Temporal and Spatial Variations of PM$_{2.5}$ during CRPAQS Winter Intensives

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Bethel Island
Sierra Nevada Foothills
Fresno
Angiola
Bakersfield

Intensive Operating Periods

• Four IOPs
  – Dec. 15-18, 2000
  – Jan. 4-7, 2001

• Five sampling periods during each IOP
  – 0000 to 0500 PST
  – 0500 to 1000 PST
  – 1000 to 1300 PST
  – 1300 to 1600 PST
  – 1600 to 2400 PST
## Commonly Applied Chemical Analysis Methods

<table>
<thead>
<tr>
<th>Observables</th>
<th>Chemical Analysis Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass</td>
<td>- Gravimetric Analysis</td>
</tr>
<tr>
<td>Elements (Na to U)</td>
<td>- X-Ray Fluorescence (XRF)</td>
</tr>
<tr>
<td>Anions (Cl(^{-}), NO(_3)^{-}, SO(_4)^{2-})</td>
<td>- Ion Chromatography (IC)</td>
</tr>
<tr>
<td>Ammonium (NH(_4)^{+})</td>
<td>- Automated Colorimetry (AC)</td>
</tr>
<tr>
<td>Soluble Sodium (Na(^{+}))</td>
<td>- Atomic Absorption Spectrophotometry (AAS) (flame or graphite)</td>
</tr>
<tr>
<td>Soluble Potassium (K(^{+}))</td>
<td></td>
</tr>
<tr>
<td>Carbon (OC, EC)</td>
<td>- Thermal/Optical Reflectance (TOR)</td>
</tr>
</tbody>
</table>
Spatial Variations of 24-hr PM$_{2.5}$

- Concentration (µg/m$^3$)
- Bethel Island
- Sierra NV Foothills
- Fresno
- Angiola
- Bakersfield

Components:
- Unidentified mass
- Trace elements
- Ammonium nitrate
- Ammonium sulfate
- Elemental carbon
- Organic material
- Crustal material
PM$_{2.5}$ Material Balance at Bethel Island

0000-0500 PST
- Unidentified mass, 0%
- Trace elements, 4%
- Crustal material, 2%
- Ammonium nitrate, 40%
- Organic material, 46%
- Ammonium sulfate, 1%
- Elemental carbon, 12%

PM$_{2.5}$ measured/calculated mass = 21.1 / 22.1 µg/m$^3$

0500-1000 PST
- Unidentified mass, 0%
- Trace elements, 4%
- Crustal material, 2%
- Ammonium nitrate, 40%
- Organic material, 46%
- Ammonium sulfate, 1%
- Elemental carbon, 12%

PM$_{2.5}$ measured/calculated mass = 22.3 / 23.8 µg/m$^3$

1000-1300 PST
- Unidentified mass, 2%
- Trace elements, 5%
- Crustal material, 2%
- Ammonium nitrate, 55%
- Organic material, 30%
- Ammonium sulfate, 0%
- Elemental carbon, 6%

PM$_{2.5}$ measured/calculated mass = 33.3 / 34.4 µg/m$^3$

1300-1600 PST
- Unidentified mass, 0%
- Trace elements, 4%
- Crustal material, 2%
- Ammonium nitrate, 66%
- Organic material, 30%
- Ammonium sulfate, 3%
- Elemental carbon, 6%

PM$_{2.5}$ measured/calculated mass = 31.3 / 34.4 µg/m$^3$

1600-2400 PST
- Unidentified mass, 5%
- Trace elements, 2%
- Crustal material, 1%
- Ammonium nitrate, 48%
- Organic material, 34%
- Ammonium sulfate, 1%
- Elemental carbon, 10%

PM$_{2.5}$ measured/calculated mass = 37.4 / 35.5 µg/m$^3$

0000-2400 PST
- Unidentified mass, 0%
- Trace elements, 3%
- Crustal material, 2%
- Ammonium nitrate, 48%
- Organic material, 38%
- Ammonium sulfate, 1%
- Elemental carbon, 10%

