Source Apportionment of PM$_{2.5}$ at Three Urban Sites Along Utah’s Wasatch Front

Robert Kotchenruther, Ph.D.
EPA Region 10
October 6, 2011
Motivation for this analysis:

• Utah and Idaho share a PM2.5 nonattainment area in the Cache Valley, north of Salt Lake City.

• There are very few speciated PM2.5 measurements in the Cache Valley, so Utah/Idaho will be using speciation data from sites along the Wasatch Front (closer to Salt lake City) as surrogates for PM2.5 speciation in the Cache Valley.

• Limited comparisons of speciation data between the Cache Valley and Wasatch Front sites indicate that chemical speciation is similar on wintertime high PM2.5 days (>50% ammonium nitrate).

• It is hoped that a better understanding of sources impacting sites along the Wasatch Front will inform the possible range of sources impacting PM2.5 in the Cache Valley.

• To date no one has conducted a recent source apportionment analysis of PM2.5 for sites along the Wasatch Front.
Map and location of PM2.5 Speciation monitors

PM2.5 Speciation Monitors used in source apportionment analysis:

• Bountiful, Utah
  AQS site identifier 490110004
  lat & lon: 40.902967, -111.884467

• Salt Lake City, Utah
  AQS site identifier 490353006
  lat & lon: 40.736389, -111.872222

• Lindon, Utah
  AQS site identifier 490494001
  lat & lon: 40.341389, -111.713611
Comparison of Cache Valley PM2.5 Speciation and that in Salt Lake City:

A speciation monitor was recently installed in the Cache Valley (Logan) starting in the 2010/2011 winter.

<table>
<thead>
<tr>
<th>5 - Day Average PM2.5 &gt; 25 ug/m3</th>
<th>% NH4</th>
<th>%NO3</th>
<th>%SO4</th>
<th>%EC</th>
<th>%OC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Logan (Cache Valley)</td>
<td>22.0%</td>
<td>46.8%</td>
<td>3.3%</td>
<td>4.4%</td>
<td>17.8%</td>
</tr>
<tr>
<td>Salt Lake City</td>
<td>16.8%</td>
<td>41.1%</td>
<td>4.8%</td>
<td>3.6%</td>
<td>21.9%</td>
</tr>
</tbody>
</table>

(Source: Utah DEQ)
Details of this source apportionment work:

Source apportionment model:
Positive Matrix Factorization (PMF, EPA v4.0beta)

Data:
- chemically speciated PM2.5 data, 24-HR average
- ~4 years 5/2007 – 5/2011, starting after switch in carbon sampling method (switched to URG3000N)
- Sites: Bountiful (227 samples), Salt Lake City (429 samples), and Lindon (228 samples)
- 28 chemical species: OC & EC thermal fractions, NO3, SO4, NH4, trace metals and soil elements.

Method:
Each site modeled separately and results compared
What is Positive Matrix Factorization (PMF)??

A form of principal component analysis (factor analysis).

**Model input ->**
Aerosol total mass, chemical composition, and measurement uncertainties

**Model process ->**
Looks for systematic patterns in the day-to-day chemical variations so that the data variability can be explained by a smaller subset of factors.

These ‘factors’ are often interpreted as ‘sources’ of aerosol.

**Model output ->**
- Each factor’s chemical ‘fingerprint’
- Factor mass contributions to each sample
What is Positive Matrix Factorization (PMF)?? (continued)

Model interpretation ->

What is at PMF model ‘Factor’? Possibilities are:

- A single source (e.g. industrial facility)

- A source category (e.g. a bunch of sources that have very similar chemical fingerprints and emissions patterns – e.g., cars, trucks, wood burning sources)

- Multiple sources or source categories grouped together (PMF may group together multiple sources because of insufficient variability in emissions, chemical fingerprint, and/or temporal/spatial resolution)
PMF Results for the Wasatch Front
An ammonium chloride aerosol factor is a surprising result, not found at other locations in the U.S., but found at all 3 sites along the Wasatch front.

