Form, Composition and Trends in Ultrafine Particulate Matter

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Background and Introduction:

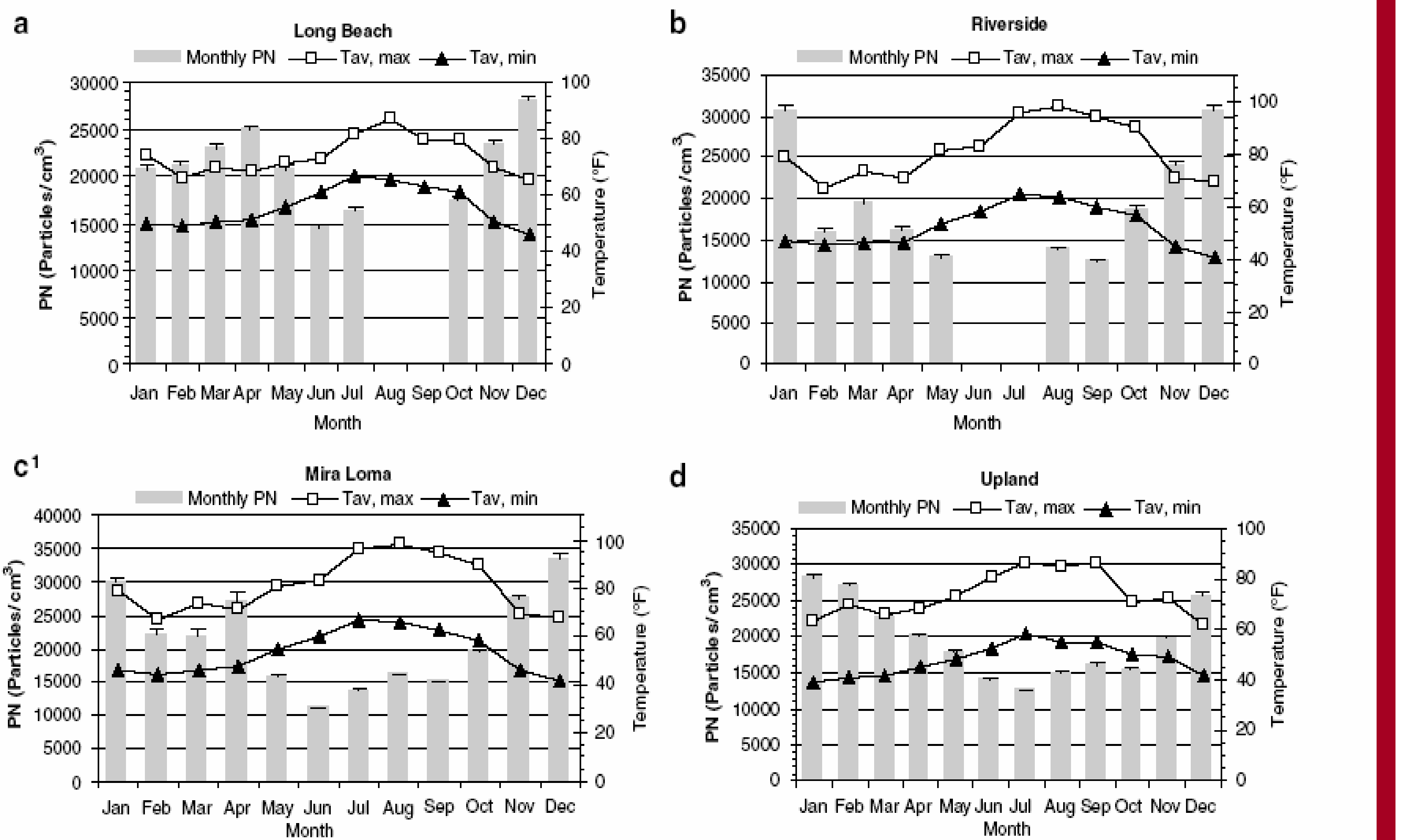
- A rapidly increasing epidemiological and toxicological evidence links cardio-respiratory health effects and exposures to ultrafine particles (Peters et al., 1997; Li et al., 2002 and 2003; Xia et al., 2004)

- PM from Mobile Sources ; major thrust area of the Southern California Particle Center and Supersite (SCPCS).

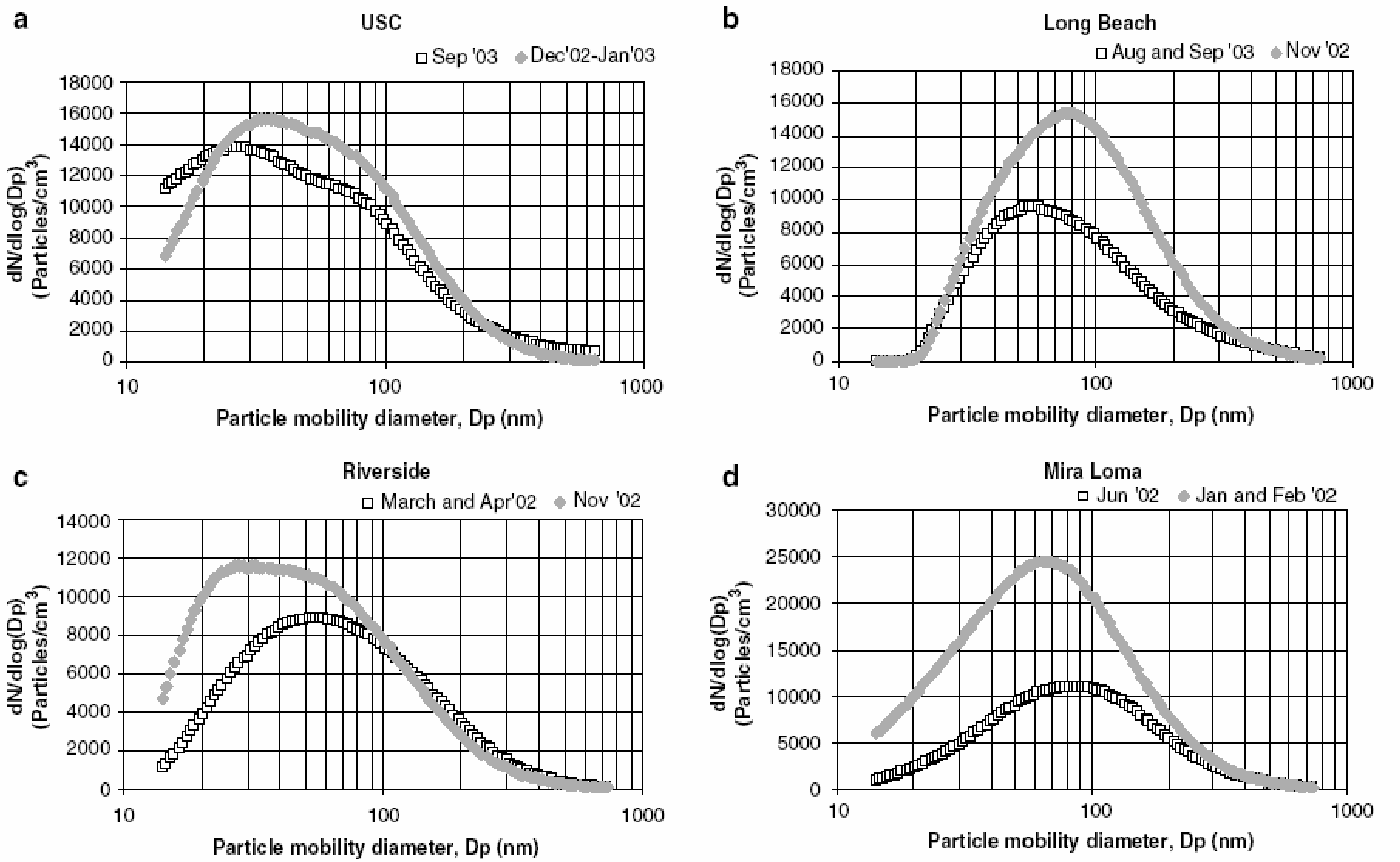
- Emphasis on : particle emission levels, particle transport and transformation away from the source --- busy roads and freeways, penetration to indoor environments, ultimately health effects

- Over 90 refereed journal publications in 5 years on ultrafine PM sources, formation mechanisms, physical and chemical properties and toxicity

- This presentation summarizes research findings on physical and chemical characteristics of ultrafine PM generated by our SCPCS.



