

US EPA ARCHIVE DOCUMENT

Sources, Composition, Variability and Toxicological Characteristics of Coarse (PM10-2.5) Particles in Southern California

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Co- Investigators:

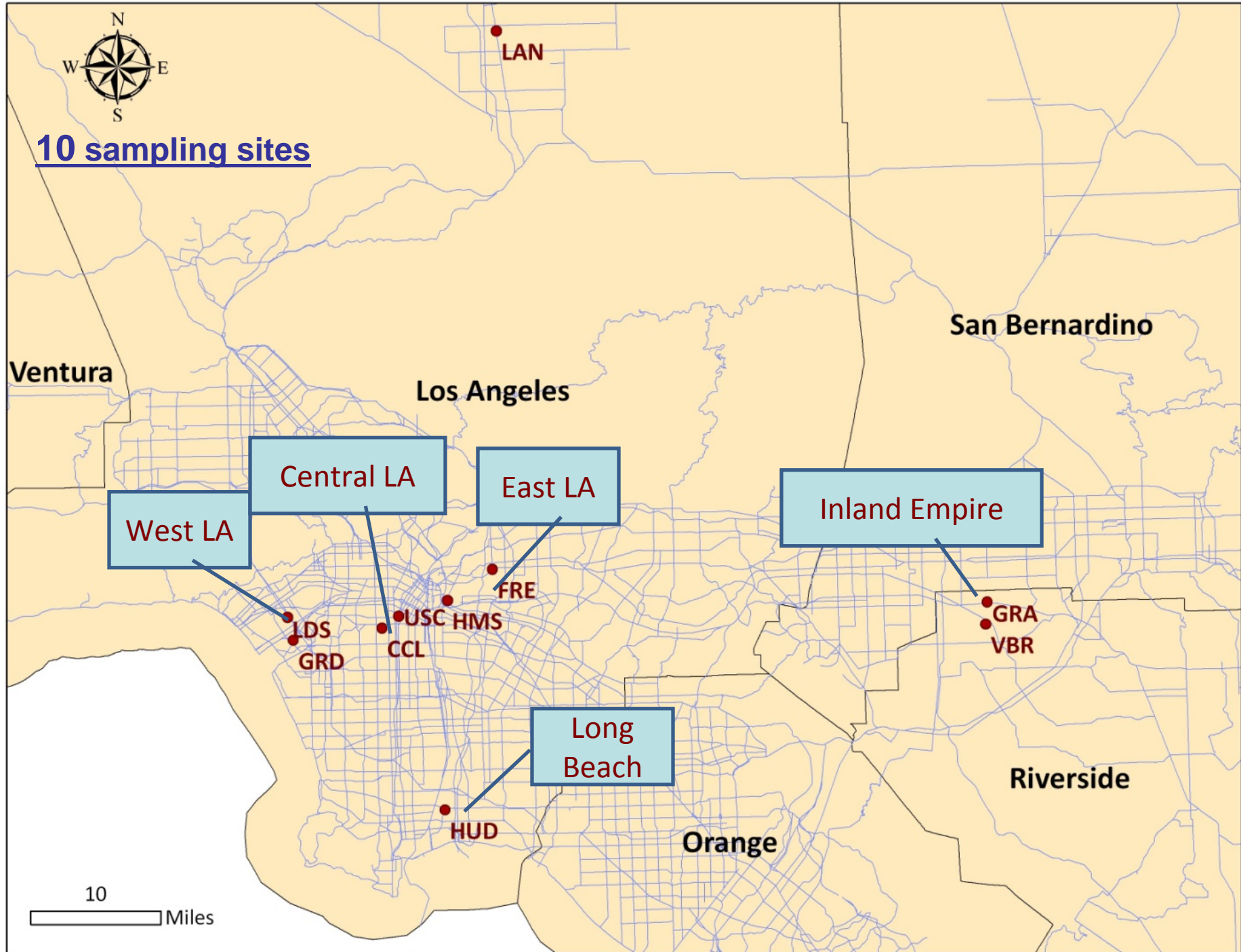
- Jamie J. Schauer, Martin Schafer; University of Wisconsin-Madison
- John R. Froines, Arthur K. Cho, Andre Nel, Ning Li : University of California- Los Angeles

Study Objectives:

- The objective of this study is to provide the much-needed information on the relationships between coarse particulate matter (PM) sources, spatial and seasonal characteristics, and toxicity in Southern California.
- The proposed multidisciplinary research in exposure assessment and toxicology activities will be integrated with other major efforts currently under way in Southern California.
- These include :
 - the EPA-supported Southern California Particle Center (SCPC)
 - the Multi-Ethnic Study of Atherosclerosis Air Pollution Study (MESA Air)

Research Questions:

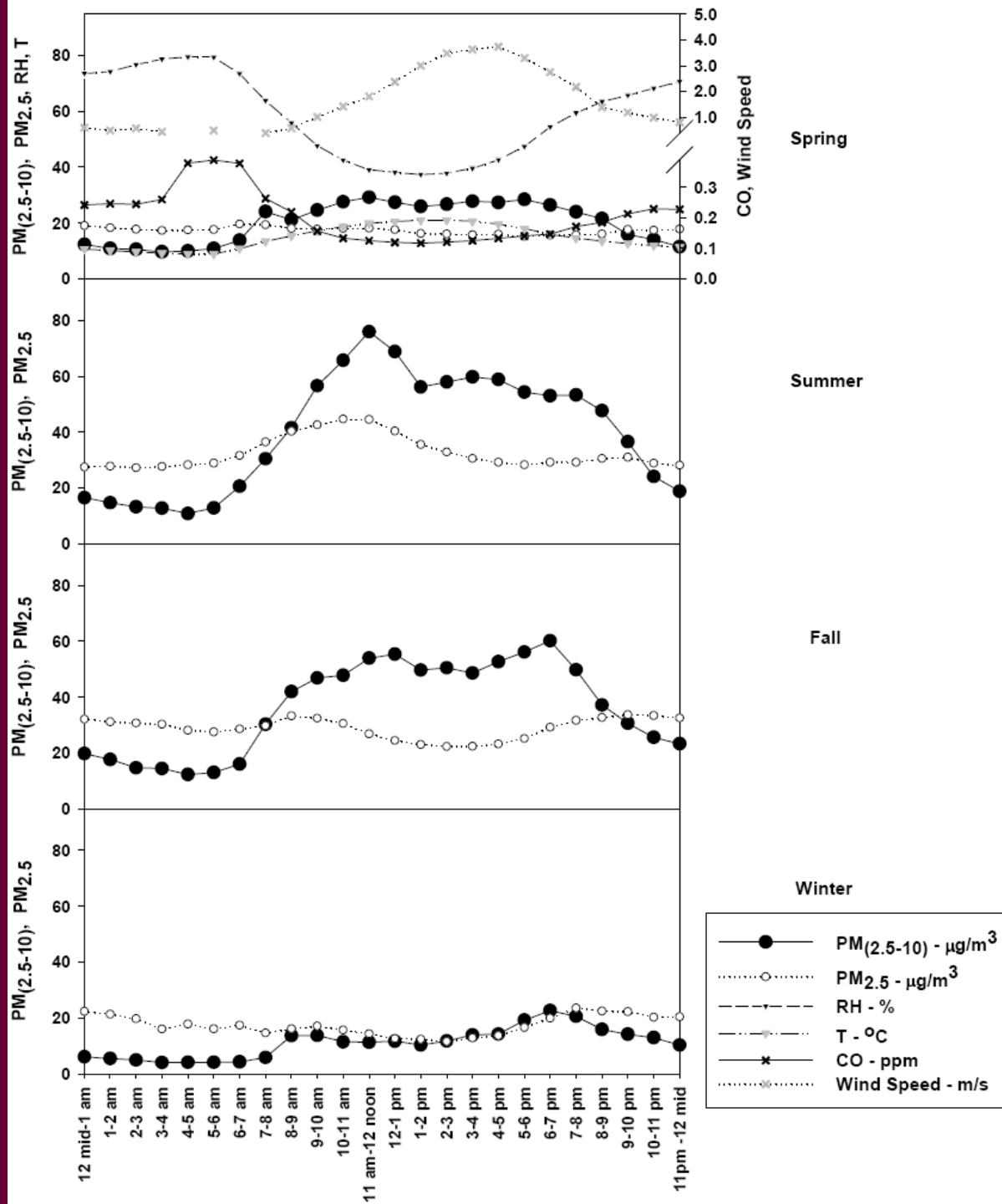
- a. What are the spatial, diurnal and seasonal differences in coarse PM mass and chemical composition found in rural and in urban areas of the Los Angeles Basin?
- b. How do the physico-chemical and toxicological characteristics of coarse PM measured near schools with minority populations compare to those of other urban and rural areas? (community of Long Beach)
- c. What is the fraction of chemically speciated PM that penetrates indoors?
- d. How do the chemical characteristics of coarse PM collected in each of the above environments and over different seasons determine and influence their toxicity?
- e. How does coarse PM toxicity differ from that of fine and ultrafine PM, measured in studies undertaken by the PIs, and sponsored separately by the SCPC?



10 sampling sites

10 Miles

VBR Site



- Low overnight CPM concentrations with rapid rise in the morning.
- Summer and Fall CPM concentrations higher than spring and winter.
- CO peak prior to the morning rise in CPM concentrations – probable contribution by vehicles via road dust resuspension
- Concentrations generally inversely proportional to RH

Lancaster (desert) site

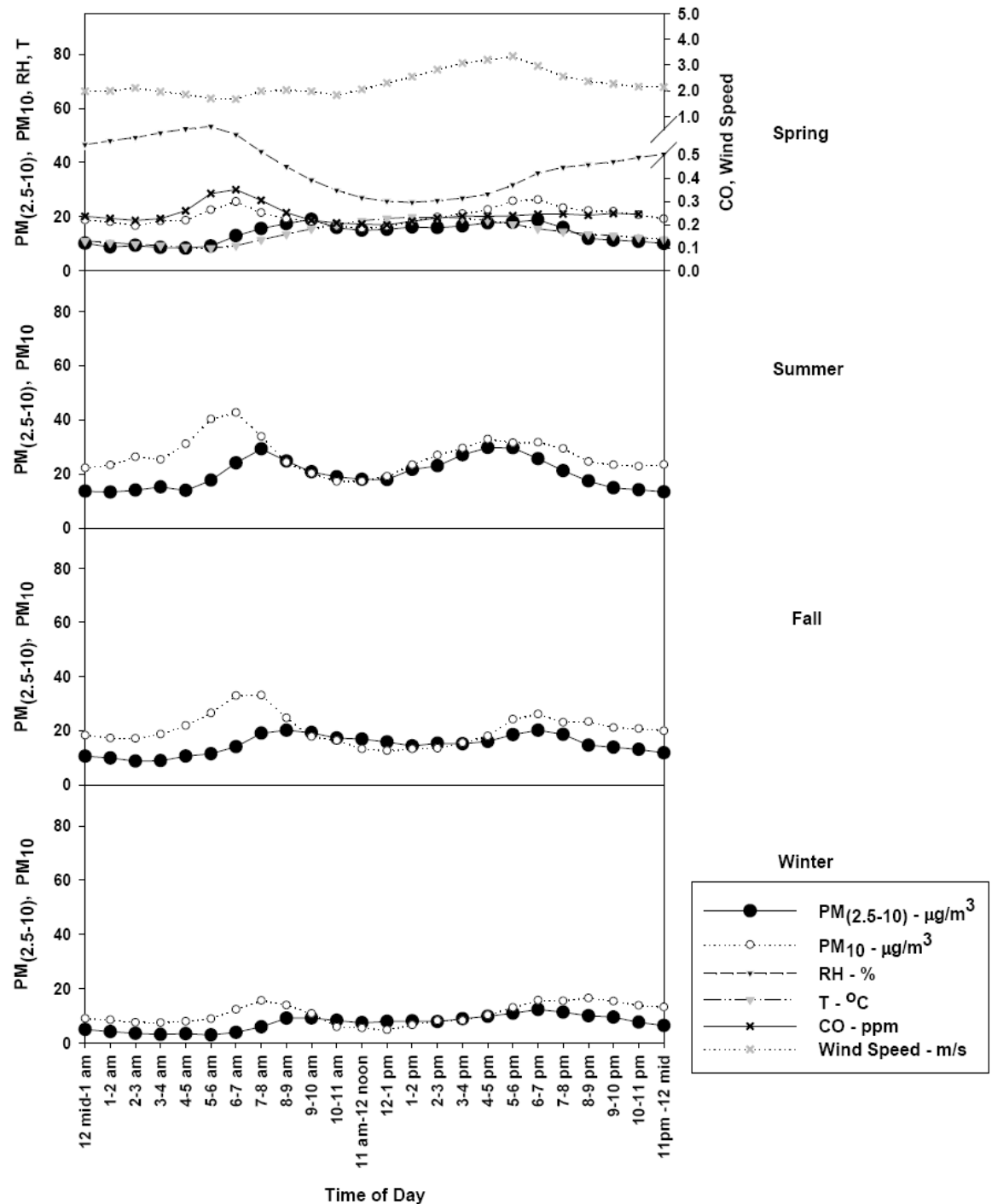
- Less seasonal variability than in VBR.

