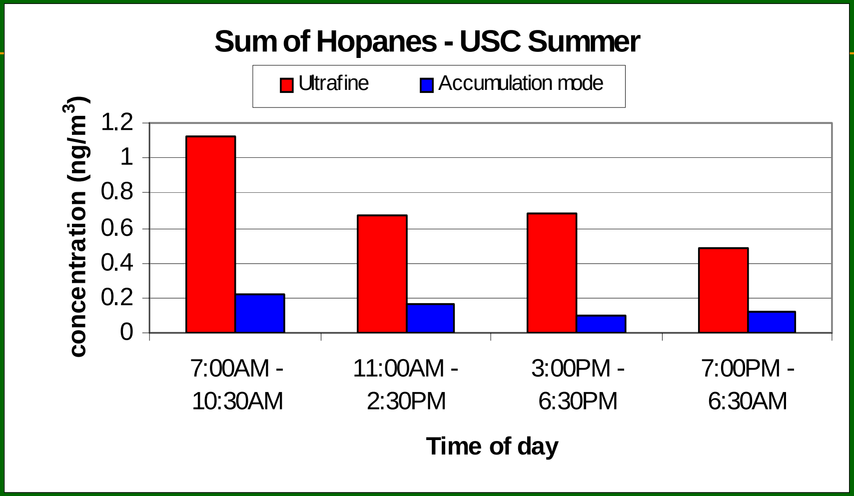
Figure 4. Evaluation of the USC High Volume Low Cutpoint Impactor with an Uncoated Quartz Substrate and Different Types of Test Aerosols

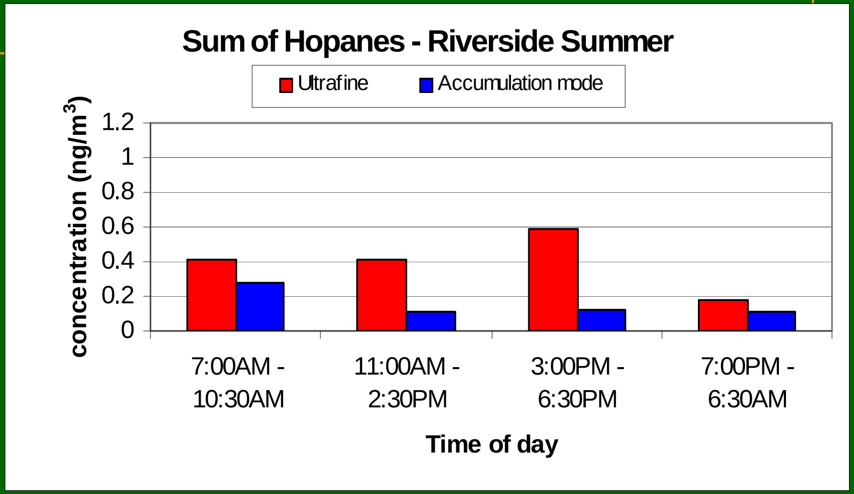
[redacted]

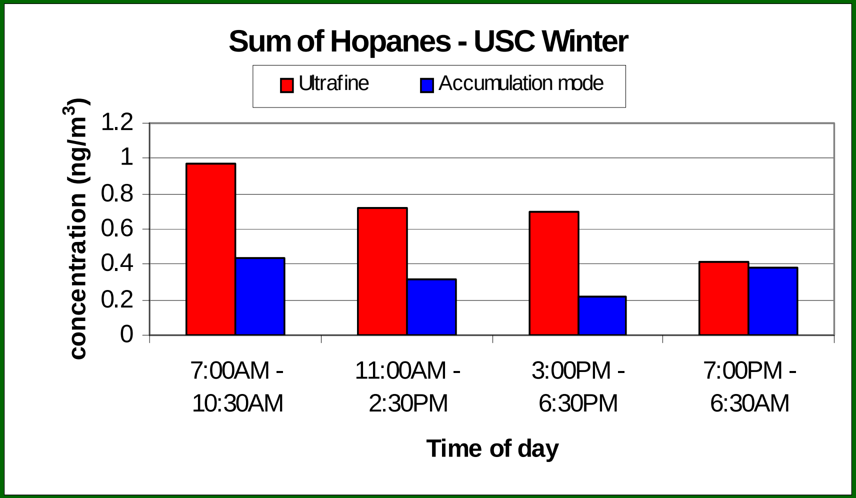


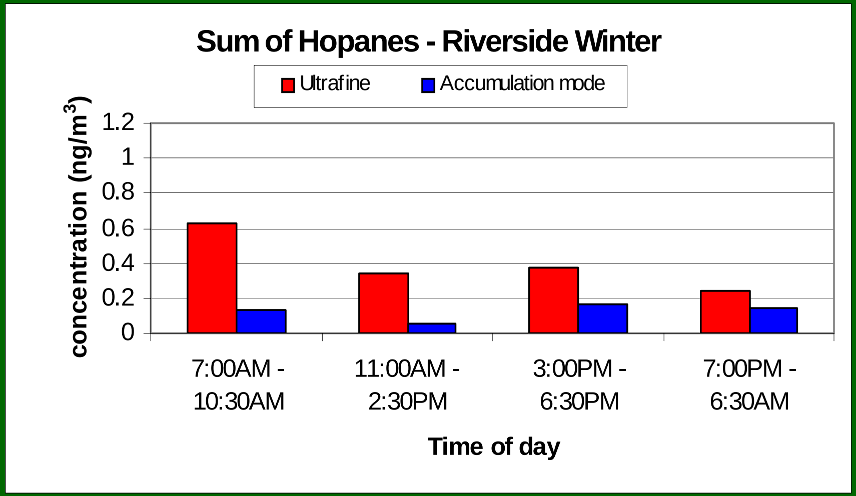
Ultrafine Organics – Vehicular Emissions

Sum of three predominant hopanes:
17a(H),21b(H)-hopane, 17a(H),21b(H)-29-norhopane, 22,29,30-trisnorneohopane


Sum of Hopanes - USC Summer

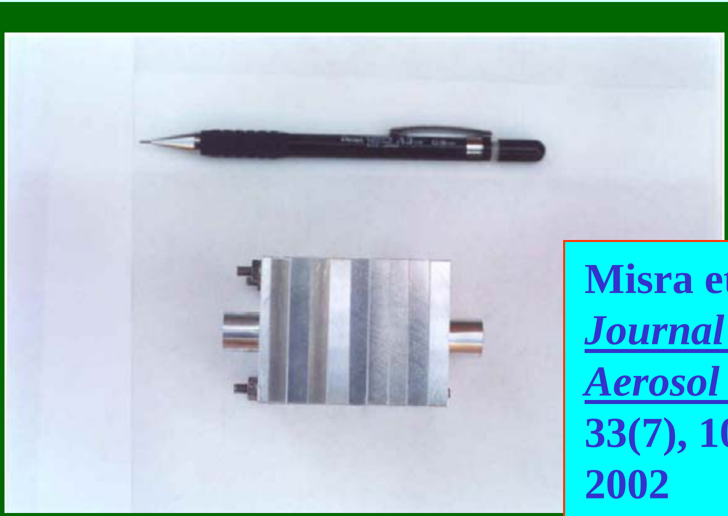

Sum of Hopanes - Riverside Summer


Sum of Hopanes - USC Winter


Sum of Hopanes - Riverside Winter

- **Higher at USC (downtown) than Riverside (inland)**
- **Enriched in ultrafine mode at both locations**

Personal Cascade Impactor



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

- Time integrated samples in 5 size ranges (2.5 - 10; 1-2.5; 0.5 –1.0; 0.2 - 0.5; and < 0.2 μm)

- Currently testing for combined ICP/MS and GC/MS on a single substrate, will provide enough data for source apportionment of personal exposure to PM of different sizes

Contribution of a Source with a Known Tracer, I, to personal exposures in the size range j

(j : <0.2, 0.2 - 0.5, 0.5 -1.0, 1 - 2.5, 2.5 - 10 µm)

