Defining Atmospheric Aerosol Sources using Thermal Desorption Aerosol GC/MS-FID (TAG)

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National Oceanic and Atmospheric Administration: ICARTT 2004
California Air Resources Board: SOAR 2005

ISSUE
(why study aerosols?)

• **Atmospheric Aerosols (PM$_{2.5}$):**
  – Decreases Atmospheric Visibility
  – Affects H$_2$O Budget
  – Affects Global Energy Balance
  – Detrimental to Human Health

• Organic portion (avg. 20-50% of total mass) is helpful in determining and understanding:
  – Particle sources
  – Particle formation processes

• Past PM$_{2.5}$ measurements:
  – In-Situ particle (no individual compound separation)
  – Filter collection (12 to 24-hour time resolution)
• Atmospheric Aerosols (PM$_{2.5}$):
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  - Affects Global Energy Balance
  - Longest Lifetime of all aerosol sizes

Olympus Aerial Surveys, Inc.
• Atmospheric Aerosols (PM$_{2.5}$): Detrimental to Human Health
  Deposition efficiency of inhaled particles in the respiratory tract.

Naso-Oro-Pharyngeal-Laryngeal (NOPL)
- Bulk of ETS mass in this size range
- Wood and meat smoke
- Secondary Organic Aerosols

Tracheobronchial (TB)

Pulmonary (no cleaning mechanism)
- Bulk of ETS mass in this size range
- Wood and meat smoke
- Secondary Organic Aerosols

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(what needs improvement?)

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• Creates a need for an instrument capable of:
  – Separating / Identifying / Quantifying individual organic marker compounds from ambient PM$_{2.5}$
  – In-Situ, Automated measurements
  – 1-hour time resolution (to track diurnal changes)
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Thermal Desorption Aerosol GC/MS-FID (TAG)
**APPROACH**

TAG: **Thermal Desorption Aerosol GC/MS-FID**

1. **Collection technique:**
   - Inertial Impaction (30°C)

2. **Sample transfer:**
   - Thermal Desorption (50-300°C)

3. **Chemical separation:**
   - Gas Chromatography

4. **Compound identification:**
   - Mass Spectrometry (Quadrupole)

5. **Compound quantification:**
   - Flame Ionization Detection
TAG Applications To Date

• **In-Laboratory Trial Runs**
  - UC Berkeley
    • ambient sampling on campus
  - ADI in Berkeley
    • ambient sampling in business district

• **Field Sampling**
  - ICARTT 2004, Chebogue Point, Nova Scotia
    • Ambient sampling downwind of United States and Canada
  - SOAR 2005, Riverside, California
    • Ambient sampling downwind of Los Angeles
ICARTT campaign at Chebogue Point during summer of 2004.
- Full range of meteorological, radiation, trace gas, and aerosol measurements
- TAG analysis focused on period of July 26 – Aug.15, 2004 (~3 weeks)
- Hourly data (750 chromatograms x 2 detectors)
- Manual calibration with directly applied standards
- Automated filtered and zero air blanks

Location: Chebogue Point, Nova Scotia. August 7, 2004
Sample time: 0.5 hour
Sample Volume: 0.25 m³
Thermal Desorption: 50-300°C
GC oven temp. range shown here: ~ 45°C to 300°C

Total Organic Aerosol = (Resolved Compounds + Unresolved Compounds + Non-Eluting Compounds)

Resolved compounds will determine the aerosol source
Individual TAG Compounds vs. Aerosol Mass Spectrometer (AMS) Total Organics and Total $\text{SO}_4^{2-}$

**Compound: A**
- 4-Pentenoic acid, 2-acetyl-2,3-dimethyl-,ethyl ester ($\text{C}_{11}\text{H}_{18}\text{O}_3$)

**Compound: B**
- 1,6-Dioxaspiro[4,4]nonane-2,7-dione ($\text{C}_7\text{H}_8\text{O}_4$)

AMS data supports the fact that these two compounds represent two different events.

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AMS data (Aerodyne Research, Inc.: Worsnop et al.)
FACTOR ANALYSIS

• Data in Principal Component Factor Analysis
  – 37 resolved TAG organic compounds
  – O3, CO, Radon
  – AMS (Organic carbon, $\text{SO}_4^{2-}$,$\text{NO}_3^-$,$\text{NH}_4^+$)

• See how these 44 components vary with each other
  – Factor analysis finds some underlying process or source type

• Have identified 6 major organic aerosol sources
  – Factor 1: Isoprene Oxidation
  – Factor 2: US Outflow type 1
  – Factor 3: Local Alkane Emission
  – Factor 4: US Outflow type 2
  – Factor 5: Terpene Oxidation
  – Factor 6: Marine or Dairy
6 Particle Sources

- Isoprene Oxidation
- US Outflow 1
- Local Alkane
- US Outflow 2
- Terpene Oxidation
- Marine or Dairy

- Shade of wedge = Intensity of events
- Length of wedge = Frequency of events

NOAA-NESDIS/OAR Emission Inventory Mapviewer: [http://map.ngdc.noaa.gov/website/al/emissions/viewer.htm](http://map.ngdc.noaa.gov/website/al/emissions/viewer.htm)
AMS speciation during TAG-defined events

**Isoprene Oxidation**
- $\text{NO}_3^- \quad 5\%$
- $\text{NH}_4^+ \quad 6\%$
- $\text{SO}_4^{2-} \quad 6\%$

**US Outflow 1**
- $\text{NO}_3^- \quad 2\%$
- $\text{NH}_4^+ \quad 14\%$
- $\text{Organics} \quad 33\%$
- $\text{SO}_4^{2-} \quad 51\%$

