The Chemical Composition of PM2.5
to support PM Implementation

Neil Frank
AQAG/AQAD USEPA

For Presentation at
EPA State / Local / Tribal Training Workshop: PM 2.5 Final Rule Implementation and 2006 PM 2.5
Designation Process
June 20-21
Topics

• How do we derive FRM PM2.5 composition
• How does avg composition vary by region, by season and over time
• Variation within urban areas
• What are the local vs regional components and how does this relate to potential emission sources
• Differences between peak day and average composition
What is the composition of PM2.5 and where does it come from?

Major components
- Ammonium Sulfate
- Ammonium Nitrate
- Organic Carbonaceous Mass
- Elemental Carbon
- Crustal Material

The chemistry is complicated and particle formation is dependent on other pollutants and atmospheric conditions.

From: The Particle Pollution Report: Current Understanding of Air Quality and Emissions through 2003
To estimate urban PM2.5 composition

• Use measurements from routine monitoring networks
  – STN, SLAMS (=CSN)

• Make adjustments to represent FRM mass

• FRM mass does not equal the simple sum of the measured components
  [i.e. PM2.5 ≠ AmmSul + AmmNitr + OCM + EC + Crustal]
6 Nitrate Study Sites, 2003

FRM doesn’t retain all ambient nitrates
Monthly and Annual Average NO₃, 2003

Cleveland, OH

FRM (red bar and black line)
STN (total bar)

Birmingham, AL

PM2.5 mass also includes particle bound water (at mass weighing conditions)

Reconstructed Fine Mass
RCFM (reflects ambient)

SANDWICH (reflects FRM PM2.5)

Sulfate  Nitrate  TCM  Crustal  Passive
SANDWICH
more than a cute acronym

• What is the SANDWICH Approach?
  – Sulfate, Adjusted Nitrate, Derived Water, Inferred Carbon Hybrid material balance approach
    • for estimating PM2.5 mass composition as if it was measured by the PM2.5 FRM.
    • The approach uses a combination of speciation measurements and modeled speciation estimates to represent FRM PM2.5.

• Why is it needed?
  – The FRM defines the regulatory indicator of PM2.5.
  – FRM mass may not retain all nitrate, and includes particle bound water and other components not estimated directly with STN measurements.
  – To estimate FRM PM2.5 composition including FRM carbonaceous mass without “fudge” factors.
  – To help QC speciation measurements

• SANDWICH is the default method in EPA modeling guidance to define baseline PM2.5
  – for SMAT (speciated modeled attainment test)
  – “FRM” composition with the peer-reviewed “SANDWICH” technique used in CAIR and PM2.5 RIA

Conceptual Overview of Mass Balance Approaches

(1) Approach using measurements and calculated values

Distribute unknown (or scale all down) equally

(2) SANDWICH
(a) W. Reduced Nitrates

(b) With added water

Sulfate mass increases

(c) Plus filter contamination (= FRM “blank”)

(d) Remaining unknown mass is assigned to carbon

* Default SANDWICH can be modified to consider other components, like salt. This reduces estimate of TCM.
Annual Average Composition (2002-04) in East NA areas

Less nitrate and more sulfate mass with SANDWICH

<table>
<thead>
<tr>
<th>area</th>
<th>area_annual_dv</th>
</tr>
</thead>
<tbody>
<tr>
<td>NA area: Johnstown, PA</td>
<td>15.3</td>
</tr>
<tr>
<td>NA area: Martinsburg, WV-Hagerstown, MD</td>
<td>16.1</td>
</tr>
<tr>
<td>NA area: Parkersburg-Marietta, WV-OH</td>
<td>15.2</td>
</tr>
<tr>
<td>NA area: Reading, PA</td>
<td>16.1</td>
</tr>
<tr>
<td>NA area: Steubenville-Weirton, OH-WV</td>
<td>17</td>
</tr>
<tr>
<td>NA area: Wheeling, WV-OH</td>
<td>15.1</td>
</tr>
</tbody>
</table>

• NA area without STN data (02-04)

Black outlined pies had collocated FRM and speciation
Annual Average Composition (2002-04) in West NA areas
Less nitrate and more carbon mass with SANDWICH

Black outlined pies have collocated FRM and speciation
FRM composition can be very different than constructed mass from speciation measurements.

Rubidoux, CA (2005)

Over-estimates FRM mass

Less nitrate mass
More sulfate and carbon

Gray line shows \( \{ \text{OCMmb} - \text{OCM14} \} \)
FRM composition can be very different than constructed mass from speciation measurements.

