Recent Findings from EPA/ORD Ambient Measurement Research

Tim Watkins

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General Approach Ambient Measurement Research

Research Questions:
- What measurement studies are needed to address model needs/uncertainties?
- What methods are needed to conduct measurement studies?

Models:
- Conduct measurement studies to inform models

Measurements:
- Conduct measurement studies to inform models

Methods:
- Apply methods in measurement studies

Products for Air Quality Management Activities
Ambient Measurement Research Questions and Activities

Source Apportionment
How do sources impact ambient air concentrations?

- Characterize pollutant composition for identification of source markers
- Characterize spatial/temporal distribution of ambient pollutants
- Characterize relationships between ambient, indoor, personal concentrations

Exposure Assessment
How do ambient concentrations impact actual human exposures?
Locations of ORD’s Ambient Measurement Research Field Studies

Many studies in locations with NAAQS non-attainment issues.
Source Apportionment Tools
Elements of Source Apportionment Research
Sampling Time Resolution for providing data for local and regional source apportionment

- 24 hour time resolution
  - Filter based sampling

- 12 hour time resolution
  - Sequential Filter based sampling

- 1 hour or less time resolution
  - Semi-continuous analyzer

Reduced mixing of sources due to lower variability in wind direction
High Time Resolution Ambient Sampling

The **Aerosol Ion Monitor (AIM)** enables high time resolution determination of PM$_{2.5}$ anions (sulfate and nitrate), cations (ammonium and sodium), and precursor gas species. Within the AIM, ambient PM samples are collected and extracted, and ion analysis is conducted using IC. The automated instrument provides concentration measurements every hour.

The **Semi-continuous Elements in Aerosol Sampler (SEAS)** provides inorganic concentration measurements of ambient PM$_{2.5}$ aerosols. The sampler runs in unattended mode and provides concentration measurements on a 30-minute basis. Near-real time reporting supports source apportionment studies, health studies, and development of effective mitigation strategies.

**Time-of-Flight Aerosol Mass Spectrometry (TOF-AMS)** provides real-time elemental and/or chemical analysis of single aerosol particles. High-time resolution results provided by TOF-AMS enables in-situ characterization of complex aerosol formation and reaction processes which cannot be achieved by other measurement methods.
Analytical Techniques

**High Resolution ICP-MS** provides high sensitivity analysis to quantify a large number of soluble inorganic species. High resolution capability provides Se and K without interference that are important source tracers and isotope ratios provide additional source apportionment capability. Complements measurements made by the EPA XRF.

**X-Ray Fluorescence (XRF)** provides moderate sensitivity analysis for inorganics. Rapid multi-element, non-destructive technique. Minimal sample preparation and high sample throughput. Provides total elemental concentrations to complement soluble metals analysis by ICP-MS.

**Scanning Electron Microscopy (SEM)** with **Energy-Dispersive X-Ray Spectroscopy (EDS)** provides individual particle characterization (size, composition, and morphology). Complements bulk analyses (XRF) by providing particle size distribution and within-particle elemental relationships. Computer-Controlled SEM can characterize hundreds of particles per hour without operator assistance.

**GCMS with high sensitivity Selective Ion Monitoring (SIM)** provides organic analysis with low method detection limits (pg/m³ at 10 liter/min, 24 h). Demonstrated ability to quantify organic source markers in ambient and personal exposure sample.
EPA Receptor Models

- **EPA Chemical Mass Balance**
  - Quantify Sources with measured profiles and calculated profiles from other EPA receptor models

- **EPA Unmix and EPA Positive Matrix Factorization (PMF)**
  - Calculate source profiles and quantify sources using only sample data

- **EPA Air Pollution Transport to Receptor (APTR)**
  - Identify the location of sources and their impact using wind speed, wind direction, trajectories
  - Regional and Local Analyses

Receptor models are mathematical algorithms developed for identifying and quantifying the sources of ambient air contaminants (and their effects) at a receptor location, primarily on the basis of concentration measurements made at the receptor.
Source Apportionment Findings
Source Sample Collection at U.S. Steel Granite City Works in St. Louis

Profiles used in the CMB model and for source identification of PMF and Unmix results for St. Louis, Dearborn, and Cleveland Studies

Samples resuspended by Desert Research Institute, collected on filters, and analyzed by EPA with EDXRF, ICP-MS, IC, OC/EC, organic speciation, and SEM-EDX
St. Louis Advanced Monitoring Initiative Project

These and other results have been used by the State of Illinois and the State of Missouri to inform efforts to reduce PM$_{2.5}$ emissions

*Unexplained Mass contains nitrate and OC/EC compounds*
Additional Information from SEM Analyses