PM$_{2.5}$ measured/calculated mass = 28.0 / 28.3 µg/m$^3$
PM$_{2.5}$ Material Balance at Sierra Nevada Foothills

**0000-0500 PST**
- Unidentified mass: 0%
- Trace elements: 4%
- Crustal material: 3%
- Ammonium nitrate: 34%
- Organic material: 58%
- Ammonium sulfate: 1%
- Elemental carbon: 9%

PM$_{2.5}$ measured/calculated mass = 12.0 / 13.1 µg/m$^3$

**1000-1300 PST**
- Unidentified mass: 0%
- Trace elements: 5%
- Crustal material: 4%
- Ammonium nitrate: 49%
- Elemental carbon: 5%
- Ammonium sulfate: 1%
- Organic material: 39%

PM$_{2.5}$ measured/calculated mass = 18.8 / 19.7 µg/m$^3$

**1600-2400 PST**
- Unidentified mass: 1%
- Trace elements: 3%
- Crustal material: 2%
- Ammonium nitrate: 47%
- Elemental carbon: 8%
- Ammonium sulfate: 1%
- Organic material: 39%

PM$_{2.5}$ measured/calculated mass = 26.5 / 26.3 µg/m$^3$

**0500-1000 PST**
- Unidentified mass: 0%
- Trace elements: 6%
- Crustal material: 5%
- Ammonium nitrate: 40%
- Elemental carbon: 9%
- Ammonium sulfate: 1%
- Organic material: 52%

PM$_{2.5}$ measured/calculated mass = 12.2 / 13.8 µg/m$^3$

**1300-1600 PST**
- Unidentified mass: 0%
- Trace elements: 5%
- Crustal material: 3%
- Ammonium nitrate: 64%
- Elemental carbon: 5%
- Ammonium sulfate: 5%
- Organic material: 39%

PM$_{2.5}$ measured/calculated mass = 21.4 / 25.7 µg/m$^3$

**0000-2400 PST**
- Unidentified mass: 0%
- Trace elements: 4%
- Crustal material: 3%
- Ammonium nitrate: 47%
- Elemental carbon: 8%
- Ammonium sulfate: 2%
- Organic material: 43%

PM$_{2.5}$ measured/calculated mass = 18.9 / 20.0 µg/m$^3$
PM$_{2.5}$ Material Balance at Fresno

**0000-0500 PST**
- Unidentified mass, 7%
- Trace elements, 2%
- Crustal material, 1%
- Ammonium nitrate, 25%
- Organic material, 53%
- Ammonium sulfate, 0%
- Elemental carbon, 12%

PM$_{2.5}$ measured/calculated mass = 75.2 / 69.9 µg/m$^3$

**1000-1300 PST**
- Unidentified mass, 0%
- Trace elements, 4%
- Crustal material, 2%
- Ammonium nitrate, 60%
- Organic material, 31%
- Ammonium sulfate, 6%
- Elemental carbon, 4%

PM$_{2.5}$ measured/calculated mass = 57.8 / 61.3 µg/m$^3$

**1600-2400 PST**
- Unidentified mass, 12%
- Trace elements, 1%
- Crustal material, 1%
- Ammonium nitrate, 29%
- Organic material, 45%
- Ammonium sulfate, 1%
- Elemental carbon, 10%

PM$_{2.5}$ measured/calculated mass = 96.9 / 84.9 µg/m$^3$

**0500-1000 PST**
- Unidentified mass, 0%
- Trace elements, 3%
- Crustal material, 1%
- Ammonium nitrate, 38%
- Organic material, 47%
- Ammonium sulfate, 0%
- Elemental carbon, 11%

PM$_{2.5}$ measured/calculated mass = 48.5 / 49.0 µg/m$^3$

**1300-1600 PST**
- Unidentified mass, 0%
- Trace elements, 4%
- Crustal material, 2%
- Ammonium nitrate, 59%
- Organic material, 29%
- Ammonium sulfate, 11%
- Elemental carbon, 5%

