SOURCES, COMPOSITION, VARIABILITY AND TOXICOLOGICAL CHARACTERISTICS OF COARSE ($PM_{2.5-10}$) PARTICLES IN SOUTHERN CALIFORNIA

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Presentation to US EPA, March 18, 2013

Acknowledgements

- Co- Investigators
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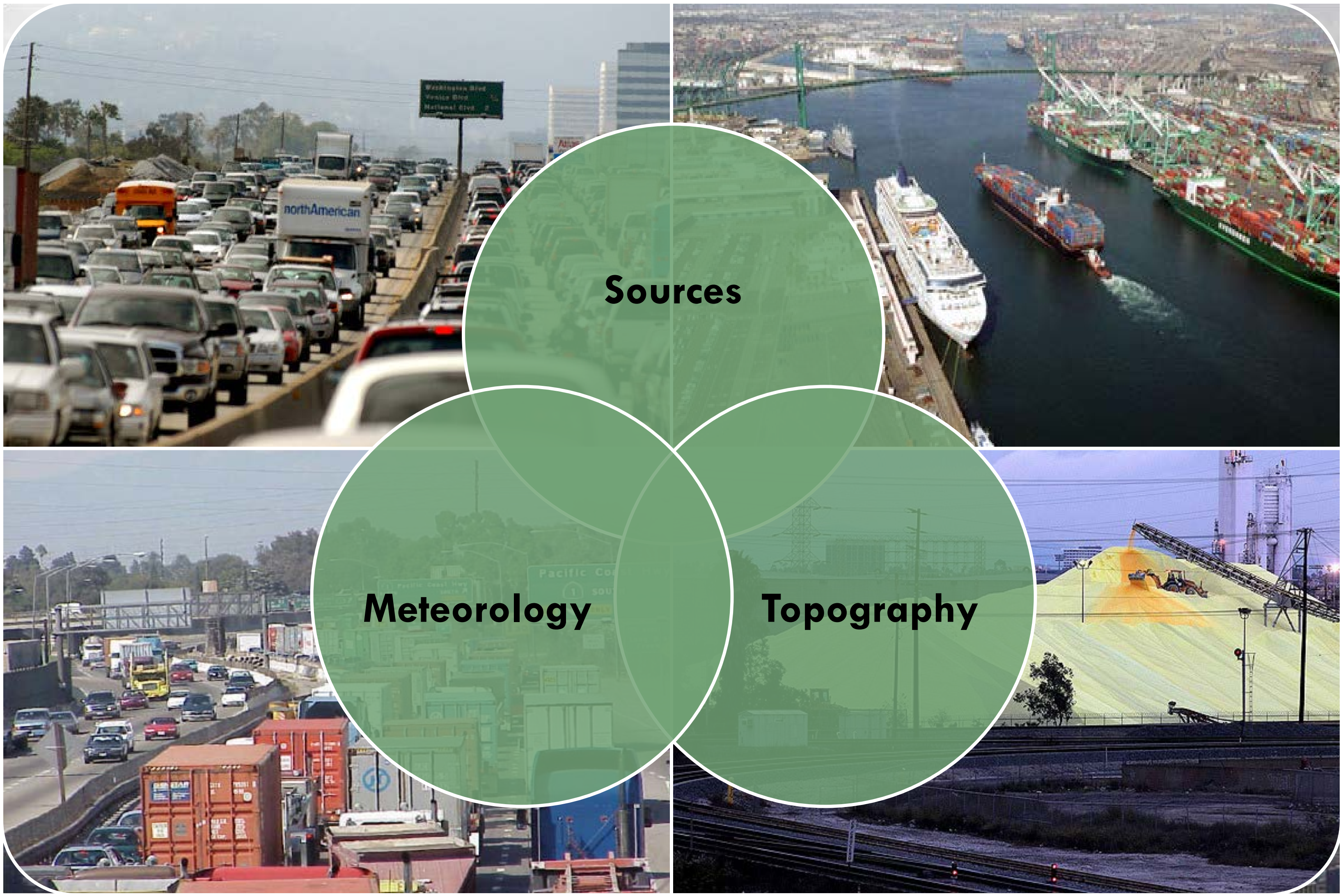
  - University of Wisconsin Madison: James Schauer, Martin Shafer
  - UCLA: Arthur Cho , Ning Li
  - **EPA Agreement Number:** RD-83374301-0
  - **Project Period:** November 1, 2008 to October 31, 2012

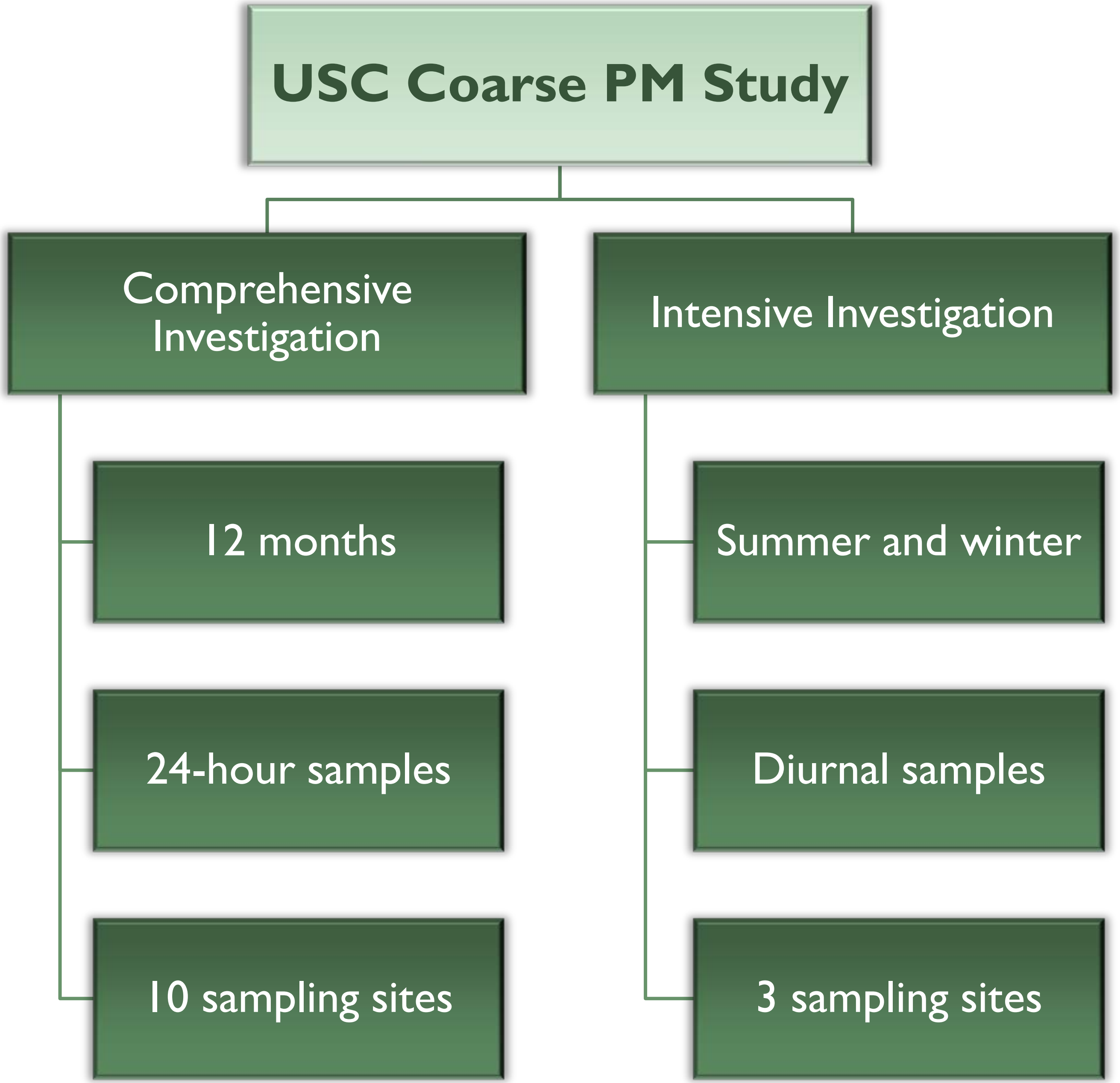
Outline

- **Introduction**
  - Rationale
  - Objectives
  - Project Methodology
- **Key Findings/Results**
  - Physical Characterization of Coarse PM (CPM)
  - Chemical Characterization of CPM
  - Toxicological Characterization CPM
  - Trends in CPM Concentration and Chemical Speciation
- **Conclusions**
  - Limitations
  - Recommendations

Objectives

- What are the spatial, diurnal and seasonal differences in coarse PM mass and chemical composition in rural and in urban areas of the Los Angeles Basin?
- What is the fraction of chemically speciated PM that penetrates indoors?
- How do the chemical characteristics of coarse PM collected in each of the above environments determine their toxicity?
- What are the trends of coarse PM mass and composition over the past 15+ yrs of monitoring in the LA Basin?
- What would be the most effective ways of regulating coarse PM?


Sources
Meteorology
Topography
northAmerican


USC Coarse PM Study
Comprehensive Investigation
Intensive Investigation
12 months
24-hour samples
10 sampling sites
Summer and winter
Diurnal samples
3 sampling sites

Physical Characterization

- What causes the spatial and seasonal trends in CPM mass?
- Has the mass concentration changed over the years?
- Is PM_{10} a good surrogate of CPM?

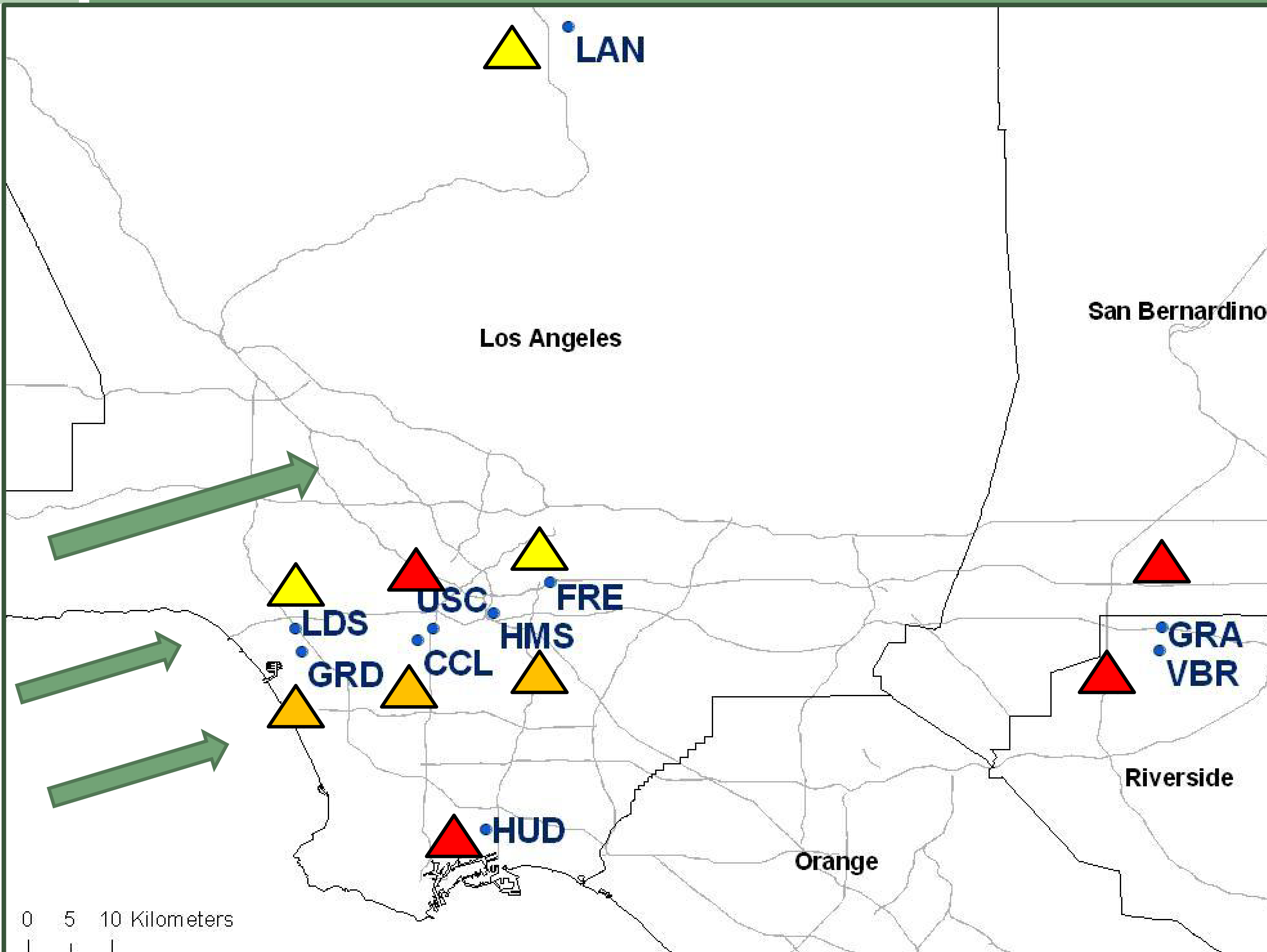
Chemical Characterization

- Is the chemical composition of CPM different from $PM_{2.5}$?
- What are the sources and formation mechanisms of CPM?
- Has the chemical profile of coarse particle changed over the years?

Toxicological Characterization

- What are driving the toxicity of coarse particles?
- Is there a link between source, composition and toxicity of CPM?