[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/cm3)
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
c
Riverside
March and Apr'02
Nov '02
14000
d
Mira Loma
Jun '02
Jan and Feb '02
30000
25000
20000
15000
10000
5000

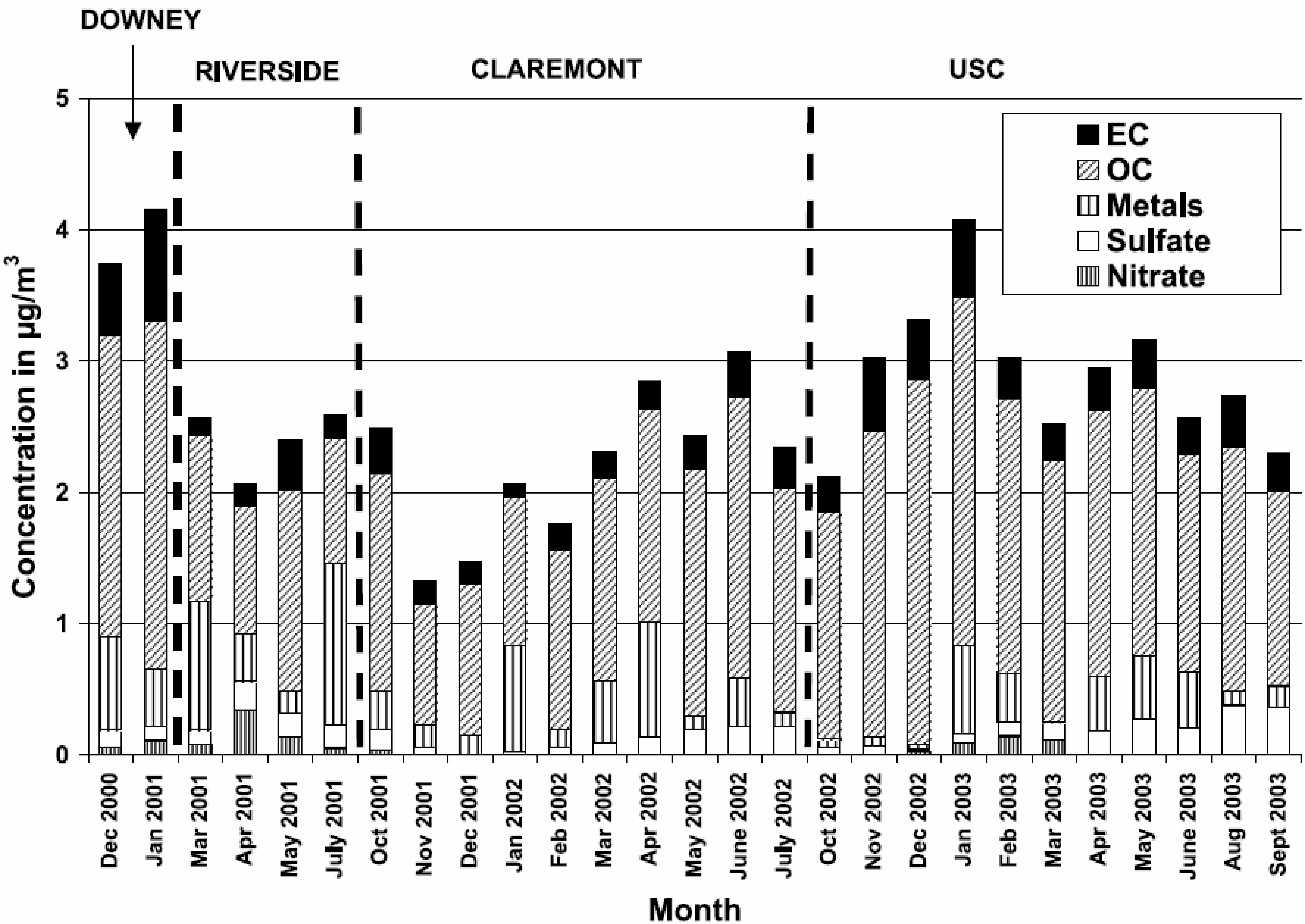


Figure 5. Monthly average PM chemical composition in the ultrafine mode.

TABLE 6. Light-Duty Vehicle and Heavy-Duty Diesel Emission Factors ($mg\ kg^{-1}$) of Fuel Burned (average ± standard deviation)[a]

	mode		
	coarse (2.5—10 μm)	accumulation (0.18—2.5 μm)	ultrafine (<0.18 μm)
Light-Duty			
mass	7.7 ± 1.6	40 ± 8	27.1 ± 3.2
OC	2.4 ± 0.9	7.4 ± 2.3	**
EC	1.0 ± 0.6	2.6 ± 1.2	26.8 ± 3.1
nitrate	0.6 ± 0.3	0.42 ± 0.2	1.2 ± 0.9
sulfate	0.8 ± 0.4	1.1 ± 0.9	2.7 ± 1.8
Mg	0.4 ± 0.2	0 ± 0	0 ± 0
Al	0.2 ± 0.4	0 ± 0	0.1 ± 0.1
Si	1.6 ± 1.3	0.1 ± 0.1	0.3 ± 0.1
Ca	0.8 ± 0.3	0.4 ± 0.2	0.3 ± 0.0
Fe	10.4 ± 3.1	3.7 ± 0.9	1.23 ± 0.50
Ti	0.3 ± 0.2	0.2 ± 0.1	0.1 ± 0.0
Ba	1.2 ± 0.9	0.3 ± 0.2	0 ± 0
Heavy-Duty			
mass	75 ± 15	304 ± 62	711 ± 65
OC	12.3 ± 2.6	19.0 ± 5.6	*b*
EC	66 ± 17	306 ± 44	403 ± 32
nitrate	0.4 ± 0.0	4.5 ± 1.0	1.8 ± 0.9
sulfate	1.9 ± 0.5	10.7 ± 0.4	37 ± 9
Mg	−8.2 ± 6.3	0.0 ± 0.0	0.0 ± 0.0
Al	−12.2 ± 1.9	0.0 ± 0.0	0.6 ± 0.2
Si	−51 ± 44	0.6 ± 0.1	0.6 ± 0.3
Ca	−30 ± 9	0.3 ± 0.1	0.2 ± 0.1
Fe	−154 ± 58	4.3 ± 2.0	2.8 ± 0.9
Ti	−3.3 ± 1.7	1.3 ± 0.2	0.8 ± 0.1
Ba	−15.2 ± 3.5	0.9 ± 0.1	0.0 ± 0.0

[a] Negative values reflect the higher tunnel entrance levels relative to exit levels. [b] Not presented due to a substantial organic adsorption artifact.

LDV and HDV Emission factors from the Caldecott Tunnel study

(Geller et al, ES&T, 2005)

HDV emissions are 10-30 fold higher for:

- **Mass**
- **EC**
- **Sulfate**

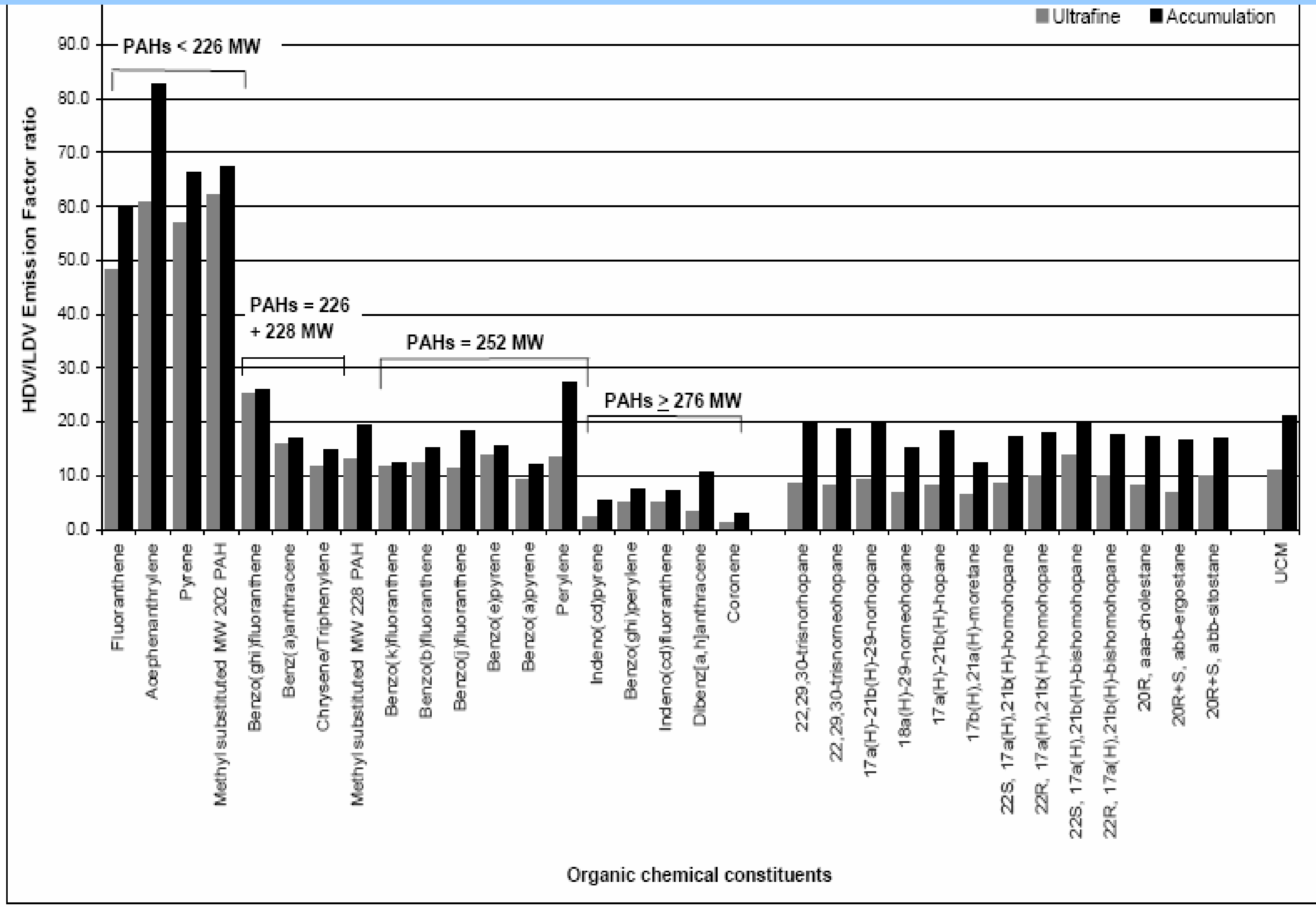
TABLE 7. Comparison of the Current Measured Concentrations of CO_2 and Emission Factors of $PM_{2.5}$ and PN to Measurements Made in Previous Studies at the Caldecott Tunnel

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	$1.285 \pm 0.2^{*}$	*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

PAH, Hopane and Steranes Emission factors for HDV and LDV; (Phuleria et al, ES&T, 2006, in press)



Note: EF ratio for PAHs < 226 may be overestimated due to positive adsorption artifact in ultrafine size modes.

