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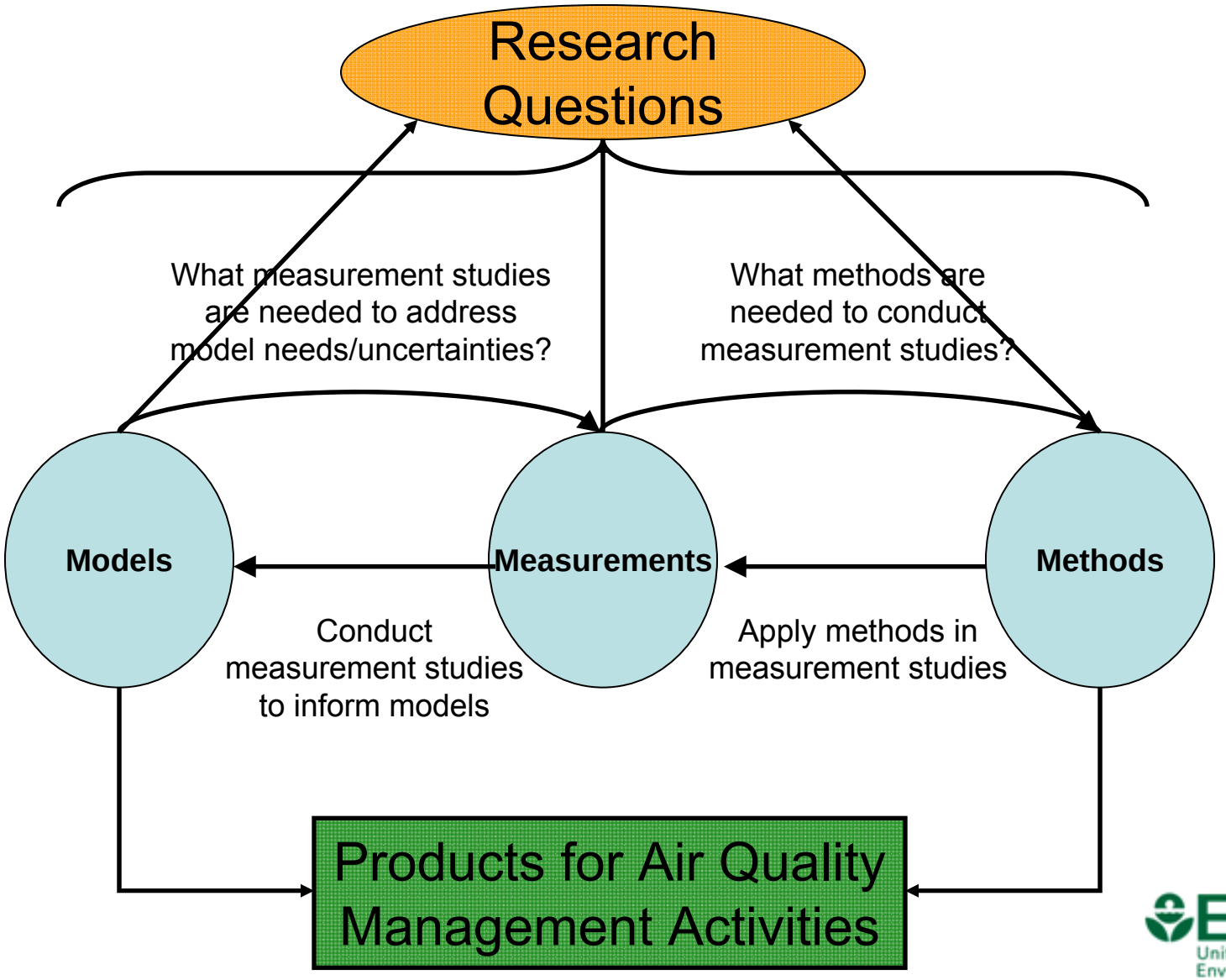
# Recent Findings from EPA/ORD Ambient Measurement Research

*Tim Watkins*

*National Air Monitoring Conference*
*Nashville, TN*
*November 3, 2009*

**Office of Research and Development**
**National Exposure Research Laboratory**

# General Approach Ambient Measurement Research



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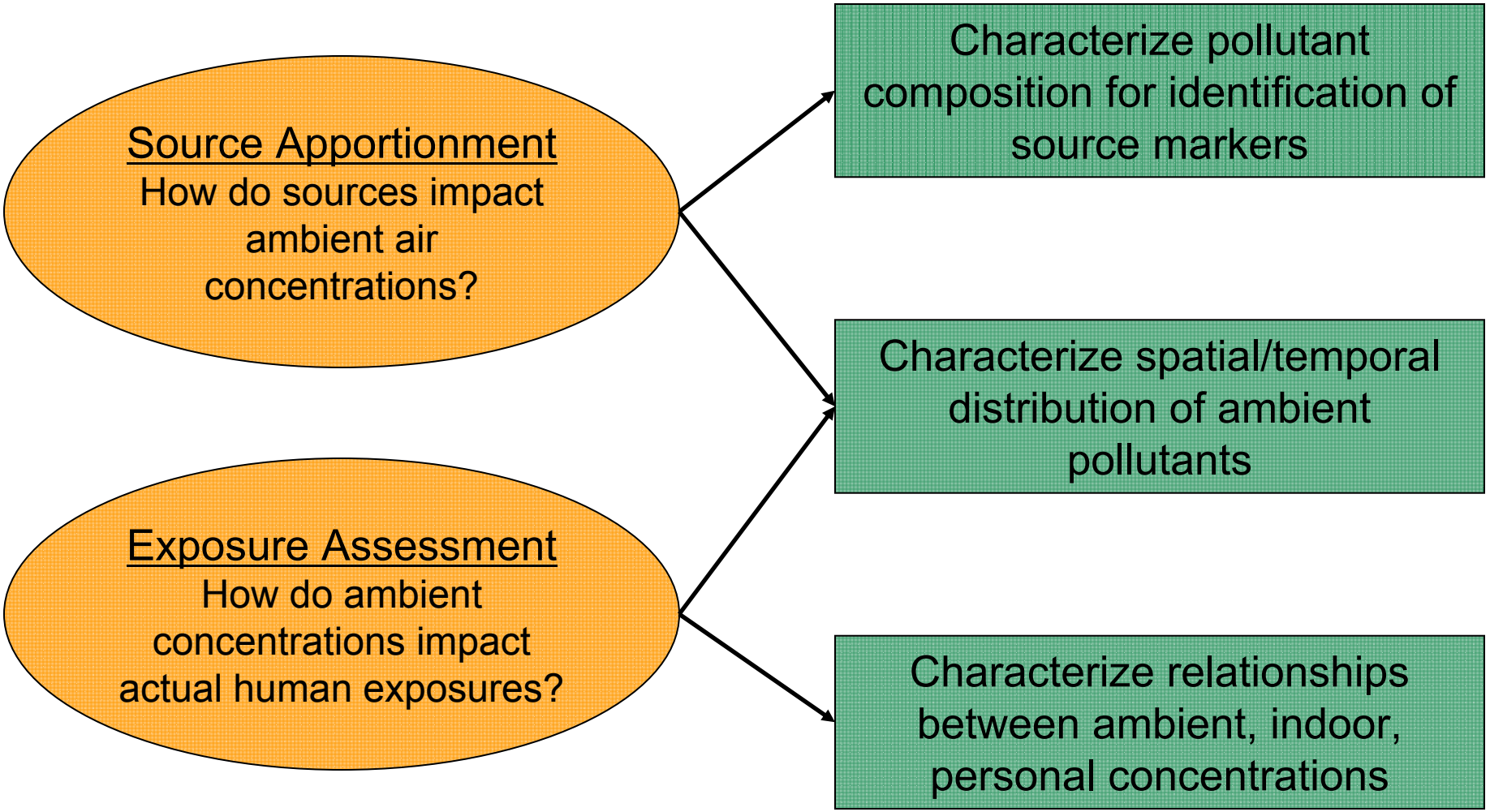
# Ambient Measurement Research Questions and Activities



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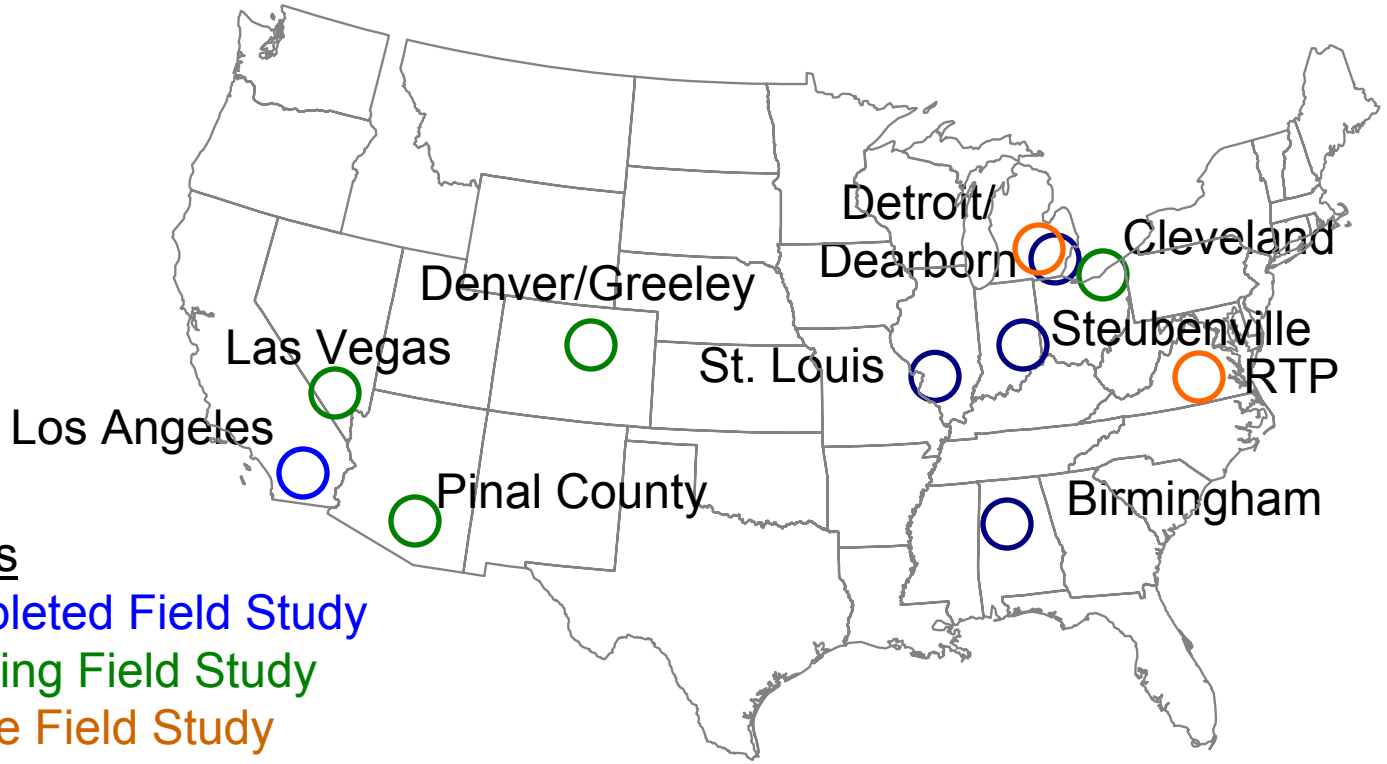
# Locations of ORD's Ambient Measurement Research Field Studies




Status
Completed Field Study
Ongoing Field Study
Future Field Study

Many studies in locations with NAAQS non-attainment issues.



