SEASONAL AND SPATIAL VARIATION IN CHEMICAL COMPOSITION OF ULTRAFINE PARTICLES IN SOUTHERN CALIFORNIA

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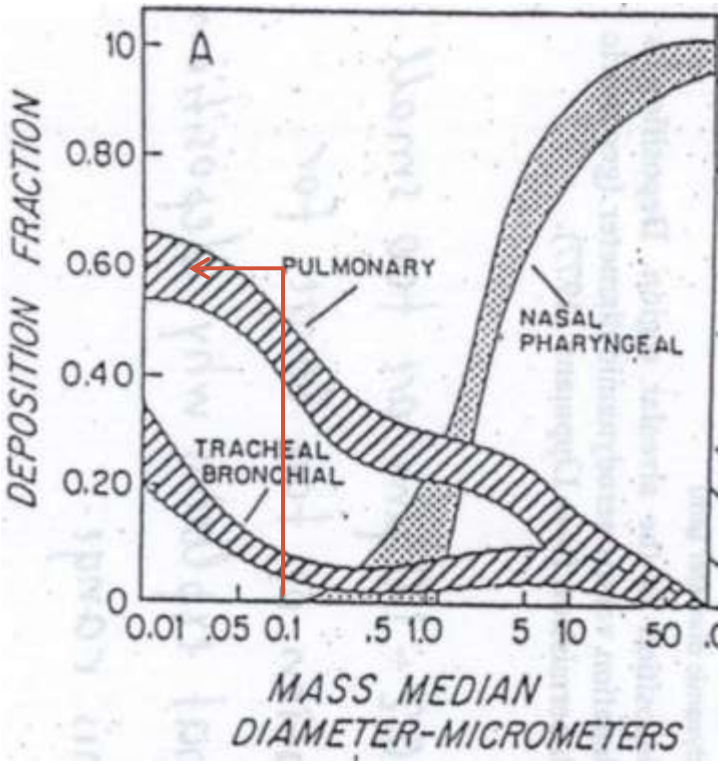
Why study ultrafine particles (UFP)?

- Current regulatory efforts are focused on reducing PM_{10} and $PM_{2.5}$
- But, UFP dominate particle number concentrations and have a large surface area relative to $PM_{2.5}$ or $PM_{2.5-10}$ and a high pulmonary deposition efficiency.



→UFP can carry substantial amounts of toxic air pollutants (e.g. OC, PAHs and transition metals)

Objectives

- What is the spatial and seasonal variation in UFP mass and chemical composition in the Los Angeles Basin?
- How do the chemical characteristics of UFP in urban sites compare to those in rural or receptor sites?
- What are the major primary and secondary sources of UFP at each site and what is their seasonal variability?
- What is the seasonal and spatial distribution of UFP toxicity as measured by chemical (DTT) and cellular redox activity assays (ROS)?
- How are the chemical characteristics of UFP associated with at the above environments associated with the measured toxicity of UFP?

Sampling Sites

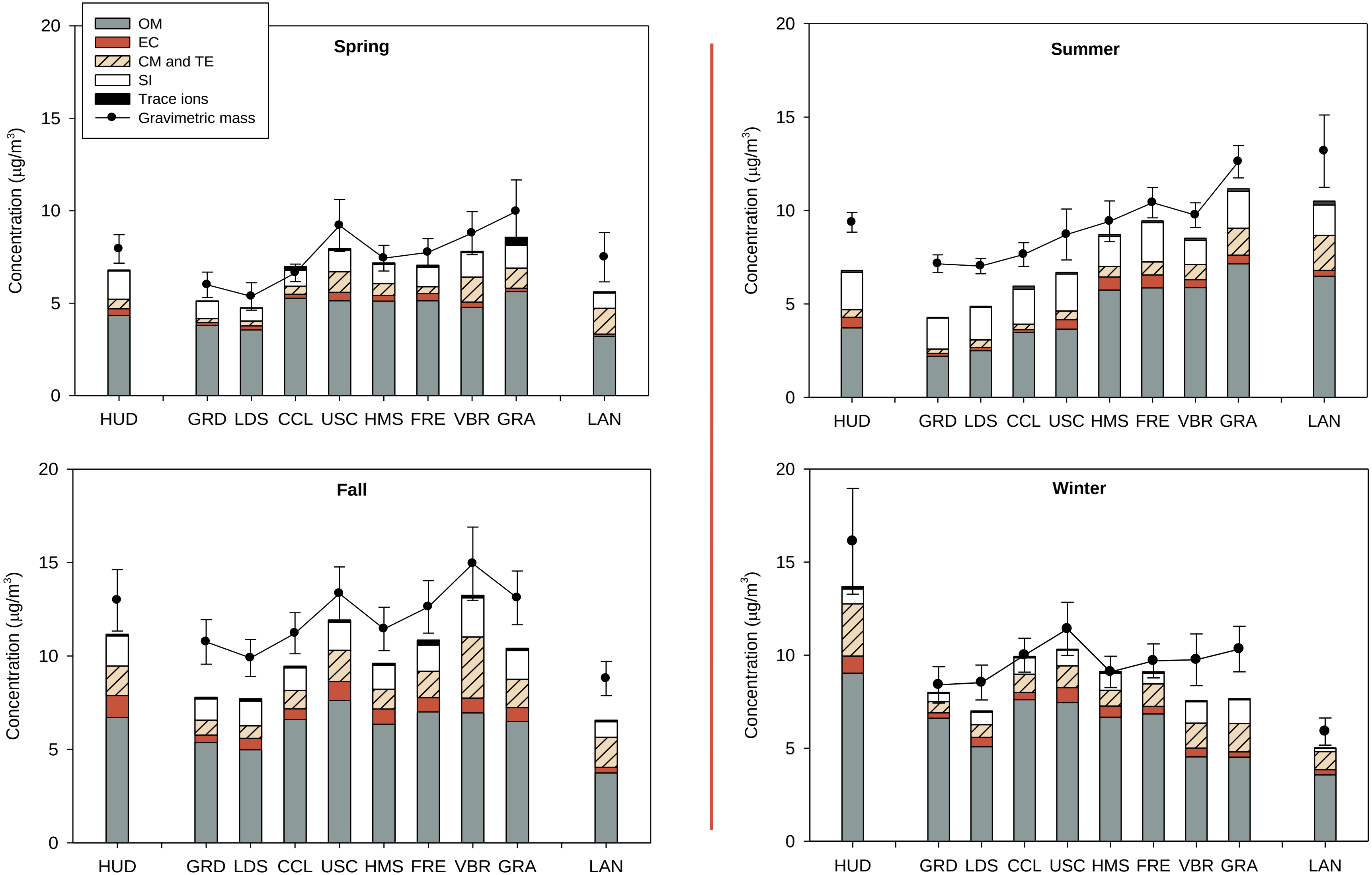
Methodology

- 24-hr weekly samples (dp<0.25 um) concurrently collected at 10 sampling sites from April 2008 to March 2009.
- Sioutas Personal Cascade Impactor Sampler (PCIS)