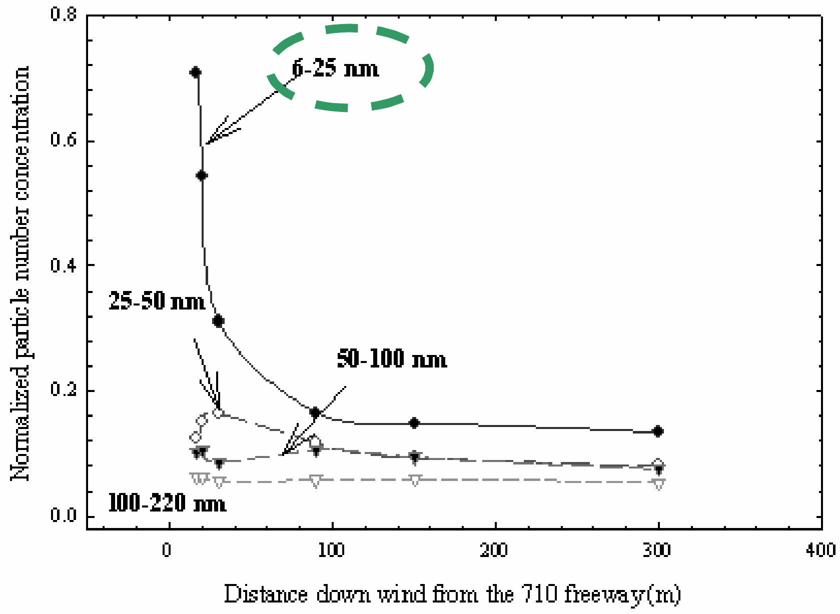
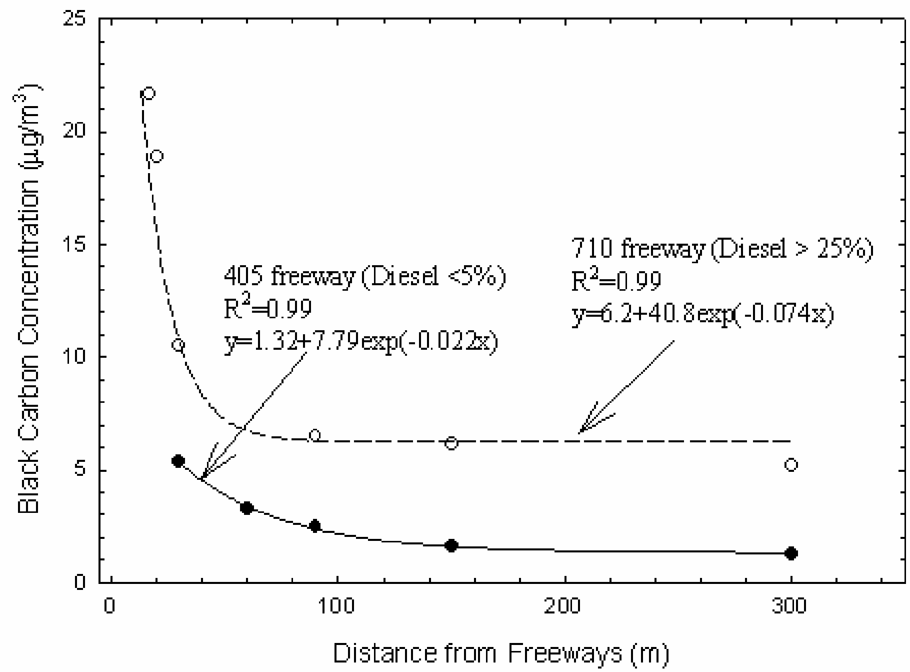


Figure 5. Normalized particle number concentration for different size ranges as a function of distance to the 710 freeway.

The decrease is more pronounced for the smallest particles

EC concentrations are much higher in the diesel traffic freeway



(b)