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# Source Apportionment Tools

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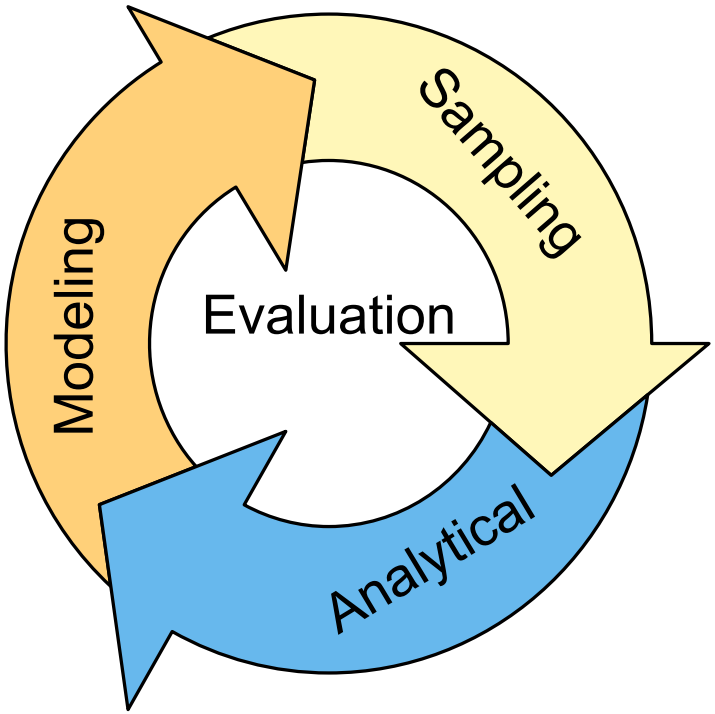
# Elements of Source Apportionment Research



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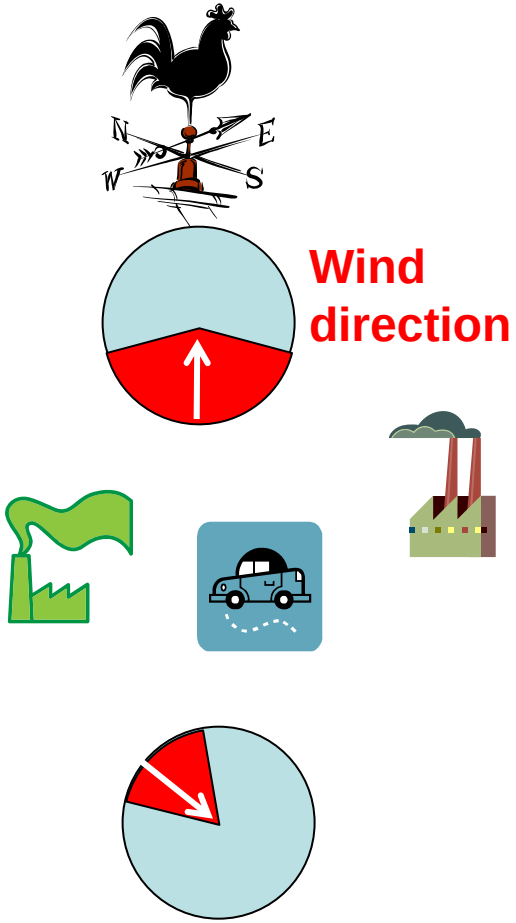
# Sampling Time Resolution for providing data for local and regional source apportionment

- 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.

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# 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-destrutive 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/$m^3$ at 10 liter/min, 24 h). Demonstrated ability to quantify organic source markers in ambient and personal exposure sample.



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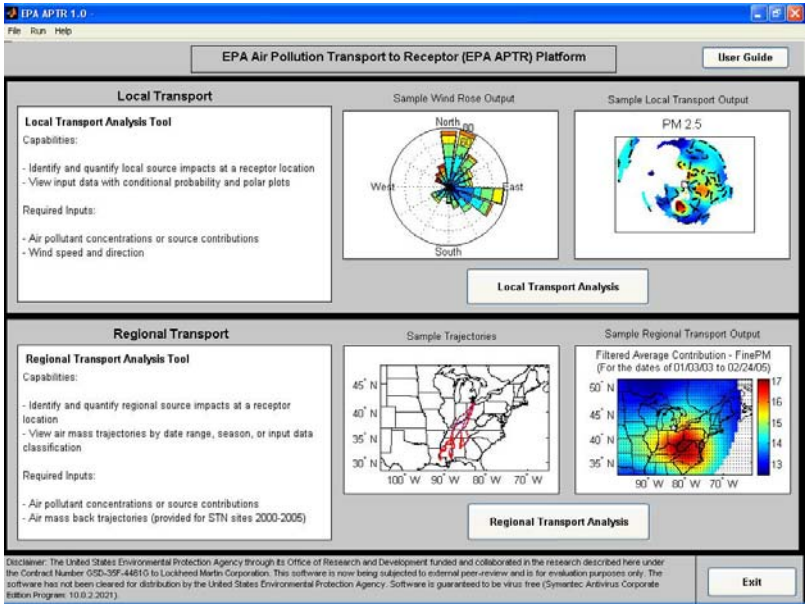
# EPA Receptor Models

- **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

**EPA Air Pollution Transport to Receptor (APTR)**




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.



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# Source Apportionment Findings

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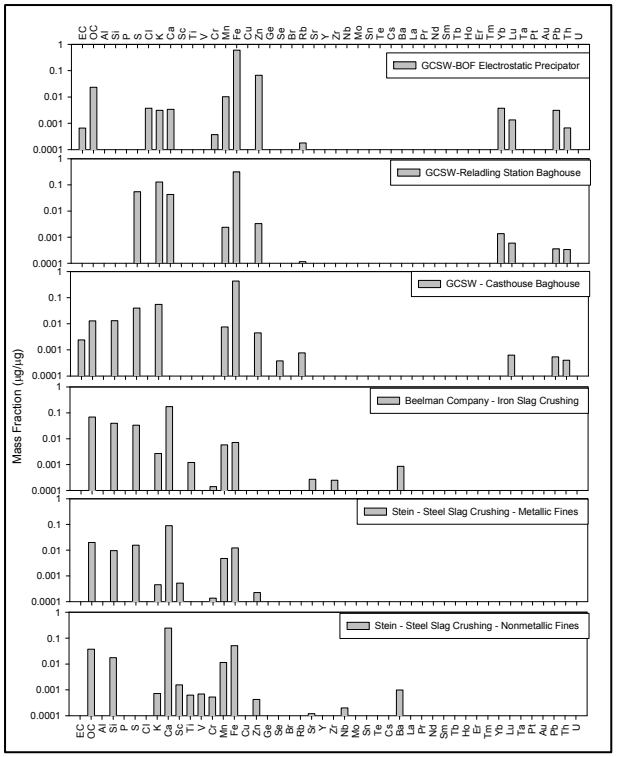
# Source Sample Collection at U.S. Steel Granite City Works in St. Louis

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

Coal fines conveyor

ESP controlling Basic Oxygen Furnace




**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**



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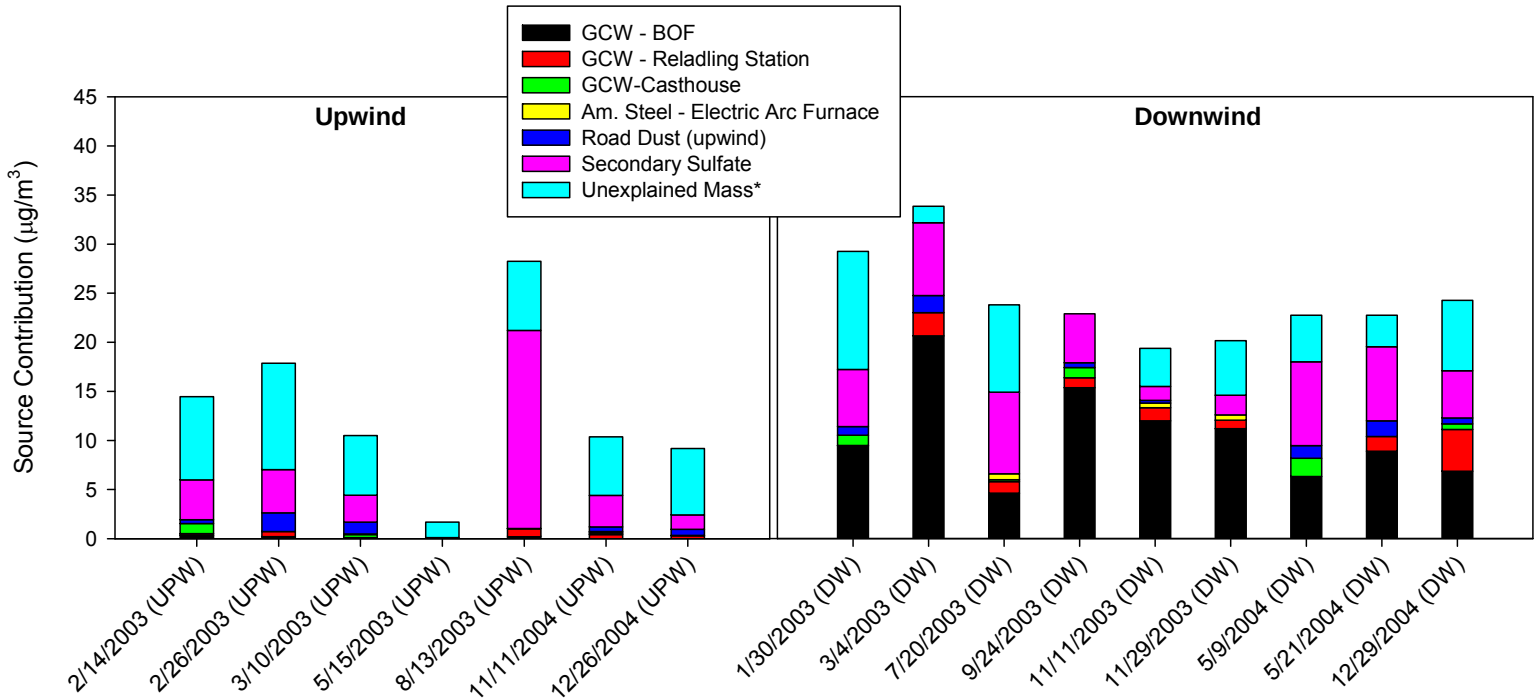
# St. Louis Advanced Monitoring Initiative Project