St. Louis Pilot Study (Nov. 3-6, 2006)

- 9 Passive Aerosol Samplers collected upwind and downwind of Granite City facility, 1-day & 3-day exposures
- Downwind samples were enriched relative to upwind for several metal-rich particle classes
Analysis of 30 minute St. Louis SEAS Data with EPA Unmix
## St. Louis APTR Results

<table>
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<tr>
<th>Sector (center)</th>
<th>Percentage</th>
<th>Mean</th>
<th>N</th>
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<tr>
<td>339-52 (369)</td>
<td>9.46</td>
<td>0.095</td>
<td>131</td>
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<tr>
<td>53-110 (75)</td>
<td>9.42</td>
<td>0.094</td>
<td>53</td>
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<tr>
<td>111-165 (134)</td>
<td>14.18</td>
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<tr>
<td>166-190 (208)</td>
<td>1.07</td>
<td>0.011</td>
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<tr>
<td>191-294 (273)</td>
<td>60.92</td>
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<td>173</td>
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<tr>
<td>295-338 (313)</td>
<td>4.95</td>
<td>0.049</td>
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<td>316-48 (362)</td>
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<td>49-128 (89)</td>
<td>16.25</td>
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<td>129-144 (198)</td>
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<td>145-190 (283)</td>
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<td>191-315 (314)</td>
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<th>Mean</th>
<th>N</th>
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<td>351-1 (360)</td>
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<tr>
<td>2-60 (60)</td>
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<td>61-120 (95)</td>
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<td>121-190 (145)</td>
<td>13.29</td>
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<td>191-260 (225)</td>
<td>20.34</td>
<td>0.207</td>
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<tr>
<td>261-350 (295)</td>
<td>36.8</td>
<td>0.374</td>
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</table>

**Zn Source**

**Cu-Pb Source**

**Steel Source**

[Image of maps showing Zn, Cu-Pb, and Steel sources]
Regional Source Contributions in St. Louis

The PMF biomass burning regional impact in $\mu g/m^3$ evaluated using EPA Air Pollution Transport to Receptor (APTR). The impact of forest fires is shown in Season 3 (summer) on the St. Louis Supersite (bottom left).
Evaluation of the SEAS in Dearborn, MI

**Arsenic**
- $y = 0.9009x + 0.0206$
- $R^2 = 0.9063$

**Vanadium**
- $y = 1.014x + 0.0022$
- $R^2 = 0.9984$

**Atm Conc ng/m³**
- V by EPA SEAS
- V by UMi SEAS
Steubenville Source Apportionment Study: Impact of Coal Fired Utility Boilers

- Coal-fired power plant near Steubenville, OH
  - Source profile measurements
  - High-time resolution (30-minute) sampling
  - Application of advanced receptor models
  - Determine local vs. regional contributions for SO$_2$, PM, and mercury (Hg)

Local impact of power plant quantified for SO$_2$ in Steubenville

Annualized Steubenville Source Apportioned Mercury Wet Deposition Results

<table>
<thead>
<tr>
<th>Year</th>
<th>Measured</th>
<th>PMF Estimated CFUB* Contribution</th>
<th>UNMIX Estimated CFUB* Contribution</th>
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<tbody>
<tr>
<td>2003</td>
<td>13.5</td>
<td>Mean = 9.1 (5-95% Ω) = (6.4 – 14.7)</td>
<td>Mean = 9.9 (5-95% Ω) = (5.9 – 15.1)</td>
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<tr>
<td>2004</td>
<td>19.7</td>
<td>Mean = 13.1 (5-95% Ω) = (9.3 – 21.4)</td>
<td>Mean = 15.5 (5-95% Ω) = (9.1 – 23.1)</td>
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</tbody>
</table>

*Coal-fired Utility Boiler
Urban vs. Rural/Remote TOF-AMS Measurements

- OOA corresponds to SOA

Zhang, Jimenez, et al., GRL, 34, L13801, 2007
Organic Markers Near a Roadway (RTP, NC)
Findings Related to Spatial and Temporal Distributions
Ambient Coarse Particle Variability in Greeley, CO (Rural)

Site pair in Greeley, CO using TEOM 1405-DF
• 24 hr average correlation is 0.95
• 1 hr average correlation is 0.65
• longer averaging time reduced noise of measurement

Source: Mike Hannigan
Ambient Coarse Particle Variability in Los Angeles, CA

- For 14 of 18 outdoor sites, correlation (r) with central monitor > 0.71
- Distance between sites didn’t impact correlation.
- Location of sources impacted correlation.