The Issue of PM Volatility and Why it is Important

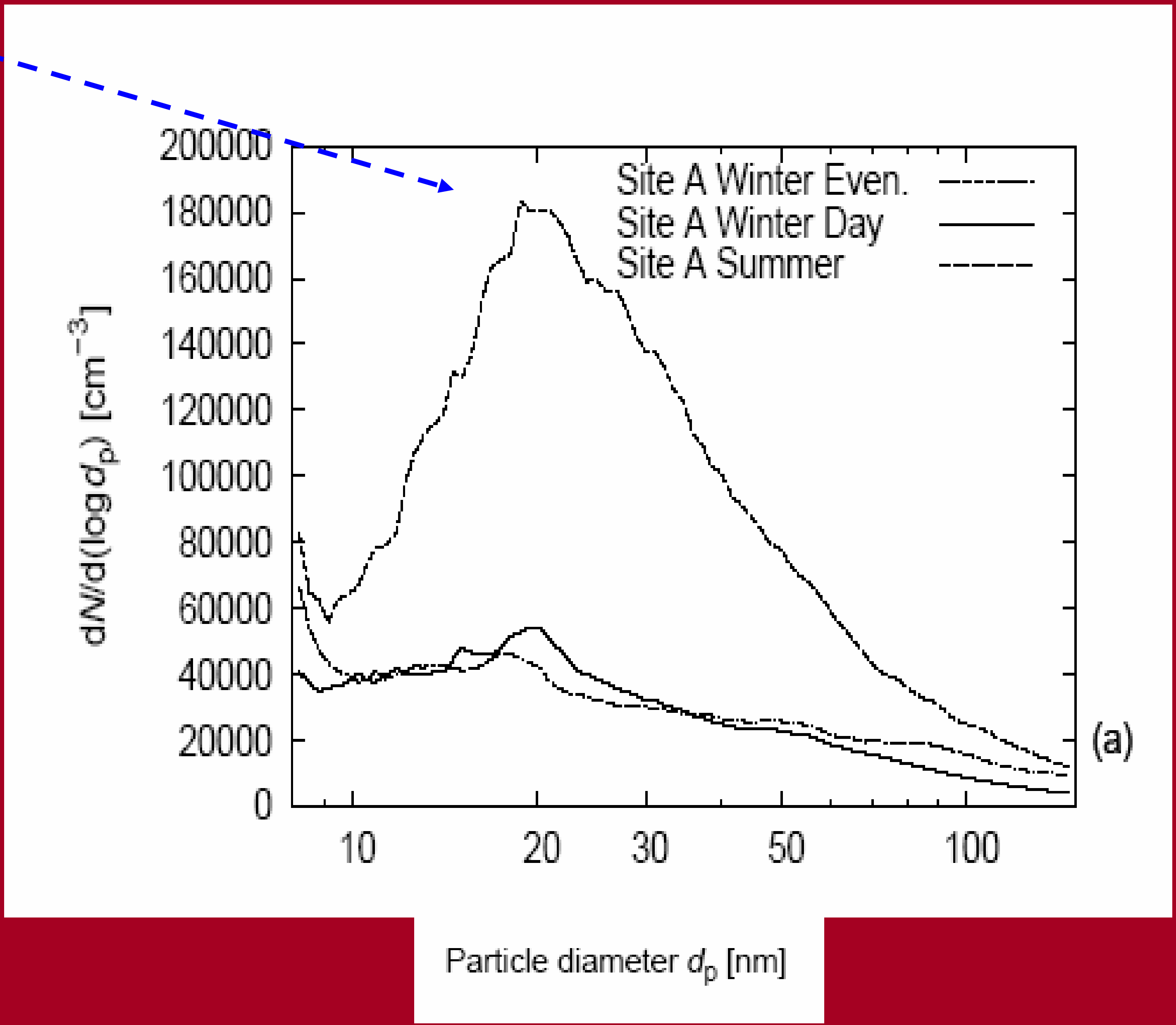
•**Exposure and health Implications**

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

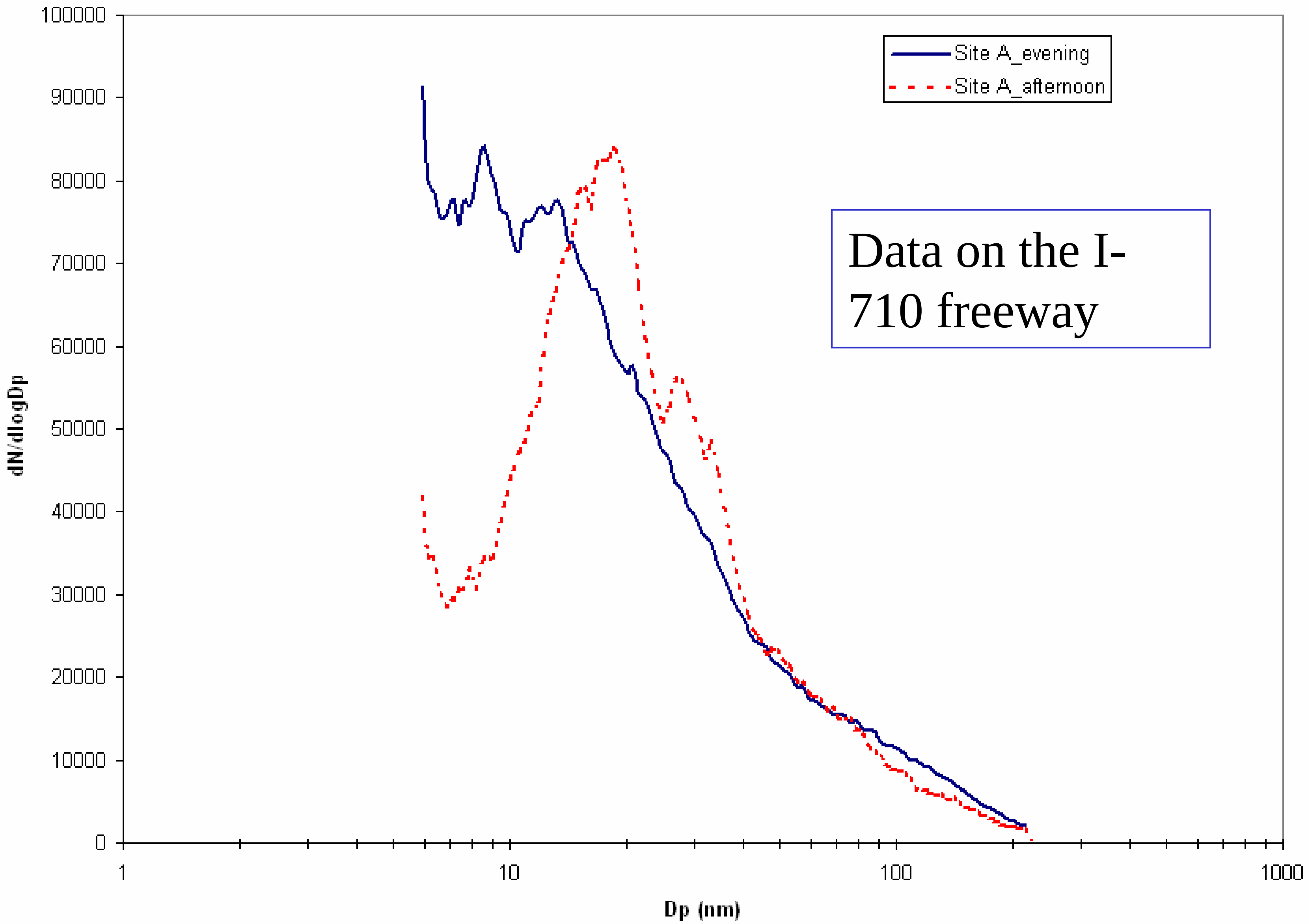
• The semi-volatile component of these particles may likely be present in its gaseous phase or associated with smaller sizes in indoor environments

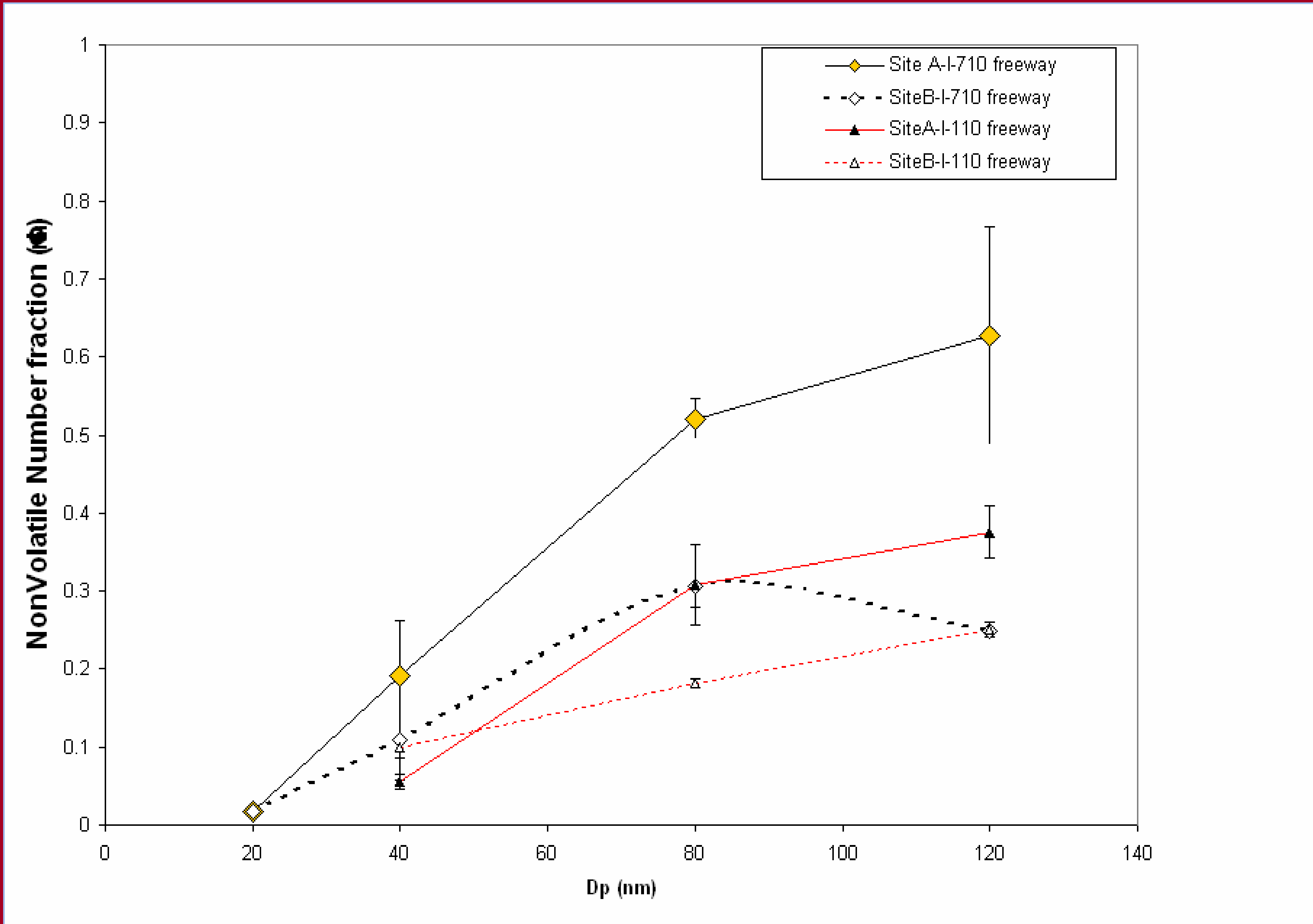
• Finally, given that the majority of people's exposure during commute will be dominated to these particles, it would be useful to know whether the non-volatile or semi-volatile material is more toxic.