- Two distinct CPM peaks – in the early morning and evening coinciding with commute periods - re-suspension of road dust

- Lowest concentrations in winter.

- Low overnight concentration.

- CPM constitutes a major fraction of PM_{10} .



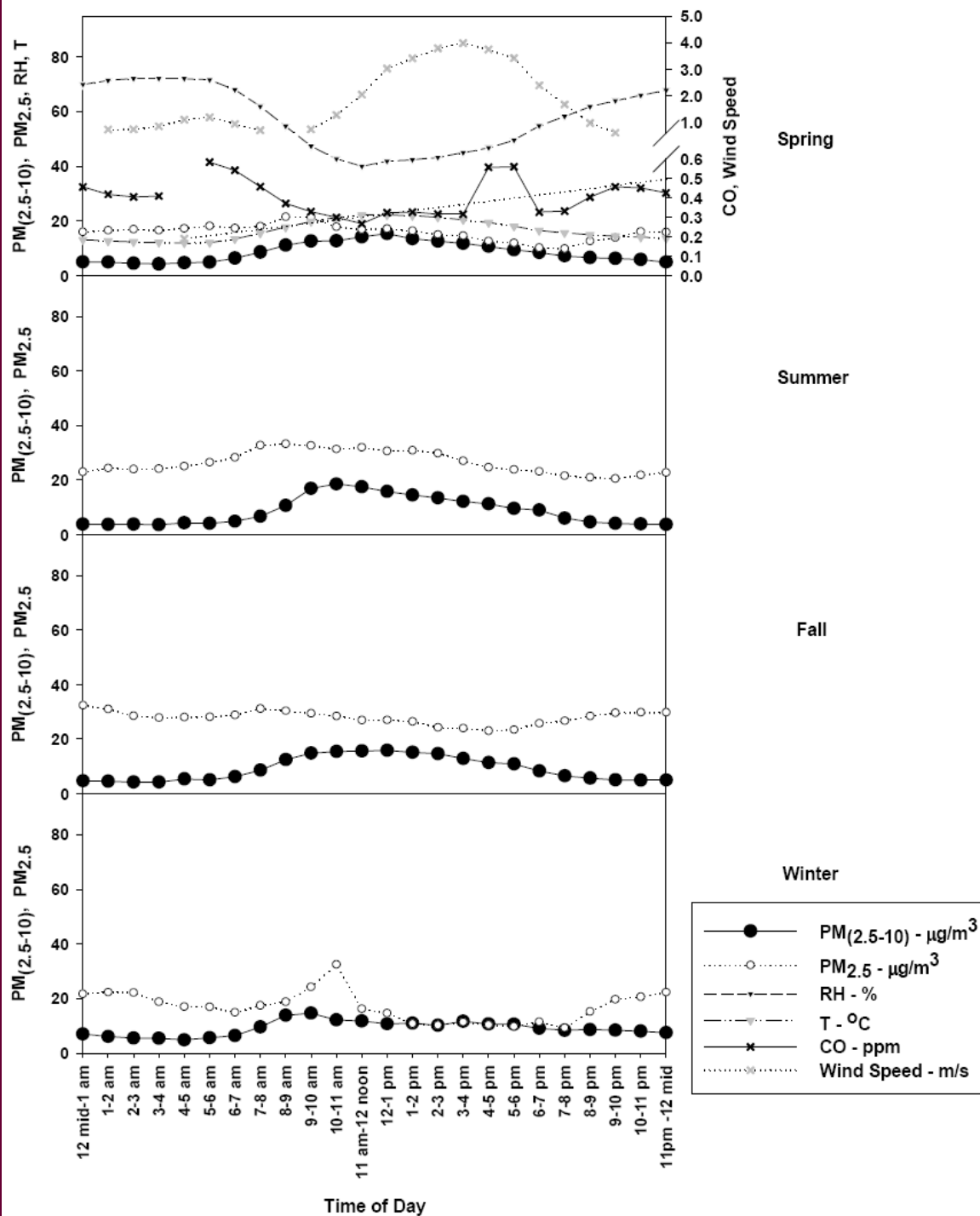
USC (central LA) site

- Somewhat intermediate of VBR and LAN.

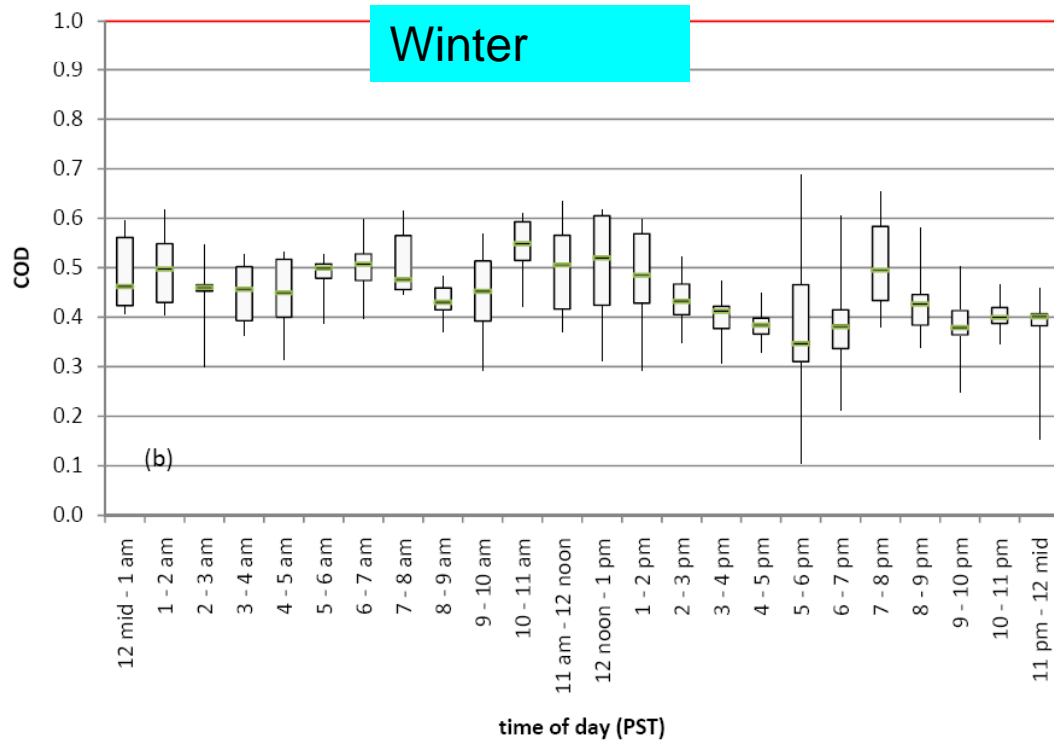
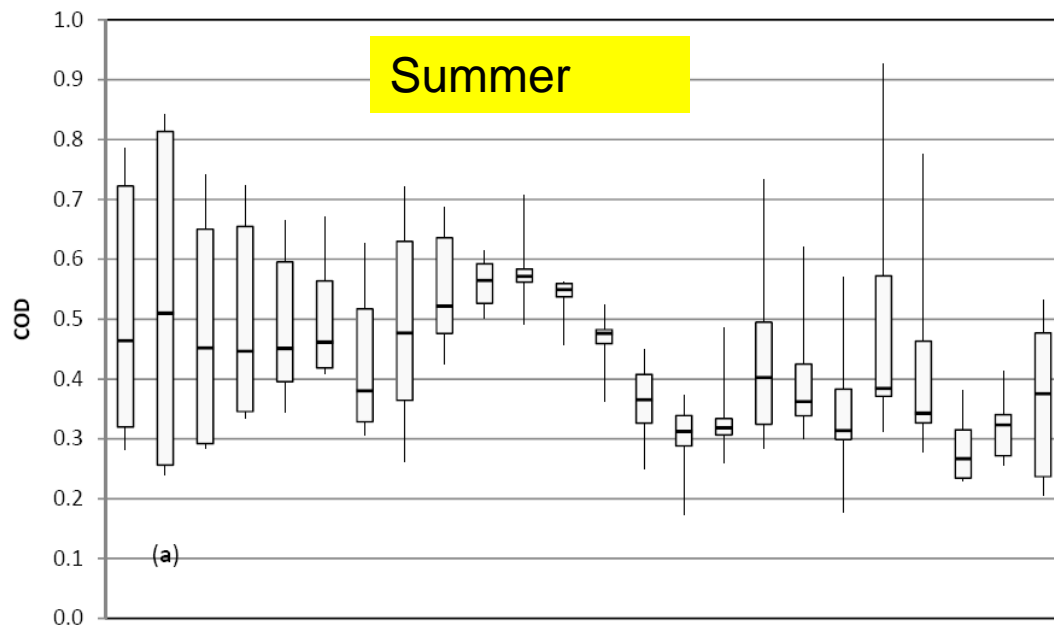
- Low overnight CPM concentration with a mid-morning peak, following the morning commute.

- Lower peak daytime concentrations throughout the year compared to the other sites.

- $PM_{2.5}$ constitutes a major fraction of PM_{10} , although CPM becomes important during middle of the day.



Spatial Variability



- High CODs during middle of the day and somewhat reduced COD values in the early and late evenings.

- Higher summer CODs in the morning, compared to the winter.

- Variability in sources on sub-km scales can produce quantifiably different ambient concentrations leading to considerably different exposures to CPM concentrations.

