Ambient Fine Aerosol Measurements and Seasonal Positive Matrix Factorization (PMF) Analysis of Organic Aerosol in Downtown Atlanta, Georgia using the Aerodyne Aerosol Chemical Speciation Monitor (ACSM)

13th Annual AMS Users Meeting, 2012

Sri Hapsari Budisulistiorini1, Manjula R. Canagaratna2, Philip L. Croteau2, Wendy J. Marth1, Karsten Baumann3, Eric S. Edgerton3, Stephanie L. Shaw4, Eladio M. Knipping5, John Jansen6, Roger L. Tanner7, Douglas R. Worsnop2, John T. Jayne2, Avram Gold1 and Jason D. Surratt1,*

1Department of Environmental Sciences and Engineering, Gillings School of Global Public Health, The University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599, USA
2Aerodyne Research, Inc., Billerica, Massachusetts 01821, USA
3Atmospheric Research & Analysis, Inc., Cary, North Carolina 27513, USA
4Electric Power Research Institute, Palo Alto, California, USA
5Electric Power Research Institute, Washington, DC, USA
6Southern Company, 600 N. 18th St., P.O. Box 2641, Birmingham, AL 35291-8195
7Environmental Technologies, Tennessee Valley Authority, CEB 1C, P.O. Box 1010, Muscle Shoals, Alabama 35662, USA
Sampling Location

Southeastern Aerosol Research and Characterization (SEARCH) Network

Jefferson Street (JST) site
- Mixed industrial-residential area
- ~4.2 km northwest of downtown Atlanta
- Collocated measurements:
  - 24-hr: PM$_{2.5}$ filter samples, PM$_{10}$ & gaseous ammonia
  - Continuous: particles, gaseous & meteorological conditions

ACSM operation:
- Sampling inlet: PM$_{2.5}$ cyclone
- Sample drying: 50-tube Nafion dryer (Perma Pure PD-50T-24)
- Sampling flow rate: 3 L min$^{-1}$
- Data analysis:
  - CE = 0.5
  - acsm_local_1443

http://www.atmospheric-research.com/studies/SEARCH/
Total organic aerosol (OA) is on average $11.2 \pm 4.8$ (μg m$^{-3}$)
Summer 2011 PMF Analysis

External Independent Measurements

- CO
- EC
- NOx

- NO3⁻
- O₅=NO₂+O₃

- SO₄²⁻
- NH₄⁺

- SO₄²⁻
- NO

Factor’s Time Series

- r ~0.8

Factor’s Mass Spectra

- r ~0.8
- HOA
- NO3⁻
- O₅=NO₂+O₃

- r ~0.9
- SO₄²⁻
- NH₄⁺

- r ~0.9
- LV
- IEPOX

- r ~0.8
- IEPOX-OA
- m/z
IEPOX Chemistry

(Paulot et al., 2009; Surratt et al., 2010; Lin et al., 2012)

(Surratt et al., 2010; Chan et al., 2010)
IEPOX-OA Factor vs. BSOA Tracers

IEPOX-OA is strongly correlated with individual IEPOX-derived SOA tracers

IEPOX-OA is not well correlated with \( \alpha \)-pinene and biomass burning tracers

IEPOX-OA is strongly correlated with sum of IEPOX-derived SOA tracers
IEPOX-OA Factor vs. IEPOX-derived SOA Mass Spectra

$m/z$ 82 can be associated with IEPOX-OA factor
Total OA is on average $10.1 \pm 8.9$ (μg m$^{-3}$)
Fall 2011 PMF Analysis

External Independent Measurements

- CO
- EC
- NO\textsubscript{x}
- NO\textsubscript{3}^{-}
- O\textsubscript{x}=NO\textsubscript{2}+O\textsubscript{3}
- SO\textsubscript{4}\textsuperscript{2-}
- NH\textsubscript{4}^{+}

Factor’s Time Series

- COEC vs. NO\textsubscript{x}
- r \approx 0.9

Factor’s Mass Spectra

- NO\textsubscript{x} vs. O\textsubscript{x}=NO\textsubscript{2}+O\textsubscript{3}
- SO\textsubscript{4}\textsuperscript{2-} vs. NH\textsubscript{4}^{+}

Avg. total PMF factors = 11.1 ± 10 \, \mu g \, m^{-3}
Avg. HOA = 3.9 ± 7.2 \, \mu g \, m^{-3}
Avg. SV-OOA = 5.1 ± 4.2 \, \mu g \, m^{-3}
Avg. LV-OOA = 2.1 ± 1.1 \, \mu g \, m^{-3}
PMF Factors are not well correlated to BBOA and/or IEPOX-derived SOA tracers
Winter 2011 NR-PM$_1$