## Chemical Mass Balance Results – VFW Site (Granite City, IL)




**Unexplained Mass contains nitrate and OC/EC compounds*

**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**



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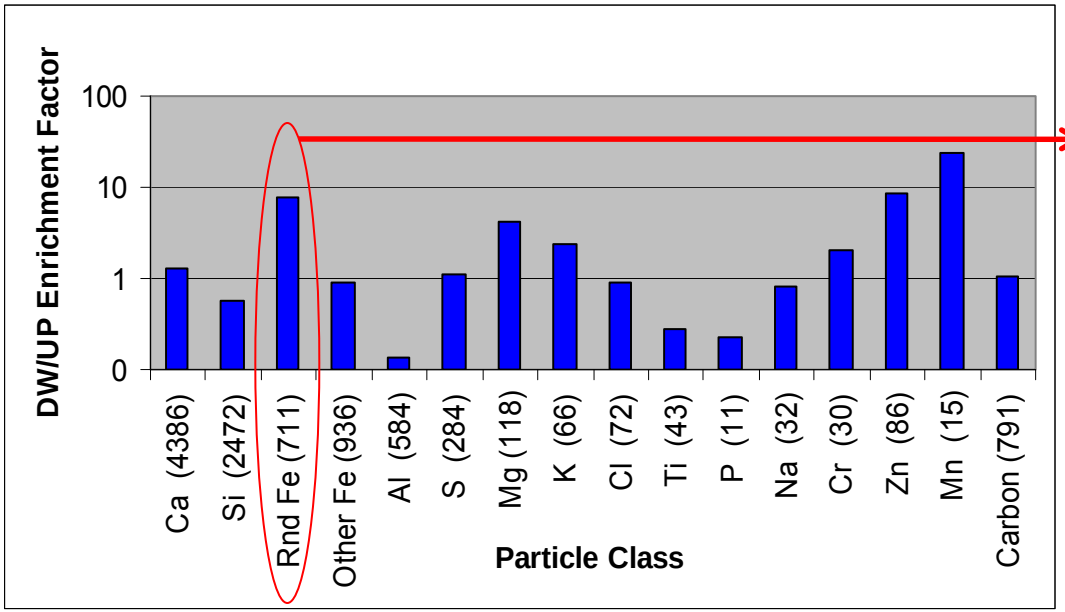
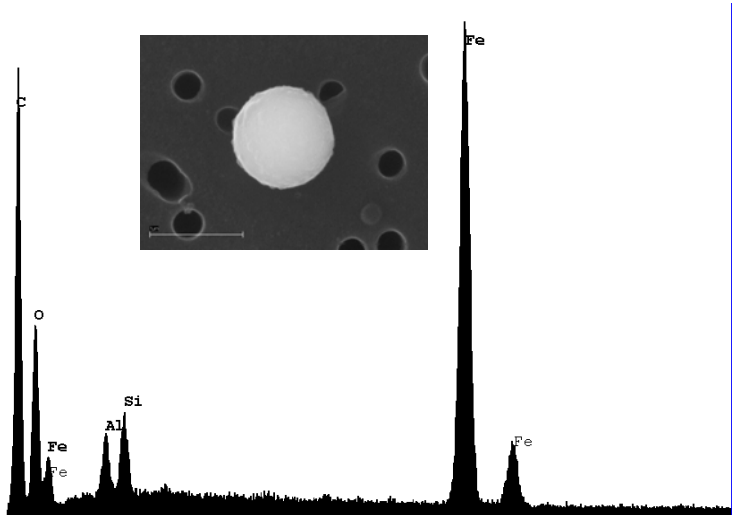
# Additional Information from SEM Analyses

## 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**




**EPA Scanning Electron Microscopy**



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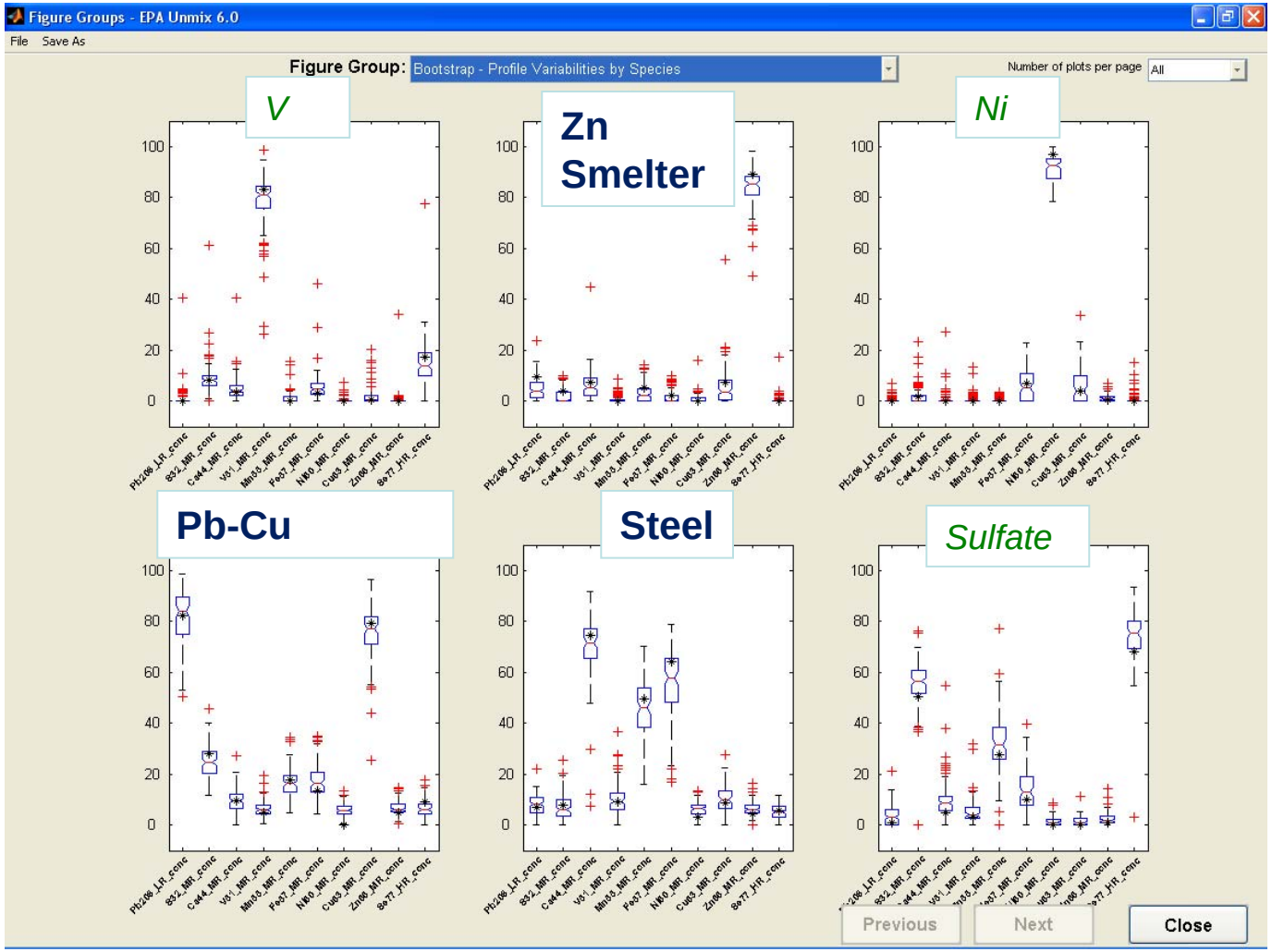
# Analysis of 30 minute St. Louis SEAS Data with EPA Unmix



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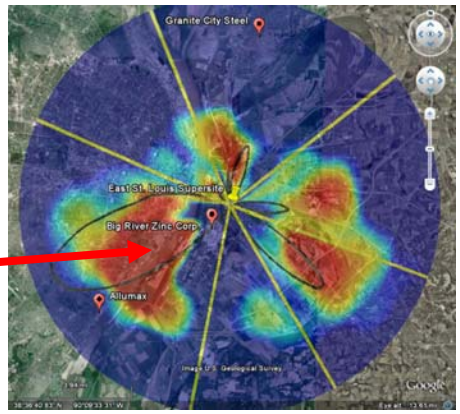
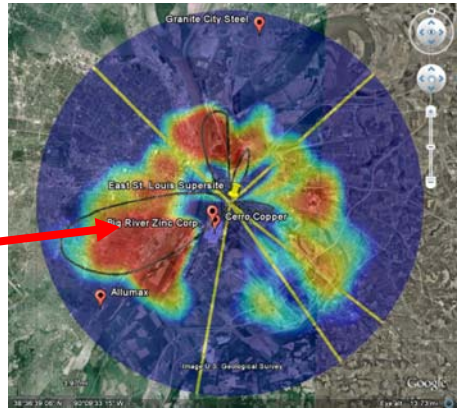
# St. Louis APTR Results

| Sector (center) | Percentage | Mean | N |
|---|---|---|---|
| 339-52 (369) | 9.46 | 0.095 | 131 |
| 53-110 ( 75) | 9.42 | 0.094 | 53 |
| 111-165 (134) | 14.18 | 0.142 | 36 |
| 166-190 (208) | 1.07 | 0.011 | 23 |
| 191-294 (273) | 60.92 | 0.609 | 173 |
| 295-338 (313) | 4.95 | 0.049 | 16 |



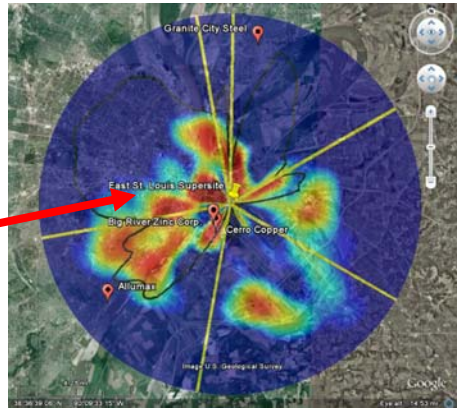

Zn Source

| Sector (center) | Percentage | Mean | N |
|---|---|---|---|
| 316-48 (362) | 25.2 | 0.254 | 145 |
| 49-128 ( 89) | 16.25 | 0.164 | 64 |
| 129-144 (198) | 3.29 | 0.033 | 10 |
| 145-190 (283) | 4.36 | 0.044 | 43 |
| 191-315 (314) | 50.91 | 0.514 | 170 |




Cu-Pb Source

| Sector (center) | Percentage | Mean | N |
|---|---|---|---|
| 351-1 (360) | 3.64 | 0.037 | 32 |
| 2-60 ( 60) | 11.49 | 0.117 | 53 |
| 61-120 ( 95) | 14.43 | 0.147 | 41 |
| 121-190 (145) | 13.29 | 0.135 | 108 |
| 191-260 (225) | 20.34 | 0.207 | 85 |
| 261-350 (295) | 36.8 | 0.374 | 113 |




Steel Source

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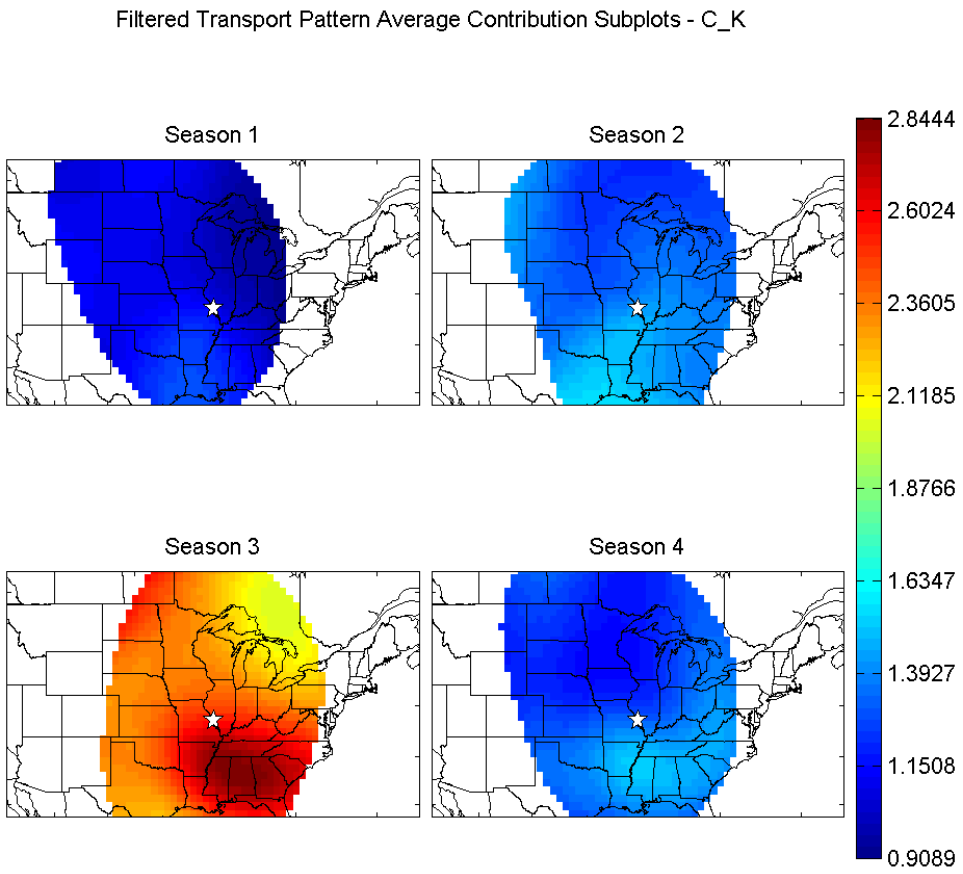
# Regional Source Contributions in St. Louis




The PMF biomass burning regional impact in μg/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).



