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

Missouri Department of Natural Resources,
Air Pollution Control Program and
Environmental Services Program

Washington University, St. Louis

U. S. EPA

Introduction

- The St. Louis Community Air Project (CAP) and the Blair St. National Air Toxics Trends Station (NATTS) have measured elevated concentrations of airborne arsenic in St. Louis. Data showed some correlation with wind direction.
- These elevated arsenic concentrations are consistent with an excess cancer risk from inhalation of airborne arsenic.
- This Community-Scale Air Toxics Monitoring Project is intended to identify and locate arsenic emission sources in the St. Louis area.

Summary of CAP and NATTS Monitoring Results

- CAP: average arsenic concentration ~ detection limit ~ 1/100,000 cancer benchmark = 0.002 ug/m3
- Blair St. and Arnold PM2.5 STN: arsenic average about 0.002 ug/m3
  - (Bonne Terre about 0.001 ug/m3)
- Blair St. NATTS: average arsenic concentration ~ 0.002 to 0.001 ug/m3; detection limit ~ 0.00002 ug/m3 = 0.02 ng/m3

Excess Cancer Risk for Arsenic (PM_{10} and $PM_{2.5}$) Based on Blair St. Monitoring Data

Size Category	Year	Annual Arithmetic Mean ($\mu g/m^3$)	Risk-Based Concentration (Risk = 1E-06, 70-Year) ($\mu g/m^3$)	Excess Cancer Risk (1E-06)
PM_{10} (NATTS, analyzed by ICPMS)				
	2004	0.001660	2E-04	8
	2005	0.002330	2E-04	12
	2006	0.001060	2E-04	5
	2007	0.001120	2E-04	6
$PM_{2.5}$ (STN, analyzed by XRF)				
	2004	0.0029	2E-04	15
	2005	0.0026	2E-04	13
	2006	0.0017	2E-04	9
	2007	0.0015	2E-04	8

Project Goals

- Help identify the area where sources of arsenic compounds are located, if not the sources themselves, and the climatology involved.
- Provide information on the adequacy of existing emission inventories.
- Provide results for other toxic metals, including lead, to help determine whether concentrations are near levels of concern, and where source areas may be.

Project Plan

- **Phase I. Spatially and Temporally Enhanced 24-hour Integrated Measurements**
  - 1-in-3 day PM10 sampling and metals analysis by ICPMS at 4 sites in the St. Louis area for 1 year (MDL~0.02-0.03 ng/m3, 24-hr samples)
- **Phase II. High Time Resolution Measurements**
  - Time-resolved near-real-time analysis at six sites in the St. Louis area for 1 month at each site (MDL<0.1 ng/m3, possibly as low as 0.01 ng/m3, 2-hr samples)
- **Data Analysis and Reporting**
  - Source apportionment, source identification, model comparisons