PM$_{2.5}$ measured/calculated mass = 43.3 / 47.9 µg/m$^3$

**0000-2400 PST**
- Unidentified mass, 3%
- Trace elements, 2%
- Crustal material, 1%
- Ammonium nitrate, 36%
- Organic material, 46%
- Ammonium sulfate, 2%
- Elemental carbon, 10%

PM$_{2.5}$ measured/calculated mass = 68.9 / 66.7 µg/m$^3$
**PM$_{2.5}$ Material Balance at Angiola**

**0000-0500 PST**
- Unidentified mass, 5%
- Trace elements, 2%
- Crustal material, 2%
- Organic material, 17%
- Elemental carbon, 4%
- Ammonium sulfate, 1%
- Ammonium nitrate, 68%

PM$_{2.5}$ measured/calculated mass = 40.7 / 38.8 µg/m$^3$

**0500-1000 PST**
- Unidentified mass, 4%
- Trace elements, 2%
- Crustal material, 2%
- Organic material, 20%
- Elemental carbon, 5%
- Ammonium sulfate, 1%
- Ammonium nitrate, 67%

PM$_{2.5}$ measured/calculated mass = 38.2 / 36.8 µg/m$^3$

**1000-1300 PST**
- Unidentified mass, 1%
- Trace elements, 3%
- Crustal material, 5%
- Organic material, 16%
- Elemental carbon, 3%
- Ammonium sulfate, 3%
- Ammonium nitrate, 70%

PM$_{2.5}$ measured/calculated mass = 51.9 / 51.6 µg/m$^3$

**1300-1600 PST**
- Unidentified mass, 3%
- Trace elements, 0%
- Crustal material, 6%
- Organic material, 19%
- Elemental carbon, 3%
- Ammonium sulfate, 2%
- Ammonium nitrate, 67%

PM$_{2.5}$ measured/calculated mass = 59.7 / 59.4 µg/m$^3$

**1600-2400 PST**
- Unidentified mass, 13%
- Trace elements, 1%
- Crustal material, 6%
- Organic material, 15%
- Elemental carbon, 3%
- Ammonium sulfate, 1%
- Ammonium nitrate, 60%

PM$_{2.5}$ measured/calculated mass = 69.8 / 60.6 µg/m$^3$

**0000-2400 PST**
- Unidentified mass, 1%
- Trace elements, 2%
- Crustal material, 5%
- Organic material, 17%
- Elemental carbon, 3%
- Ammonium sulfate, 3%
- Ammonium nitrate, 65%

PM$_{2.5}$ measured/calculated mass = 54.6 / 50.6 µg/m$^3$
**PM$_{2.5}$ Material Balance at Bakersfield**

### 0000-0500 PST
- **Unidentified mass, 2%**
- **Crustal material, 2%**
- **Trace elements, 2%**
- **Ammonium nitrate, 52%**
- **Elemental carbon, 9%**
- **Ammonium sulfate, 0%**

PM$_{2.5}$ measured/calculated mass = 66.0 / 64.5 µg/m$^3$

### 1000-1300 PST
- **Unidentified mass, 0%**
- **Crustal material, 3%**
- **Trace elements, 3%**
- **Ammonium nitrate, 80%**
- **Elemental carbon, 4%**
- **Ammonium sulfate, 1%**

PM$_{2.5}$ measured/calculated mass = 68.0 / 78.4 µg/m$^3$

### 1600-2400 PST
- **Unidentified mass, 14%**
- **Crustal material, 2%**
- **Trace elements, 2%**
- **Ammonium nitrate, 49%**
- **Elemental carbon, 7%**
- **Ammonium sulfate, 0%**

PM$_{2.5}$ measured/calculated mass = 90.0 / 77.8 µg/m$^3$

### 0500-1000 PST
- **Unidentified mass, 0%**
- **Crustal material, 2%**
- **Trace elements, 2%**
- **Organic material, 30%**
- **Ammonium nitrate, 59%**
- **Elemental carbon, 8%**
- **Ammonium sulfate, 0%**