Birmingham, AL (2005)

RCFM

Under-estimates FRM mass

Less nitrate mass
More sulfate and carbon

Gray line shows \{OCMmb - OCM14\}
Quarterly PM2.5 Composition in Eastern NA areas, 2002-04

Note: Many areas do not have speciation data and some at a different site

No speciation data in 2002-04
Quarterly PM2.5 Composition in NA areas, 2002-04

Many areas do not have speciation data and some at a different site
Quarterly PM2.5 Composition in Western NA areas, 2002-04
1st and 4th quarters have higher concentrations (except LA)
Composition Can Vary Within the NA Area

“Generally” the extra component is carbon

For some cities, there are gradients in non-C components

<table>
<thead>
<tr>
<th></th>
<th>Allen Pk</th>
<th>Dearborn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfate Mass</td>
<td>5.5</td>
<td>7.4</td>
</tr>
<tr>
<td>Carbonaceous Mass</td>
<td>5.5</td>
<td>7.1</td>
</tr>
<tr>
<td>Nitrate</td>
<td>2.4</td>
<td>2.9</td>
</tr>
<tr>
<td>Crustal Material</td>
<td>0.4</td>
<td>2.7</td>
</tr>
<tr>
<td>PM2.5</td>
<td>14.22</td>
<td>20.56</td>
</tr>
</tbody>
</table>
What to do if speciation is not at the DV site?

Accounting for differences in within-area speciation profiles

Speciation location (Ann Avg=14.9 ug/m3)

- SANDWICH
  - Sulfate_mass: 7.98
  - Nitrate_mass: 1.11
  - TCM: 0.49
  - Passive: 0.71

- SANDWICH_PacMan
  - Sulfate_mass: 7.98
  - Nitrate_mass: 1.11
  - TCM: 0.49
  - Passive: 0.71

DV site (16.3 ug/m3)

- SANDWICH_PacMan
  - Sulfate_mass: 7.98
  - Nitrate mass: 1.40
  - TCM: 0.71
  - Passive: 0.49

1.4 ug/m3 is unknown

Baltimore (Essex speciation site) is not at DV site, 2002 speciation data

When DV site does not have speciation data, the unknown mass may or may not be TCM. It could be crustal material (as we observe in Birmingham and Detroit) or possibly Nitrate.
Regional Trends in PM2.5 Composition, 2002-2006

Compositional changes in some regions

- Lower nitrates and sulfates. Increasing Carbon
- Lower nitrates and sulfates
- Lower nitrates and sulfates
- Lower nitrates and sulfates

Reduced Nitrates, Sulfates & Carbon

No change Sulfates. Decreasing Nitrates Increasing Carbon

DRAFT
SANDWICH data are now available on Air Explorer

http://www.epa.gov/airexplorer/
The Urban Excess
Urban PM2.5 is Composed of Urban and Regional Components

Baltimore PM2.5 compared to Upwind rural site illustrates urban/rural contributions

Based on constructed mass (not SANDWICH), *March 01 – Feb 02*
Urban PM2.5 is Composed of Urban and Regional Components

**Sulfates**
- Most from regional sources

**Carbon**
- Large PM2.5 component
- Local contribution (40-70%)

**Nitrates**
- 10-30% of PM2.5
- Some east avg. ambient nitrates ~4 ug/m³
- Local contribution ≥ 50%

*From Particle Pollution Report, 2003
Comparing single urban and rural locations*
Carbon and Nitrates dominate the average local urban excess Composition of Eastern PM2.5 Non-Attainment Areas

* Indicates areas with > 30% UE nitrates

* Carbon
* Sulfates
* Nitrates
* Crustal
High Day vs. Average Composition

Average Concentration is based on all days but is strongly influenced by the highest concentration days
Composition on Annual Average and High PM2.5 Days

Some source categories and regional influences may be more important for high concentration days

- Comparing average of 5 highest days during 2003, regional sources of sulfates and nitrates are larger contributors to peak day concentrations than to annual average (selected city analysis)
- Composition can vary from high day to high day
- Carbon can be smaller as % -- but still larger in absolute concentration values -- compared to the average

This analysis shows PM2.5 Composition of the ambient aerosol (not adjusted to represent FRM mass)
Percent of 2003-05 FRM Days > 35 ug/m³ by Month
Based on all sites which violate 24-hr NAAQS
“Example” Composition for High Days [“Warm” Season (May-Sept) & “Cold”]
But sites can be different within each “domain”

Pies represent average of 3 highest days per year per season, using SANDWICH
More Details about PM2.5
Chemical Composition for the IMW

Industrial Midwest
- Generally nitrate dominated winter-time values in northern areas
- Sulfate dominated episodes in summer (region-wide)