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

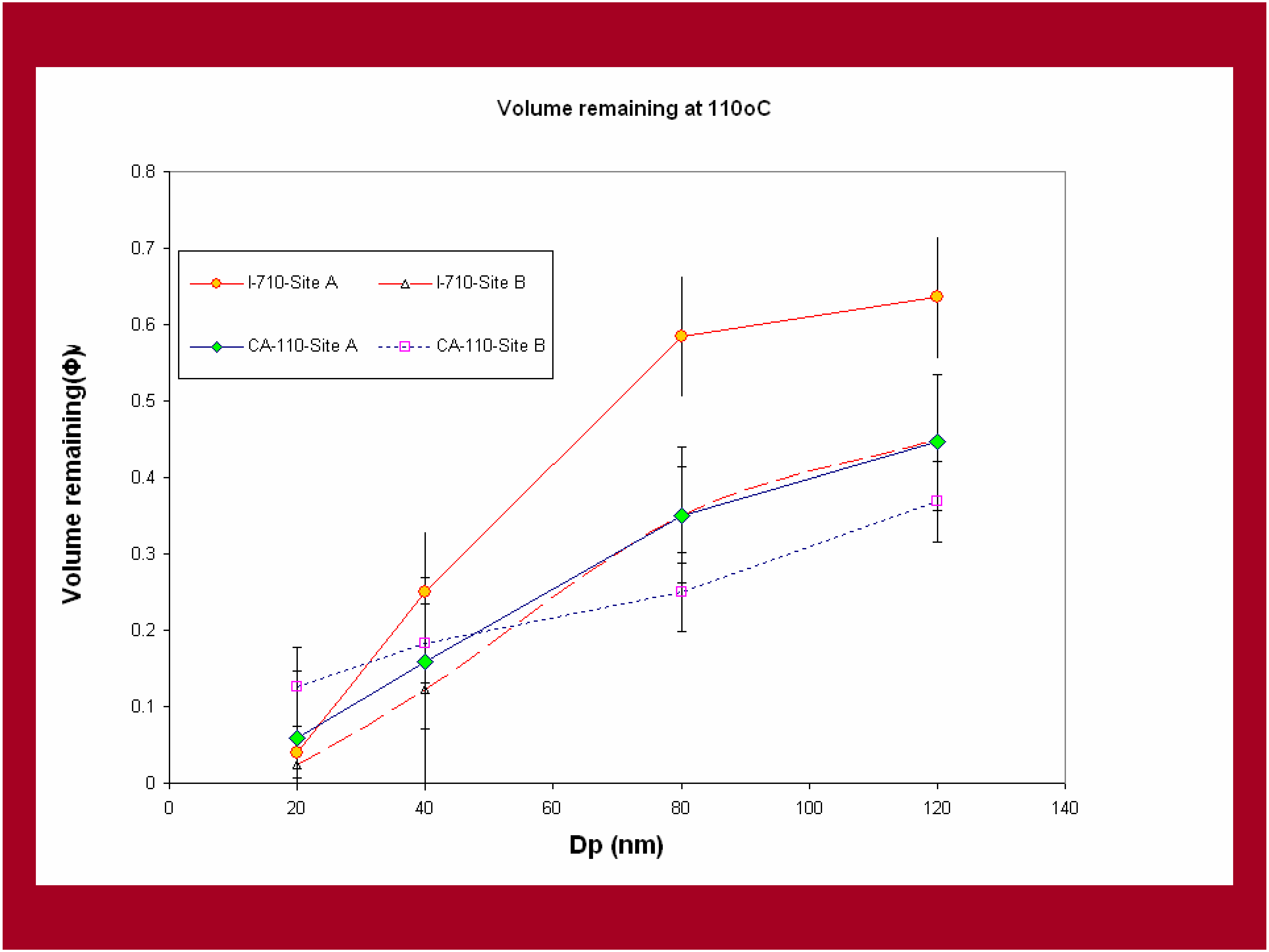


Kuhn et al., 2005, Atmos. Environ.

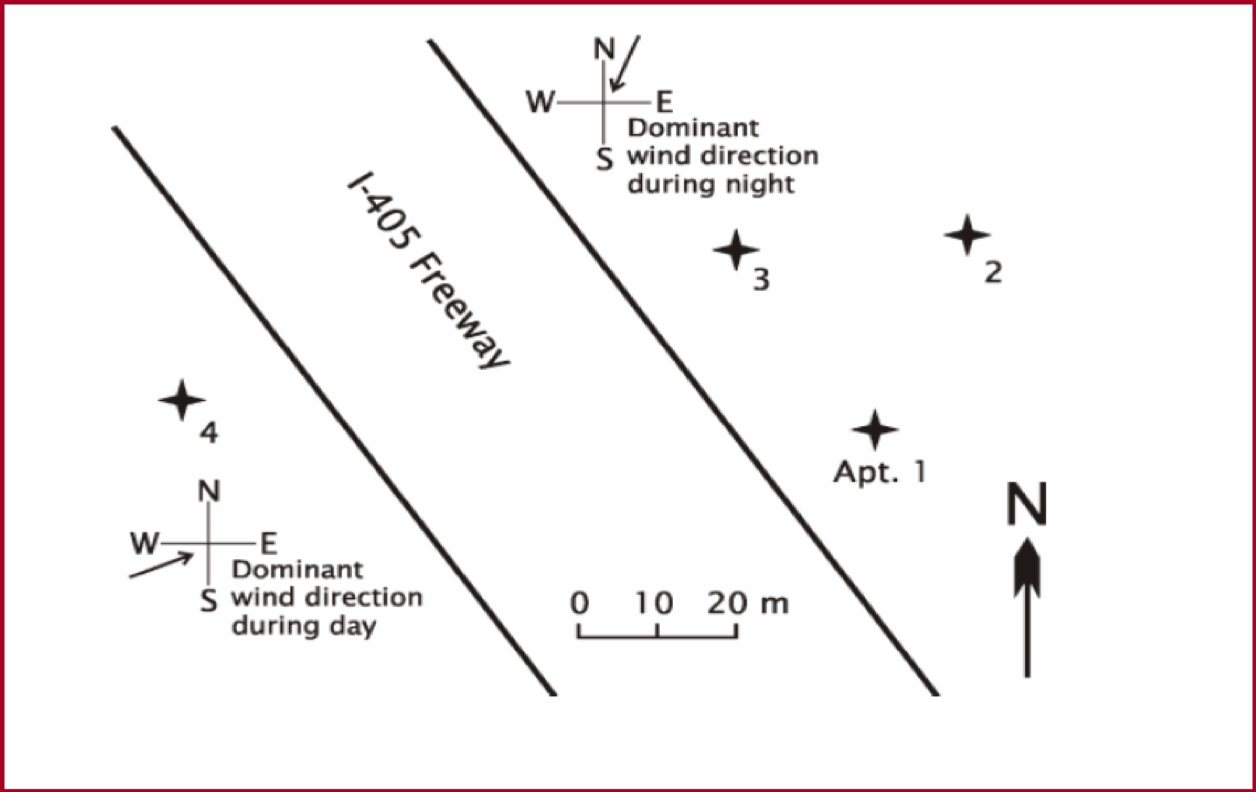

100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
dN/dlogDp
1
10
100
1000
Dp (nm)
Site A_evening
Site A_afternoon
Data on the I-710 freeway



NonVolatile Number fraction (Φ)
Dp (nm)
Site A-I-710 freeway
SiteB-I-710 freeway
SiteA-I-110 freeway
SiteB-I-110 freeway
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
0
20
40
60
80
100
120
140


Volume remaining at 110oC
I-710-Site A
I-710-Site B
CA-110-Site A
CA-110-Site B
Volume remaining(Φ)
Dp (nm)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0
20
40
60
80
100
120
140

What is the Impact of Mobile Sources In Indoor Environments?

