Measurement and Data Analysis for Source Attribution of Ambient Particulate Matter Arsenic and Other Air Toxics Metals in St. Louis

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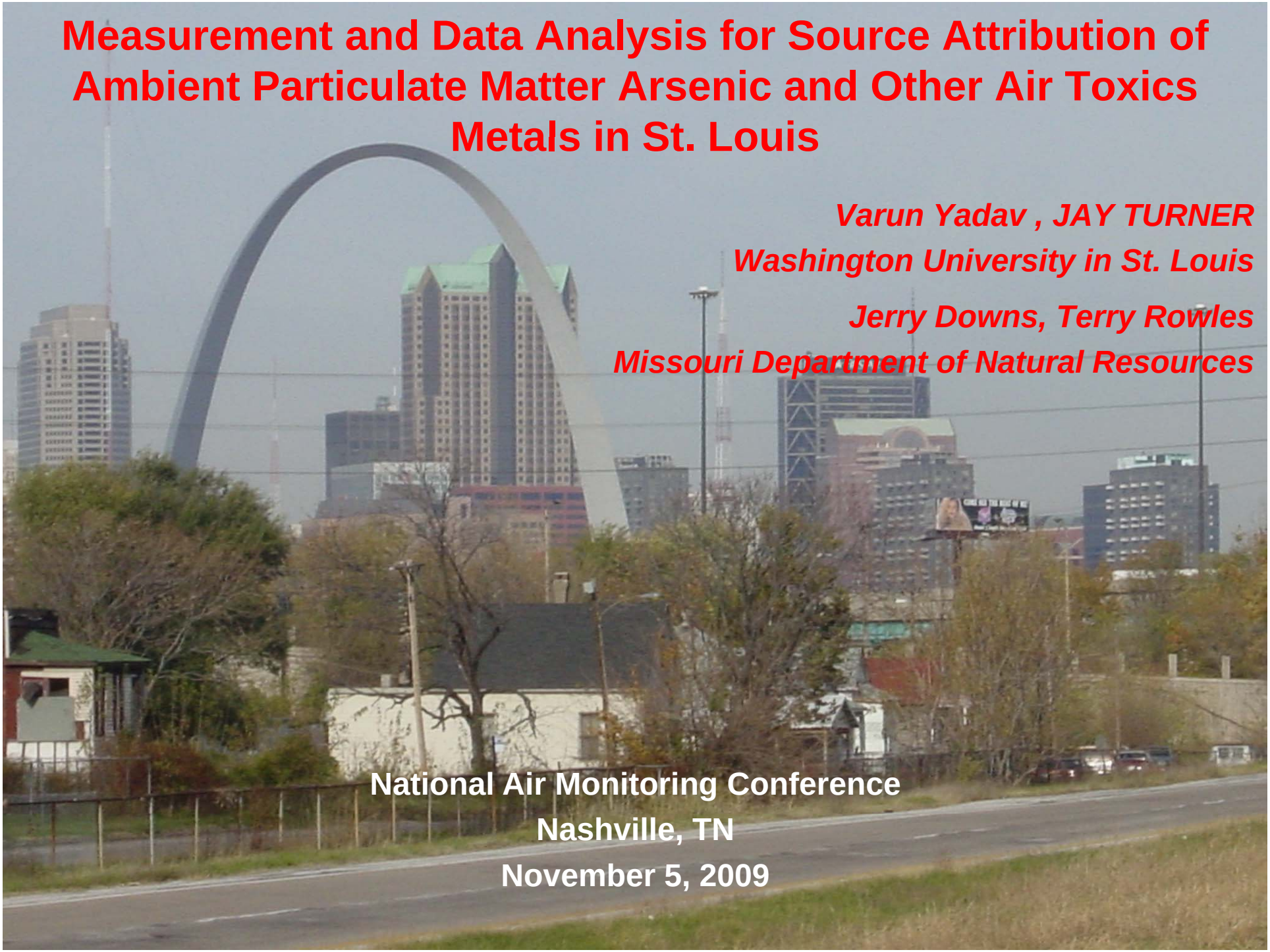


National Air Monitoring Conference

Nashville, TN

November 5, 2009

Motivation

The St. Louis Community Air Project (CAP)

- identified six hazardous air pollutants of concern including arsenic, *however*…
- poor data quality for $PM_{2.5}$ arsenic from speciation network data
- PM_{10} air toxics metals routinely measured at only one site (1-in-6 day)

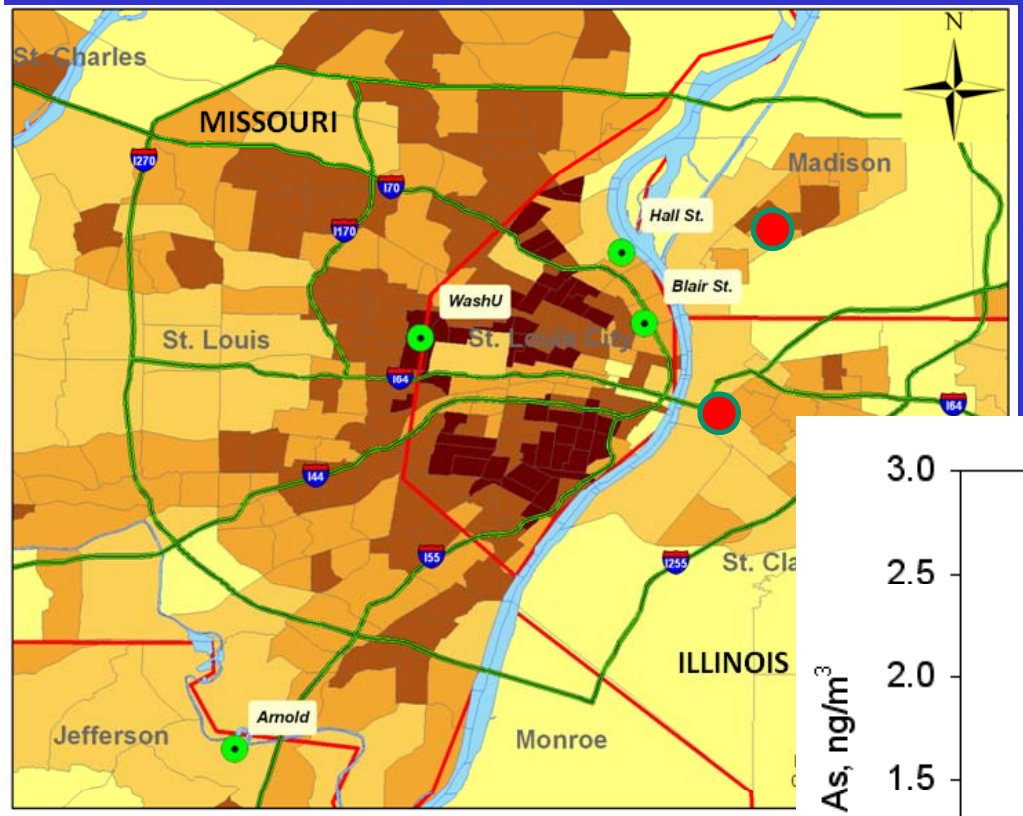
Objectives

Community Air Toxics Grant from USEPA

- Phase I
  - four site network of HiVol PM_{10} samplers
  - one year at 1-in-3 days
  - hot acid extraction and analysis by ICP-MS
- Phase II
  - high(er) time resolution measurements
  - six one-month deployments of CES Xact 620
  - *Xact performance evaluation (already shown this week)*

Filter Network Monitoring Sites

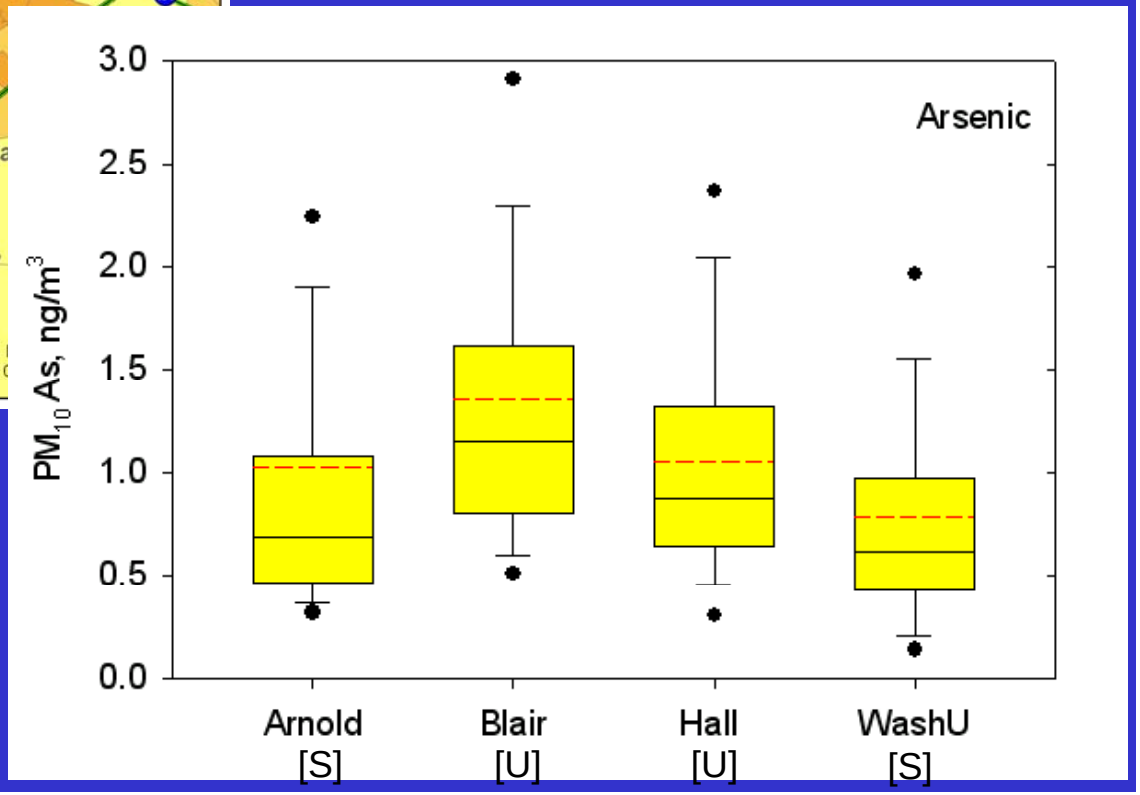
4 × Missouri (1-in-3), 2 × Illinois (1-in-6)



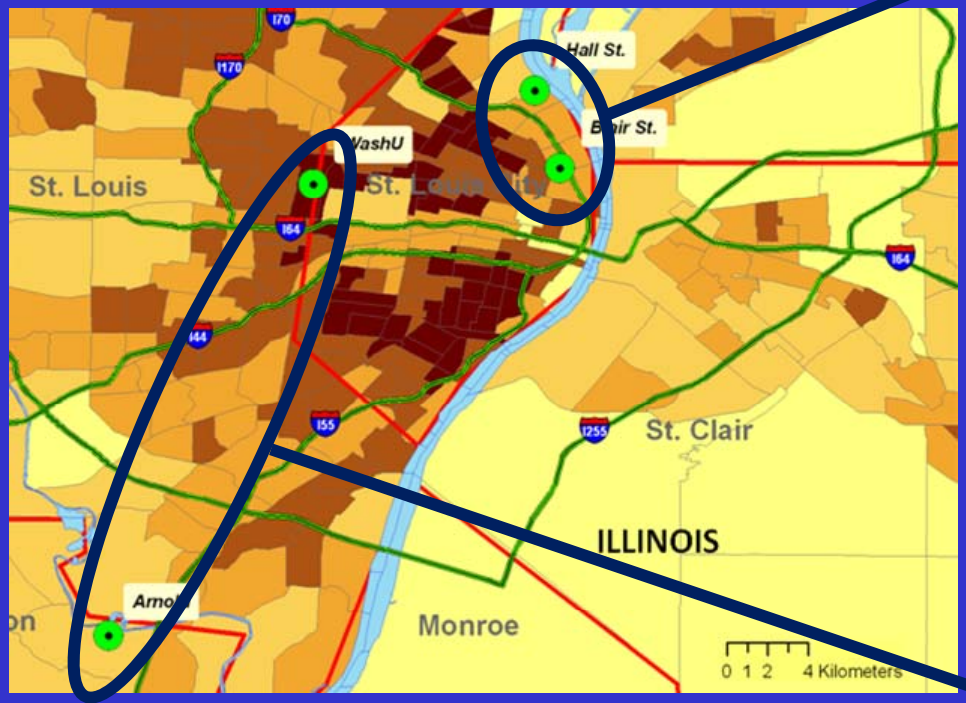
Pop. Density (#/sq. mile)