PM$_{2.5}$ measured/calculated mass = 57.6 / 58.9 µg/m$^3$

### 1300-1600 PST
- **Unidentified mass, 0%**
- **Crustal material, 3%**
- **Trace elements, 2%**
- **Organic material, 24%**
- **Elemental carbon, 3%**
- **Ammonium nitrate, 6%**
- **Ammonium sulfate, 6%**

PM$_{2.5}$ measured/calculated mass = 61.2 / 72.6 µg/m$^3$

### 0000-2400 PST
- **Unidentified mass, 1%**
- **Crustal material, 2%**
- **Trace elements, 2%**
- **Organic material, 28%**
- **Elemental carbon, 7%**
- **Ammonium nitrate, 58%**
- **Ammonium sulfate, 1%**

PM$_{2.5}$ measured/calculated mass = 71.9 / 70.9 µg/m$^3$
Elevated PM$_{2.5}$ mass coincides with elevated nitrate and OC

- **Mass**
  - Y-axis: Mass Concentration (µg/m$^3$)

- **NO$_3^-$**
  - Y-axis: Nitrate Concentration (µg/m$^3$)

- **OC**
  - Y-axis: Concentration (µg/m$^3$)

Legend:
- Black: Angiola
- Pink: Bakersfield
- Green: Bethel Island
- Blue: Fresno
- Purple: Sierra NV
Crustal species are elevated at the Angiola and Bakersfield sites.
Example of a Nitrate Episode – IOP 3 (Jan. 4-7, 2001)

- **Bethel Island**
  - Concentration (µg/m³)
  - Time of Day (PST)

- **Sierra Nevada Foothills**
  - Concentration (µg/m³)
  - Time of Day (PST)

- **Fresno**
  - Concentration (µg/m³)
  - Time of Day (PST)

- **Angiola**
  - Concentration (µg/m³)
  - Time of Day (PST)

- **Bakersfield**
  - Concentration (µg/m³)
  - Time of Day (PST)

Legend:
- Unidentified Mass
- Trace elements
- Ammonium nitrate
- Ammonium sulfate
- Elemental carbon
- Organic material
- Crustal material

Analysis:
- The concentration of nitrate and related compounds varies throughout the day, with peaks observed during certain times.
- The highest concentrations are typically observed during the afternoon hours (1300-1600 PST).
- Trace elements and unidentified mass show lower concentrations compared to other components.

Conclusion:
- Nitrate episodes are a significant contributor to air pollution, particularly in urban and industrial areas.
- Understanding the temporal dynamics of these episodes is crucial for effective air quality management.
Diurnal Variations by Species – IOP 3 (Jan. 4-7, 2001)

- **Mass**
- **Organic Carbon**
- **Nitrate**
- **Elemental Carbon**

**Locations:**
- Angiola
- Bakersfield
- Bethel Island
- Fresno
- Sierra NV

**Concentration (µg/m³) Time periods:**
- 0000–0500
- 0500–1000
- 1000–1300
- 1300–1600
- 1600–2400

**Concentration ranges:**
- Mass: 0–200 µg/m³
- Organic Carbon: 0–100 µg/m³
- Nitrate: 0–100 µg/m³
- Elemental Carbon: 0–10 µg/m³
PM$_{2.5}$ nitrate accounts for $\sim$50% of mass at all sites except Fresno during IOP 3 (Jan. 4-7, 2001)

- **Bethel Island**
  - Unidentified Mass
  - Trace elements
  - Ammonium nitrate
  - Ammonium sulfate
  - Elemental carbon
  - Organic material
  - Crustal material

- **Sierra Nevada Foothills**

- **Fresno**

- **Angiola**

- **Bakersfield**

- **Bethel Island**
  - Measured mass and species (µg/m³)
  - PM2.5 Mass
  - Nitrate
  - Organic Carbon
  - Elemental Carbon