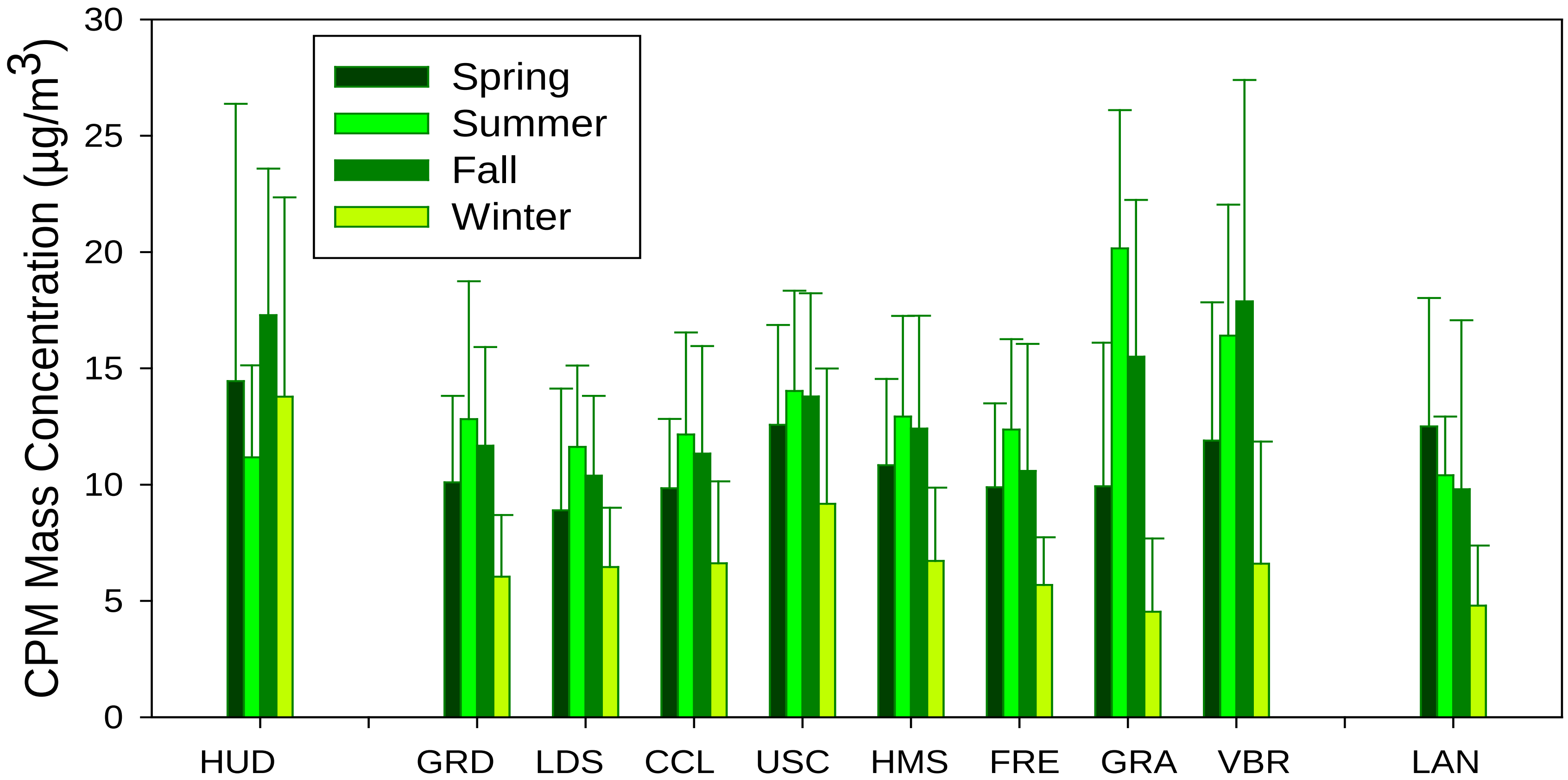
Mass Concentration - Overview



Annual mean CPM levels

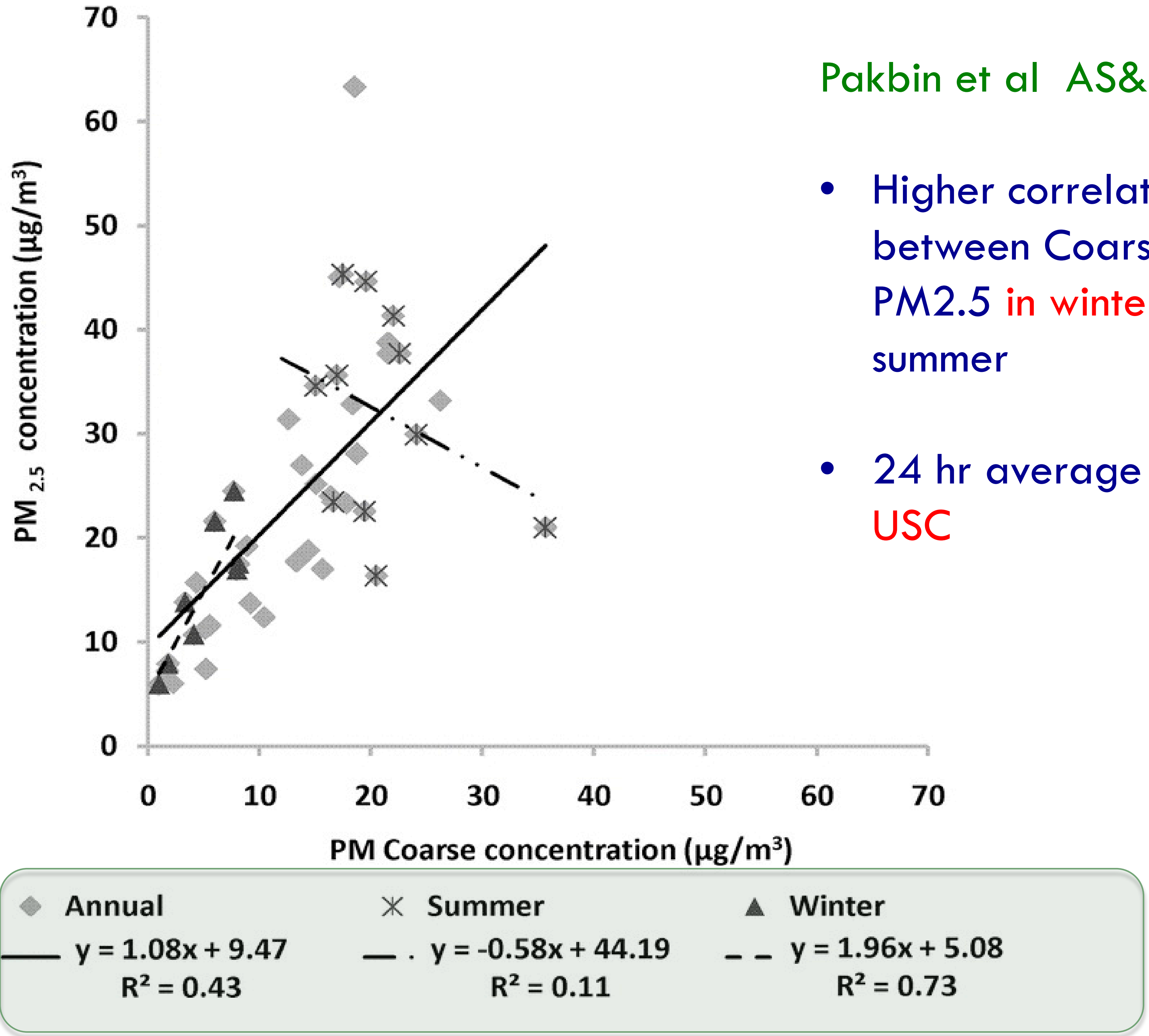
- 0-10 μg/m^3
- 10-12 μg/m^3
- 12-15 μg/m^3

Spatial and Seasonal Trends in CPM Mass (*Cheung et al 2010*)



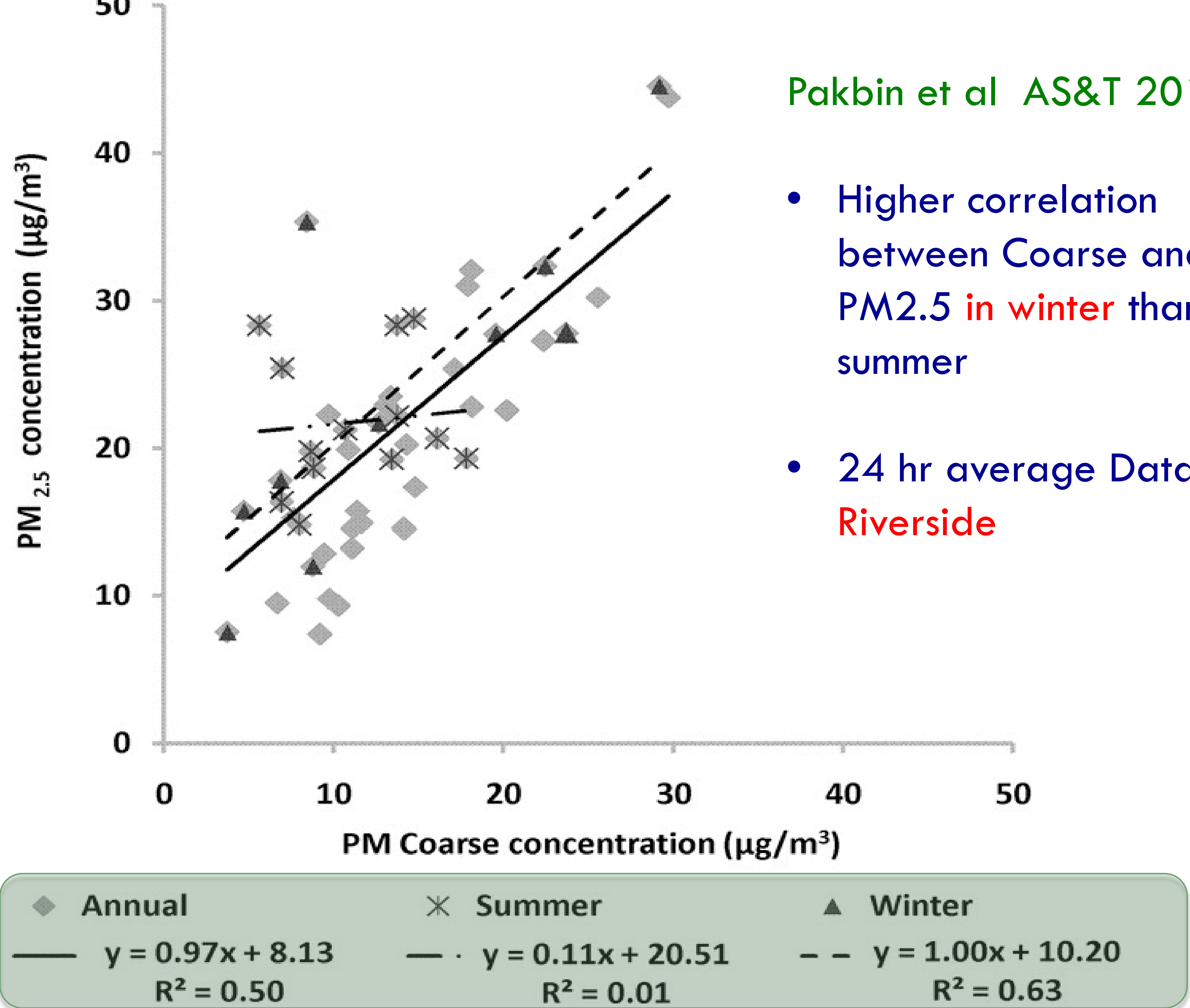
Long Beach ➜ West LA ➜ Central LA ➜ East LA ➜ Riverside ➜ Lancaster

Moving from coast to inland



Pakbin et al AS&T 2010

- Higher correlation between Coarse and PM2.5 in winter than summer
- 24 hr average Data at USC

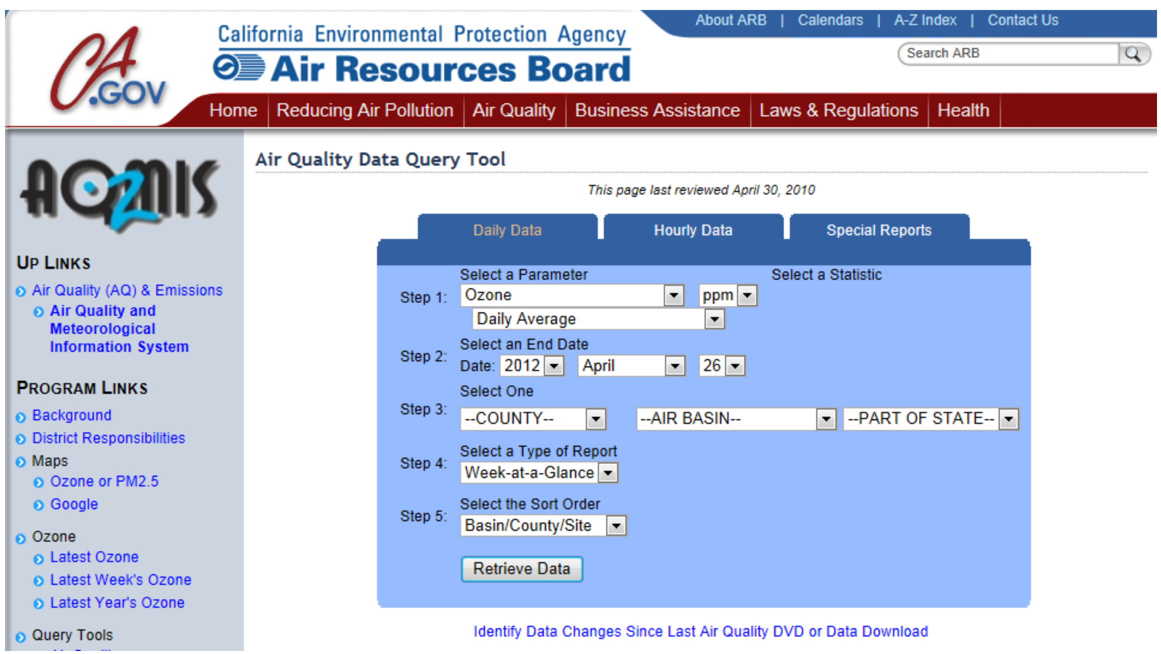


Pakbin et al AS&T 2010

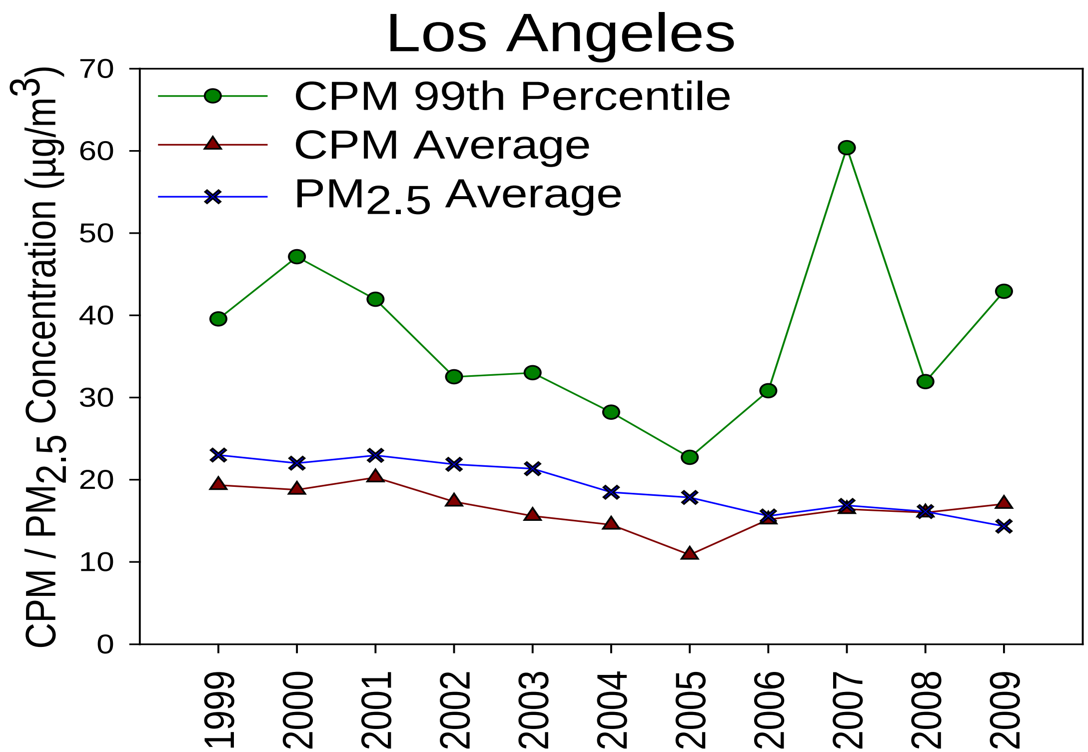
- Higher correlation between Coarse and PM2.5 in winter than summer
- 24 hr average Data at Riverside