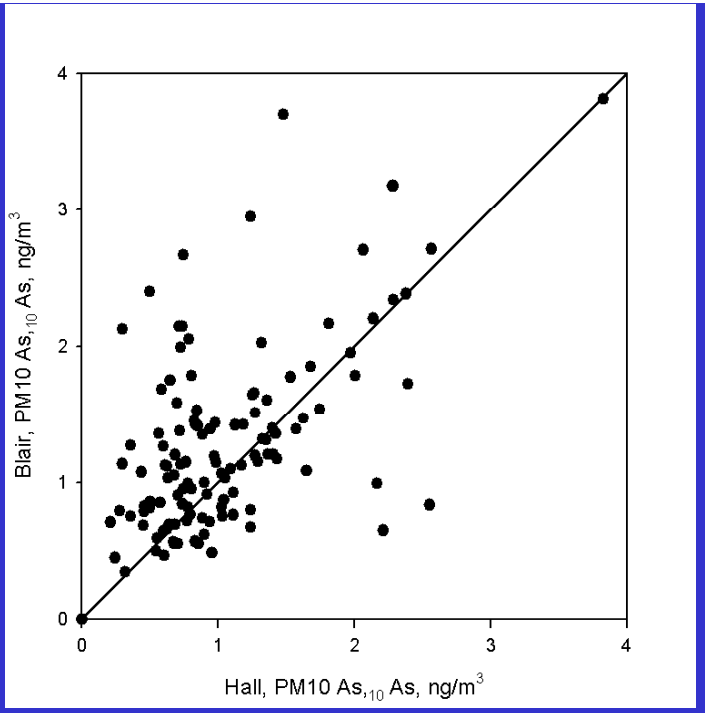
- 0 - 599
- 600 - 1723
- 1724 - 3833
- 3834 - 7792
- 7793 - 15224

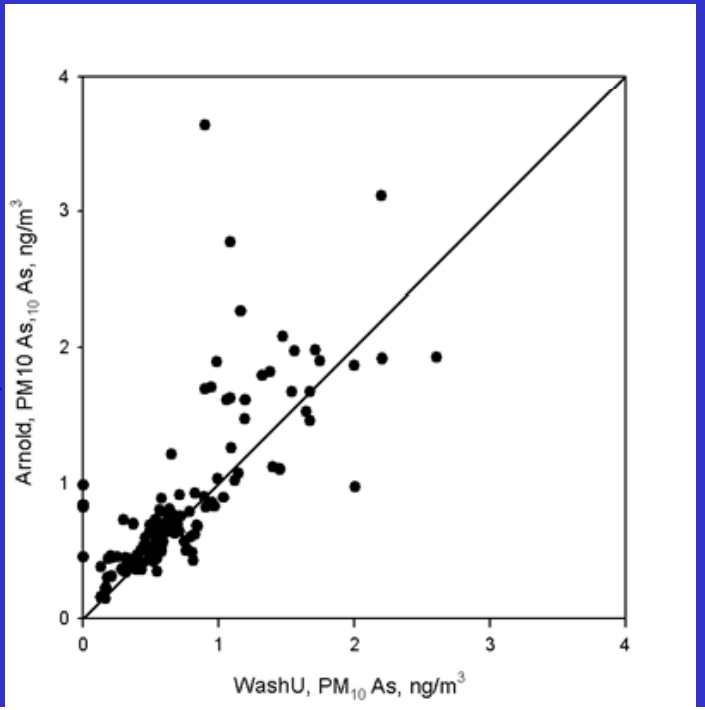
U = Urban
S = Suburban



Intersite Variability





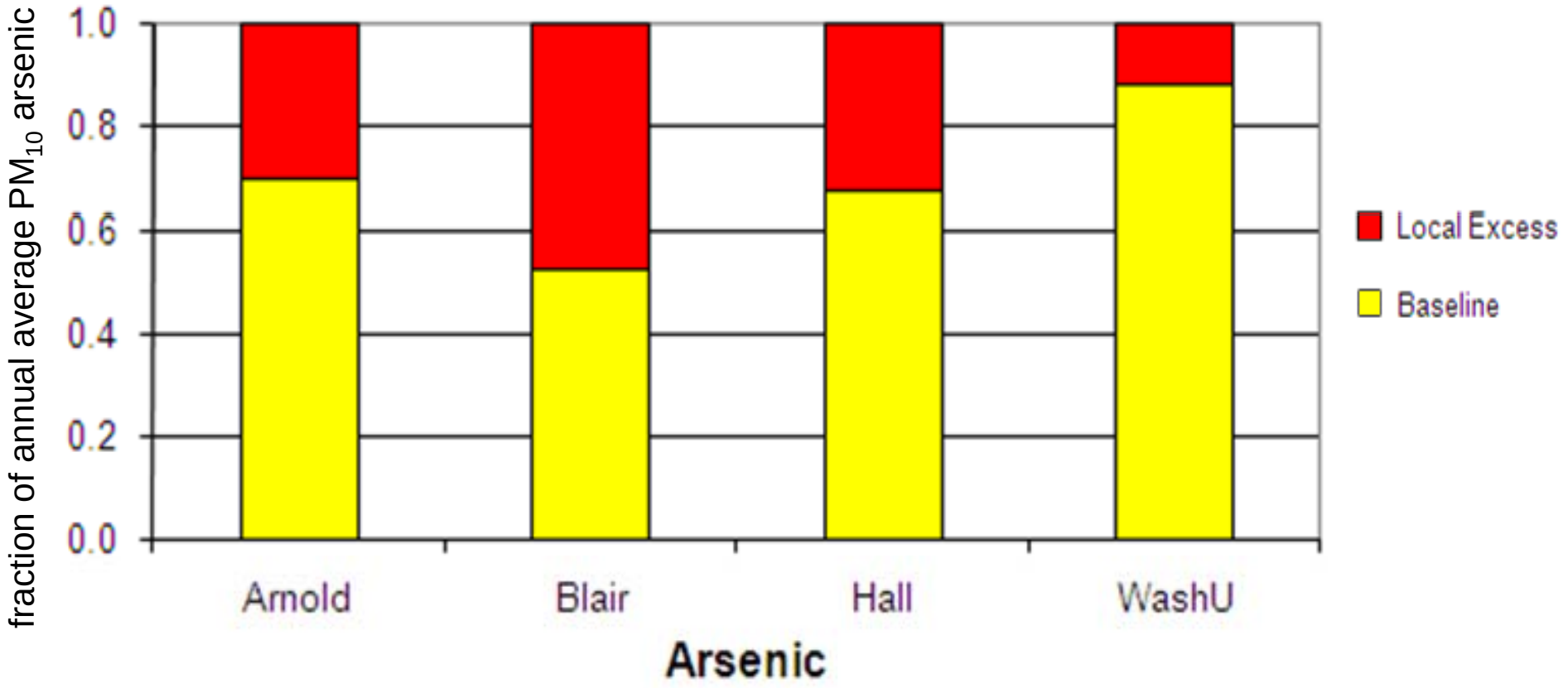


variability (proximate urban sites)

>

variability (distance suburban sites)

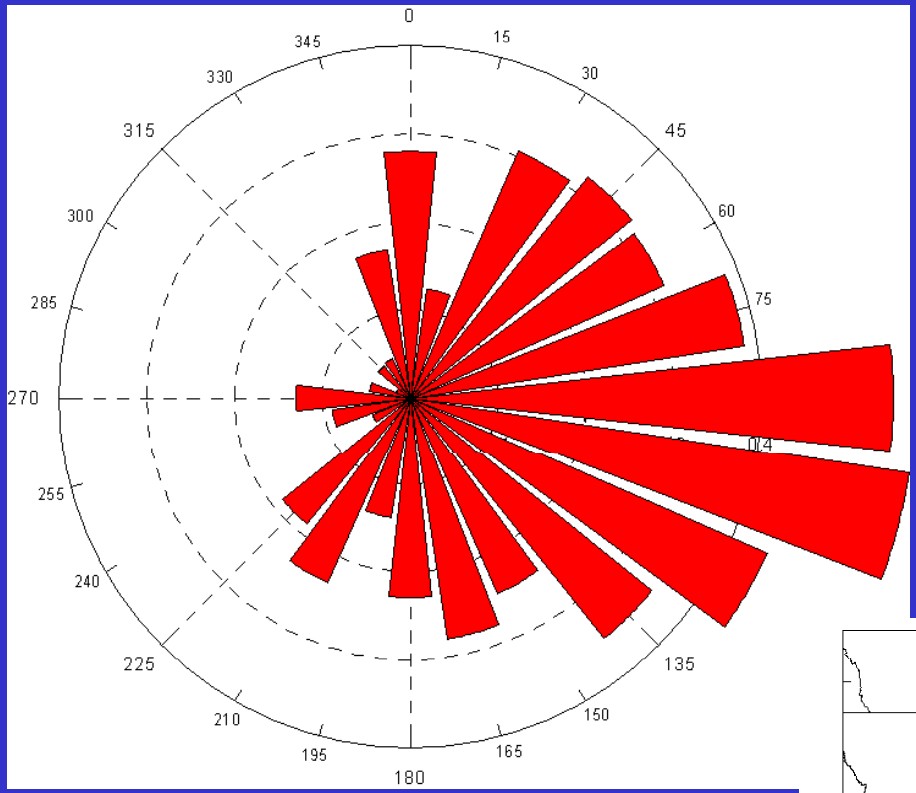
Baseline and Excess Contributions to PM_{10} Arsenic



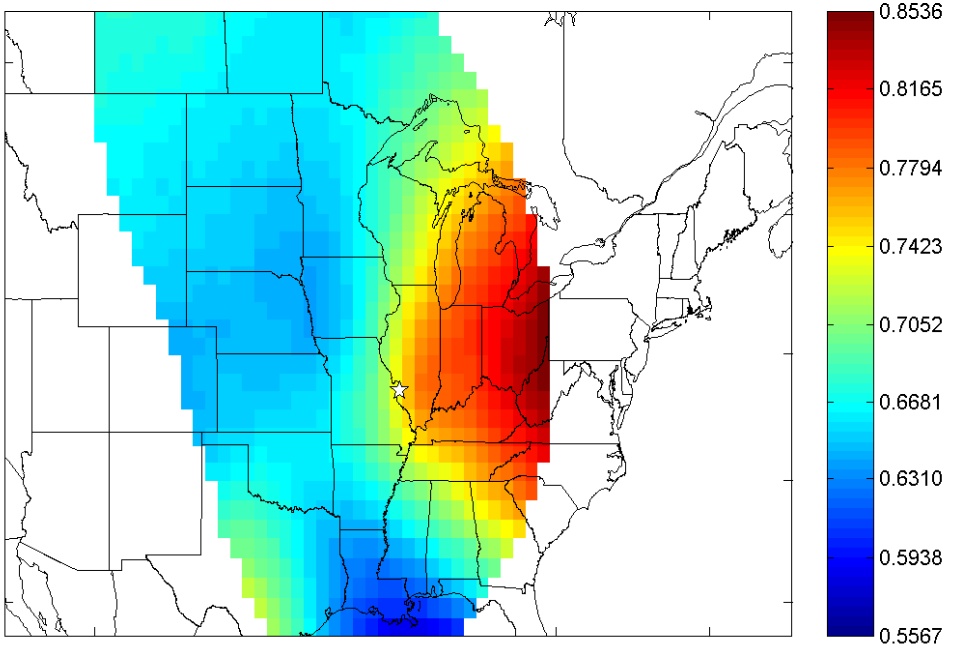
Baseline = regionally transported?