TABLE 3

Pearson correlation coefficients (R) for the regression analysis of PM_{10-2.5} and PM_{2.5} (PM₁₀ at Lancaster) with other measured parameters

Pearson Correlation Coefficient (R)										
Site	Season	Parameter	CO	NO	NO ₂	NO _x	PM ₁₀ (LAN)/ PM _{2.5} (USC/VBR)	RH	T	Wind speed
LAN	<i>Spring</i>	PM _{10-2.5}	-0.21	-0.26	-0.50	-0.38	0.26	-0.78	0.77	0.58
		PM ₁₀	0.61	0.28	0.39	0.37	1.00	0.11	-0.08	0.45
	<i>Summer</i>	PM _{10-2.5}	-0.06	-0.21	-0.20	-0.19	0.45	-0.45	0.54	0.50
		PM ₁₀	0.39	0.24	0.50	0.45	1.00	0.46	-0.35	-0.07
	<i>Fall</i>	PM _{10-2.5}	0.07	0.03	-0.19	-0.07	0.22	-0.53	0.51	0.82
		PM ₁₀	0.95	0.81	0.88	0.89	1.00	0.61	-0.59	-0.18
	<i>Winter</i>	PM _{10-2.5}	-0.06	-0.27	-0.08	-0.19	0.45	-0.68	0.64	-0.43
		PM ₁₀	0.79	0.44	0.79	0.63	1.00	0.26	-0.26	-0.32
USC	<i>Spring</i>	PM _{10-2.5}	-0.53	-0.57	-0.71	-0.52	0.15	-0.97	0.98	0.62
		PM _{2.5}	0.03	0.42	0.48	0.51	1.00	0.06	0.02	-0.43
	<i>Summer</i>	PM _{10-2.5}	0.00	-0.05	0.13	0.01	0.73	-0.94	0.96	0.72
		PM _{2.5}	0.31	0.46	0.58	0.53	1.00	-0.60	0.68	0.26
	<i>Fall</i>	PM _{10-2.5}	-0.39	-0.36	-0.19	-0.36	-0.46	-0.98	0.95	-0.23
		PM _{2.5}	0.53	0.63	0.68	0.69	1.00	0.56	-0.57	-0.04
	<i>Winter</i>	PM _{10-2.5}	-0.44	-0.41	-0.18	-0.38	-0.05	-0.72	0.72	-0.05
		PM _{2.5}	0.41	0.46	0.05	0.40	1.00	0.35	-0.33	-0.38
VBR	<i>Spring</i>	PM _{10-2.5}	-0.82	-0.50	-0.83	-0.67	-0.48	-0.94	0.93	0.77
		PM _{2.5}	0.56	0.62	0.53	0.60	1.00	0.46	-0.48	-0.80
	<i>Summer</i>	PM _{10-2.5}	-0.65	-0.40	-0.72	-0.61	0.64	-0.95	0.94	0.81
		PM _{2.5}	-0.08	0.16	-0.10	0.01	1.00	-0.51	0.56	0.22
	<i>Fall</i>	PM _{10-2.5}	-0.78	-0.65	-0.67	-0.72	-0.45	-0.88	0.90	0.76
		PM _{2.5}	0.56	0.34	0.69	0.60	1.00	0.68	-0.66	-0.85
	<i>Winter</i>	PM _{10-2.5}	-0.33	-0.46		-0.25	0.13	-0.48	0.59	-0.06
		PM _{2.5}	0.53	0.45		0.66	1.00	0.70	-0.57	-0.66

CPM Mass Reconstruction Methodology

Chemical components were grouped into five categories:

- minerals and trace elements (MIN and TE),
- organic matter (OM),
- elemental carbon (EC)
- sea salt (SS),
- inorganic aerosol (IA) – non SS sulfate, nitrate, ammonium

MIN represents the sum of typical crustal metals- Al, K, Fe, Ca, Mg, Ti and Si.

$$\text{MIN} = 1.89\text{Al} + 1.21 \text{K} + 1.43 \text{Fe} + 1.4 \text{Ca} + 1.66 \text{Mg} + 1.7 \text{Ti} + 2.14\text{Si}$$

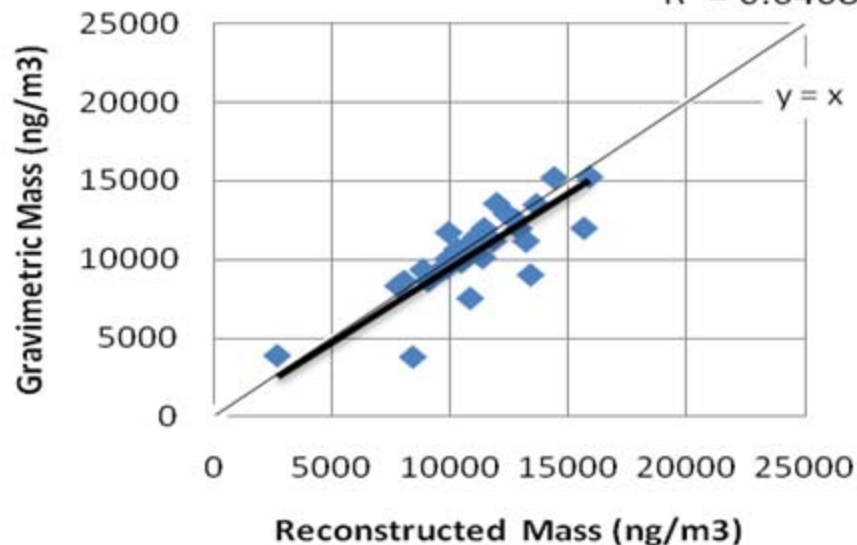
(*Elemental Si was estimated by multiplying Al using a factor of 3.41*)

$$\text{SS} = \text{Na}^+ + \text{ssCl}^- + \text{ssMg}^{2+} + \text{ssK}^+ + \text{ssCa}^{2+} + \text{ssSO}_4^{2-}$$

where $\text{ssCl}^- = 1.8 \text{Na}^+$, $\text{ssMg}^{2+} = 0.12 \text{Na}^+$, $\text{ssK}^+ = 0.036 \text{Na}^+$, $\text{ssCa}^{2+} = 0.038 \text{Na}^+$,
and $\text{ssSO}_4^{2-} = 0.252 \text{Na}^+$

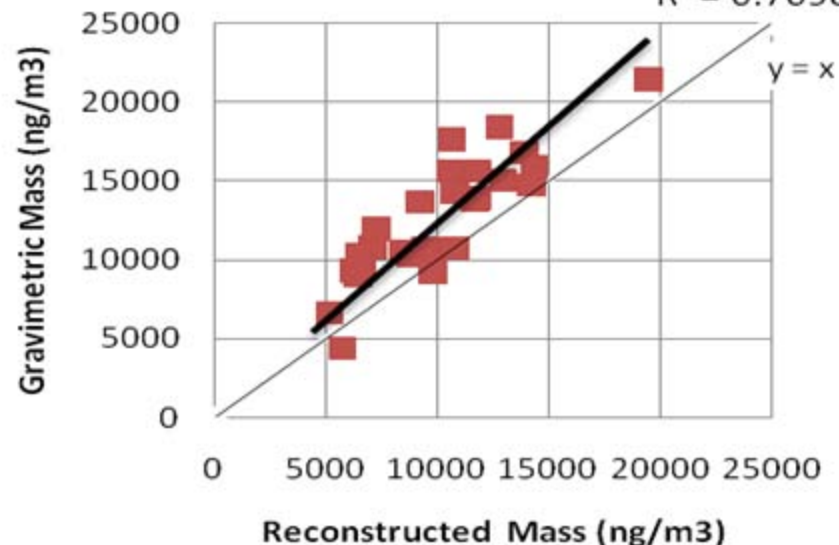
SPRING (MAR, APR, MAY)

$$y = 0.9414x$$
$$R^2 = 0.6408$$



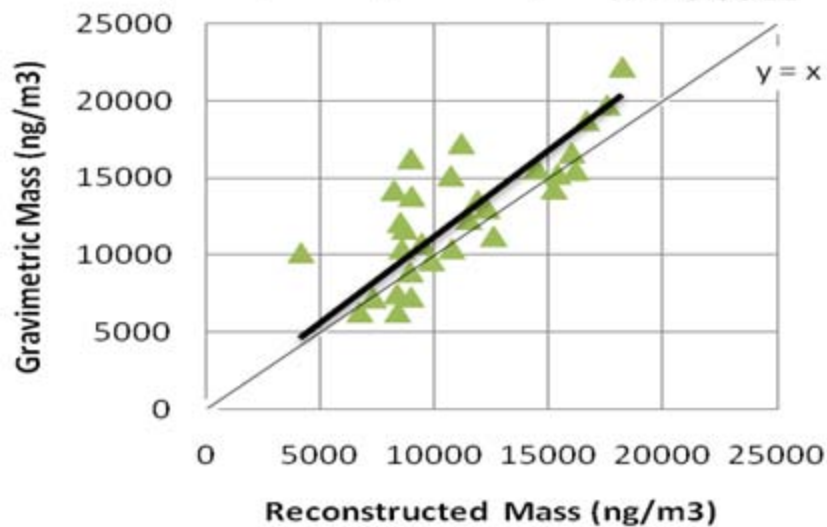
SUMMER (JUN, JUL, AUG)

$$y = 1.2314x$$
$$R^2 = 0.7098$$



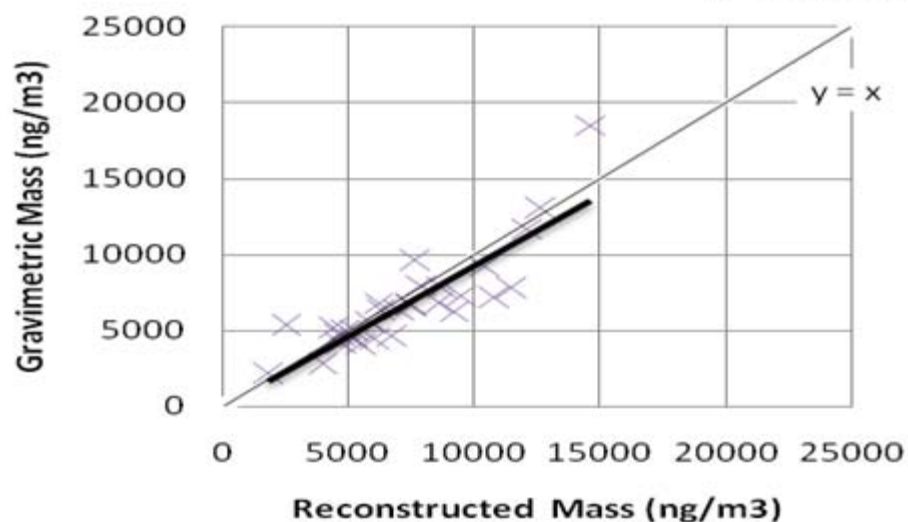
FALL (SEP, OCT, NOV)

$$y = 1.1209x$$
$$R^2 = 0.5521$$

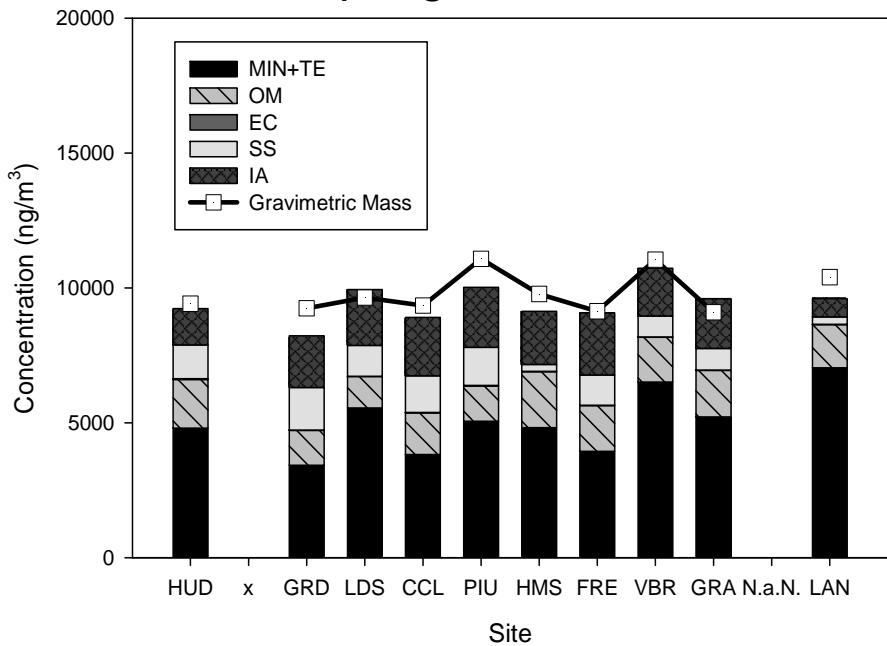


WINTER (DEC, JAN, FEB)