Historical Trend

- PM_{10} and $PM_{2.5}$ data from CARB
- $PM_{10-2.5}$ concentrations from the subtraction method
- Year 1999 to 2009, 24-hr concentration

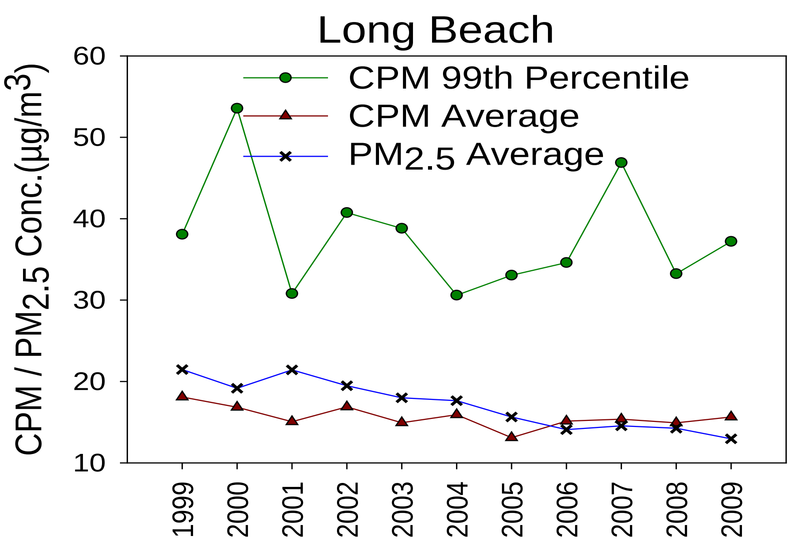


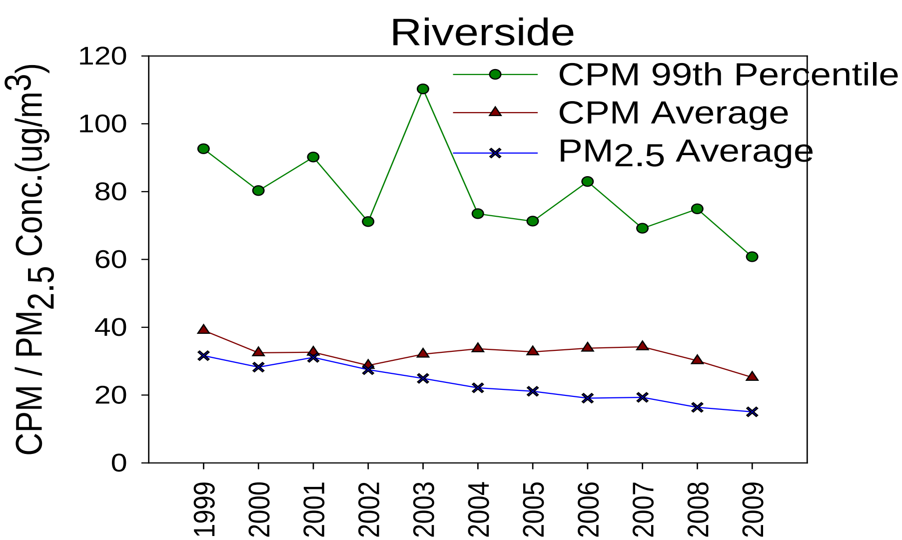
Historical Trends



Downtown LA		Linear Regression	R^2	p
PM_{10}	Average	y = -1.33(±0.12) x + 57.4(±1.6)	0.86	<0.001
$PM_{10-2.5}$				
	Average	y = -0.39(±0.23) x + 18.9(±1.5)	0.25	0.11
$PM_{2.5}$	Average	y = -0.92(±0.09) x + 24.6(±0.64)	0.91	<0.001

Historical Trends in Other LAB Areas

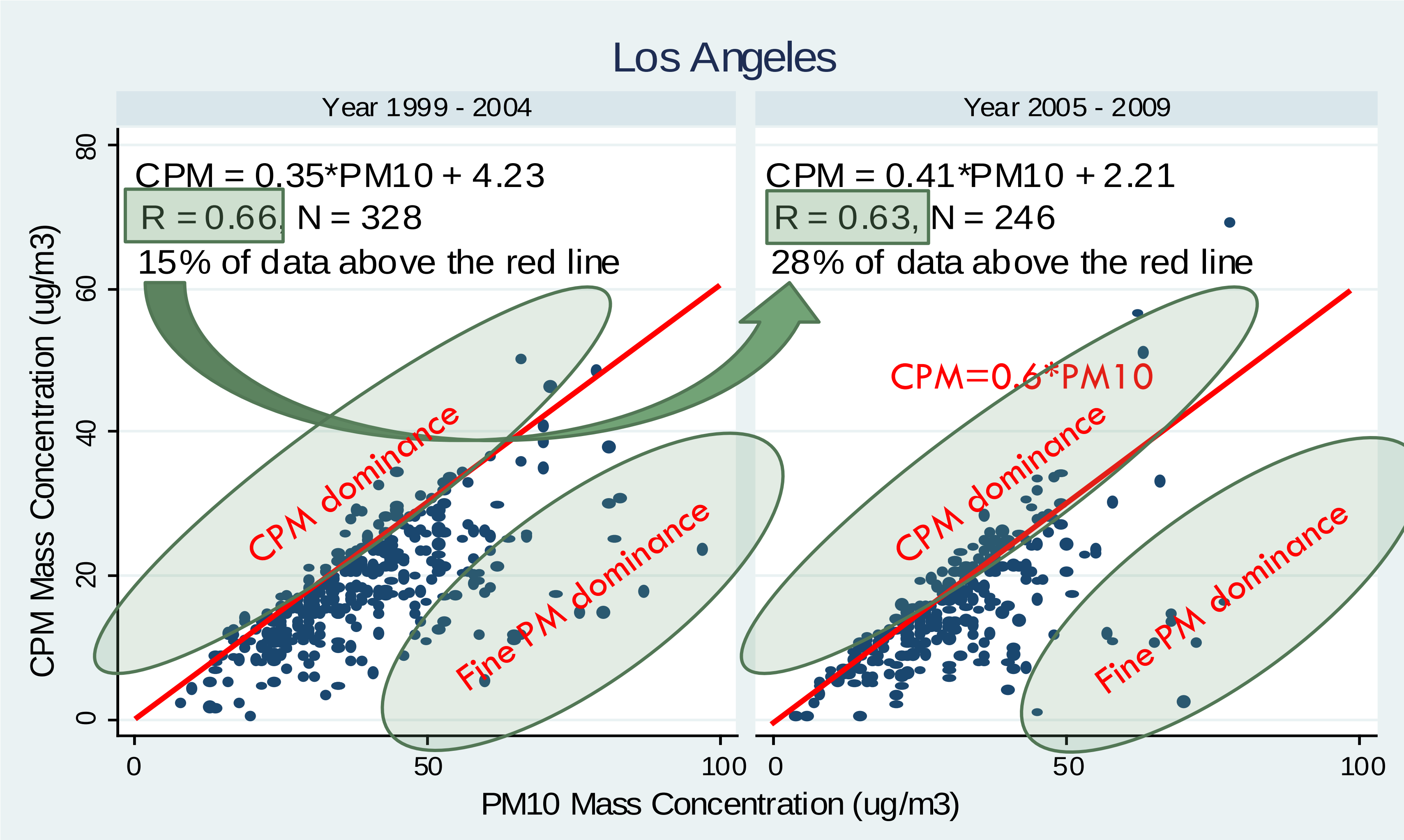




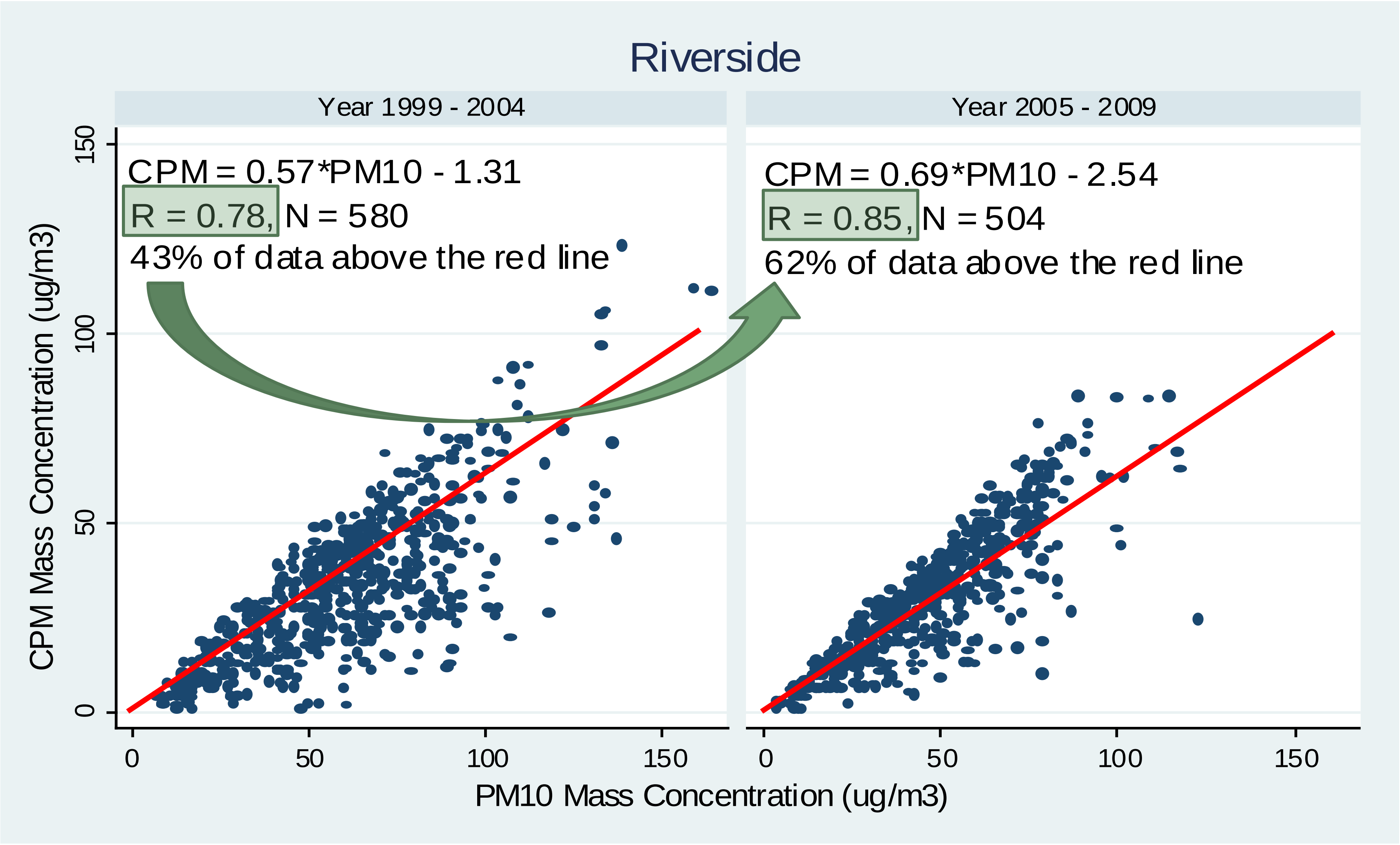
Long Beach		Linear regression	R^2	p
PM_{10}	Average	y = -0.76(±0.11) x + 44.8(±1.4)	0.72	<0.001
$PM_{10-2.5}$				
	Average	y = -0.22(±0.11) x + 17.0(±0.74)	0.31	0.07
$PM_{2.5}$	Average	y = -0.87(±0.09) x + 22.4(±0.61)	0.91	<0.001

Riverside		Linear regression	R^2	p
PM_{10}	Average	y = -1.76(±0.23) x + 84.6(±3.0)	0.75	<0.001
$PM_{10-2.5}$				
	Average	y = -0.57(±0.29) x + 35.7(±2.0)	0.30	0.08
$PM_{2.5}$	Average	y = -1.69(±0.12) x + 33.5(±0.84)	0.96	<0.001

PM_{10} as a Surrogate of CPM



PM_{10} as a Surrogate of CPM



Summary

- Seasonal and spatial trend
- PM_{10} is a generally good surrogate for CPM
- The significant decrease in PM_{10} is driven mostly by fine PM

Physical Characterization

- What causes the spatial and seasonal trends in CPM mass?
- Has the mass concentration changed over the years?
- Is PM_{10} a good surrogate of CPM?

