Urban Sources of Fine Particles

A Look At Biomass Smoke Emissions

MARAMA Monitoring Committee
Prof. Monica Mazurek, Civil & Environmental Engineering Department
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Markers for source apportionment

Simoneit et al. 1980, JAPCA 30, 387-390

Contamination of the Lake Tahoe Air Basin by High Molecular Weight Petroleum Residues

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The atmosphere of the Lake Tahoe air basin is contaminated with high molecular weight (> C20) petroleum hydrocarbons. Aerosol samples were collected by high-volume filtration and the solvent-soluble organic matter was analyzed. The relative concentrations of petroleum residues found were as follows: winter > summer and day > night. This contamination is primarily due to the poorer combustion of diesel and home heating fuels at that altitude and during periods of colder climate.
Petroleum biomarkers

- Characterization of crude oils
- Geochemical evidence for oil field evaluation
- Distribution patterns of homologs of large organic sources
Fossil bacteria and microbiota became today’s petroleum
PM origin from petroleum >>

Lake Tahoe winter PM hopanes & steranes

Southern California Bight sediment hopanes & steranes

Figure 3. Relative distribution histogram for extended diterpanes and triterpanes (based on the m/z 191 mass chromatograms of the GC/MS data) for an example of Lake Tahoe aerosol and a sediment from the Southern California Bight which is contaminated by petroleum seepage. (a) Sample 3, Sugarpine Point State Park, winter; (b) Sample 193, Santa Barbara Basin (reference 5). The R and S diastereomers are also indicated and C₂₈ hopane I is 1.

Simoneit et al. 1980, JAPCA 30, 387-390
Receptor modeling and CMB-MM

Professor Glen Cass
Urban sources of fine PM

Los Angeles, CA fine particle emissions inventory

- Oil-fired boiler
- Autos (non- and catalyst-equipped)
- Heavy-duty diesel trucks
- Home heating furnace
- Home fireplace
- Roofing tar pots
- Road dust
- Tire dust
- Brake dust
- Cigarette smoke
- Meat cooking operations
- Vegetation (cultivated, native)

Mathematical Models Accounting for Individual Emission Contributions from Discrete Urban Sources
Urban sources of fine PM2.5

- Emissions inventories for major sources PM2.5
- Ambient fine particle sampling network for a complete annual cycle
- Source emission tests to produce chemical mass balance profiles

Credit: Schauer et al., *Atmos. Environ.*, 1996
Chemical Mass Balance-Molecular Marker Model (CMB-MM)

Modeled source contribution >>

Mass balance for Downtown Los Angeles, 1982, Schauer et al., 1996
Urban plume markers

- Motor vehicle exhaust (hopanes & steranes)
- Cooking emissions (cholesterol)
- Biomass/cellulose combustion (levoglucosan)
- Elemental carbon
What is the organic composition of PM 2.5?

What are its sources?

What components are directly emitted vs. secondary?

NY, NJ CT Fine Particulate Matter Study (NYSERDA) >> NYDEC, NJDEP, CTDEP, SUNY-Albany

Toll Plaza 13, NJ Turnpike Elizabeth, NJ >> 220,000 motor vehicles per day
SOAP 2002-2007 Field Program

PM2.5

SOAP ’02-’03 10 composites per site
SOAP ’05-’07 16 composites per site

Population (Thousands)

- > 2000
- 1401 - 2000
- 1001 - 1400
- 801 - 1000
- 501 - 800
- 201 - 500
- 100 - 200
- 0 - 100
- SOAP Sampling Site

Locations:
- Westport, CT
- Pinnacle State Park, NY
- Bronx, NY
- Queens, NY
- Elizabeth, NJ
- Chester, NJ
Alkanes

- n-pentacosane
- n-hexacosane
- n-heptacosane
- n-octacosane
- n-nonacosane
- n-triacontane
- n-hentriacontane
- n-dotriacontane
- anteiso-triacontane
- iso-hentriacontane
- anteiso-hentriacontane
- iso-dotriacontane
- anteiso-dotriacontane
- iso-tritriacontane
- phytane
- pristane

