Use of Passive PM Samples in Source Apportionment

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Project Team and Contributors

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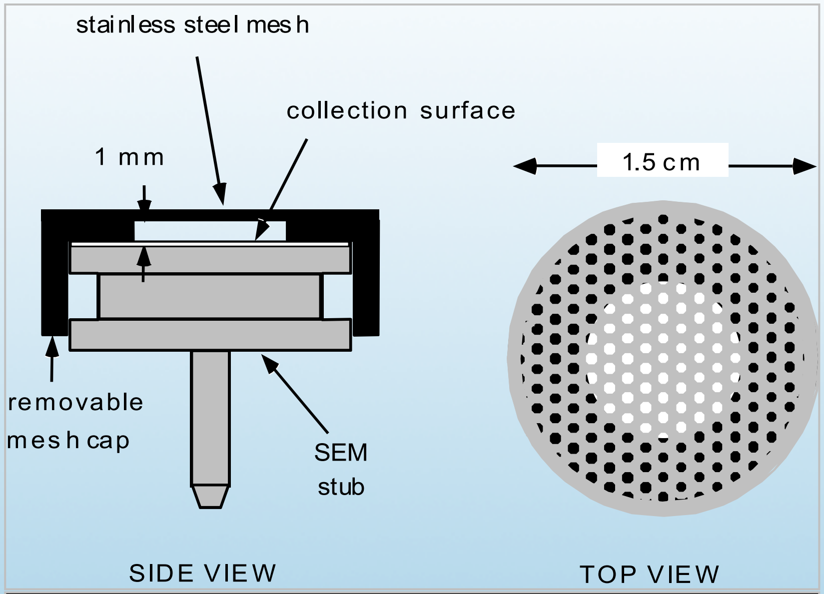
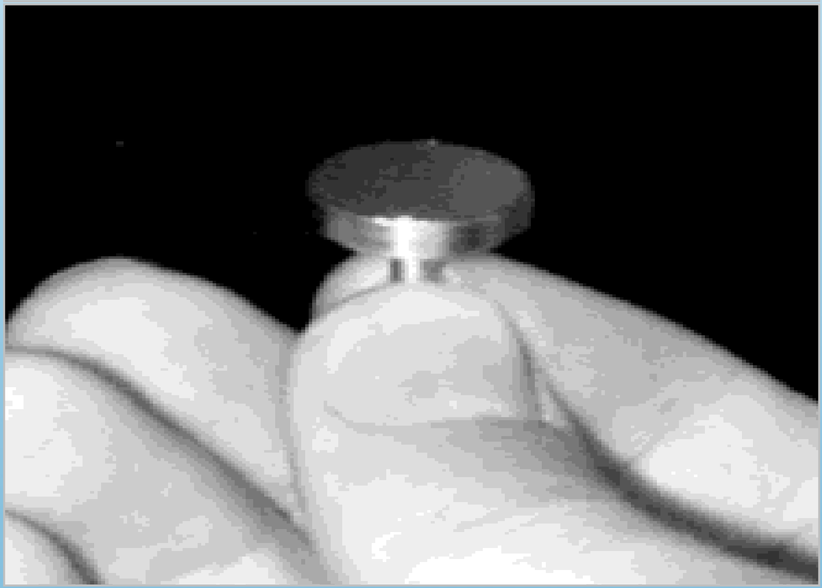
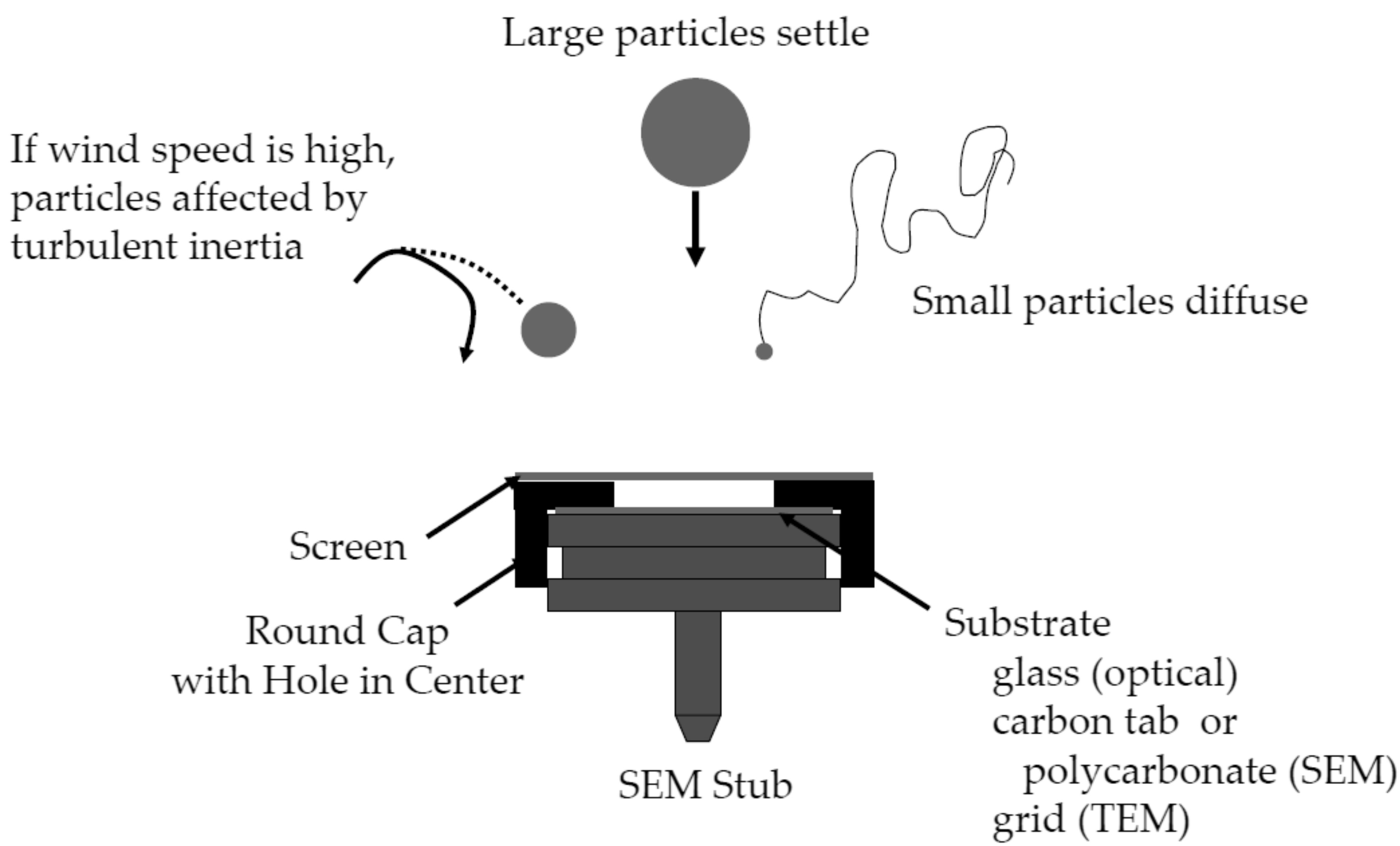
Passive Samplers





- Passive samplers are intended to monitor ambient, indoor, or occupational aerosols over a period of hours to weeks and have the potential to be used as an area monitor or as a personal sampler
- Longer sampling times of the passive sampler improve assessments of long-term mean exposures
- Passive samplers are cheaper and easier to operate than conventional samplers and, therefore, a larger number of passive samplers can be deployed.
- Enable more representative measurements (easy to deploy many duplicate samples)

How it works?