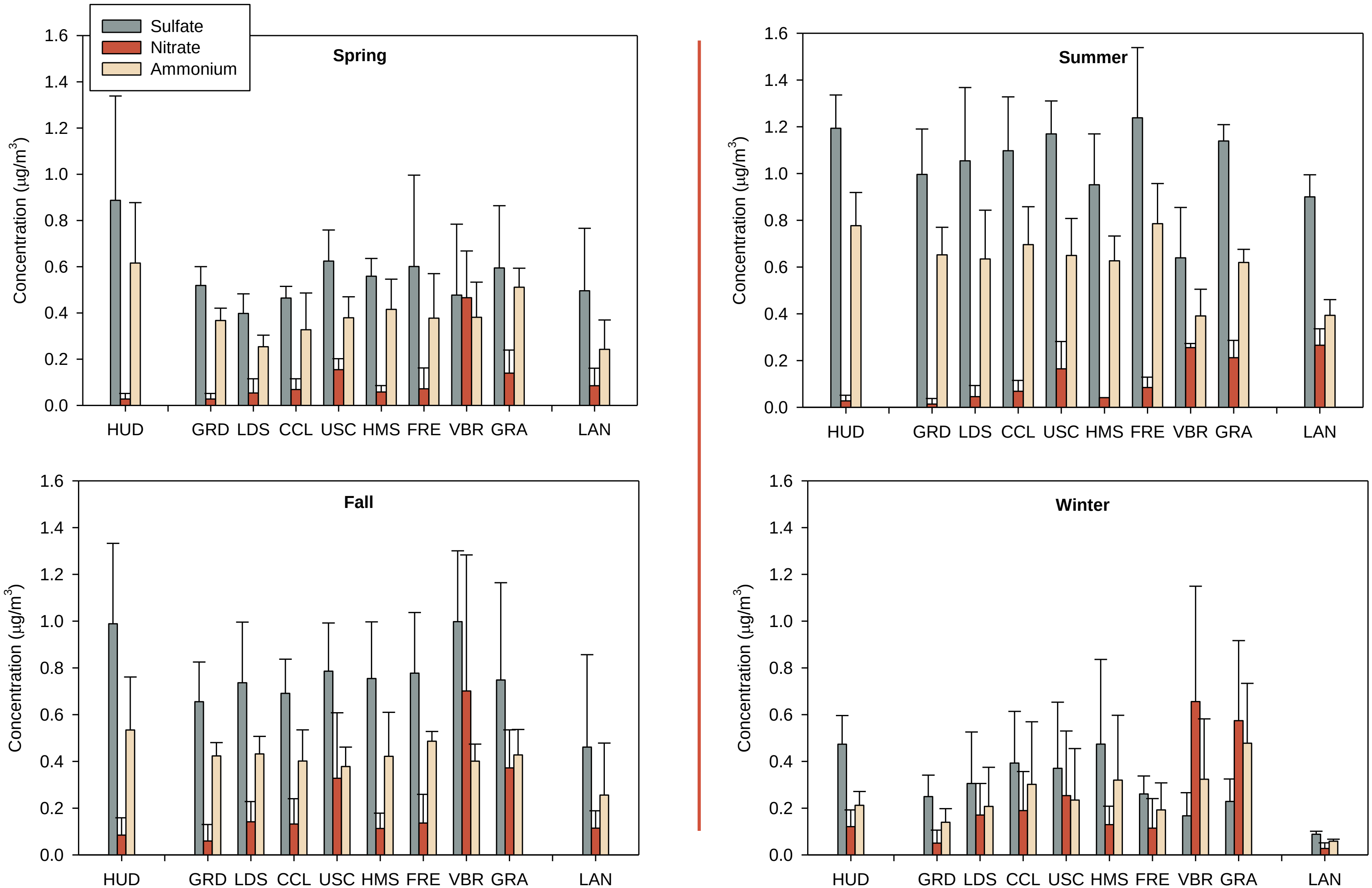
Meteorology

		Temperature (°C) Average ± stdev	Wind (vector-average)	
			Speed (m/s) (calm%)	Prevailing direction
Long Beach	Spring	16.3±5	1.6(4.1)	**SW**
	Summer	21.3±3.8	1.9(3.3)	**SW**
	Fall	19.9±4.9	1.2(5.6)	W
	Winter	13.8±5	0.7(2.9)	NW
Western LA	Spring	15±4.4	1.7(9.8)	**W**
	Summer	19.4±2.7	0.7(26.2)	**W**
	Fall	19±4.2	0.2(50.2)	NE
	Winter	13.9±4.8	0.2(26.2)	NW
Central & Eastern LA	Spring	17.2±5.8	2.1(0.6)	**SW**
	Summer	22.8±4.8	3.6(1.2)	**SW**
	Fall	20.9±5.7	1.6(4.6)	SW
	Winter	14.1±5.6	1.5(0.6)	NE
Riverside	Spring	17.4±6.7	2.6(5)	NW
	Summer	25.6±6.4	3.6(2.7)	**W**
	Fall	22±7.1	1.6(6.5)	NW
	Winter	13.8±6.1	1.3(3.9)	N
Lancaster	Spring	15.2±6.6	4.1(13.5)	**W**
	Summer	27.9±5.4	4.3(11.6)	**W**
	Fall	18.8±7.3	1.5(30.5)	W
	Winter	8.7±4.7	1.5(33.6)	W