Source: Costas Sioutas
Variability of Particle Measurements in RTP, NC

Temporal and Spatial PM Variability

- Per 10-2.5
- Amb 10-2.5

Temporal and Spatial PM Variability

- Per 2.5
- Amb 2.5

Variability of Particle Measurements in RTP, NC
Spatial variability of PM$_{10-2.5}$ measured over 3-week study period in Cleveland, OH
Seasonal and Spatial Variability for Coarse PM Observed in the Detroit Exposure and Aerosol Research Study (DEARS)
Spatial Variability Varies by Pollutant in DEARS

Residential Outdoor Concentration

Ambient Concentration at Central Site Monitor

Season 1 (Summer) •
Season 2 (Winter) •
Variability of Air Pollutants Near LAX

• Los Angeles International Airport (LAX)
  • Mobile monitoring platform
  • High time resolution sampling: particle number, size distribution, black carbon, NO\textsubscript{x}, particulate PAHs
  • Determine extent of airport emissions downwind into surrounding neighborhood

Site locations: A--Upwind, B--500m downwind of landing, C--Taxiway, D--Takeoff, E--900m downwind of takeoff

Time series of mobile monitoring data showing high spatial and temporal variability in concentrations near LAX

Source: Costas Sioutas
Findings Related to Personal Exposure – Ambient Relationships
DEARS Personal and Ambient PM2.5 Relationships

Central Site PM2.5 versus Personal PM2.5 in EMA 6
[all seasons]

- $y = 0.3363x + 13.731$
- $R^2 = 0.0232$

Site impacted by highway

Central Site PM2.5 versus Personal PM2.5 in EMA 7
[seasons 1 & 2 only]

- $y = 0.4029x + 5.083$
- $R^2 = 0.3253$

Site impacted by regional air

Note differences in $r^2$
Personal, Indoor, Outdoor, and Ambient Relationships: Particles
Personal, Indoor, Outdoor, and Ambient Relationships: Air Toxics
## Effect of Residential Characteristics (% Increase in Mean Concentration)

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<thead>
<tr>
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<tbody>
<tr>
<td>Benzene</td>
<td>Indoor</td>
<td>46</td>
<td>44</td>
<td>6</td>
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<tr>
<td></td>
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<td>115</td>
<td>45</td>
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<tr>
<td>Toluene</td>
<td>Indoor</td>
<td>48</td>
<td>51</td>
<td>37</td>
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<td></td>
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<tr>
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## Effect of Personal Activities (% Increase in Mean Concentration)

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Location</th>
<th>Gas space heater</th>
<th>Solvent usage</th>
<th>Candles or incense</th>
<th>Dryclean (7 d. prior)</th>
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<tbody>
<tr>
<td>Benzene</td>
<td>Indoor</td>
<td></td>
<td></td>
<td>-27</td>
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<tr>
<td></td>
<td>Personal</td>
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<td>Toluene</td>
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<td>-30</td>
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<td>64</td>
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<td>-30</td>
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<td></td>
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<td>m,p-Xylenes</td>
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<tr>
<td></td>
<td>Personal</td>
<td>10</td>
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Products for Air Quality Management Activities
Federal Reference and Equivalency Program Update

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<th>Designation</th>
<th>PM$_{10}$</th>
<th>PM$_{2.5}$</th>
<th>PM$_{10-2.5}$</th>
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<th>NO$_2$</th>
<th>SO$_2$</th>
<th>CO</th>
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Receptor Model and Instructional Material Releases

- **Source Apportionment Model Releases**
  - EPA Positive Matrix Factorization (PMF) 3.0 Software & User Guide
  - EPA Unmix 6.0 Software & User Guide
  - EPA CMB 8.2 Software and User Guide
  - EPA Air Pollution Transport to Receptor 1.0 alpha

**Software and User Guide Links**

Unmix: [http://www.epa.gov/heasd/products/unmix/unmix.htm](http://www.epa.gov/heasd/products/unmix/unmix.htm)

PMF: [http://www.epa.gov/heasd/products/pmf/pmf.htm](http://www.epa.gov/heasd/products/pmf/pmf.htm)

CMB: [http://www.epa.gov/scram001/receptor_cmb.htm](http://www.epa.gov/scram001/receptor_cmb.htm)
Future Directions
Near Term Future Directions for ORD Ambient Air Research

- Continue Data Analyses
  - Detroit/Dearborn
  - Birmingham
  - Steubenville

- Ongoing and Planned Field Work
  - Cleveland Multiple Air Pollutant Study (CMAPS)
  - Near Roadway
    - Las Vegas
    - Detroit
    - RTP, NC

- Federal Reference and Equivalency
  - Lead
  - Visibility

- Science to Achieve Results (STAR) - Extramural Grants
  - New air pollution research centers
  - Source emissions
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