Organic Carbon Mass Balance and Source Apportionment of Primary Organic Carbon in the Pittsburgh Region using Molecular Markers

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February 10, 2005: AAAR Specialty Conference, Platform #16B-3
Outline of this talk

- Overview of PAQS molecular marker database
- Source profile selection: a visualization technique
  - Polycyclic aromatic hydrocarbons (PAH)
  - Hopanes and EC
  - Wood smoke tracers
- PAQS source apportionment results
- Variability in apportioned OC
  - Effect of the OC/tracer ratio
- PAQS organic carbon mass balance
Organic molecular markers

- Combustion sources: similar bulk composition
- Organic compounds:
  - Highly source specific
  - Small fraction of emissions

Examples
- Cholesterol: meat-cooking
- Hopanes: petroleum biomarkers
  - Engine exhaust, other fossil fuel combustion

Cholesterol
(0.03 – 1% of cooking OC)

Norhopane
(0.0006% - 0.11% of vehicle OC)
Organic molecular markers at PAQS

July 2001-June 2002

- ~ 125 24-hr quartz/PUF samples
- 100+ compounds by GC-MS (Wolfgang Rogge, FIU)
PAQS ambient tracer data: well-correlated

\[ y = 0.72x \quad R^2 = 0.95 \]

\[ y = 1.74x + 0.25 \quad R^2 = 0.65 \]

\[ y = 0.63x + 0.51 \quad R^2 = 0.58 \]

\[ y = 0.69x \quad R^2 = 1.00 \]

\[ y = 0.83x \quad R^2 = 1.00 \]

\[ y = 0.24x \quad R^2 = 0.95 \]

\[ y = 2.25x \quad R^2 = 1.00 \]

\[ y = 0.63x + 0.51 \quad R^2 = 0.58 \]
Source apportionment using CMB

Critical issues
- Atmospheric stability
- Source completeness
- Representative source profiles
- Analytical accuracy and precision

\[ c_i = \sum_{k} \alpha_{i,k} S_k + e_i \]
Source profile selection and OC apportionment

- Source profiles should explain the ambient distribution of multiple tracers

- Cannot fit OC: no “SOA profile”

- Use OC/tracer ratio
Visualization ambient tracers with scatter plots and ratio-ratio plots

(a) Source 1
Ambient data

(b) Source 1
Ambient data

(c) Source 1
Ambient data
Source 2

(d) Source 1
Source 2
75% Source 2

(e) Source 1
Ambient data
Source 2
Source 3

(f) Source 1
Source 2
Source 3
Ambient data
2-source mixing lines
Tracers dominated by a single source:
PAH and coke oven emissions

Indeno(1,2,3-cd)pyrene/ Benzo(e)pyrene

Benzo(fl)anthracene
Benzofluoranthenes
Benzo(a)pyrene
Coronene
Benzo(g,h,i)perylene

Other PAH (ng/m³)

Indenopyrene (ng/m³)

y = 2.25x  
R² = 1.00

y = 0.83x  
R² = 1.00

y = 0.69x  
R² = 1.00

y = 0.24x  
R² = 0.95

Related….
Poster 17PB-2
Tracers from two major sources: hopanes and EC; vehicular emissions

$y = 0.72x$
$R^2 = 0.95$

Related... Posters 17PB-3, 12PD-27
Two vehicular source profile scenarios

(a) "NFRAQS"
- Gasoline:diesel 1:1
- Ambient summer
- "NFRAQS gasoline"
- "NFRAQS diesel"

(b) "Cass"
- Mixing: diesel + non-catalytic gasoline
- Mixing: diesel + catalytic gasoline
- "Cass diesel"
- Non-catalytic gasoline
Wood smoke: no unique source profile?

- Fine NE-US hardwood: lev./OC 10.8-16.8%
- Fine NE-US softwood average lev./OC 7.0%

Resin Acids/Levoglucosan
Syringaldehyde/Levoglucosan

Ambient (sized to levoglucosan concentration)
Mixing lines for wood smoke source profiles

Resin Acids/Levoglucosan

Syringaldehyde/Levoglucosan

Three possible pairs:

<table>
<thead>
<tr>
<th>Softwood</th>
<th>Hardwood</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fine</td>
<td>Fine</td>
</tr>
<tr>
<td>Hays</td>
<td>Fine</td>
</tr>
<tr>
<td>Hays</td>
<td>Schauer</td>
</tr>
</tbody>
</table>

Schauer oak 60%
Hays foliar loblolly pine 40%
levoglucosan/OC = 16.3%

Fine NE-US: Softwood 100%
levoglucosan/OC 7%

Fine NE-US hardwood average

Hays foliar fuel: loblolly pine
Source profiles and molecular markers used for PAQS CMB Analysis

- **Base Profiles**
  - Softwood & Hardwood: Fine et al. 2001 average profiles
    - Levoglucosan, sum of 4 resin acids, syringaldehyde
  - Coke production: PAQS
    - 4 PAH
  - Meat cooking: Rogge et al. 1991 meat frying
    - Cholesterol
  - Road dust, cigarettes, vegetative detritus: Rogge et al. 1993 & 1994
    - Iron, iso-Hentriacontane, anteiso-Dotriacontane, and C-29, C-31 and C-33 n-alkanes