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- Generally nitrate dominated winter-time values in northern areas
- Sulfate dominated episodes in summer (region-wide)

Northern Site (Grand Rapids, MI)

24hr DV= 37 ug/m³

Southern Site (Indianapolis, IN)

24hr DV= 38 ug/m³

Number inside pie is the “top 3” average concentration, ug/m³

Note: Passive is PM2.5 unrelated to emissions
<table>
<thead>
<tr>
<th>Location</th>
<th>24-hr DV (ug/m³)</th>
<th>Annual DV (ug/m³)</th>
<th>Existing NA Area</th>
<th>Total 3 yr obs</th>
<th>&quot;Cold&quot; days &gt; 30</th>
<th>&quot;Warm&quot; days &gt; 30</th>
<th>Avg conc. - top 3 values/yr</th>
<th>Sulfate, Nitrate, EC, OCMmb, Crustal, Passive Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indianapolis, IN</td>
<td>38</td>
<td>15.4</td>
<td>Indianapolis, IN</td>
<td>280</td>
<td>3</td>
<td>15</td>
<td>36.9, 37.9</td>
<td>Crustal Passive</td>
</tr>
<tr>
<td>Grand Rapids, MI</td>
<td>36</td>
<td>16.6</td>
<td>Charleston, WV</td>
<td>49</td>
<td>0</td>
<td>9</td>
<td>0.0, 35.9</td>
<td>Sulfate, Nitrate, EC, OCMmb, Crustal, Passive Average</td>
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<tr>
<td>Elkhart, IN</td>
<td>36</td>
<td>14.6</td>
<td></td>
<td>47</td>
<td>2</td>
<td>1</td>
<td>41.8, 40.8</td>
<td>Sulfate, Nitrate, EC, OCMmb, Crustal, Passive Average</td>
</tr>
<tr>
<td>Detroit (Dearborn), MI</td>
<td>37</td>
<td>13.1</td>
<td></td>
<td>171</td>
<td>5</td>
<td>5</td>
<td>42.5, 38.2</td>
<td>Sulfate, Nitrate, EC, OCMmb, Crustal, Passive Average</td>
</tr>
<tr>
<td>Detroit (Allen Park), MI</td>
<td>44</td>
<td>18.2</td>
<td></td>
<td>139</td>
<td>12</td>
<td>9</td>
<td>38.0, 43.2</td>
<td>Sulfate, Nitrate, EC, OCMmb, Crustal, Passive Average</td>
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<tr>
<td>Buffalo, NY</td>
<td>40</td>
<td>15.1</td>
<td></td>
<td>327</td>
<td>8</td>
<td>11</td>
<td>44.2, 38.5</td>
<td>Sulfate, Nitrate, EC, OCMmb, Crustal, Passive Average</td>
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<tr>
<td>Milwaukee, WI</td>
<td>37</td>
<td>13.8</td>
<td></td>
<td>135</td>
<td>3</td>
<td>5</td>
<td>37.3, 36.7</td>
<td>Sulfate, Nitrate, EC, OCMmb, Crustal, Passive Average</td>
</tr>
<tr>
<td>Grand Rapids, MI</td>
<td>36</td>
<td>13.5</td>
<td></td>
<td>161</td>
<td>5</td>
<td>1</td>
<td>39.0, 41.1</td>
<td>Sulfate, Nitrate, EC, OCMmb, Crustal, Passive Average</td>
</tr>
<tr>
<td>Pittsburgh, PA</td>
<td>39</td>
<td>15.5</td>
<td>Pittsburgh-Beaver Valley, PA</td>
<td>291</td>
<td>2</td>
<td>10</td>
<td>31.6, 40.8</td>
<td>Sulfate, Nitrate, EC, OCMmb, Crustal, Passive Average</td>
</tr>
<tr>
<td>Liberty, PA</td>
<td>68</td>
<td>20.8</td>
<td>Pittsburgh-Beaver Valley, PA</td>
<td>109</td>
<td>7</td>
<td>11</td>
<td>50.5, 55.7</td>
<td>Sulfate, Nitrate, EC, OCMmb, Crustal, Passive Average</td>
</tr>
</tbody>
</table>

Note: Map shows existing NA areas & new violation sites.