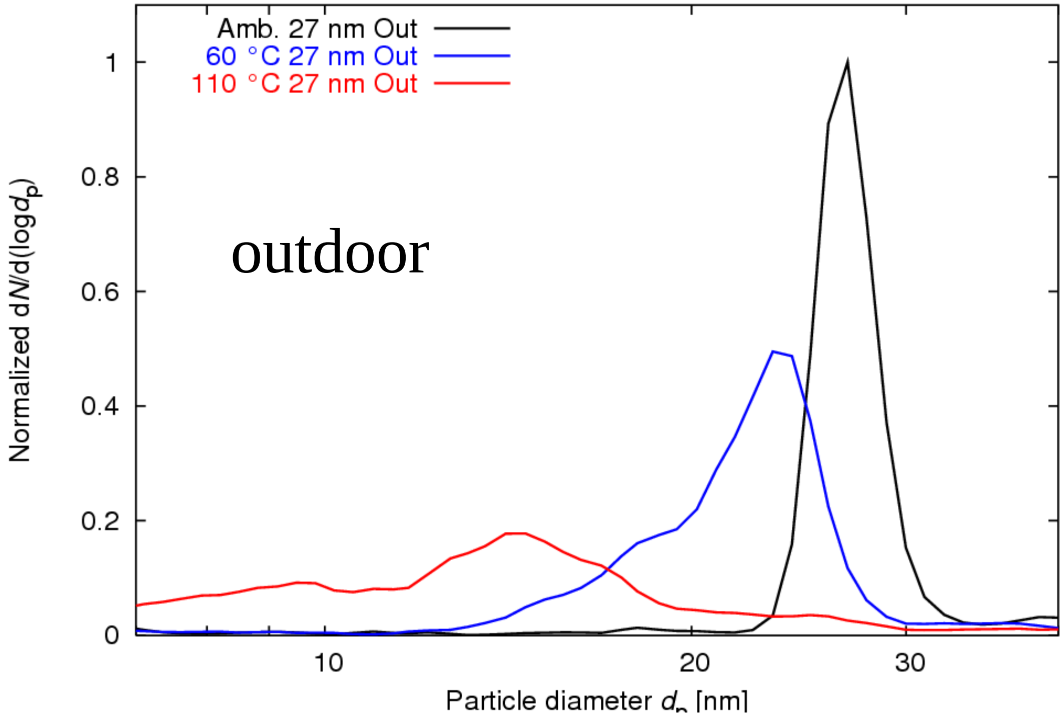


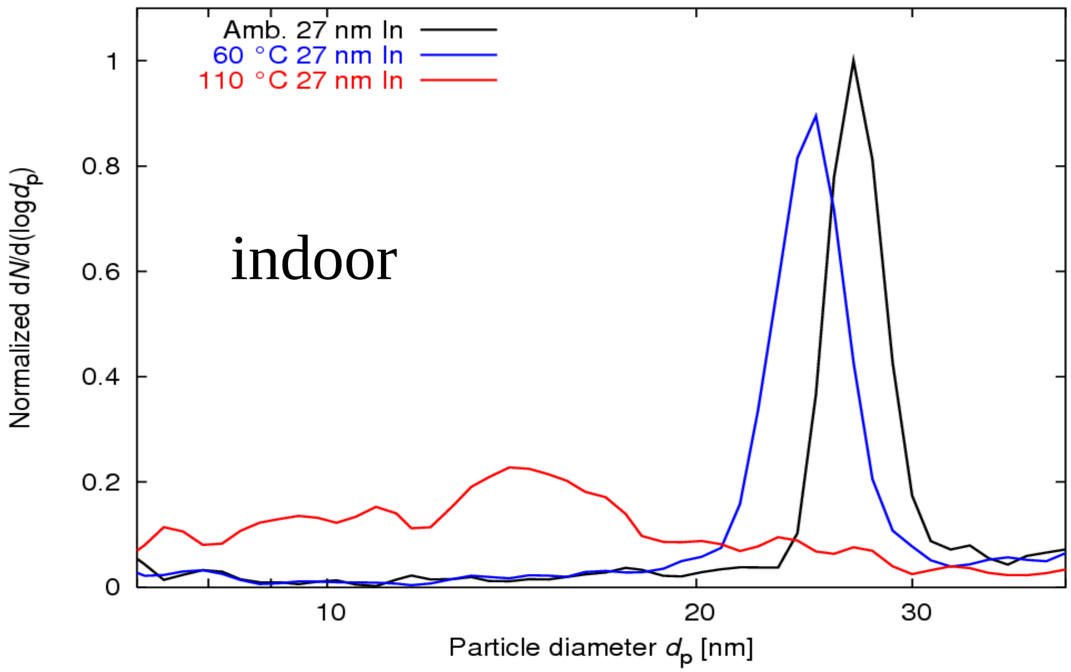
- 4 residences in proximity of I-405
- No indoor sources during tests
- 3 ventilation conditions tested

(Zhu et al., J Aerosol Science, 2004)

Indoor – Outdoor Comparisons

- It is evident that indoor particles of the same size are less volatile indoors
- This is because they may have already shrunk to that size from a larger outdoor particle





-Non volatile volume fraction of indoor PM consistently higher than outdoors.

- Volatility increases with decreasing particle size both indoors and outdoors

T. Kuhn et al. / Aerosol Science 36 (2005) 291–302

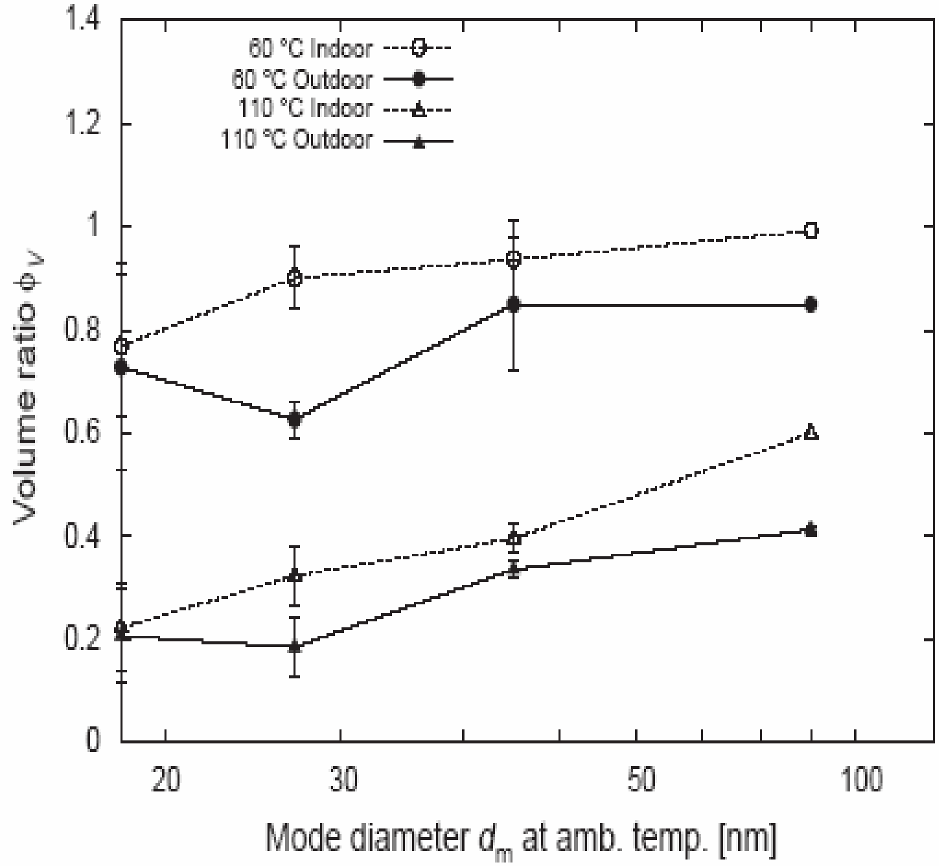
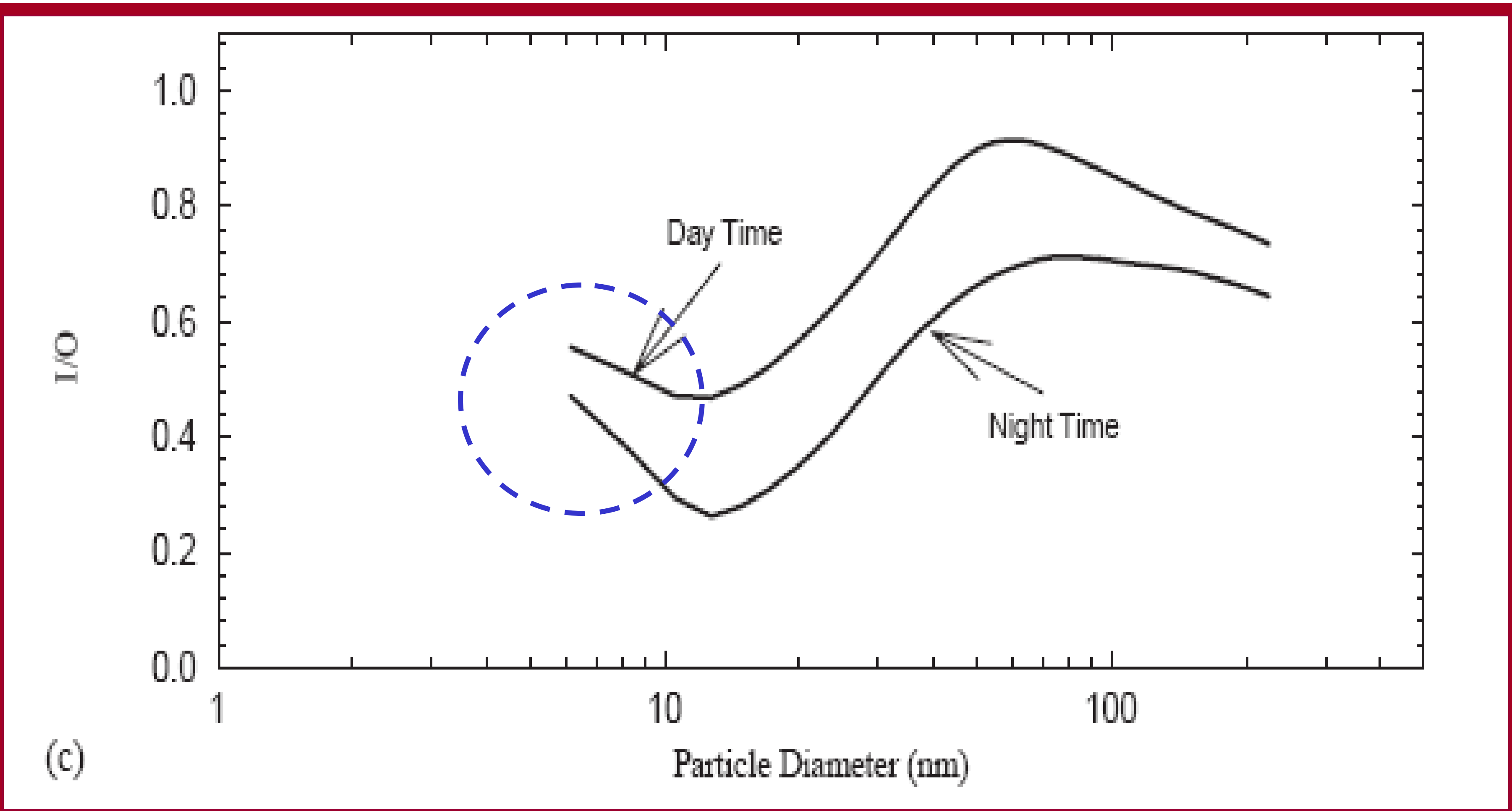


Fig. 6. Comparison of fractions ϕ_V for outdoor and indoor aerosols at Apt. 1.