Willis, R., Norris, G., Watkins, T., Sawvel, E., Boysen, D., Kumar, N., Peters, T., Casuccio, G., Characterization of coarse PM using Passive samplers, NAAMC, 2009

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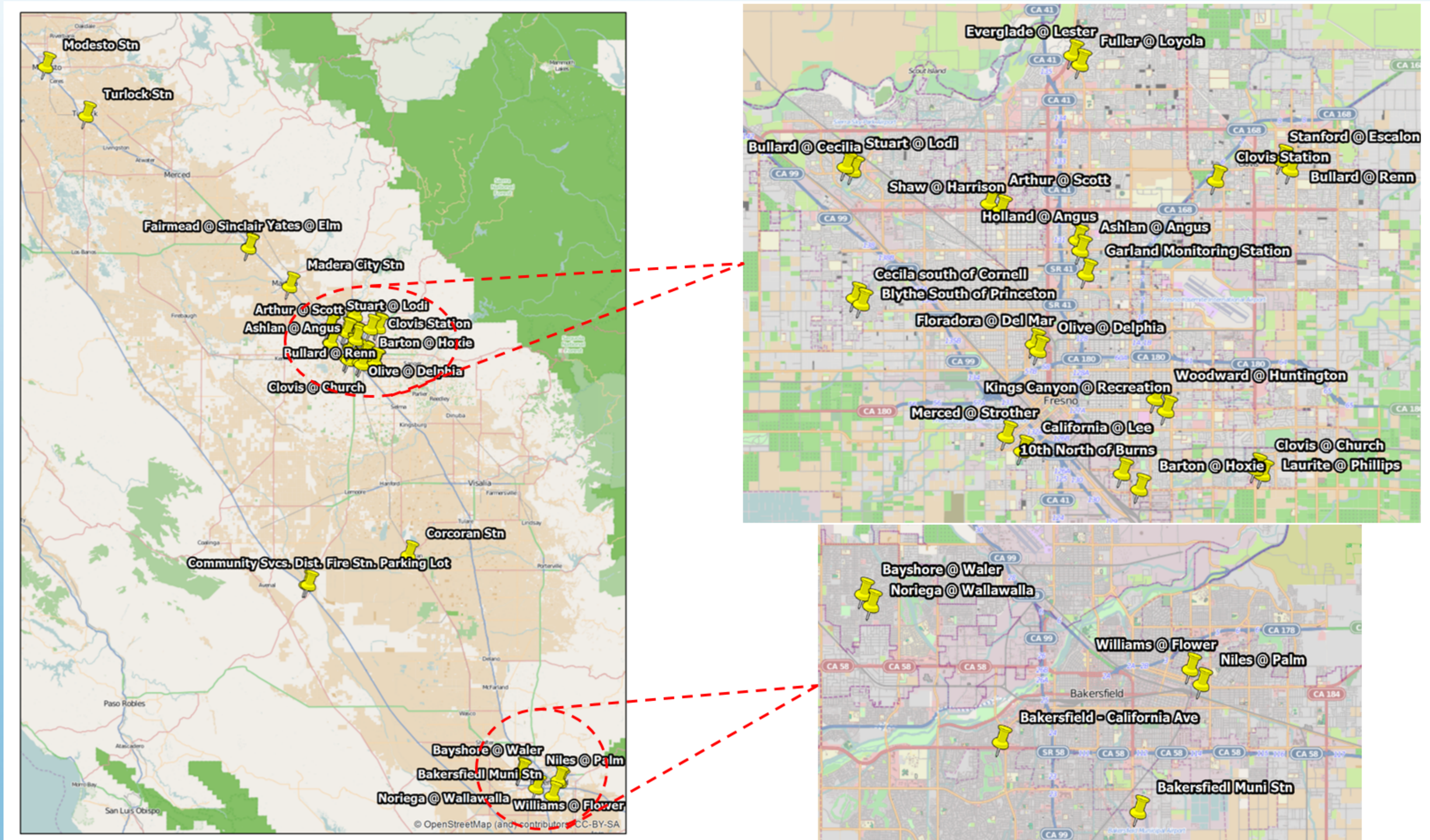
Sampler Deployment



Computer Controlled Scanning Electron Micrograph (CCSEM)

Computer Controlled Scanning Electron Microscopy (CCSEM):

- **Scanning Electron Microscope (SEM):**

  Scintillation counter from the emitted electrons gives the morphology (Particle size and Shape), and determines the boundary of the particle from backscattered electrons
- **Digital Scan Generator (DSC):**

  Electrons from the microscope beam that are directly scattered by the particle can be used for particle imaging (shape, image)
- **Energy Dispersive X-Ray (EDX):**

  Characteristic X-rays emitted (photon counts)

  Typical elements: Na, Mg, Al, Si, P, S, CI, K, Ca, Ti, V, Cr, Mn, Fe, Cu, Ni, Zn, Pb, and Br (composition, density)
- Flux measurements and a semi-empirical deposition velocity model can be used to estimate average concentration and size distribution of particles to which the passive samplers were exposed

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Why Classify Particles into Groups

Fluoresced X-rays used for the compositional measurements rarely can be used to provide accurate elemental concentrations in individual particles.

It is possible to use the qualitative or semi-quantitative data to obtain new quantitative variables based on the classification of the particles into homogeneous particle types.

Chemical information derived is semi quantitative, but can serve as the basis for classification of the particles into homogeneous particle types

Particle Classification using Neural Networks

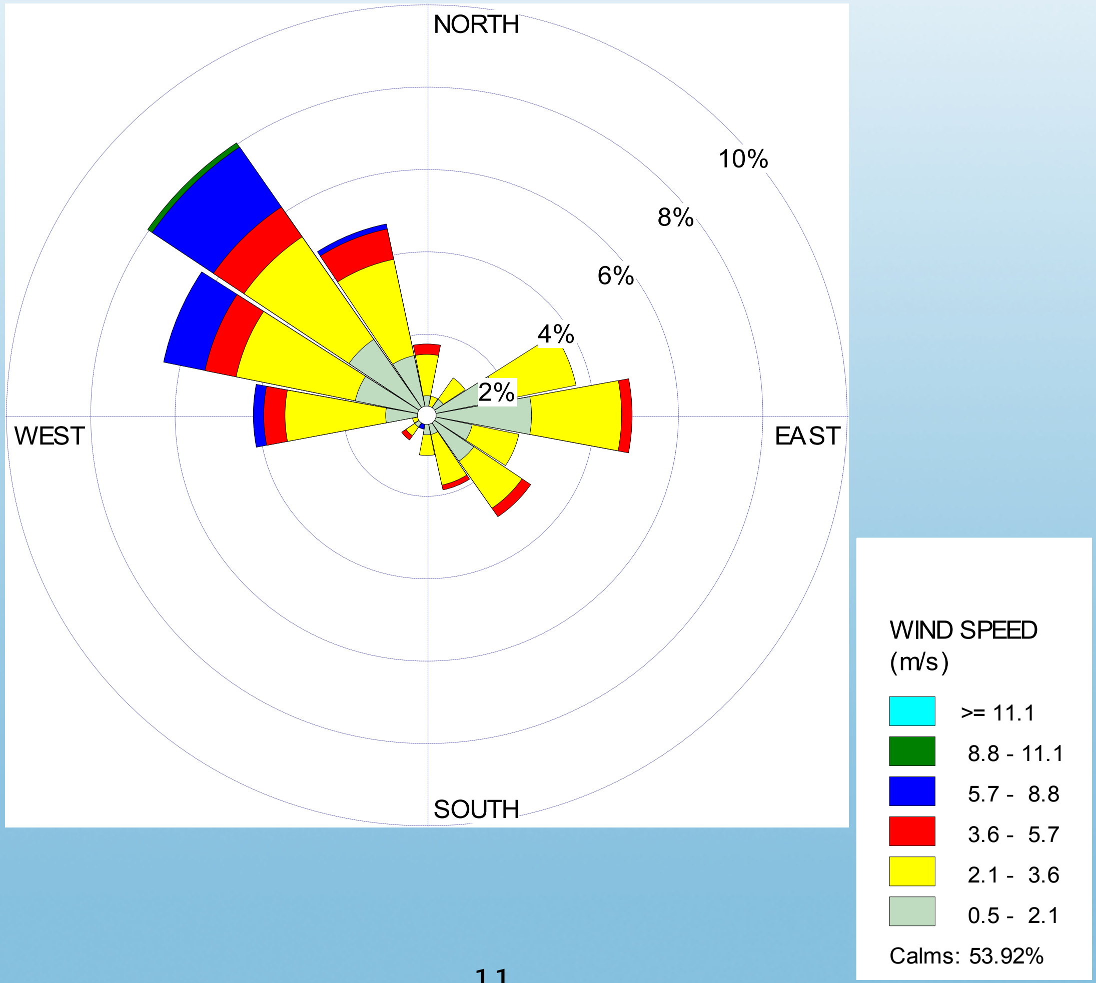
- Adaptive resonance theory can be applied to group particles of similar composition together (pattern recognition).
- These particle classes or groups represent the types of particles present in the air.
- The mass of particles in a given class is a quantitative measure of particle composition