• Other factors typical of urban U.S. locations.
• Factors are very similar site to site, suggesting relative homogeneity of sources in airshed.

<table>
<thead>
<tr>
<th>Factors for this study</th>
<th>10 factors</th>
<th>11 factors</th>
<th>12 factors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium Nitrate</td>
<td>✓</td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>Ammonium Chloride</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Wood Smoke</td>
<td>✓</td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>OP rich</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Gasoline Vehicles</td>
<td>Not found</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Ammonium Sulfate</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Diesel I</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Fugitive Dust I</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Fugitive Dust II</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Fireworks</td>
<td>✓</td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>Industrial/Urban</td>
<td>✓</td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>Diesel II</td>
<td>Not found</td>
<td>Not found</td>
<td>✓</td>
</tr>
</tbody>
</table>
Results: Mass impacts during winter high PM2.5 days

- Similar mass impacts site to site.
- Ammonium chloride factor is significant, 8-15% under winter high PM2.5 conditions.
- Is ammonium chloride aerosol a reasonable result?
Ambient Ammonium Chloride Aerosol: Ambient ammonium chloride aerosol has been previously documented and studied in lab analyses.

Sample of literature references where ambient ammonium chloride was observed:

- Yoshizumi and Okita (1983) found NH₄Cl concentrations between 7.76 - 15.5 ug/m³ in Riverside, CA.

- Pio and Harrison (1987) found NH₄Cl concentrations up to 10 ug/m³ in Northwest England.

- Possanzin et al. (1992) found NH₄Cl represents approximately one-fifth of NH₄NO₃ and one-tenth of the total ammonium species by mass in Rome, Italy.

(Most references appear to be from the 1980’s and 1990’s).
Ammonium Chloride Aerosol Chemistry:

Pio and Harrison (1987) determined that the thermodynamics of \( \text{NH}_4\text{Cl} \) formation is very similar to that of \( \text{NH}_4\text{NO}_3 \).

\[
\text{NH}_3(g) + \text{HCl}(g) \leftrightarrow \text{NH}_4\text{Cl}(s) \\
\text{NH}_3(g) + \text{HNO}_3(g) \leftrightarrow \text{NH}_4\text{NO}_3(s)
\]

Both have reversible reactions and similar dependency on temperature and RH.

**From Pio and Harrison (1987):**

\( \text{NH}_4\text{Cl}(s) \) is slightly more volatile than \( \text{NH}_4\text{NO}_3(s) \)

[for the same \( \text{NH}_3(g) \) concentration. equilibrium concentrations of \( \text{HCl}(g) \) are 1.5-2 times higher than \( \text{HNO}_3(g) \) levels]

Taking typical atmospheric concentrations of gaseous \( \text{NH}_3 \) and \( \text{HCl} \), it is unlikely that \( \text{NH}_4\text{Cl} \) aerosol will exist at temperatures much above 10 deg C.
Ammonium Chloride Aerosol Chemistry:

\[ \text{NH}_3(g) + \text{HCl}(g) \leftrightarrow \text{NH}_4\text{Cl}(s) \]

**What might be sources of HCl(g) in the Wasatch Front?**

- Chlorine replacement in reactions with NaCl aerosol releases HCl(g)
  
  \[
  \text{H}_2\text{SO}_4(g) + 2\text{NaCl}(s) \rightarrow 2\text{HCl}(g) + \text{Na}_2\text{SO}_4(s) \\
  \text{HNO}_3(g) + \text{NaCl}(s) \rightarrow \text{HCl}(g) + \text{NaNO}_3(s)
  \]

  The Salt Lake has high NaCl concentrations. Heavy road salting is done in the winter in the Salt Lake City area.

- MagCorp (a magnesium chloride plant) is a known large point source of chlorine the Salt Lake airshed (~40 miles west of Salt Lake City)

- Poorly controlled coal combustion is a known historical source of HCl(g).