Total OA is on average 6.9 ± 6.5 (μg m$^{-3}$)

Note: JST unadjusted continuous data
Winter 2011 PMF Analysis

External Independent Measurements

- CO
- EC
- NO\textsubscript{x}
- NO\textsubscript{3}^-
- O\textsubscript{x}=NO\textsubscript{2}+O\textsubscript{3}
- SO\textsubscript{4}^{2-}
- NH\textsubscript{4}^+

Factor’s Time Series

<table>
<thead>
<tr>
<th>Mass Concentration (µg m\textsuperscript{-3})</th>
<th>r \approx 0.9</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="graph.png" alt="Graph" /></td>
<td></td>
</tr>
</tbody>
</table>

Factor’s Mass Spectra

<table>
<thead>
<tr>
<th>Mass (m/z)</th>
<th>HOA</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="graph.png" alt="Graph" /></td>
<td></td>
</tr>
<tr>
<td>Mass (m/z)</td>
<td>SV-OOA</td>
</tr>
<tr>
<td><img src="graph.png" alt="Graph" /></td>
<td></td>
</tr>
<tr>
<td>Mass (m/z)</td>
<td>LV-OOA</td>
</tr>
<tr>
<td><img src="graph.png" alt="Graph" /></td>
<td></td>
</tr>
</tbody>
</table>

Avg. total PMF factors = 7.6 ± 7.4 µg m\textsuperscript{-3}
Avg. HOA = 2.0 ± 3.7 µg m\textsuperscript{-3}
Avg. SV-OOA = 3.3 ± 4.0 µg m\textsuperscript{-3}
Avg. LV-OOA = 2.2 ± 1.1 µg m\textsuperscript{-3}

HOA & LV-OOA decrease while SV-OOA increases
Total OA is on average $8.1 \pm 3.9$ (μg m$^{-3}$)

Problem in nitrogen-species measurement
Spring 2012 PMF Analysis

External Independent Measurements

Factor’s Time Series

Factor’s Mass Spectra

COEC

NO\textsubscript{x}

\textsubscript{SO}_4\textsuperscript{2-}

\textsubscript{NH}_4\textsuperscript{+}

\textsubscript{NO}_3\textsuperscript{-}

O\textsubscript{x}=\textsubscript{NO}_2+\textsubscript{O}_3

\textsubscript{NO}_3

\textsubscript{O}_x=\textsubscript{NO}_2+\textsubscript{O}_3

\textsubscript{SO}_4\textsuperscript{2-}

\textsubscript{NH}_4\textsuperscript{+}

r \sim 0.8

Avg. total PMF factors = 9.2 \pm 4.6 \mu g m^{-3}

Avg. HOA = 1.5 \pm 1.9 \mu g m^{-3}

Avg. SV-OOA = 4.5 \pm 3.3 \mu g m^{-3}

Avg. LV-OOA = 3.2 \pm 1.0 \mu g m^{-3}

Both SV-OOA & LV-OOA do not show significant peak of \textit{m/z} 82 \rightarrow variation was not detected?
Diurnal Variations

Summer 2011

Fall 2011

Spring 2012

Winter 2011

Anthropogenic emission & inorganic fractions influence HOA & SV-OOA
PMF Factors Relative Contribution to OA

Warmer months: biogenic SOA factor was detected & LV-OOA increases

Colder months: SV-OOA is dominant & HOA increases
Questions remain

• CE & RIE changed seasonally?

• Detection limit shifted?

• Can shorter-term PMF analysis better capture the transition of biogenic SOA?

• O/C parameterization from AMS (Aiken et al., 2008) for ACSM?
Summary

1. ACSM has overall fine performance for continuous 1-year long sampling
   • Good correlation with collocated measurements but absolute concentrations are off for certain species

2. Seasonal PMF analysis suggest that
   • Significant increase of POA, represented as HOA factor, was observed during cold season, i.e., fall and winter.
   • SOA, represented as sum of OOA factors, is dominant for the entire year (all four seasons).
   • BVOC influences in SOA, observed as IEPOX-OA factor, was found only during summer season when isoprene is abundant.
   • Biomass burning influence in SOA was not detected which probably because the smoke did not arrive at JST site, or it dissipated along the way

3. Biogenic factor(s) cannot be resolved in PMF analysis
Acknowledgements

University of North Carolina at Chapel Hill
• Dr. Jason Surratt (PhD Advisor)
• Dr. Avram Gold
• Dr. Zhenfa Zhang
• Wendy Marth