Map of Phase I Sampling Sites

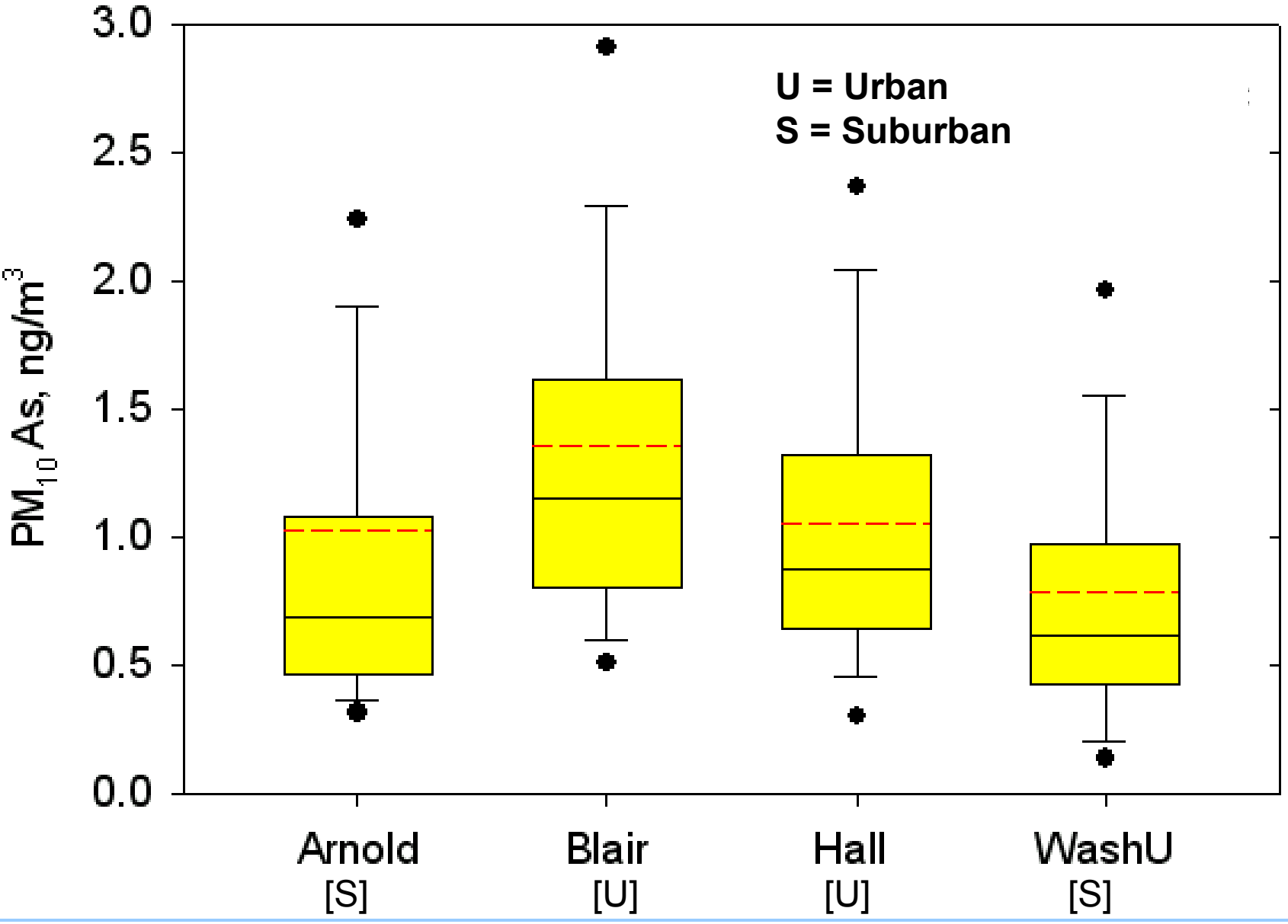
Blair Street

Hall Street

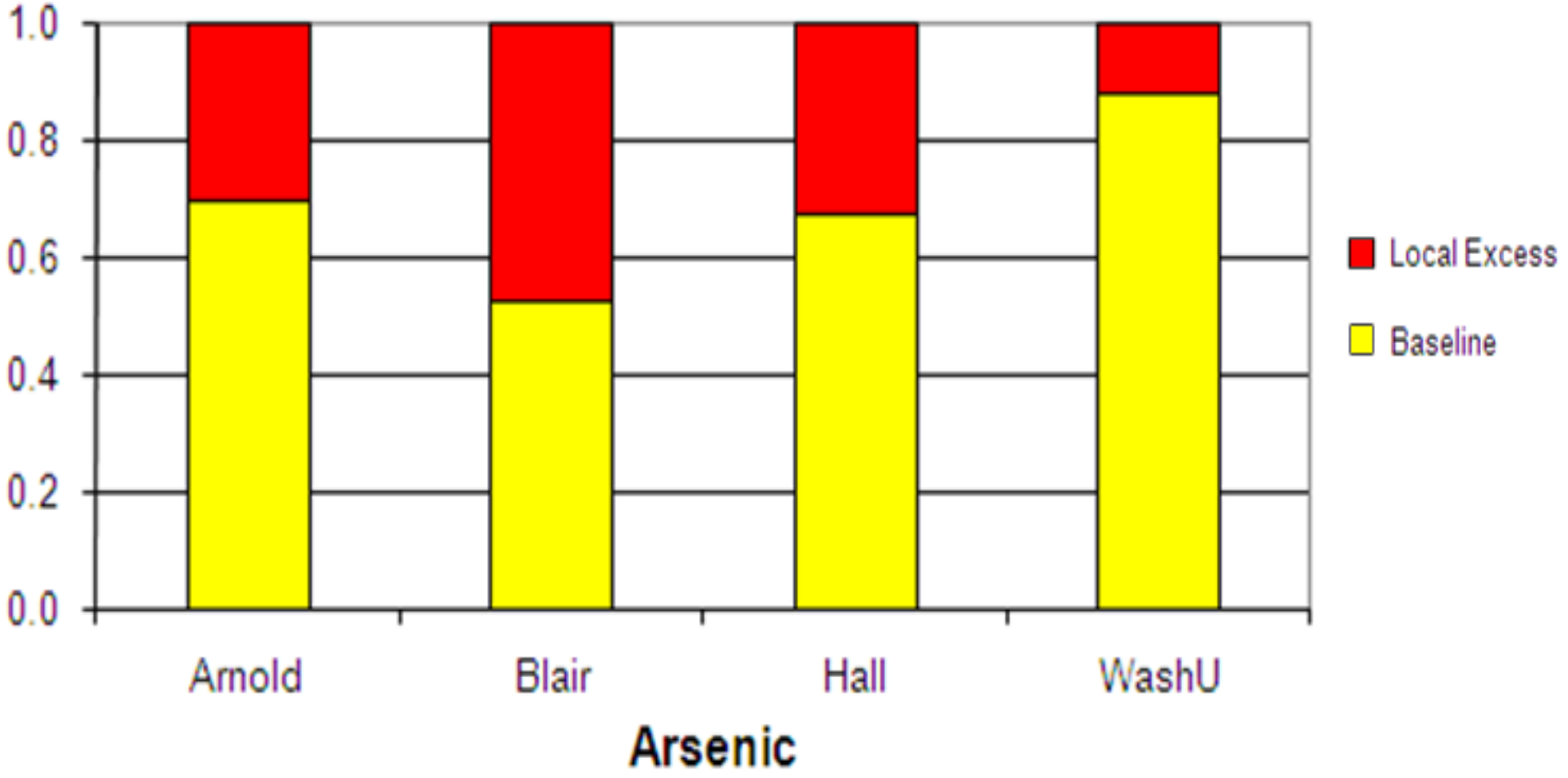