Excess = locally emitted?

Baseline PM_{10} Arsenic

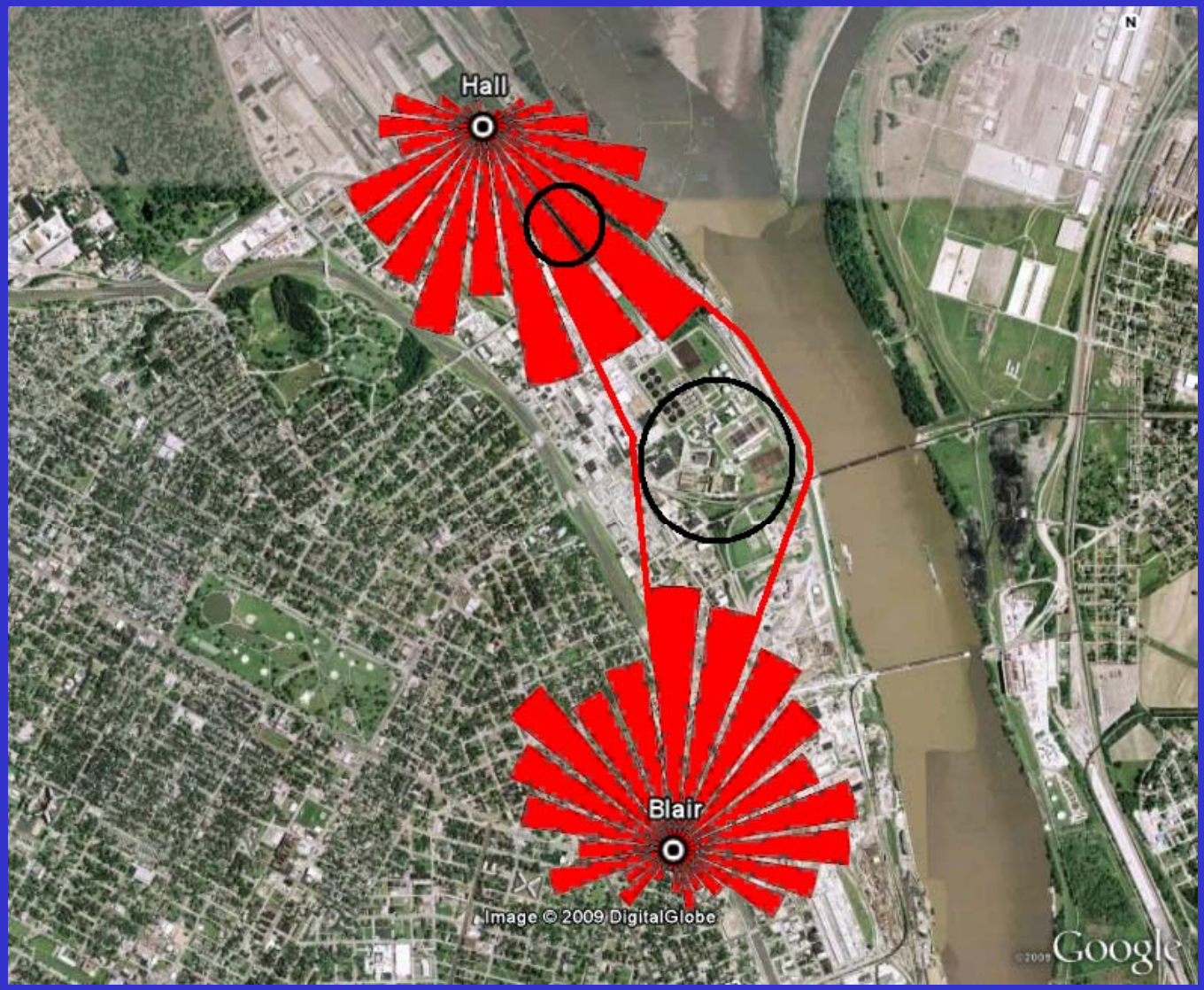


conditional probability function (CPF)
(24-hour As, hourly winds)



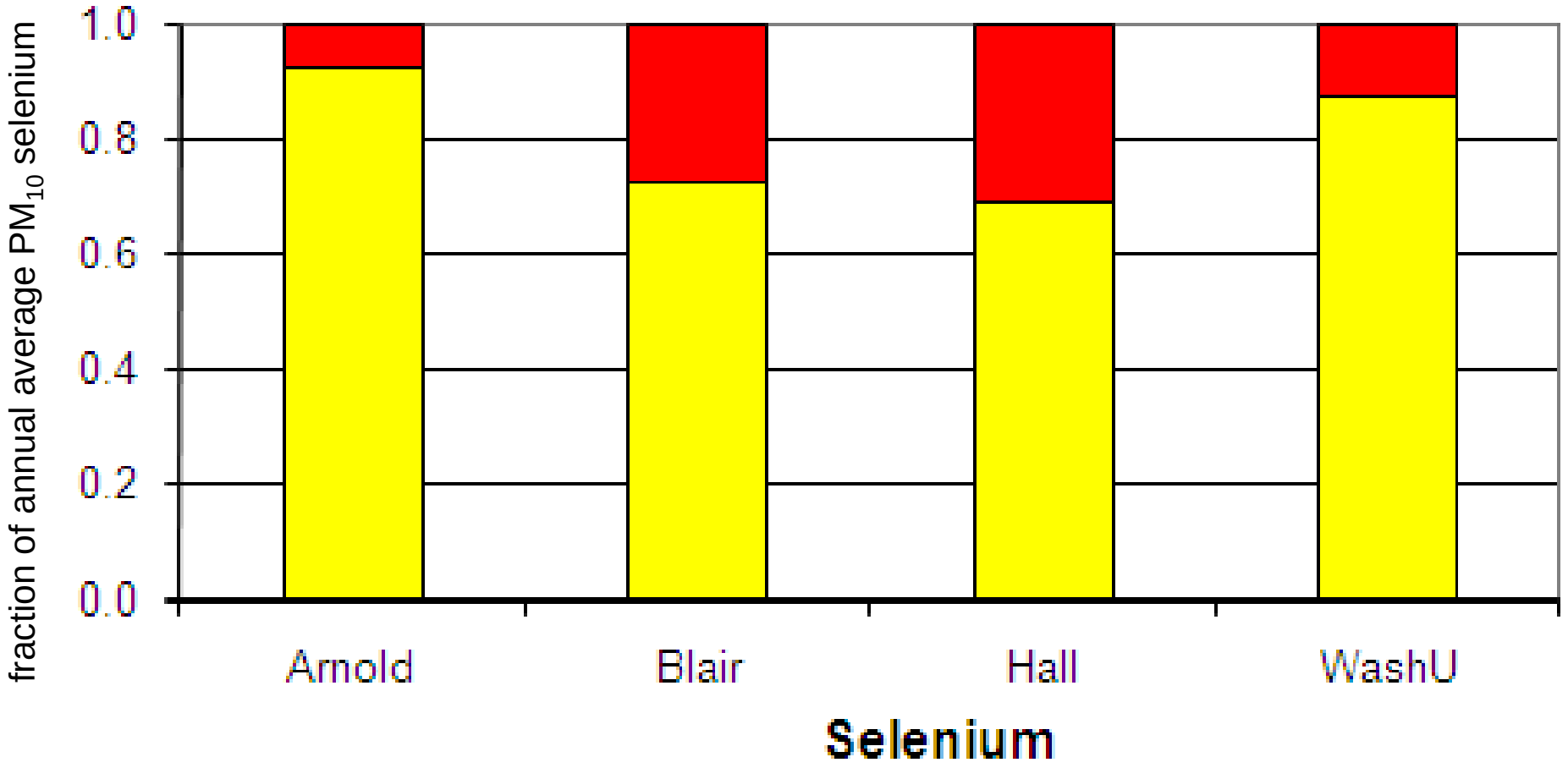
quantitative transport bias analysis
(QTBA)
(24-hour As, 3-day back trajectories)

Excess PM_{10} Arsenic at Urban Sites



conditional probability function plots (24-hour As, hourly winds)

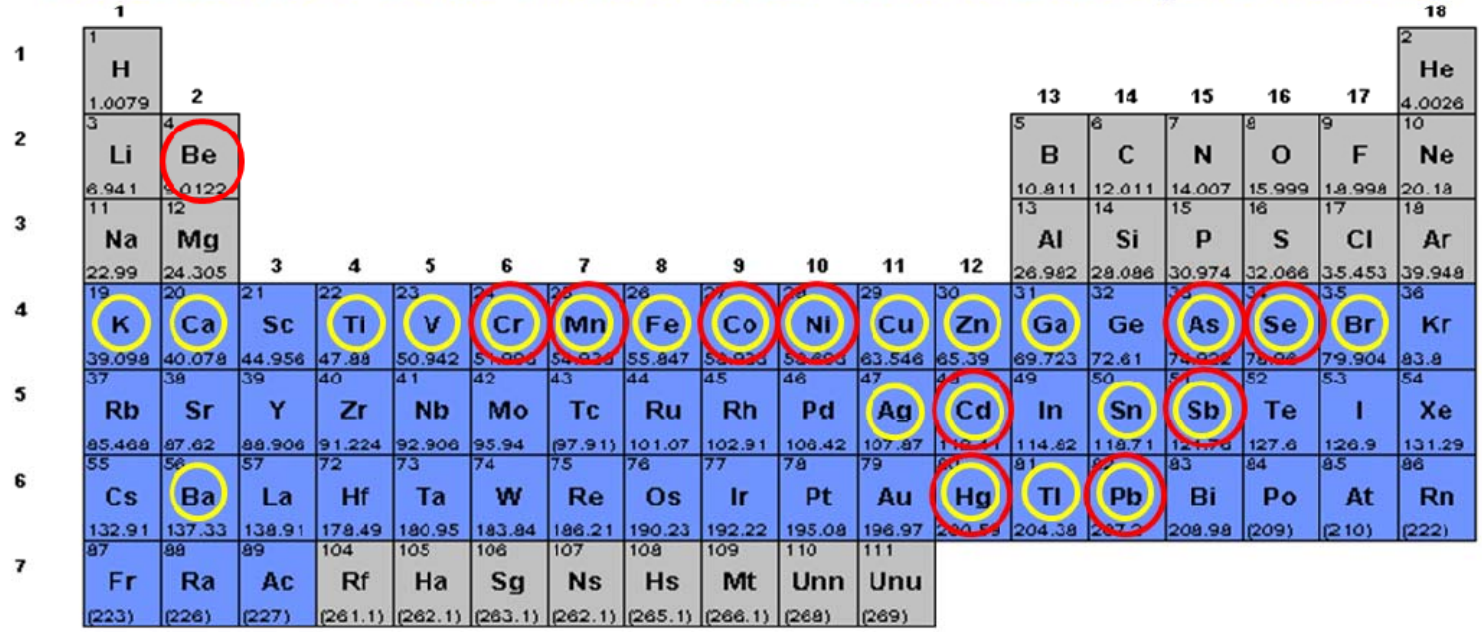
Baseline and Excess Contributions to PM_{10} Selenium



Cooper Environmental Services (CES) Xact 620

- particle collection on a filter tape
- analysis by x-ray fluorescence (XRF)
- continuous data time series at user-defined intervals
- Missouri DNR instrument optimized for As, Hg, and Pb at remote areas