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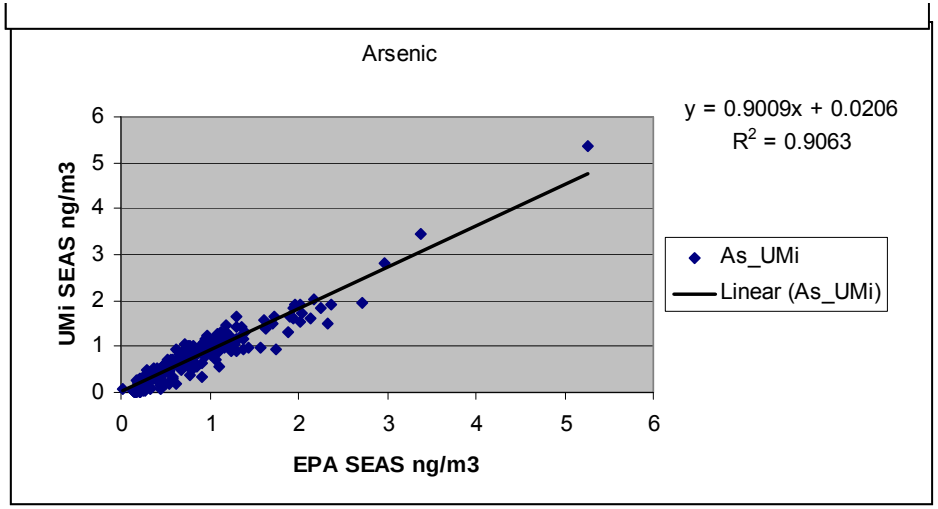
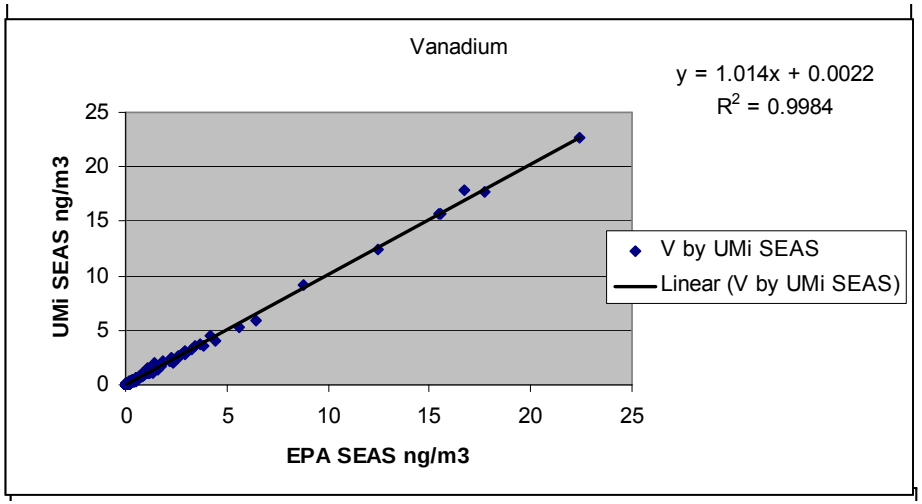
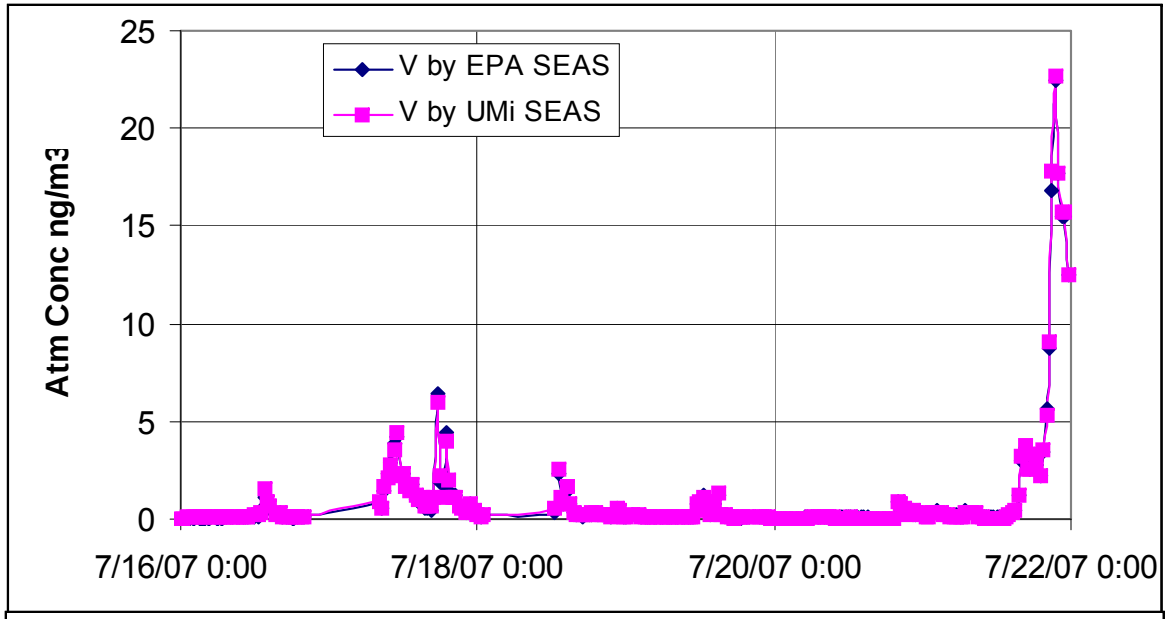
# Evaluation of the SEAS in Dearborn, MI



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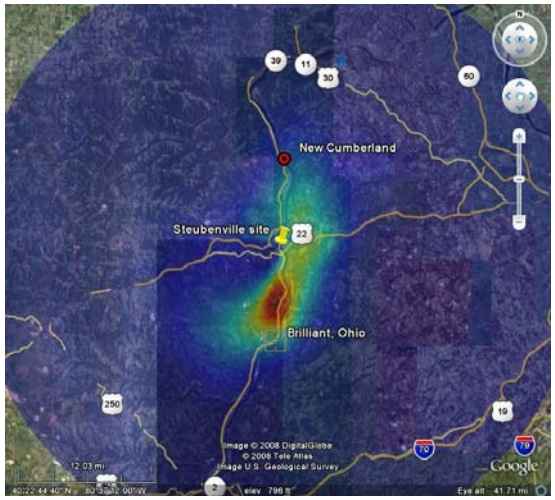
# Steubenville Source Apportionment Study: Impact of Coal Fired Utility Boilers

*Local impact of power plant quantified for $SO_2$ in Steubenville*




- 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)

**Annualized Steubenville Source Apportioned Mercury Wet Deposition Results**

| Year | Measured | PMF Estimated CFUB* Contribution | UNMIX Estimated CFUB* Contribution |
|---|---|---|---|
| 2003 | 13.5 | Mean = 9.1 (5-95% Ω) = (6.4 – 14.7) | Mean = 9.9 (5-95% Ω) = (5.9 – 15.1) |
| 2004 | 19.7 | Mean = 13.1 (5-95% Ω) = (9.3 – 21.4) | Mean = 15.5 (5-95% Ω) = (9.1 – 23.1) |

***Coal-fired Utility Boiler**



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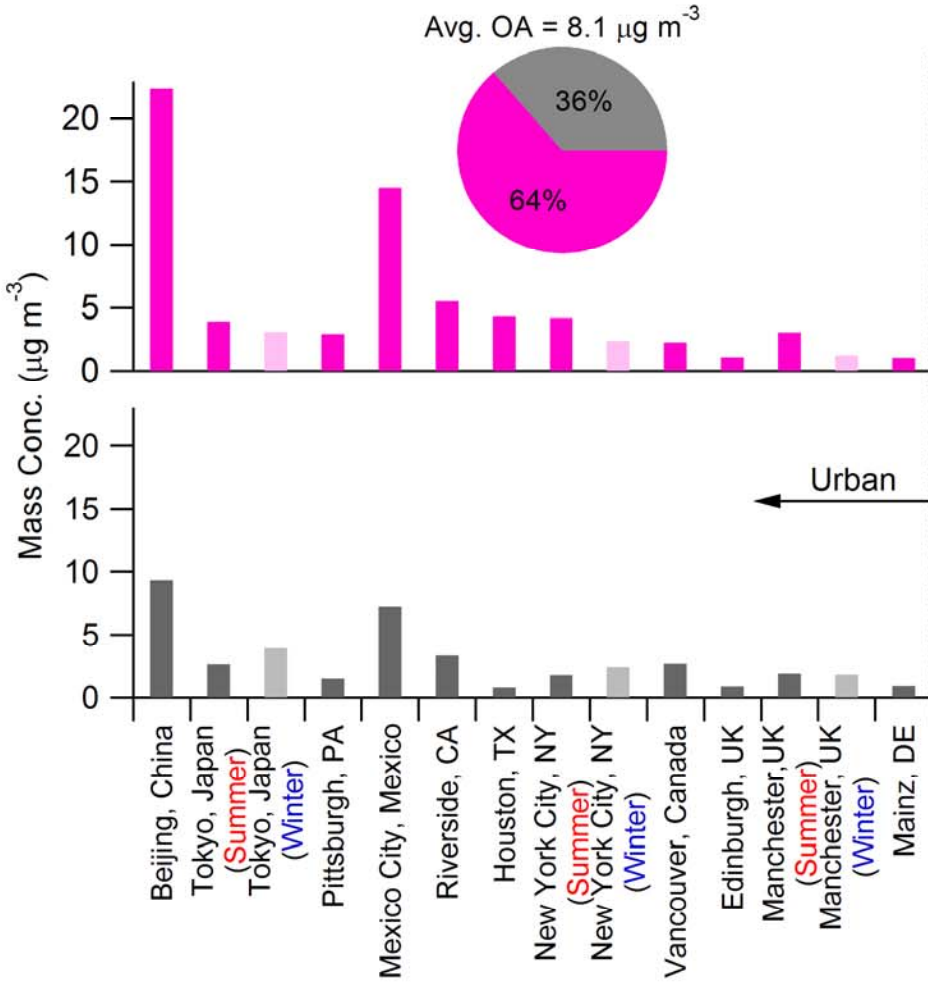
# Urban vs. Rural/Remote TOF-AMS Measurements




Oxygenated OA (OOA)

Hydrocarbon-like OA (HOA)