Washington University

Arnold West

Arsenic Concentration by Site

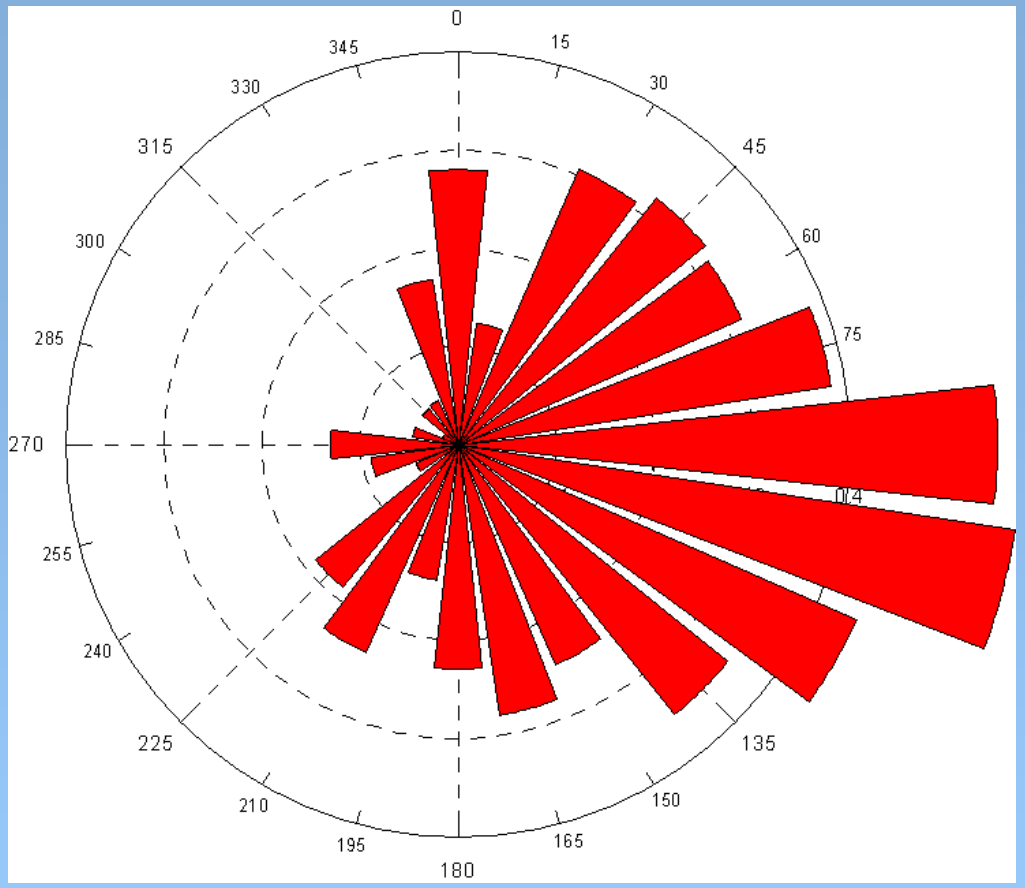


Contributions of Baseline and Excess