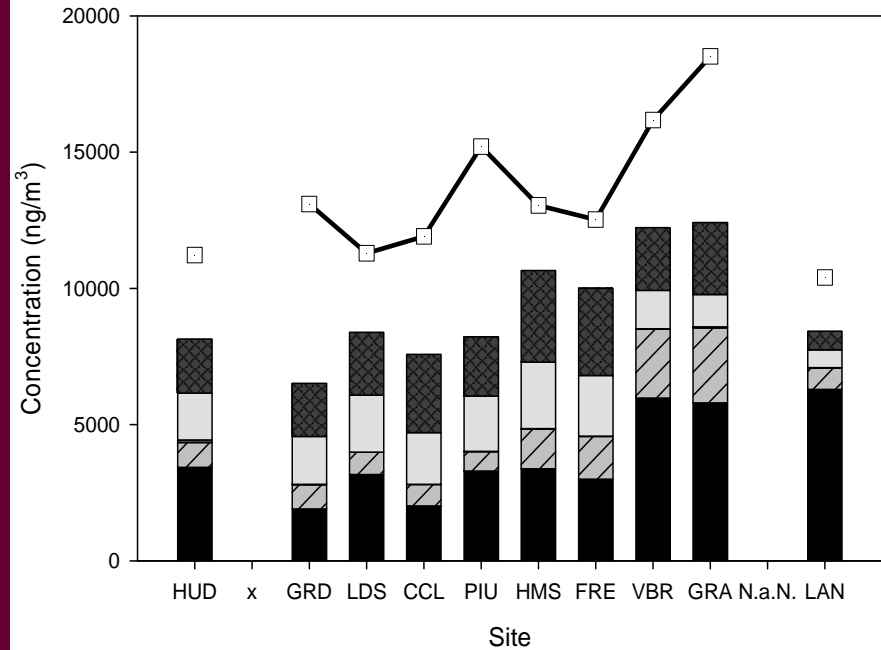
$$y = 0.928x$$
$$R^2 = 0.7461$$



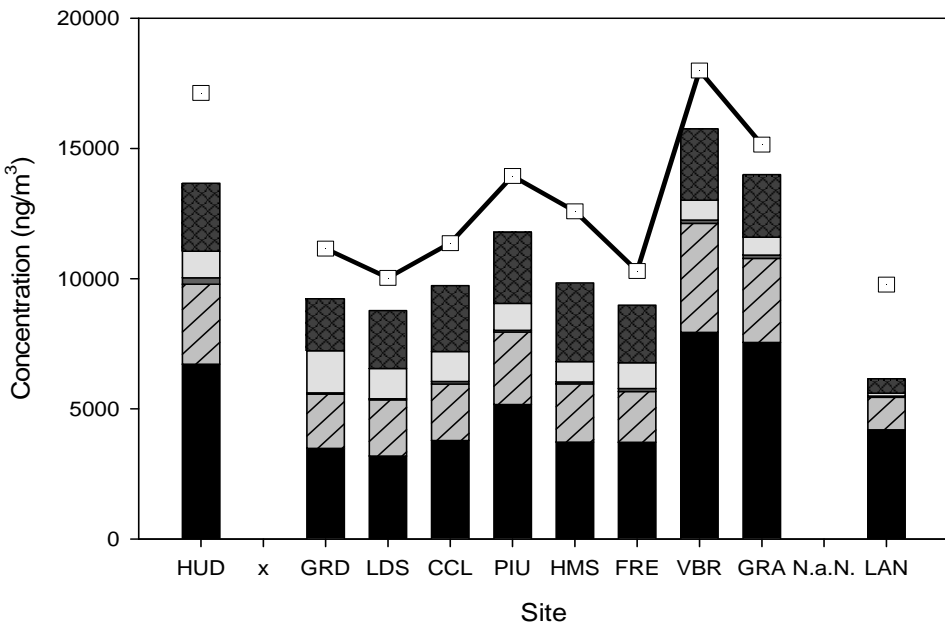
Spring



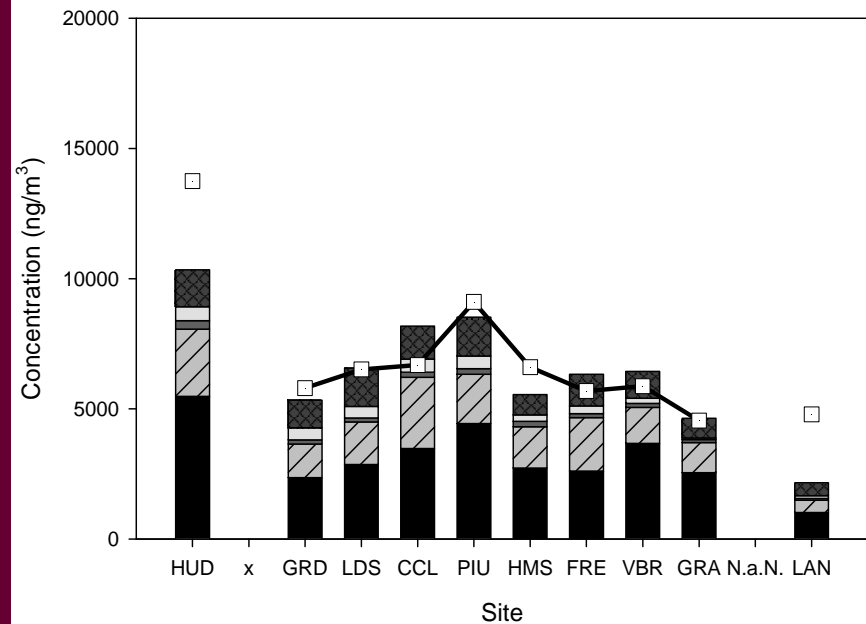
Summer



Fall

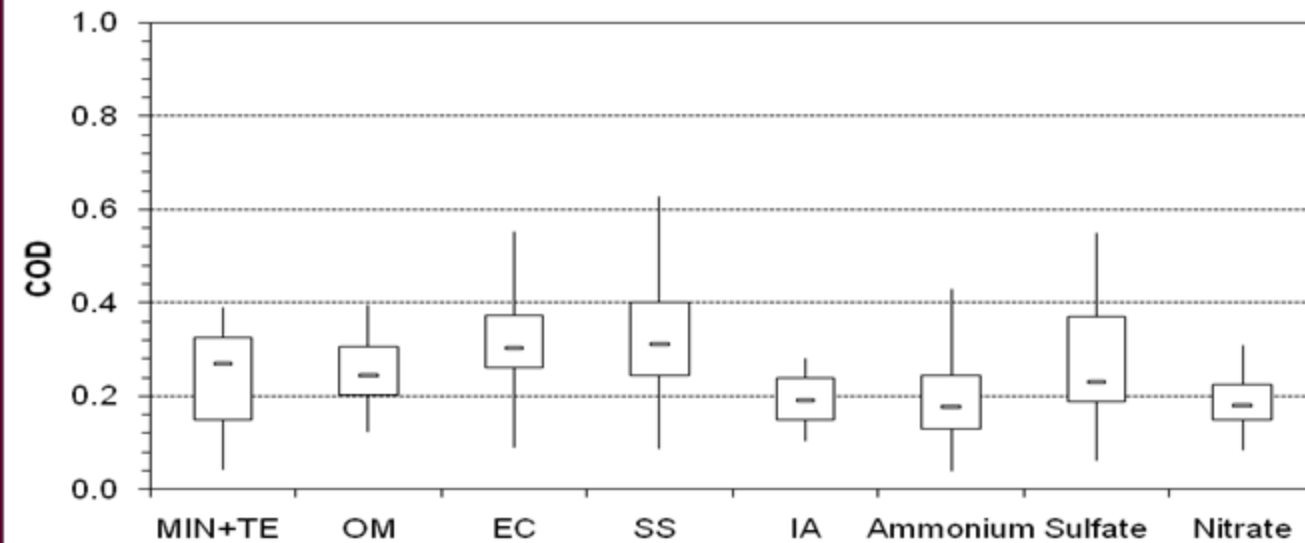
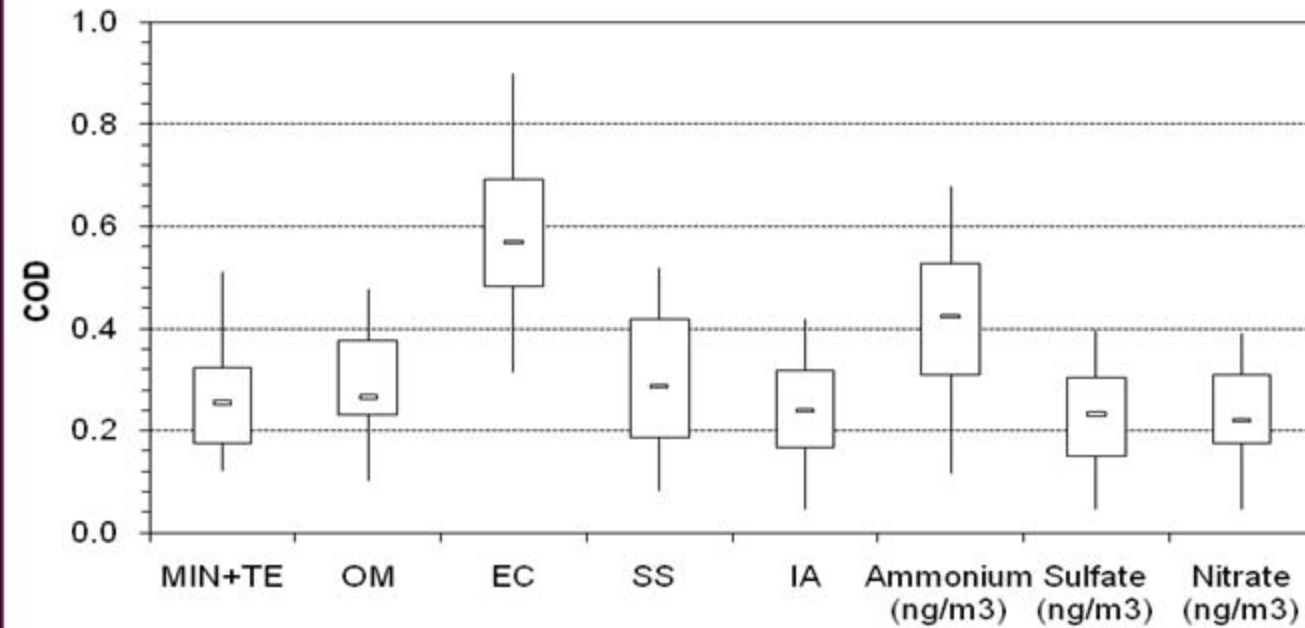