$$C_{ij} = [\, X_{pers,\, IJ} / X_{outdoor,\, IJ} \,] * PM_{pers,\, IJ}$$

Amount of PM
mass measured in
size range J

on personal sample

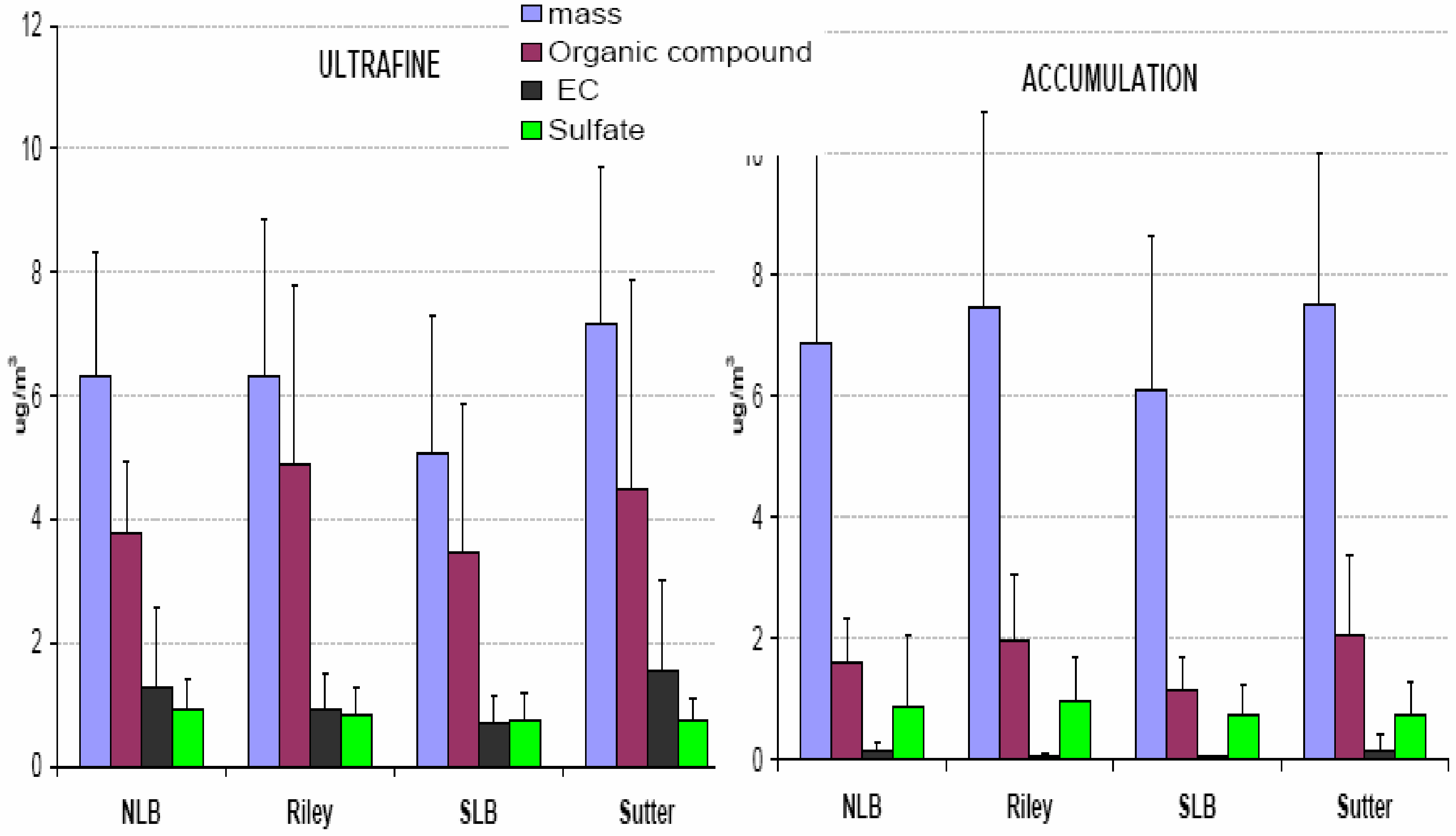
Amount of
tracer I in
size range J

on personal
sample

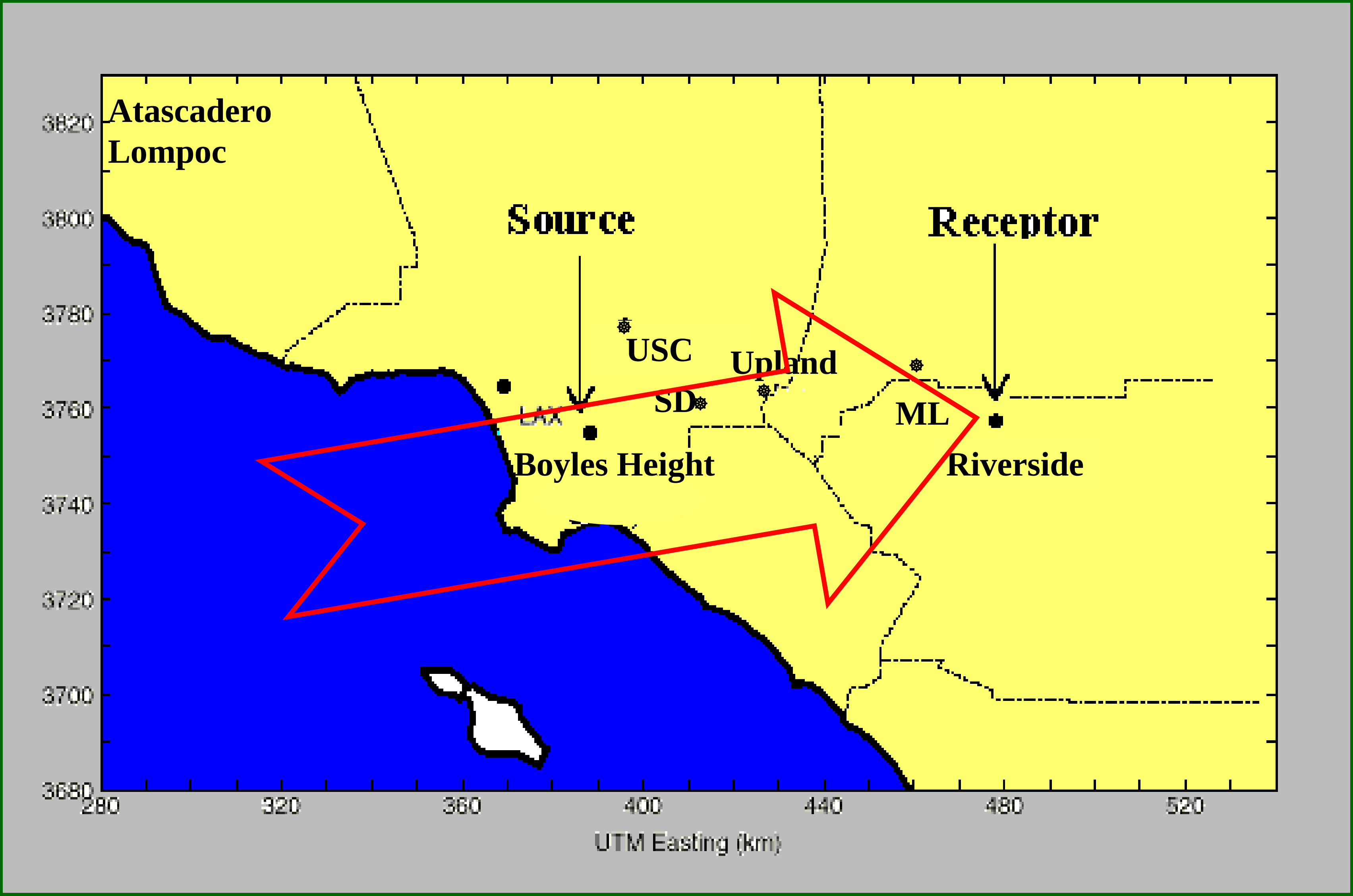
Amount of
tracer I in
size range J

on outdoor
sample

Average PM Species Measured in Children in 4 Sites of Long Beach - winter



Source and Receptor Areas in the Los Angeles Basin



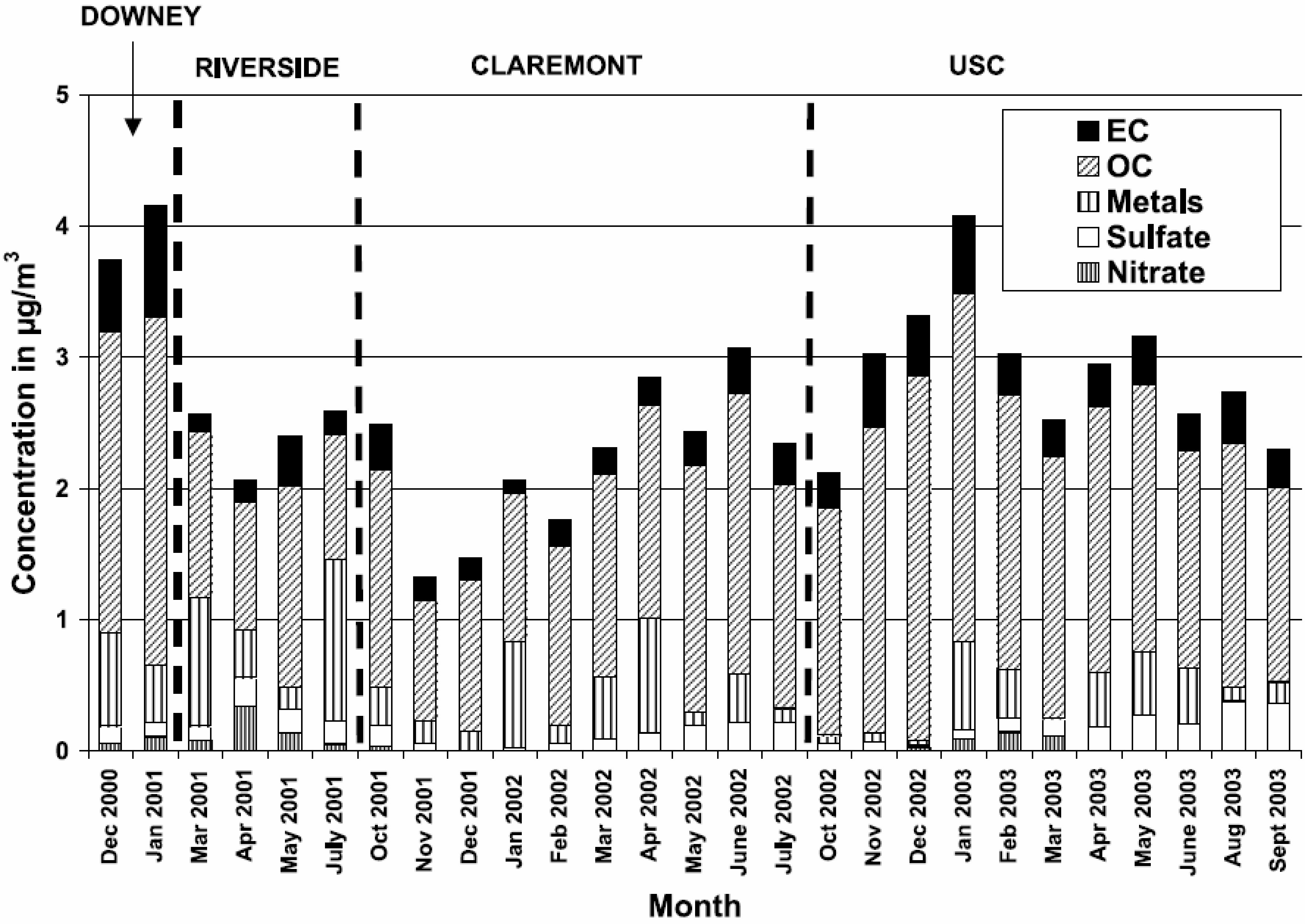
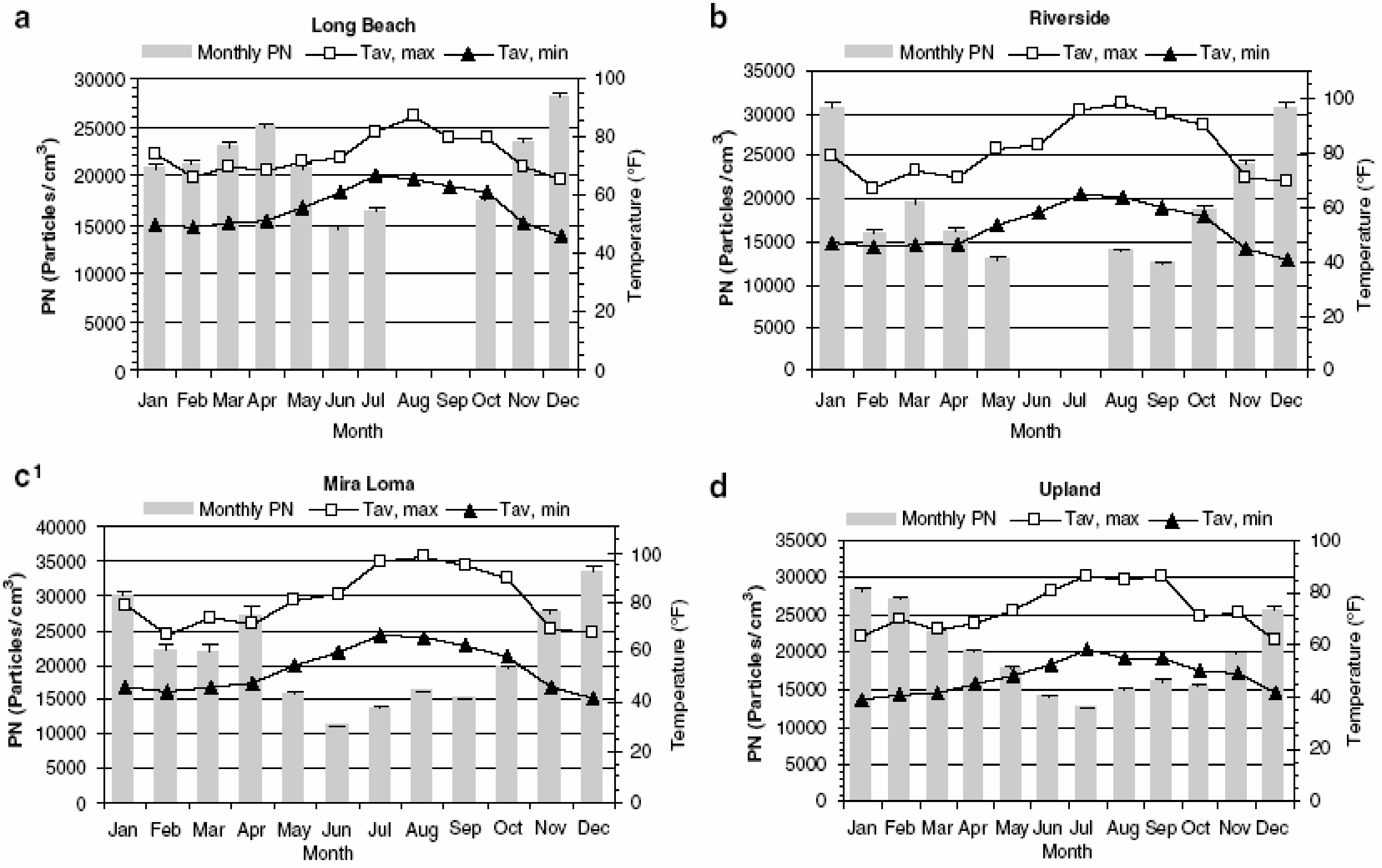
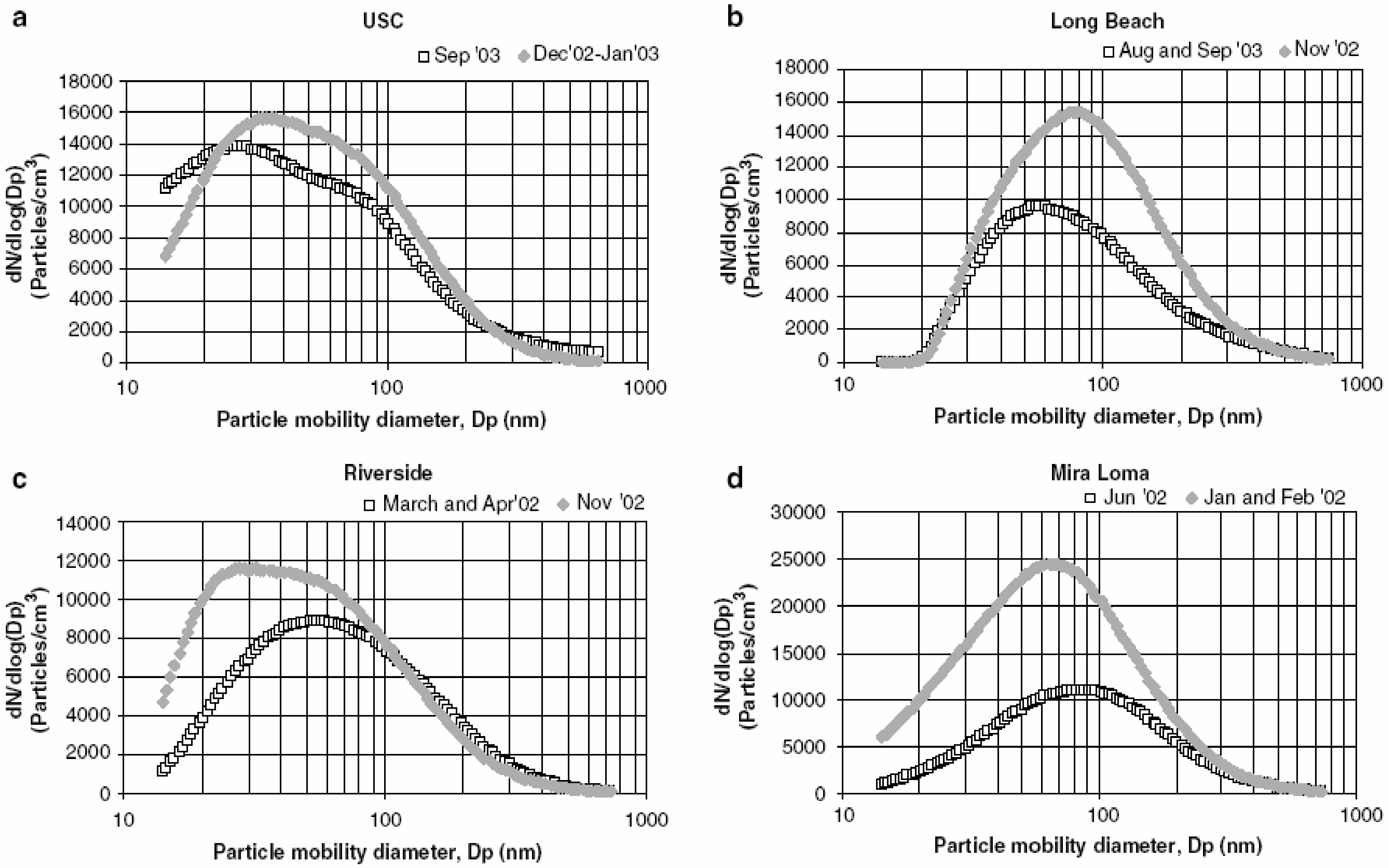