ELEMENTS THE XACT CAN MEASURE (IN BLUE)



measured by Xact in this study

EPA Air Toxics PM metals

Xact Performance Evaluation

HiVol PM_{10} / quartz filter,
NATTS digestion protocol

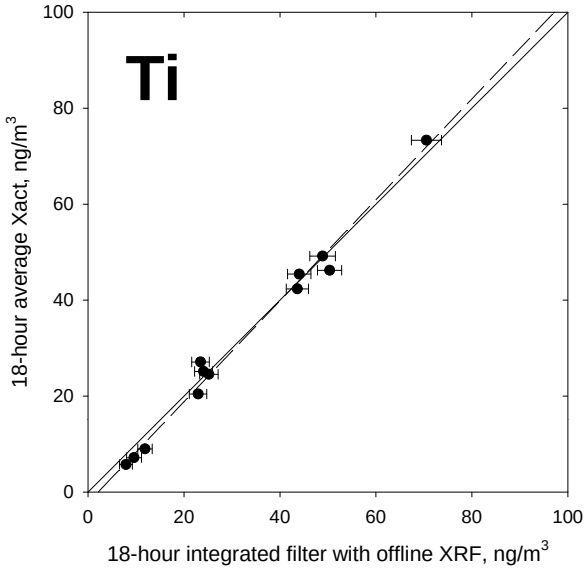
ICP-MS: As, Pb, Se…

LowVol PM_{10} (FRM) / Teflon filter

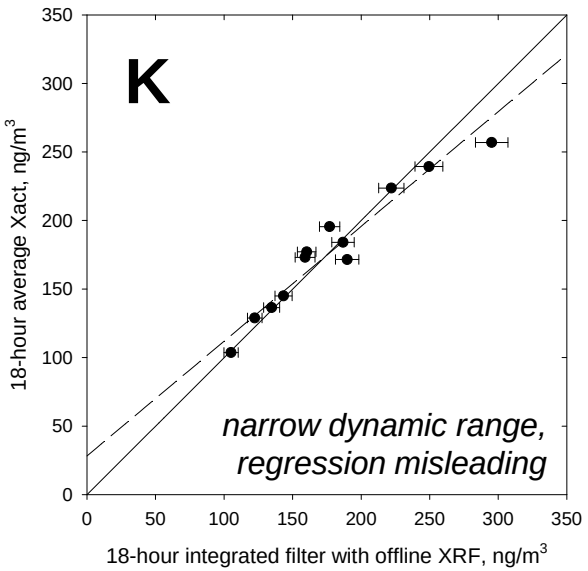
XRF: Ca, Fe, K, Mn, Pb, Ti…

Xact vs. LowVol PM_{10} FRM / XRF

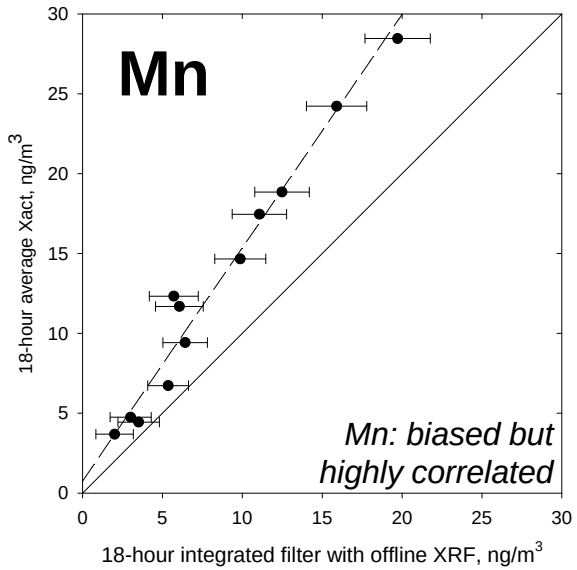
Xact = (1.05 ± 0.04)×filter + (-2.2 ± 2.8)



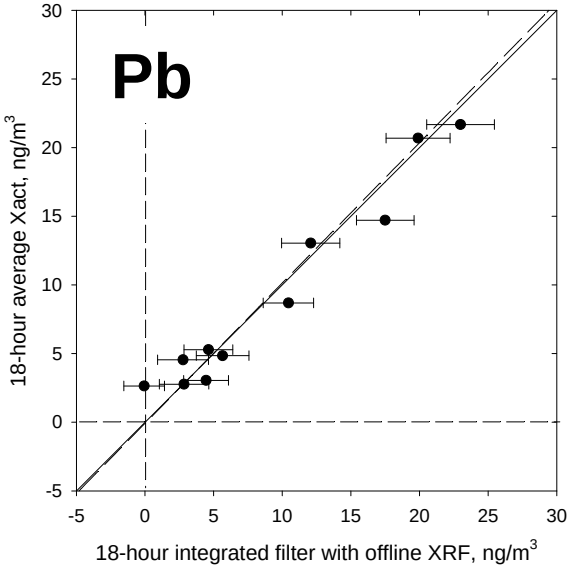
Xact = (0.84 ± 0.21)×filter + (28 ± 25)



Xact = (1.46 ± 0.18)×filter + (0.7 ± 1.6)

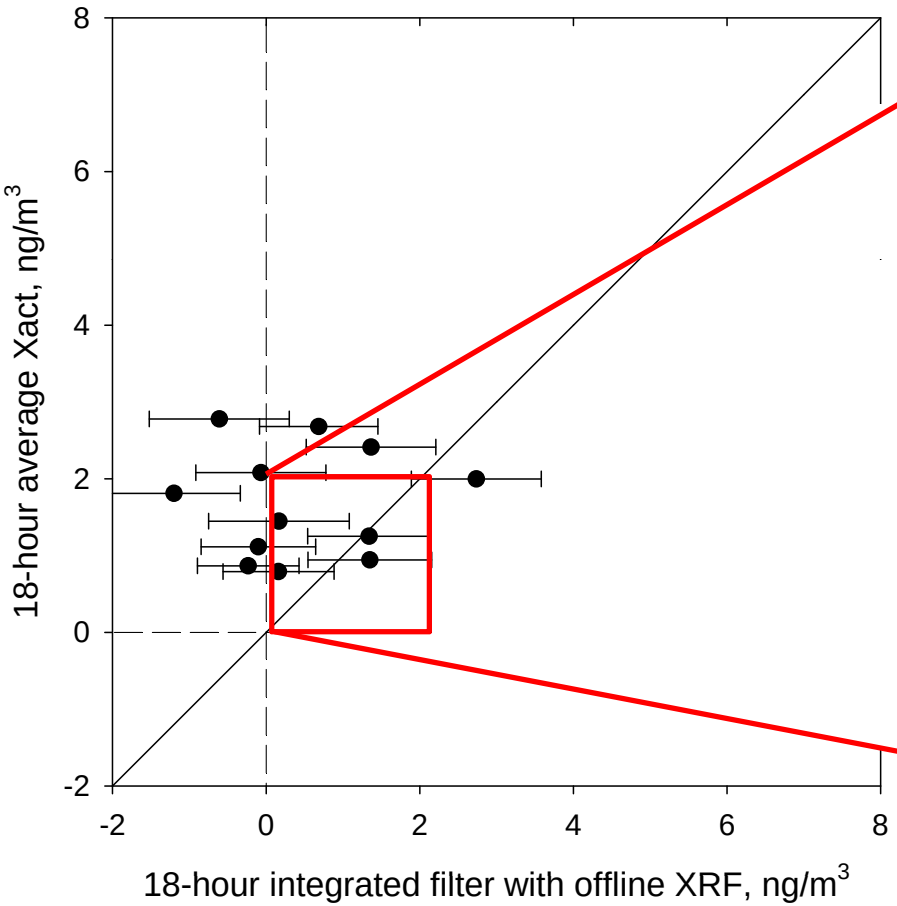


Xact = (1.02 ± 0.10)×filter + (-0.1 ± 1.8)

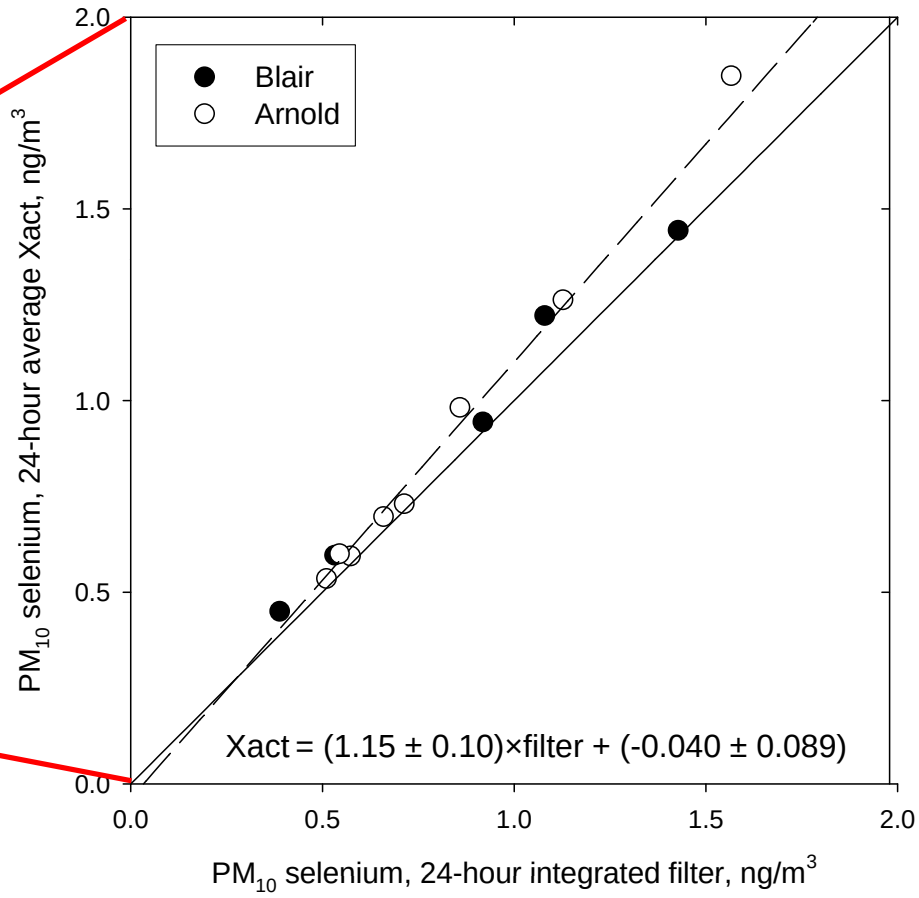


Selenium: Xact vs. Filter-Based Measurements

Xact vs. LowVol filter / lab XRF



Xact vs. HiVol filter / lab ICP-MS

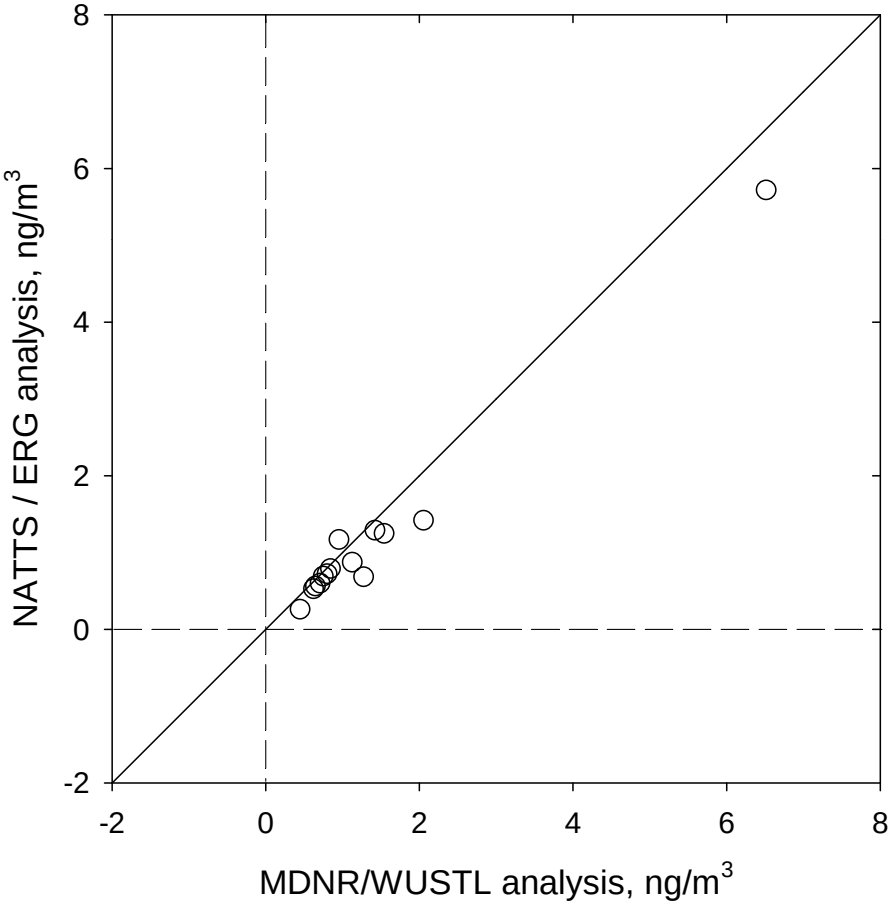


Se: favorable comparison between Xact and PM_{10} HiVol samples with analysis by ICP-MS