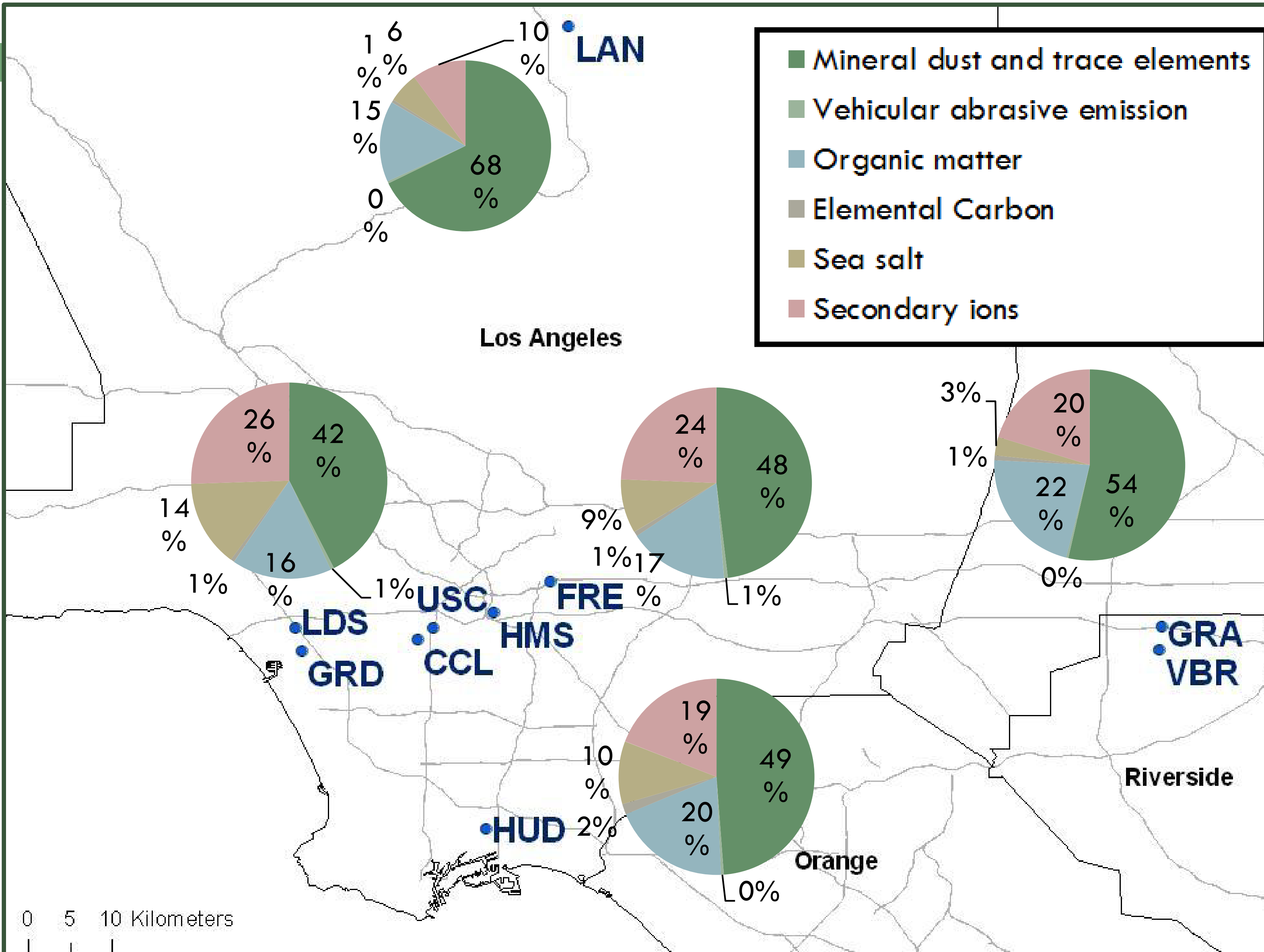
Chemical Characterization

- Is the chemical composition of CPM different from $PM_{2.5}$?
- What are the sources and formation mechanisms of CPM?
- Has the chemical profile of coarse particle changed over the years?

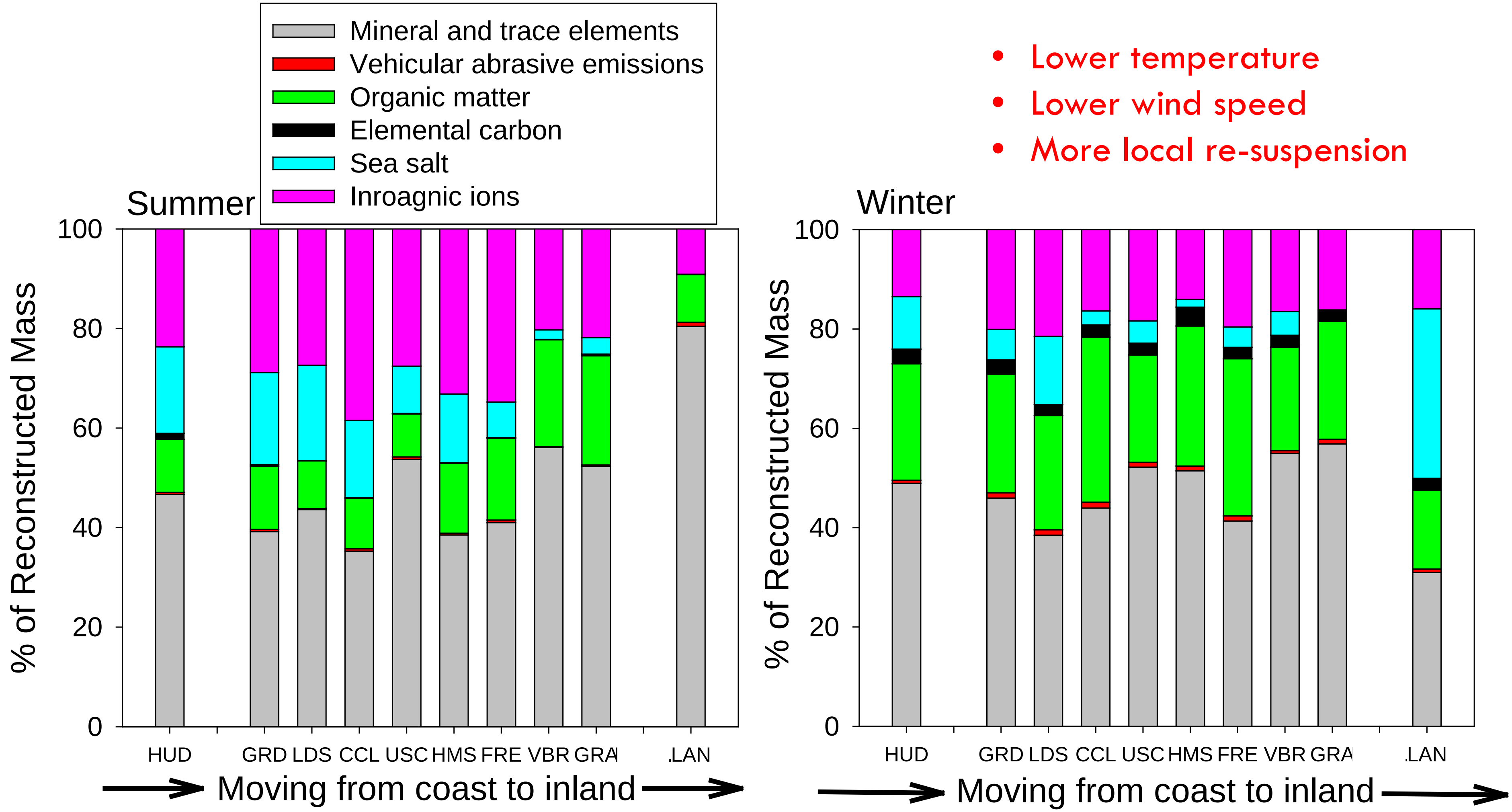
Toxicological Characterization

- What are driving the toxicity of coarse particles?
- Is there a link between source, composition and toxicity of CPM?

Chemical Composition - Overview

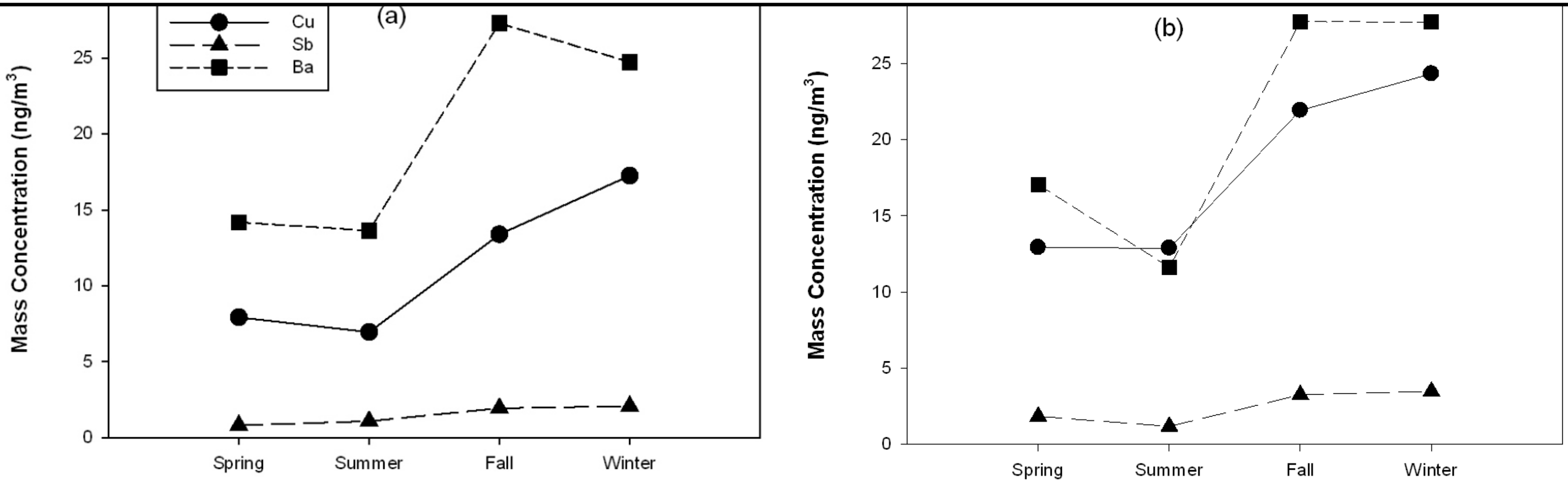


Seasonal and Spatial Trend

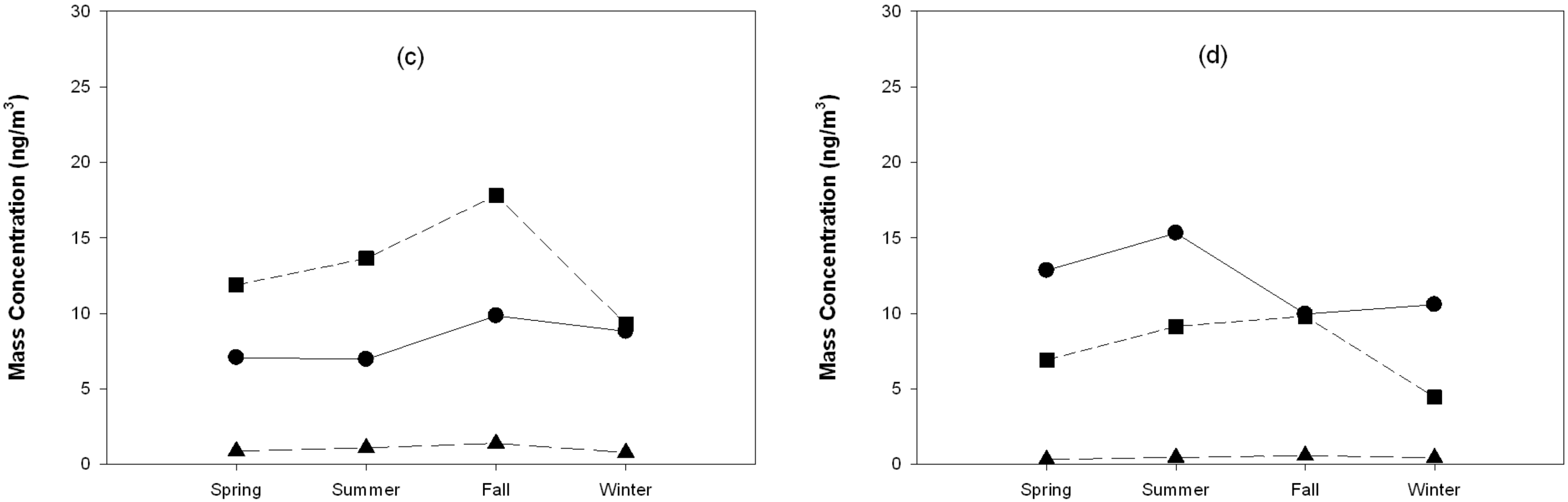


- Lower temperature
- Lower wind speed
- More local re-suspension

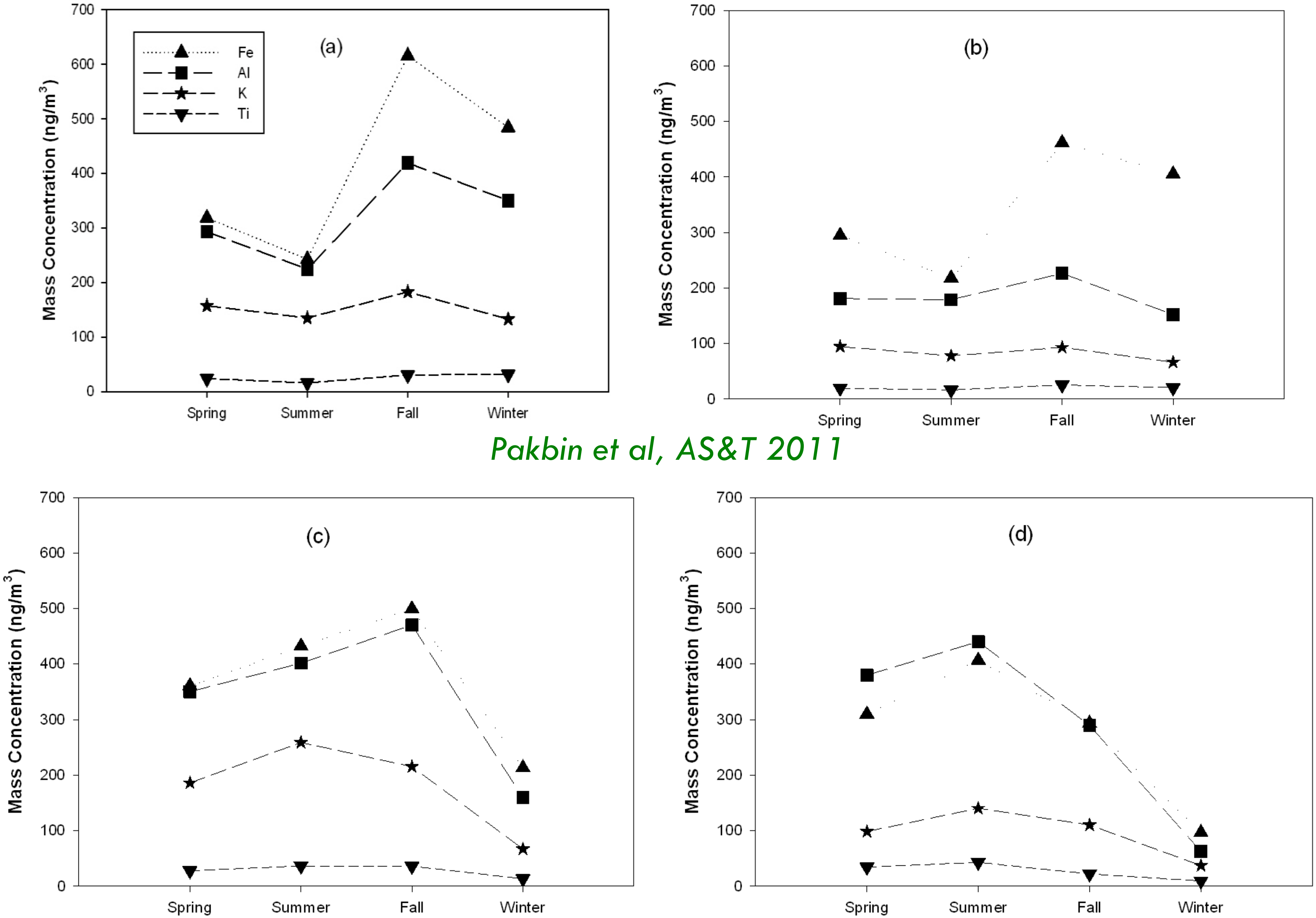
Temporal variation of abrasive vehicular tracers (Cu, Sb, Ba) in different sampling site clusters: (a) Los Angeles cluster, (b) Long Beach, (c) Riverside cluster, and (d) Lancaster.