Conditional Probability Function

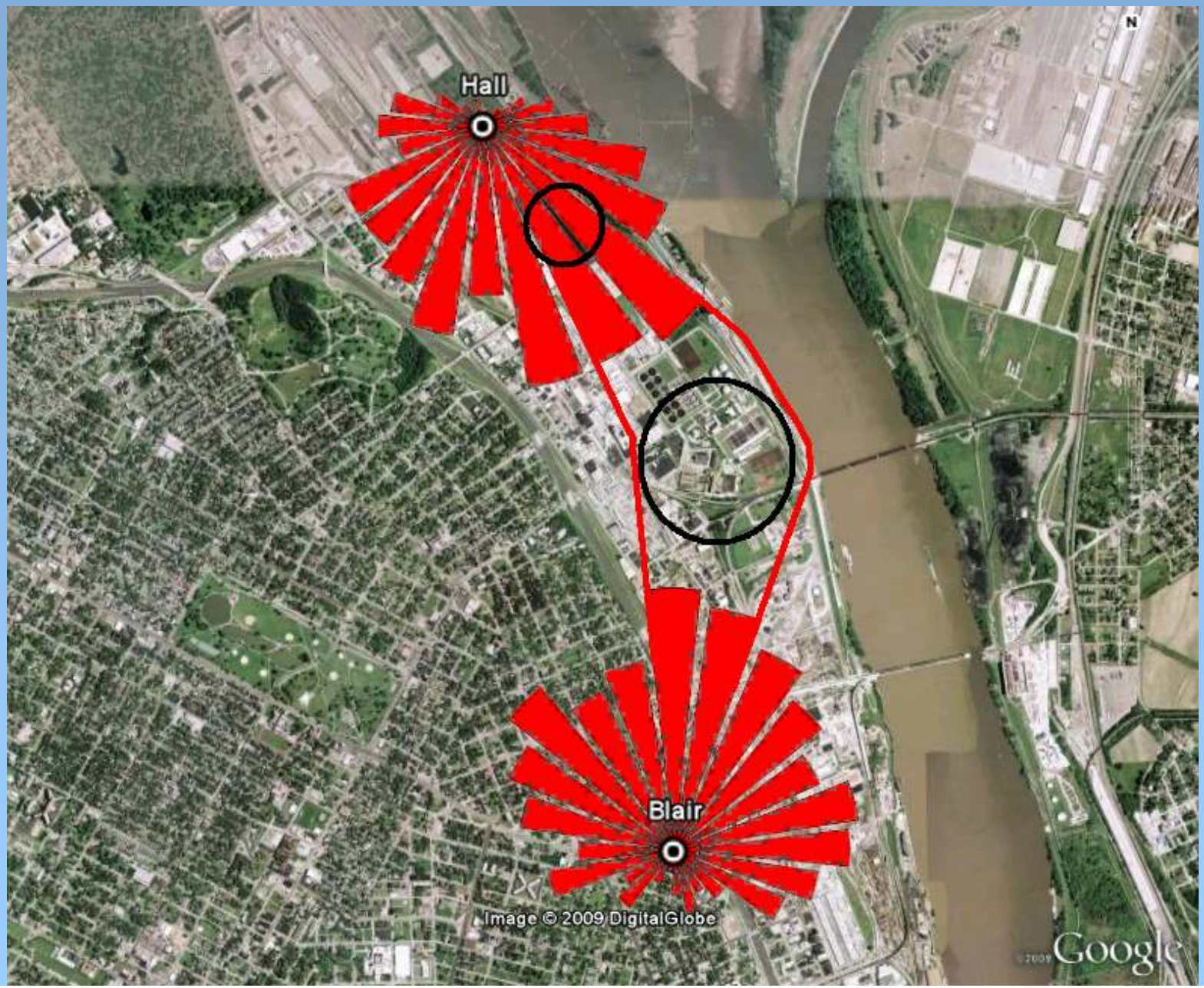
Probabilty of “high concentration day” from a wind direction



