Characterizing Ambient Fine Particulate Matter Mass in St. Louis

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- Four year campaign, core monitoring site in East St. Louis, IL
  - Two years of measurements with a subset of the initial monitoring platform (6/2003 – 3/2005)

- Data collection and analysis to support:
  - Development and evaluation of monitoring methods
  - Exposure and health effects studies
  - Source apportionment and SIP planning
SIP Planning Support Grant to WUSTL

1. Coordination
2. Organic Carbon Source Apportionment
3. Data Harmonization & Episodes Analysis
4. Urban / Rural Contrast & Intraurban Variability
5. Transport Regimes Analysis
6. Refinements to PM$_{2.5}$ Mass Apportionment
7. Soil / Road Dust Characterization

Many of these analyses designed to support (model validation) or complement (weight-of-evidence) chemical transport modeling

Subcontractors:
- University of Wisconsin (Schauer group)
- Sonoma Technology, Inc.
STL Fine PM Mass Apportionment Studies

<table>
<thead>
<tr>
<th>Site</th>
<th>Period</th>
<th>Method</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 sites in STL area (RAPS)</td>
<td>5/75-4/77</td>
<td>PMF2</td>
<td>Kim &amp; Hopke (2005)</td>
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<td>10 sites in STL area (RAPS)</td>
<td>7/76-8/76</td>
<td>CMB</td>
<td>Dzubay et al. (1980)</td>
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<td>Carondelet (Six-Cities Study)</td>
<td>1979-1988</td>
<td>APCA</td>
<td>Laden et al. (2000)</td>
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<tr>
<td>Blair Street (STN)</td>
<td>4/01-4/02</td>
<td>CMB</td>
<td>Kenski &amp; Koerber (2002)</td>
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<td>Blair Street (STN)</td>
<td>4/01-4/02</td>
<td>PMF*</td>
<td>Coutant &amp; Swinton (2002)</td>
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<td>8/00-7/01</td>
<td>PMF*</td>
<td>Battelle (2003)</td>
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<td>(insert)</td>
<td>EPA PMF</td>
<td>MDNR (internal) (2005)</td>
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<td>East St. Louis (STL-SS)</td>
<td>6/01-5/03</td>
<td>PMF2</td>
<td>Lee et al. (2006)</td>
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* Version of PMF to be determined
** Sensitivity studies and refinements to the apportionment of Lee, Hopke and Turner (2006)

Acknowledgement: Mike Davis (EPA Region VII) for draft synthesis of the contemporary STL PM$_{2.5}$ mass apportionment studies
East St. Louis Fine PM Mass Apportionment by Positive Matrix Factorization (PMF) (Lee et al. 2006)

Measured Species Contributions to PM$_{2.5}$

- SO$_4^{2-}$: 23%
- NH$_4^+$: 11%
- NO$_3^-$: 12%
- OM: 31%
- EC: 9%
- crustal: 3%
- other: 3%
- unaccounted: 8%

Factor Contributions to PM$_{2.5}$

- sulfuric 33%
- nitrate 15%
- gasoline 16%
- diesel 2%
- lead 1%
- copper 1%
- nitric 1%
- soil 4%
- steel 7%
- other 3%
Carbon in the Hopke Group Apportionments

East St. Louis

IMPROVE carbon fractions

Arnold Blair

NIOSH OC/EC
Reconciling the Hopke Group (Clarkson) Apportionments

Different data collection and analysis methods (especially carbon); consistent source apportionment methodology

(*) Soil: Arnold includes separate Ca-rich factor; Blair = soil + non-soil industrial
(**) Nonferrous Metals: Arnold includes steel processing
NR = factor not resolved
Sulfate factor... Is this gradient from sulfate ion concentration, or from other species present in the sulfate factor?

(*) Soil: Arnold includes separate Ca-rich factor; Blair = soil + non-soil industrial
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Nitrate factor... *Is this gradient from nitrate ion concentration, or from other species present in the nitrate factor?*

- Nitrate factor
- Sulfate
- Nitrate
- Mobile source
- Soil
- Steel production
- Nonferrous metals
- Biomass
- "Carbon-rich sulfate"

(*) Soil: Arnold includes separate Ca-rich factor; Blair = soil + non-soil industrial
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Mobile source factor... gradient seems backwards; highest in suburbs and lowest in urban core.

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<th>Arnold</th>
<th>East St. Louis</th>
<th>Blair Street</th>
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<tbody>
<tr>
<td>Sulfate</td>
<td>6.1</td>
<td>6.0</td>
<td>6.2</td>
</tr>
<tr>
<td>Nitrate</td>
<td>2.3</td>
<td>2.2</td>
<td>2.1</td>
</tr>
<tr>
<td>Mobile Source</td>
<td>4.0</td>
<td>4.1</td>
<td>4.2</td>
</tr>
<tr>
<td>Soil*</td>
<td>3.5</td>
<td>3.6</td>
<td>3.7</td>
</tr>
<tr>
<td>Steel Production</td>
<td>2.8</td>
<td>2.9</td>
<td>3.0</td>
</tr>
<tr>
<td>Nonferrous Metals*</td>
<td>1.3</td>
<td>1.4</td>
<td>1.5</td>
</tr>
<tr>
<td>Biomass</td>
<td>0.9</td>
<td>1.0</td>
<td>1.1</td>
</tr>
<tr>
<td>&quot;Carbon-rich Sulfate&quot;</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
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*Soil/crustal factor... difficult to assess consistency due to admixing with other sources (see footnote)*

