Use of Passive PM Samples in Source Apportionment

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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?

If wind speed is high, particles affected by turbulent inertia.

Large particles settle.

Small particles diffuse.

Screen

Round Cap with Hole in Center

SEM Stub

Substrate:
- glass (optical)
- carbon tab
- polycarbonate (SEM)
- grid (TEM)

Samplers were deployed in 38 sites for about 4 weeks in Summer and in Winter Seasons. Units were deployed on telephone poles or other similar structures.
Computer Controlled Scanning Electron Micrograph (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, Cl, 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
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

**Wind Speed (m/s) Distribution:***

- Calm: 53.92%
- 0.5 - 2.1: 2%
- 2.1 - 3.6: 4%
- 3.6 - 5.7: 8%
- 5.7 - 8.8: 6%
- 8.8 - 11.1: 4%
- >= 11.1: 2%
# Fine Particle (PM2.5) Class Groupings

- Winter 2013

<table>
<thead>
<tr>
<th>No.</th>
<th>Likely Source Type</th>
<th>Elements – PM2.5</th>
<th>Total Mass (pg)</th>
<th>Average (D_p) (µm)</th>
<th>Total Conc. (ng/m³)</th>
<th>Particle Count</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Soil/Crustal</td>
<td>Na Al Si K Ti Fe</td>
<td>55.94</td>
<td>0.57</td>
<td>2.10</td>
<td>149</td>
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<tr>
<td>2</td>
<td>Aged Sea-Salt</td>
<td>C Na Mg P Cl Ti Fe Ni Cu</td>
<td>207.58</td>
<td>0.64</td>
<td>5.51</td>
<td>362</td>
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<tr>
<td>3</td>
<td>Biogenic</td>
<td>C P K Ni Cu</td>
<td>723.93</td>
<td>0.78</td>
<td>13.72</td>
<td>637</td>
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<tr>
<td>4</td>
<td>Soil/Crustal</td>
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<td>0.82</td>
<td>8.85</td>
<td>578</td>
</tr>
<tr>
<td>5</td>
<td>Soil/Crustal with Metals</td>
<td>Na Mg Al Si P K Ti Mn Fe Ni Cu</td>
<td>2628.88</td>
<td>1.03</td>
<td>14.42</td>
<td>713</td>
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<tr>
<td>6</td>
<td>Tire and Brake Wear</td>
<td>C Mg Al Cl Ca Ti Cr Fe Ni Cu</td>
<td>2824.99</td>
<td>1.02</td>
<td>17.98</td>
<td>761</td>
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<tr>
<td>7</td>
<td>Industrial/Metals</td>
<td>Na P Ca Ti Cr Mn Ni Cu Zn</td>
<td>2862.38</td>
<td>1.08</td>
<td>17.21</td>
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<td>8</td>
<td>Industrial/Metals</td>
<td>Mg Al Si P K Mn Fe Zn</td>
<td>2967.83</td>
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<td>16.16</td>
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<td>9</td>
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<tr>
<td>10</td>
<td>Ca &amp; K - Bearing Sulfur and Chloride Aerosol</td>
<td>P S Cl K Ca Cr Cu</td>
<td>3007.51</td>
<td>1.01</td>
<td>19.85</td>
<td>875</td>
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<td>11</td>
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<td>C P Cl K Ca Cr Mn</td>
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<td>12</td>
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<td>958</td>
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<td>13</td>
<td>Metallic Traffic Emissions</td>
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<td>19</td>
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<td>20</td>
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<td>C S Ca</td>
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<td>23</td>
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<td>4461.66</td>
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<td>23.01</td>
<td>919</td>
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</table>
## WINTER PM$_{2.5}$ GROUPED BY LIKELY SOURCE CATEGORY

<table>
<thead>
<tr>
<th>Likely Source Type</th>
<th>Class Grouping No.</th>
<th>Total Mass (pg)</th>
<th>Average $D_p$ (µm)</th>
<th>Particle Count</th>
<th>Total Conc (ng/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metallic Traffic Emissions</td>
<td>13, 22, 23</td>
<td>11,882</td>
<td>1.11</td>
<td>2,565</td>
<td>63.01</td>
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<td>Metals/Crustal</td>
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<td>10,194</td>
<td>1.12</td>
<td>2,355</td>
<td>55.37</td>
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<td>Biomass Combustion</td>
<td>11, 21</td>
<td>7,105</td>
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<td>Industrial/Metals</td>
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<td>3,824</td>
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<td>Vehicle Engine Emissions</td>
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<td>3,760</td>
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<td>Mineral Dust</td>
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<td>3,412</td>
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<td>Crustal</td>
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<td>3,390</td>
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<td>Aged Sulfur-Bearing Carbon Particles</td>
<td>12</td>
<td>3,199</td>
<td>0.98</td>
<td>958</td>
<td>23.14</td>
</tr>
<tr>
<td>Ca &amp; K - Bearing Sulfur and Chloride Aerosol</td>
<td>10</td>
<td>3,008</td>
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<td>875</td>
<td>19.85</td>
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<tr>
<td>Tire and Brake Wear</td>
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<td>2,825</td>
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<td>Soil/Crustal with Metals</td>
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<td>2,629</td>
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<td>Biogenic</td>
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<td>724</td>
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<td>637</td>
<td>13.72</td>
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<tr>
<td>Aged Sea-Salt</td>
<td>2</td>
<td>208</td>
<td>0.64</td>
<td>362</td>
<td>5.51</td>
</tr>
</tbody>
</table>
Winter PM2.5 Particle Size Distribution