Arsenic – Methods Comparisons

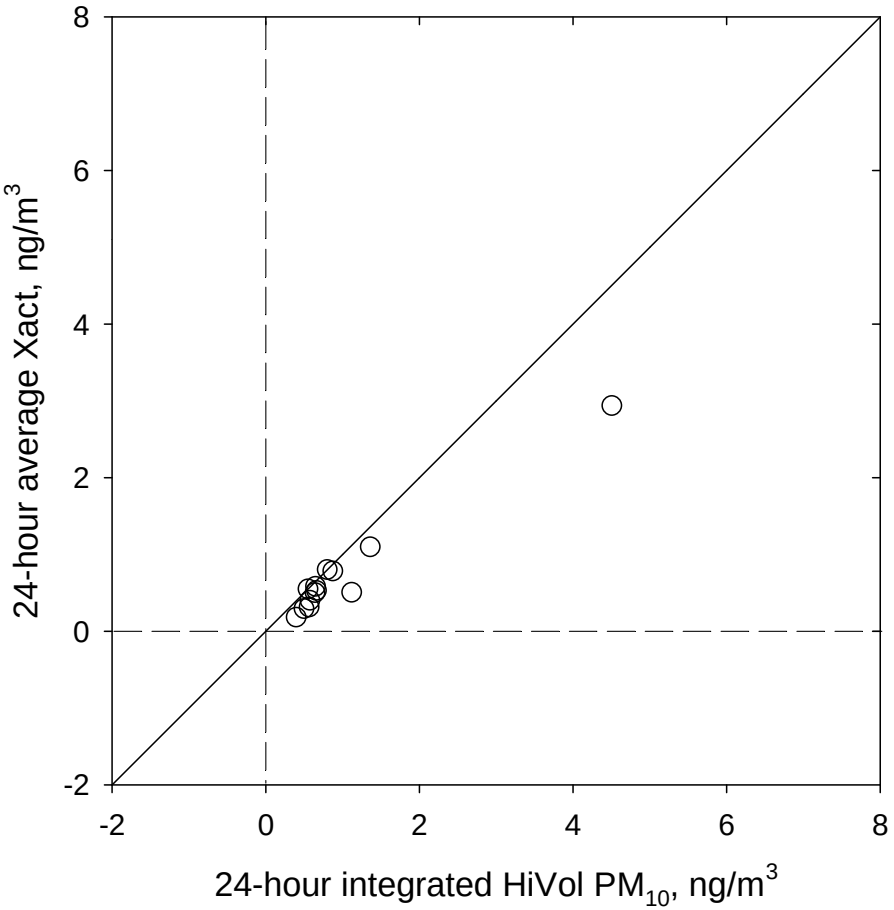
Collocated HiVol Samplers

Blair site, 4th Quarter 2008



Xact vs. WUSTL HiVol

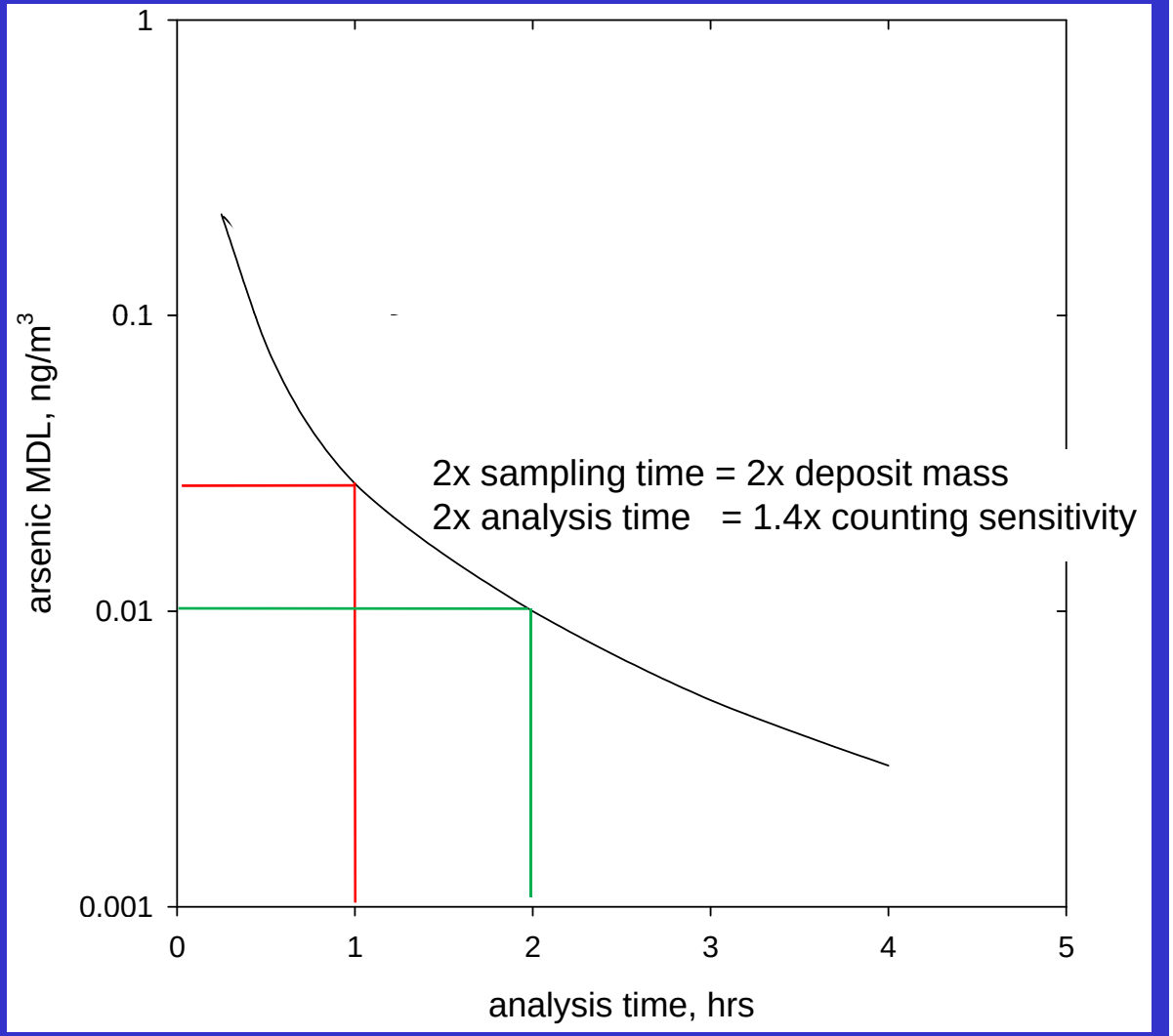
Dec 2008 / Jan 2009



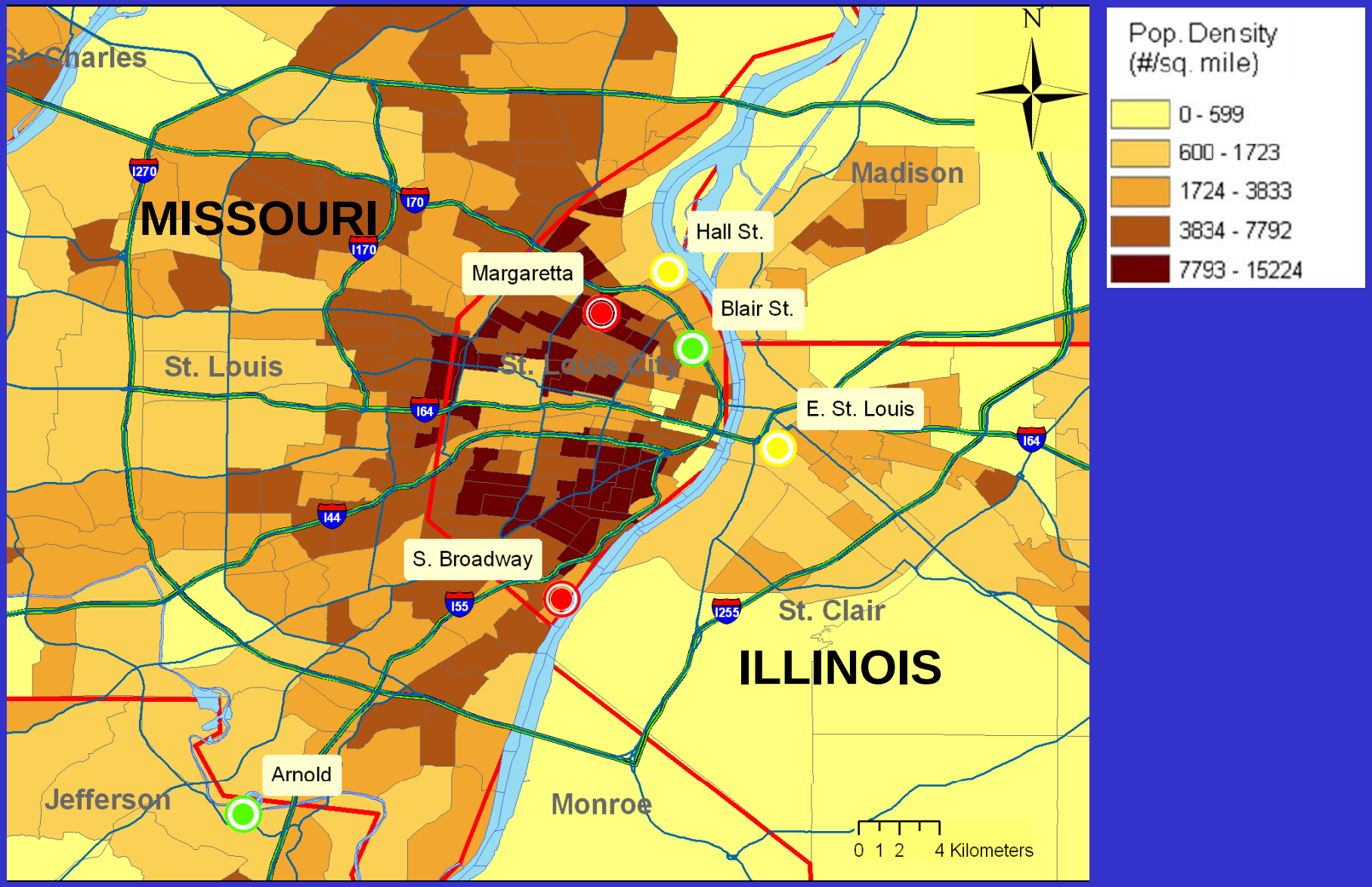
As: favorable comparison between Xact and PM_{10} HiVol samples with analysis by ICP-MS.