- **Motor Vehicle Scenarios**
    - fleet average gasoline: combination of summer low, medium, and high emitter profiles
    - fleet average diesel: combination of diesel profiles
  - Case 2: Cass
    - Schauer et al. 2002 non-catalytic gasoline
    - Schauer et al. 2002 catalytic gasoline
    - Average diesel: Schauer et al. 1999, Fraser et al. 2002
  - Vehicle fitting species
    - NFRAQS - 4 hopanes + EC
    - Cass - 4 hopanes, EC, and C-24 & C-26 n-alkanes

**Related…**

**Posters**
17PB-1, 2
12PD-26
CMB results for March 12, 2002 (NFRAQS)

- Gasoline: 26.0 +/- 6.9%
- Veg. Detritus: 1.5 +/- 0.3%
- Hardwood: 5.1 +/- 1.4%
- Cigarettes: 0.3 +/- 0.1%
- Cooking: 7.1 +/- 1.7%
- Coke: 2.7 +/- 0.3%
- Diesel: 7.0 +/- 3.2%
- Softwood: 16.9 +/- 3.7%
- Road-dust: 7.1 +/- 1.4%
- Unapportioned: 26.4%

R² 0.99
X² 0.53
DF 9
OC 4.1 µg-C/m³
96 daily measurements between July 2001 and June 2002
Average $R^2$ of 0.90
$\chi^2 \leq 6.3$

Confidence:
- Cass: 10 to 17 degrees of freedom
- NFRAQS: 10 to 14 degrees of freedom
- 90% or better confidence based on the $\chi^2$
  - Just one day with 88% confidence (Cass)
- Two days not confidently resolved with NFRAQS
CMB results with the NFRAQS vehicular profiles

- Diesel
- Gasoline
- Wood smoke
- Coke ovens
- Meat-cooking
- Other primary
- Unapportioned
- Overapportioned
CMB results with the Cass vehicular profiles

<table>
<thead>
<tr>
<th>Diesel</th>
<th>Gasoline</th>
<th>Wood smoke</th>
<th>Coke oven</th>
</tr>
</thead>
<tbody>
<tr>
<td>Meat-cooking</td>
<td>Other primary</td>
<td>Unapportioned</td>
<td>Overapportioned</td>
</tr>
</tbody>
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- Diesel
- Gasoline
- Wood smoke
- Coke oven
- Meat-cooking
- Other primary
- Unapportioned
- Overapportioned
Annual Average Apportionment

**NFRAQS**
42% OC apportioned

- Diesel: 8.0%
- Gasoline: 12.8%
- Wood smoke: 6.1%
- Coke ovens: 1.7%
- Meat-cooking: 7.5%
- Other primary: 5.7%
- Unapportioned: 58.1%

**CASS**
65% OC apportioned

- Diesel: 6.0%
- Non-Cat. Gas: 3.5%
- Unapportioned: 35.4%
- Catalytic Gas: 33.3%
- Wood smoke: 6.3%
- Meat-cooking: 8.3%
- Coke oven: 1.8%
- Other primary: 5.5%

OC = 3.0 ug C/ m³
Why is there so much more gasoline OC in the Cass solution?

OC/Hopane ratio of Schauer Catalytic profile: a factor of 10-100 larger than other profiles

Published Gasoline Vehicle Profiles
CMB results with the NFRAQS vehicular profiles: Gasoline OC highly seasonal
Seasonal variations in vehicle marker concentrations

Potential Explanations
- Seasonal non-vehicular source of EC
- Seasonal change in source profiles
- Chemistry

Related... Talk 18C-5
Effect of vehicular fleet composition: NFRAQS

**High-emitter**
- \( y = 1.19x \)
- \( R^2 = 0.99 \)

**Low-emitter**
- \( y = 0.58x \)
- \( R^2 = 0.81 \)

<table>
<thead>
<tr>
<th>Profile</th>
<th>OC/norhopane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td>880</td>
</tr>
<tr>
<td>High</td>
<td>3236</td>
</tr>
<tr>
<td>Average</td>
<td>2715</td>
</tr>
</tbody>
</table>
Seasonal variation in gasoline contribution
OC Mass Balance

Majority of OC is primary but many issues remain

Still gaps in summer:
• Seasonally varying emission profiles
• Oxidation of tracer
• Underestimating SOA with EC ratio technique
• Organic artifacts
  • …..
Conclusions

- Molecular markers in Pittsburgh consistent with source profiles for vehicular exhaust and coke oven emissions
  - No unique source profile set for wood smoke?
- NFRAQS v/s “Cass” vehicular apportionment: factor of three difference for gasoline OC
- Uncertainties in tracer/OC ratios
  - Especially for gasoline source profiles
- Seasonal variations in vehicular tracers
  - Changes in emission profiles
  - Atmospheric processing
Conclusions

- A large fraction of the fine organic PM is primary
  - “Traditional” primary sources + primary biological
- Secondary organic aerosol
  - Summer: ~30% of OC
  - Winter: <10% of OC
- Mass balance closure issues
Acknowledgements

- The US EPA Supersites program
- The US DOE/NREL
- AAAR travel grant for R.

- Spyros Pandis, Neil Donahue, Cliff Davidson
- Mark Hernandez
- Eric Lipsky, Sarah Rees, Juan Cabada, Charles Stanier, Tim Raymond, Wei Tang, Ann E. Wittig, Lisa Clarke, Natalie Pekney, Emily Weitkamp, Satoshi Takahama
- Leonard Lucas, Dave Wynne
- Gary Norris, Matt Fraser, Phil Fine, John Watson, Barbara Zielinska
- Paul Solomon, Tami Bond

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