Comparison Between Particulate Matter Sampled at Urban and Rural Locations in the San Joaquin Valley: Continuous Measurement of Single Particle Size and Composition

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Goals of ATOFMS CRPAQS Studies

• Use ATOFMS at 2 locations (Fresno and Angiola) to measure the temporal variability of individual particle composition and size (30-60 minute temporal resolution).

• Determine composition differences in rural (Angiola) vs. urban (Fresno) locations.

• Determine major sources in the different regions

• Study effects of fog processing on particle composition
**ATOFMS**

**Diode Pumped Nd:YAG Lasers**

**Ellipsoidal Mirrors**

**Particles**

**PMTs**

**C\textsubscript{n}H\textsubscript{m}^+ (organic species)**

**Metals (Fe, V, Pb)^+**

**Nd:YAG Laser**

**C\textsubscript{n}H\textsubscript{m}^- (organic species)**

**Nitrates, sulfates, phosphates, chloride Metal oxides**
Ozone(g) versus HMS(particles)

HMS formation: \( \text{HCHO}_\text{(aq)} + \text{HSO}_3^-\text{(aq)} \rightarrow \text{HOCH}_2\text{SO}_3^- \)


Ozone(g) versus HMS(particles)

December 1, 2000-December 8, 2001
Motivation for SVOC measurements

- High fraction of SVOC associated with PM in central California region
- ATOFMS measures nitrate, sulfate, carbon (EC vs. OC), metals, phosphates, etc.
  - Correlations established with PM$_{2.5}$, nitrate, sulfate, ammonium mass on long (MOUDI 4 hr.) and short (30 minute) timescales
- Can ATOFMS be used to measure temporal variability of semivolatile organic species?
  - Proposed as contributors to health effects
  - Many are aromatic, PAH, and derivitized (i.e. nitrated) species with known mutagenicity and carcinogenicity
  - ATOFMS highly sensitive to aromatic compounds ($\lambda = 266$ nm)
Nitrate Mass (Angiola, January 2001)

Data provided by Susanne Hering
Temporal Evolution (Angiola)
PAH and Aromatic Marker Ions
January 9-February 4, 2001

ATOFMS Counts

Date/Time

Date

# particles (supermicron)
200 to 210
220 to 230
250 to 260
170 to 180
150 to 160
Nitrate Mass (Fresno)
January 9-February 4, 2001

Data provided by Susanne Hering
PAH mass (PAS), # of PAH, # of Biomass (-45) particles (ATOFMS)

January 9-February 4, 2001
PAH mass (PAS) vs. # of Biomass (K) particles
January 9-February 4, 2001
Semivolatile Species (Fresno)
BAM vs. TEOM
January 9, 2001-February 4, 2001

Date/Time

µg/m³
Fresno Semivolatile OC Particles
Digital Histogram Spectra

~100% have K⁺-biomass core (both sub- and super-µm particle sizes)
Temporal Evolution of Positive Ions
Fresno, CA
12:00 2/2/01 - 10:00 2/4/01

Area{115} > 50

ATOFMS Counts

Date/Time

0

2/2/01 12:00 2/2/01 18:00 2/3/01 0:00 2/3/01 6:00 2/3/01 12:00 2/3/01 18:00 2/4/01 0:00 2/4/01 6:00

Noon Midnight Date/Time Noon Midnight

0 50 100 150 200 250 300

2/2/01 12:00 2/2/01 18:00 2/3/01 0:00 2/3/01 6:00 2/3/01 12:00 2/3/01 18:00 2/4/01 0:00 2/4/01 6:00
Temporal Evolution of Positive Ions
Fresno, CA

ATOFMS Counts

Date/Time

Noon
Midnight

Area\{115\} > 50
Area\{128\} > 50
Temporal Evolution of Positive Ions
Fresno, CA

- Area{115} > 50
- Area{128} > 50
- Area{139} > 50
Temporal Evolution of Positive Ions
Fresno, CA

Temporally evolving ion counts from Fresno, CA, showing the temporal evolution of positive ions. The plot indicates the ATOMS counts over a specific period from 2/2/01 12:00 to 2/4/01 6:00. The data is categorized by different areas, with the following symbols:
- Area{115} > 50
- Area{128} > 50
- Area{139} > 50
- Area{152} > 50

The y-axis represents the ATOMS counts, ranging from 0 to 300, and the x-axis represents the date and time from 2/2/01 to 2/4/01.
Temporal Evolution of Positive Ions
Fresno, CA

Area{115} > 50
Area{128} > 50
Area{139} > 50
Area{152} > 50
Area{165} > 50
Temporal Evolution of Positive Ions

Fresno, CA

Graph showing the temporal evolution of positive ions with different areas marked for comparison. The x-axis represents date and time, and the y-axis represents ATOFMS counts.
Temporal Evolution of Negative Ions
Fresno, CA

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ATOFMS Counts

Temporal Evolution of Negative Ions

Fresno, CA

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ATOFMS Counts

Date/Time

Area{-109} > 50
Temporal Evolution of Negative Ions
Fresno, CA

ATOFMS Counts

Date/Time

Noon
Midnight

Area{-109} > 50
Area{-137} > 50
Area{-151} > 50
Temporal Evolution of Negative Ions (Fresno, CA)

Date/Time

Temporal Evolution of Negative Ions (Fresno, CA)

- Area{-109} > 50
- Area{-123} > 50
- Area{-137} > 50
- Area{-151} > 50
- Area{-163} > 50
- Area{-177} > 50
- Area{-191} > 50

ATOFMS Counts

Noon
Midnight
Date/Time
Noon
Midnight
Temporal Evolution of Negative Ions
Fresno, CA

Gas-to-particle partitioning at night
Primary emissions during day or SOA formation?)
Temporal Evolution of Negative Ions
Fresno, CA (12/1/00-2/4/2001)

AOFMS Counts

Date/Time

Area{-109} > 50
Area{-123} > 50
Area{-137} > 50
Area{-151} > 50
Area{-163} > 50
Area{-177} > 50
Guaiacol (methoxy phenols)

R=CH₃, C₂H₅

**Most likely assignments based on Schauer et al. (2001) and Silva et al. (2000).**
Conclusions

- HMS(particles) anti-correlated with ozone measurements

- Correlation observed between K\(^+\) (core), m/z -45 (sugars + levoglucosan), PAH, and semivolatile aromatic species

- During stagnation (fog) episodes, build-up of K\(^+\)/biomass particles coupled with nitrates, sulfates, and SVOC (more EC observed in rural area)

- Major SVOC ion peaks compared to off-line chemical analysis results (Schaer and Cass) suggest methoxy phenols as major components of SVOC

- Particles more internally mixed in rural location (i.e. aged with significant SOA), whereas in urban location sources are still (for the most part) apparent
Future Plans

• Finish quantitation of ATOFMS data upon comparison with MOUDI data (see poster)
• Quantify ATOFMS data at higher time resolution using semi-continuous PM data (EC, OC, sulfate, nitrate)
• Scale ATOFMS counts using SMPS/APS
• Continue comparison with other gas, particle, and meteorological data
• Perform source apportionment using single particle signatures to assess relative impact of biomass burning (relative to other local sources)
• Long term goal: compare ATOFMS quantitative data with model/s (i.e. source oriented external mixture model with M. Kleeman)
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