- **Nitrates** - important in the North sub-Region.
- **Sulfates** and **warm season** in the South portion.
Mid Atlantic Region
Generally Sulfate dominated episodes everywhere in summer
Fewer Nitrate contributed winter-time values
(except in SE. PA)
Sulfates dominate high Summer days
Nitrates - important on fewer cold days
South East Region
Mostly sulfate dominated + OC episodes, in summer
-- shows influence of biogenics and other SOA
Fewer cold-season exceedances (& are driven by carbon)

Existing NA: Birmingham, AL

New 24hr Violation: Phenix City, AL (Columbus, GA area)
Sulfates and carbon during summer
Carbon more important on fewer cold days

Note: Columbus area designated Attainment in 2005 on basis of spatial averaging.
Southwestern US

- Speciation data (from El Paso) suggest emission sources creating crustal and carbon
- Shows effect of aridity and wind

PM2.5 speciation - 02/02/2003

Las Cruces, NM
24hr DV=36
Ann DV=10.4

24hr DV=42 (not pop- oriented?)
Ann DV=17.3

Nitrate data was not available for this site
Southern California
- Nitrates dominate High PM2.5 in LA.
- Carbon (summer) and also nitrates (winter) in Calexico
  - Lower % crustal on high days

**Downwind of LA: Rubidoux, CA**

- **AVG**
- **Avg High 3 Cold**: 70
- **Avg High 3 Warm**: 45

**Border Site: Calexico, CA**

- **AVG**
- **Avg High 3 Cold**: 32
- **Avg High 3 Warm**: 34

24hr DV= 65 ug/m³ 24hr DV= 39 ug/m³
Composition Varies Across this Diverse CA Domain
Middle California
- Carbon in Northern Central Valley
  - from RWC?
- Nitrates dominate High PM2.5 in lower SJV

Northern Central Valley (e.g. Sacramento)
- 24hr DV= 45 ug/m3
- No warm season exceedances

Southern SJV (e.g. Bakersfield, CA)
- 24hr DV= 58 ug/m3
- No warm season exceedances
Chico, CA

Sacramento, CA

Modesto, CA

Fresno, CA

Bakersfield, CA

Nitrates dominate peak days in Southern SJV
Carbon is big contributor in N. Central Valley (RWC)
North West

- Carbon dominates Libby (from RWC?)
- Nitrates are also found on high winter days in Missoula (and elsewhere, e.g. Boise)
  -- mobile and valley influence or?
- Summer days are flagged fires
  • (not concurred?)

Missoula, MT (traffic influenced)

Libby, MT (RWC)

24hr DV = 41 ug/m³

No warm season exceedances

24hr DV = 44 ug/m³
Difficult to predict composition from nearby locations
(e.g. Missoula composition is similar to Boise but different than Libby)

New violation locations without STN data

Composition Varies. Only Carbon at some locations. Nitrate is evident at other sites. Many Viol sites wo STN

Libby, MT

Missoula, MT
High PM2.5 in Utah

- Consistently more Nitrates on high days
- SLC has similar % Sulfates as ann avg
- Lindon – one summer exceedance
  - unflagged fire?
Many Violating Locations in UT
Nitrates seems to dominate peaks

Ogden-Clearfield CBSA
- Logan (Cache Co.)
- Ogden (Weber Co.)
- Bountiful (Davis Co.)

SLC
- SLC
- Spanish Fork City

Provo-Orem CBSA
- Lindon
- Provo

24hr DV >35 (& Ann DV>15) wo STN FRM wo 24hr viol
24hr ONLY violation (wo STN)  STN NA area 24hr ONLY STN viol
24-hrDV>35ug/m3 at STN (red square=only 24-hr eligible)
High PM2.5 in Alaska (Fairbanks)
- 50% carbon on winter exceedance day
- Two summer exceedances are flagged fires (not concurred)
### Potential Source Influences by Season and Scale

<table>
<thead>
<tr>
<th>Season &amp; Affected Domains</th>
<th>Major PM2.5 Components</th>
<th>Source category</th>
<th>Typical Scales of Influence</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Regional</td>
</tr>
<tr>
<td>Cold</td>
<td>Nitrate</td>
<td>EGU (NOx)</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ag (NH₃)</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mobile (NOₓ+NH₃)</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>Sulfate</td>
<td>EGU (SO₂)</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>Carbon</td>
<td>Mobile, Area/RWC, Industry</td>
<td>✓</td>
</tr>
<tr>
<td>Crustal</td>
<td>Industry, Mobile</td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>Warm</td>
<td>Sulfate</td>
<td>EGU (SO₂)</td>
<td>✓</td>
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<tr>
<td></td>
<td>Carbon</td>
<td>Mobile, Area, Industry, Biogenics and Smoke</td>
<td>✓</td>
</tr>
<tr>
<td>Crustal</td>
<td>Mobile, Area, Industry</td>
<td></td>
<td>*</td>
</tr>
</tbody>
</table>

Underlined text indicates dominant season for the domain.
Carbon includes OC and EC.
*Sometimes occurs