Optimizing the Sampling Time Interval

- depends on study objectives!
- trade-offs between time resolution and frequency above MDL
- Blair Street (STL)
  - 1-hour: 56%>MDL
  - 2-hour: 86% > MDL

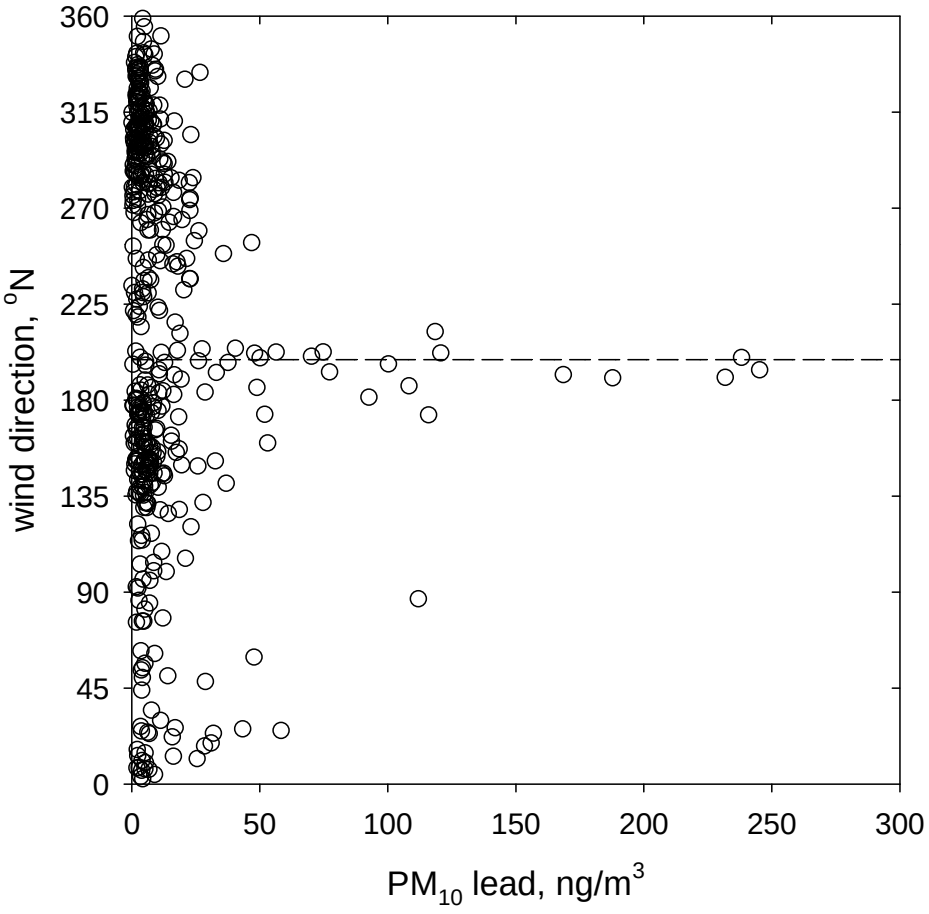


Xact Monitoring Sites

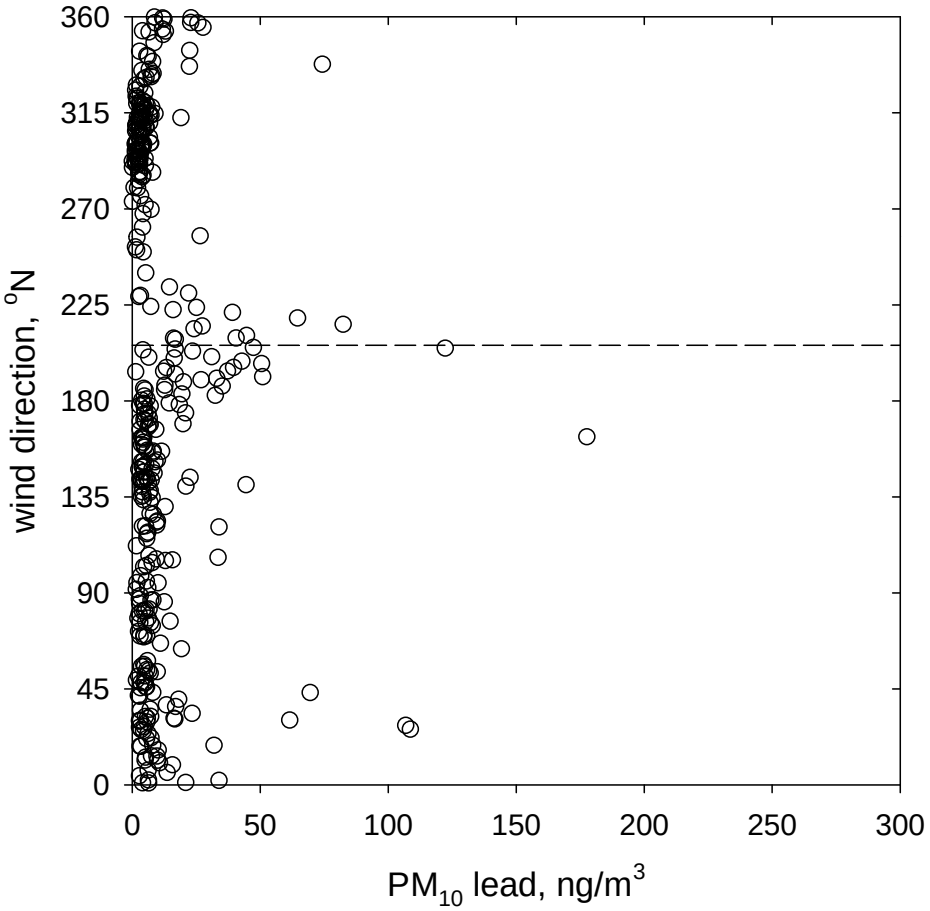


PM_{10} Lead by Xact (2-hour resolution)

BLAIR

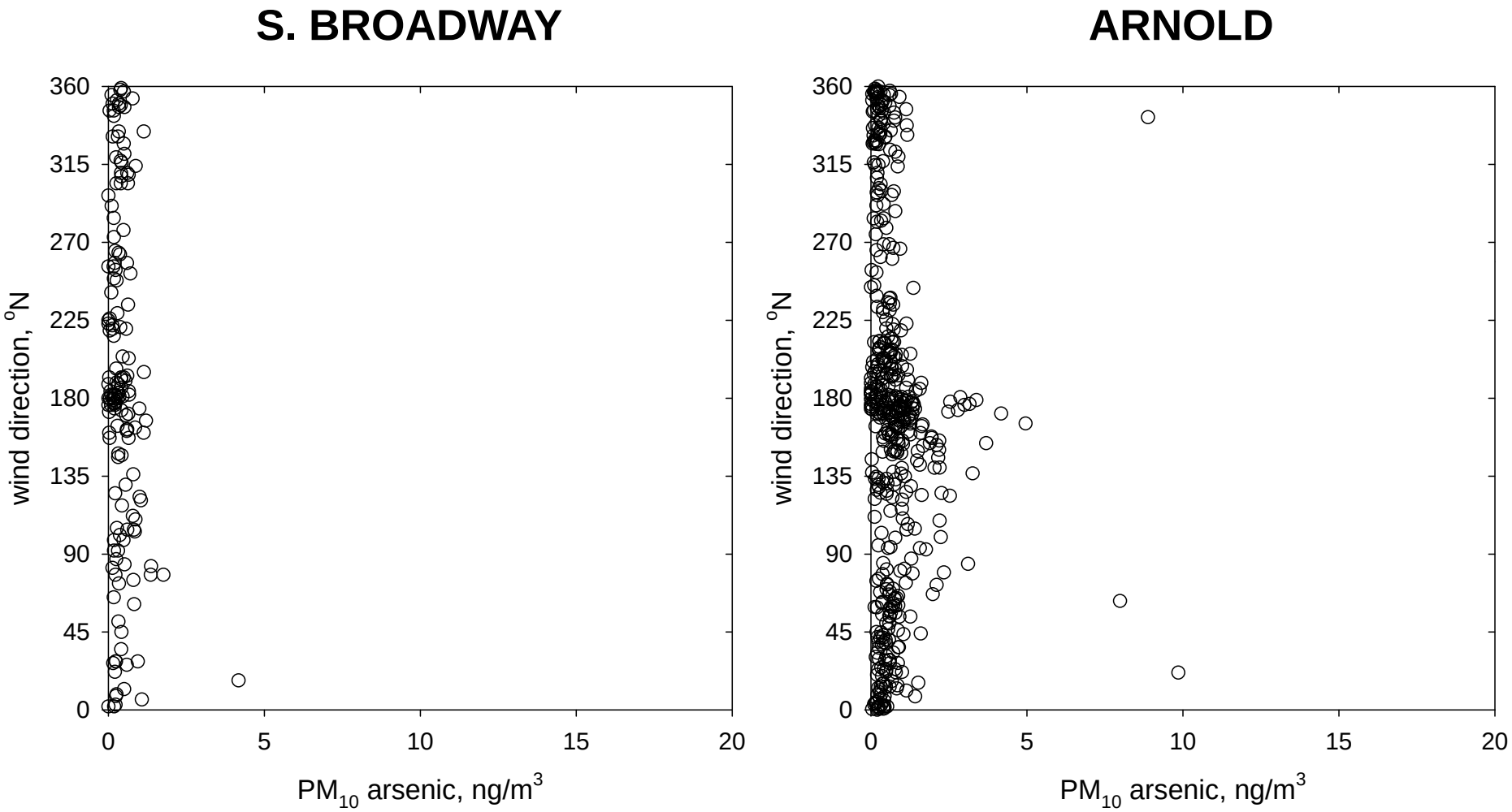


ARNOLD



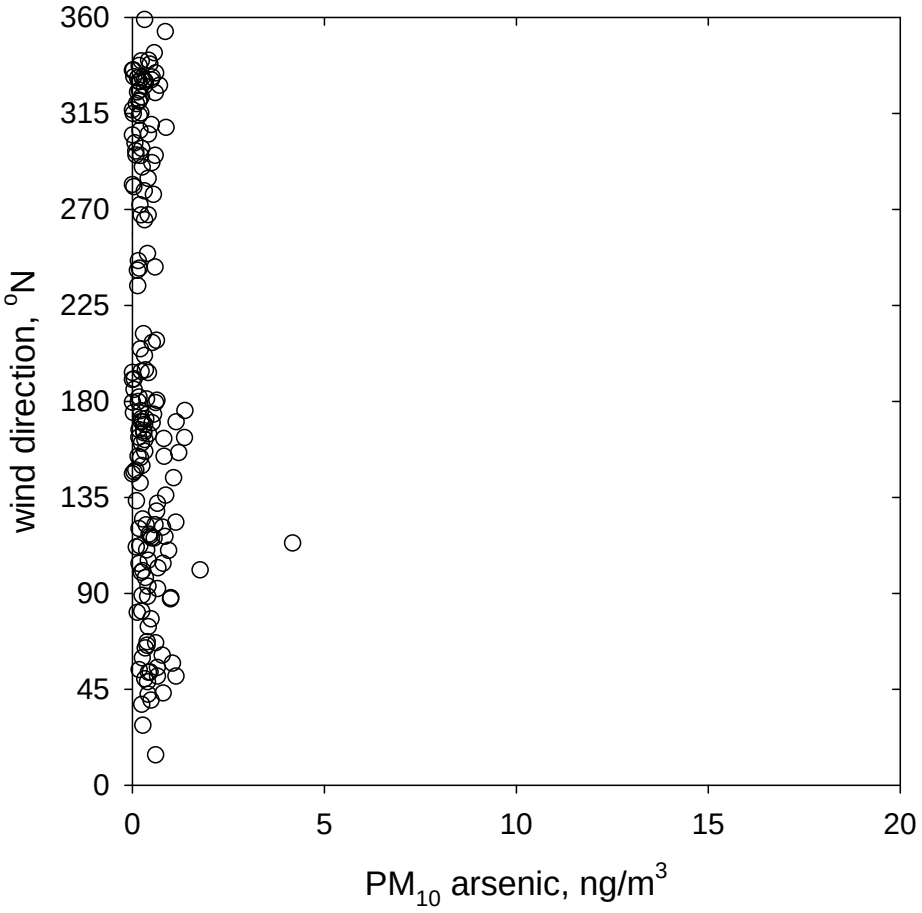
Dashed line is bearing of Doe Run – Herculaneum lead smelter

PM_{10} Arsenic by Xact (2-hour resolution)