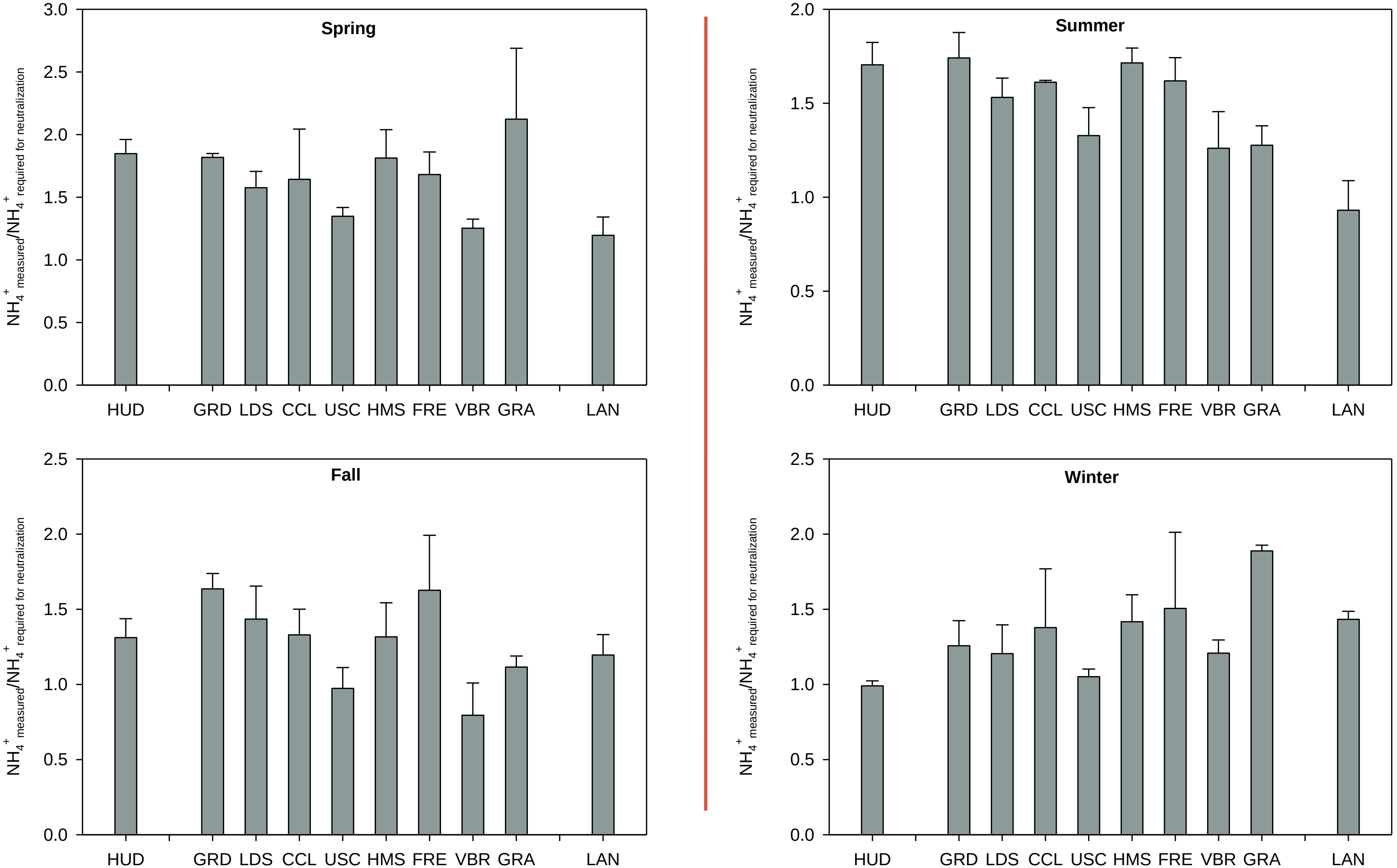
UFP Mass and Chemical Composition



Secondary Ions (Sulfate, Nitrate, Ammonium)



Ion Balance



Spring
Summer
Fall
Winter
NH_4^+ measured/NH_4^+ required for neutralization
HUD
GRD
LDS
CCL
USC
HMS
FRE
VBR
GRA
LAN
0.0
0.5
1.0
1.5
2.0
2.5
3.0

Metals & Elements: Principal Component Analysis (PCA)

Elements	Principal Component				
	PC1	PC2	PC3	PC4	PC5
Rb	.949	.173	-.030	.135	.078
Mg	.946	.187	.028	.135	.081
Al	.919	.224	.059	.135	.109
K	.907	.235	.075	.130	.041
Mn	.886	.347	.024	.143	.109
Ca	.856	.358	.048	.212	.117
Ti	.850	.403	.025	.094	.081
Na	.848	.075	.223	.097	.146
Li	.808	.249	.014	.323	.086
Fe	.768	.583	-.010	.136	.136
Sr	.683	.586	.042	.184	.066
Co	.627	.276	.461	.056	.297
Rh	.282	.868	.017	.173	.136
Ba	.422	.835	-.002	.142	.060
Sb	.243	.793	-.016	.350	.026
Cu	.221	.756	-.005	.144	.150
Mo	.257	.714	.170	.191	.389
As	.339	.511	.068	.455	.062
Zn	.452	.478	.477	.327	.033
S	.049	-.201	.874	-.047	.003
La	.254	.170	.847	.049	-.017
V	-.170	.031	.808	-.029	.232
Cd	.137	.225	.105	.869	.007
Ag	.193	.229	-.133	.687	.063
Pb	.381	.538	.063	.624	.123
Cr	.281	.218	-.022	.044	.871
Ni	.128	.207	.492	.087	.810
Eigenvalue	14.68	2.95	2.62	1.35	0.98*
% Variance	35.808	20.782	10.921	9.224	6.992

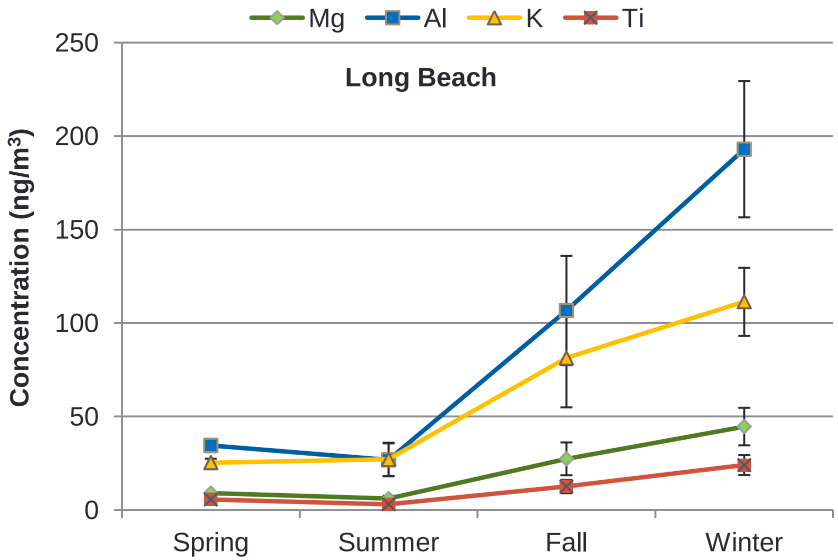
Principal Components (PC)

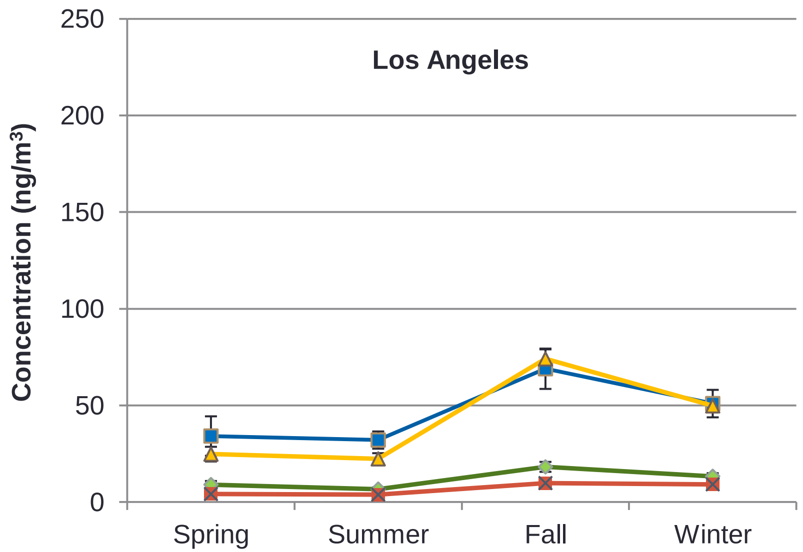
- PC1: road dust
- PC2: vehicular abrasion
- PC3: ship emissions
- PC4: gasoline exhaust
- PC5: industrial emissions

