Fine Particulate Matter in the San Joaquin Valley: Review of Modeling Results From CRPAQS

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Mechanistic Air Quality Models

- Photo-chemistry
- Transport
- Fog Processing
- Chemical Reactions

Gas-Phase Emissions
Aerosol Emissions
Condensation & Evaporation
Deposition

Particles of each size, source, and age are tracked separately.

Figure courtesy of Prakash Bhave, U.S. EPA
## Chemical Mechanism

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constants</th>
<th>Species</th>
<th>Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO + NO + O₂</td>
<td>3.085E-10</td>
<td>NO₂</td>
<td>335 Active Species</td>
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<tr>
<td>O₃ + NO = O₂ + O₂</td>
<td>2.61E-02</td>
<td></td>
<td>15 Steady State Radicals</td>
</tr>
<tr>
<td>O₂ + H₂O = H₂O₂ + O</td>
<td>2.344E-08</td>
<td></td>
<td>1500 Chemical Reactions</td>
</tr>
<tr>
<td>+300,000 grid cells</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Basic Particle Chemistry

VOC = Volatile Organic Compounds (benzene, ethanol, formaldehyde, …)
SOC = semi-volatile organic compounds (mostly unknown)
Primary PM = particulate matter emitted directly from sources (trace metals – aluminum, silicon, iron, nickel, etc, elemental carbon, organic carbon)
CRPAQS PM2.5 Mass

Black Line – measurements

Blue Line – predictions

Red Shading – Mid 50% Quantile within 10km of monitor

Major trends are captured at most stations

Under-prediction of mass at Angiola and Bakersfield near the end of the episode

Source: Q. Ying, J. Lu, P. Allen, P. Livingstone, A. Kaduwela, and M. Kleeman “Modeling Air Quality During the California Regional PM10/PM2.5 Air Quality Study (CRPAQS) Using the UCD/CIT Source-Oriented Air Quality Model – Part I. Base Case Model Results.”, Atmos. Env., 42, pg8954-8966, 2008.
Relative Component Contributions to PM

Average and standard deviation of predictions and observations is based on 55 samples

Urban locations (Fresno and Bakersfield)
Predictions and observations match except for nitrate under-prediction at Bakersfield

Rural location (Angiola)
OC under-prediction. What primary sources are we missing? What SOA formation mechanisms are we missing?

Source: Q. Ying, J. Lu, P. Allen, P. Livingstone, A. Kaduwela, and M. Kleeman "Modeling Air Quality During the California Regional PM10/PM2.5 Air Quality Study (CRPAQS) Using the UCD/CIT Source-Oriented Air Quality Model – Part I. Base Case Model Results.", Atmos. Env., 42, pg8954-8966, 2008.
Grid Model vs. CMB Source Apportionment

Angiola

**Dust sources removed from grid model

Fresno

**Dust sources removed from grid model

Source: Q. Ying, J. Lu, A. Kaduwela, and M. Kleeman “Modeling Air Quality During the California Regional PM10/PM2.5 Air Quality Study (CRPAQS) Using the UCD/CIT Source-Oriented Air Quality Model – Part II. Regional Source Apportionment of Primary Airborne Particulate Matter.”, Atmos. Env 42, pp8967-8978, 2008.
Regional EC Source Contributions

Urban hotspots

Diesel dominates

Source: Q. Ying, J. Lu, A. Kaduwela, and M. Kleeman "Modeling Air Quality During the California Regional PM10/PM2.5 Air Quality Study (CRPAQS) Using the UCD/CIT Source-Oriented Air Quality Model – Part II. Regional Source Apportionment of Primary Airborne Particulate Matter.", Atmos. Env., 42, pp8967-8978, 2008.
Regional OC Source Contributions

Urban hotspots

Wood smoke dominates

Source: Q. Ying, J. Lu, A. Kaduwela, and M. Kleeman “Modeling Air Quality During the California Regional PM10/PM2.5 Air Quality Study (CRPAQS) Using the UCD/CIT Source-Oriented Air Quality Model – Part II. Regional Source Apportionment of Primary Airborne Particulate Matter.”, Atmos. Env., 42, pp8967-8978, 2008.
Spectrum of Reactive Nitrogen Compounds

- NO, NO2, NO3, N2O5, HONO, PAN, HNO3

**Direct Emissions**

**Reactive Intermediate Products**

**Stable End Product From Atmospheric Chemistry**

- HNO₃ + NH₃ → NH₄NO₃

**Direct Emissions**

**Particle Phase Nitrate**
Nighttime/Winter Nitrate Formation

- $\text{NO} \xrightarrow{O_3} \text{NO}_2 \xrightarrow{O_3} \text{NO}_3 \xrightarrow{} \text{N}_2\text{O}_5 \xrightarrow{\text{H}_2\text{O}} 2\text{HNO}_3$

- Main oxidant is $O_3$ – favors low sunlight intensity, wet conditions
Equilibrium Dissociation Constant for Ammonium Nitrate

Ammonium nitrate will not form when $[\text{NH}_3] \times [\text{HNO}_3] < K_p$

$$K_p = [\text{NH}_3]_{\text{gas}} \times [\text{HNO}_3]_{\text{gas}}$$
Source Apportionment of Secondary PM

Regional Nitrate Source Contributions
Regional NH4+ Source Contributions

Source: Q. Ying, J. Lu, A. Kaduwela, and M. Kleeman “Modeling Air Quality During the California Regional PM10/PM2.5 Air Quality Study (CRPAQS) Using the UCD/CIT Source-Oriented Air Quality Model – Part III. Regional Source Apportionment of Secondary and Total Airborne PM2.5 and PM0.1.”, Atmos. Env., 42, pp8967-8978, 2008.
Regional PM2.5 (primary + secondary) Source Contributions

Source: Q. Ying, J. Lu, A. Kuduwea, and M. Kleeman “Modeling Air Quality During the California Regional PM10/PM2.5 Air Quality Study (CRPAQS) Using the UCD/CIT Source-Oriented Air Quality Model – Part III. Regional Source Apportionment of Secondary and Total Airborne PM2.5 and PM0.1.”, Atmos. Env., 43, pp419-430, 2009.
How Much PM Does Each Region Contribute to Other Regions?