Pakbin et al, AS&T 2011

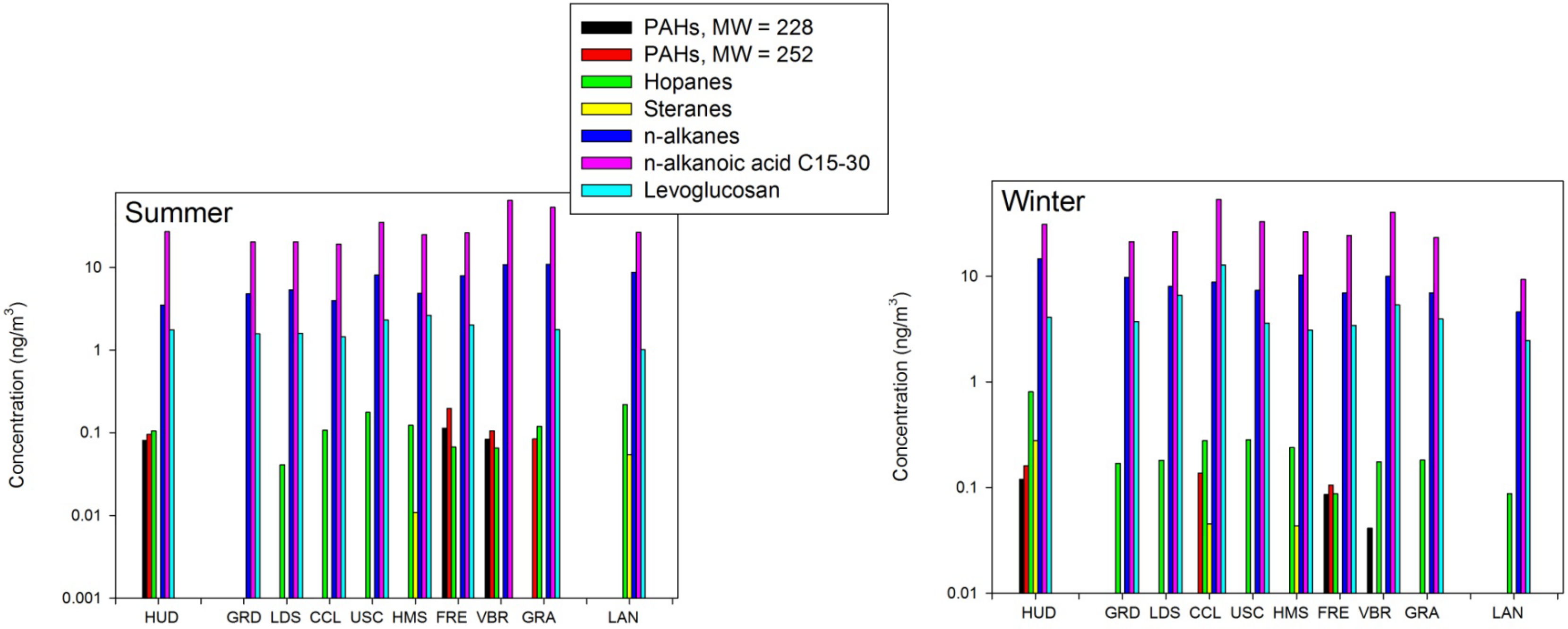


Temporal variation of selected mineral dust tracers (Fe, Al, K, Ti) in different sampling site clusters: (a) Los Angeles cluster, (b) Long Beach, (c) Riverside cluster, and (d) Lancaster.



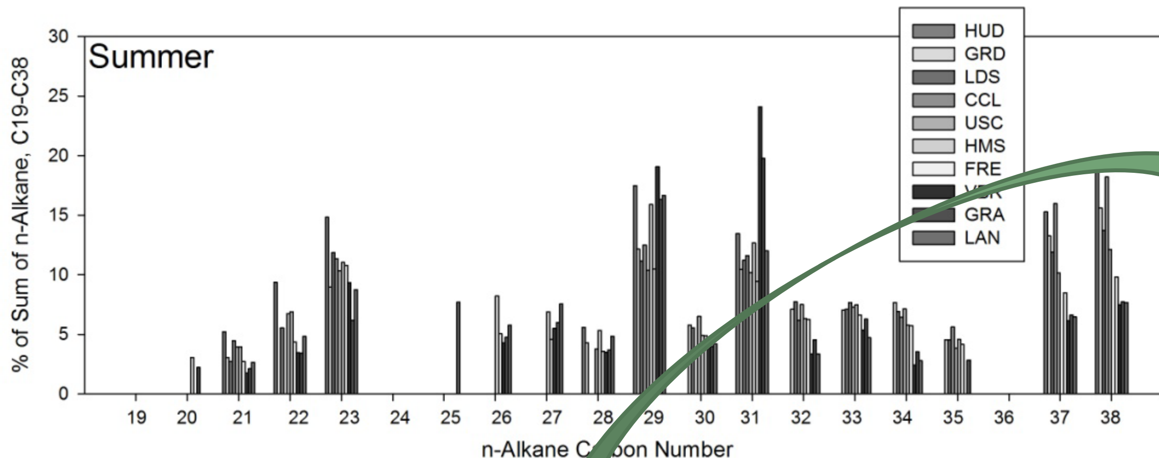
Pakbin et al, AS&T 2011

Organics

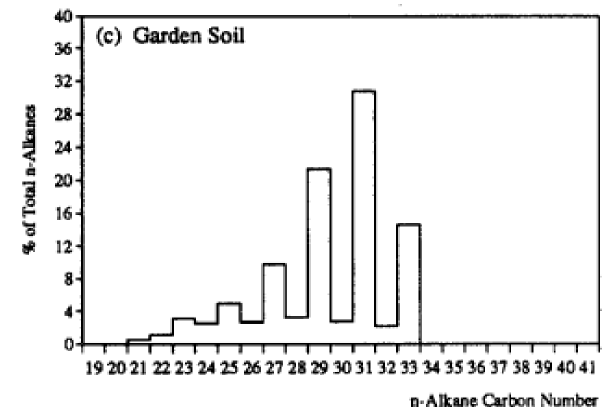


- Hopanes, steranes and PAHs, mostly in trace levels / undetected
- Alkanes and alkanoic acids are the two most dominant components
- Levoglucosan is still significant in CPM, with higher levels in winter

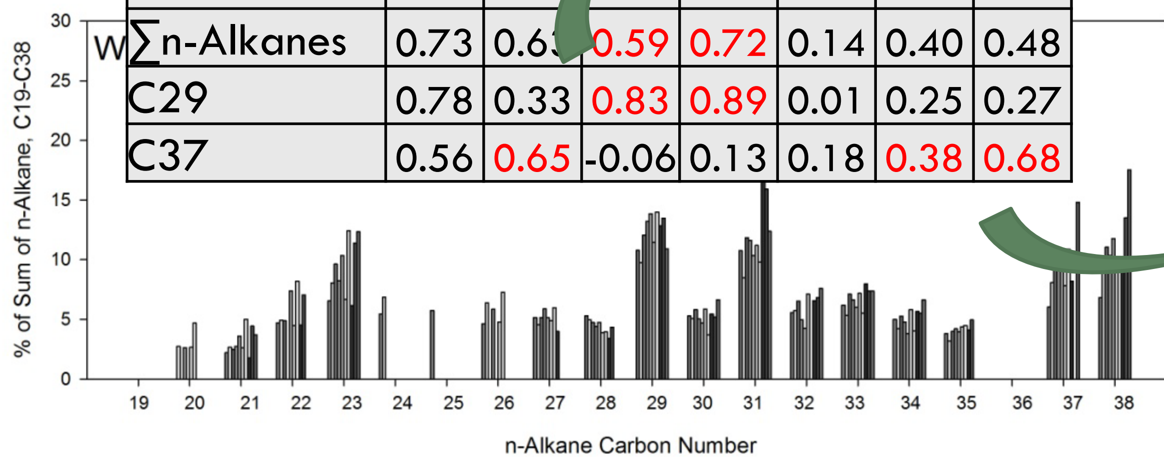
Organics – n-alkanes

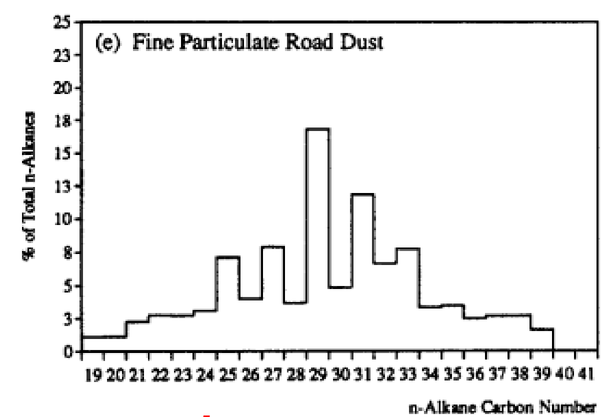


- Similar to the source profiles of:



	OC	EC	Al	Ti	Cu	Zn	Ba
∑n-Alkanes	0.73	0.63	0.59	0.72	0.14	0.40	0.48
C29	0.78	0.33	0.83	0.89	0.01	0.25	0.27
C37	0.56	0.65	-0.06	0.13	0.18	0.38	0.68

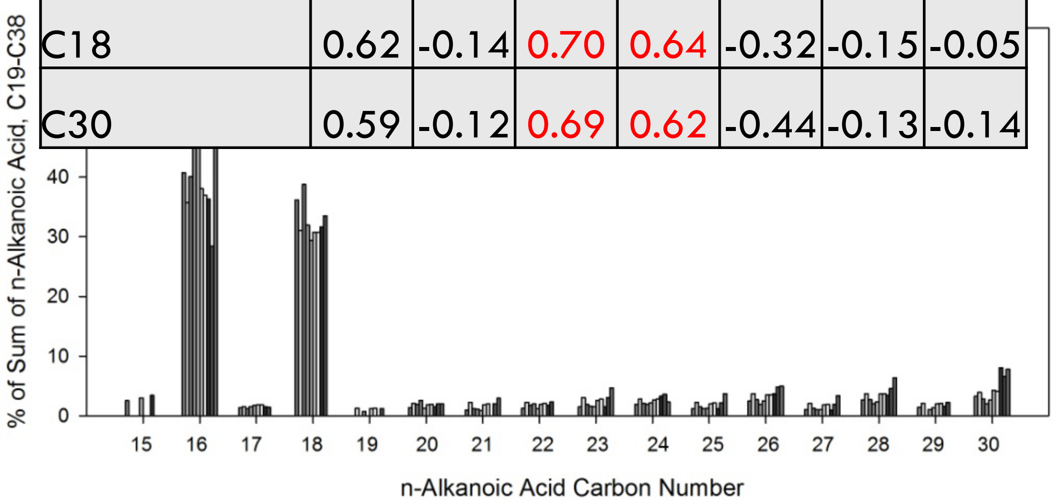




Cheung et al, Atmos Environ 2011

Organics – n-alkanoic acids

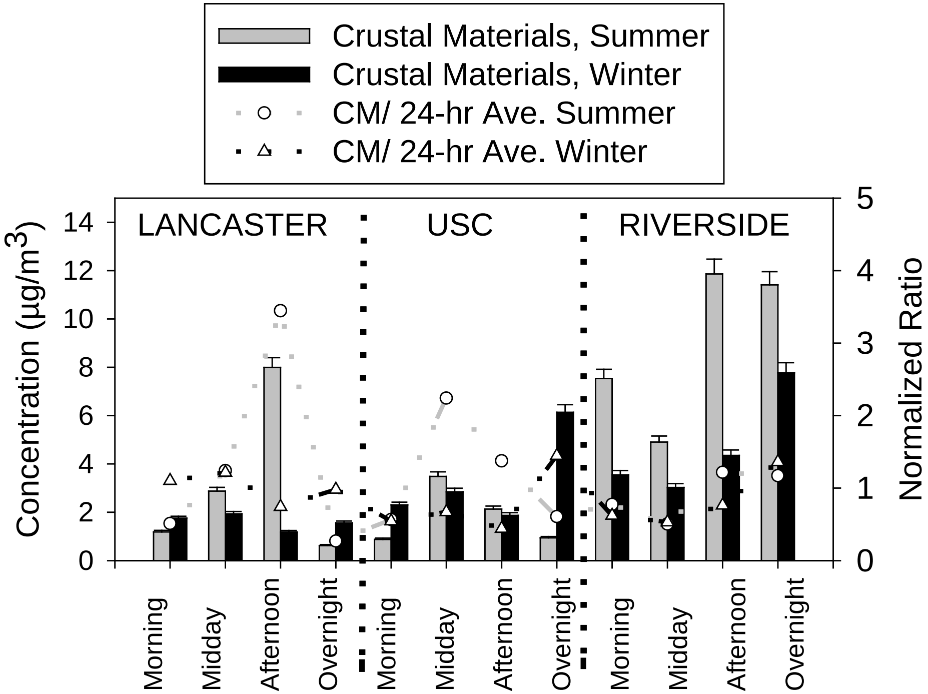
	OC	EC	Al	Ti	Cu	Zn	Ba
∑n-Alkan.Acids	0.74	0.11	0.68	0.71	-0.11	0.19	0.32
C18	0.62	-0.14	0.70	0.64	-0.32	-0.15	-0.05
C30	0.59	-0.12	0.69	0.62	-0.44	-0.13	-0.14