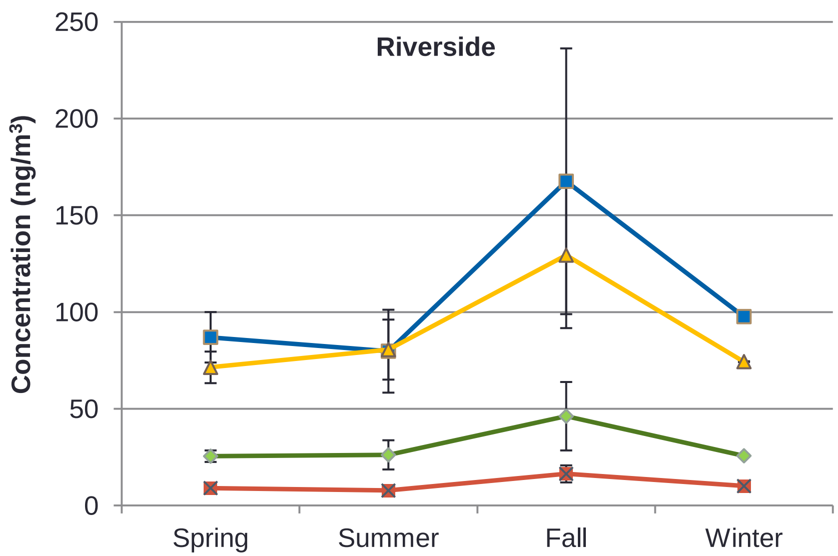
- ***A note on road dust***: UFP largely originate from tires, and not road pavement. The particles consist most likely of mineral oils from the softening filler and fragments of the carbon-reinforcing filler material (soot agglomerates).

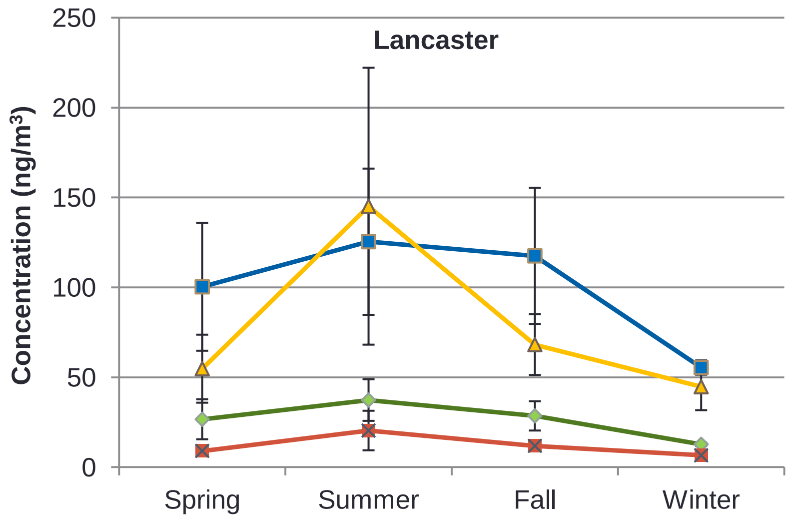
- See the work by Gustafsson group (Swedish National Road and Transport Research Institute)

