Character of Baltimore PM as derived from detailed Characterization of Molecular Organic Source Markers in 3-hr Samples

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Problem:

No knowledge available about the diurnal concentration patterns and dynamics of organic compounds associated with PM2.5

Time resolved data needed for:

• Health Effects Studies
• Atmospheric Chemistry
• Source/Receptor Reconciliation
• Regional Scale Atmospheric Transport Modeling

Approach:

• Design and test sequential multi-channel PM2.5 sampler
• 3-Hourly sampling with Filter/PUF in Baltimore during a Summer 2002 and Winter 2002/2003
• Analyze Filter and PUF for organic constituents using GC/MS
System for 3-Hourly PM2.5 Sampling

Marple PM2.5 Inlet Impactor

2 meter

Trailer Roof

Ceiling

Electronic Timer

Sequential Control Module

Pressure Gauges

Leak Test Pump

Leak Test Air Outlet

PUF

Filter Holder: Ø 125 mm

PUF Holder: Ø 103 mm, L=25cm

2" Electric Actuated Ball Valve

2" Electric Actuated Ball Valve

Air Condition

Primary Pump

Primary Pump

2 meter

Air Condition
## Major Organic Source Marker

<table>
<thead>
<tr>
<th>Source Markers</th>
<th>Source Indicators</th>
<th>Major Source Type</th>
<th>Associated Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>Odd-Carbon n-Alkanes (&gt;C_{25})</td>
<td>Leaf Surface Waxes</td>
<td>Burning of Vegetative Detritus, Soil Dust, Vegetarian Cooking</td>
<td></td>
</tr>
<tr>
<td>Even-Carbon n-Alkanic Acids (&gt;C_{23})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Even-Carbon n-Alkanes</td>
<td>Plastic Waste Burning</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cholesterol</td>
<td>Palmitic &amp; Stearic Acids, Palmitoleic &amp; Oleic Acids</td>
<td>Meat Cooking</td>
<td></td>
</tr>
<tr>
<td>Levoglucosan</td>
<td>Phytosterol: β-Sitosterol, Stigmasterol, Campesterol</td>
<td>Biomass Burning (Cellulose)</td>
<td>Wildfires, Forest Fires</td>
</tr>
<tr>
<td>Resin Acids</td>
<td></td>
<td>Soft Wood Burning</td>
<td></td>
</tr>
<tr>
<td>Syringyl Derivatives</td>
<td></td>
<td>Hard Wood Lignin</td>
<td></td>
</tr>
<tr>
<td>Saccharides: Mucose, Sucrose, α-, β-Glucose</td>
<td>Fugitive Dust from Cultivated Land</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iso-, Anteiso-Alkanes (&gt;C_{26})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hopanes &amp; Steranes</td>
<td>n-Alkanes (&lt; C_{25}), Alkylcyclohexanes, PAHs</td>
<td>Vehicular Emission</td>
<td>Heavy Oil Burning</td>
</tr>
</tbody>
</table>
Biogenic Aerosol Sources

Primary Organic Aerosol:
- Waxy Substances
- Biopolymer Breakdown
- Resin Acids
- PAHs
- Waxy Substances
- Phytosterols
- Sugars

Secondary Organic Aerosol:
- Nopinone
- Norpinic Acid
- Norpinonic Acid
- Pinonic Acid
- Pinic Acid

Monoterpenes: e.g. α- & β-Pinene

OH·

O3

NO3·

Secondary Organic Aerosol:
- Nopinone
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- Norpinonic Acid
- Pinonic Acid
- Pinic Acid

Monoterpenes: e.g. α- & β-Pinene

OH·

O3

NO3·
Particulate (PM2.5) Leaves Surface Abrasion Products

**n-Alkanes**
- Green Leaves
- Dead Leaves

**Carbon Number**
- 0
- 1
- 2
- 3
- 4
- 5
- 6
- 7
- 8
- 9
- 10
- 11
- 12
- 13
- 14
- 15
- 16
- 17
- 18
- 19
- 20
- 21
- 22
- 23
- 24
- 25
- 26
- 27
- 28
- 29
- 30
- 31
- 32
- 33
- 34
- 35
- 36

**n-Alkanoic Acids**
- Green Leaves
- Dead Leaves

Sources: Waxes on Leaf Surfaces, Burning of Vegetative Detritus, Soil Dust, Vegetarian Cooking

2006 National Air Monitoring Conference - Nov.6-9 in Las Vegas - PM Supersite Baltimore - Wolfgang F. Rogge, Ph.D., P.E., FIU, Miami, FL
Ambient Concentrations of n-Alkanes for Summer 2002 - Short Time Compositional Changes of Organic Compounds in PM2.5

Mainly Vehicular Exhaust

Waxy Leaf Surface Abrasions

Plastic Burning

July 2002

August 2002

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Organic Markers in Wood Smoke

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Major</td>
<td>Cellulose</td>
<td>40 – 50%</td>
</tr>
<tr>
<td></td>
<td>Hemicelluloses</td>
<td>25 – 35%</td>
</tr>
<tr>
<td></td>
<td>Lignins</td>
<td>30 – 40%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20 – 30%</td>
</tr>
<tr>
<td>Minor</td>
<td>Extraneous Substances</td>
<td>4 – 10%</td>
</tr>
<tr>
<td></td>
<td>Resins</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Gums</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fats, waxes, starches, terpenes,</td>
<td></td>
</tr>
<tr>
<td></td>
<td>tannins, phenolics, pectins,</td>
<td></td>
</tr>
<tr>
<td></td>
<td>sugars, sapins, mucilages,</td>
<td></td>
</tr>
<tr>
<td></td>
<td>glycosides, essential oils,</td>
<td></td>
</tr>
<tr>
<td></td>
<td>sterols, others</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Inorganics (Ash)</td>
<td>&lt; 1%</td>
</tr>
</tbody>
</table>

• **Marker for Cellulose Burning: Levoglucosan**
  
  Cellulose is the abundant organic polymer on earth, found in any wood, vegetative detritus, biomass, etc.