Winter



COD for CPM chemical groups

**Spring and
summer**

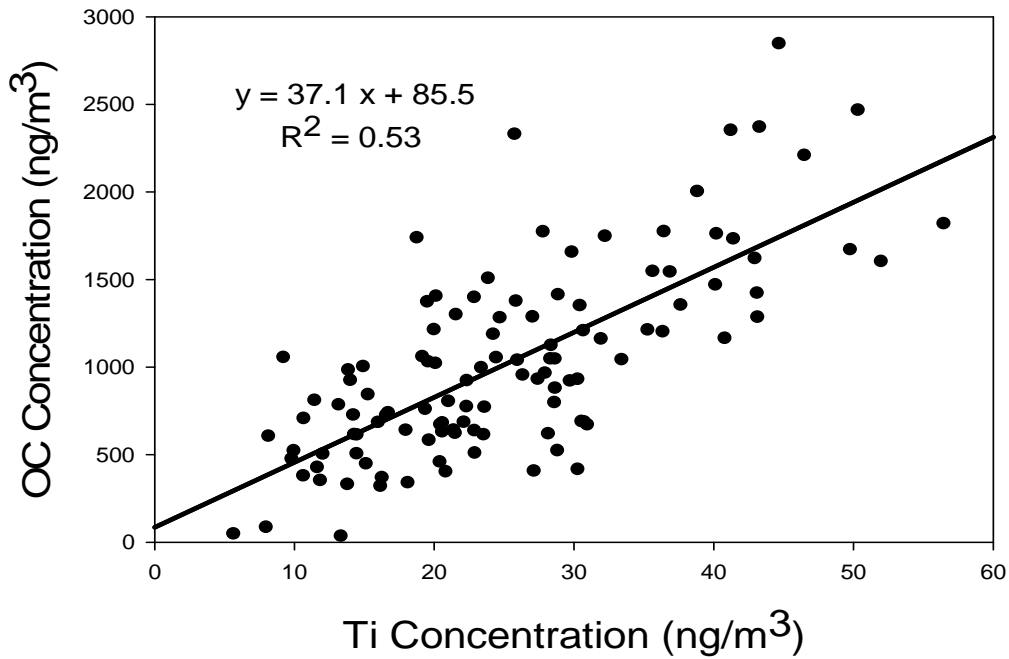


Fall and Winter

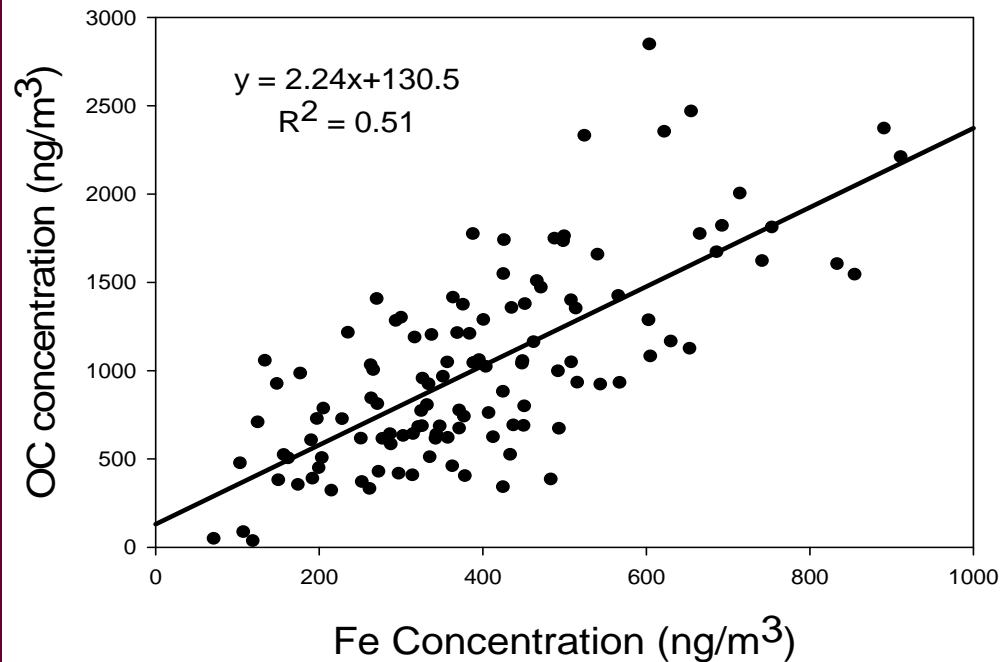
Regression analysis of OC vs. selected species in a) spring and summer and b) fall and winter

	$y=mx+c$	R
OC-MIN+TE	$0.08x+518.27$	0.54
OC-EC	$-1.73x+914.9$	-0.21
OC-SS	$-0.01x+858.4$	-0.02
OC-IA	$0.09x+637.02$	0.21
OC-Ti	$31.26x+127.59$	0.68
OC-Fe	$2.11x+183.55$	0.58

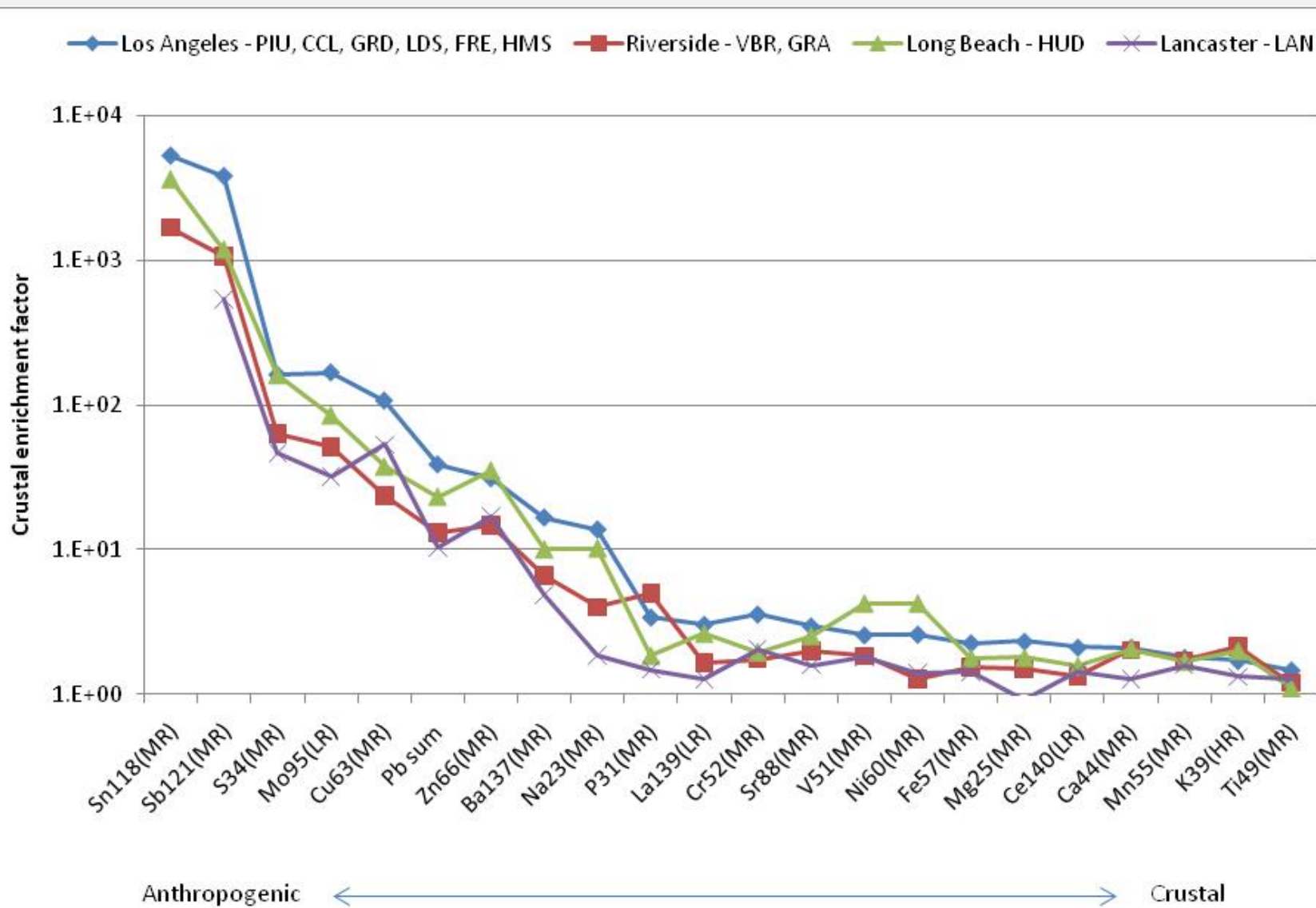
	$y=mx+c$	R
OC-MIN+TE	$0.21x+296.52$	0.72
OC-EC	$2.97x+755.73$	0.43
OC-SS	$0.19x+1041.74$	0.16
OC-IA	$0.30x+632.65$	0.46
OC-Ti	$39.16x+114.91$	0.76
OC-Fe	$2.39x+48.18$	0.74



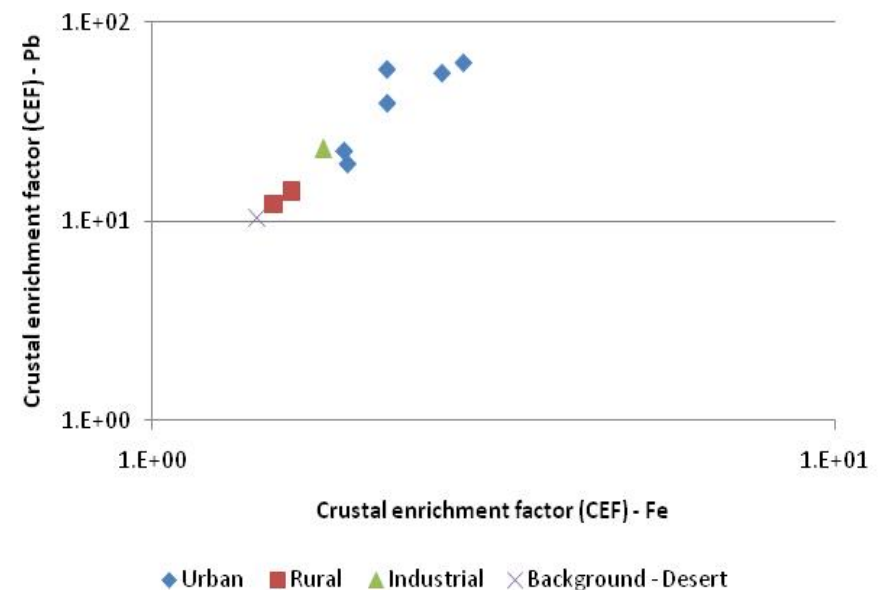
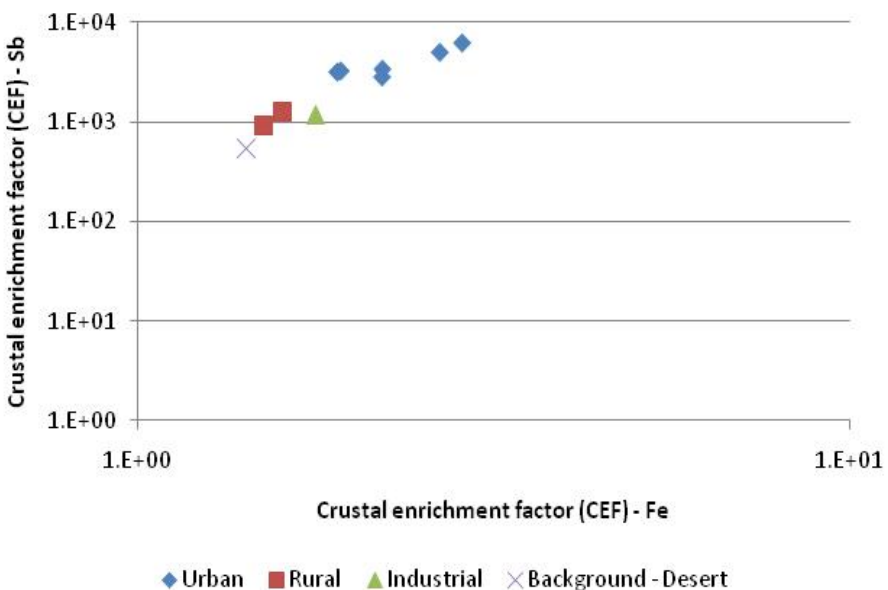
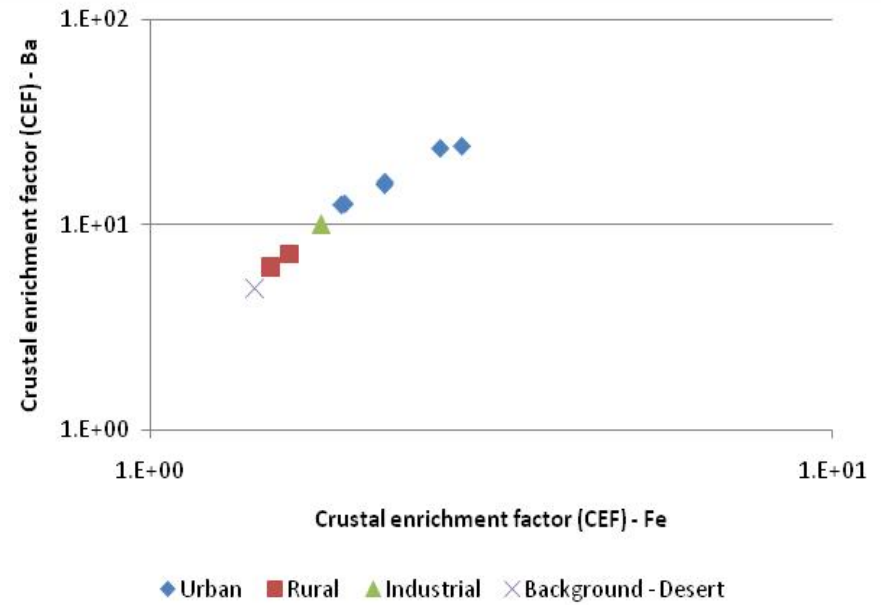
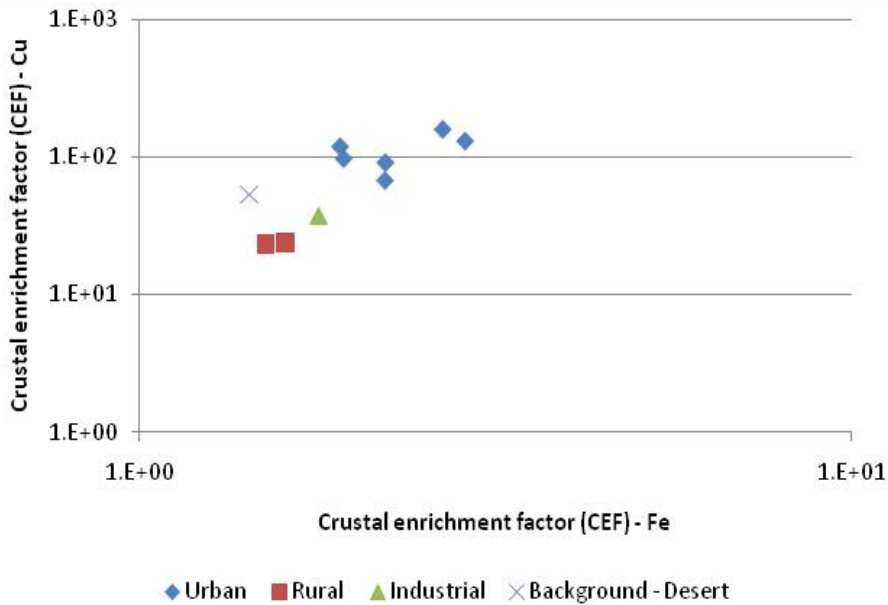
A significant fraction of measured OC in coarse PM is clearly associated with road dust