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Steelmaking Factor

Steel production… relatively large at East St. Louis but small at Blair; not resolved at Arnold

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Nonferrous Metals Processing Factor

Nonferrous metals (zinc, lead, copper)... in aggregate similar contributions across all three sites

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PM$_{2.5}$ mass, µg/m$^3$

- Sulfate
- Nitrate
- Mobile source
- Soil*
- Steel production
- Nonferrous metals**
- Biomass
- "Carbon-rich sulfate"
Biomass Burning Factor

Biomass burning... not resolved at Blair, not resolved in published East St. Louis apportionment but subsequent work by Hopke group suggests it can be resolved

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“Carbon-Rich Sulfate” Factor

Carbon-rich sulfate factor… 15-20% of mass at East St. Louis… what does it represent?

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PMF with Consistent Carbon Representation

- **East St. Louis**
- ** Arnold Blair**
- **East St. Louis**

**IMPROVE carbon fractions**

**NIOSH OC/EC**
(*) Soil: Arnold includes separate Ca-rich factor; Blair = soil + non-soil industrial
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Apportionments with NIOSH OC/EC at all Sites

**Intraurban gradients still exist! Regional plus local contributions and/or measurement artifacts?**

PM$_{2.5}$ mass, µg/m$^3$

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Interpretation of Carbon-Rich Sulfate Factor

- Factor profile predominantly carbon, some sulfate
  - Relatively high EC/OC ratio suggests unaged carbon and thus likely local sources
  - However, modeled apportionments using different representations for carbon suggests the factor represents regional sources
- Reconcile East St. Louis TC apportionment with urban/rural contrast, August-November 2001 measurements (Park Hills)
Monitoring Locations: 8/17/01 – 11/20/01

East St. Louis (IL) is approximately 3 km east of the City of St. Louis (MO) central business district. Park Hills (MO) is a predominantly rural site ~100 km south/southwest of the St. Louis urban core.
Sulfate at the Urban and Rural Sites

PM-2.5 sulfate, µg/m³

- Park Hills
- East St. Louis
Urban/Rural Analysis Objective
- Examining the Total Carbon Attribution -

Measured Regional TC (Park Hills)
Urban/Rural Analysis Objective
- Examining the Total Carbon Attribution -

Modeled Urban TC (PMF using ESL data)

Measured Regional TC (Park Hills)
Urban/Rural Analysis Objective
- Examining the Total Carbon Attribution -

Modeled Urban TC (PMF using ESL data)

Measured Regional TC (Park Hills)

? =

Measured Urban TC (East St. Louis)
PMF-Modeled Urban Excess for Carbon

- PMF model does indeed capture the STL “urban excess” for carbon.
Daily Total Carbon Reconstruction

- Negative ESL concentrations indicate that Park Hills + modeled urban TC overestimated the measured ESL TC
Dramatic increase is in the gasoline factor contribution during this period.
PMF-Modeled Urban Excess for Carbon

- Agreement is better for the 11-factor solution (wood smoke factor)
Comparing Blair (City of St. Louis – urban) to Bonne Terre (rural), there is an OC urban excess at Blair on virtually every sampling day May - September only, 2003 & 2004

May - September only, 2003 & 2004

\[
\frac{OC(Blair)}{OC(Bonne Terre)} = 1.9
\]

\[
\frac{TCM(Blair)}{TCM(Bonne Terre)} = 2.0
\]

Assuming urban plumes do not impact the rural site, then nearly 100% urban excess for the summer months!
Fine Particulate Matter Carbon in St. Louis

• From the carbon attribution in the PMF mass apportionment modeling (East St. Louis)...
• From the average of daily differences between observed urban and rural carbon burdens (Arnold, Blair)
  – Annual average, at East St. Louis and Arnold*:
    • Regionally transported carbon: ~50%
    • Locally emitted/generated carbon: ~50%
  – Summertime average, at Blair Street*:
    • Regionally transported carbon: ~50%
    • Locally emitted/generated carbon: ~50%
      (currently working on annual average)
  – *Results for Arnold and Blair Street sensitive to how the data is conditioned (urban excess could be as low as 35-40%)
• What are the sources of the locally emitted/generated carbon?
  – Fine PM mass apportionment not designed to answer this question
  – Need more-sophisticated approaches…
Towards more specificity in representing carbon

- OC/EC
- Thermal carbon fractions
- Speciated organics
Primary OC Apportionment by CMB (Schauer Group, U. Wisconsin)

- East St. Louis, 1-in-6 day data with organic speciation by extraction-GCMS, June 2001 – May 2003
- CMB apportionment assumes we know all of the primary OC sources and have representative source profiles!

- PMF resolved eight factors including one mobile source factor, also two point source factors and secondary organic aerosol (SOA) not in CMB
Summary

• St. Louis – Midwest Supersite program has collected a wealth of data for fine particle physical and chemical properties
• Together with the state/local routine monitoring data, there is substantial information to support in PM$_{2.5}$ SIP planning for the St. Louis area
• Ultimate goal is a defensible control strategy
  – Currently analyzing the observational data to provide technical support towards that effort
• East St. Louis Fine PM Mass Apportionment
  – Use of allied data (in this case, paired urban/rural data) provided significant insights into the original apportionment