Descriptive Model of PM Pollution in Baltimore as derived from Analysis of Components of Discrete Episodes at the Ponca St. Supersite

John Ondov
Department of Chemistry and Biochemistry
University of Maryland, College Park, MD 20742
jondov@umd.edu; 301 405 1859

www.chem.umd.edu/supersite
Baltimore Supersite Study Area

Typical MidAtlantic Seaport City
- Populous, heavy industry, So. Baltimore
- Complex meteorology
- Major N.-S. transportation corridor

End member Washington - Boston Megalopolis

Variable Aerosol age
- local, 50 km, 100’s km source regions
- Appalachian Cloud-processed sulfate

Environmental Justice
- Downtown, weakly influenced
- So. Baltimore 10-X PAH, Metals
- 1.7-X deaths via pulmonary disease

Interpretive Context
- 25 yrs receptor modeling in region
- EPA and AEOLOS studies in Baltimore
- IMPROVE site, Shennandoah Nat. Park

Health Effects Studies
- JHU & UMAB
Strategically located to assess urban, industrial, and traffic influences
Measurements

- Primary Site: Ponca St., East Baltimore
  9.5 months: March – November, 2003
- Maximum temporal, size, compositional resolution
  - PM2.5, EC, OC, Nitrate, Sulfate,
  - Metals, Organic compounds
  - PAMS VOC, CO, NO$_x$, NO, NO$_2$, O$_3$
  - LIDAR, Single Particle MS
  - SMPS + APS size distributions 10 nm to 20 µm
- Measurement resolution 5 min, 10 min, 30 min, 1 hr, 3 hr, plus 24 Hr FRM mass and speciation
Interpretive Context

• PM air pollution may be viewed as occurring in a series of discrete meteorologically driven discrete episodes
• Transients often caused by one or two components
• Local vs. distant sources indicated by
  – Temporal behavior of constituents and marker species
  – Size distribution parameters
  – Detailed Analysis of episodes
Outline

- PM2.5 Episodes in 2002 (30 min data)
- Summary of major features of 6 worst
- Detailed description of highly time resolved data for worst summer and cool weather episodes
- Features of major components
30-min PM$_{2.5}$ Concentrations: 2002

show: series of discrete episodes of hours to 2 or 3 days duration

Canadian Smoke

reconstructed

A

B

C

D

E
### PM2.5 Statistics: 9.5 months, 2002

<table>
<thead>
<tr>
<th></th>
<th>w/Canadian Smoke</th>
<th>w/o Canadian Smoke*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Daily means:</td>
<td>3.5 to 85.6</td>
<td>3.5 to 64</td>
</tr>
<tr>
<td>Annual mean</td>
<td>16.9</td>
<td>15.8±13</td>
</tr>
<tr>
<td>No. daily exceedences</td>
<td>2</td>
<td>~1</td>
</tr>
<tr>
<td>No. daily means &gt; 30 µg/m³</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td>(i.e., 16.9 + 13)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*6 worst episodes described in Park et al., 2005
2 will be described in this talk*

*Episode B; M\maximum 30 min concentration was 198 µg/m³*
### Characteristics of Six Worst PM2.5 Episodes
**Baltimore Supersite, Ponca St., 2002**

<table>
<thead>
<tr>
<th>Episode</th>
<th>Date</th>
<th>Type</th>
<th>Ozone (ppb)</th>
<th>Ambient temp (°C)</th>
<th>Relative humidity (%)</th>
<th>Maxima NOx and CO, ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Avg.</td>
<td>Range</td>
<td>Avg.</td>
<td>Range</td>
</tr>
<tr>
<td>A</td>
<td>June 24-25</td>
<td>Regional Haze</td>
<td>84</td>
<td>26-132</td>
<td>29.8</td>
<td>23.7-35.4</td>
</tr>
<tr>
<td>B</td>
<td>July 6-8</td>
<td>Canadian Smoke</td>
<td>-</td>
<td>-</td>
<td>25.6</td>
<td>19.7-33.8</td>
</tr>
<tr>
<td>C</td>
<td>July 18-19</td>
<td>Regional Haze</td>
<td>70</td>
<td>14-91</td>
<td>29</td>
<td>23.2-34.0</td>
</tr>
<tr>
<td>D</td>
<td>Aug. 12-14</td>
<td>Reg Haze + Local Traffic</td>
<td>76</td>
<td>22-122</td>
<td>29.2</td>
<td>21.6-35.6</td>
</tr>
<tr>
<td>E</td>
<td>Oct. 2-5</td>
<td>Regional Haze</td>
<td>35</td>
<td>1-57</td>
<td>24.8</td>
<td>17.5-30.4</td>
</tr>
<tr>
<td>F</td>
<td>Nov. 20-21</td>
<td>Local Traffic</td>
<td>2</td>
<td>0-6</td>
<td>8.4</td>
<td>3.1-14.5</td>
</tr>
</tbody>
</table>

1. Ozone mixing ratios represent measurements made between 10:00 and 20:00 hours.

---

**Episode durations:** 2 to 4 days  
**Summer haze:** high O$_3$, hot, low NOx & CO  
**Fall local sources:** low O$_3$, cool, high NOx & CO
Table 2. Concentrations of PM2.5 mass and major chemical species for 6 pollution episodes.