Figure 5. Monthly average PM chemical composition in the ultrafine mode.

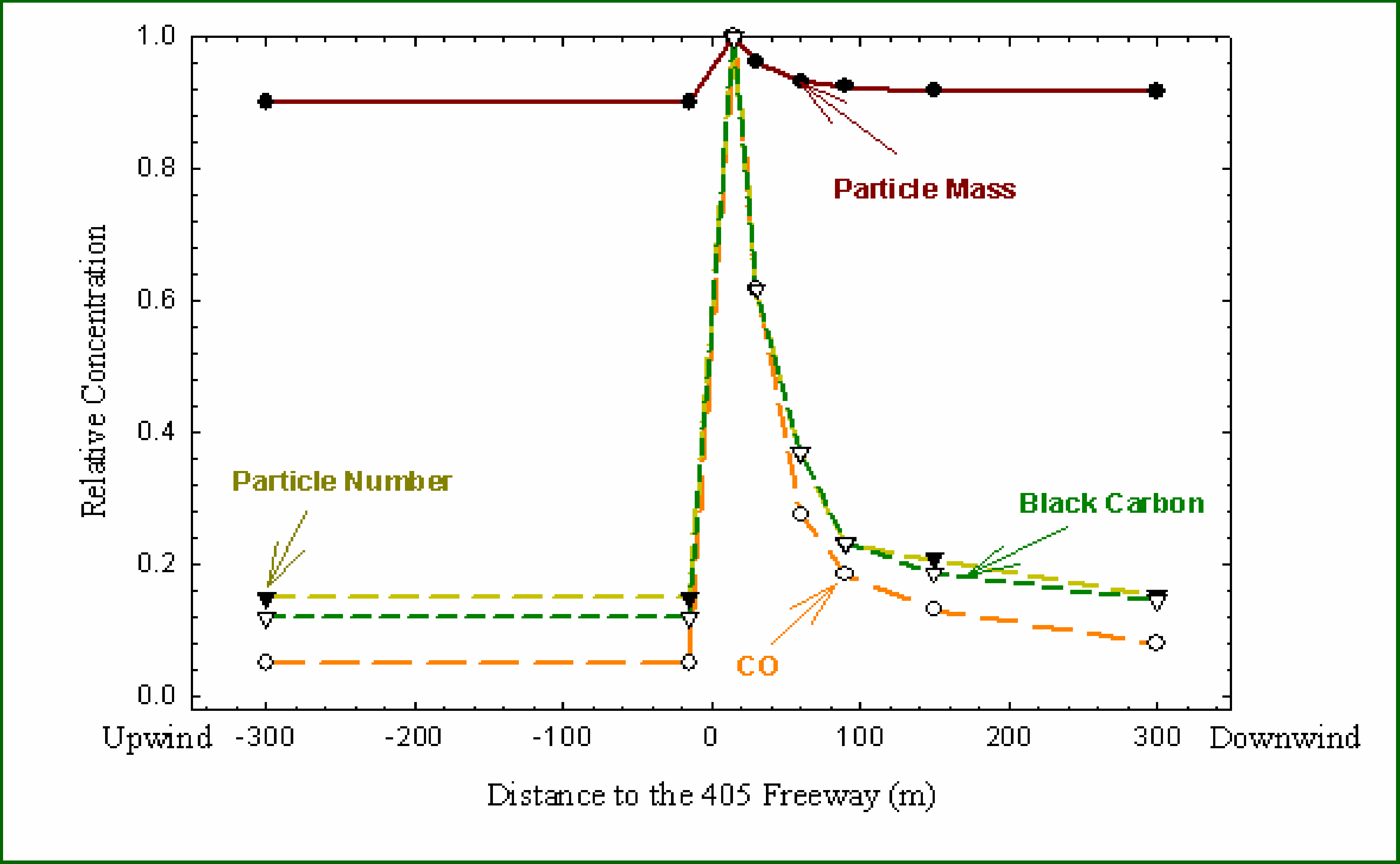


[1] The temperature data for Mira Loma was not available. The data plotted above was taken from the nearest available site Riverside firestation (around 10 kms east of Mira Loma)


a
USC
□ Sep '03 ◆ Dec'02-Jan'03
dN/dlog(Dp) (Particles/cm^3)
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
10
100
1000
Particle mobility diameter, Dp (nm)
b
Long Beach
□ Aug and Sep '03 ◆ Nov '02
dN/dlog(Dp) (Particles/cm^3)
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
10
100
1000
Particle mobility diameter, Dp (nm)
c
Riverside
□ March and Apr'02 ◆ Nov '02
dN/dlog(Dp) (Particles/cm^3)
14000
12000
10000
8000
6000
4000
2000
0
10
100
1000
Particle mobility diameter, Dp (nm)
d
Mira Loma
□ Jun '02 ◆ Jan and Feb '02
dN/dlog(Dp) (Particles/cm^3)
30000
25000
20000
15000
10000
5000
0
10
100
1000
Particle mobility diameter, Dp (nm)

Relative Particle Number, Mass, Black Carbon, CO Concentration, Vs. Downwind Distance from Freeway , but not by the same degree

(Zhu et al., JAWMA 52:1032-1042, 2002)