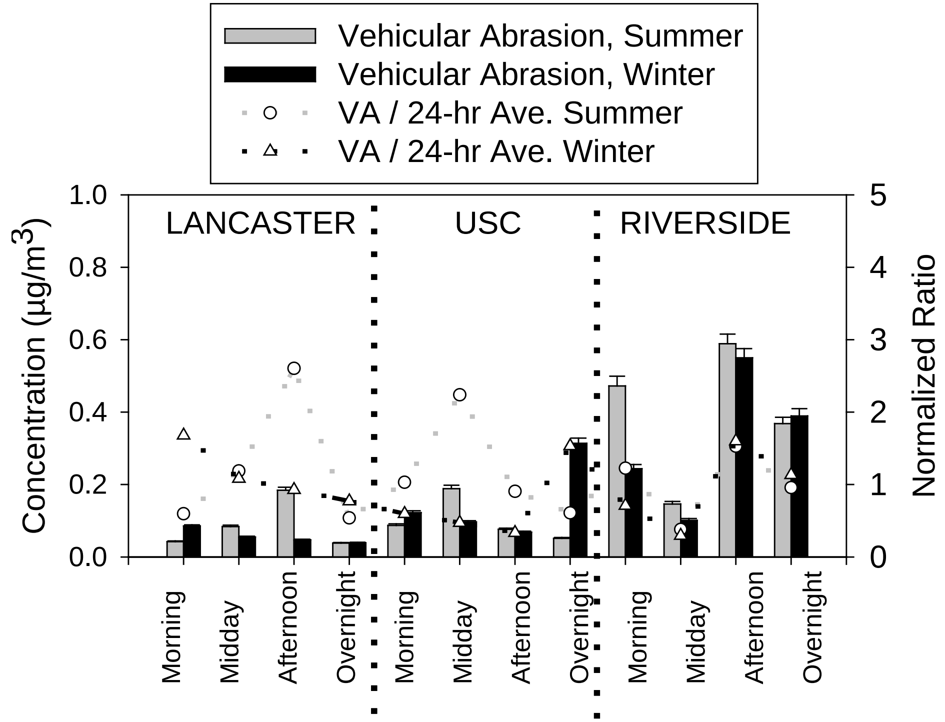


- Similar to the source profiles of:
  - Road dust
  - Green leaf debris
  - Tire wear
- Al and Ti – crustal materials
- EC-tailpipe exhaust
- Cu, Zn and Ba- vehicular abrasive emissions

Cheung et al, Atmos Environ 2011

Diurnal Trends

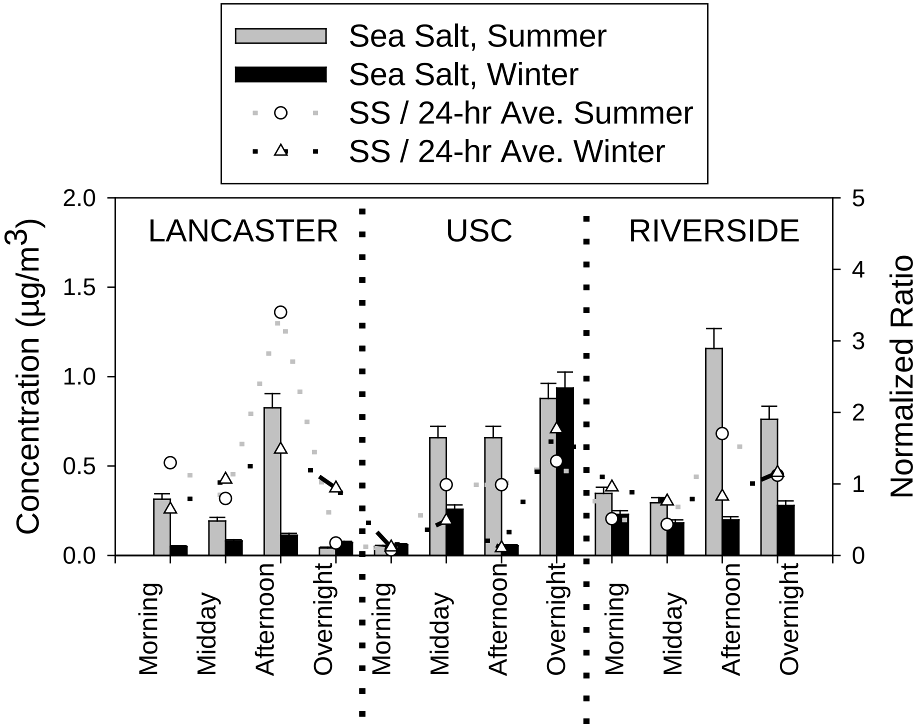


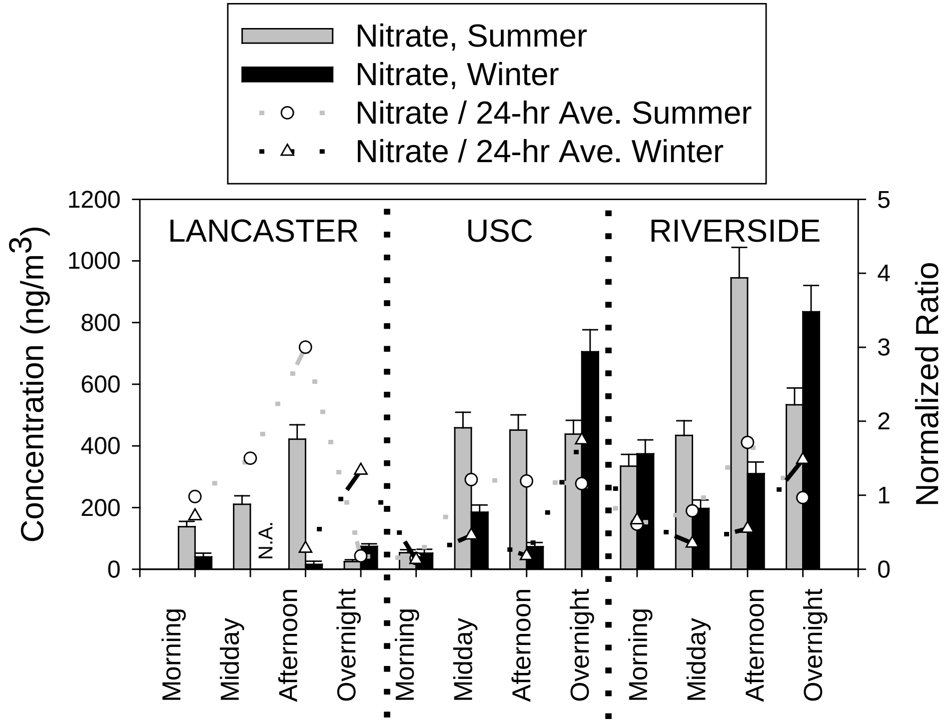


- In summer, higher levels in midday / afternoon
- In winter, overnight peaks, near-freeway re-suspension

Cheung et al, Roy Soc Chem, JEM- 2012

Diurnal Trends





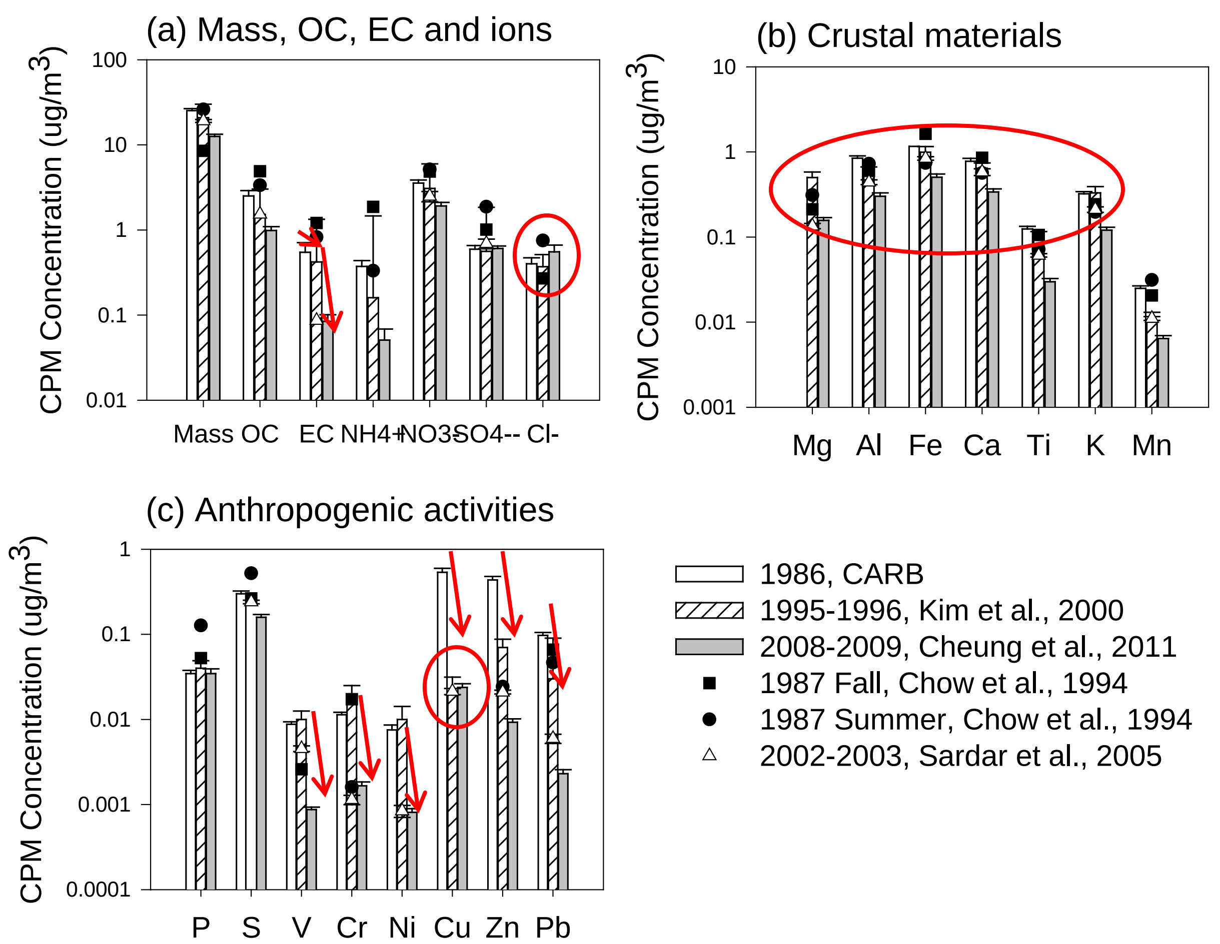
- Sea salt and nitrate follows similar diurnal trend
- Nitrate formation
  - In summer, sea salt depletion
  - In winter, depletion in addition to reactions with mineral dust and ammonium

Cheung et al, Roy Soc Chem, JEM- 2012

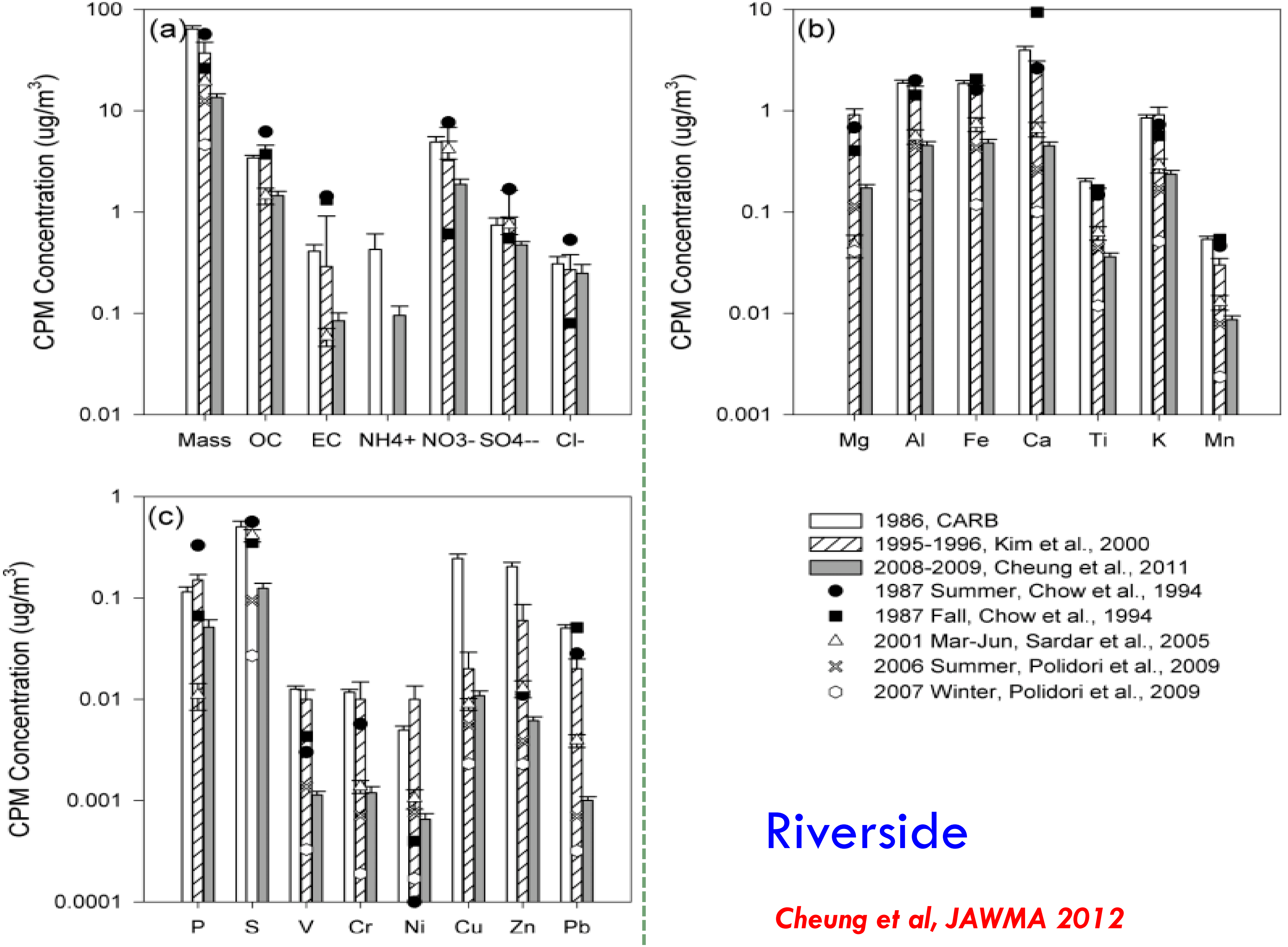
Historical Trends in CPM in the LA Basin

- Historical chemical composition
  - Peer-reviewed journals
  - Government agency database

