Recent Source Apportionment Analyses and Understanding Differences in STN and IMPROVE Data

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Background

- EPA established STN to characterize urban PM$_{2.5}$ and to assist identifying out-of-attainment area of new NAAQS.

- Advanced source apportionment studies are needed for identifying source, developing effective control strategies, and source-specific adverse health effect studies.

- STN data have major challenges due to the way the samples have been analyzed.
Challenges in STN data

- OC concentrations were not blank corrected.
- 4 different types of samplers, 3 carbon analyzers, 2 ICs for anions, 3 ICs for cations, 5 XRFs for metals were used.
- Method detection limits (MDL) and uncertainties were not reported.
Outline

- OC blank corrections
- Error structure estimation for the source apportionment study, i.e. PMF
- NJ source apportionment studies
- Gasoline vs diesel emissions in STN and IMPROVE
Since trip and field blank values were below MDL, STN data were not blank corrected.

Tolocka et al. (Aerosol Sci. Technol. 2001) reported a positive artifact in STN OC from the comparison among STN, FRM, and VAPS samplers.

For the integrated OC blank conc., Tolocka et al. approach was tested using 13 STN data measured at NY, NJ, VT.

The intercepts of the regression of OC against PM$_{2.5}$ are considered to be integrated OC blank conc.

- Reported STN OC was blank corrected by subtracting estimated OC blank conc.

PM$_{2.5}$ mass concentrations versus OC concentrations for four STN sites.
OC Blank Correction

- Rural sites have lower OC blank conc.
- Urban areas have higher OC blank conc.
- Indication of the positive artifact from the adsorption of gaseous organic matter by quartz filters

<table>
<thead>
<tr>
<th>Monitoring site</th>
<th>OC blank (µg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Burlington, VT</td>
<td>1.83</td>
</tr>
<tr>
<td>Whiteface, NY</td>
<td>1.02</td>
</tr>
<tr>
<td>Rochester, NY</td>
<td>1.67</td>
</tr>
<tr>
<td>Buffalo, NY</td>
<td>1.44</td>
</tr>
<tr>
<td>Pinnacle State Park, NY</td>
<td>1.25</td>
</tr>
<tr>
<td>NY Botanical Garden, NY</td>
<td>1.41</td>
</tr>
<tr>
<td>IS52, NY</td>
<td>1.85</td>
</tr>
<tr>
<td>Canal St., NY</td>
<td>2.44</td>
</tr>
<tr>
<td>Queens College, NY</td>
<td>1.57</td>
</tr>
<tr>
<td>Chester, NJ</td>
<td>1.35</td>
</tr>
<tr>
<td>New Brunswick, NJ</td>
<td>1.49</td>
</tr>
<tr>
<td>Camden, NJ</td>
<td>1.65</td>
</tr>
<tr>
<td>Elizabeth Lab., NJ</td>
<td>2.19</td>
</tr>
</tbody>
</table>
PMF analysis depends on the estimated uncertainty for each of the measured conc.

Comprehensive set of error structure for the PMF studies are required.

General fractional error was estimated by comparing available conc. and associated analytical errors.

The comparison between measured conc. and associated uncertainties, and estimated error structure
Positive Matrix Factorization (PMF)

- General receptor modeling problem

\[ X = GF + E \]

- PMF uses variations in PM composition over time to extract features

- PMF can deduce source profiles as well as source contributions (Paatero, P. Chemom.Intell.Lab.Syst. 1997)

**X**: a data matrix with \( n \) samples and \( m \) size intervals

**G**: a factor contribution matrix with \( n \) samples and \( p \) factors

**F**: a factor profile matrix with \( m \) size intervals and \( p \) factors

**E**: a residual matrix
Conditional Probability Function (CPF)

- Analyzing source contribution versus wind direction
- Probability that a given factor contribution from a given wind direction will exceed a predetermined threshold criterion (upper 25% of contribution)

\[
CPF_{\Delta \theta} = \frac{m_{\Delta \theta}}{n_{\Delta \theta}}
\]

- \( m_{\Delta \theta} \): number of occurrence from wind sector \( \Delta \theta \) that are upper 25% of source contributions
- \( n_{\Delta \theta} \): total number of occurrence from the same wind sector

- Sources are likely to be located in the directions that have high CPF values
Conditional Probability Function (CPF)

- Brigantine, NJ IMPROVE PM$_{2.5}$ study (Kim and Hopke, J. Geophys. Res. 2004)
To examine the use of estimated error structure, four NJ STN data were analyzed by PMF.

Six to eight sources including gasoline vehicle and diesel emissions were identified.
**NJ PMF studies**

- Elizabeth, NJ
- June 2001 – Nov. 2003
- 216 samples, 32 species
- PMF identified 8 sources including 3 motor vehicle sources

![Pie chart showing source contributions to PMF studies.](chart-image-url)
NJ PMF studies

- New Brunswick, NJ
  - Feb. 2001 – Nov. 2003
  - 235 samples, 28 species
  - PMF identified 8 sources including 3 motor vehicle sources
NJ PMF studies

- Camden, NJ
  - June 2001 – Sep. 2003
  - 146 samples, 29 species
  - PMF identified 7 sources including 2 motor vehicle sources
NJ PMF studies

- Chester, NJ
  - June 2001 – Nov. 2003
  - 140 samples, 28 species
  - PMF identified 6 sources including 2 motor vehicle sources
NJ PMF studies

- Source contributions of airborne soil
  - July 4, 2002 may be caused by Sahara dust storm
  - April 22, 2001 was likely Asian dust storm
NJ PMF studies

- Highway emissions at Elizabeth
  - Impacts from Highways 57 and 95

- Local motor vehicle at New Brunswick
  - Impacts from local road and tollgate
NJ PMF studies

- Aged sea salt at 3 sites
  - CPF plots indicate higher contributions of aged sea salt from the direction of Atlantic Ocean
Motor vehicle emissions

- Motor vehicle is a significant source of PM$_{2.5}$, and it would be useful if the diesel and gasoline vehicle emissions could be separated.

Previously, source apportionment studies with IMPROVE data including total OC/EC could not always separate diesel emissions from gasoline emissions. (Song et al., Atmos. Environ. 35, 2001)
PMF was applied to daily integrated ambient PM$_{2.5}$ compositional data including 8 carbon fractions collected at four monitoring sites across US: Washington, DC; Atlanta, GA; Seattle, WA; and Brigantine, NJ.

Motor vehicle emissions were separated into fractions identified as gasoline and diesel emissions containing carbon fractions whose abundances were different between the two sources.
Gasoline emissions include the lower temperature carbon fractions (OC1 - OC4). No weekday/weekend variation.
**IMPROVE Diesel emission**

- Diesel emissions contain large amounts of the EC1
- Strong weekday/weekend variation: mostly from vehicles operating on weekdays (delivery trucks, commuter buses)
Gasoline and diesel emissions were separated with STN OC/EC abundances between the two sources.

- Diesel emissions contain large amounts of EC.
- Diesel emissions have strong weekday/weekend variation.
Gasoline vs diesel emissions in STN

- Diesel emissions were not always separated with IMPROVE OC/EC

- We seem to be able more often to find ‘diesel’ signature with STN OC/EC

- This may be due to the STN OC/EC doing a better job of excluding refractory OC from EC (different temperature steps, reflectance vs transmittance)
Acknowledgment

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- Dr. Y. Qin