Road Dust

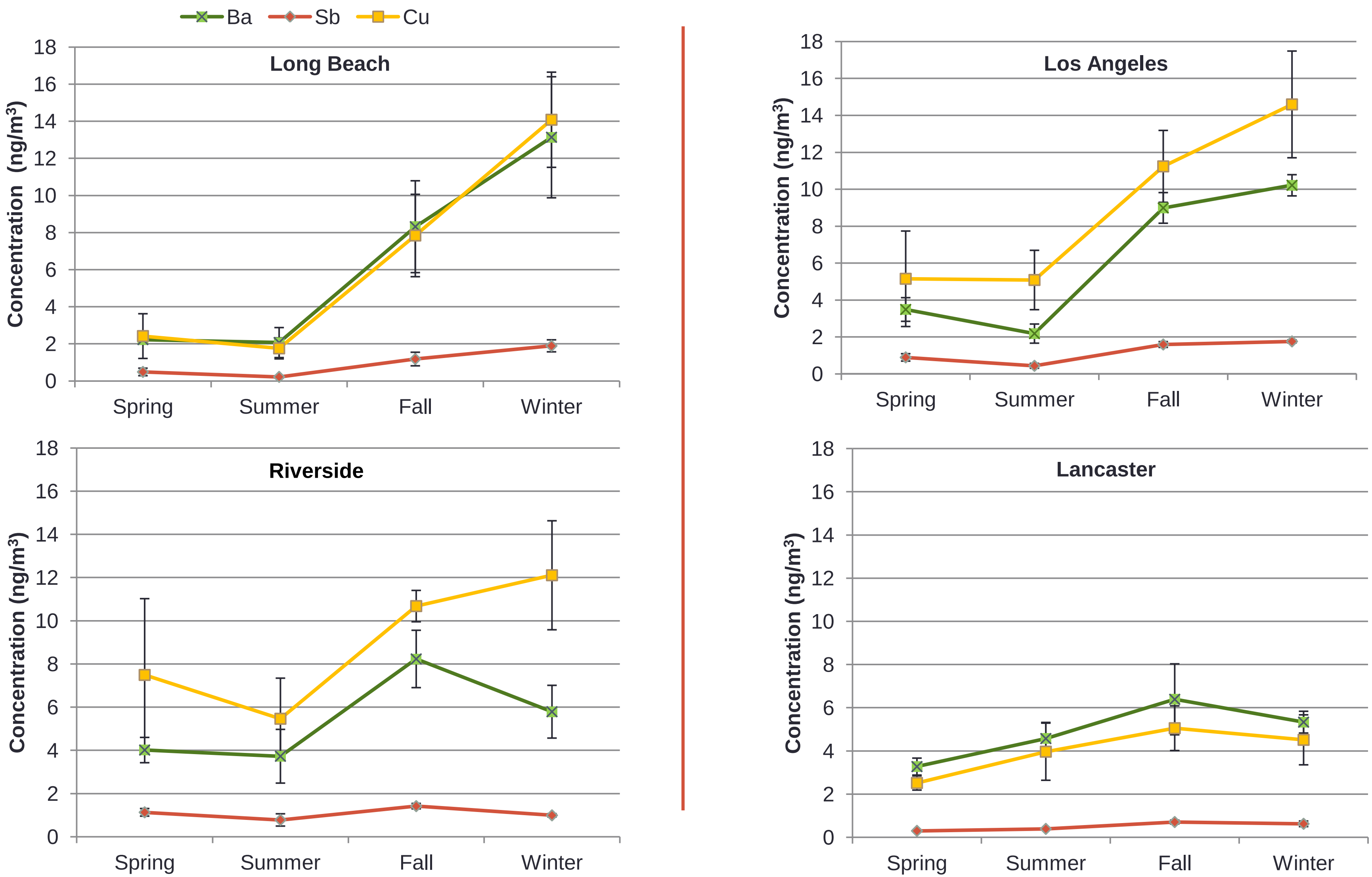

Mg
Al
K
Ti
Long Beach
Concentration (ng/m³)
250
200
150
100
50
0
Spring
Summer
Fall
Winter