<table>
<thead>
<tr>
<th>Episode</th>
<th>Interval</th>
<th>PM2.5, µg/m³</th>
<th>Constituent expressed as indicated, µg/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>TEOM</td>
<td>(NH₄)₂SO₄</td>
</tr>
<tr>
<td>A</td>
<td>Episode Avg.¹</td>
<td>N/A</td>
<td>55¹, 62²</td>
</tr>
<tr>
<td>Regional Haze</td>
<td>Episode Range¹</td>
<td>N/A</td>
<td>43 - 77</td>
</tr>
<tr>
<td>Bkgnd³</td>
<td>N/A</td>
<td>24</td>
<td>8.3</td>
</tr>
<tr>
<td>Bkgnd Range</td>
<td></td>
<td>22 - 27</td>
<td>5.8 - 10</td>
</tr>
<tr>
<td>B</td>
<td>Episode Avg.¹</td>
<td>57¹, 86²</td>
<td>55¹, 82²</td>
</tr>
<tr>
<td>Canadian Smoke Episode Range¹</td>
<td></td>
<td>20 - 180</td>
<td>20 - 174</td>
</tr>
<tr>
<td>Bkgnd³</td>
<td>19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bkgnd Range</td>
<td></td>
<td>15 - 17</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>Episode Avg.¹</td>
<td>49¹, 52²</td>
<td>49¹, 53²</td>
</tr>
<tr>
<td>Regional Haze</td>
<td>Episode Range¹</td>
<td>24 - 72</td>
<td>23</td>
</tr>
<tr>
<td>Bkgnd³</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bkgnd Range</td>
<td></td>
<td>12 - 37</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>Episode Avg.¹</td>
<td>42¹, 57²</td>
<td>8.9 - 52²</td>
</tr>
<tr>
<td>Regional Haze + Local Traffic</td>
<td>Episode Range¹</td>
<td>36 - 73</td>
<td>11</td>
</tr>
<tr>
<td>Bkgnd³</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bkgnd Range</td>
<td></td>
<td>9.8 - 12</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>Episode Avg.¹</td>
<td>35¹, 35²</td>
<td>6.5 - 22</td>
</tr>
<tr>
<td>Regional Haze</td>
<td>Episode Range¹</td>
<td>8.9 - 52²</td>
<td></td>
</tr>
<tr>
<td>Bkgnd³</td>
<td>12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bkgnd Range</td>
<td></td>
<td>6.5 - 22</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>Episode Avg.¹</td>
<td>32¹, 32²</td>
<td>34¹, 32²</td>
</tr>
<tr>
<td>Local Traffic</td>
<td>Episode Range¹</td>
<td>9.1 - 87</td>
<td>14.5 - 83</td>
</tr>
<tr>
<td>Bkgnd³</td>
<td>9.6</td>
<td></td>
<td>4.7</td>
</tr>
<tr>
<td>Bkgnd Range</td>
<td></td>
<td>7.8 - 12</td>
<td>13 - 14</td>
</tr>
</tbody>
</table>

¹Average concentration during period of elevation
²Highest midnight to midnight (24-hr) average during episode
³Average before and after episode
⁴Estimated, see text.