Particle Characterization And Classification

- Results from Data Crunching
  - Class memberships – mass, average diameter, count
  - Particle size distribution
  - Significant classes for each neighborhood
  - Additional modeling to calculate mass concentrations

CLASSIFICATION OF WINTER SAMPLES

Meteorology During 2013 Winter Campaign



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Fine Particle (PM2.5) Class Groupings - Winter 2013

No.	Likely Source Type	Elements – PM2.5																	Total Mass (pg)	Average D_P (µm)	Total Conc. (ng/m³)	Particle Count
1	Soil/Crustal		Na		Al	Si				K		Ti			Fe				55.94	0.57	2.10	149
2	Aged Sea-Salt	C	Na	Mg					Cl			Ti			Fe	Ni			207.58	0.64	5.51	362
3	Biogenic	C					P			K						Ni	Cu		723.93	0.78	13.72	637
4	Soil/Crustal		Na	Mg	Al	Si					Ca		Cr	Mn	Fe				792.64	0.82	8.85	578
5	Soil/Crustal with Metals		Na	Mg	Al	Si						Ti		Mn	Fe	Ni	Cu		2628.88	1.03	14.42	713
6	Tire and Brake Wear	C		Mg	Al				Cl		Ca	Ti	Cr		Fe	Ni	Cu		2824.99	1.02	17.98	761
7	Industrial/Metals		Na				P				Ca	Ti	Cr	Mn		Ni	Cu	Zn	2862.38	1.08	17.21	787
8	Industrial/Metals			Mg	Al	Si	P			K				Mn	Fe			Zn	2967.83	1.07	16.16	788
9	Metals/Crustal		Na		Al	Si			Cl			Ti					Cu		2998.75	1.10	17.19	690
10	Ca & K - Bearing Sulfur and Chloride Aerosol						P	S	Cl	K	Ca		Cr				Cu		3007.51	1.01	19.85	875
11	Biomass Combustion	C					P		Cl	K	Ca		Cr	Mn					3103.68	1.02	26.49	992
12	Aged Sulfur-Bearing Carbon Particles	C						S	Cl			Ti	Cr	Mn				Zn	3199.37	0.98	23.14	958
13	Metallic Traffic Emissions	C	Na	Mg	Al										Fe		Cu		3284.51	1.08	18.43	787
14	Crustal		Na	Mg	Al	Si			Cl	K		Ti	Cr				Cu		3390.05	1.09	19.47	850
15	Mineral Dust			Mg		Si	P				Ca	Ti				Ni			3412.37	0.98	20.83	1000
16	Metals/Crustal		Na		Al	Si		S						Mn	Fe	Ni	Cu	Zn	3474.21	1.07	19.67	945
17	Soil/Crustal				Al		P	S			Ca	Ti		Mn					3589.64	1.05	21.26	1002
18	Metals/Crustal		Na	Mg	Al	Si	P			K			Cr	Mn		Ni			3720.88	1.17	18.51	720
19	Vehicle Engine Emissions	C					P		Cl			Ti	Cr			Ni		Zn	3760.43	1.06	27.14	1068
20	Construction Materials/ Gypsum							S			Ca								3823.75	0.99	24.63	1053
21	Biomass Combustion		Na		Al			S		K	Ca		Cr	Mn					4001.10	1.13	21.14	884
22	Metallic Traffic Emissions		Na	Mg			P	S				Ti			Fe			Zn	4135.37	1.13	21.57	859
23	Metallic Traffic Emissions		Na	Mg		Si	P					Ti	Cr	Mn	Fe	Ni	Cu		4461.66	1.12	23.01	919

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WINTER $PM_{2.5}$ GROUPED BY LIKELY SOURCE CATEGORY

Likely Source Type	Class Grouping No.	Total Mass (pg)	Average D_P (µm)	Particle Count	Total Conc (ng/m3)
Metallic Traffic Emissions	13, 22, 23	11,882	1.11	2,565	63.01
Metals/Crustal	9, 16, 18	10,194	1.12	2,355	55.37
Biomass Combustion	11, 21	7,105	1.08	1,876	47.63
Industrial/Metals	7, 8	5,830	1.07	1,575	33.37
Soil/Crustal	1, 4, 17	4,438	1.00	1,729	32.21
Construction Materials/ Gypsum	20	3,824	0.99	1,053	24.63
Vehicle Engine Emissions	19	3,760	1.06	1,068	27.14
Mineral Dust	15	3,412	0.98	1,000	20.83
Crustal	14	3,390	1.09	850	19.47
Aged Sulfur-Bearing Carbon Particles	12	3,199	0.98	958	23.14
Ca & K - Bearing Sulfur and Chloride Aerosol	10	3,008	1.01	875	19.85
Tire and Brake Wear	6	2,825	1.02	761	17.98
Soil/Crustal with Metals	5	2,629	1.03	713	14.42
Biogenic	3	724	0.78	637	13.72
Aged Sea-Salt	2	208	0.64	362	5.51

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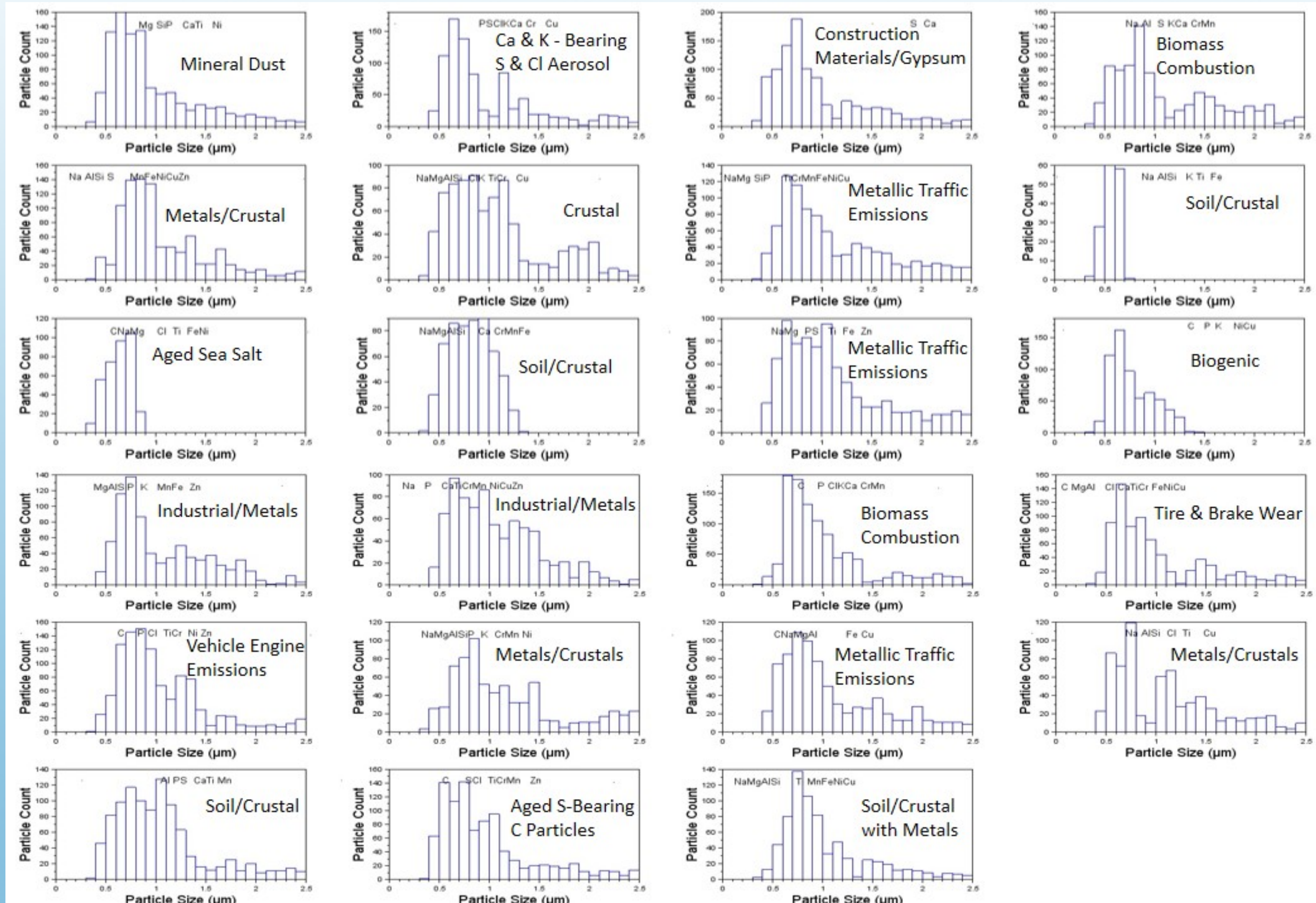
Winter PM2.5 Particle Size Distribution