• **Markers for Lignins from Hardwood Burning: Syringyl Derivatives (Syringaldehyde, Acetosyringone, Syringic acid)**
  
  Second most abundant organic polymer on earth:
  
  Hardwoods have about 50% guaiacyl and 50% syringyl units
  Softwoods have 90% – 100% guaiacyl units

• **Markers for Softwood Burning: Resin Acids [dehydroabietic acid (major), 7-oxo-dehydroabietic acid, pimaric acid, abietic acid, etc.]**
### Estimating Ambient OC Contributions from Wood Burning

<table>
<thead>
<tr>
<th>Fuel Type</th>
<th>Combustor</th>
<th>OC/Levoglucosan</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardwood</td>
<td>Fire Place</td>
<td>7.8</td>
<td>Fine et al., 2001</td>
</tr>
<tr>
<td>Softwood</td>
<td>Fire Place</td>
<td>13.1</td>
<td>Fine et al., 2001</td>
</tr>
<tr>
<td>Hardwood</td>
<td>Fire Place</td>
<td>7.4</td>
<td>Fine et al., 2002</td>
</tr>
<tr>
<td>Softwood</td>
<td>Fire Place</td>
<td>23.5</td>
<td>Fine et al., 2004a</td>
</tr>
<tr>
<td>Hardwood</td>
<td>Fire Place</td>
<td>5.5</td>
<td>Fine et al., 2004b</td>
</tr>
<tr>
<td>Softwood</td>
<td>Wood Stove</td>
<td>8.1</td>
<td>Fine et al., 2004b</td>
</tr>
<tr>
<td>Hardwood</td>
<td>Fire Place</td>
<td>8.1</td>
<td>Schauer et al., 2001</td>
</tr>
<tr>
<td>Softwood</td>
<td>West US</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td>Hardwood</td>
<td>West-Midwest US</td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td>Softwood</td>
<td>West US</td>
<td>3.9</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>6.6 ± 3.2</td>
<td></td>
</tr>
</tbody>
</table>

\[
% \text{ Ambient OC from Wood Burning} = \left( \frac{OC}{\text{Levoglucosan}_{\text{Woodsmoke}}} \right)_{\text{Ambient}} \left( \frac{\text{Levoglucosan}}{OC} \right)_{\text{Ambient}}
\]

\[
% \text{ Ambient OC from Wood Burning} = 6.6 \pm 3.2 \left( \frac{\text{Levoglucosan}}{OC} \right)_{\text{Ambient}}
\]
Estimating Ambient OC Contributions from Wood Burning

% OC from Wood Burning

November 2002

February 2003
Baltimore Supersite:

Secondary Biogenic Atmospheric Reaction Products: Nopinone, Pinonic Acid, Norpinonic Acid

Schematics for the formation routes of secondary biogenic reaction products following the ozonolysis of $\alpha$-pinene and $\beta$-pinene.

(from Kamens)
Nopinone: Secondary Biogenic Reaction Products - Summer 2002
Nopinone: Secondary Biogenic Reaction Products - Summer 2002

![Graph showing Nopinone and % Rel. Humidity for July and August 2002]
Major Organic Compounds associated with PM2.5 Cooking Emissions

Number of Experiments in ( )
From: Rogge et al., Emission Factors for Residential Cooking

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Diurnal Cooking Activities over 48 Hours

Local Cooking Source

Distant Cooking Source (travel time 8 hrs) + Local Cooking Source
Ambient Concentrations of Palmitoleic Acid, Oleic Acid, and Cholesterol
Summer 2002

Any Daily Patterns?
Organic Markers for Vehicle Exhaust: Hopanes & Steranes

Squirrel Hill Tunnel, Pittsburgh

Tunnel vs. Ambient

Ambient concentrations in ng/m3

Tunnel Emission Factors in µg/Kg of Fuel
Organic Markers for Vehicle Exhaust: Hopanes & Steranes

1. Alkylcyclohexanes
2. n-Alkanes (C19-C25)
3. PAHs

How do ambient concentration patterns for the Hopanes compare to:

- Alkylcyclohexanes?
- n-Alkanes (C19-C25)?
- PAHs?
Conclusions:

• For the very first time, insight into the daily patterns of atmospheric organic compounds associated with PM2.5 with an 3 hourly time-resolution

• For Summer 2002: 18 days of data available

• For Winter 2002-03: 17 days of data available

• For 111 individual organic compounds, about 62,000 data points have been generated

• Although, only a very short view into the data set has been presented, already several interesting aspects about the atmospheric dynamic of fine particle bound organic compounds have been demonstrated:

  • Compositional changes of organic matter associated with PM2.5 occurs with a time scale of less than 3 hours

  • With very few exceptions, no diurnal concentration patterns have been found for individual organic compounds, indicating that PM2.5 at the sampling site is impacted by sources close and far

  • Wood smoke markers are also detectable in summer time

  • Wood smoke from softwood burning and hardwood burning can be distinguished well using resin acids and phenolic derivatives from the syringyl type “building blocks” in lignins

  • Vehicular marker concentrations (hopanes) compare very well to n-alkanes (C19-C25) and alkylcyclohexanes and is responsible for most of the PAH emissions