POLLUTION PROCESSING BY RADIATION FOGS DURING THE CALIFORNIA REGIONAL PM10/PM2.5 AIR QUALITY STUDY (CRPAQS)

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SJV fogs

- Dense, widespread radiation fogs occur during winter
  - Moist air trapped in valley by thermal inversion
  - Radiative cooling produces fogs
- Fogs affect particles by
  - Production of non-volatile solute mass
  - Scavenging and deposition

Evaporation

Gases

Fog Drops

Fog Drops

Deposition

Particles
Past Studies of SJV fogs - I

- Nitrate and ammonium typically major species
  - pH high
  - Important organic carbon contributions
  - Nitrite and sulfate also present
  - Composition variable in time and space
Past Studies of SJV fogs - II

- Deposition of inorganic ions important
  - sulfate production ~ balances sulfate deposition
- How do fogs process OC?
Fog Measurements
CRPAQS Fog Episodes

- Several fog episodes
- Shallow fog layer
- Large drops
CRPAQS Fog Organics

- Organic carbon is key component of CRPAQS fogs
- ~75% of OC is dissolved
- Fogs process soluble and insoluble OC

n-alkanoic acids - Angiola, 12/17/00

[Graph showing n-alkanoic acids with ng/mL on the y-axis and C9 to C26 on the x-axis, with blue for insolubles and red for solubles]
CRPAQS Fog Organics - II

- Many organic compounds present
  - PM source tracers
- Lots of high molecular weight material
Fog Dissolved Organic Carbon Composition

- MW > 1000
- 1000 > MW > 500
- Formaldehyde
- Formate
- Acetate
- Diacids (C2-C5)
- n-alkanes (C11-C40)
- n-alkanoic acids (C9-C33)
- PAH + oxy-PAH
- Other MW < 500

 DICARBOXYLS
 Levoglucosan
 DON
Drop size dependence

- Most species enriched in small drops
  - $\text{NO}_2^-$ is an exception
- Can impact
  - Deposition
  - Aqueous chemistry
Fog Deposition

- Deposition velocity, $V_d = \text{Flux}/C$
- Much faster than dry deposition
- Removal $\sim 1 \, \mu\text{g/m}^3\cdot\text{hr}$
New PM production

- High pH promotes rapid rxn. of dissolved SO$_2$ to
  - sulfate
  - hydroxymethanesulfonate

\[ \text{Typical Fog Conditions} \]
Summary

• Fogs interact strongly with aerosol particles and soluble trace gases
  – Nitrogen dominated
  – 100s of organic species
  – Distributed between solution and insoluble fraction
• Main effect of fogs on PM is scavenging and removal
  – Can reduce airborne concentration by >1 \( \mu g/m^3 \cdot hr \)
  – Dep velocities depend on solute distribution across drop size spectrum
  – SOA production?
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CRPAQS Fog Deposition

- Fog event fluxes range from 10s to 1000s of µg/m²
- Assuming a 100 m deep fog, concentrations would decrease typically
  - ~ 0.5 µg/m³/hr sulfate
  - ~ 1 µg/m³/hr nitrate
  - ~ 1 µg/m³/hr ammonium
  - ~ 0.7 µgC/m³/hr TOC
- Remember, fog solutes can be volatile or non-volatile

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<th>NO₃⁻ (µg/m²)</th>
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Particle and gas scavenging

- Particles scavenged by nucleation, diffusion, impaction, interception
- Soluble gases partition to drop
CMU Modeling (Fahey and Pandis)

• Fog model reasonably predicts
  – Bulk fog composition
  – Size-dependence
  – Deposition fluxes