NEIGHBORHOOD SIGNIFICANT PARTICLE CLASS MEMBERSHIPS, WINTER $PM_{2.5}$

	1st		2nd		3rd	
	Likely Source	Mass (pg)	Likely Source	Mass (pg)	Likely Source	Mass (pg)
Bakersfield Neighborhoods	Metallic Traffic Emissions	145	Crustal	114	Metals/Crustal	114
Bullard HS	Metallic Traffic Emissions	146	Metallic Traffic Emissions	144	Construction Materials/Gypsum	140
Calwa	Biomass Combustion	140	Metallic Traffic Emissions	135	Metallic Traffic Emissions	122
Central HS East Campus	Metallic Traffic Emissions	102	Vehicle Engine Emissions	76	Crustal	73
Clovis neighborhood	Biomass Combustion	198	Construction Materials/Gypsum	186	Metallic Traffic Emissions	170
Clovis West Neighborhood	Biomass Combustion	139	Vehicle Engine Emissions	101	Crustal	97
Edison HS	Metallic Traffic Emissions	139	Metallic Traffic Emissions	136	Mineral Dust	116
Fairmead-Madera County	Metallic Traffic Emissions	143	Construction Materials/Gypsum	115	Vehicle Engine Emissions	112
Figarden Loop	Metallic Traffic Emissions	164	Crustal	150	Metallic Traffic Emissions	141
Fresno Garland Station	Metals/Crustal	194	Metallic Traffic Emissions	148	Mineral Dust	122
Fresno HS	Metallic Traffic Emissions	215	Metallic Traffic Emissions	134	Crustal	133
Kettleman City-Kings County	Soil/Crustal with Metals	121	Mineral Dust	116	Biomass Combustion	115
McLane Neighborhood	Metallic Traffic Emissions	156	Crustal	129	Biomass Combustion	121
Roosevelt HS	Metallic Traffic Emissions	117	Construction Materials/Gypsum	114	Soil/Crustal with Metals	107
Sunnyside Neighborhood	Metals/Crustal	131	Construction Materials/Gypsum	119	Tire and Brake Wear	115

SPATIAL HETEROGENEITY ANALYSIS

VARIABILITY OF PARTICLE CLASSES

- Spatial heterogeneity examined by calculating the coefficient of divergence (COD) and Pearson correlation coefficient (COR).
- Both calculated using mass of each particle class from each sample
- COD ranges from 0 to 1
  - Greater than 0.2 suggests heterogeneity
  - Greater than 0.4 suggests strong heterogeneity
- COR ranges from 0 to 1
  - Approaching 1 suggests correlation
  - Approaching 0 suggests divergence

COD and COR Averages

		Grand Average of All Sites					
		Min COD	Max COD	Avg COD	Min COR	Max COR	Avg COR
PM_{10}	Winter	0.51	0.80	0.61	0.13	0.74	0.45
	Summer	0.18	0.51	0.27	0.46	0.92	0.82
$PM_{2.5}$	Winter	0.29	0.75	0.42	0.09	0.74	0.41
	Summer	0.21	0.60	0.36	0.07	0.81	0.44

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VARIABILITY SUMMARY

- COD results
  - Very high heterogeneity in winter
  - Winter PM_{10} more heterogeneous than $PM_{2.5}$
  - Summer samples slightly less heterogeneous than winter
- COR results
  - Winter samples less correlated than summer
  - Summer PM_{10} samples well correlated while $PM_{2.5}$ samples were not

Heterogeneity of Particle Classes - 1

- A quantitative measure of spatial heterogeneity can be examined by calculating the coefficient of divergence (COD) and/or Pearson correlation coefficient (COR).
- COD and COR can be calculated using the particle class mass concentrations or particle class mass at all the sampling sites studied in this work.
- The COD averages ranged between 0.34 and 0.71, suggesting strong heterogeneity in the $PM_{2.5}$ samples in Winter Samples, although the degree of heterogeneity was somewhat lesser than the heterogeneity in the PM10 samples.

SOURCE APPORTIONMENT

WHY ADDITIONAL GROUPING ANALYSIS?

- ART 2A alone provided too many classes
- Needed additional step to obtain source profiles and their contributions
- Positive Matrix Factorization (PMF) widely used for source apportionment