- 3 year-long studies
  - 1986-87, CARB
  - 1995-96, AQMD
  - 2008-09, EPA/USC

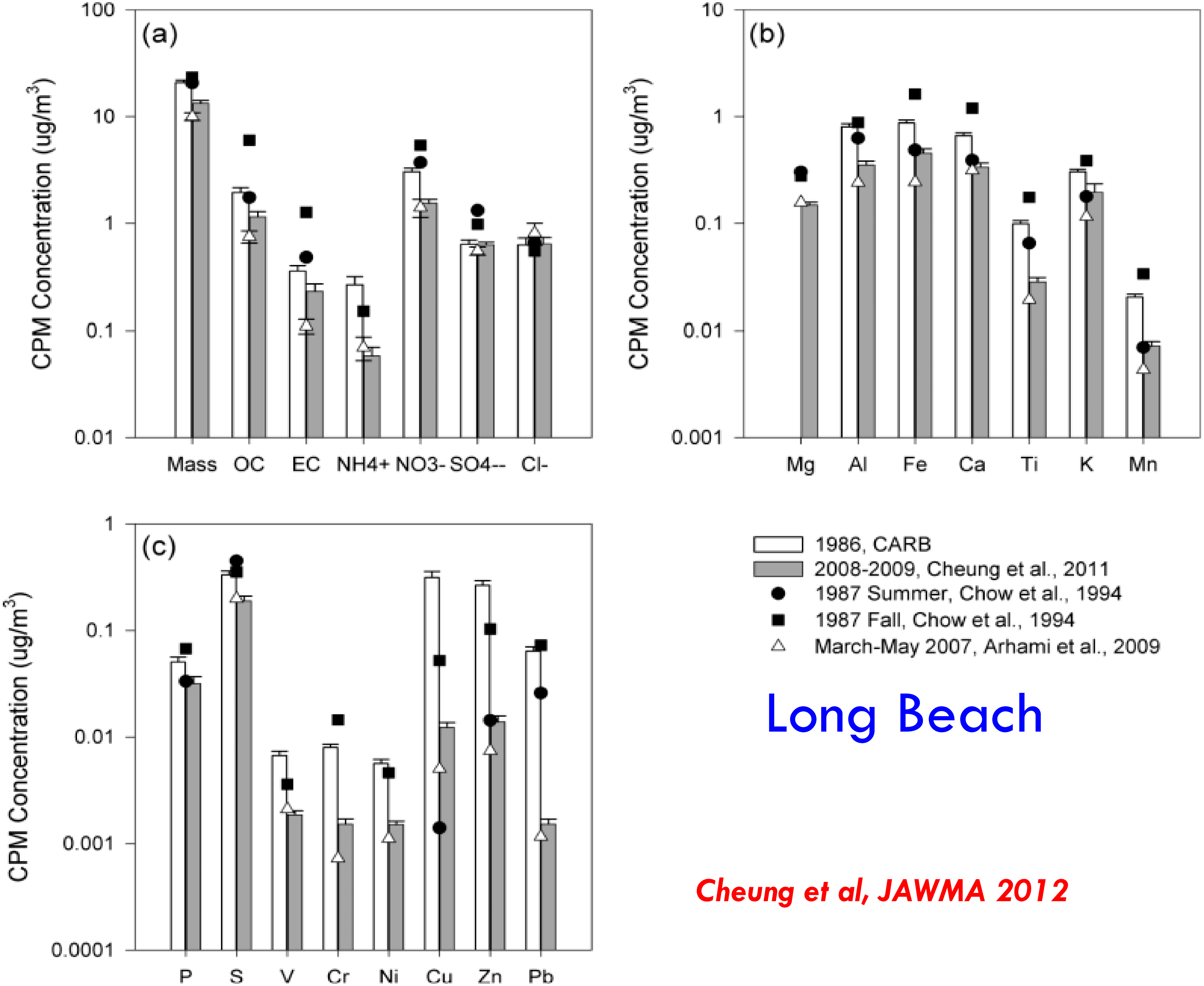


Cheung et al, JAWMA 2012



Riverside

Cheung et al, JAWMA 2012



Long Beach

Cheung et al, JAWMA 2012

Summary

- Mineral dust is the most dominant group, with higher fractions in inland areas
- Organic matter mostly arises from soil and biological materials
- Combustion emissions have decreased considerably even in CPM in the last decade
- Significant diurnal trend and contrasting primary re-suspension mechanism in summer and winter

Physical Characterization

- What causes the spatial and seasonal trends in CPM mass?
- Has the mass concentration changed over the years?
- Is PM_{10} a good surrogate of CPM?

Chemical Characterization

- Is the chemical composition of CPM different from $PM_{2.5}$?
- What are the sources and formation mechanisms of CPM?
- Has the chemical profile of coarse particle changed over the years?

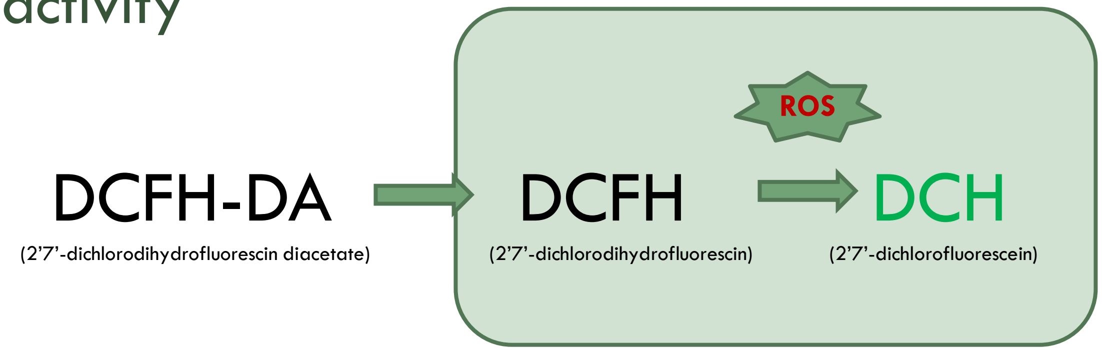
Toxicological Characterization

- What are driving the toxicity of coarse particles?
- Is there a link between source, composition and toxicity of CPM?

Cellular ROS Assay

- A Cell-based Method
  - Alveolar macrophage (AM)
  - Measures total ROS activity

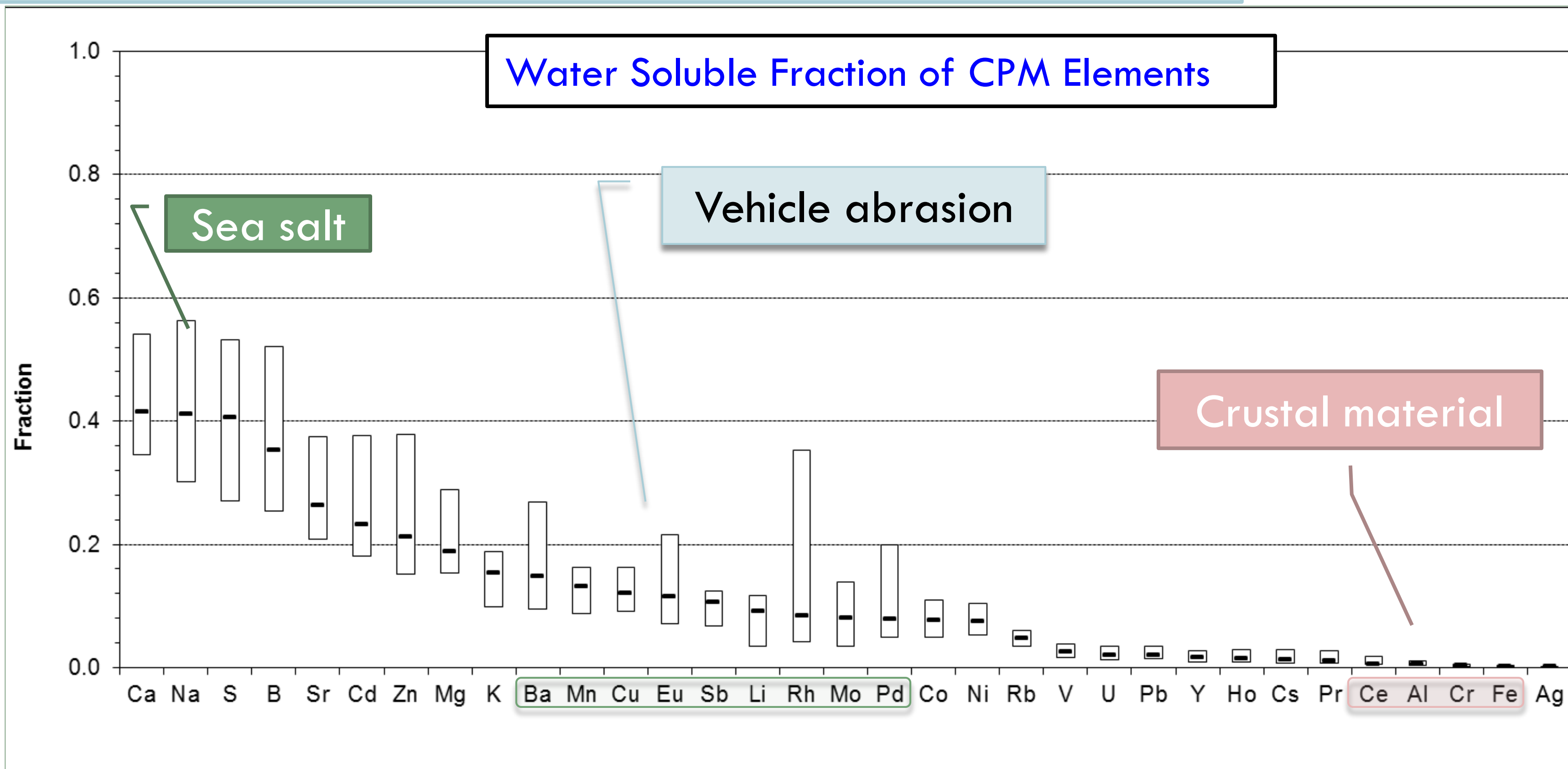
- Method
  1) Water extraction
  2) Filtration
  3) Add DCFH-DA solution of AM cell culture
  4) Exposure of AM cells to PM extracts
  5) Measure the increase of fluorescence in treated samples every 30 mins for an incubation time of 150 mins, and compared with untreated controls



PM Induced-ROS Formation

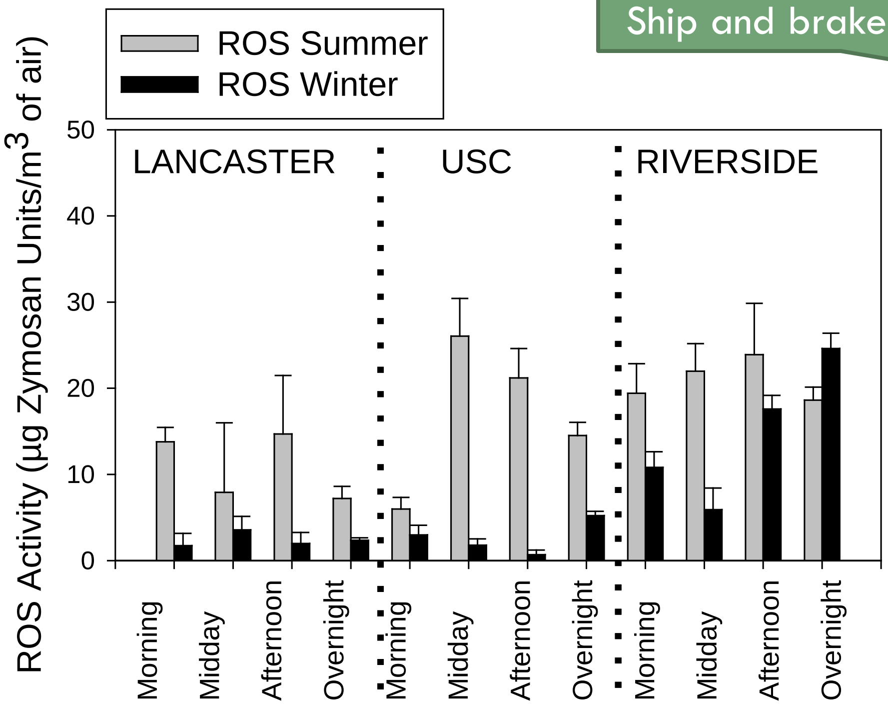
Cheung et al ES&T 2012

- Particle-cell interaction
  1. Fine/Coarse PM enter cells by phagocytosis.
  2. Ultrafine PM, organic compounds enter by diffusion.
  3. Water-soluble ions enter by ion channels, carrier molecules.



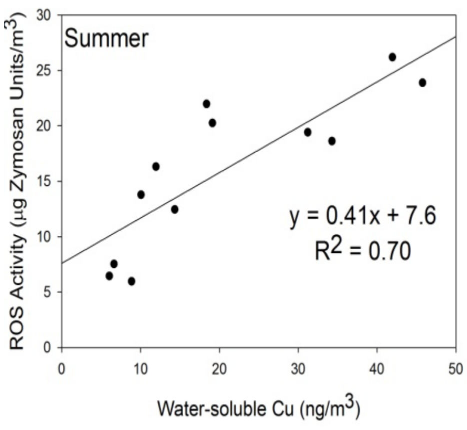
Cheung et al ES&T 2012

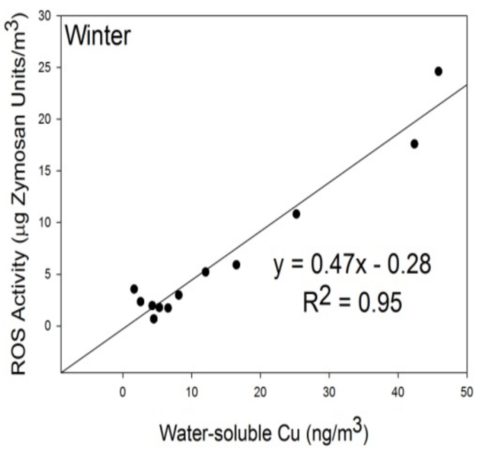
ROS Activity in Coarse Particles



Ship and brake wear — Catalytic converter wear — Brake wear

	WS-V	WS-Pd	WS-Cu	WS-Rh	WS-Ti	WS-Al
ROS	0.74	0.78	0.73	0.64	0.14	0.16
WS-V		0.86	0.67	0.64	0.15	0.27
WS-Pd			0.85	0.86	0.11	0.34
WS-Cu				0.71	0.12	0.28
WS-Rh					0.07	0.53
WS-Ti						0.06