**Local Alkane**
- $\text{NO}_3^- \quad 4\%$
- $\text{NH}_4^+ \quad 11\%$
- $\text{SO}_4^{2-} \quad 21\%$
- $\text{Organics} \quad 64\%$

**US Outflow 2**
- $\text{NO}_3^- \quad 7\%$
- $\text{NH}_4^+ \quad 12\%$
- $\text{SO}_4^{2-} \quad 25\%$
- $\text{Organics} \quad 56\%$

**Terpene Oxidation**
- $\text{NO}_3^- \quad 5\%$
- $\text{NH}_4^+ \quad 10\%$
- $\text{SO}_4^{2-} \quad 8\%$
- $\text{Organics} \quad 77\%$

**Marine or Dairy**
- $\text{NO}_3^- \quad 6\%$
- $\text{NH}_4^+ \quad 11\%$
- $\text{SO}_4^{2-} \quad 16\%$
- $\text{Organics} \quad 67\%$

Chart size scaled to average aerosol concentration for each factor
ICARTT CONCLUSIONS

- TAG instrument successfully deployed

- First in-situ hourly measurements of speciated ambient organic aerosol composition

- Analysis of 37 TAG compounds
  - See 6 distinct source types, each with different organic marker compounds

- Organic aerosol in Nova Scotia is consistently composed of mostly oxygenated compounds that are both biogenic and anthropogenic in origin
SOAR 2005 Status
Riverside, CA

• Overview
  – 5 weeks in summer, 5 weeks in fall
  – Large suite of aerosol instrumentation

• TAG identified over 300 ambient compounds w/ various sources
  – Gasoline
  – Diesel
  – Plastics
  – Biogenics
  – Pesticides
  – Wood combustion
  – Plus many secondary organic sources

• Still integrating chromatograms
  – 1,530 hours from summer and fall
  – 2 detectors
  – 300 compounds
  – 918,000 peaks to integrate
Interesting Discoveries in Berkeley

Methamphetamine

Nighttime in the warehouse district

Caffeine

Morning on Campus
Berkeley Ambient Air
2/7/06
22:30-24:00

Total Ion Abundance

Retention Time (min)
Future Plans for TAG

- Development
  - 2 Dimensional TAG w/ TOF mass spectrometer (STTR grant)
    • Increase number of compounds from several hundred to several thousand
  - Online Chemical Derivatization Technique
    • Analyze more polar compounds
  - Commercialize 1 dimensional TAG (phase 3 of SBIR grant)
    • TSI
      • Marketing as a tool in atmospheric science, drug enforcement, and chemical warfare detection

- Planned Atmospheric Science Studies
  - Pittsburgh, PA (urban aerosol)
  - Blodgett Forest, CA (biogenic aerosol)
  - San Joaquin Valley, CA (agriculture influenced aerosol)
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Radon Data
U. Washington, Bothell
Dan Jaffe, Isaac Bertschi

Backtrajectories
NOAA
Allen White

Funding:
Department of Energy: Global Change Education Program
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National Oceanic and Atmospheric Administration: ICARTT 2004
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For Detailed TAG description:

ASIDE: Compounds collected in Nova Scotia are extremely oxygenated. Difficult to identify using only mass spectra database.

The dotted red line represents equivalent abundance between graphs A and B.

A) Oxygenated Compounds

B) Hydrocarbon like Compounds

Berkeley, CA
Winter Evening 2004
Resolved Compounds Matched by Palisade library: 85%

Nova Scotia, Canada
Summer Evening 2004
Resolved Compounds Matched by Palisade library: 50%
Table 3. Impact periods of TAG factors during July 26 – August 15, 2004.

<table>
<thead>
<tr>
<th>Factor Description</th>
<th>Source</th>
<th>Avg. Windspeed (m s⁻¹)</th>
<th>Avg. Duration (h)</th>
<th>Percentage of Total Time (%)</th>
<th>Avg. Aerosol Concentration (μg m⁻³)</th>
<th>Avg. Organics Concentration (μg m⁻³)</th>
<th>Relative Importance for Organics</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1 Isoprene Oxidation</td>
<td>3.3</td>
<td>6.7</td>
<td>10.5</td>
<td>6.8</td>
<td>5.7</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>F2 U.S. Outflow 1</td>
<td>4.7</td>
<td>31.0</td>
<td>6.9</td>
<td>21.9</td>
<td>7.3</td>
<td>0.84</td>
<td></td>
</tr>
<tr>
<td>F3 Local Alkane</td>
<td>1.7</td>
<td>6.5</td>
<td>11.6</td>
<td>4.3</td>
<td>2.8</td>
<td>0.54</td>
<td></td>
</tr>
<tr>
<td>F4 U.S. Outflow 2</td>
<td>4.0</td>
<td>4.3</td>
<td>7.6</td>
<td>6.0</td>
<td>3.3</td>
<td>0.43</td>
<td></td>
</tr>
<tr>
<td>F5 Terpene Oxidation</td>
<td>2.4</td>
<td>3.6</td>
<td>8.9</td>
<td>4.0</td>
<td>3.1</td>
<td>0.46</td>
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</tr>
<tr>
<td>F6 Marine or Dairy</td>
<td>1.5</td>
<td>3.1</td>
<td>6.9</td>
<td>4.3</td>
<td>2.9</td>
<td>0.33</td>
<td></td>
</tr>
</tbody>
</table>

All values calculated using dominant factor > 1σ criteria, except average duration and percentage of total time which were calculated using f > 1σ criteria. Aerosol concentrations calculated using sum of all AMS aerosol species reported (i.e. organic carbon, sulfate, nitrate, and ammonium). Relative Importance for Organics is calculated as the product of Avg. Organics Concentration times the Percentage of Total Time, normalized to Factor 1. This value provides a relative scale to compare each factor’s contribution to total organic aerosol loading at Chebogue Point.