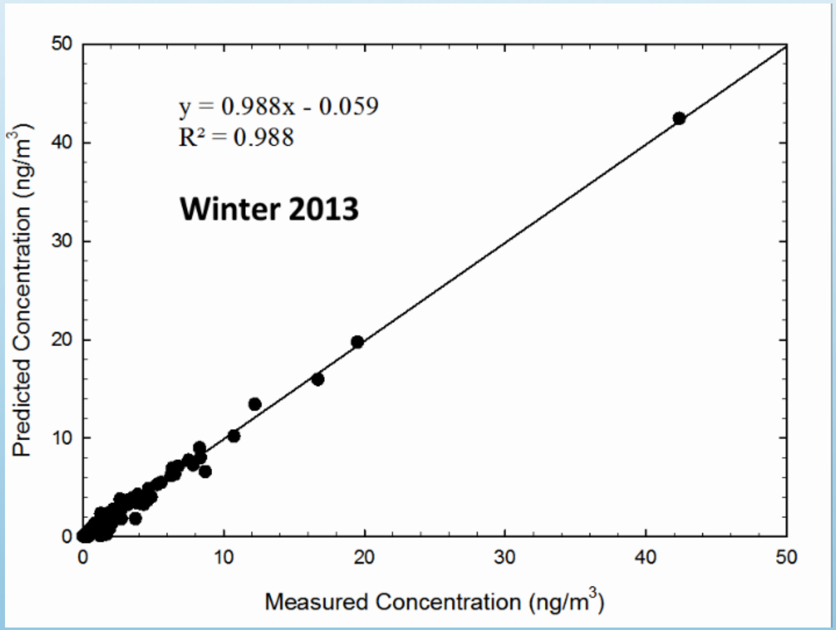
POSITIVE MATRIX FACTORIZATION

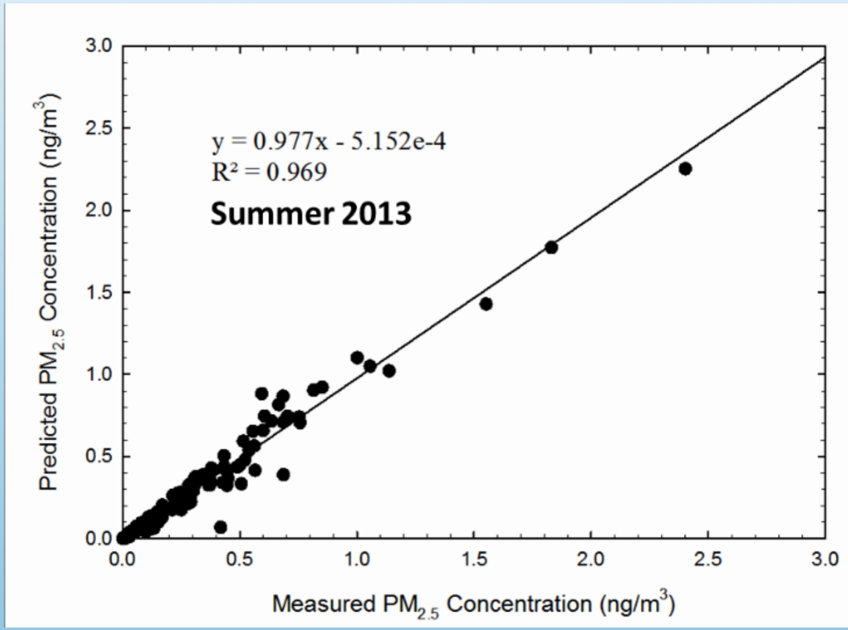
- Sources and receptors follow mass conservation
- Goal of PMF is to find the true dimensionality of the sources and the relationship between each chemical species/particle clusters
- Multiple class memberships could have been generated from the same source
- PMF helps determine the actual number of sources in the total mass of PM measured at each site

DATA PROCESSING FOR PMF

- Samples were averaged for each site
- Particle masses in each class and in each site were summed up in the 5 size ranges
  - 0.2-0.5 μm, 0.5-1.0 μm, 1.0-1.5 μm, 1.5-2.0 μm, 2.0-2.5 μm
  - This provides the data for the “X” Matrix
  - Zero or empty cells in the “X” matrix were replaced with one third of the least significant value present in each particle class membership of the concentration matrix
- Uncertainties (“S” Matrix) for each class membership was calculated as 5% of the measured concentration plus one third of the least significant value