California Legislation on School Sites

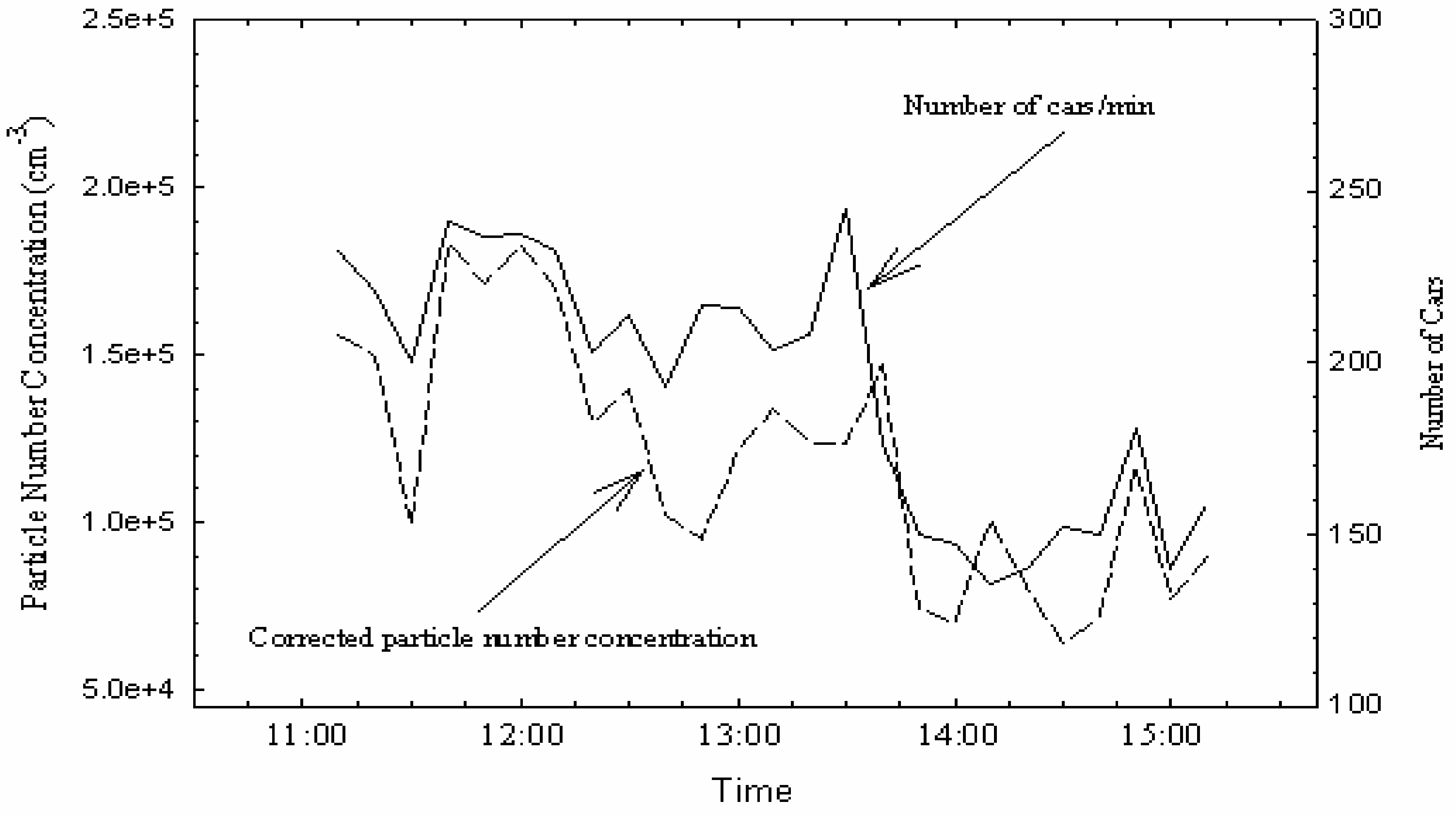
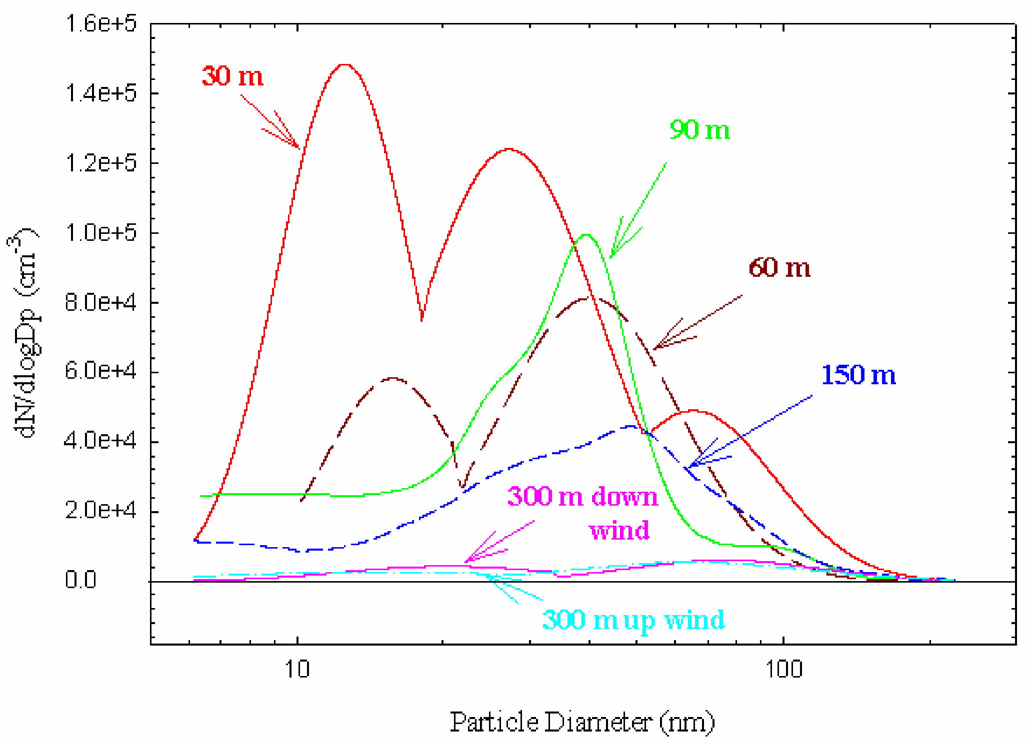
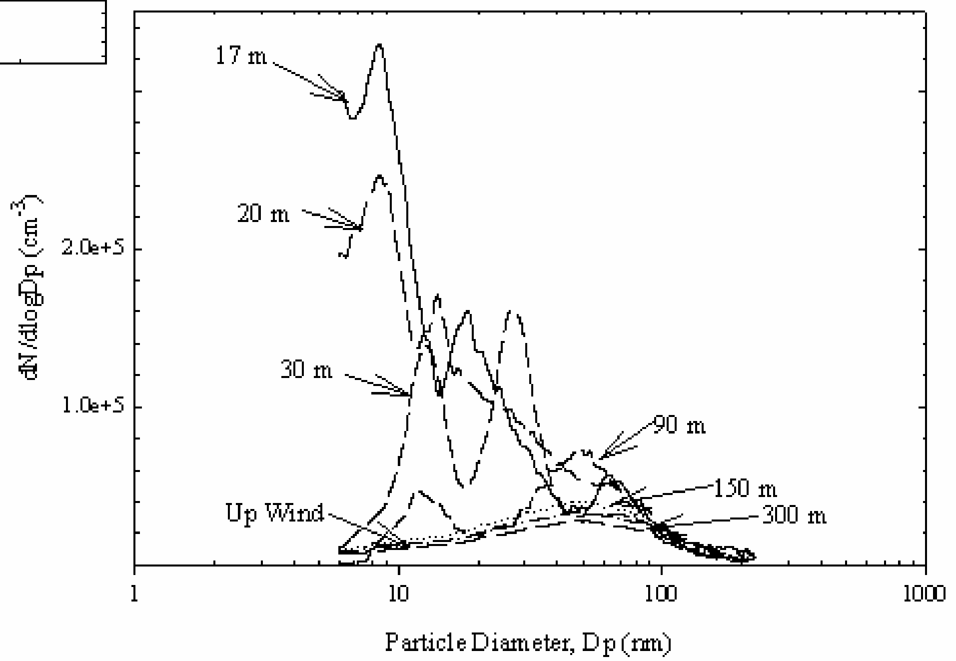


Figure 3. Correlation between traffic density and measured total particle number concentration, corrected for wind velocity at 30 m downwind from the freeway.



Significant changes occur in size distribution of PM with distance from roadway

Generally, number concentration decreases and particle size increases with distance (Zhu et al., 2002b)



I-710 (mostly diesel)

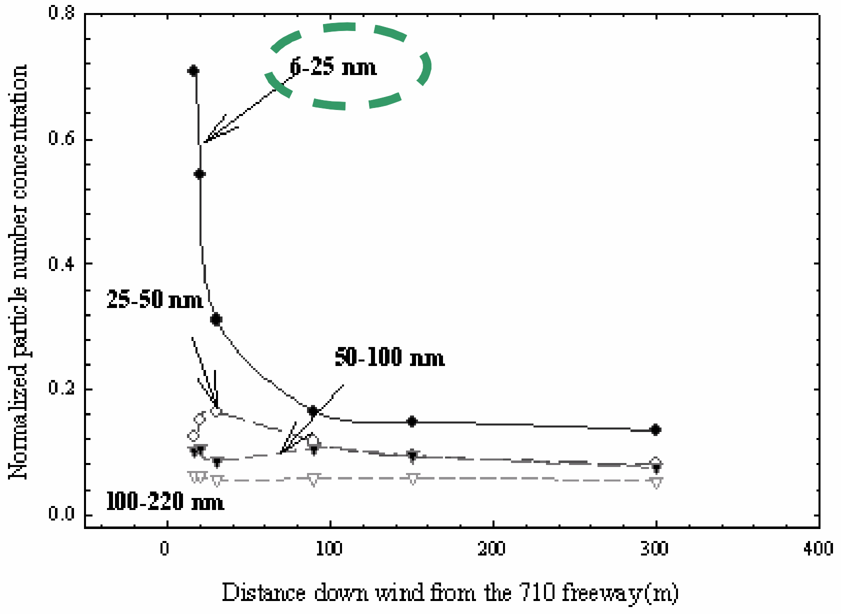
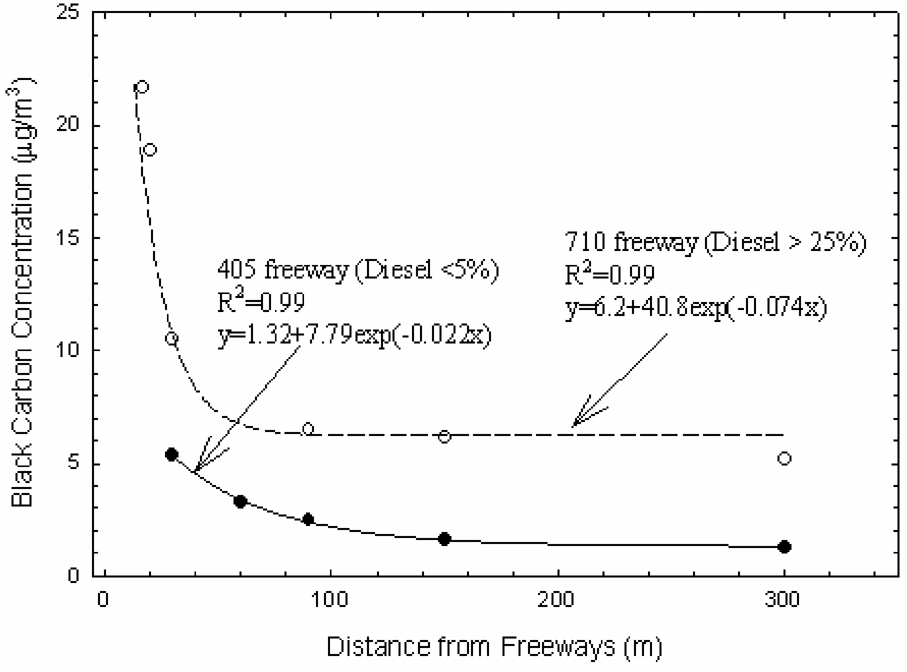


Figure 5. Normalized particle number concentration for different size ranges as a function of distance to the 710 freeway.