- OOA corresponds to SOA



Zhang, Jimenez, et al., GRL, 34, L13801, 2007

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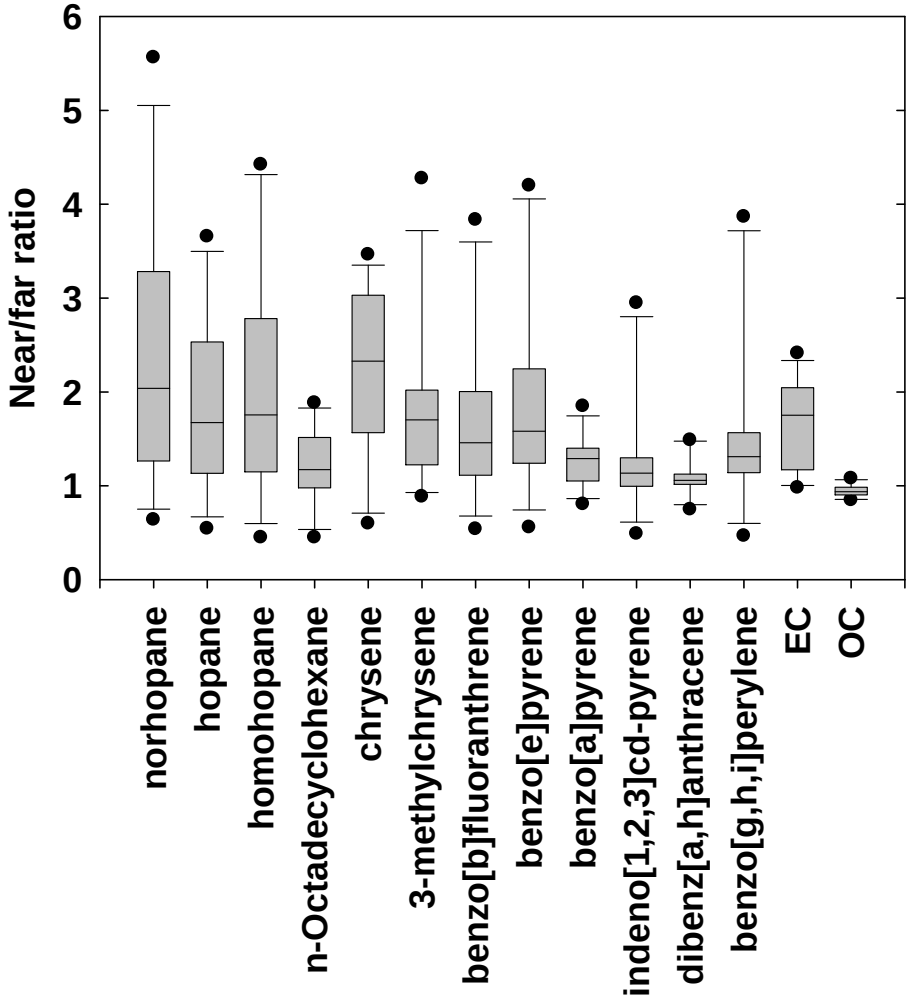
# Organic Markers Near a Roadway (RTP, NC)



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# Findings Related to Spatial and Temporal Distributions

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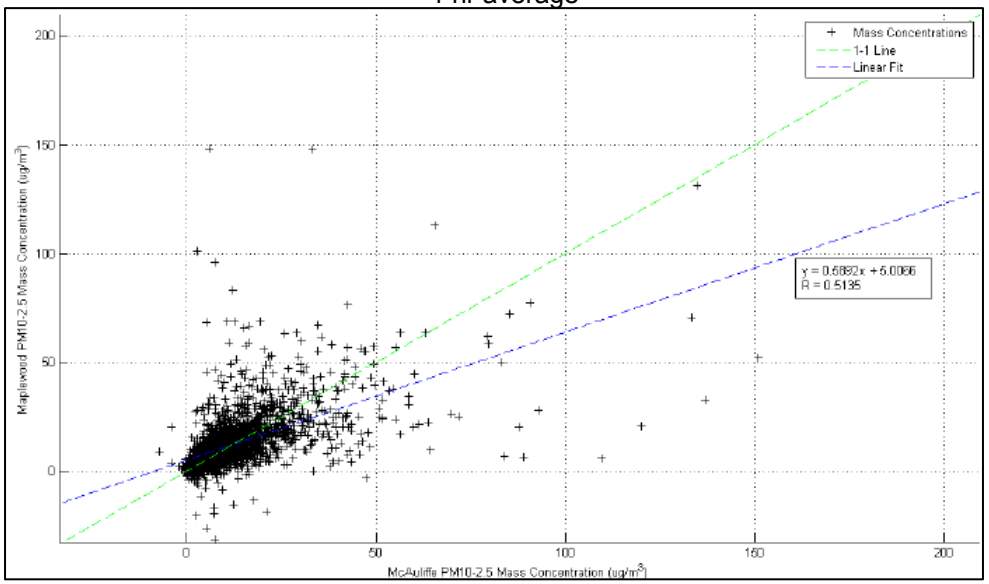
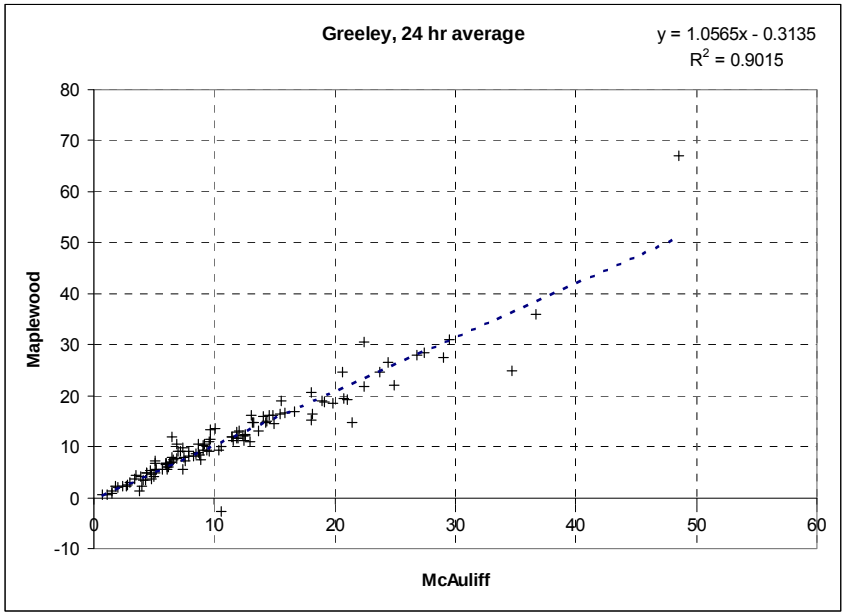
National Exposure Research Laboratory

# Ambient Coarse Particle Variability in Greeley, CO (Rural)

1 hr average




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



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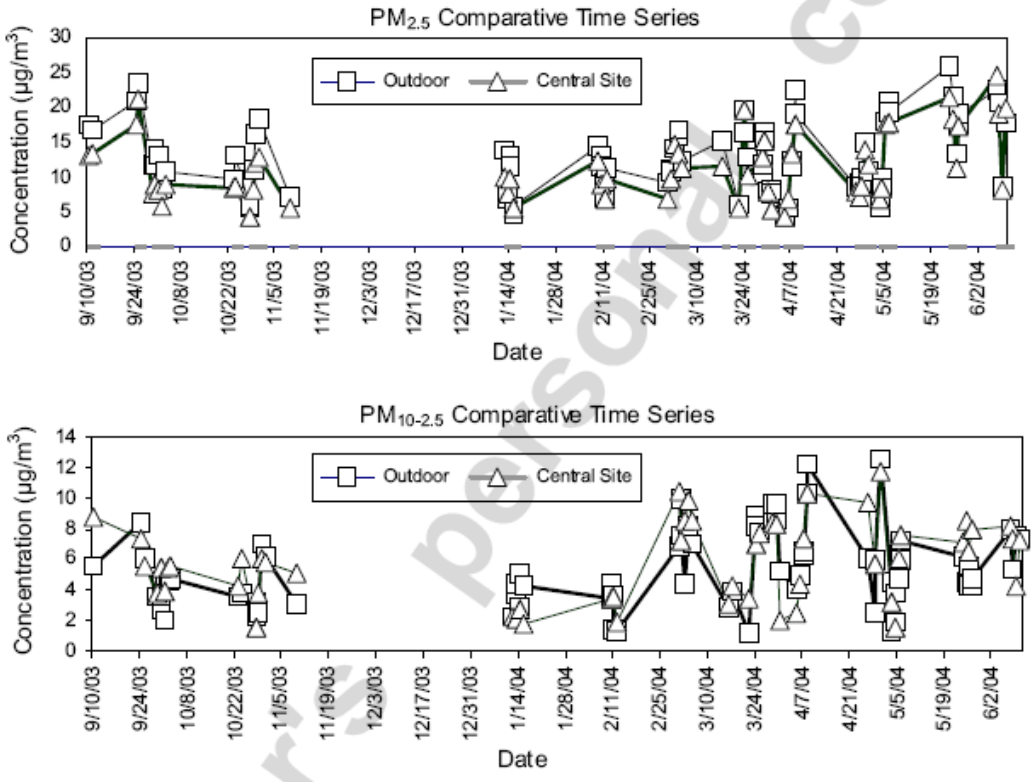
# Ambient Coarse Particle Variability in Los Angeles, CA




- 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



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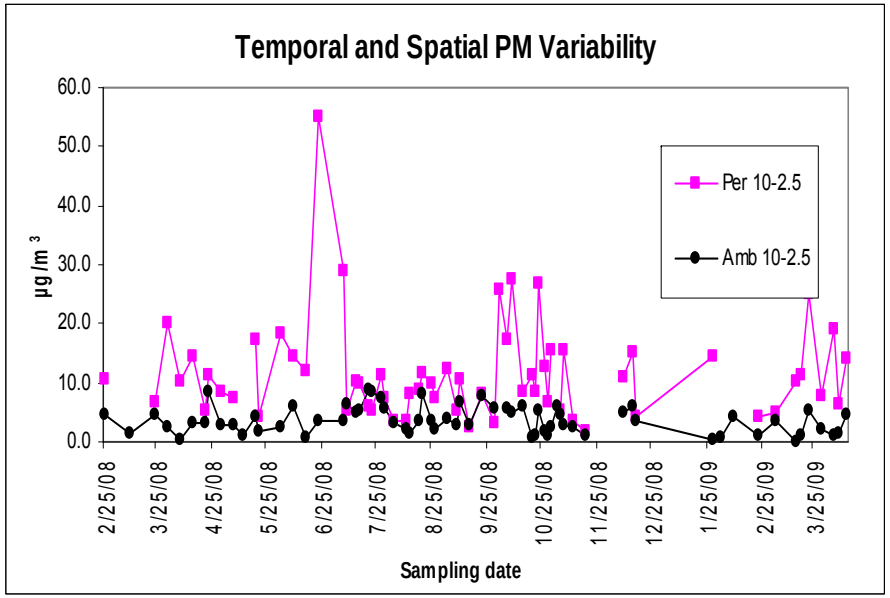
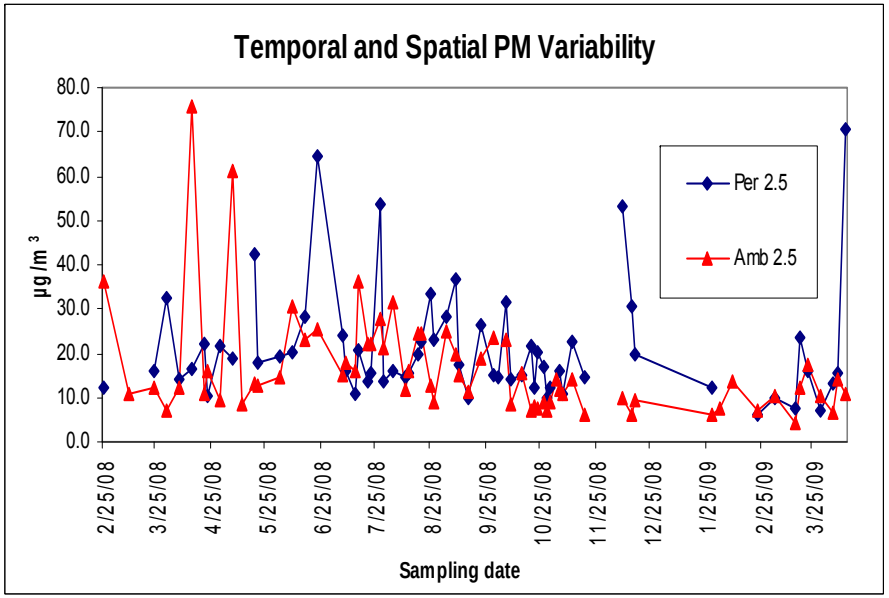
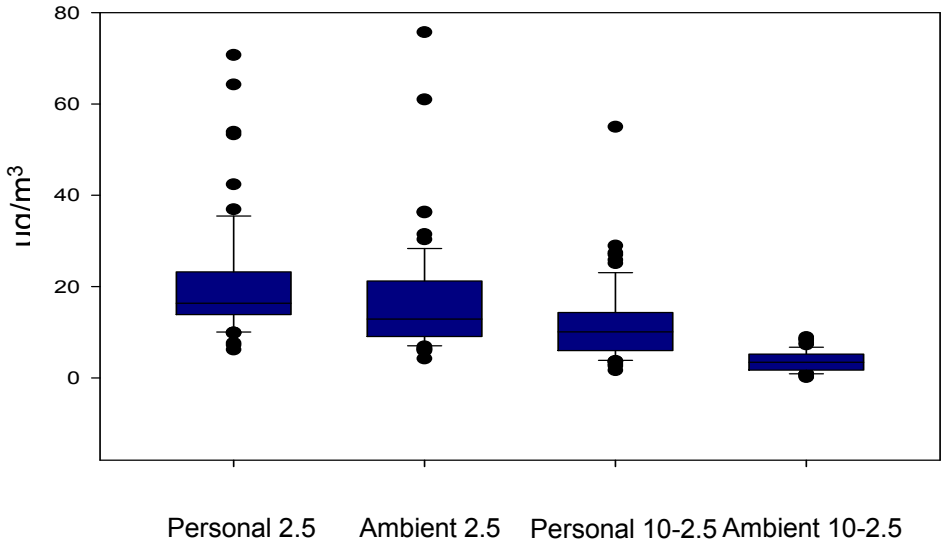
# Variability of Particle Measurements in RTP, NC