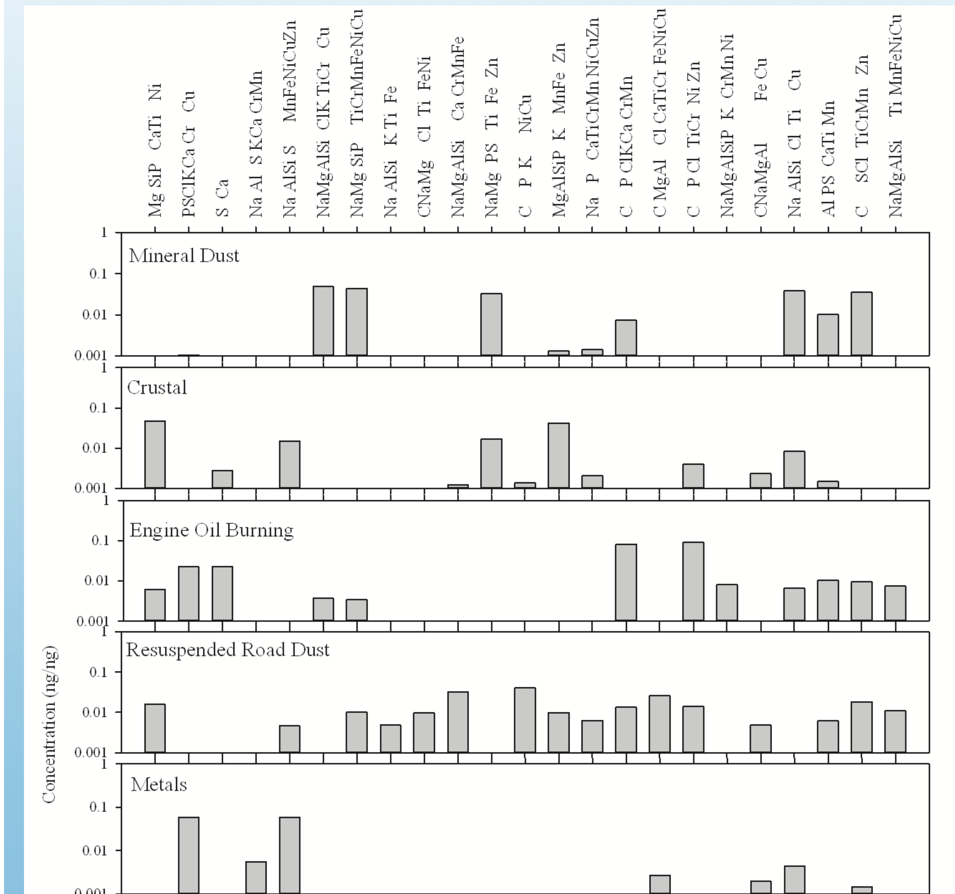
CORRELATION BETWEEN MEASURED AND PREDICTED $PM_{2.5}$ MASS

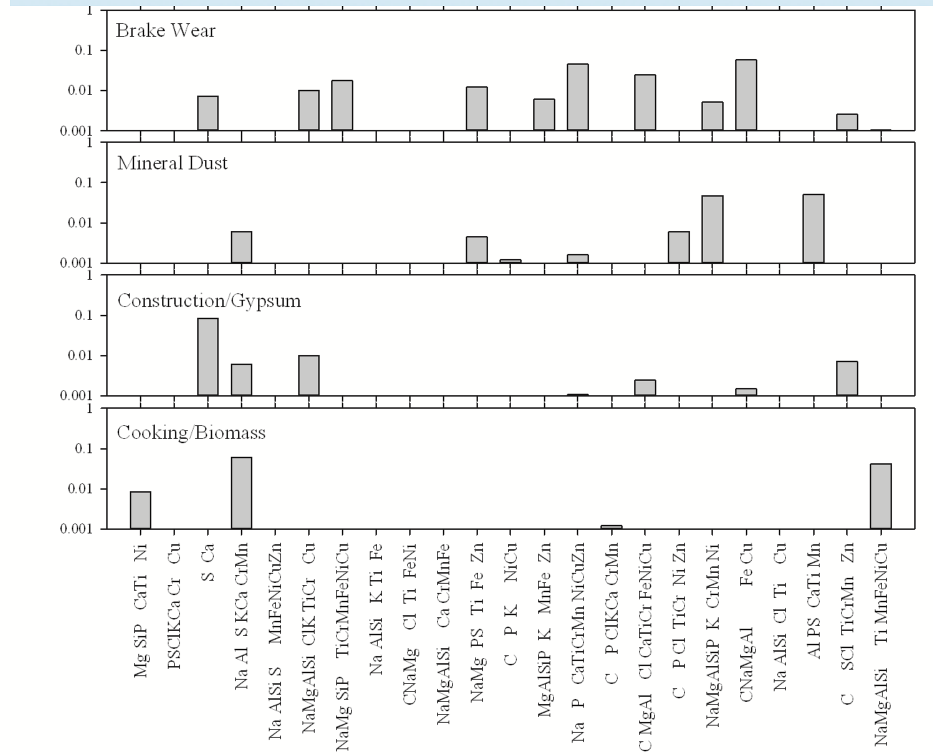




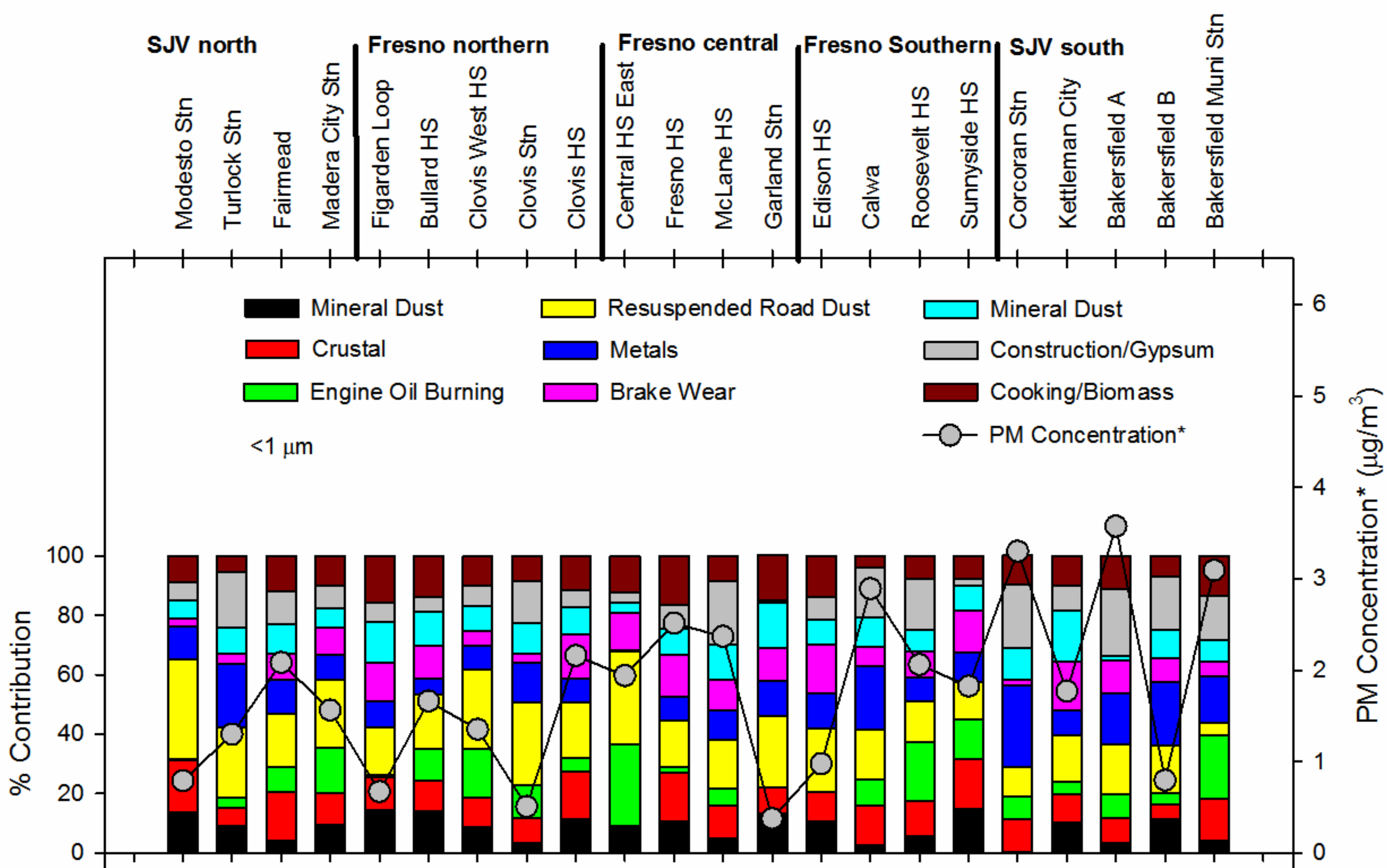
WINTER $PM_{2.5}$ SAMPLE SOURCE PROFILES

PMF grouped 23 classes into 9 source categories