Crustal enrichment factors (CEF) of individual metals in different regions

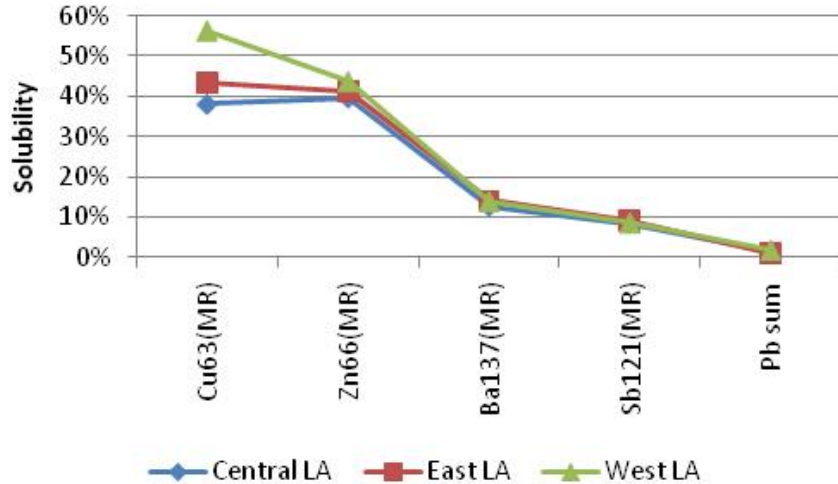


Correlation between crustal enrichment factors of Fe, Ba, Cu and Pb using the reference element Al.

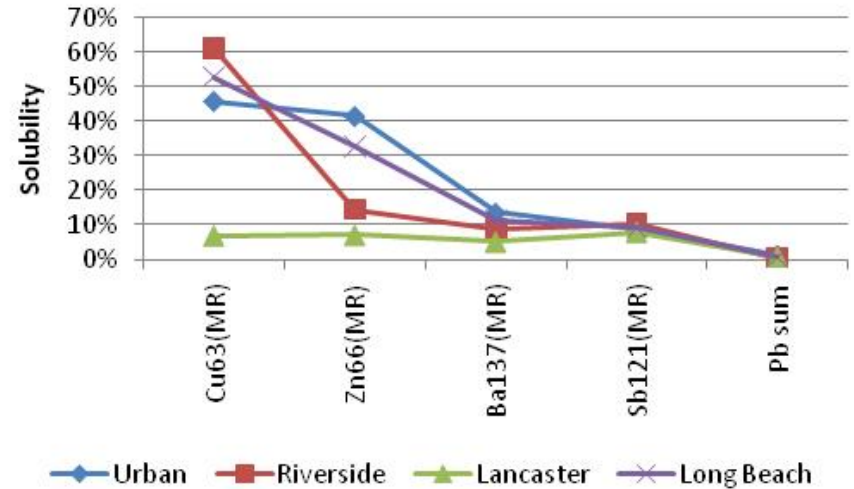


Water-solubility

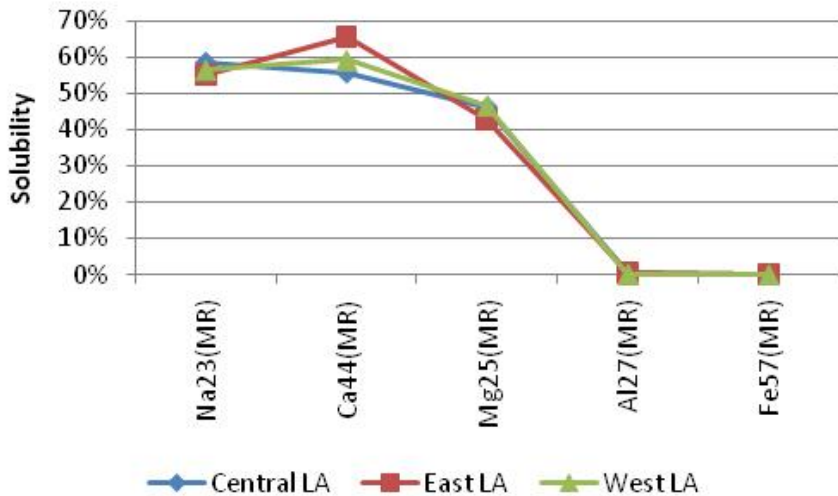
Break Wear - Solubility - Urban



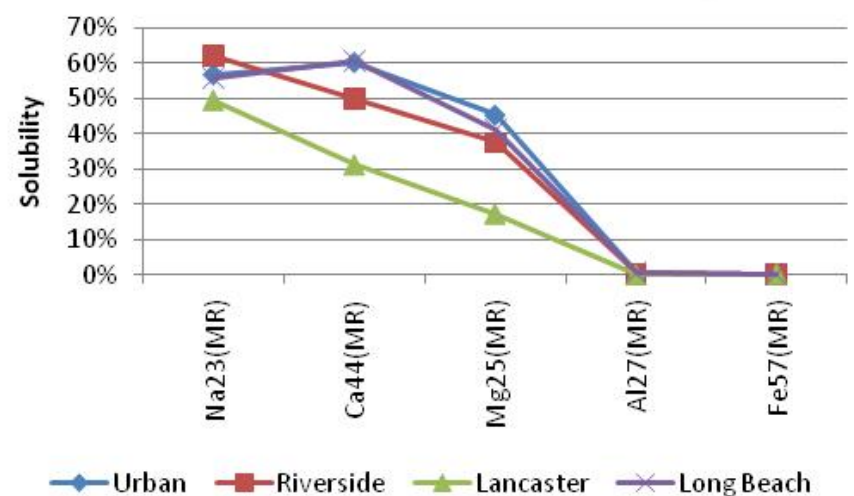
Break Wear - Solubility



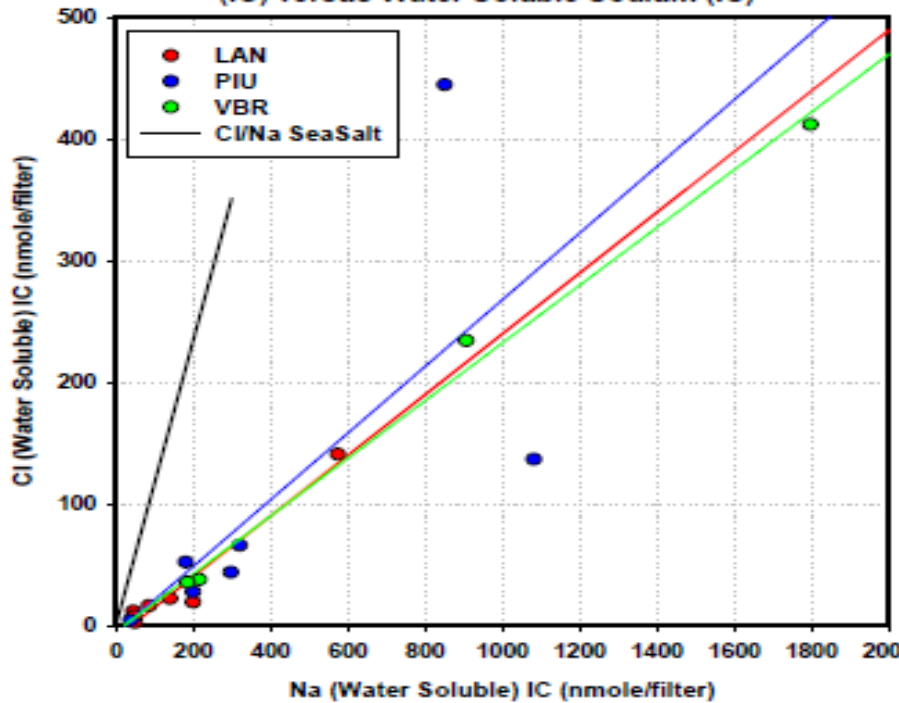
Crustal materials - Solubility - Urban



Crustal materials - Solubility



Summer Intensive - Water Soluble Chloride (IC) versus Water Soluble Sodium (IC)