PM2.5 Nitrate

Source: Q. Ying, and M. Kleeman
"Regional Contributions to Airborne Particulate Matter in Central California During a Severe Pollution Episode", Atmos. Env., 43, 1218-1228, 2009.
Regional Contributions to SJV PM2.5 Nitrate Between Dec 15, 2000 – Jan 7, 2001

- SJV: 68%
- Bay Area: 3%
- Sacramento Region: 4%
- Northern Sacramento Valley: 3%
- Sierra Mountains: 2%
- Sacramento Region: 4%
- Bay Area: 3%
- Upwind Boundary: 18%
- Other: 2%
Nitrate Control Options

Maximum 24-hr average PM2.5 nitrate concentrations response to NOx and VOC controls on December 31, 2000 using the SAPRC 90 chemical mechanism. Solid line with dots represents estimated emissions control trajectory since the year 2000 and dashed line with dots represents projected emissions controls through the year 2020 based on the California Almanac for Emissions.
Control Strategy Effectiveness

Research vs. Regulatory Models

- Research Model
  - Develop new techniques
  - Emphasis on science
  - Usually increased computational burden

- Regulatory Model
  - Accepted techniques
  - Emphasis on practical application for SIP
EXTRA SLIDES
PM2.5 Concentrations in the SJV

PM2.5 Seasonal Variation in the SJV

Daytime/Summer Nitrate Formation

- \( NO \overset{O_3}{\rightarrow} NO_2 \overset{OH}{\rightarrow} HNO_3 \)

- Main oxidant is OH – requires high sunlight, VOC rich environment
OC Region Contributions

Ammonium Region Contributions

Nitrate Region Contributions

(a) Modesto

(b) Fresno

(c) Bakersfield

Distribution of Transport Distances

PM2.5
Ammonium

Source: Q. Ying, and M. Kleeman
"Regional Contributions to Airborne Particulate Matter in Central California During a Severe Pollution Episode",
## Nitrate Regional Contribution Summary

<table>
<thead>
<tr>
<th>Source</th>
<th>BC</th>
<th>Bay Area</th>
<th>Sac</th>
<th>SJV</th>
<th>SJV</th>
<th>SJV</th>
<th>SacV</th>
<th>Sierra</th>
<th>Other</th>
<th>SUM</th>
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<tbody>
<tr>
<td>Bay Area</td>
<td>R1</td>
<td>2.1%</td>
<td>1.5%</td>
<td>1.8%</td>
<td>1.4%</td>
<td>0.4%</td>
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<td>Sac</td>
<td>R2</td>
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<td>1.3%</td>
<td>0.3%</td>
<td>0.3%</td>
<td>0.0%</td>
<td>0.1%</td>
<td>0.1%</td>
<td>0.8%</td>
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<td>N SJV</td>
<td>R3</td>
<td>1.3%</td>
<td>0.3%</td>
<td>0.8%</td>
<td>1.7%</td>
<td>1.0%</td>
<td>0.0%</td>
<td>0.1%</td>
<td>0.4%</td>
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<tr>
<td>C SJV</td>
<td>R4</td>
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<td>0.8%</td>
<td>0.9%</td>
<td>1.7%</td>
<td>17.7%</td>
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<tr>
<td>S SJV</td>
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<td>3.1%</td>
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<td>N SacV</td>
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<td>Sierra</td>
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<tr>
<td>Other</td>
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<td>3.9%</td>
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<td>0.6%</td>
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<tr>
<td>SUM</td>
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<td>8.2%</td>
<td>29.3%</td>
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<td>6.0%</td>
<td>1.6%</td>
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<td>100.0%</td>
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</table>

Nitrate Control Options

Maximum 24-hr average PM2.5 nitrate concentrations response to NOx and VOC controls on December 31, 2000 using the SAPRC 90 chemical mechanism. Solid line with dots represents estimated emissions control trajectory since the year 2000 and dashed line with dots represents projected emissions controls through the year 2020 based on the California Almanac for Emissions.
Partial Answers

• **Primary vs. secondary PM 2.5 species**
  – Elemental carbon (EC), organic carbon (OC), ammonium nitrate

• **Sources of PM 2.5 in the region?**
  – Wood smoke (OC) and diesel engines (EC) in urban areas
  – Diesel engines (nitrate) and gasoline engines (nitrate) contribute regionally
  – Agricultural activities (ammonium) contribute regionally
Partial Answers

• Why do they concentrate in winter?
  – Lower mixing depths, colder temperature, home heating

• Where and when do PM 2.5 concentrations vary in the Valley?
  – Transport can be a factor, but mostly local emissions cause local air pollution

• What types of control measures have been most successful?
  – Restrictions on residential wood combustion
  – Restrictions on NO emissions
Acknowledgements

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