PAHs (22 total)

- benzo[b]fluoranthene
- benzo[k]fluoranthene
- benzo[e]pyrene
- indeno[1,2,3-cd]pyrene
- indeno[1,2,3-cd]fluoranthene
- retene
- coronene

Acids

- 21 n-alkanoic acids
  (with C_{10} to C_{30})
- 10 aliphatic dicarboxylic acids
  (C_{3} to C_{10})
- 1 aromatic polycarboxylic acid
- cis-9-n-octadecenoic acid

Other

- hopanes
- steranes
- Combined
  - nonanal
  - diterpenoids
  - sterols
  - cholesterol
  - 7H-benz[de]anthracen-7-one
  - benz[a]anthracene-7,12-dione

Over 100 individual organic markers quantified in SOAP 2002-2007 PM2.5 ambient samples
A biomarker for the pyrolysis of cellulose ($\text{C}_6\text{H}_{10}\text{O}_5$)

- Is produced from man-made and natural combustion activities
- Is unique as a smoke marker, stability in aqueous phase << solid phase
- Is associated with particulate phase because of MW (162 amu)
- Is a polar compound that is soluble in water, alcohols, acetone
- Emission rates measured from different cellulose combustion sources
Interannual concentration differences could be due to meteorological conditions and/or emission source strength.
Quebec Wildfires July 2, 2002

Higher regional smoke concentrations found for SOAP 2002-2003 due to persistent wildfires in the western US and Canada.

Levoglucosan was 10 times higher than any sample for SOAP 2002-2003.
## Levoglucosan SOAP 2002-2007

### U.S. Winter Concentrations Comparison

<table>
<thead>
<tr>
<th>Reference</th>
<th>Location (Study Period)</th>
<th>Levoglucosan, ng/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sheesley et al. (2007)</td>
<td>Charlotte, NC (Mid-October – December, 2003)</td>
<td>196</td>
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<tr>
<td>Gorin et al. 2006</td>
<td>Fresno, CA (12/25/03-1/15/04)</td>
<td>600</td>
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<tr>
<td>This Study</td>
<td>Queens, NY (winter)</td>
<td>37.7</td>
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<tr>
<td>This Study</td>
<td>Elizabeth, NJ (winter)</td>
<td>6.7</td>
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<td>This Study</td>
<td>Chester, NJ (winter)</td>
<td>24.2</td>
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<td>Westport, CT (winter)</td>
<td>120.9</td>
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<td>This Study</td>
<td>Bronx, NY (January, 2006)</td>
<td>84.3</td>
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<td>Pinnacle State Park, NY (January, 2006)</td>
<td>113.0</td>
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<td>Bronx, NY (January, 2007)</td>
<td>85.6</td>
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<td>Pinnacle State Park, NY (January, 2007)</td>
<td>45.5</td>
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</table>
U.S. EPA Speciate Emission Rates

% Levoglucosan/OC

% Levoglucosan/EC
Conversion to % Ambient PM$_{2.5}$ OC Mass

$$\% \ OC = \frac{ng \ levoglucosan}{m^3} \times \frac{m^3}{\mu g \ OC} \times \frac{\mu g \ OC}{100 \ ng \ levoglucosan} \times 100\%$$

Emission factor averaged from Fine et al. 2001
Wood Smoke Estimate

SOAP 2002-2003
% OC mass from wood smoke

SOAP 2005-2007
% OC mass from wood smoke
More wood smoke emissions studies needed to improve chemical speciation and mass emission factors from biomass fuels from home heating, commercial cooking, fugitive sources (solid waste, structural fires, agricultural, food carts), and biofueled power plants.

Collaboration with U.S. EPA Biomass Emissions R&D Program (Gullett and Hays) provides fine PM emissions from wood and pellet stoves used in the NE US.

Search for additional biomarkers that can be used in combination with levoglucosan to identify emission sources.
Thank you

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