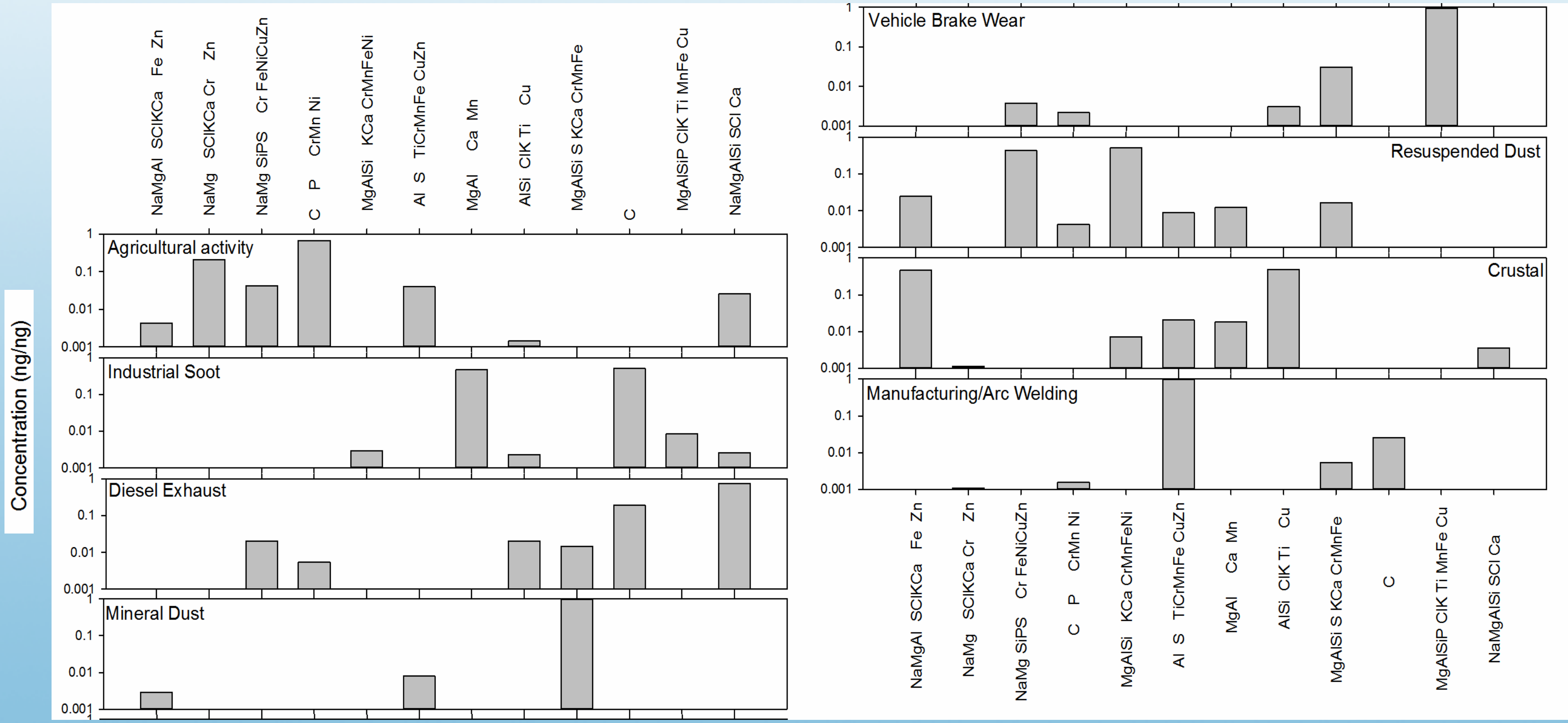


NEIGHBORHOOD SOURCE CONTRIBUTIONS AND CONCENTRATIONS, WINTER $PM_{2.5}$

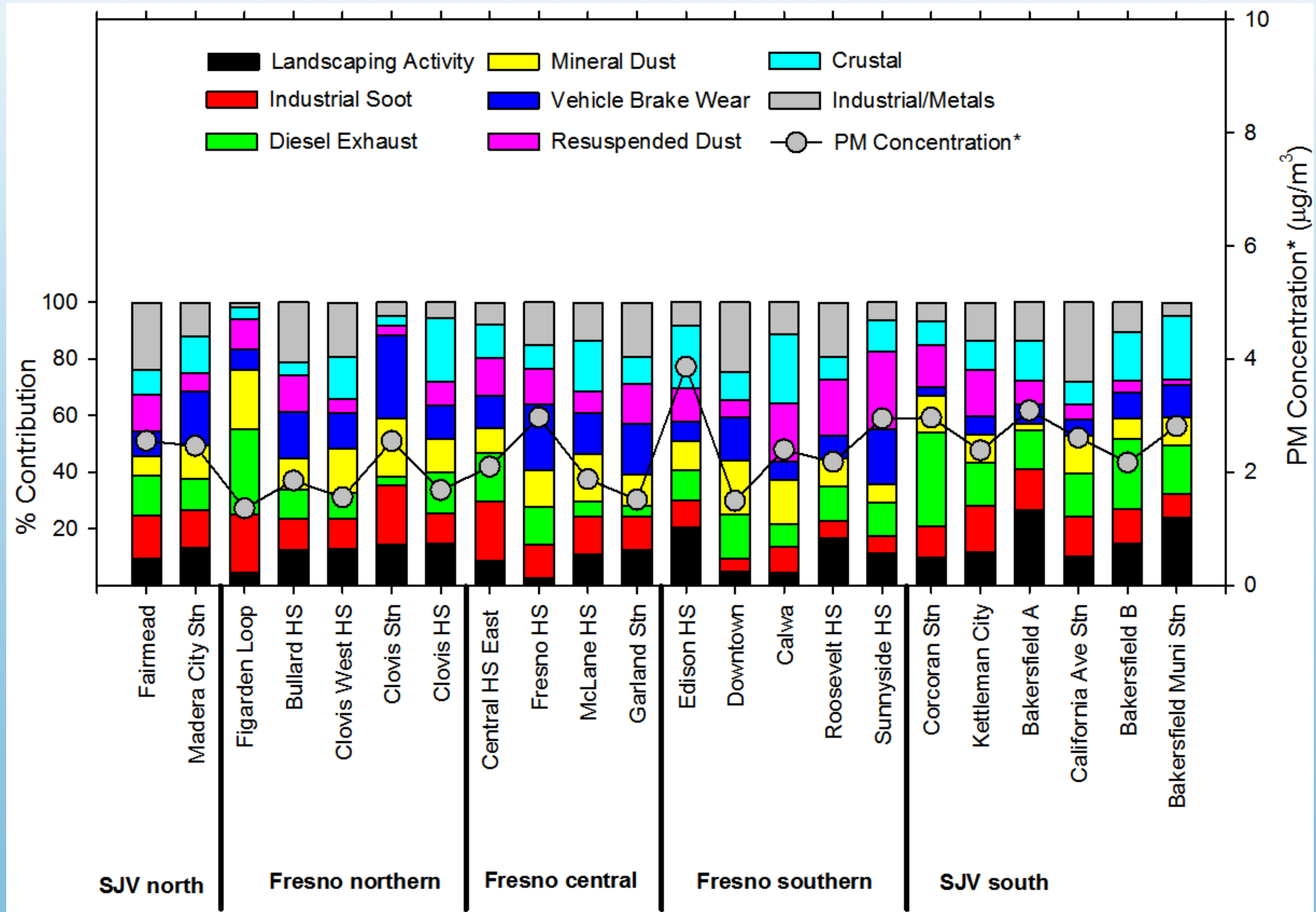


SUMMER PM$_{2.5}$ SAMPLE SOURCE PROFILES

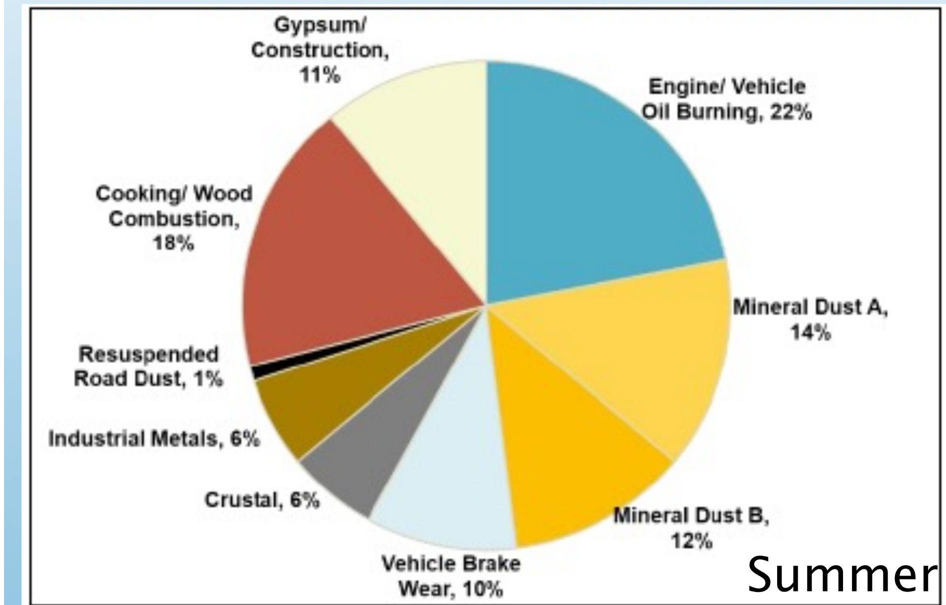
PMF grouped 12 classes into 8 source categories