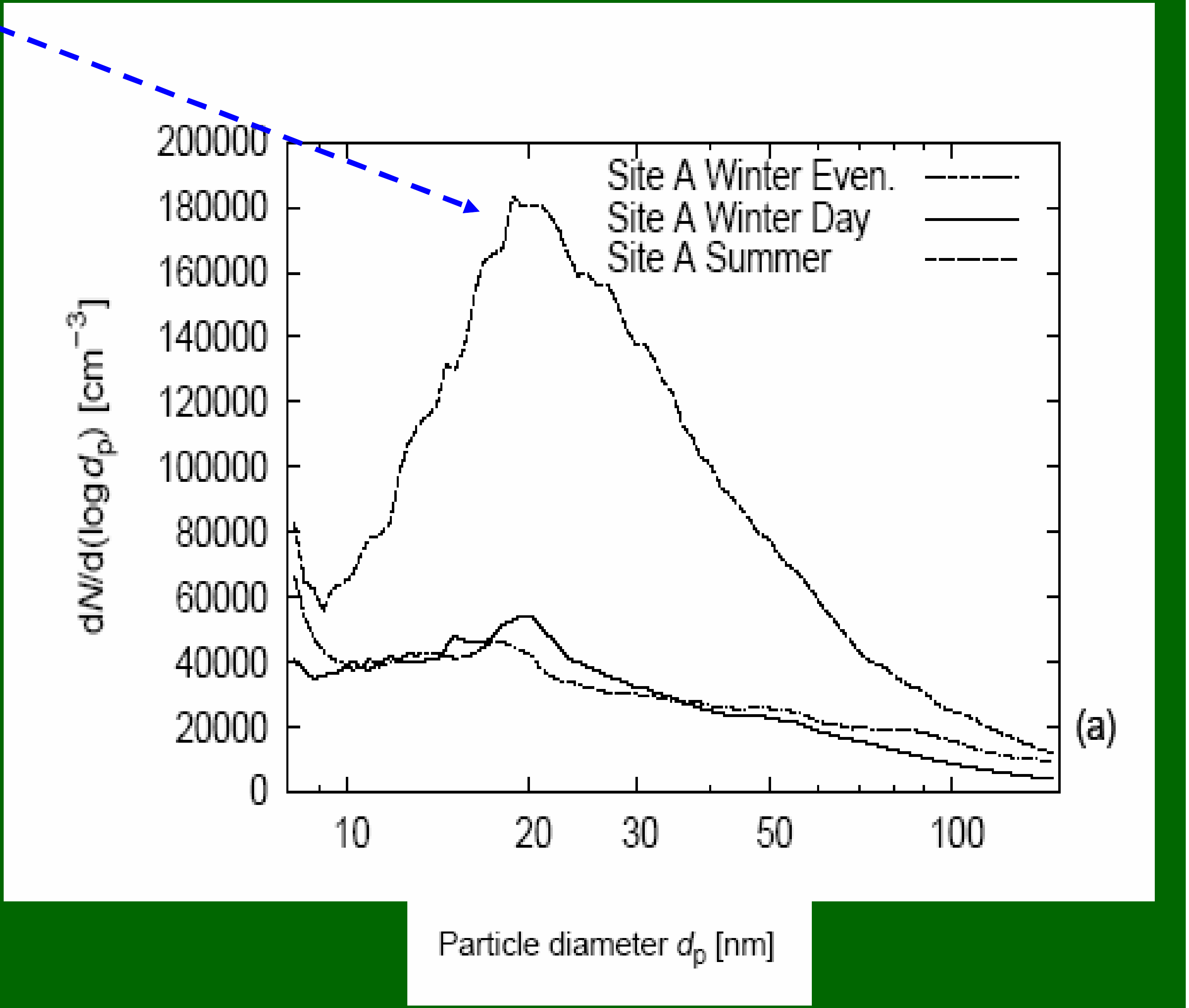
The decrease is more pronounced for the smallest particles

EC concentrations are much higher in the diesel traffic freeway



(b)

Major differences in PN between day vs. evening in winter suggest condensation or semi-volatile species as a major aerosol formation mechanism



Kuhn et al., 2005, Atmos. Environ.

The Issue of PM Volatility and Why it is Important

- **Exposure and Health Implications**

- Exposure and dose of semi-volatile species may differ according to whether they are in the gas or particle phases.

- The semi-volatile component of these particles may likely be present in its gaseous phase or associated with smaller sizes in indoor environments

- Finally, given that the majority of people's exposure during commute will be dominated to these particles, it would be useful to know whether the non-volatile or semi-volatile material is more toxic.

Impacts on Effective Control Strategies

- Impact on new emissions control technologies that better protect the public health.

- This is because particle traps remove non-volatile soot particles but not always the precursors of the smaller semi-volatile particles

- Also, the reduction of the larger, non-volatile particles from the exhaust may increase the formation-emission of the smaller, semi-volatile PM

- Our recent studies at the Caldecott tunnel showed that while PM mass emitted by LDV and HDV decreased by 50-70% over the past 7 yrs in California, particle numbers increased by 2-3 fold. See:

  - ***Geller, M.D., Sardar, S., Fine, P.M. and Sioutas, C. "Measurements of Particle Number and Mass Concentrations in a Roadway Tunnel Environment". Environmental Science and Technology, in press***

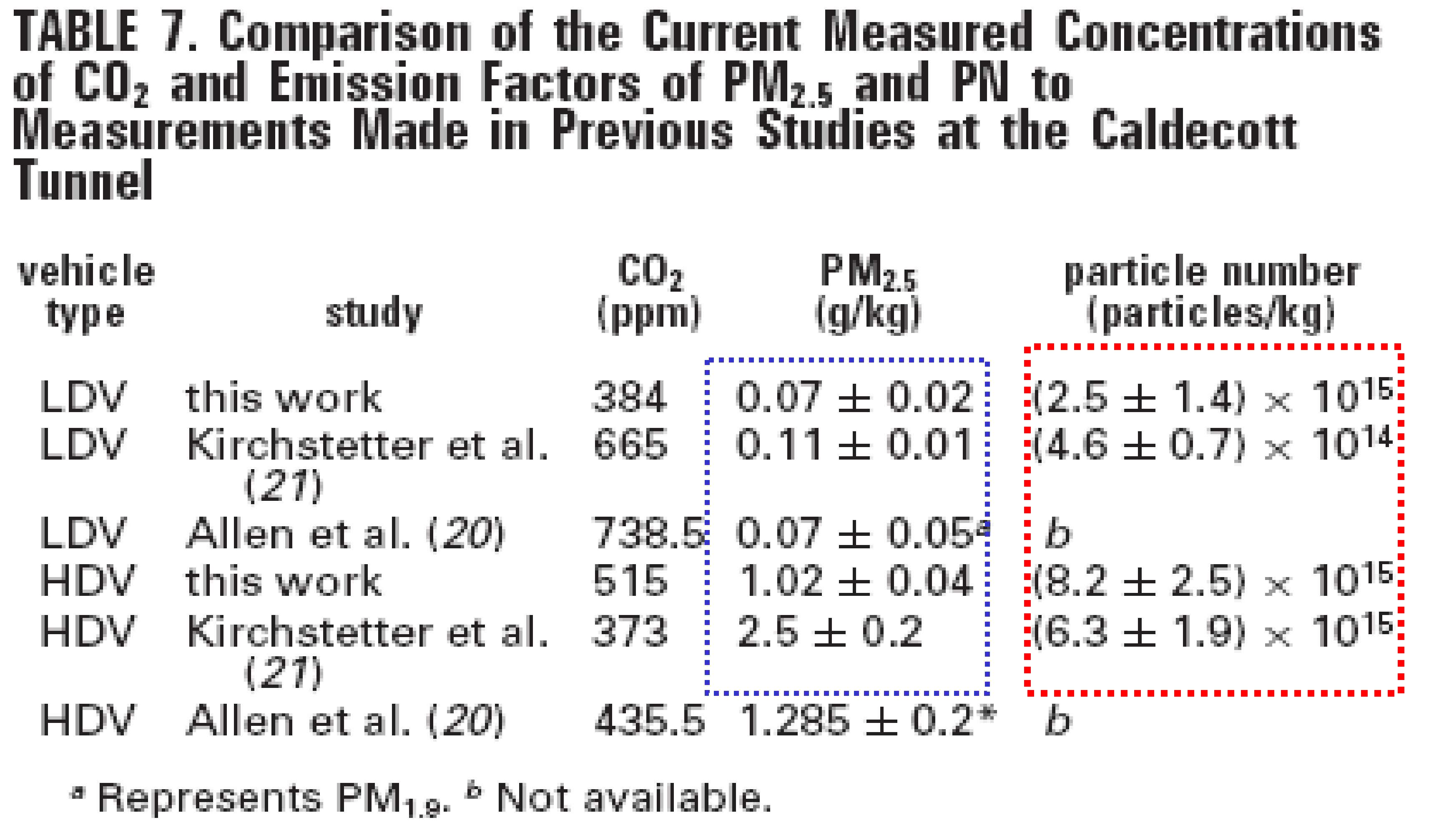


TABLE 7. Comparison of the Current Measured Concentrations of CO_2 and Emission Factors of $PM_{2.5}$ and PN to Measurements Made in Previous Studies at the Caldecott Tunnel

vehicle type	study	CO_2 (ppm)	$PM_{2.5}$ (g/kg)	particle number (particles/kg)
LDV	this work	384	0.07 ± 0.02	$(2.5 \pm 1.4) \times 10^{15}$
LDV	Kirchstetter et al. (*21*)	665	0.11 ± 0.01	$(4.6 \pm 0.7) \times 10^{14}$
LDV	Allen et al. (*20*)	738.5	0.07 ± 0.05^{a}	*b*
HDV	this work	515	1.02 ± 0.04	$(8.2 \pm 2.5) \times 10^{15}$
HDV	Kirchstetter et al. (*21*)	373	2.5 ± 0.2	$(6.3 \pm 1.9) \times 10^{15}$
HDV	Allen et al. (*20*)	435.5	1.285 ± 0.2*	*b*

[a] Represents $PM_{1.9}$. [b] Not available.

- ➢$PM_{2.5}$ emissions have declined by 37% (LDV) and 60% (HDV) since 1997
- ➢PN emissions have increased
  - ➢Factor of 5.4 for LDV
  - ➢Factor of 1.3 for HDV