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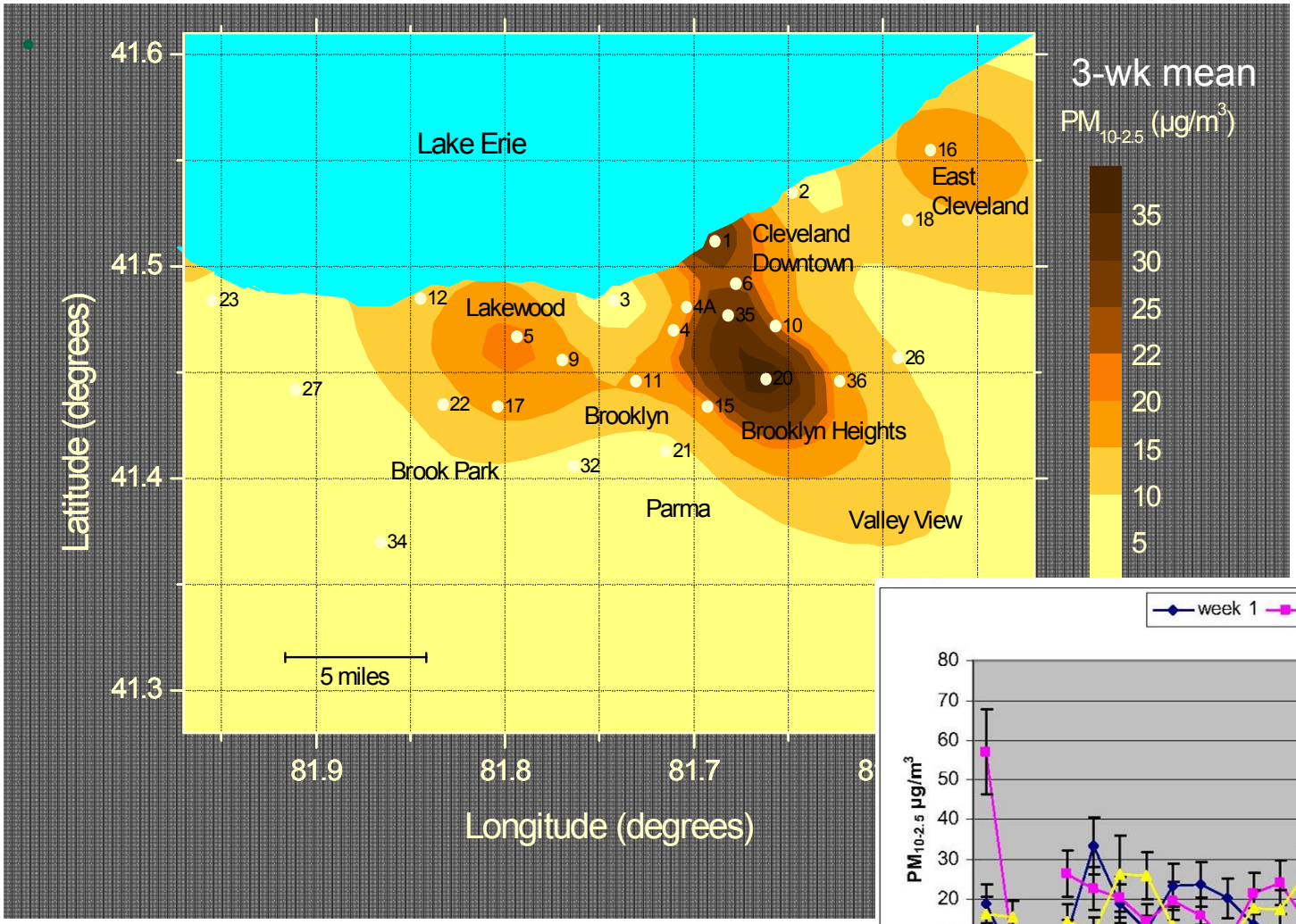
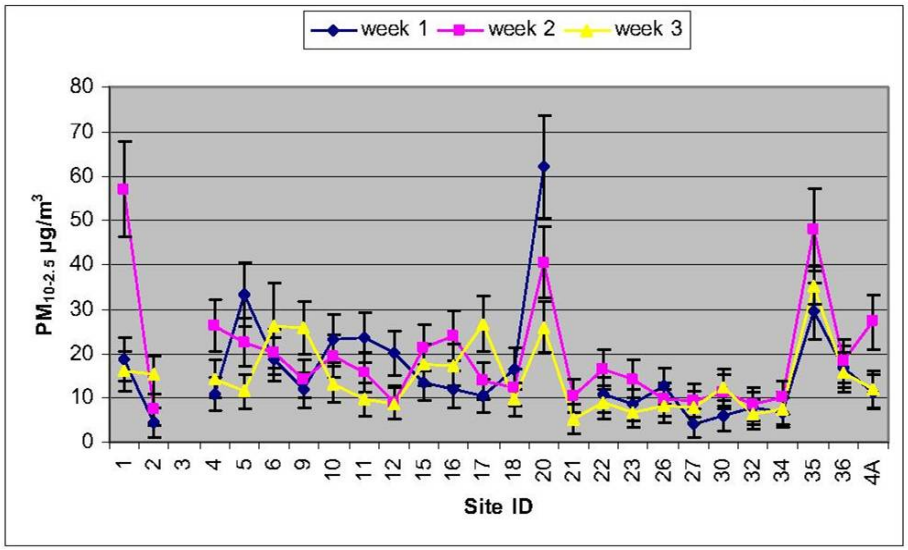
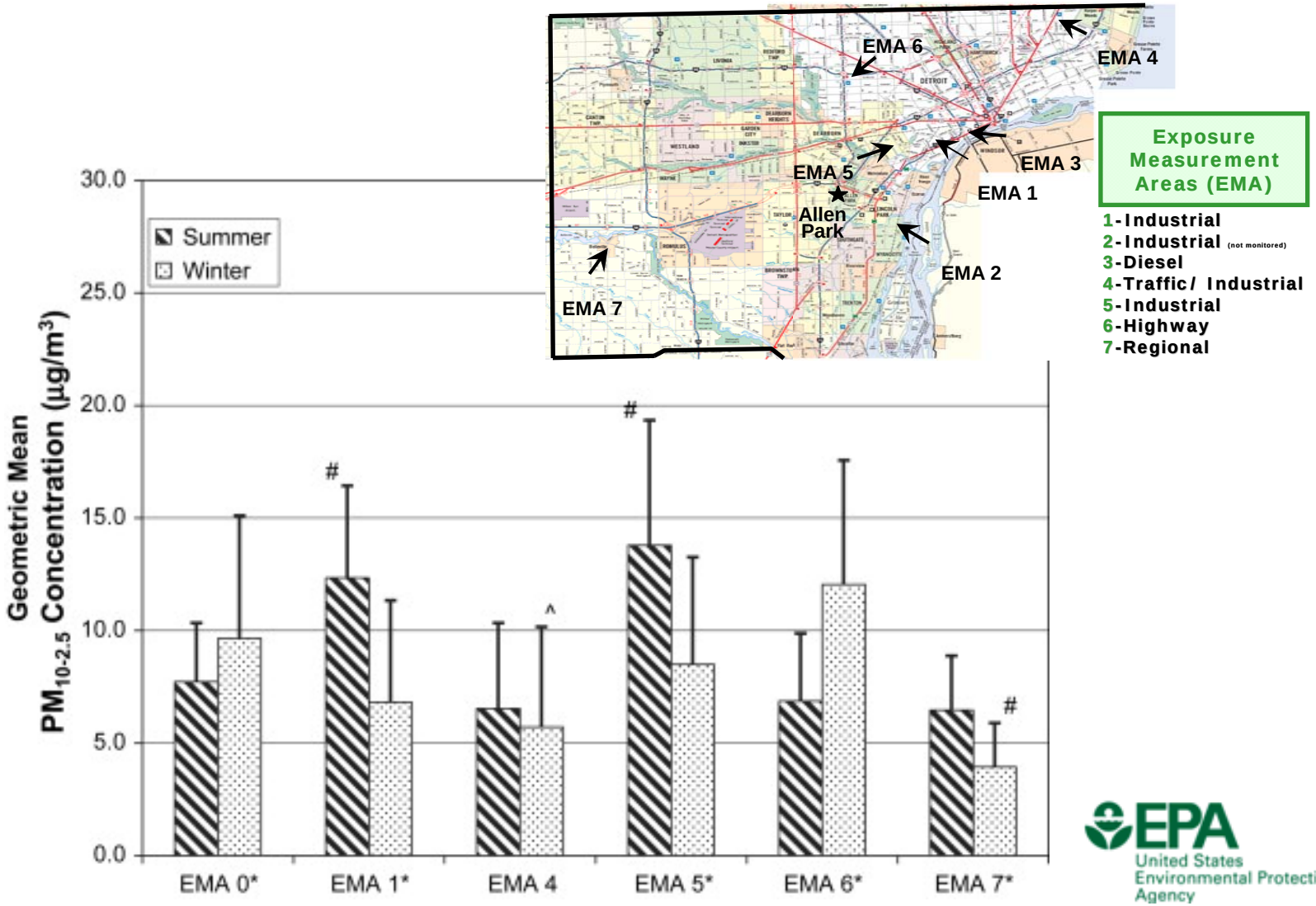
# Spatial variability of $PM_{10-2.5}$ measured over 3-week study period in Cleveland, OH