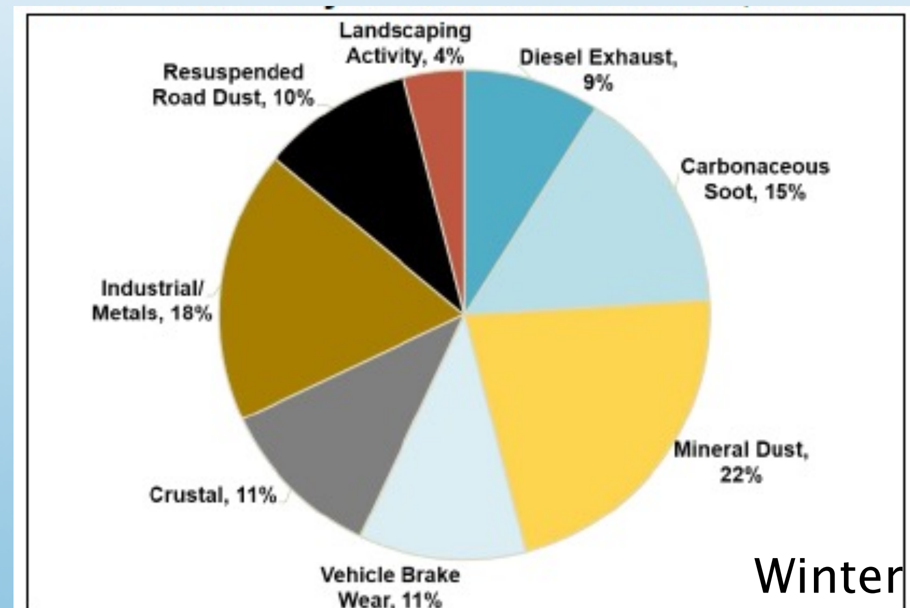


NEIGHBORHOOD SOURCE CONTRIBUTIONS AND CONCENTRATIONS, SUMMER PM



Summary of Identified Sources





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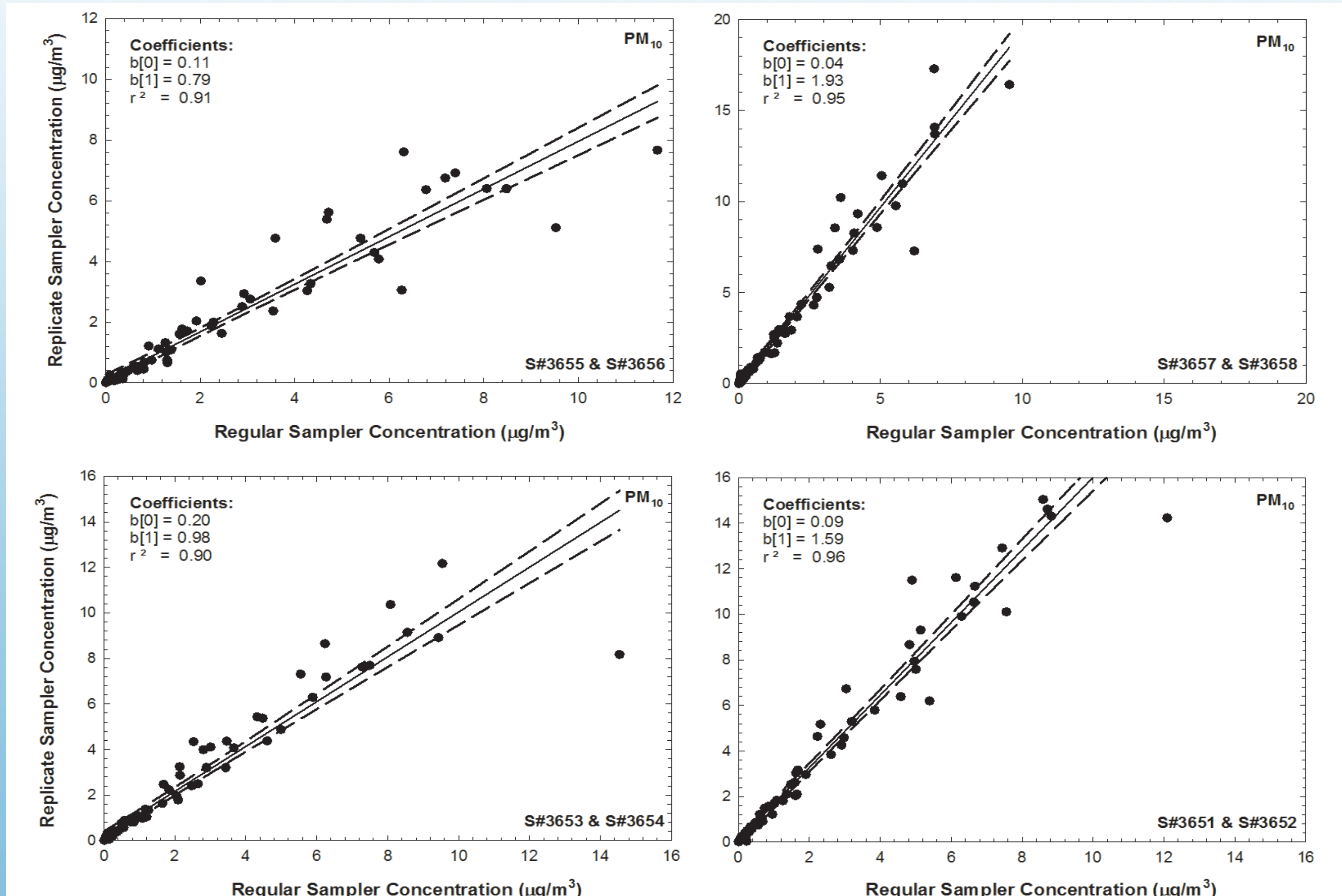
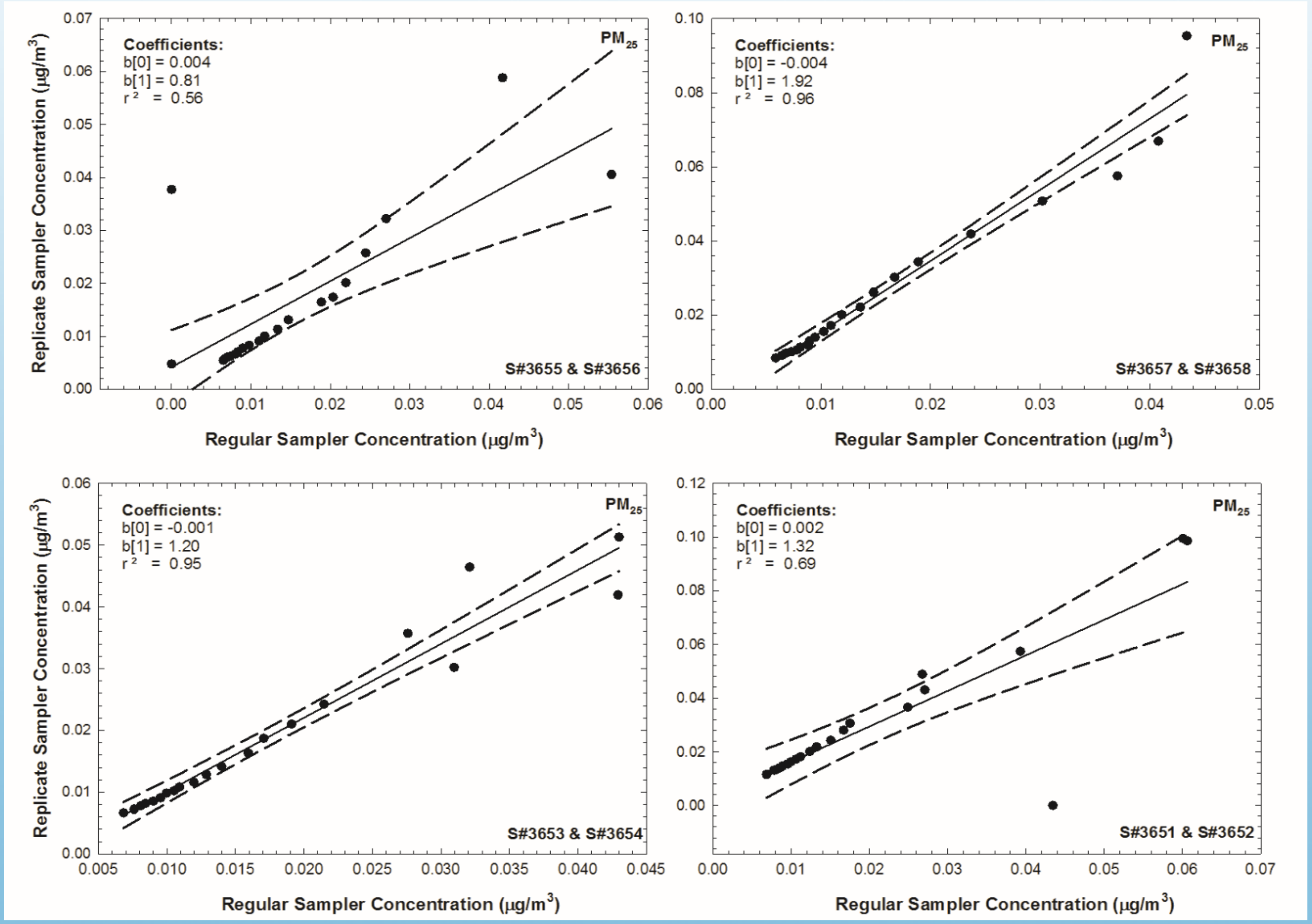
REPLICATE SAMPLES

Replication Sample Correlation – PM10



Replicate Sample Correlation – PM2.5



CONCLUSIONS AND SUMMARY - 1

- Considerable heterogeneity in both composition and concentration were observed between adjacent sites as indicated by composition profiles in each neighborhood and the coefficient of divergence.
- Combustion particles including engine oil and biomass combustion, biological, and brake and tire wear were the major sources of the fine particles.
- Mineral dust and crustal materials were major sources in the larger size group.

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CONCLUSIONS AND SUMMARY - 2

- Strong seasonal variability both in compositional source profiles and spatial distribution of PM mass and species were exhibited in Summer and Winter Samples
- Spatial heterogeneity was more pronounced in the Winter
  samples than in Summer samples
- Hybrid method of combining ART-2A and PMF provided more useful results than just particle classification using ART-2A

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