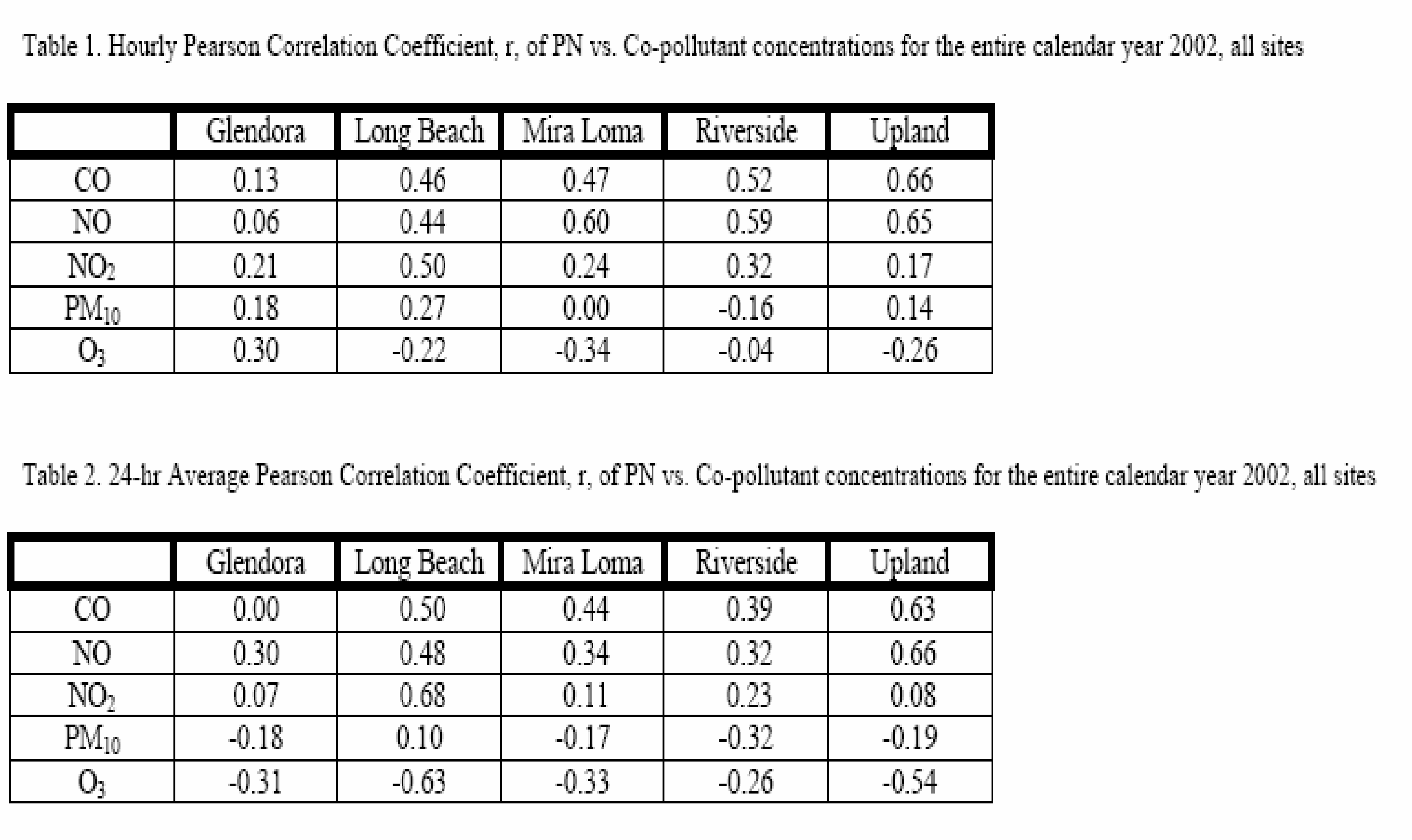


Table 1. Hourly Pearson Correlation Coefficient, r, of PN vs. Co-pollutant concentrations for the entire calendar year 2002, all sites

	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_2	0.21	0.50	0.24	0.32	0.17
PM_{10}	0.18	0.27	0.00	-0.16	0.14
O_3	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_2	0.07	0.68	0.11	0.23	0.08
PM_{10}	-0.18	0.10	-0.17	-0.32	-0.19
O_3	-0.31	-0.63	-0.33	-0.26	-0.54

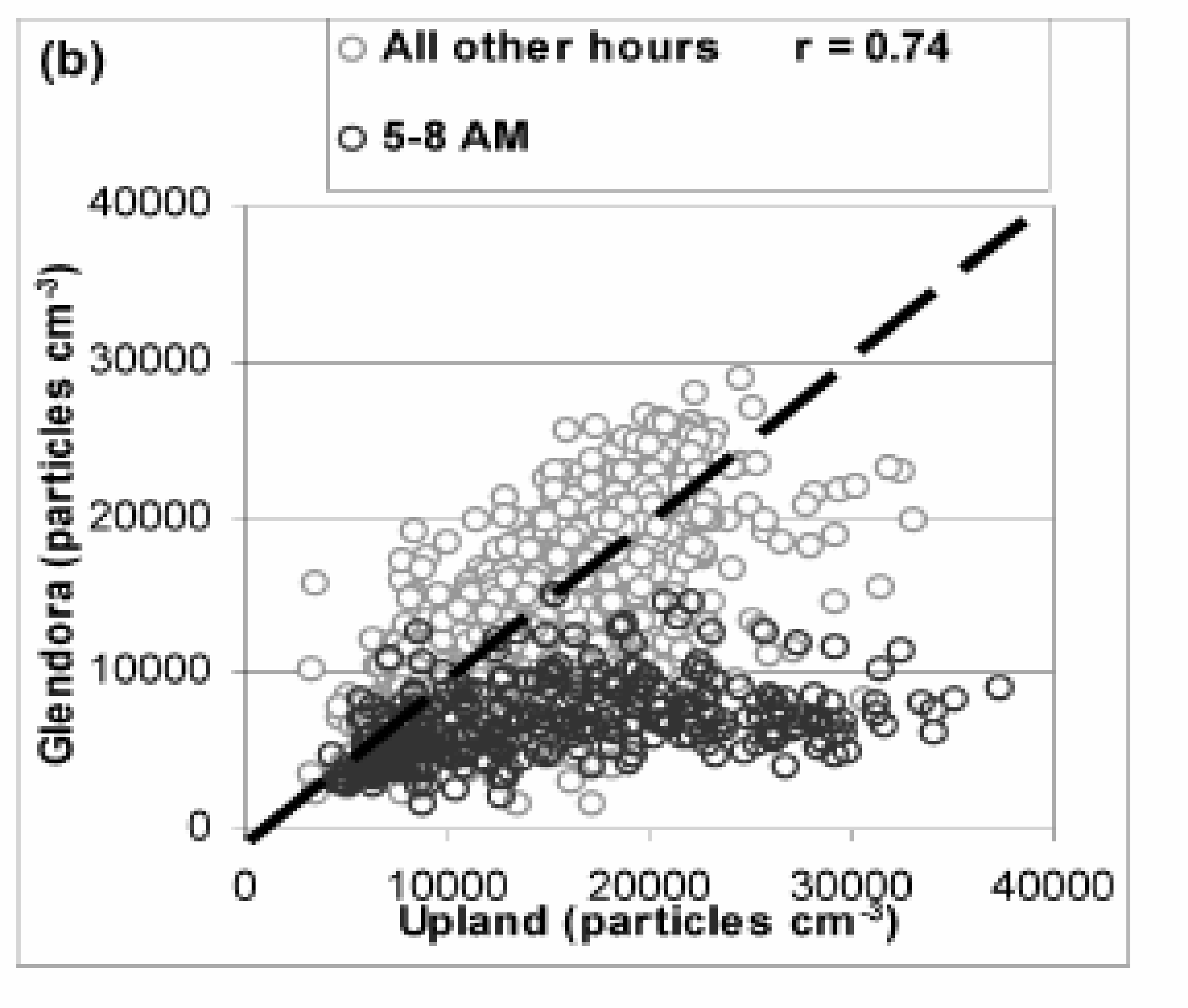
- Generally low to moderate correlations between PN and gaseous co pollutants as well as PM10

- Hourly associations > 24 hr associations

- *(Sardar et al, JAWMA, 2004)*

Spatial Inhomogeneity of Ultrafine PM

Sardar et al, JAWMA, 2004



Data in Glendora and Upland, 2002

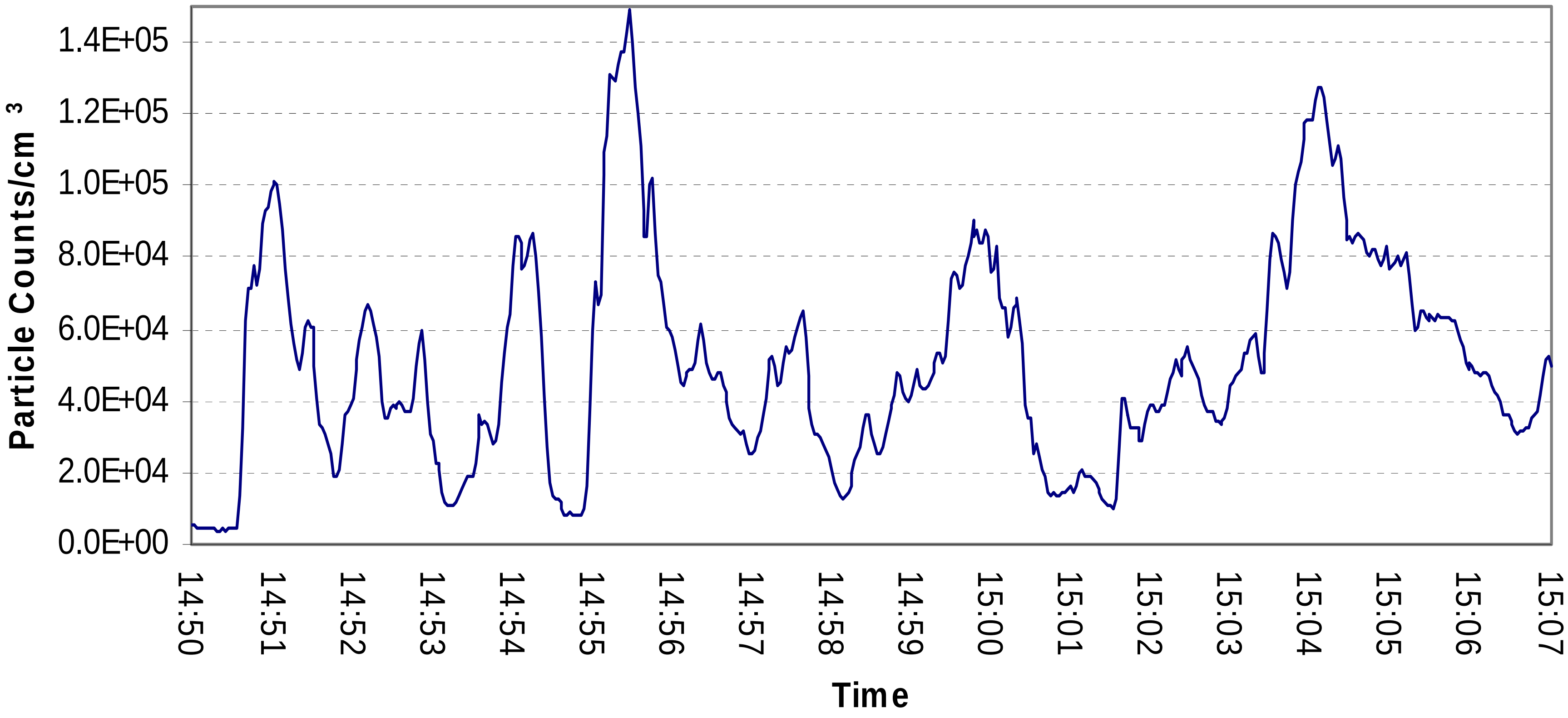
a) No lag time
b) One hour lag time
c) Two hour lag time
d) Three hour lag time.