Los Angeles
Concentration (ng/m³)
250
200
150
100
50
0
Spring
Summer
Fall
Winter

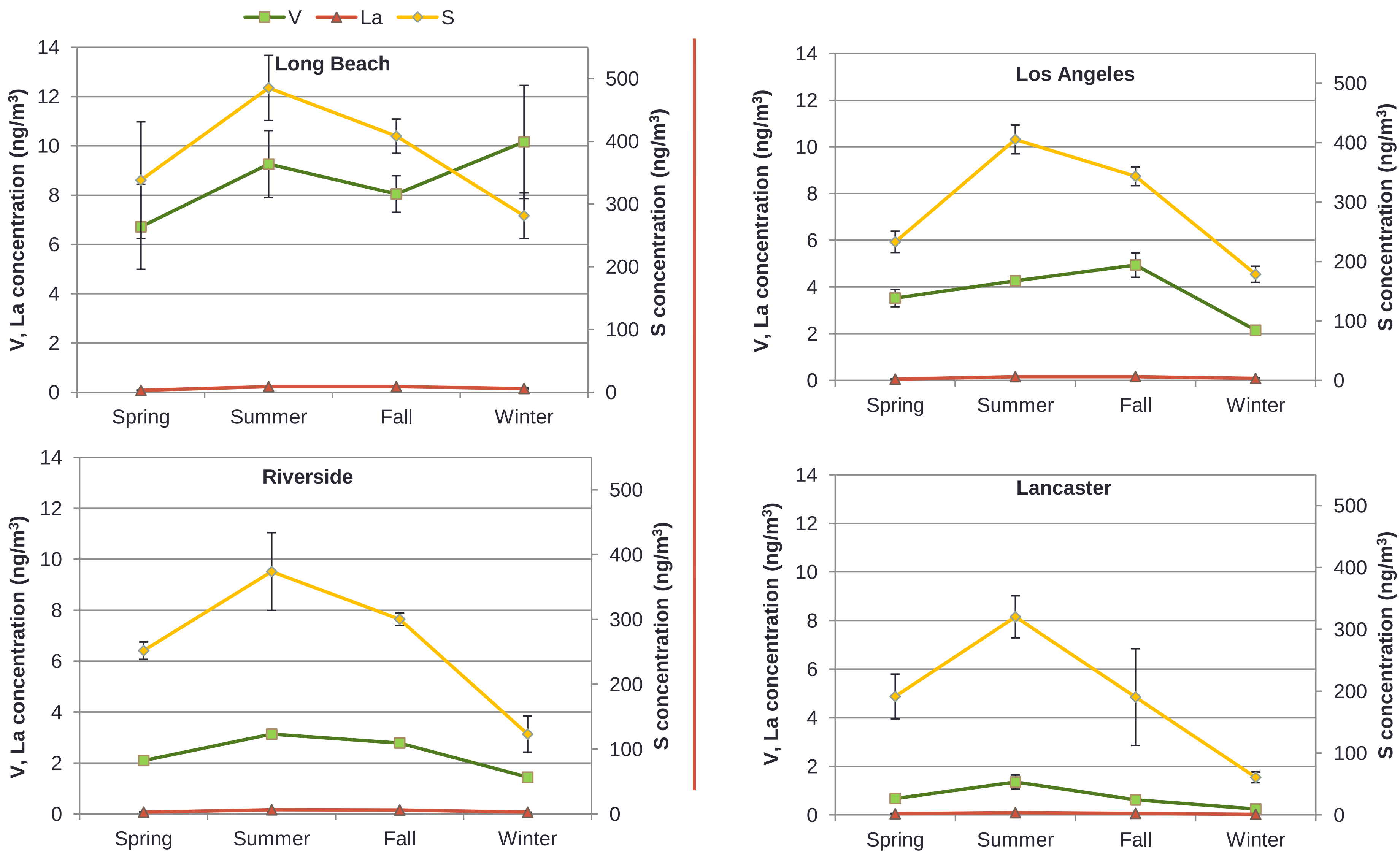

Riverside
Concentration (ng/m³)
250
200
150
100
50
0
Spring
Summer
Fall
Winter


Lancaster
Concentration (ng/m³)
250
200
150
100
50
0
Spring
Summer
Fall
Winter

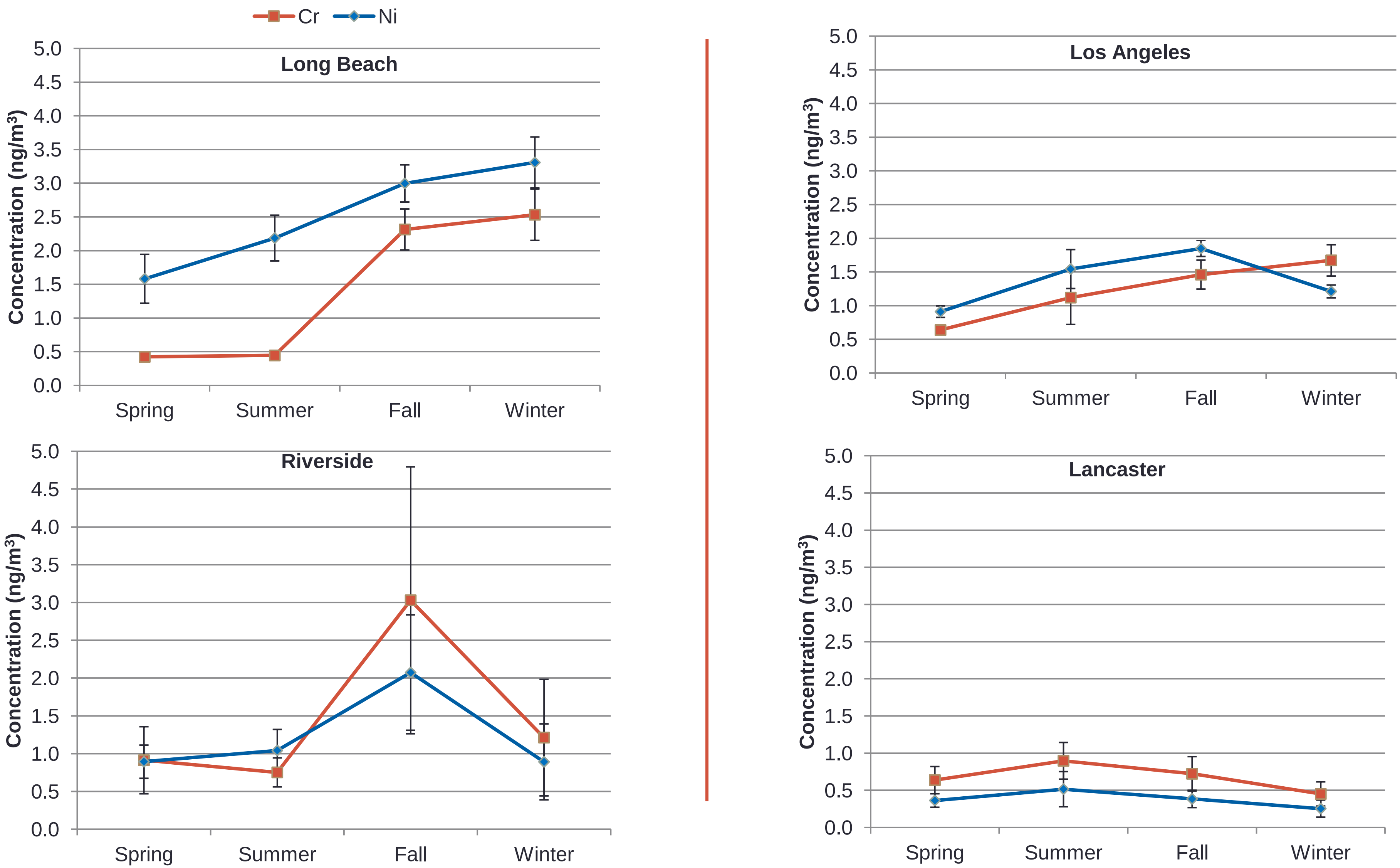
Vehicular Abrasion



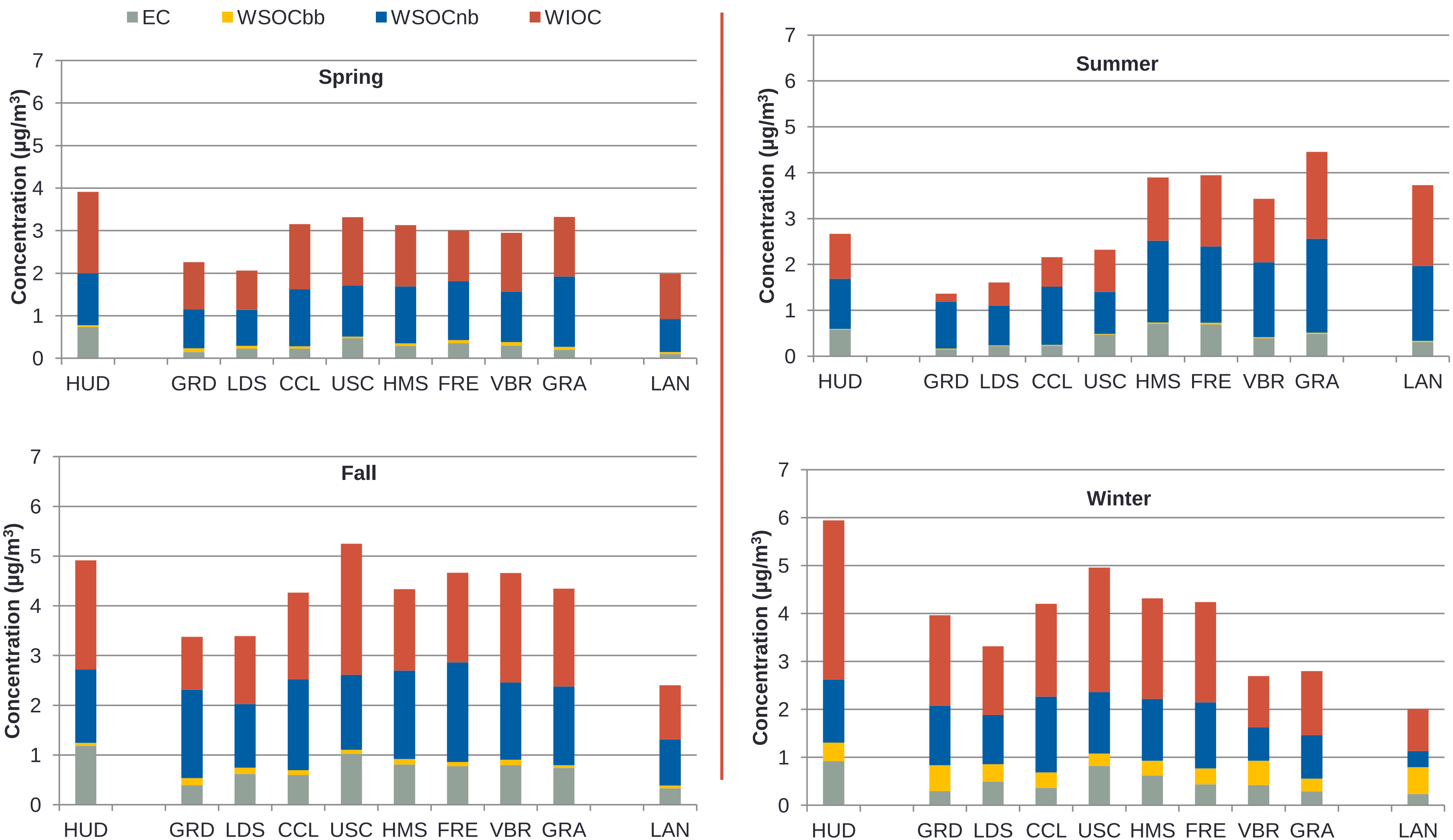
Ship Emissions



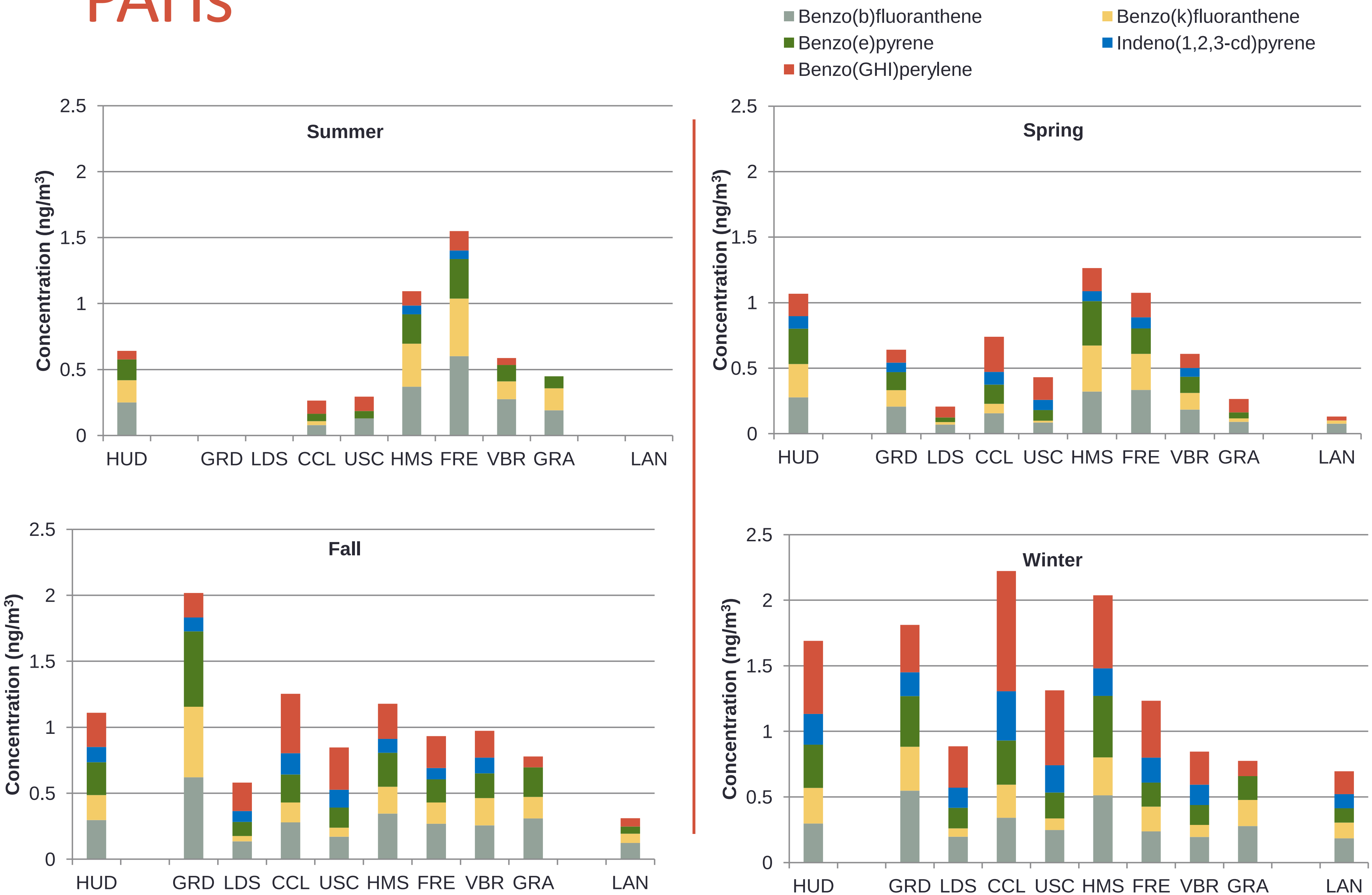
Industrial Emissions



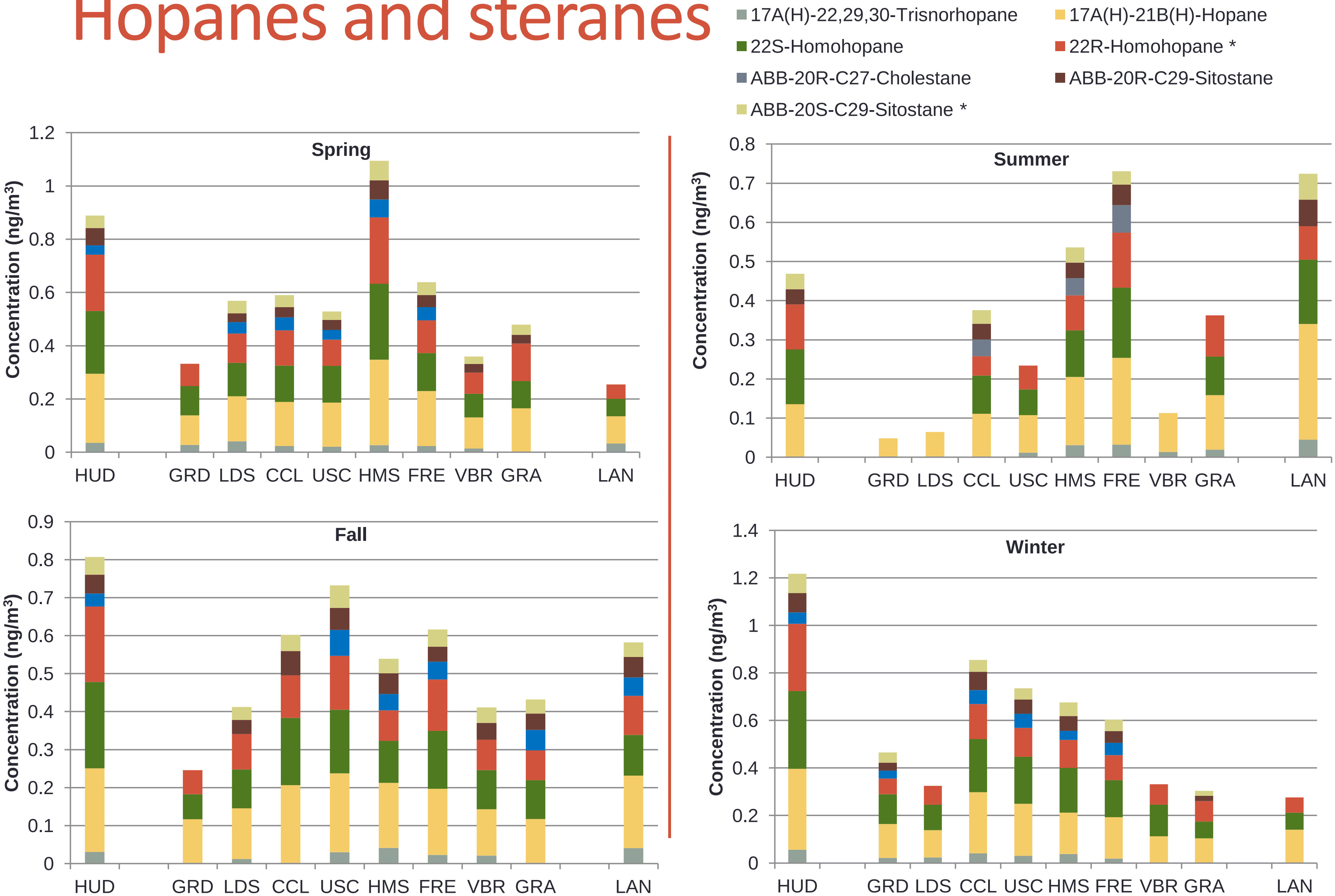
Carbonaceous Compounds



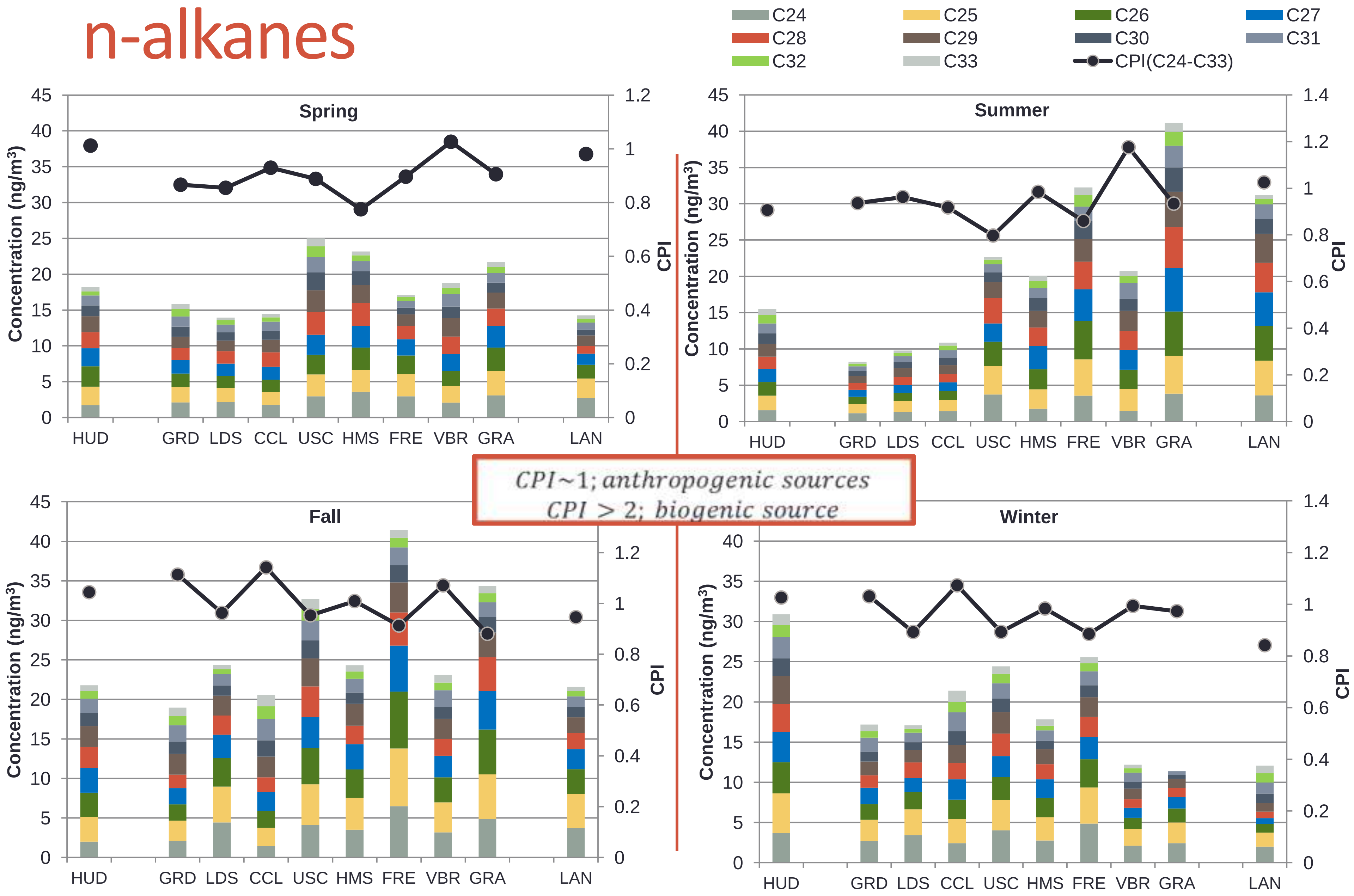
PAHs


Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(e)pyrene
Indeno(1,2,3-cd)pyrene
Benzo(GHI)perylene
Summer
Spring
Fall
Winter
Concentration (ng/m³)
0
0.5
1
1.5
2
2.5
HUD
GRD
LDS
CCL
USC
HMS
FRE
VBR
GRA
LAN

Hopanes and steranes



n-alkanes


C24
C25
C26
C27
C28
C29
C30
C31
C32
C33
CPI(C24-C33)
Spring
Summer
Fall
Winter