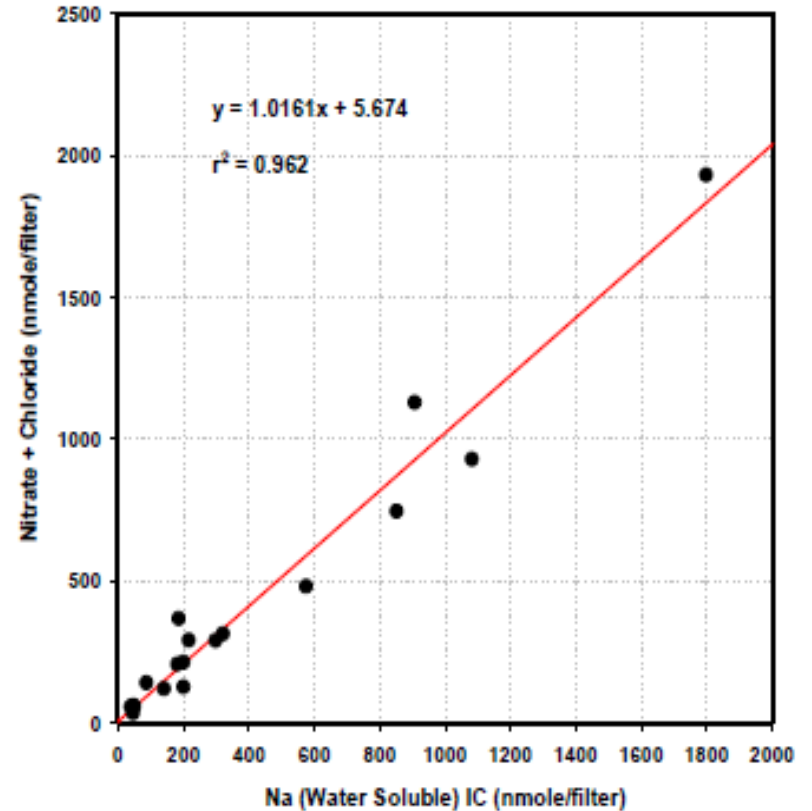
Clear evidence of Na depletion

←

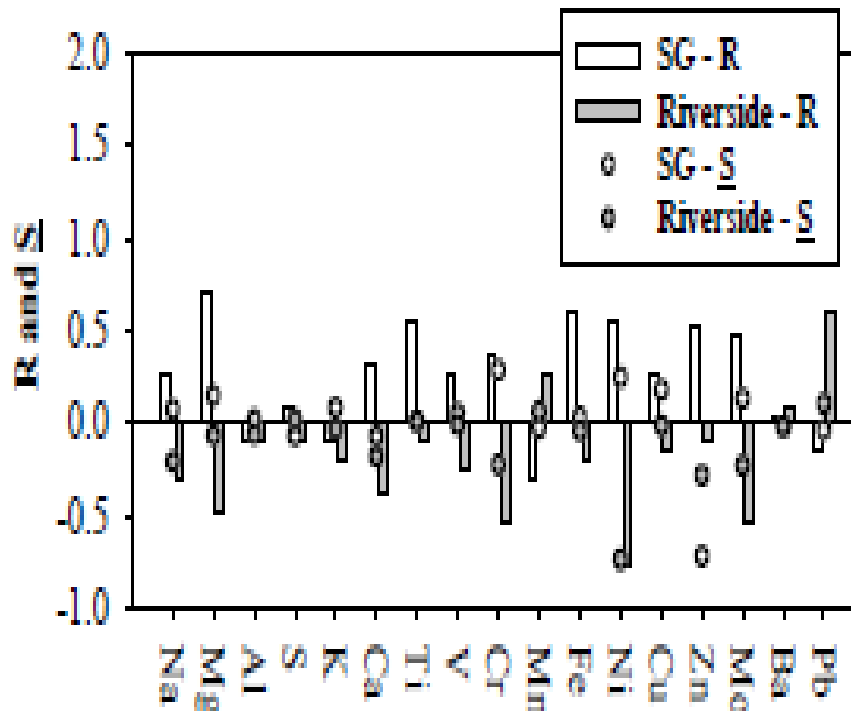
Almost all Na is in the form of NaCl and NaNO₃- so NaCl is depleted by reactions with HNO₃ to form NaNO₃

→

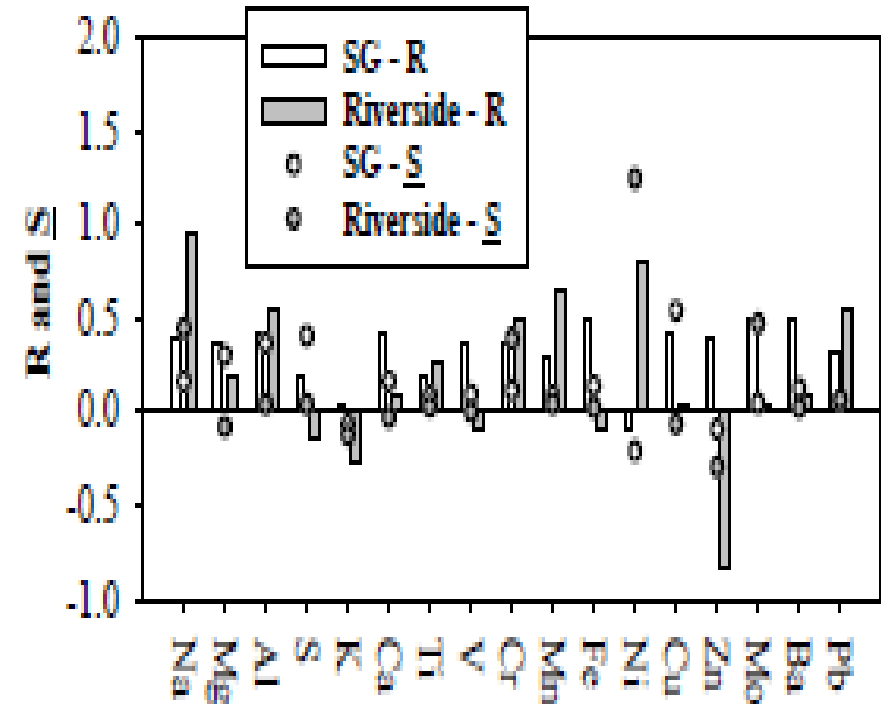
Summer Intensive - Water Soluble Sodium (IC) versus Nitrate + Chloride



Coarse - Warmer Season



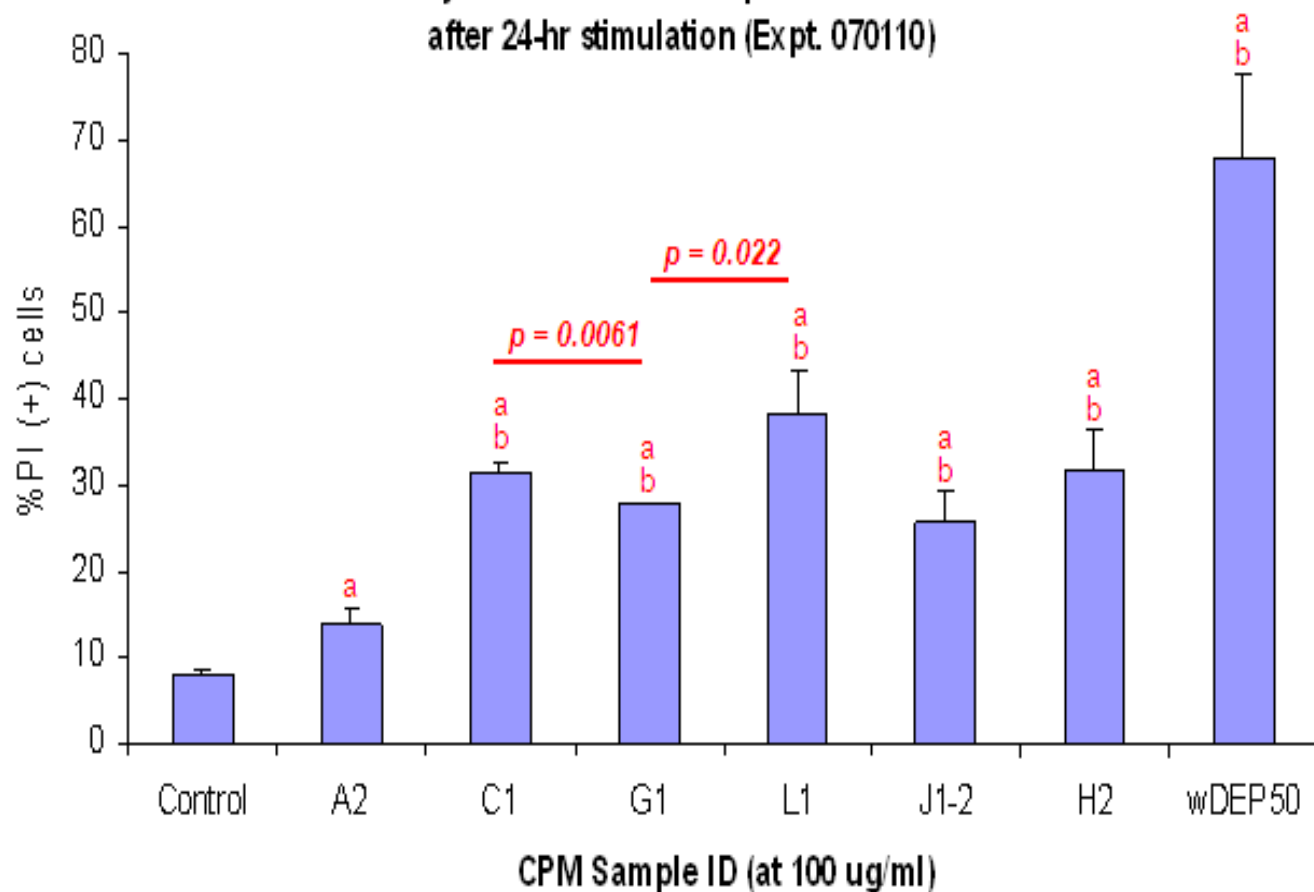
Coarse - Cooler Season



- Indoor vs Outdoor coarse PM correlations (R) and I/O level (S)
- data collected in 2 retirement communities (San Gabriel – SG and Riverside (R) during a panel study (CHAPS- PI R Delfino)
- Unlike PM_{2.5}, R and S values are in general much lower for coarse PM

Polidori et al - Atmospheric Chemistry and Physics, 9, 4521-4536, 2009

Teh toxicity of various CPM samples in RAW 264.7 cells
after 24-hr stimulation (Expt. 070110)