- Mineral Dust
- Ca & K - Bearing S & Cl Aerosol
- Construction Materials/Gypsum
- Biomass Combustion
- Metals/Crustal
- Crustal
- Metallic Traffic Emissions
- Soil/Crustal
- Aged Sea Salt
- Metallic Traffic Emissions
- Biogenic
- Industrial/Metals
- Industrial/Metals
- Biomass Combustion
- Tire & Brake Wear
- Vehicle Engine Emissions
- Metals/Crustals
- Metallic Traffic Emissions
- Metals/Crustals
- Soil/Crustal
- Aged S-Bearing C Particles
- Soil/Crustal with Metals
## Neighborhood Significant Particle Class Memberships, Winter PM$_{2.5}$

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

<table>
<thead>
<tr>
<th></th>
<th>Min COD</th>
<th>Max COD</th>
<th>Avg COD</th>
<th>Min COR</th>
<th>Max COR</th>
<th>Avg COR</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PM&lt;sub&gt;10&lt;/sub&gt;</strong></td>
<td>Winter</td>
<td>0.51</td>
<td>0.80</td>
<td>0.61</td>
<td>0.13</td>
<td>0.74</td>
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<td></td>
<td>Summer</td>
<td>0.18</td>
<td>0.51</td>
<td>0.27</td>
<td>0.46</td>
<td>0.92</td>
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<tr>
<td><strong>PM&lt;sub&gt;2.5&lt;/sub&gt;</strong></td>
<td>Winter</td>
<td>0.29</td>
<td>0.75</td>
<td>0.42</td>
<td>0.09</td>
<td>0.74</td>
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<tr>
<td></td>
<td>Summer</td>
<td>0.21</td>
<td>0.60</td>
<td>0.36</td>
<td>0.07</td>
<td>0.81</td>
</tr>
</tbody>
</table>
VARIABILITY SUMMARY

- COD results
  - Very high heterogeneity in winter
  - Winter $\text{PM}_{10}$ more heterogeneous than $\text{PM}_{2.5}$
  - Summer samples slightly less heterogeneous than winter

- COR results
  - Winter samples less correlated than summer
  - Summer $\text{PM}_{10}$ samples well correlated while $\text{PM}_{2.5}$ 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 2013

\[ y = 0.988x - 0.059 \]
\[ R^2 = 0.988 \]

Summer 2013

\[ y = 0.977x - 5.152\times10^{-4} \]
\[ R^2 = 0.969 \]
**Winter PM\textsubscript{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

- Agricultural activity
- Industrial Soot
- Diesel Exhaust
- Mineral Dust
- Vehicle Brake Wear
- Resuspended Dust
- Crustal
- Manufacturing/Arc Welding
NEIGHBORHOOD SOURCE CONTRIBUTIONS AND CONCENTRATIONS, SUMMER PM
Summary of Identified Sources

Summer

- Engine/Vehicle Oil Burning: 22%
- Resuspended Road Dust: 1%
- Cooking/Wood Combustion: 18%
- Industrial/Metals: 6%
- Crustal: 6%
- Mineral Dust B: 12%
- Vehicle Brake Wear: 10%
- Mineral Dust A: 14%
- Gypsum/Construction: 11%

Winter

- Landscaping Activity: 4%
- Diesel Exhaust: 9%
- Resuspended Road Dust: 10%
- Carbonaceous Soot: 15%
- Industrial/Metals: 18%
- Crustal: 11%
- Mineral Dust: 22%
- Vehicle Brake Wear: 11%
REPLICATE SAMPLES
Replication Sample Correlation – PM10

Coefficients:
- S#3655 & S#3656:
  - b[0] = 0.11
  - b[1] = 0.79
  - $r^2 = 0.91$
- S#3657 & S#3658:
  - b[0] = 0.04
  - b[1] = 1.93
  - $r^2 = 0.96$

Coefficients:
- S#3653 & S#3654:
  - b[0] = 0.20
  - b[1] = 0.68
  - $r^2 = 0.90$
- S#3651 & S#3652:
  - b[0] = 0.09
  - b[1] = 1.59
  - $r^2 = 0.96$
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.
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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