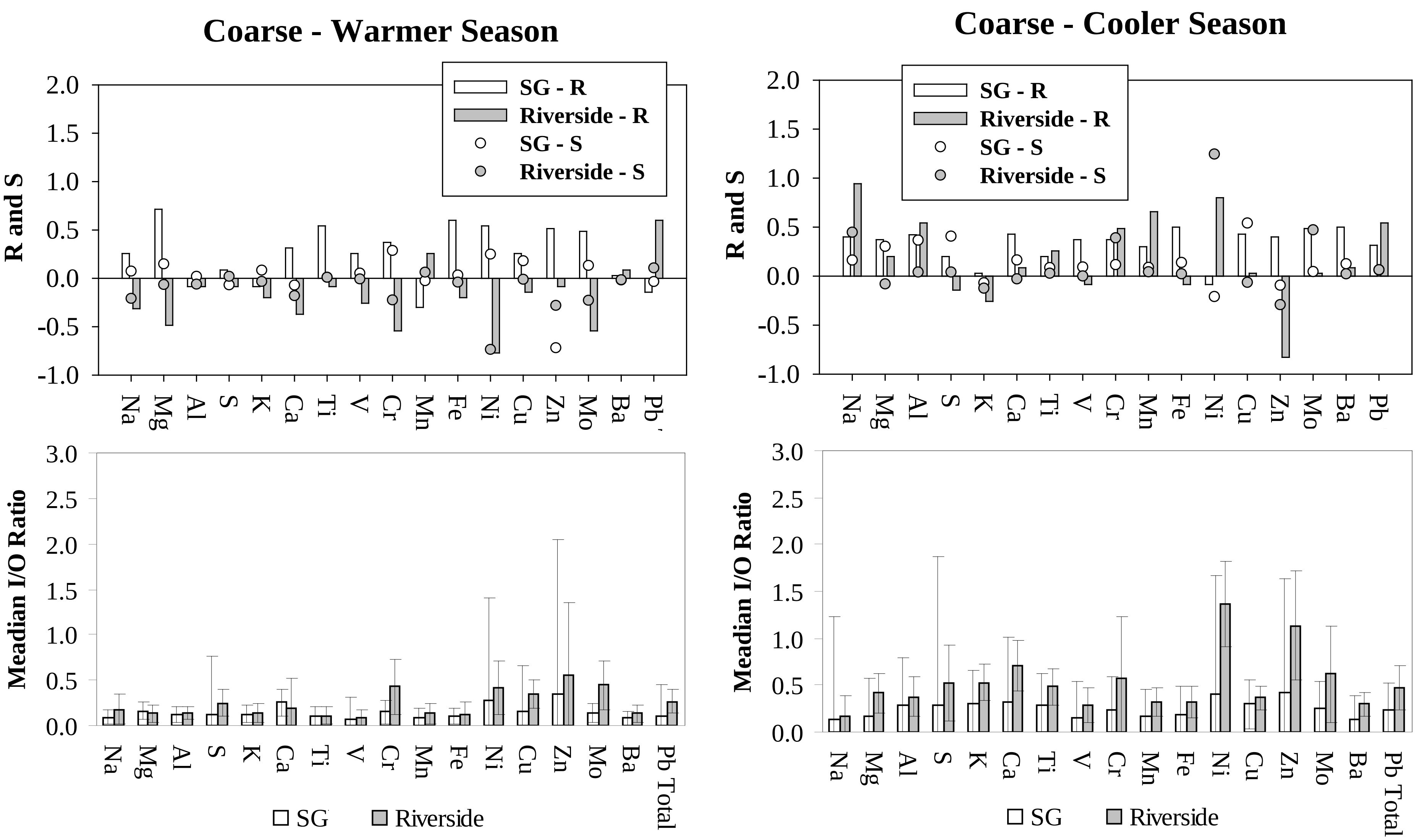
Summary

- Water solubility in crustal vs. anthropogenic elements
- Distinct ROS activity and profile in summer vs. winter
- The water-soluble fraction of four elements (V, Pd, Cu and Rh) displayed the highest associations with ROS activity (R^2>0.60).

Limitations

- Generalizability
- Toxicological assessment
- Penetration in Indoor Environments

Indoor vs Outdoor CPM Ratios and Correlation (Polidori et al, 2009)

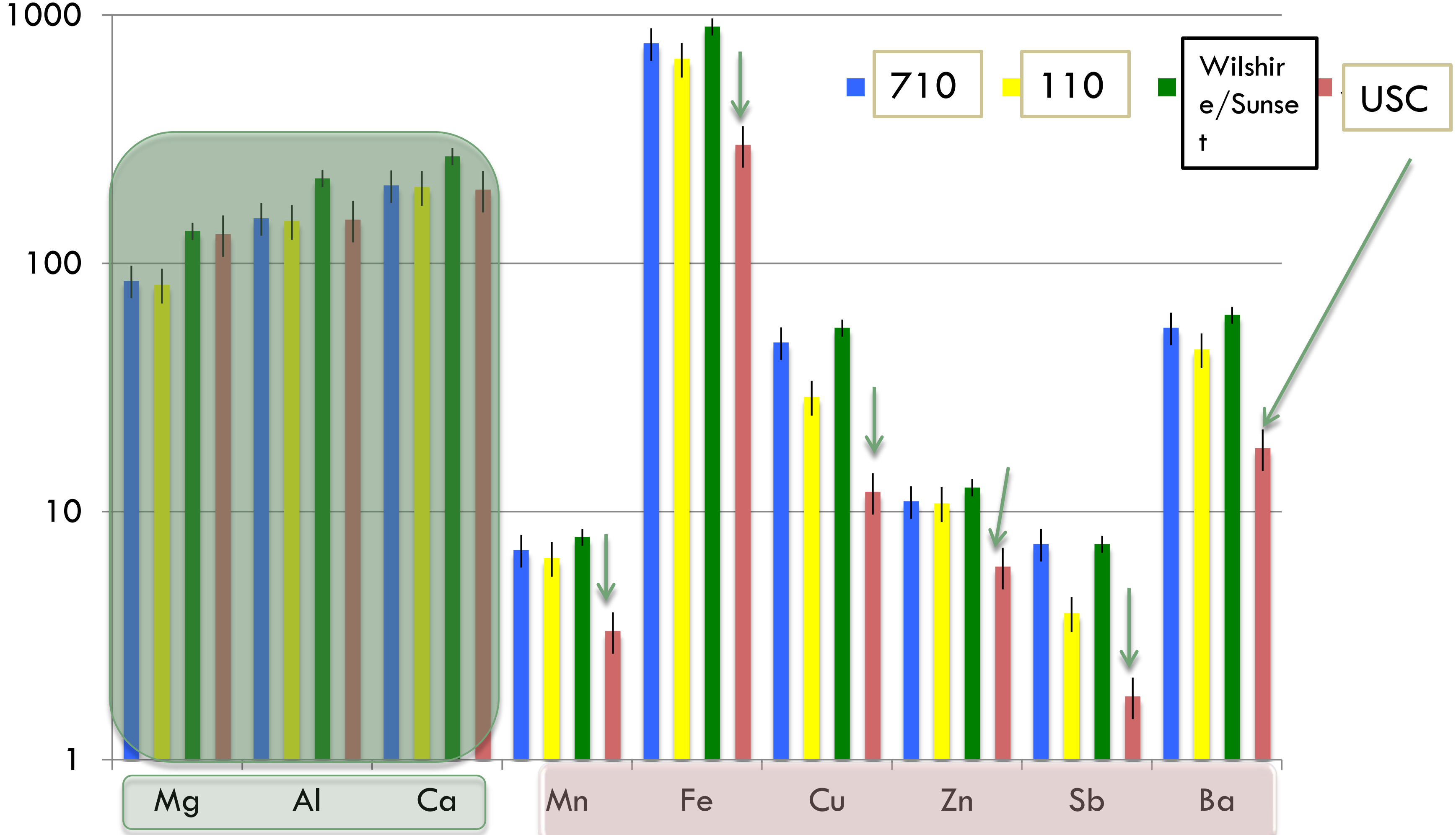


Coarse PM have very low I/O ratios and low (often negative) I/O correlations (R)

SG: San Gabriel   R; Pearson Coefficient   S; regression slope

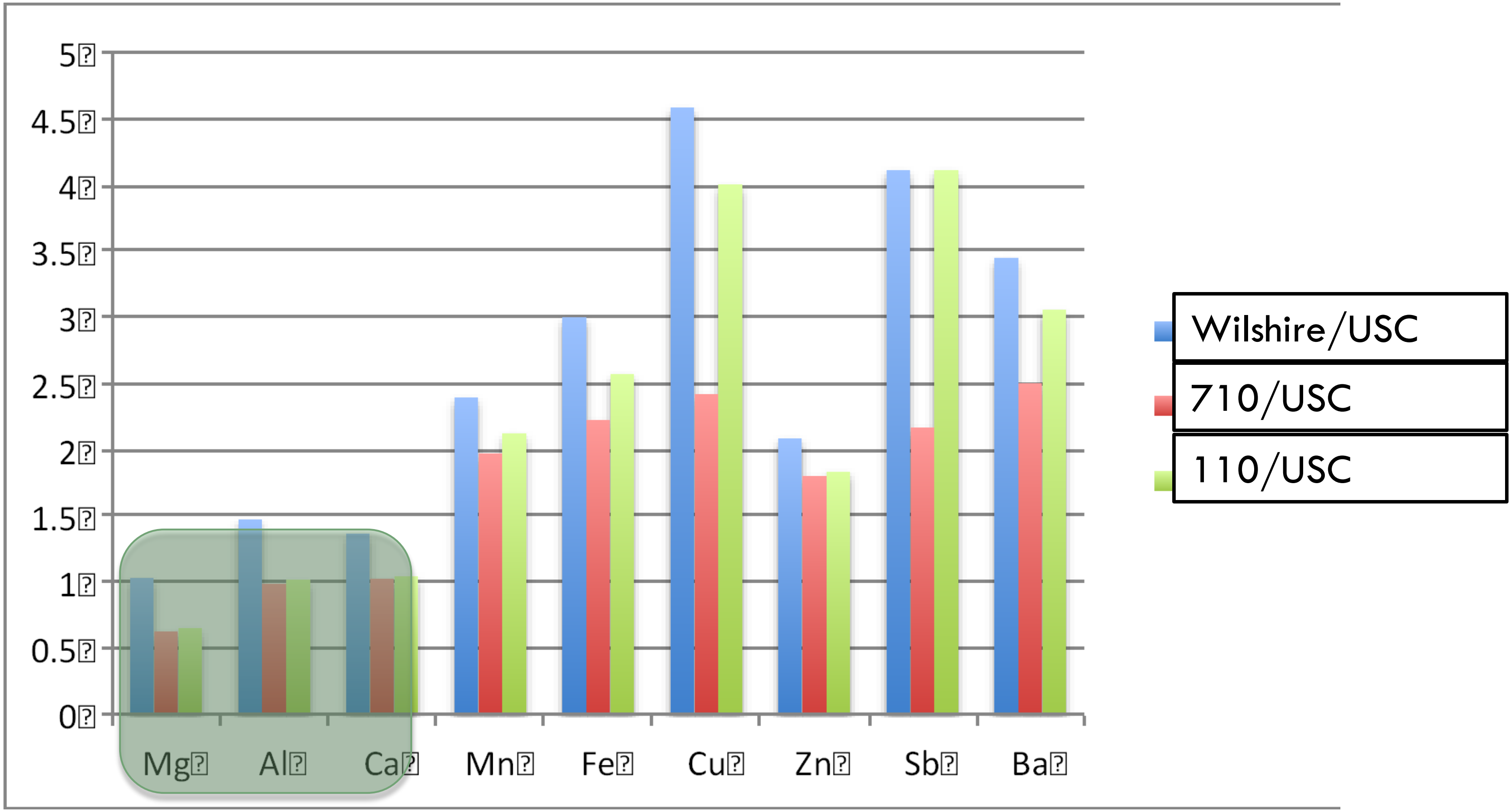
Riverside

Coarse PM Elements and Metals in Freeways, Busy Streets and Urban Background in LA (Kam et al 2012)



<u>Crustal elements</u>
Very similar concentrations

<u>Road dust, vehicular abrasion, tire and break wear</u> – USC on average 20%-40% of other areas- highest levels at Wilshire and Sunset Blvds.

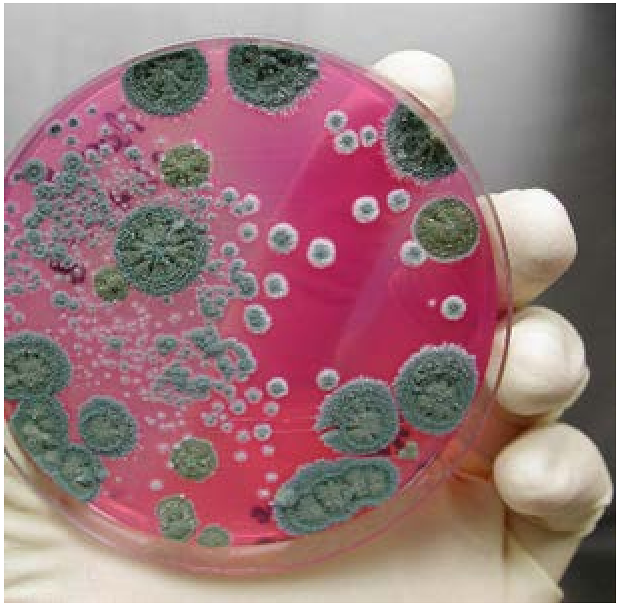


Ratios of Coarse PM in Various LA Freeways and busy streets vs USC (urban background site)- from *Kam et al Atmos Environ 2012*

2-5 fold higher levels of CPM-bound metals from road dust in busy streets compared to urban background

Recommendations on Future Aerosol Research

- Bioaerosols
  - Quantification of fungi, bacteria, plant pollen, and spore materials



- Road dust
  - Focused-characterization
  - In-vivo exposures

  Increasingly important, given difficulties controlling non-tailpipe exhaust

Journal Papers (peer-reviewed)

- Polidori, A., Cheung, K. L., Arhami, M., Delfino, R. J., Schauer, J. J. and Sioutas, C. Relationships between size-fractionated indoor and outdoor trace elements at four retirement communities in southern California. *Atmos Chem Phys* **2009**. 9 (14): p/ 4521-4536.
- 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*, **2010**. 44(7): p. 514-525.
- Moore, K.F., Verma, V. Minguillon, 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*, **2010**. 44(7): p. 526-540.
- Pakbin P., Ning, Z., Shafer M. M., Schauer J. J., and Sioutas C. Seasonal and Spatial Characteristics of Trace Elements and Metals in Coarse Particulate Matter in the Los Angeles Area. *Aerosol Science and Technology*, **2011**. 45(8): p. 949-956.
- Cheung K.L., Daher N., Kam W., Shafer M.M., Ning Z., Schauer J.J., Sioutas C. Spatial and Temporal Variation of Chemical Composition and Mass Closure of Ambient Coarse Particulate Matter ($PM_{10-2.5}$) in the Los Angeles Area. *Atmospheric Environment*, **2011**. 45(16): p. 2651-2662.
- Cheung, K., Shafer, M.M. Schauer, J.J. and Sioutas, C. Diurnal trends in coarse particulate matter composition in the Los Angeles Basin. *Journal of Environmental Monitoring*, **2011**,13, : 3277-3287.
- Cheung, K., Shafer, M.M. Schauer, J.J. and Sioutas, C. Historical trends in the mass and chemical species concentrations of coarse particulate matter (PM) in the Los Angeles Basin and relation to sources and air quality regulations. *Journal of the Air & Waste Management Association*, **2012**: *62*(5), 541-556.
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- Cheung, K., Olson, M.R., Shelon, B., Schauer, J.J. and Sioutas, C. Seasonal and spatial variations of individual organic compounds of coarse particulate matter in the Los Angeles Basin. *Atmospheric Environment*, **2012** ,59:pp 1–10.
- Wang, Dongbin, et al. "Development of a Two-Stage Virtual Impactor System for High Concentration Enrichment of Ultrafine, PM2. 5, and Coarse Particulate Matter." *Aerosol Science and Technology* 47.3 (**2013**): 231-238.