PM2.5, µg/m³
- **bkgnd mean**
  - *Summer* ~20 ~60
  - *Fall* ~14 ~34

- **Summer** more sulfate
- **Fall** comparable OM
- **Fall** more EC, nitrate
<table>
<thead>
<tr>
<th>Episode</th>
<th>Interval¹</th>
<th>(NH₄)₂SO₄²⁻</th>
<th>Constituent, %</th>
<th>OM²</th>
<th>EC</th>
<th>NH₄NO₃²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Episode Avg.</td>
<td>65</td>
<td>29</td>
<td>2.3</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Episode Range</td>
<td>54 - 78</td>
<td>20 - 34</td>
<td>1.0 - 5.3</td>
<td>1.1 - 9.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Bkgnd</td>
<td>37</td>
<td>51</td>
<td>4.7</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Bkgnd Range</td>
<td>30 - 43</td>
<td>32 - 59</td>
<td>2.6 - 8.5</td>
<td>1.3 - 1.5</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>Episode Avg.</td>
<td>13</td>
<td>81</td>
<td>3</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Episode Range</td>
<td>3.8 - 30</td>
<td>65 - 92</td>
<td>1.4 - 6.2</td>
<td>1.2 - 9.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Bkgnd</td>
<td>25</td>
<td>70</td>
<td>2.8</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Bkgnd Range</td>
<td>15 - 36</td>
<td>60 - 81</td>
<td>2.6 - 3.0</td>
<td>1.2 - 1.7</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>Episode Avg.</td>
<td>71</td>
<td>25</td>
<td>2.1</td>
<td>2.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Episode Range</td>
<td>46 - 79</td>
<td>19 - 50</td>
<td>1.1 - 6.3</td>
<td>1.0 - 6.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Bkgnd</td>
<td>42</td>
<td>48</td>
<td>4.9</td>
<td>6.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Bkgnd Range</td>
<td>19 - 67</td>
<td>25 - 64</td>
<td>1.9 - 18</td>
<td>1.7 - 19</td>
<td></td>
</tr>
</tbody>
</table>

¹Averages reflect periods when concentrations were elevated. Background values represent compositions before and after the episode.
²Estimated; see text.
# Table 3, continued.

<table>
<thead>
<tr>
<th>Episode</th>
<th>Interval¹</th>
<th>(NH₄)₂SO₄²</th>
<th>Constituent, %</th>
<th>OM²</th>
<th>EC</th>
<th>NH₄NO₃²</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>Episode Avg.</td>
<td>49</td>
<td>42</td>
<td>3.8</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Episode Range</td>
<td>22 - 71</td>
<td>26 - 62</td>
<td>1.6 - 9.3</td>
<td>1.1 - 16</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Bkgnd</td>
<td>34</td>
<td>56</td>
<td>5.6</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Bkgnd Range</td>
<td>24 - 42</td>
<td>50 - 62</td>
<td>5.0 - 6.5</td>
<td>3.0 - 8.2</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>Episode Avg.</td>
<td>62</td>
<td>27</td>
<td>6</td>
<td>5.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Episode Range</td>
<td>47 - 77</td>
<td>19 - 34</td>
<td>2.9 - 11</td>
<td>1.4 - 13</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Bkgnd</td>
<td>44</td>
<td>44</td>
<td>6.4</td>
<td>5.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Bkgnd Range</td>
<td>30 - 55</td>
<td>38 - 51</td>
<td>3.7 - 11</td>
<td>2.2 - 12</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>Episode Avg.</td>
<td>22</td>
<td>41</td>
<td>9.6</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Episode Range</td>
<td>12 - 31</td>
<td>27 - 65</td>
<td>4.2 - 17</td>
<td>7.8 - 42</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Bkgnd</td>
<td>34</td>
<td>35</td>
<td>6.9</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Bkgnd Range</td>
<td>29 - 37</td>
<td>34 - 37</td>
<td>6.6 - 7.6</td>
<td>20 - 30</td>
<td></td>
</tr>
</tbody>
</table>

¹Averages reflect periods when concentrations were elevated. Background values represents compostions before and after the episodoe.
²Estimated; see text.
PM Episode A
June 24-26, 2002

Summer Haze Episode, dominated by Sulfate, OM
Influence of Local sources evident
Episode A: June 24-25: Sulfate Haze Event

Worst Episode in 9.5 month study (except Canadian Smoke)

Aged Local, regional, fresh local components

- Local power plants
  44 - 31 = 13 µg/m³
- Inter-regional transport
  31 - 6 = 25 µg/m³
- Aged Local,
  24 - 6 = 18 µg/m³
- Bkgnd, 6 µg/m³

18:00 06/25

1.5 hrs after local winds shift to 170° at 3m/s = 16.2 km/h

Local power plant 15 km plumes raise sulfate concs.

Aged secondary accumulation mode

Bkgnd, 6 µg/m³

Fresh power plant accumulation mode
Some important points

• Arguably, sources in the local region contributed substantial amounts of sulfate on day 1
• Arrival of polluted air mass increases sulfate 7x relative to background on day 2
• OC increase only 1.5x over background, to 10 µg/m³.