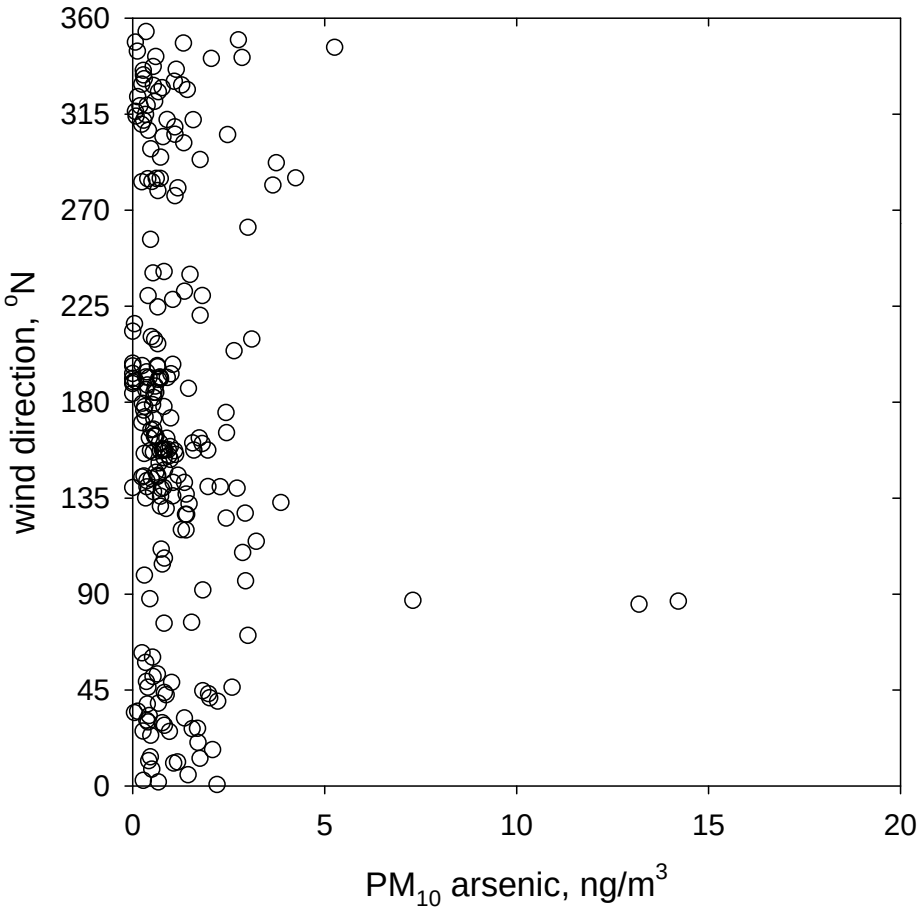


PM_{10} Arsenic by Xact (2-hour resolution)

MARGARETTA

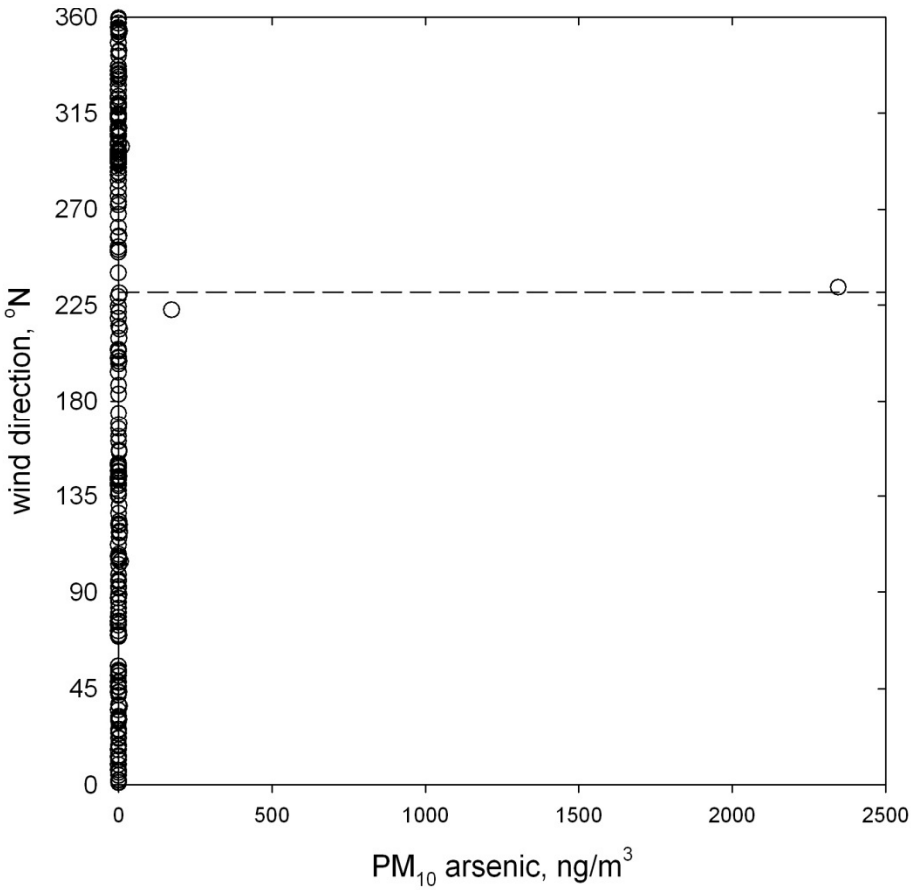


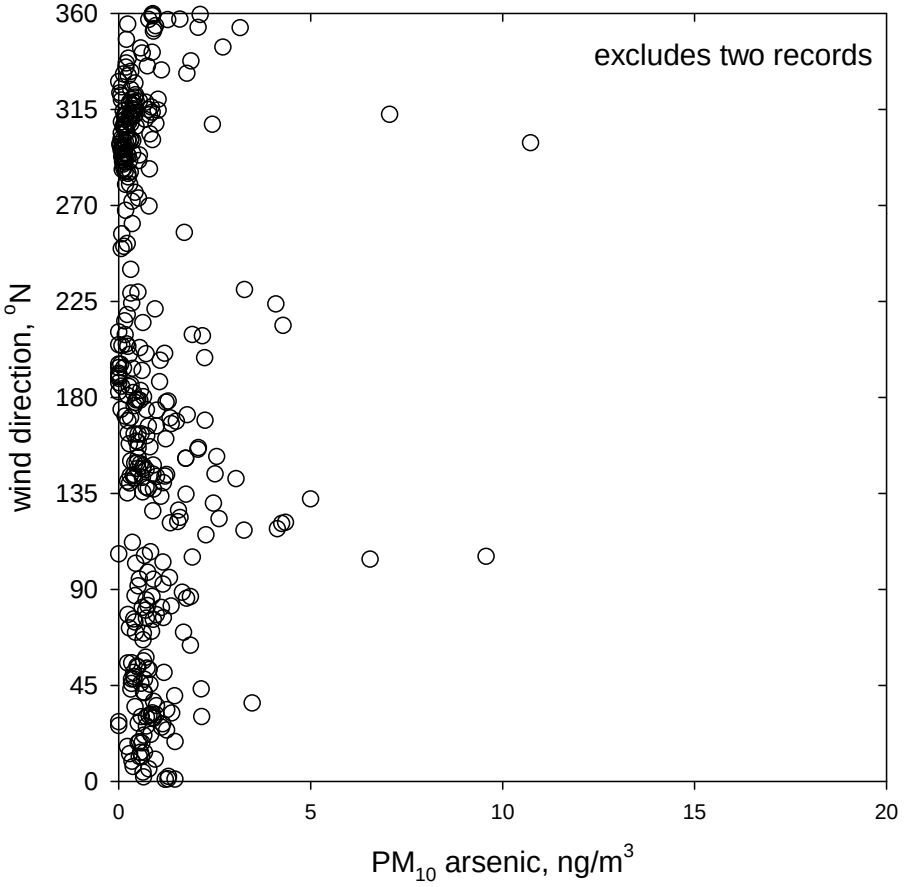
HALL



PM_{10} Arsenic by Xact (2-hour resolution)

EAST ST. LOUIS

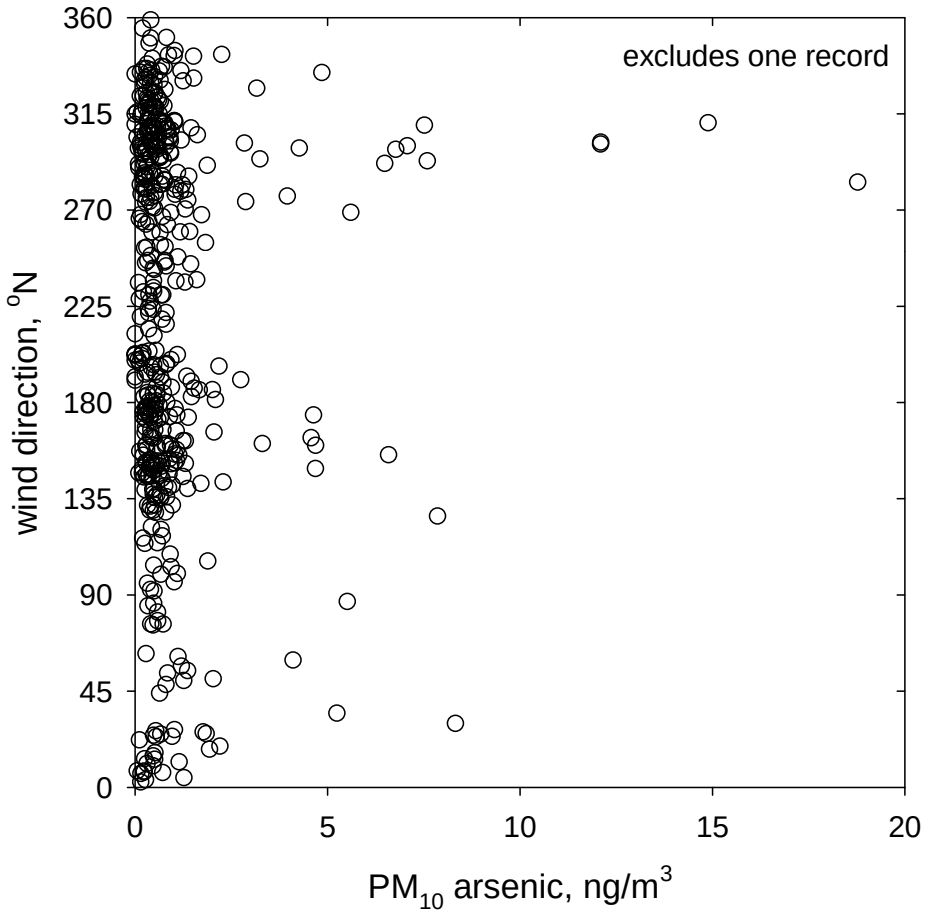




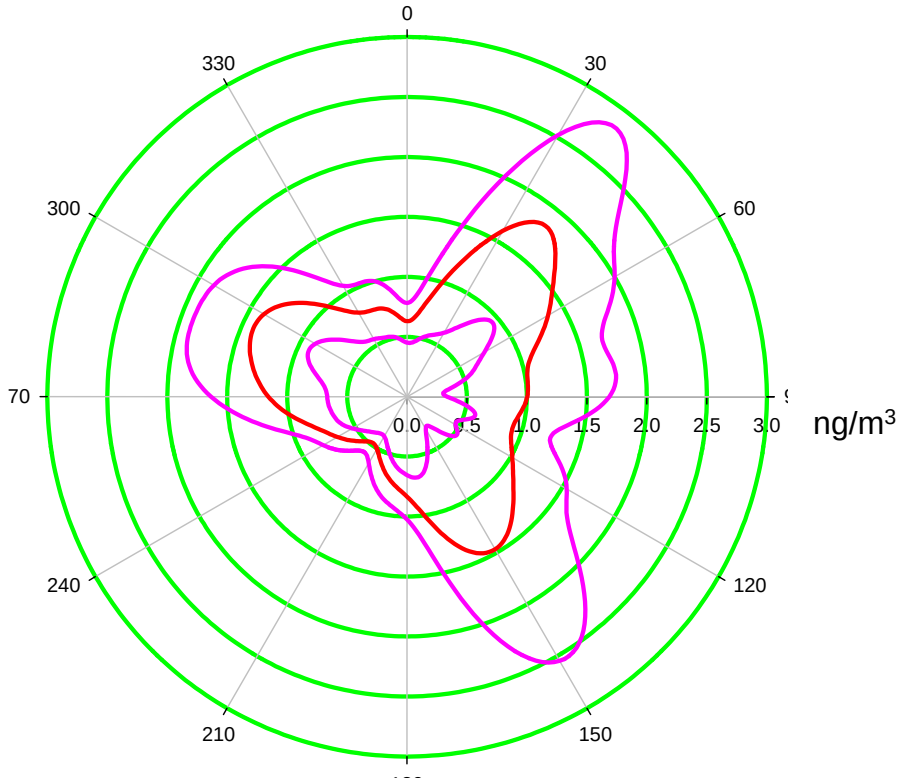
2-hour spike exceeding 2.5 $\mu g/m^3$ arsenic!