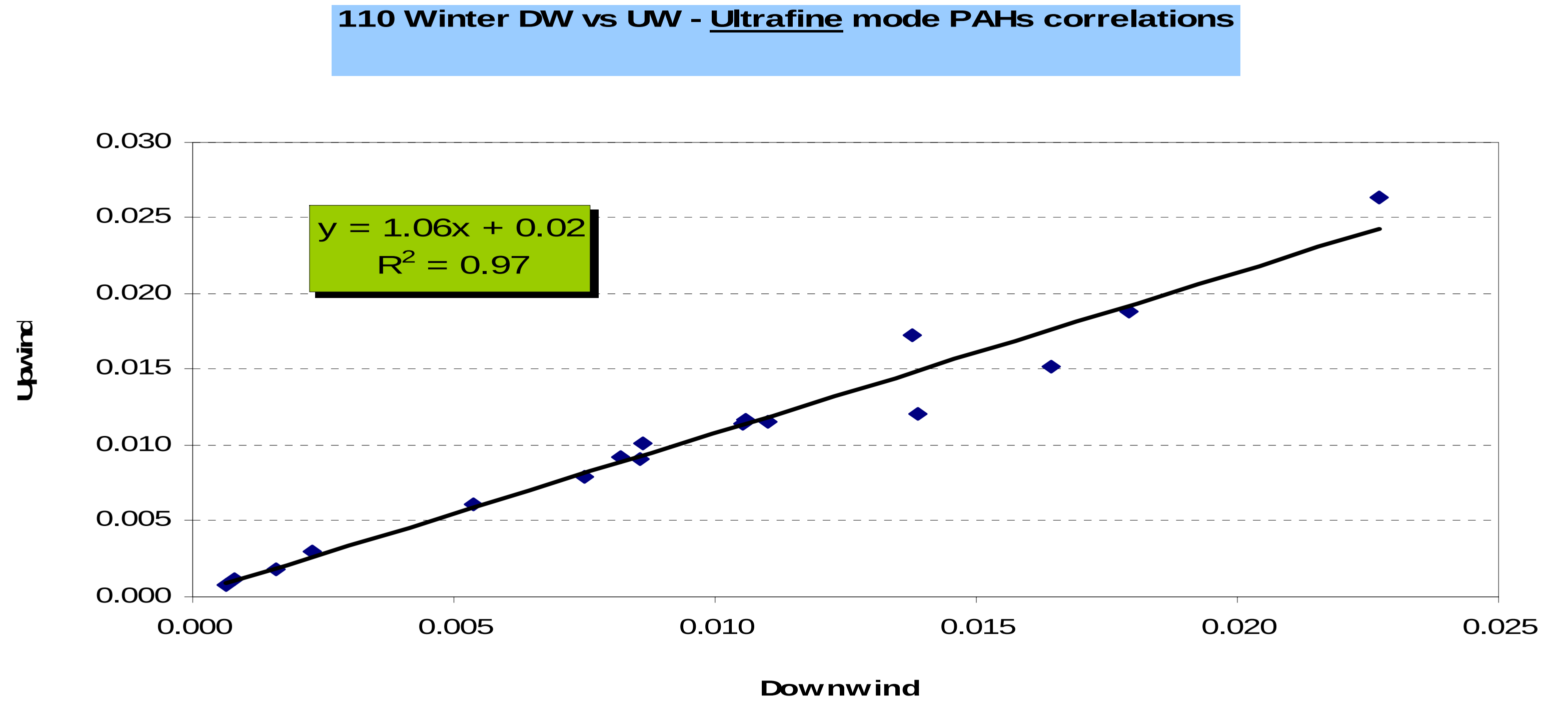
- For particles less than 20 nm, I/O ratios, penetration factors and deposition rates did not follow the trend of theoretical classic aerosol theory.

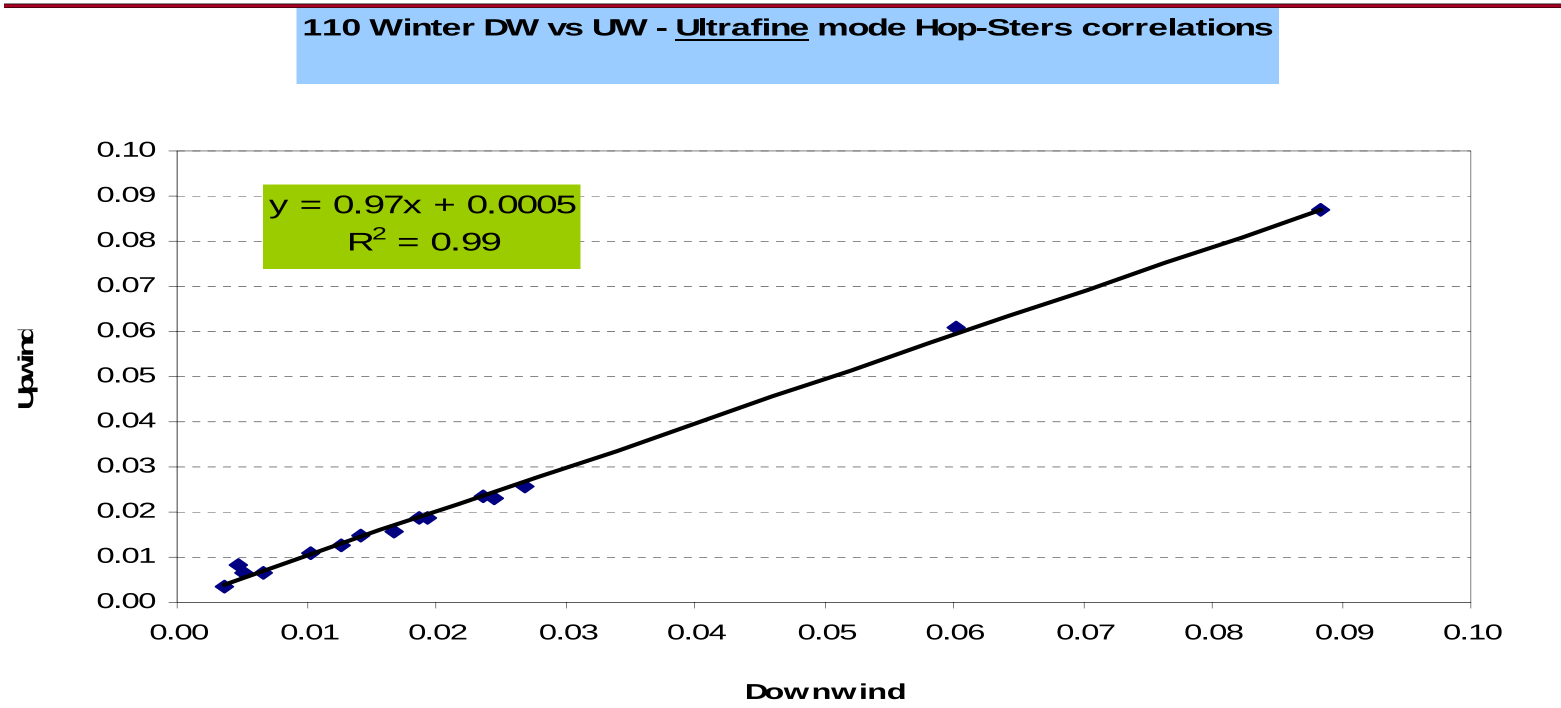
- Possible reason may be the unique, semi-volatile, nature of freeway ultrafine particles.

(Zhu et al., J Aerosol Science, 2004)

Chemical Speciation of PM at the CA-110 LDV only Freeway

	Coarse		Accumulation		Ultrafine			Coarse		Accumulation		Ultrafine	
	A	B	A	B	A	B		A	B	A	B	A	B
Mass							**S**						
Mean	7.60	4.92	13.98	10.62	6.00	5.04	Mean	0.08	0.06	0.34	0.27	0.03	0.06
SD	0.66	0.58	11.13	5.48	1.54	1.17	SD	0.05	0.02	0.34	0.22	0.01	0.03
Nitrate							**Cl**						
Mean	0.67	0.49	2.38	2.49	2.82	3.01	Mean	0.10	0.11	0.02	0.01	0.00	0.01
SD	0.55	0.48	3.20	3.79	1.62	1.42	SD	0.07	0.09	0.03	0.01	0.00	0.01
Sulfate							**K**						
Mean	0.27	0.17	0.77	0.82	1.58	1.23	Mean	0.08	0.08	0.04	0.05	0.02	0.04
SD	0.20	0.10	0.71	0.90	0.79	0.36	SD	0.04	0.02	0.01	0.01	0.01	0.01
OC							**Ca**						
Mean	1.37	0.77	2.17	2.17	14.55	10.66	Mean	0.27	0.26	0.09	0.10	0.04	0.09
SD	0.67	0.46	0.93	1.02	5.76	7.41	SD	0.10	0.04	0.03	0.04	0.02	0.04
EC							**Ti**						
Mean	0.21	0.05	0.14	0.12	1.90	1.50	Mean	0.03	0.03	0.02	0.02	0.01	0.01
SD	0.21	0.04	0.07	0.03	1.30	1.04	SD	0.01	0.01	0.01	0.01	0.00	0.01
Na							**Fe**						
Mean	0.08	0.26	0.06	0.06	0.01	0.03	Mean	0.66	0.56	0.34	0.30	0.09	0.16
SD	0.06	0.25	0.06	0.03	0.01	0.03	SD	0.16	0.17	0.10	0.15	0.05	0.08
Mg							**Cu**						
Mean	0.02	0.01	0.00	0.04	0.02	0.00	Mean	0.03	0.02	0.02	0.02	0.01	0.01
SD	0.02	0.00	0.00	0.01	0.00	0.00	SD	0.01	0.01	0.01	0.01	0.00	0.00
Al							**Zn**						
Mean	0.15	0.15	0.04	0.06	0.39	0.47	Mean	0.01	0.01	0.02	0.02	0.00	0.01
SD	0.08	0.02	0.01	0.02	0.61	0.40	SD	0.01	0.00	0.01	0.01	0.00	0.00
Si							**Ba**						
Mean	0.56	0.54	0.17	0.21	0.11	0.20	Mean	0.04	0.03	0.03	0.02	0.00	0.01
SD	0.22	0.13	0.06	0.08	0.06	0.08	SD	0.01	0.01	0.01	0.01	0.00	0.01