- Waste incineration can release HCl(g).
PMF factor ‘Ammonium Chloride’ at each location
Chemical ‘fingerprint’

- Bountiful
- Salt Lake City
- Lindon

Br  Cl  NH₄
PMF factor ‘Ammonium Chloride’ at each location

Mass impacts

<table>
<thead>
<tr>
<th>Date</th>
<th>Bountiful</th>
<th>Salt Lake City</th>
<th>Lindon</th>
</tr>
</thead>
<tbody>
<tr>
<td>4/1/2007</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7/1/2007</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10/1/2007</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1/1/2008</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4/1/2008</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7/1/2008</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10/1/2008</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1/1/2009</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4/1/2009</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7/1/2009</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10/1/2009</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1/1/2010</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4/1/2010</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7/1/2010</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10/1/2010</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1/1/2011</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4/1/2011</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Factor Monthly Average Mass Impacts (ug/m³)

- Bountiful
- Salt Lake City
- Lindon

Note:
- Mainly winter impacts agree with understood thermodynamics of secondary NH₄Cl
- Concentrations in line with those observed elsewhere
Other analysis to test the PMF finding of NH₄Cl aerosol:

**Further analysis of PMF results**

• Do NH₄Cl and NH₄NO₃ PMF factors form on the same days?
  -> look at NH₄Cl and NH₄NO₃ factor mass scatter plot

• What is the temperature dependence of the NH₄Cl factor?
  -> look at NH₄Cl factor mass vs. max daily temperature

**Outside of the PMF analysis, other data analyses**

• Are we missing any major ions that could account for the Cl?
  -> look at ion balance between available cations (+) and anions (-), is there a charge imbalance indicating possible missing ions?

• If we have ion balance, what cations are available in the sample that could be associated with Cl?
  -> look at samples with high Cl mass and see what cations could be associated with the Cl.
Are conditions conducive to a high NH$_4$NO$_3$ factor mass also conducive to a high NH$_4$Cl factor mass?

Comparing PMF ammonium nitrate and ammonium chloride factors

Conditions leading to significant NH$_4$NO$_3$ are also more conducive to NH$_4$Cl, consistent with similarity between NH$_4$NO$_3$ and NH$_4$Cl thermodynamics.
What temperatures are conducive to high NH$_4$Cl factor mass?

**Max daily temperature and ammonium chloride factor**

Significant NH$_4$Cl factor mass occurs mostly when max daily temperatures are less than 10°C, consistent with Pio and Harrison (1987) prediction about the temperature dependence of NH$_4$Cl aerosol.
Are we missing any major ions that could be associated with Cl\(^-\)? To check we can see if there is charge balance between the expected major ions: Cl\(^-\), NO\(_3^-\), SO\(_4^{2-}\), Na\(^+\), K\(^+\), NH\(_4^+\). Plotting anion charge equivalence vs. cation checks this.

anion equivalence = \([\text{Cl}^-]/35.453 + [\text{NO}_3^-]/62.005 + [\text{SO}_4^{2-}]/48.03\]
cation equivalence = \([\text{Na}^+]/23.0 + [\text{K}^+]/39.098 + [\text{NH}_4^+]/18.04\)

There is very close charge balance between the expected anions and cations, so it does not appear we are missing any major species.
When we have high Cl equivalence, what are the available cations that could be associated?

Highest Cl samples at Bountiful, ranked by Cl charge equiv.

This shows that the highest Cl concentration samples at Bountiful are mostly associated with NH₄⁺.
When we have high Cl equivalence, what are the available cations that could be associated?

Highest Cl samples at Salt Lake City, ranked by Cl charge equiv.

This shows that the highest Cl concentration samples at Salt Lake City are mostly associated with NH₄.
When we have high Cl equivalence, what are the available cations that could be associated?

Highest Cl samples at **Lindon**, ranked by Cl charge equiv.

This shows that the 2 highest Cl concentration samples at Lindon are mostly associated with NH$_4^+$, the next two highest could be associated with any of the cations.
For the Cache Valley, is there significant NH$_4$Cl?