# Seasonal and Spatial Variability for Coarse PM Observed in the Detroit Exposure and Aerosol Research Study (DEARS)



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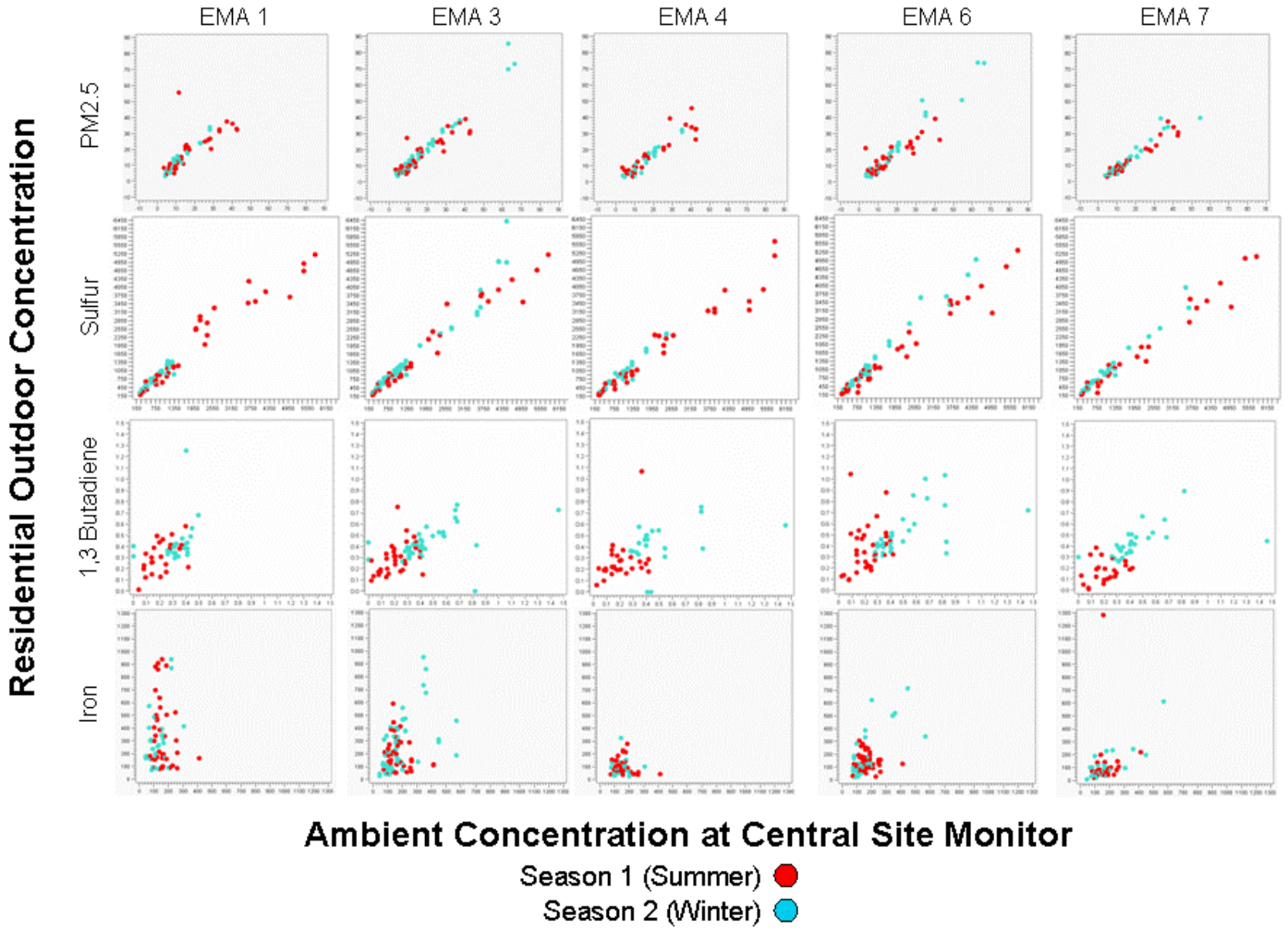
# Spatial Variability Varies by Pollutant in DEARS



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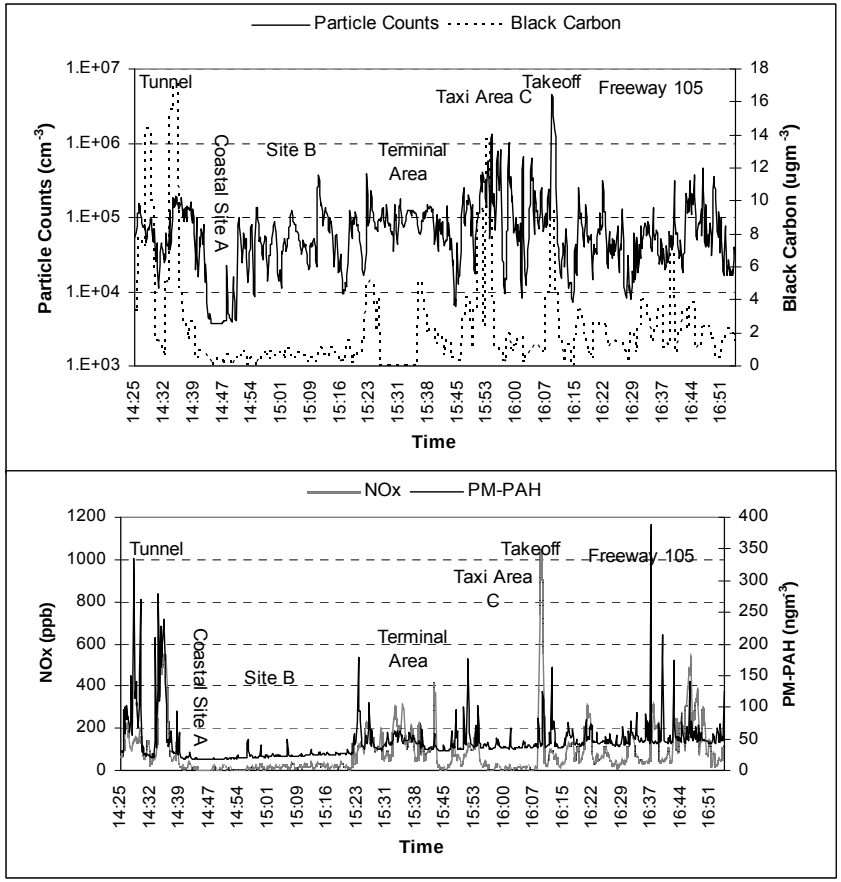
# Variability of Air Pollutants Near LAX

- Los Angeles International Airport (LAX)
  - Mobile monitoring platform
  - High time resolution sampling: particle number, size distribution, black carbon, $NO_x$, 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



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# Findings Related to Personal Exposure – Ambient Relationships

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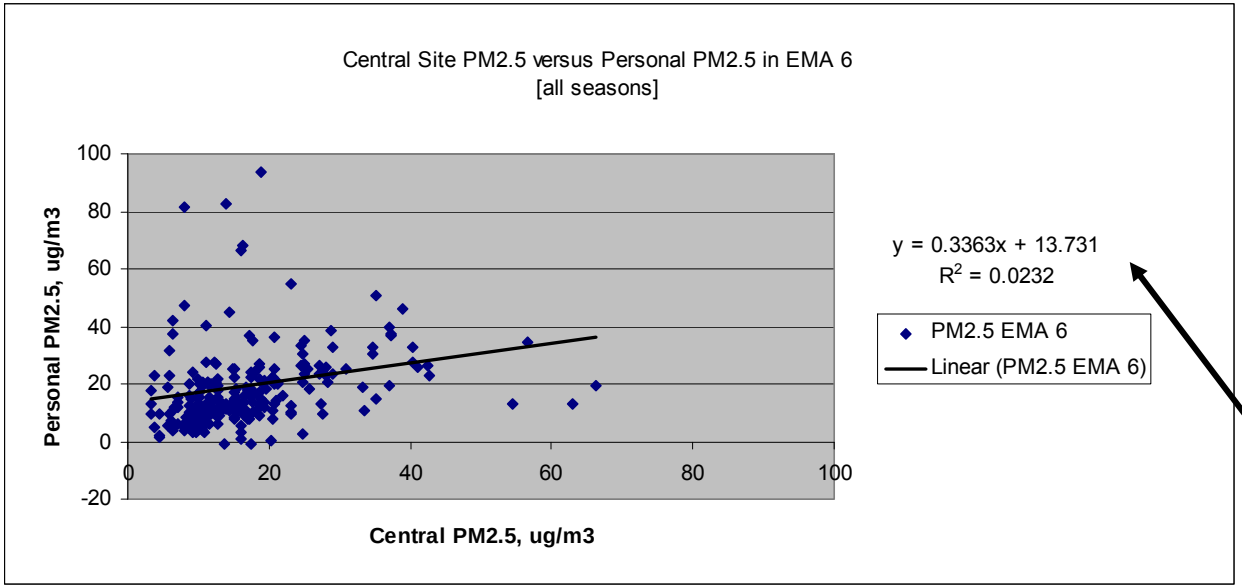
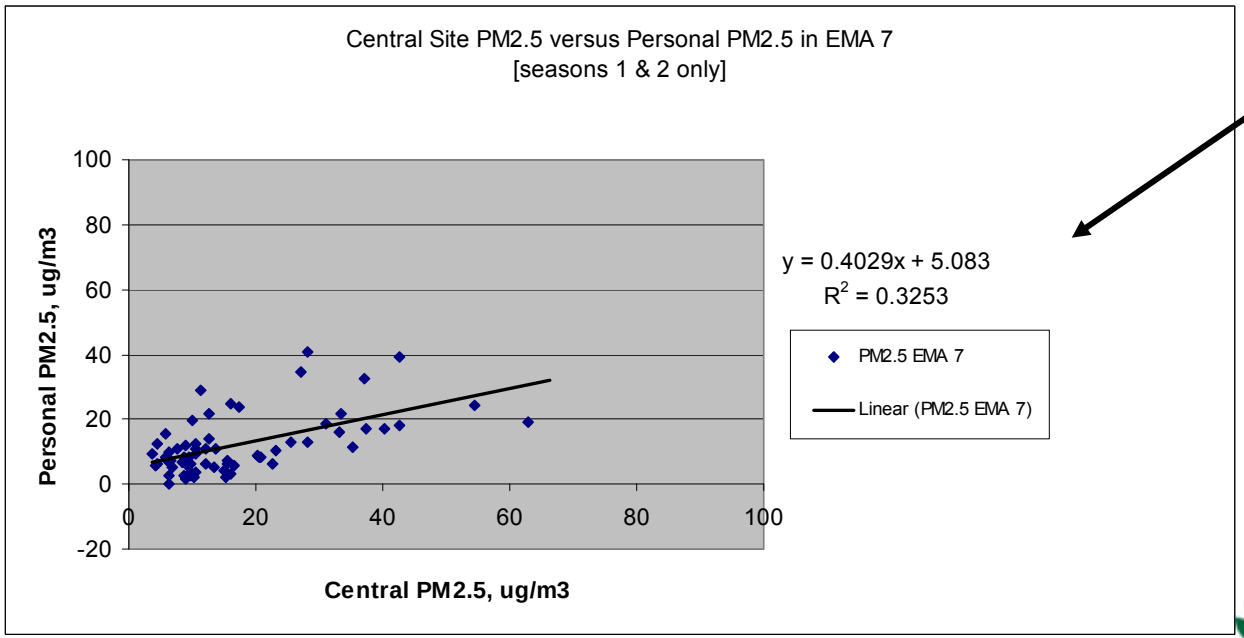
# DEARS Personal and Ambient PM2.5 Relationships