Dashed lines indicate the ideal 1:1 relationship

-Glendora and Upland are only 6 km apart

- Influence of morning traffic in Upland decreases Pearson coefficient, r, between PN in the two sites

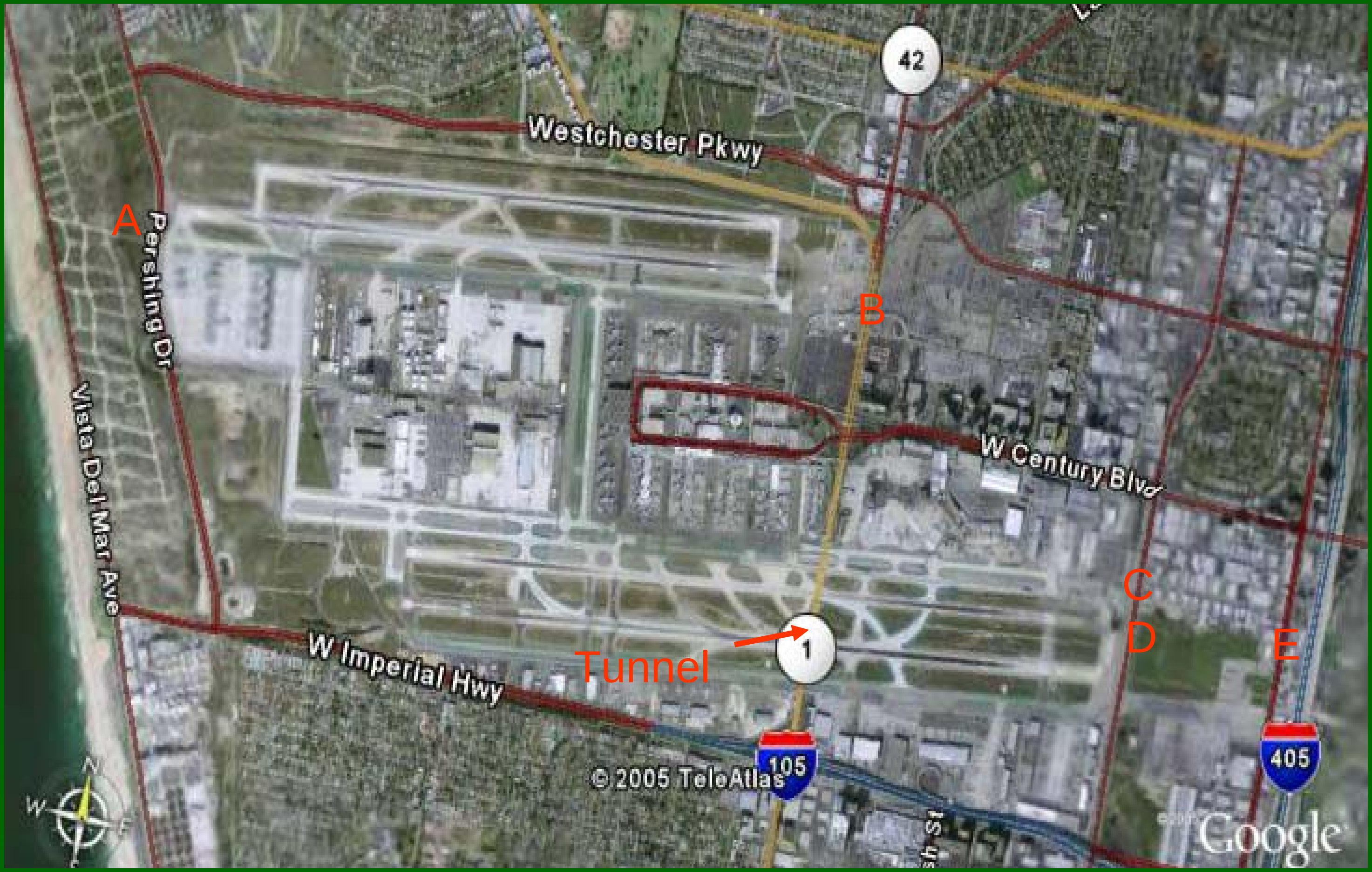
Particle Counts 500 Meters Downwind of North Runway During Landings at Site B



Freeways are not the only source of ultrafine particles!

CARB Study; Westerdahl et al., 2005

LAX Study Area

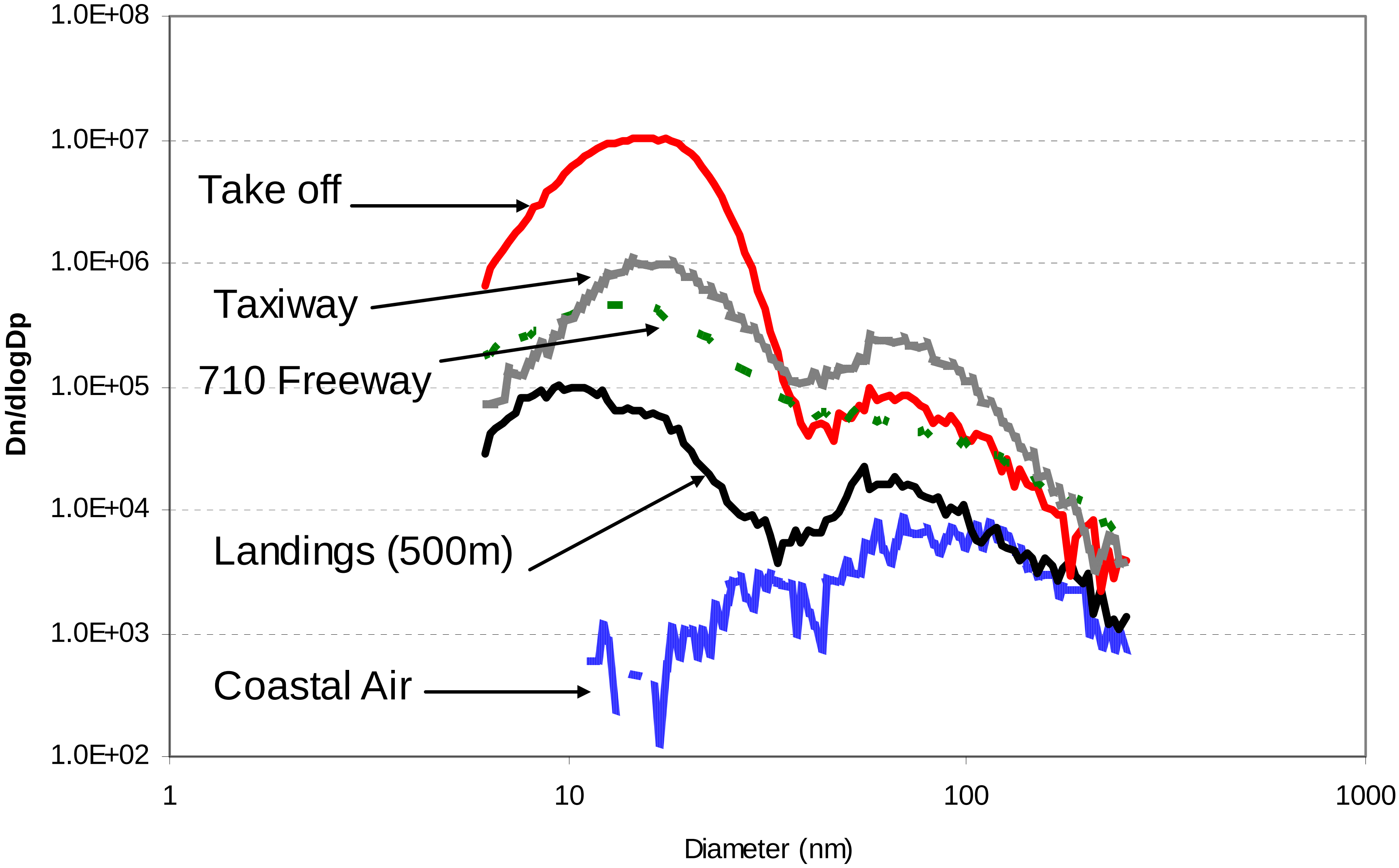


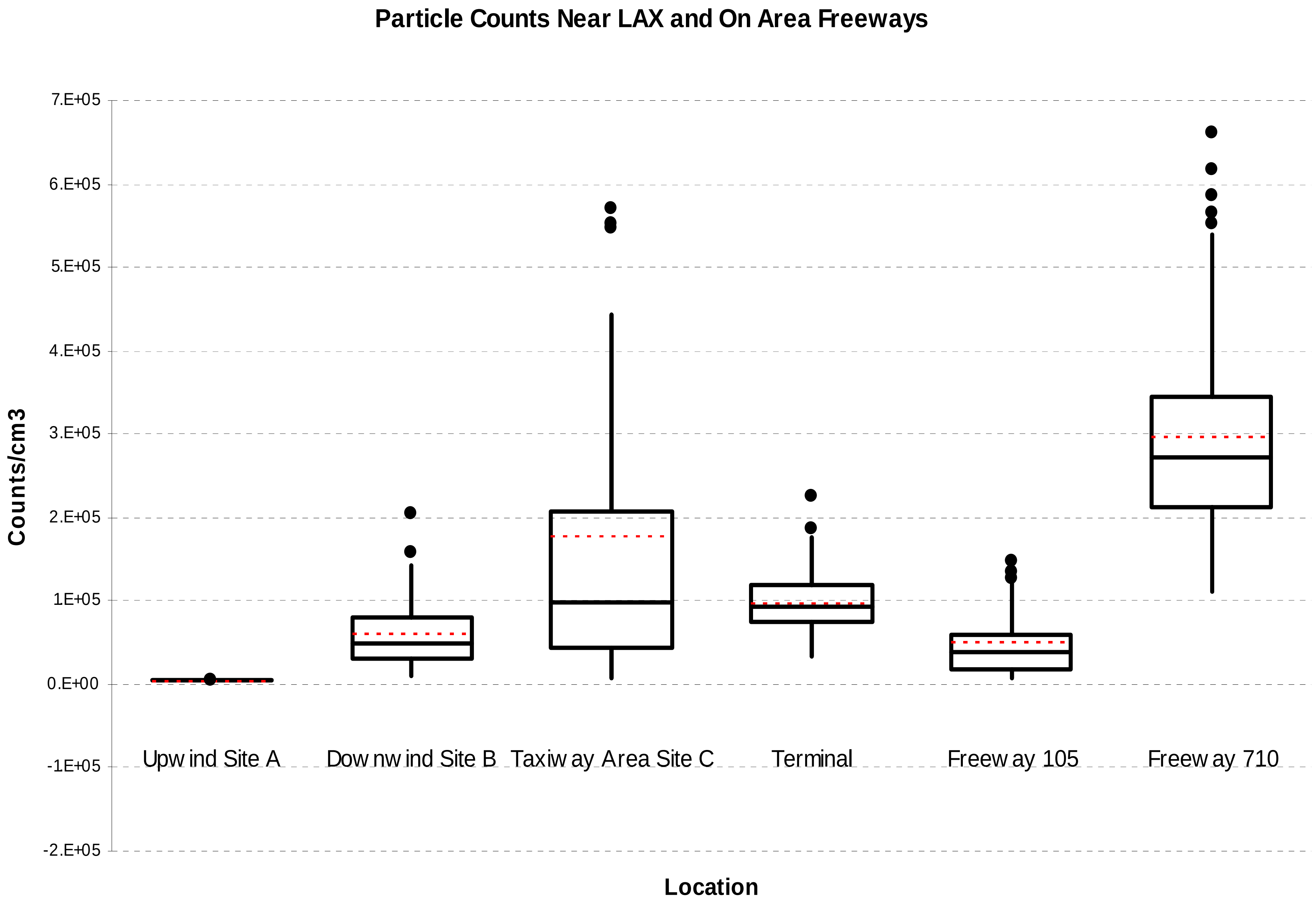
Sites

A—Upwind B—500 Meters Downwind of North Runway C—Downwind of Taxiway

D—Downwind of South Runway E—800 Meters Downwind of South Runway

Particle Number Distribution




Particle Counts Near LAX and On Area Freeways
Counts/cm3
7.E+05
6.E+05
5.E+05
4.E+05
3.E+05
2.E+05
1E+05
0.E+00
-1E+05
-2.E+05
Upwind Site A
Downwind Site B
Taxiway Area Site C
Terminal
Freeway 105
Freeway 710
Location