Electric Power Research Institute (EPRI)
• Dr. Stephanie Shaw
• Dr. Eladio Knipping

Aerodyne Research, Inc.
• Dr. John Jayne
• Dr. Doug Worsnop
• Dr. Manjula Canagaratna
• Dr. Philip Croteau
• Dr. Nga L. Ng (now at GA Tech)

Atmospheric Research & Analysis, Inc. (ARA)
• Dr. Karsten Baumann
• Eric Edgerton

Funding
Additional Slides
### Summer 2011 PMF Factors Correlation with External Data (JST Level2)

<table>
<thead>
<tr>
<th></th>
<th>IEPOX-OA</th>
<th>LV-OOA</th>
<th>SV-OOA</th>
<th>HOA</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_{TS}^+$ CO</td>
<td>0.27</td>
<td>-0.01</td>
<td>0.35</td>
<td>0.78 Primary</td>
</tr>
<tr>
<td>EC</td>
<td>0.21</td>
<td>0.00</td>
<td>0.39</td>
<td>0.83 Primary</td>
</tr>
<tr>
<td>NO$_x$</td>
<td>0.07</td>
<td>-0.06</td>
<td>0.17</td>
<td>0.83 Primary</td>
</tr>
<tr>
<td>NO$_y$</td>
<td>0.12</td>
<td>-0.04</td>
<td>0.19</td>
<td>0.85 Primary + Secondary</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>0.67</td>
<td>0.46</td>
<td>0.14</td>
<td>0.09 Secondary</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>0.65</td>
<td>0.48</td>
<td>0.22</td>
<td>0.07 Secondary</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>0.20</td>
<td>-0.12</td>
<td>0.26</td>
<td>0.63 Secondary</td>
</tr>
<tr>
<td>O$_x$ (=O$_3$+NO$_2$)</td>
<td>0.31</td>
<td>0.30</td>
<td>0.16</td>
<td>-0.36 Secondary</td>
</tr>
<tr>
<td>$r_{MS}^\dagger$ IEPOX SOA</td>
<td>0.86</td>
<td>0.66</td>
<td>0.71</td>
<td>0.30 Laboratory ACSM-1</td>
</tr>
<tr>
<td></td>
<td>0.82</td>
<td>0.57</td>
<td>0.66</td>
<td>0.32 Laboratory ACSM-2</td>
</tr>
<tr>
<td></td>
<td>0.78</td>
<td>0.44</td>
<td>0.59</td>
<td>0.37 Laboratory ACSM-3</td>
</tr>
<tr>
<td>HOA</td>
<td>0.64</td>
<td>0.32</td>
<td>0.62</td>
<td>0.73 Pittsburgh$^2$</td>
</tr>
<tr>
<td>OOA-1</td>
<td>0.89</td>
<td>0.90</td>
<td>0.91</td>
<td>0.17 Pittsburgh$^2$</td>
</tr>
<tr>
<td>OOA-2</td>
<td>0.81</td>
<td>0.78</td>
<td>0.87</td>
<td>0.54 Pittsburgh$^2$</td>
</tr>
<tr>
<td>HOA</td>
<td>0.53</td>
<td>0.23</td>
<td>0.51</td>
<td>0.78 Urban AMS$^3$</td>
</tr>
<tr>
<td>LV-OOA</td>
<td>0.84</td>
<td>0.93</td>
<td>0.89</td>
<td>0.15 Urban AMS$^3$</td>
</tr>
<tr>
<td>SV-OOA</td>
<td>0.86</td>
<td>0.60</td>
<td>0.89</td>
<td>0.50 Urban AMS$^3$</td>
</tr>
<tr>
<td>Honda emission</td>
<td>0.47</td>
<td>0.22</td>
<td>0.48</td>
<td>0.78 Laboratory AMS$^4$</td>
</tr>
<tr>
<td>Diesel emission</td>
<td>0.47</td>
<td>0.20</td>
<td>0.47</td>
<td>0.80 Laboratory AMS$^4$</td>
</tr>
</tbody>
</table>

$^\dagger$ $r_{TS}$: correlation coefficient of the PMF factor time series and the collocated particle measurement

$^\ddagger$ $r_{MS}$: correlation coefficient of the PMF factor mass spectra and the reference mass spectra from previous studies and ACSM
Summer PMF Evaluation Plots

(a) Q/Q_{exp} vs Number of Factors

(b) Q/Q_{exp} vs FPEAK

(c) Mass Frac. vs FPEAK

(d) FTime Series

(e) Mass Conc. (µg m^{-3}) vs Date and Time (Local)