Trying to get speciated PM2.5 data from Cache Valley to see.
References:


Other PMF Factors
Ammonium Nitrate Factor

Factor Profile - Run 8

Factor Profile - Run 16

Factor Profile - Run 1

Bountiful

Salt Lake City

Lindon

NH₄NO₃
Ammonium Nitrate Factor

Factor time series

Factor Mass Impacts (ug/m3)
- Bountiful
- Salt Lake City
- Lindon

Mass (ug/m3)

Month

Factor Monthly Average Mass Impacts (ug/m3)
- Bountiful
- Salt Lake City
- Lindon

Monthly mean conc.
Wood Smoke Factor

(Lindon factor omitted here)

Bountiful

Lack of K unusual, but OC1 and EC1 similar to Tacoma wood smoke factor.

Salt Lake City

Tacoma WA Wood Smoke Factor
Wood Smoke Factor

Factor time series

Factor Monthly Average Mass Impacts (ug/m3)
- Bountiful
- Salt Lake City
- Lindon

Monthly mean conc.

Seasonal pattern of mass impacts matches that expected of wood smoke from home heating.
OP Rich Factor
(Lindon factor omitted here)
The source(s) of this factor are uncertain.

? Aged POA/SOA

More heavily oxidized POA/SOA would be less volatile and perhaps more likely to char rather than volatilize during OC thermal analysis.
Gasoline Vehicles Factor (not found at Bountiful)

Similar to factors found in Zhao and Hopke, 2004
Kim et al. 2004
Maykut et al. 2003
Ammonium Sulfate Factor

Factor time series

Factor Mass Impacts (ug/m³)
- Bountiful
- Salt Lake City
- Lindon

Mass (ug/m³)

Date
4/1/2007
7/1/2007
10/1/2007
1/1/2008
4/1/2008
7/1/2008
10/1/2008
1/1/2009
4/1/2009
7/1/2009
10/1/2009
1/1/2010
4/1/2010
7/1/2010
10/1/2010
1/1/2011
4/1/2011

Monthly mean conc.

Factor Monthly Average Mass Impacts (ug/m³)
- Bountiful
- Salt Lake City
- Lindon

Mass (ug/m³)

Month
1 2 3 4 5 6 7 8 9 10 11 12
Diesel I Factor

Bountiful

Salt Lake City

Lindon

Factor Profile - Run 8

Factor Profile - Run 16

Factor Profile - Run 1

Cu, Fe, Mn, Zn, EC1
Diesel I Factor

Factor time series

Factor Mass Impacts (ug/m3)
- Bountiful
- Salt Lake City
- Lindon

Mass (ug/m3)

Date

Month

Mass (ug/m3)

Monthly mean conc.
Fugitive Dust I Factor

Factor Profile - Run 8

Bountiful

Factor Profile - Run 16

Salt Lake City

Factor Profile - Run 1

Lindon

Al, Ca, Fe, Ti, Si
Fugitive Dust II Factor
Fugitive Dust II Factor

Factor time series

Factor Mass Impacts (ug/m³)
- Bountiful
- Salt Lake City
- Lindon

Monthly mean conc.

Mass (ug/m³)

Date

Month
Fireworks Factor

Bountiful

Salt Lake City

Lindon

Cu

Mg

K
Fireworks Factor

Factor time series

Factor Mass Impacts (ug/m³)
- Bountiful
- Salt Lake City
- Lindon

Mass (ug/m³)

Date

Monthly mean conc.
Industrial/Urban Factor

Bountiful

Salt Lake City

Lindon

Cr  Pb  Ni  NO3  EC2  EC3SO4
Industrial/Urban Factor

Factor time series

Factor Mass Impacts (ug/m3)
- Bountiful
- Salt Lake City
- Lindon

Monthly mean conc.

Factor Monthly Average Mass Impacts (ug/m3)
- Bountiful
- Salt Lake City
- Lindon

Date

Mass (ug/m3)

Month
Diesel II Factor

Factor Profile - Run 1

Lindon

Cu  Mn  Zn  NO3  EC1
Diesel II Factor

Factor time series

Factor Mass Impacts (ug/m3)

Lindon

Mass (ug/m3)

Date

Monthly mean conc.

Month