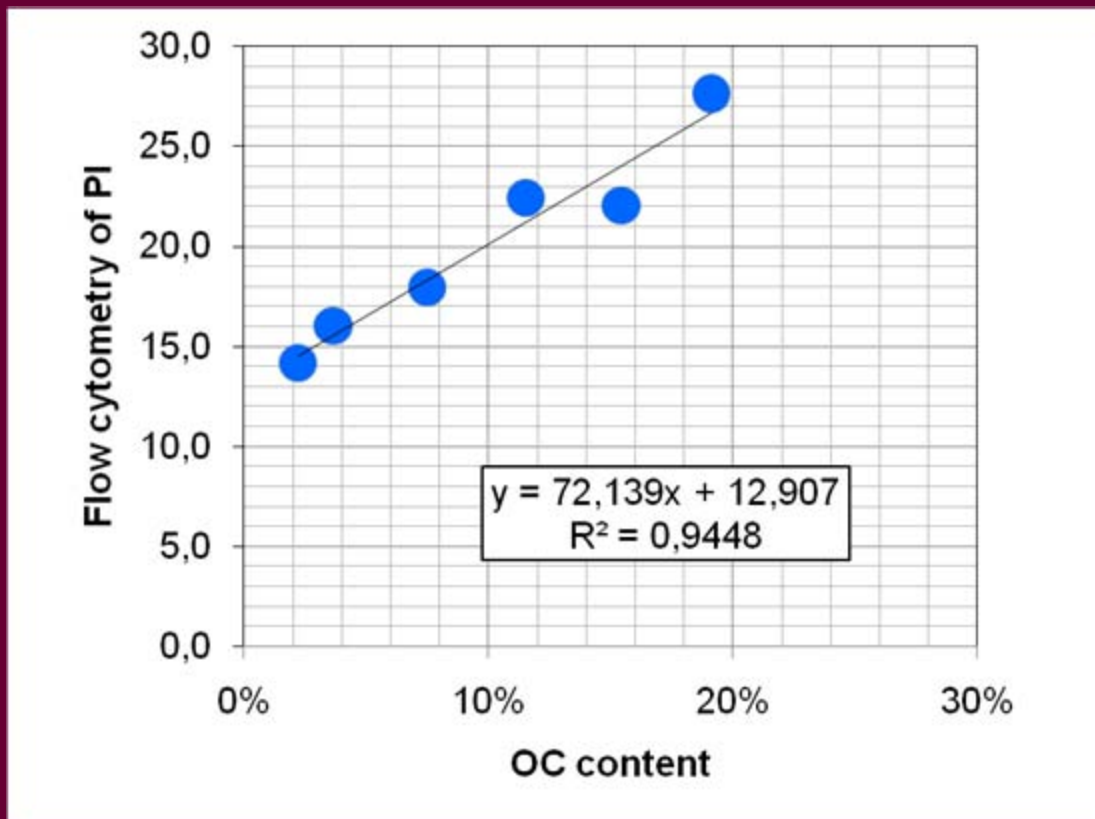


^a $p < 0.01$ compared to the Ctrl

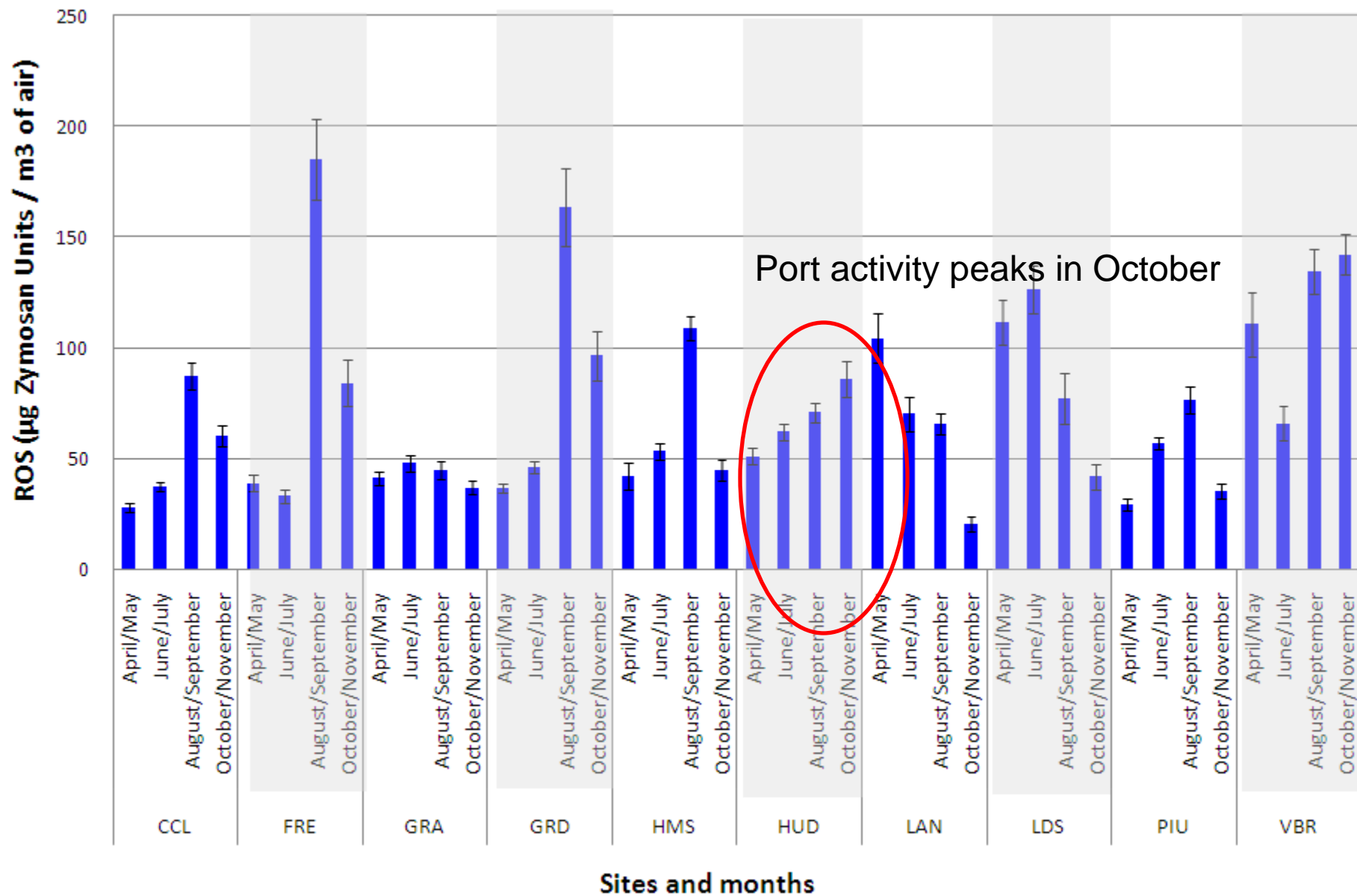
^b $p < 0.05$ compared to A2

- Flow cytometry data of CPM samples comparison with DEP and control samples

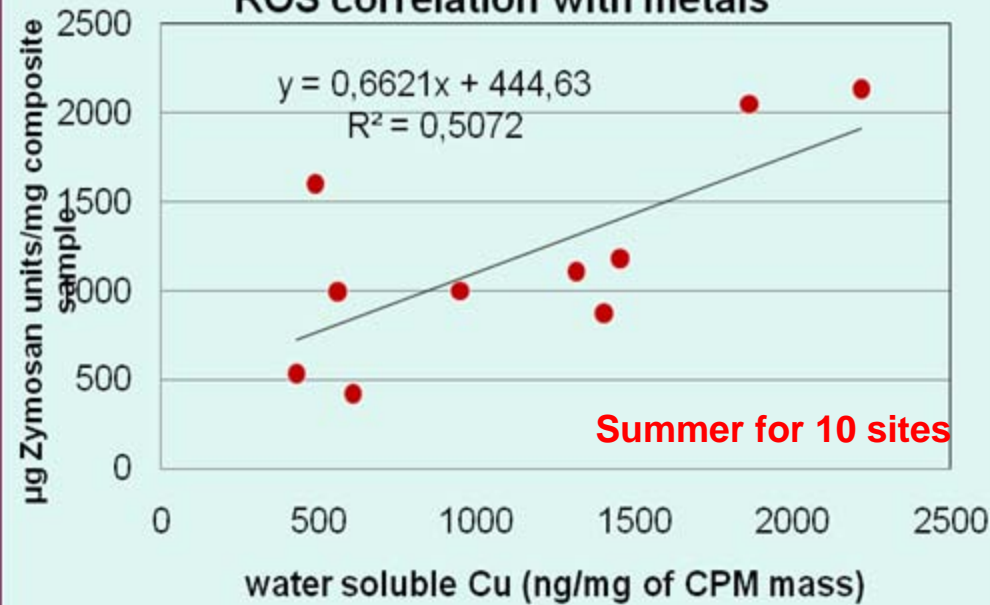
- Flow cytometry of RAW 264.7 cells stimulated with CPM after 24 hours;
- Correlation with OC fraction in total CPM mass;
- Samples to be analyzed include bi-monthly data for all ten sites;
- Preliminary data include seasonal samples from 6 sites



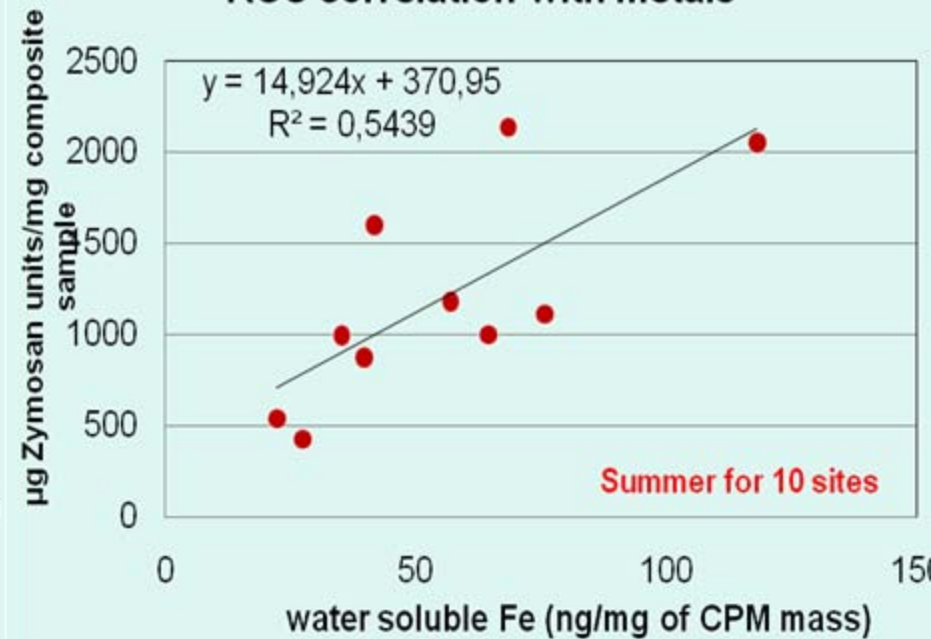
- Reactive oxygen species (ROS) data in all ten sites with ug Zymosan Units/m³ of air sampled



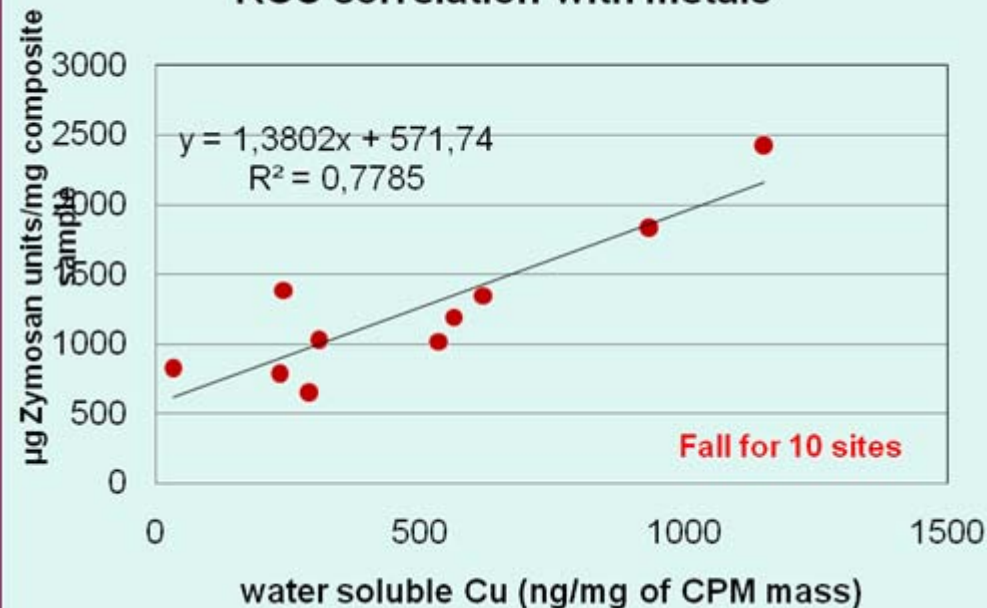
ROS correlation with metals



ROS correlation with metals



ROS correlation with metals



Conduct more detailed analyses by including ROS in principle component analysis (PCA) with water soluble metals when samples from all sites and seasons are completed

Planned and on-going work for Years 3 and 4

In 2010

- Completion of Chemical Analyses from the Winter and Summer Intensives Studies

(3 sites, USC-LAN-VBR and 4 time periods – “overnight” (12 midnight – 7 am, 7 pm – 11:59 pm), “morning commute” (7 am – 11 am), “mid-day” (11 am – 3 pm) and “afternoon” (3 pm – 7 pm).

- Sampling completed, chemical analyses to be completed by end 2010

In 2011-2012

- Chemical speciation of organics from 12 month and intensive campaigns
- Completion of DTT and ROS analyses from the above studies
- Completion of Cellular Stimulation Studies by Dr Nel;s group
- Publication of manuscripts

List of Publications

- Polidori A, Cheung K.L, Arhami M., Delfino R.J, and Sioutas C.* “Relationships Between Size- Fractionated Indoor and Outdoor Trace Elements at Four Residential Communities in Southern California”. *Atmospheric Chemistry and Physics*, 9, 4521-4536, 2009
- Pakbin P., Cheung K., Hudda N., Moore K.F, and Sioutas C.* “Spatial and Temporal Variability of Coarse (PM_{10-2.5}) Particle Concentrations in Southern California” *Aerosol Science and Technology*, 44(7):514-525, 2010
- Moore K.F, Vishal Verma V., Maria-Cruz Minguillón M.C., and Sioutas C.* “Inter- and Intra-community variability in continuous coarse particulate matter (PM_{10-2.5}) concentrations in the Los Angeles area”. *Aerosol Science and Technology*, 44(7): 526-540, 2010
- Pakbin P, Ning Z., Shafer M.M, Schauer J.J, and Sioutas C. “Chemical Speciation and Source Identification of Trace Metals for Coarse Particulate Matter in the Los Angeles Area”. Submitted to *Atmospheric Environment*, September 2010
- Cheung K., Daher N., Shafer M.M, Ning Z., Schauer J.J and Sioutas C. “Spatial and Temporal Variation of Chemical Composition and Mass Closure of Ambient Coarse (PM_{10-2.5}) Particulate Matter in the Los Angeles Area”. To be submitted to *Atmospheric Environment*, October 2010