Whereas for Episode F, local (traffic) induces 3x increase in OC!
Influence of Traffic

revealed by
characteristic size spectra, diurnal profiles
show
EC, OC, Nitrate from traffic emissions heavily influence
PM2.5 in cool, moist, low-mixing height periods
i.e., Fall, Winter, Night time
LA: Size Distributions for motor vehicle traffic

3 narrow modes in ultrafine size range

30 m downwind - trimodal

Size distribution indistinguishable from upwind at 300 m downwind

Evolution w/distance

Fresh automobile aerosol Peaks

Modal diameter changes with distance due to evaporation/condensation of volatiles

Source: LA Supersite/PM center, Sioutas
Baltimore: Ultrafine particles indicate traffic in AM
Any day, most any wind direction!
Less pronounced in afternoon, longer rush hour, greater mixing height and wind speeds

**Monday**
Feb 18

**Tuesday**
Feb 19

**Wednesday**
Feb 20

**Thursday**
Feb 21

**Friday**
Feb 22

10:00 PM

Monday morning Holiday

Leaving work early
Baltimore Ponca St: EC – Strong Diurnal Cycles
*Peaks correspond to morning Traffic*

Even in August

**Average daily profile (9.5 months)**

**OC:EC ratio increases evenings & early AM**

**Night-time chemistry?**
Baltimore Air is Heavily influenced by Traffic
(Especially in Fall/Winter/Spring months)

Ultrafine particles peak at morning rush hour (6:00 – 9:00 AM)
E-SE winds

OC & EC highly correlated w/morning traffic peak

OC a substantial fraction of PM2.5

OC highly correlated w/TEOM
Nitrate is more complicated

NOx converted to nitrate 10x faster than SO₂ to sulfate, therefore local sources much more important for nitrate

NH₄NO₃ dissociation equilibrium favors nitrate at low T, high RH

Night time radical chemistry forms nitric acid from NO₂ when temperatures are typically cooler and RH higher
Monthly trend of Nitrate concentration at Ponca

Lower concentrations in summer when ammonium nitrate more volatile
“Pure” Nitrate particles correlate with PM2.5 Nitrate peaks:
occur at high RH, low temperatures

#concentration ("pure nitrate"
50~90nm particle)

RSMSIII

R&P 8400N

These data suggest that much of the nitrate is formed by nucleation of new particles!

Tolocka et al., Submitted
But other times – much forms on “droplet” mode

Fraction of Particles in Nitrate Class vs. Size / Time of Day

Nitrate Class April 16th, 2002

Percentage of Total Spectra

- 10.0%-11.0%
- 9.0%-10.0%
- 8.0%-9.0%
- 7.0%-8.0%
- 6.0%-7.0%
- 5.0%-6.0%
- 4.0%-5.0%
- 3.0%-4.0%
- 2.0%-3.0%
- 1.0%-2.0%
- 0.0%-1.0%
Weekend patterns

Saturday
Feb. 23

Saturday night entertainment traffic or Night time chemistry?

Sunday
Feb. 24

Bars close 2:00 AM
Locally Produced Nitrate concentrations frequently observed at 30° and at wind speeds 0 to 1 m/s

Example: March 23 – 25 data

Park et al., Atmos. Environ. 39:2011, 2005:
32% of Nitrate transients were > 1 µg/m³
64% with high/NOx between 5 – 8 AM
26% between 10 PM – 2 AM
Episode F: November 20, 21
Cool Temperatures, Morning RH >90%
Winds light, variable on 20th,
Winds light, 30°, very high RH, on 21st
Episode F: November 20, 21

- Cool Temperatures, Stagnation, High RH, morning traffic peak;
- Nitrate deposits on wet particles;
- Winds from 30° all day on 21st

Highest PM2.5 max

Nitrate (lags NOx)

No obvious power plant influence; mixing hgt too low
Episode F: well correlated EC, OC, PM2.5 (Local traffic): Max conc

Winter stagnation (OC + EC)

Episode F

TEOM (µg/m³) = 7.39 EC (µg/m³) + 13.92  R²=0.85
TEOM (µg/m³) = 2.57 OC (µg/m³) + 10.53  R²=0.88
Summary

• 24-hr PM2.5 standard rarely exceeded during 2002 at Ponca st. – Episode A, max 24-hr PM2.5 was ~65 ug/m³
• 9.5-month 30-min average barely exceeded annual PM2.5 standard.
• Episodes occur during periods of stability/stagnation
  Summer episodes caused by stationary fronts; end by break by passage of cold fronts
• Local sources – traffic; So. Baltimore industry; and local regional sources contribute substantially, to EC, OC, Nitrate, especially in fall, winter, spring
• Major summer haze events; dominated by sulfate & OC – worst event after air stagnant over Ohio Valley arrived in Baltimore w/local wind direction from So. Baltimore; but Local So. Baltimore sources contributed ≥5% of PM2.5 – enough to trip standard
• Urban traffic corridor creates PM “hot spots.”