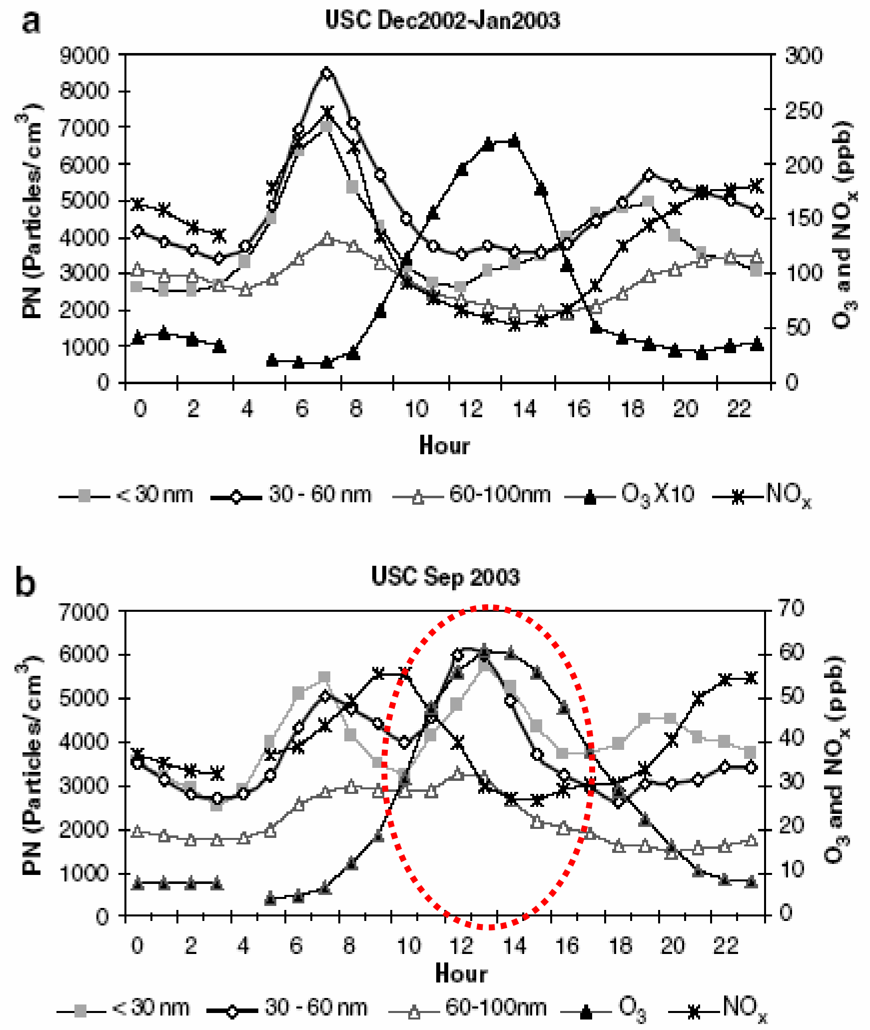


Figure 4. Diurnal trends of size-segregated particle number, O_3 and NO_x at USC during (a) Dec 2002–Jan 2003 and (b) Sep 2003.

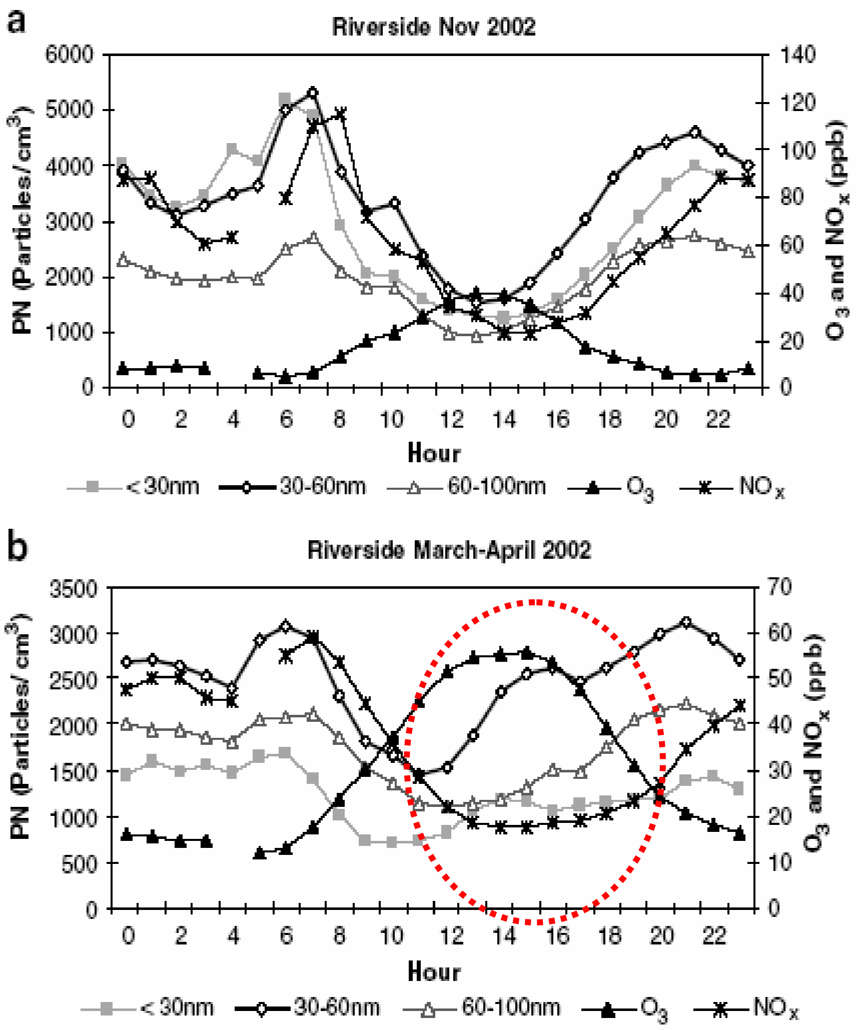


Figure 6. Diurnal trends of size-segregated particle number, O_3 and NO_x at Riverside during (a) Nov 2002 and (b) Mar–Apr 2002.

Photochemical Secondary Formation of Ultrafine PM in LA

Sardar et al., ES&T, 2005

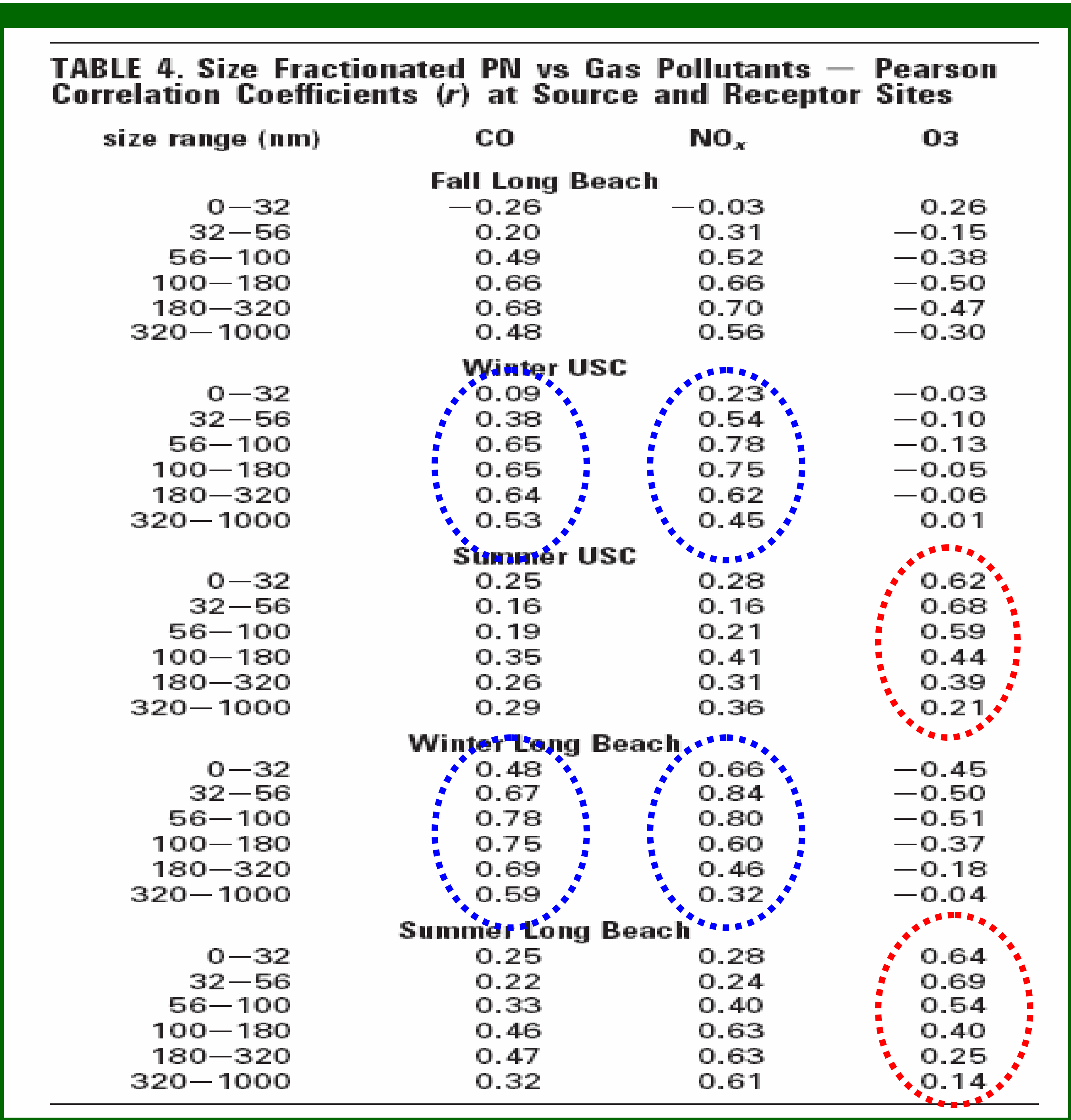


TABLE 4. Size Fractionated PN vs Gas Pollutants — Pearson Correlation Coefficients (*r*) at Source and Receptor Sites

size range (nm)	CO	NO_x	O3
	Fall Long Beach		
0−32	−0.26	−0.03	0.26
32−56	0.20	0.31	−0.15
56−100	0.49	0.52	−0.38
100−180	0.66	0.66	−0.50
180−320	0.68	0.70	−0.47
320−1000	0.48	0.56	−0.30
	Winter USC		
0−32	0.09	0.23	−0.03
32−56	0.38	0.54	−0.10
56−100	0.65	0.78	−0.13
100−180	0.65	0.75	−0.05
180−320	0.64	0.62	−0.06
320−1000	0.53	0.45	0.01
	Summer USC		
0−32	0.25	0.28	0.62
32−56	0.16	0.16	0.68
56−100	0.19	0.21	0.59
100−180	0.35	0.41	0.44
180−320	0.26	0.31	0.39
320−1000	0.29	0.36	0.21
	Winter Long Beach		
0−32	0.48	0.66	−0.45
32−56	0.67	0.84	−0.50
56−100	0.78	0.80	−0.51
100−180	0.75	0.60	−0.37
180−320	0.69	0.46	−0.18
320−1000	0.59	0.32	−0.04
	Summer Long Beach		
0−32	0.25	0.28	0.64
32−56	0.22	0.24	0.69
56−100	0.33	0.40	0.54
100−180	0.46	0.63	0.40
180−320	0.47	0.63	0.25
320−1000	0.32	0.61	0.14

Sardar et al., ES&T, 2005

-high correlation between ultrafine PM and tracers of traffic (CO, NOx) in winter

- high correlation between ultrafine PM and O_3 in summer

Future Research in Southern California

Renewed Southern California Particle Center, funded by US EPA:

- Determine the physical and chemical properties of ultrafine PM (UFP) from real-world sources, including secondary formation, to evaluate how exposure to UFP vary with respect to:
  - location, season, and particle size,
  - assess their relative toxicity.
- Assess the contributions of these outdoor sources to indoor exposure and toxicity.
- Determine the physical, chemical and toxicological characteristics of the volatile and non-volatile UFP components that originate from mobile sources.