- **Sierra Nevada Foothills**
  - Measured mass and species (µg/m³)

- **Angiola**
  - Measured mass and species (µg/m³)

- **Fresno**
  - Measured species (µg/m³)

- **Bakersfield**
  - Measured species (µg/m³)
  - Measured mass (µg/m³)
## Regional- and Urban-Scale Influences

<table>
<thead>
<tr>
<th>Dates</th>
<th>Bethel Island</th>
<th>Foothills</th>
<th>Fresno</th>
<th>Angiola</th>
<th>Bakersfield</th>
</tr>
</thead>
<tbody>
<tr>
<td>IOP 1&lt;br&gt;Dec. 15-18</td>
<td>mix</td>
<td>carbon</td>
<td>mix</td>
<td>nitrate</td>
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<td>nitrate</td>
<td>mix</td>
<td>carbon</td>
<td>nitrate</td>
<td>carbon</td>
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</tbody>
</table>
Comparison of material balance at Bethel Island and Sierra Nevada Foothills during winter 2000-01

- Unidentified mass
- Trace elements
- Ammonium nitrate
- Ammonium sulfate
- Elemental carbon
- Organic material
- Crustal material
Comparison of material balance at Fresno during winter 1999-2000 and winter 2000-01

Unidentified mass
Trace elements
Ammonium nitrate
Ammonium sulfate
Elemental carbon
Organic material
Crustal material
Comparison of material balance at Angiola during winter 1999-2000 and winter 2000-01

- Unidentified mass
- Trace elements
- Ammonium nitrate
- Ammonium sulfate
- Elemental carbon
- Organic material
- Crustal material
Comparison of material balance at Bakersfield during winter 1999-2000 and winter 2000-01
Comparison of PM$_{2.5}$ mass at Bethel Island and Sierra Nevada Foothills during winter 2000-01
Comparison of PM$_{2.5}$ mass at Fresno during winter 1999-2000 and winter 2000-01
Comparison of PM$_{2.5}$ mass at Angiola during winter 1999-2000 and winter 2000-01
Comparison of PM$_{2.5}$ mass at Bakersfield during winter 1999-2000 and winter 2000-01
Fresno urban increment to PM$_{2.5}$ nitrate at Angiola during winter 1999-2000 and winter 2000-01
Bakersfield urban increment to PM$_{2.5}$ nitrate at Angiola during winter 1999-2000 and winter 2000-01
Conclusions

- Ammonium nitrate and carbonaceous aerosol account for 85–95% of PM$_{2.5}$ mass
  - Ammonium nitrate accounts for 35–65% of PM$_{2.5}$ mass (9–43 µg/m$^3$)
  - Carbonaceous aerosol accounts for 20–56% of PM$_{2.5}$ mass (10–38 µg/m$^3$)
- Temporal variations (>20x) exceeded spatial variations (~3–4x) for major constituents over 15 IOP days, indicative of meteorological influences
- Similar 24-hr-average PM$_{2.5}$ mass (~70 µg/m$^3$) at the two urban sites
  - High carbonaceous aerosol (56%) at Fresno
  - High ammonium nitrate (59%) at Bakersfield
Conclusions (continued)

- Urban sites peak during nighttime (1600-2400 PST), carry over to early morning period (0000-0500 PST); lowest during early morning (0500-1000 PST) or afternoon (1300-1600 PST)
- Non-urban sites experience gradual concentration increases from 1000 PST to 2400 PST, with lowest during early morning (0500-1000 PST)
- Nitrate and sulfate increase ~threefold from north to south, peaking at Bakersfield
Conclusions (continued)

- Higher PM$_{2.5}$ mass and longer episodes occurred during December 1999 and January 2001 than occurred during December 2000 and January 2000

- Carbon abundances were higher during winter 2000/2001 than during winter 1999/2000 at Fresno and Bakersfield

- Regional-scale PM$_{2.5}$ (especially nitrate) dominated PM$_{2.5}$ mass at Fresno and Bakersfield