PM_{10} Arsenic at Blair by Xact (2-hour resolution)

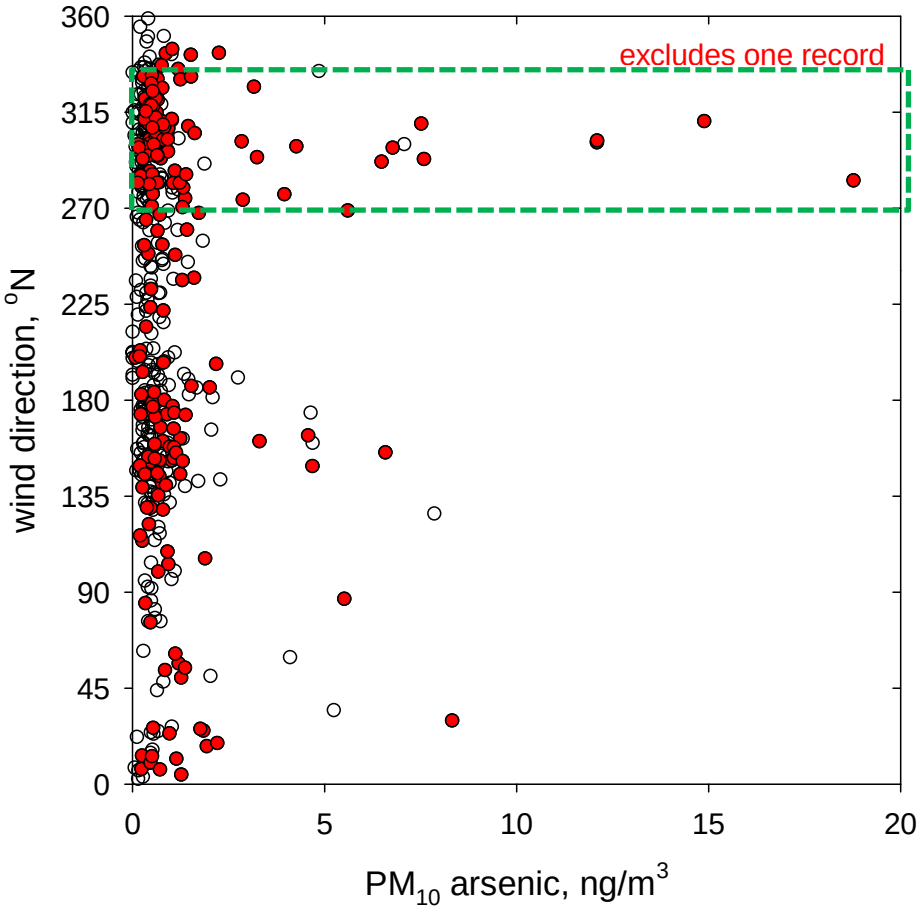
wind direction vs. concentration

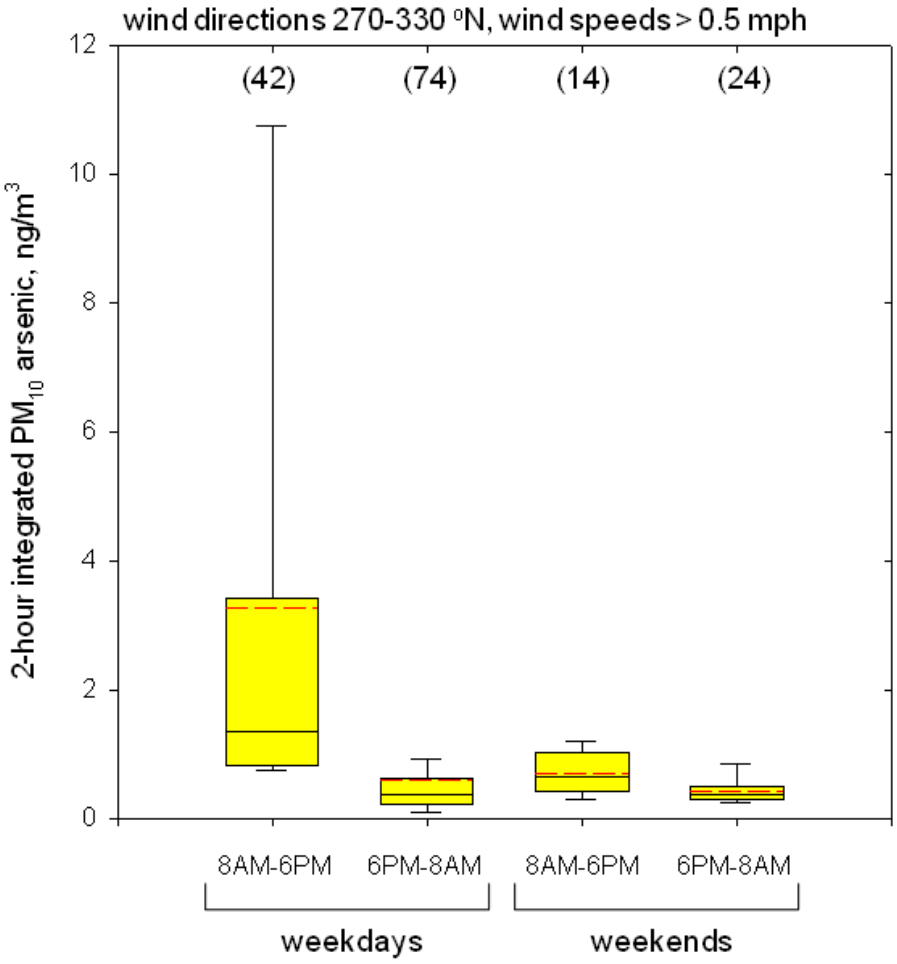


nonparametric wind regression



PM_{10} Arsenic at Blair for Winds from Northwest

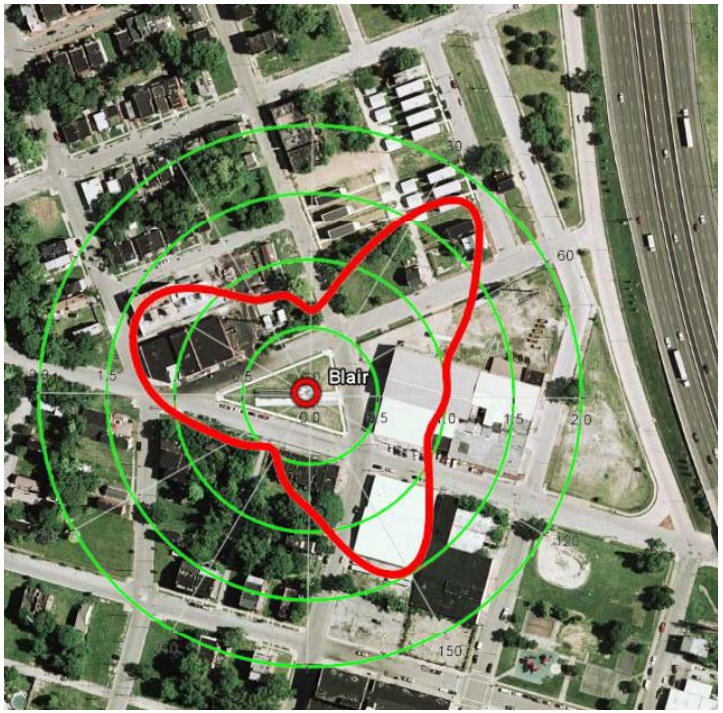


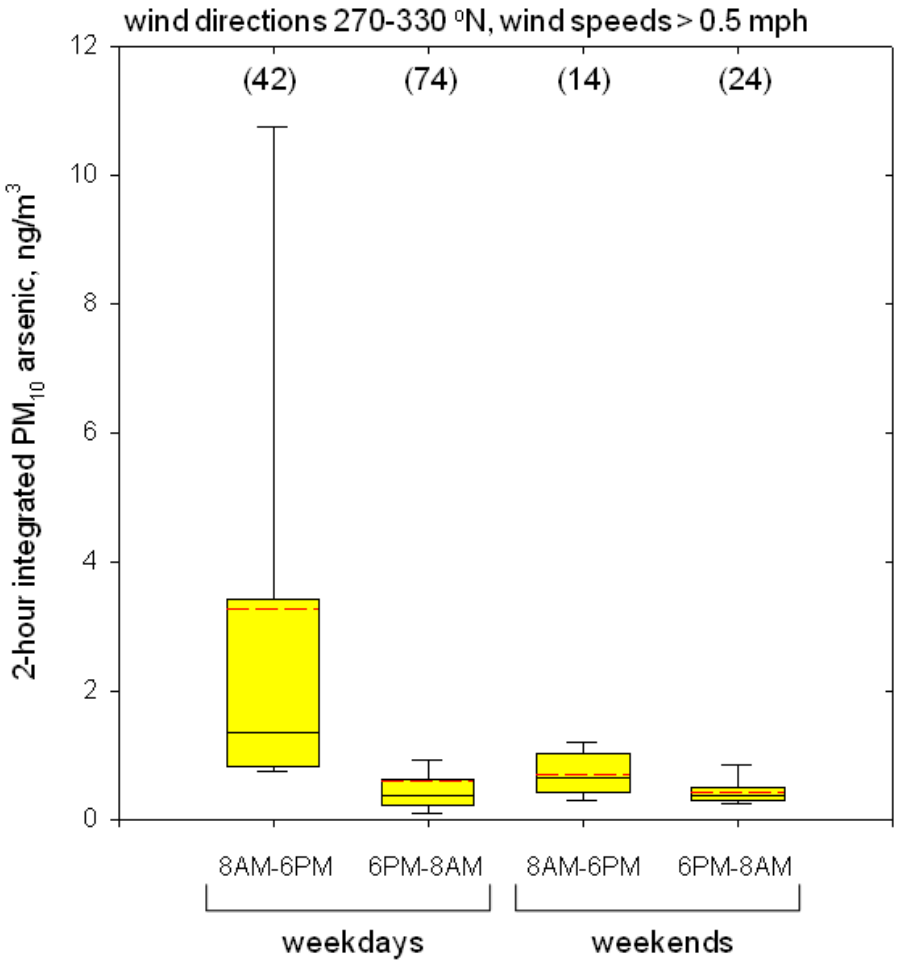


red markers = 8 AM – 6PM weekdays

PM_{10} Arsenic at Blair for Winds from Northwest

nonparametric wind regression





likely microscale impacts

Summary

- Observed urban-scale spatial gradients in PM_{10} arsenic not captured in the emissions inventory
  - Regional transport from the eastern U.S.
  - Local sources along industrial riverfront
  - Microscale impacts at the Blair Street NATTS site
- CES Xact 620 for automated ambient PM elemental analysis
  - Very promising, based on initial performance evaluation
  - Identify intermittent sources not detected by time-integrated measurements
  - How long to stay at a site? “information content” of plumes, separating local from regional contributions?

The Next Steps

- Collocated Xact measurements (MDNR and CES)
  - Herculaneum, August 2009… ***done***
  - Measurement precision, crucial data for receptor modeling
- Receptor modeling of the data sets
- Additional Xact deployments
  - Currently near lead smelter in Herculaneum (source profile)
- Expanded performance evaluation
  - Forty additional low-volume PM_{10} FRM samples, analysis by XRF and ICP-MS

Acknowledgements

- Missouri Department of Natural Resources
  - Jim Brunnert, Celeste Koon, Will Wetherell
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