Baltimore Supersite

Measurements of Elemental and Organic Carbon in PM2.5 at Ponca St. Feb./Mar. – Nov. 2002

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Objective/Scope

Characterize EC, OC, and Organic Markers during “worst” PM2.5 “Episodes”

- Ramifications for “Urban Excess” vs “Regional” control strategies

**Data discussed**

*Project period, Episodes*
EC, OC  Sunset Labs, thermal optical, 60 min
PM2.5  30° TEOM, 30 min
Met     WD, WS various, 5 min

**Two worst episodes**
Molecular Organic Markers
3-hr, Filter/PUF-GCMS (Rogge & Bernardo-Bricker)

Can local stationary or area source control reduce urban excess?
Sources affecting Ponca St. Measurements

Baltimore Supersite PM10 Sources

- Incinerator
- CFPP
- Sugar Creek Process
- Yeast Plant
- Steel Mill
- Cement
- Calcite Carbide Coke Plant
- Gypsum Plant
- CFPP/OFPP

- 190° to 200°
- 240°
- 70°
- 30°

- 0.07-23 tons/yr
- 23-61 tons/yr
- 61-243 tons/yr
- 243-510 tons/yr
- 510-924 tons/yr

Compiled by: Ondov Group, UMCP, Jan. 2002
### PM2.5 Summary Statistics
316 days, 2002

#### 30-min concentrations, µg/m³

<table>
<thead>
<tr>
<th></th>
<th>All Data</th>
<th>Without Canadian Smoke</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mean =</strong></td>
<td>16.9±13.0</td>
<td>15.8 ± 11</td>
</tr>
<tr>
<td><strong>Max =</strong></td>
<td>198</td>
<td>110</td>
</tr>
</tbody>
</table>

**Numbers of 24-hr means (without Canadian Smoke):**

- $\geq 65 \mu g/m^3$: 1
- $\geq 50$: 4
- $\geq 40$: 9
- $\geq 30$: 31

Frequency of incidences (>30 µg/m³) by type:

- 50% traffic related
- 42% sulfate haze
- 8% Canadian Smoke

**Observations:**
- Barely out of attainment for annual PM2.5 Standard
- 24-hr exceedences rare
30-min PM$_{2.5}$ Concentrations: Reveal 29 Episodes

Episodes A – F discussed in Park et al., 2004

Canadian Smoke (off scale)
Hourly EC and OC were adjusted to STN

Units: µg C/m³

EC_{STN} = 1.13 \text{EC}_{SL} + 0.44 \quad R^2 = 0.91

OC_{STN} = 1.28 \text{OC}_{SL} + 0.71 \quad R^2 = 0.95
OC statistics, Ponca st., 2002

(hourly data)

Study mean, Range

5.7 µg C/m³ 1.8 to 90 µg C/m³

(33.6±10.6% of PM2.5)

Box-Whisker plot (OC)

Canadian Smoke

OC was consistently a substantial fraction of PM2.5
EC statistics Ponca st., 2002

Study mean: 1.1 µg C/m³
(7.3±3.8% of PM2.5)

Range: 0.4 to 12 µg C/m³

Max 1-hr EC and OC 7:00 AM EST, Nov. 20th 2002
Diurnal profiles indicate large traffic Influence

Features:
- AM traffic peak; OC increases earlier than EC, CO
- OC increases relative to EC during mid-day ozone excursions, e.g., June and August
Selected Episodes

Episode C: July 17-22  Regional Haze

Episode F: Nov. 19-22  Traffic dominated
Episode C: July 17-22 Regional Haze

Main episode: Local winds from W to NW, shifting to NW to N
Episode C: OC and EC

moderate ozone

OC:EC = 1.84

3.12

2.62
Primary and Secondary OC

Episode C

Mostly Secondary OC – except for traffic induced excursions!
Episode F: November 20

7:00AM, stagnation

November stagnation (OC + EC)

Excellent Correlation: EC, OC, NOx, CO
Episode F: Low ozone, low Mixing height, cool

OC (μg C/m³), OC/EC ratio (-)

EC (μg C/m³)

OC=2.98 EC + 2.09 (R²=0.86)

OC/EC = ~3

Measurement period

OC and EC well correlated in cool, low mixing height periods
Episode F – subsidence venting of the I895/I95 corridor
Occurred after winds slowed, turned northerly, allowing subsidence venting of the I895/I95 corridor to the monitoring site.
Primary and Secondary OC

![Graph showing primary and secondary OC measurements over a 4-day period from 11/19/02 to 11/22/02. The graph compares primary (pri) and secondary (sec) OC concentrations measured in µg C/m³.]

Primary OC ≈ Secondary OC

\[
[OC]_{pri} = (OC/EC)_{pri} \times [EC]
\]

\[
[OC]_{sec} = [OC]_{tot} - [OC]_{pri}
\]
Organic Markers ("Rogge data")

Episode F
### Episode F – Traffic Markers?

<table>
<thead>
<tr>
<th>Date</th>
<th>n-Alkanes norm conc</th>
<th>Alkylcyclohexanes</th>
<th>PAHs</th>
<th>Oxy-PAHs</th>
<th>Pentacyclic Triterpanes</th>
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<tbody>
<tr>
<td>11/19/2002</td>
<td>0.0</td>
<td>0.2</td>
<td>0.4</td>
<td>0.6</td>
<td>0.8</td>
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<tr>
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<td>1.0</td>
<td>1.3</td>
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CPI = 1.0 (C27-C35) and 1.3 (C19-26) for n-alkanes, consistent with DIESEL 7.6 (C24-C33) for n-alkanoic acids; consistent with VASCULAR PLANTS!

- n-alkanes: 390 ng/m³
- n-alkanoic acids: 200 ng/m³
- PAH: 114 ng/m³

7:00 AM Peak

Fraction of Sunset OC identified: ~3%
Heterocyclic PAH

High S diesel? or coke plant?

- n-Alkanes
- S-Hetero-PAH (Dibenzothiphene)
- N-Hetero-PAH (7,8-Benzoquinoline)
- Thiazoles (Benzothiazole)

High S diesel? or coke plant?
Resin acids and steroids vs. Benzothiazole

6:00 to 9:00 AM

- Resin Acids vs. Benzothiazole
- Steroids vs. Benzothiazole (tire wear)

Data from 11/19/2002 to 11/22/2002
Syringaldehyde (as 3,4,5-trimethoxy benzaldehyde) + Acetosyringone (as 3,4,5-trimethoxyacetophene) + Syringic acid ME (as 3,4,5-trimethoxybenzoic acid, ME)
Gasoline oxidation products?

C5 – C9
e.g. Propandioic Acid

Mostly phthalic acid
6,10,14-trimethyl-2-pentadecanone
Secondary terpene oxidation products

Norpinone + Norpinonic acid + cispinonic acid
Conclusions

Part II.

Despite the hard work, only 3 to 5% of OC has been characterized!

What we thought was a largely a traffic induced episode, appears to have biomass combustion, meat cooking, and secondary terpene oxidation products, as well!

CMB would be needed to sort this out!

The 6:00 to 9:00 AM excursion may have resulted from the subsidence of highly polluted air along the I895/I95 corridor at 30°

Such “hot spots” likely exist at various locations in and around Baltimore

Part I.

The EC:OC method suggests secondary POC is ~50% of total POC, even during what we thought was largely a “traffic” induced episode. Wood combustion and meat cooking may have contributed oxygenated OM to this, but it is doubtful that these sources could have accounted for so much OC. Unidentified Mass responsible?