(f) Residual = measured - reconstructed

(g) Q/Q_{exp} contribution for each time step

(h) Q/Q_{exp} contribution for each fragment ion

(i) Boxes are ± 25% of points
### Fall 2011 PMF Factors Correlation with External Data (JST Level2)

<table>
<thead>
<tr>
<th></th>
<th>LV-OOA</th>
<th>SV-OOA</th>
<th>HOA</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>r_{TS}^†</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>0.44</td>
<td>0.39</td>
<td><strong>0.92</strong> Primary</td>
</tr>
<tr>
<td>EC</td>
<td>0.48</td>
<td>0.47</td>
<td><strong>0.91</strong> Primary</td>
</tr>
<tr>
<td>NO_x</td>
<td>0.38</td>
<td>0.34</td>
<td><strong>0.94</strong> Primary</td>
</tr>
<tr>
<td>NO_y</td>
<td>0.39</td>
<td>0.36</td>
<td><strong>0.94</strong> Primary + Secondary</td>
</tr>
<tr>
<td>SO_4^2-</td>
<td>0.35</td>
<td>0.24</td>
<td>0.62 Secondary</td>
</tr>
<tr>
<td>NH_4^+</td>
<td><strong>0.39</strong></td>
<td>0.36</td>
<td>0.15 Secondary</td>
</tr>
<tr>
<td>NO_3^-</td>
<td>0.39</td>
<td><strong>0.23</strong></td>
<td>0.36 Secondary</td>
</tr>
<tr>
<td>O_x (=O_3+NO_2)</td>
<td>0.17</td>
<td><strong>0.14</strong></td>
<td>-0.15 Secondary</td>
</tr>
<tr>
<td><strong>r_{MS}‡</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HOA</td>
<td>0.27</td>
<td>0.67</td>
<td>0.92 Pittsburgh^2</td>
</tr>
<tr>
<td>OOA-1</td>
<td>0.90</td>
<td>0.92</td>
<td>0.22 Pittsburgh^2</td>
</tr>
<tr>
<td>OOA-2</td>
<td>0.73</td>
<td>0.84</td>
<td>0.62 Pittsburgh^2</td>
</tr>
<tr>
<td>HOA</td>
<td>0.17</td>
<td>0.55</td>
<td>0.97 Urban AMS^3</td>
</tr>
<tr>
<td>LV-OOA</td>
<td>0.94</td>
<td>0.87</td>
<td>0.16 Urban AMS^3</td>
</tr>
<tr>
<td>SV-OOA</td>
<td>0.55</td>
<td>0.92</td>
<td>0.65 Urban AMS^3</td>
</tr>
<tr>
<td>BBOA</td>
<td>0.53</td>
<td>0.82</td>
<td>0.68 Urban AMS^3</td>
</tr>
<tr>
<td><strong>Honda emission</strong></td>
<td>0.15</td>
<td>0.50</td>
<td>0.96 Laboratory AMS^4</td>
</tr>
<tr>
<td><strong>Diesel emission</strong></td>
<td>0.13</td>
<td>0.49</td>
<td>0.98 Laboratory AMS^4</td>
</tr>
</tbody>
</table>

^† r_{TS} : correlation coefficient of the PMF factor time series and the collocated particle measurement

‡ r_{MS} : correlation coefficient of the PMF factor mass spectra and the reference mass spectra from previous studies and ACSM
Fall PMF Evaluation Plots

- **Plot (a)**: Graph showing Q/Q_{exp} vs. Number of Factors.
- **Plot (b)**: Graph showing Q/Q_{exp} vs. FPEAK.
- **Plot (c)**: Mass Fraction of Residual LV-OOA, SV-OOA, and HOA.
- **Plot (d)**: Time series graph with mass spectra.
- **Plot (e)**: Mass concentration comparison between measured and reconstructed total mass.
- **Plot (f)**: Residual = measured - reconstructed.
- **Plot (g)**: Q/Q_{exp} contribution for each time step.
- **Plot (h)**: Q/Q_{exp} contribution for each fragment ion.
- **Plot (i)**: Scaled residual graph with m/z values.
### Winter 2011 PMF Factors Correlation with External Data (JST Level1)