site impacted by highway




site impacted by regional air




note differences in $r^2$



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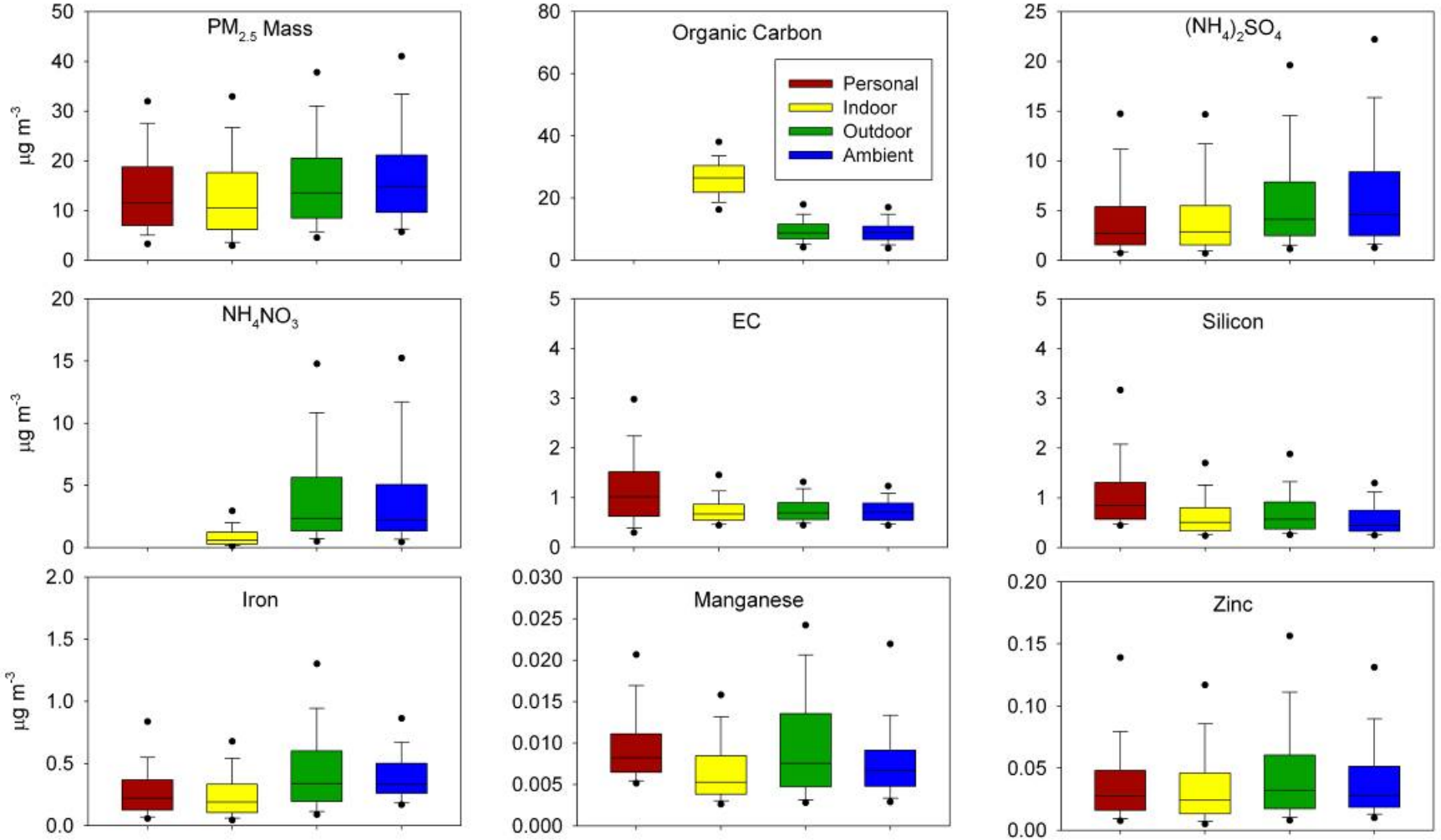
# Personal, Indoor, Outdoor, and Ambient Relationships: Particles



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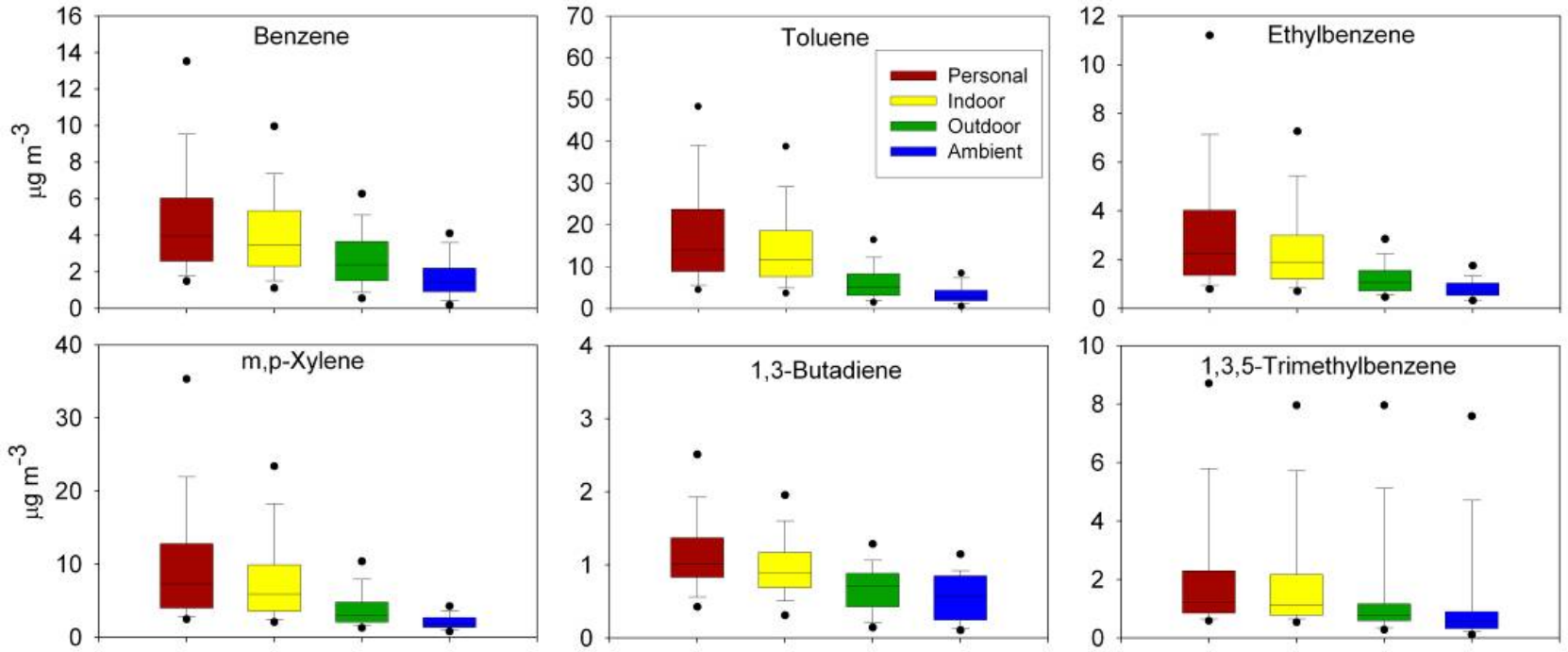
# Personal, Indoor, Outdoor, and Ambient Relationships: Air Toxics



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# Effect of Residential Characteristics
## (% Increase in Mean Concentration)

| Pollutant | Location | Attached Garage | Painting (7 d prior) | Carpet (6 mo. Prior) | Construction (6 mo. Prior) | Linoleum (6 mo. Prior) | Gas Stove |
|---|---|---|---|---|---|---|---|
| Benzene | Indoor | 46 | 44 | 6 | | 17 | |
| | Personal | 115 | 45 | | | | |
| Toluene | Indoor | 48 | 51 | 37 | 14 | 66 | |
| | Personal | | 38 | 36 | | | |
| Ethylbenzene | Indoor | 38 | 56 | 90 | 32 | 52 | |
| | Personal | | 15 | 58 | 54 | | |
| m,p-Xylenes | Indoor | 52 | 58 | 95 | 33 | 50 | |
| | Personal | 46 | 28 | 76 | 26 | | |
| Perchloroethylene | Indoor | | | | | | |
| | Personal | | | | | | |
| $NO_2$ | Personal | | | | | | 34 |
| EC | Indoor | | | | | | |



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# Effect of Personal Activities
## (% Increase in Mean Concentration)

| Pollutant | Location | Gas space heater | Solvent usage | Candles or incense | Dryclean (7 d. prior) |
|---|---|---|---|---|---|
| Benzene | Indoor | | | -27 | |
| | Personal | | | -36 | |
| Toluene | Indoor | | 38 | -30 | |
| | Personal | | | -38 | |
| Ethylbenzene | Indoor | | 64 | -30 | |
| | Personal | | 118 | -32 | |
| m,p-Xylenes | Indoor | | 65 | | |
| | Personal | | 10 | | |
| Perchloroethylene | Indoor | | | | 376 |
| | Personal | | | | 645 |
| $NO_2$ | Personal | 114 | | | |
| EC | Indoor | | | 121 | |

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# Products for Air Quality Management Activities

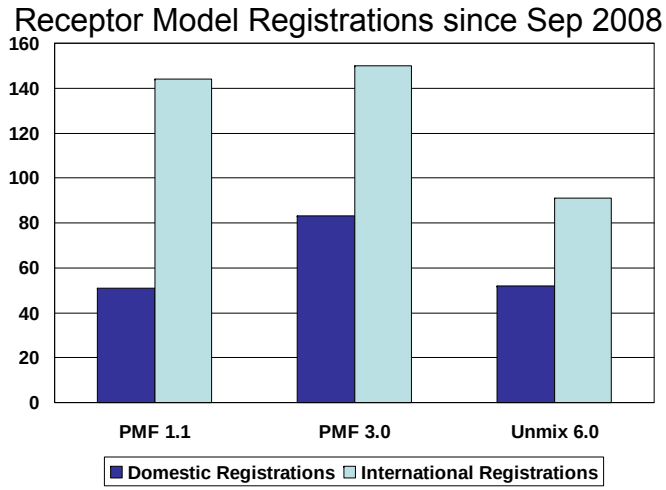
Office of Research and Development
National Exposure Research Laboratory

# Federal Reference and Equivalency Program Update

| Designation | Number of Designations by Pollutant Since 2005 | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $PM_{10}$ | $PM_{2.5}$ | $PM_{10-2.5}$ | $O_3$ | $NO_2$ | $SO_2$ | CO | Totals |
| Federal Reference Methods (FRMs) | 1 | 3 | 3 | | 4 | | 3 | 14 |
| Federal Equivalent Methods (FEMs) | 2 | 10 | 2 | 5 | | 4 | | 23 |
| Modifications to FRMs and FEMs | 12 | 3 | | 2 | 6 | 8 | 8 | 39 |

# 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

PMF: http://www.epa.gov/heasd/products/pmf/pmf.htm

CMB: http://www.epa.gov/scram001/receptor_cmb.htm



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# Future Directions

Office of Research and Development
National Exposure Research Laboratory

# Near Term Future Directions for ORD Ambient Air Research

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

Cleveland Industrial Valley

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

CMAPS Monitoring Sites Urban (GT Craig) and Background

- Federal Reference and Equivalency
  - Lead
  - Visibility

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

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