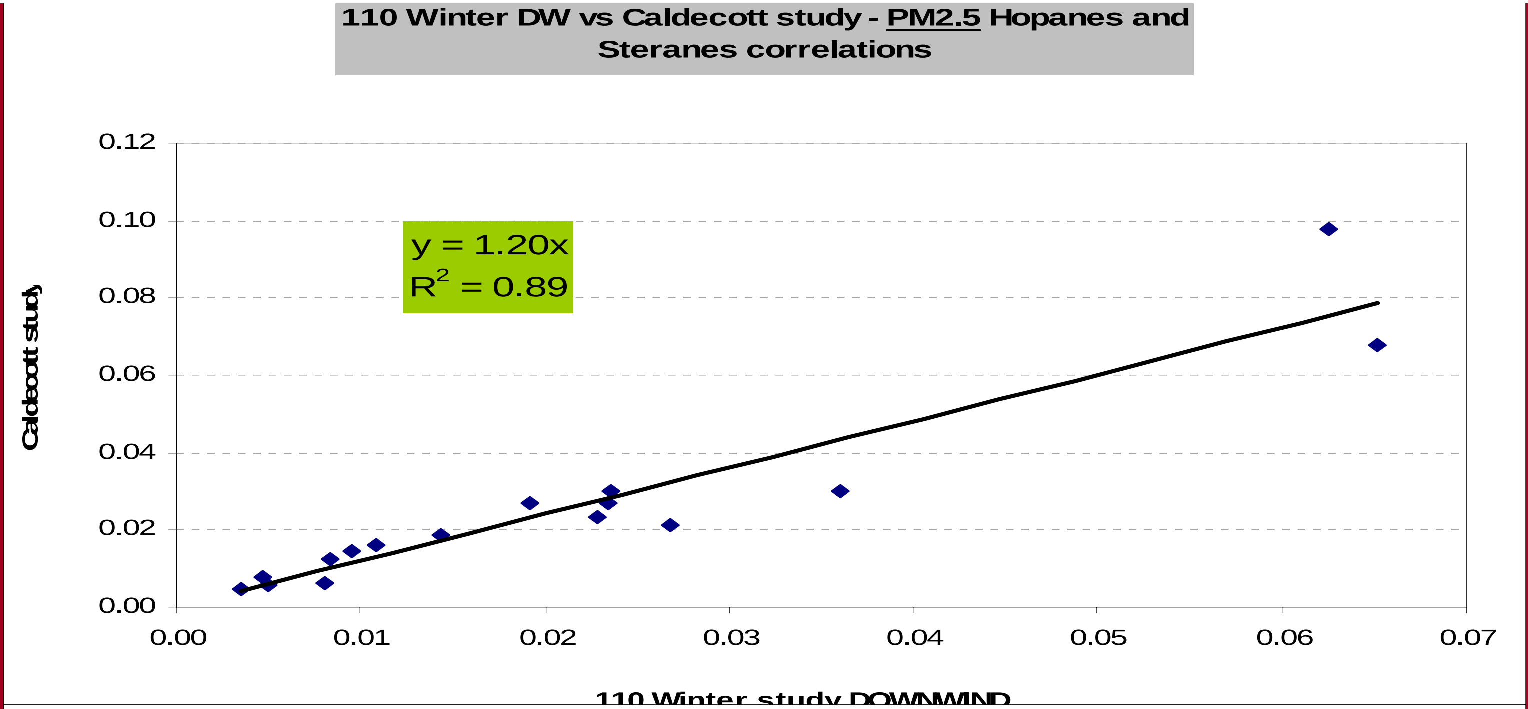


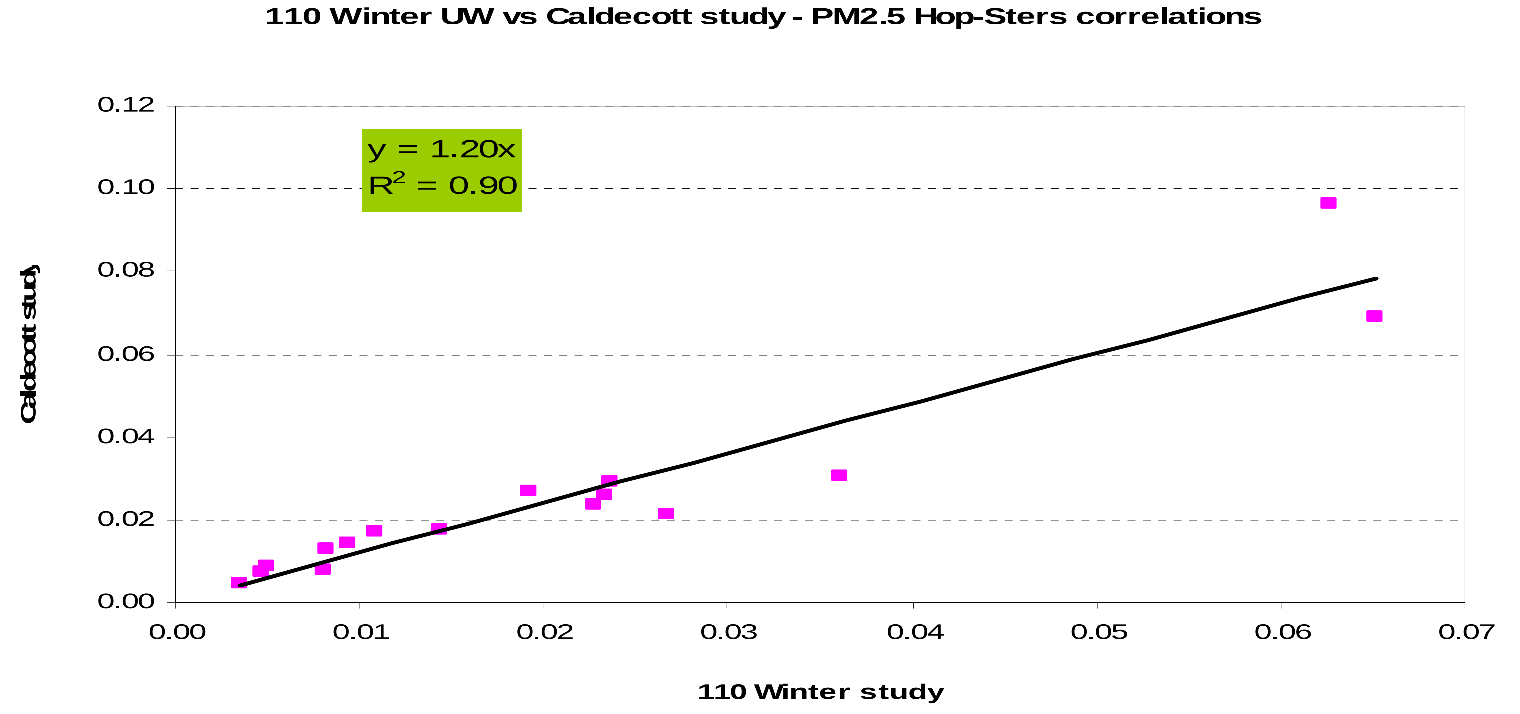
Similar PAH, hopanes and steranes levels upwind and downwind

of the CA-110 freeway

DW; downwind

UW; upwind





Similar Normalized Hopane and Steranes levels

upwind and downwind

of the CA-110 freeway to those of the LDV Caldecott Bore

(In Lieu of Conclusions) Major Research Questions to Be Addressed:

- The semi-volatile PM fraction of vehicle emissions is extremely important in terms of its contributions to human exposure

- To-date, there is no information on the relative toxicity of these particles compared to the larger, non-volatile (refractory), mostly carbonaceous fraction

- The combination of ultrafine aerosol concentrators (VACES)-thermodenuder technologies offers us a unique opportunity to study these 2 fractions separately

- Both in vivo and in vitro toxicity studies can be conducted using the VACES-thermodenuder tandem in:

    - Dynamometer facilities (heavy duty, light duty, vehicles with-without PM filter traps, catalysts, etc)
    - Roadway Tunnels
    - Proximity of freeways impacted by heavy duty (I-710) and gasoline only (I-110) traffic