<table>
<thead>
<tr>
<th></th>
<th>LV-OOA</th>
<th>SV-OOA</th>
<th>HOA</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r_{TS} ^)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>0.12</td>
<td>0.61</td>
<td>0.86</td>
</tr>
<tr>
<td>EC</td>
<td>0.18</td>
<td>0.73</td>
<td>0.87</td>
</tr>
<tr>
<td>( NO_x )</td>
<td>0.03</td>
<td>0.56</td>
<td>0.90</td>
</tr>
<tr>
<td>( NO_y )</td>
<td>0.02</td>
<td>0.55</td>
<td>0.89</td>
</tr>
<tr>
<td>( SO_4^{2-} )</td>
<td>0.25</td>
<td>0.06</td>
<td>0.11</td>
</tr>
<tr>
<td>( NH_4^+ )</td>
<td>0.42</td>
<td>0.22</td>
<td>0.11</td>
</tr>
<tr>
<td>( NO_3^- )</td>
<td>0.43</td>
<td>0.48</td>
<td>0.32</td>
</tr>
<tr>
<td>( O_3 (=O_3+NO_2) )</td>
<td>0.14</td>
<td>0.17</td>
<td>0.08</td>
</tr>
<tr>
<td>( r_{MS} ^)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HOA</td>
<td>0.27</td>
<td>0.67</td>
<td>0.92</td>
</tr>
<tr>
<td>OOA-1</td>
<td>0.90</td>
<td>0.92</td>
<td>0.22</td>
</tr>
<tr>
<td>OOA-2</td>
<td>0.73</td>
<td>0.84</td>
<td>0.62</td>
</tr>
<tr>
<td>HOA</td>
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<td>0.55</td>
<td>0.97</td>
</tr>
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<tr>
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<tr>
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<td>0.49</td>
<td>0.98</td>
</tr>
</tbody>
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\( r_{TS} \): correlation coefficient of the PMF factor time series and the collocated particle measurement

\( r_{MS} \): correlation coefficient of the PMF factor mass spectra and the reference mass spectra from previous studies and ACSM
Winter PMF Evaluation Plots

Plots:

(a) Number of Factors
(b) FPEAK
(c) Mass Fraction
(d) Time Series
(e) Mass Conc. (μg m⁻³)
(f) Residual = measured - reconstructed
(g) Q/Q_{exp} contribution for each time step
(h) Q/Q_{exp} contribution for each fragment ion
(i) Scaled Residual

Mass Spectra

Date and Time (Local)

1/10/2012
1/30/2012
2/19/2012

Boxes are ± 25% of points

m/z
## Spring 2012 PMF Factors Correlation with External Data (JST Level1)

<table>
<thead>
<tr>
<th></th>
<th>LV-OOA</th>
<th>SV-OOA</th>
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<tbody>
<tr>
<td>$r_{TS}^+$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>-0.07</td>
<td>0.43</td>
<td>0.81</td>
</tr>
<tr>
<td>EC</td>
<td>-0.12</td>
<td>0.40</td>
<td>0.80</td>
</tr>
<tr>
<td>$NO_x$</td>
<td>-0.23</td>
<td>0.25</td>
<td>0.88</td>
</tr>
<tr>
<td>$NO_y$</td>
<td>-0.21</td>
<td>0.27</td>
<td>0.88</td>
</tr>
<tr>
<td>$SO_4^{2-}$</td>
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<td>0.50</td>
<td>0.13</td>
</tr>
<tr>
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<td>0.28</td>
<td>0.26</td>
</tr>
<tr>
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<td>0.26</td>
<td>0.19</td>
</tr>
<tr>
<td>$O_x (=O_3+NO_2)$</td>
<td>0.41</td>
<td>0.13</td>
<td>-0.22</td>
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<tr>
<td>$r_{MS}^+$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HOA</td>
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<td>0.65</td>
</tr>
<tr>
<td>BBOA</td>
<td>0.53</td>
<td>0.82</td>
<td>0.68</td>
</tr>
<tr>
<td>Honda emission</td>
<td>0.15</td>
<td>0.50</td>
<td>0.96</td>
</tr>
<tr>
<td>Diesel emission</td>
<td>0.13</td>
<td>0.49</td>
<td>0.98</td>
</tr>
</tbody>
</table>

* $r_{TS}$: correlation coefficient of the PMF factor time series and the collocated particle measurement
* $r_{MS}$: correlation coefficient of the PMF factor mass spectra and the reference mass spectra from previous studies and ACSM
Spring PMF Evaluation Plots

(a) Q/Q_{exp} vs. Number of Factors

(b) Q/Q_{exp} vs. F_{PEAK}

(c) Mass Fraction of Residual LV-OOA, SV-OOA, HOA

(d) Residual Mass Spectra

(e) Measured Total Mass vs. Reconstructed Total Mass

(f) Residual = measured - reconstructed

(g) Q/Q_{exp} contribution for each time step

(h) Q/Q_{exp} contribution for each fragment ion

(i) Scaled Residual m/z vs. 25% of points