Concentration (ng/m³)
CPI
HUD
GRD
LDS
CCL
USC
HMS
FRE
VBR
GRA
LAN
0
5
10
15
20
25
30
35
40
45
0
0.2
0.4
0.6
0.8
1
1.2
1.4
CPI~1; anthropogenic sources
CPI > 2; biogenic source

α-pinene derivatives (tracers of biogenic-SOA)

Future Work

- Source apportionment of UFP at the 10 sampling sites
- Quantify the redox-activity (ROS and DTT) of UFP at the 10 sampling sites
- Examine the spatial and seasonal variation of UFP redox-activity in the Los Angeles Basin
- Relate the redox-activity of UFP to its chemical composition

Publications

1. Kam W., Liacos J., Schauer J.J., Delfino J.R and Sioutas C.*" Chemical composition of coarse, accumulation, and quasi-ultrafine PM in major roadways and arterials in Los Angeles, CA". *Atmospheric Environment*, 55 : 90-97, 2012

2. Daher N., Hasheminassab S., Shafer M.M., Schauer J.J and Sioutas C.* "Seasonal and Spatial Variability in Chemical Composition and Mass Closure of Ambient Ultrafine Particles in the Megacity of Los Angeles". *Royal Chemical Society: Environ. Sci.: Processes Impacts,* 1515: 283-295, 2013

Envision 4 more papers in 2013 (*tentative titles*):

3. Source apportionment and organic compound characterization of ambient quasi-ultrafine particulate matter in the Los Angeles Basin
4. Seasonal and Spatial Variation of Elements in quasi-Ultrafine Particles in the Los Angeles Metropolitan Area and Characterization of Their Sources
5. Seasonal and Spatial Variability in oxidative potential of ultrafine particles and its correlation with water soluble metals in the Los Angeles Metropolitan Area
6. Association of organic species with seasonal and spatial variability in redox activity (DTT) of ultrafine particles in the Los Angeles Basin

Acknowledgements

- South Coast Air Quality Management District (SCAQMD)
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