CPF Plot for Baseline Arsenic

Reference: Kim & Hopke, 2004

CPF of Excess Concentration



Phase I Summary

- St.Louis core impacted by local arsenic sources in addition to long range transport
- Excess concentration analysis identifies bearings of sources better than total concentration
- Four site, 1-in-3 day PM_{10} data provides higher spatial and temporal resolution than 1-in-6 day, single-site NATTS

Phase II. High Time Resolution Measurements

- Near-real-time analysis at six sites in the St. Louis area for 1 month at each site
  - 2-hour samples

Cooper Environmental Services
Xact 620 Ambient Air Toxic Metals Monitor

PM size-selective inlet

Temperature controlled cabinet

Heater

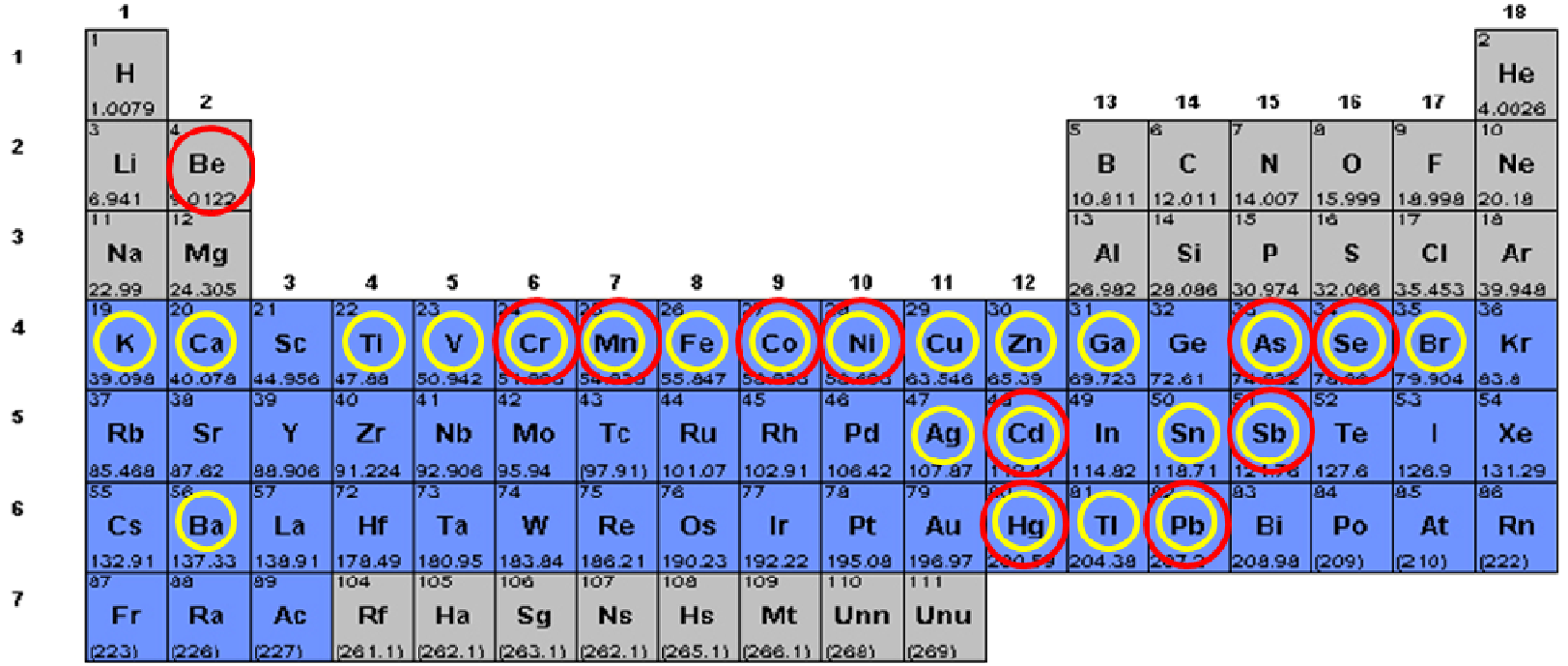
Sampling & Analysis Module

Operator interface/control panel

Flow control module

This slide provided by John Cooper, Cooper Environmental Services

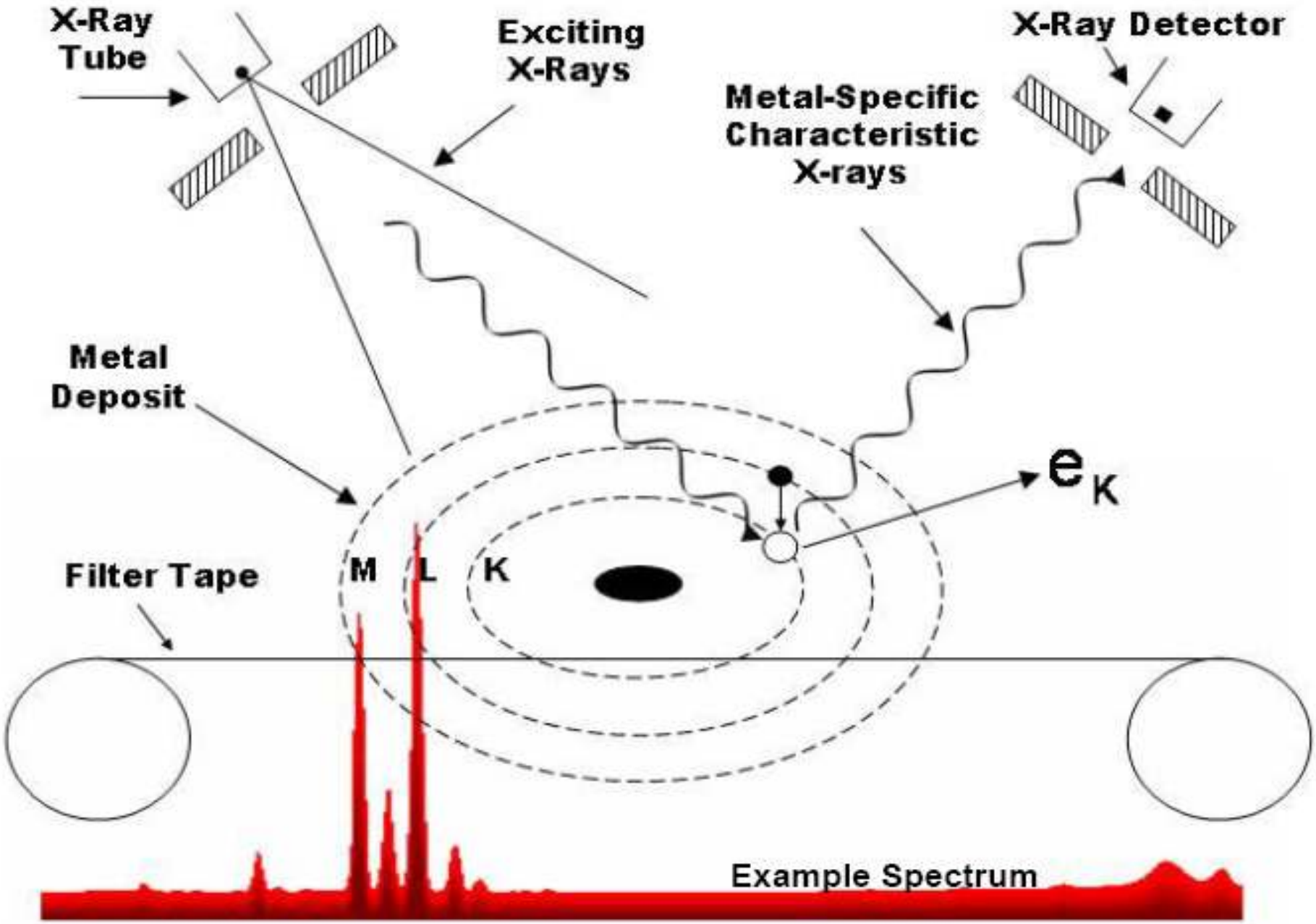
ELEMENTS THE XACT CAN MEASURE (IN BLUE)



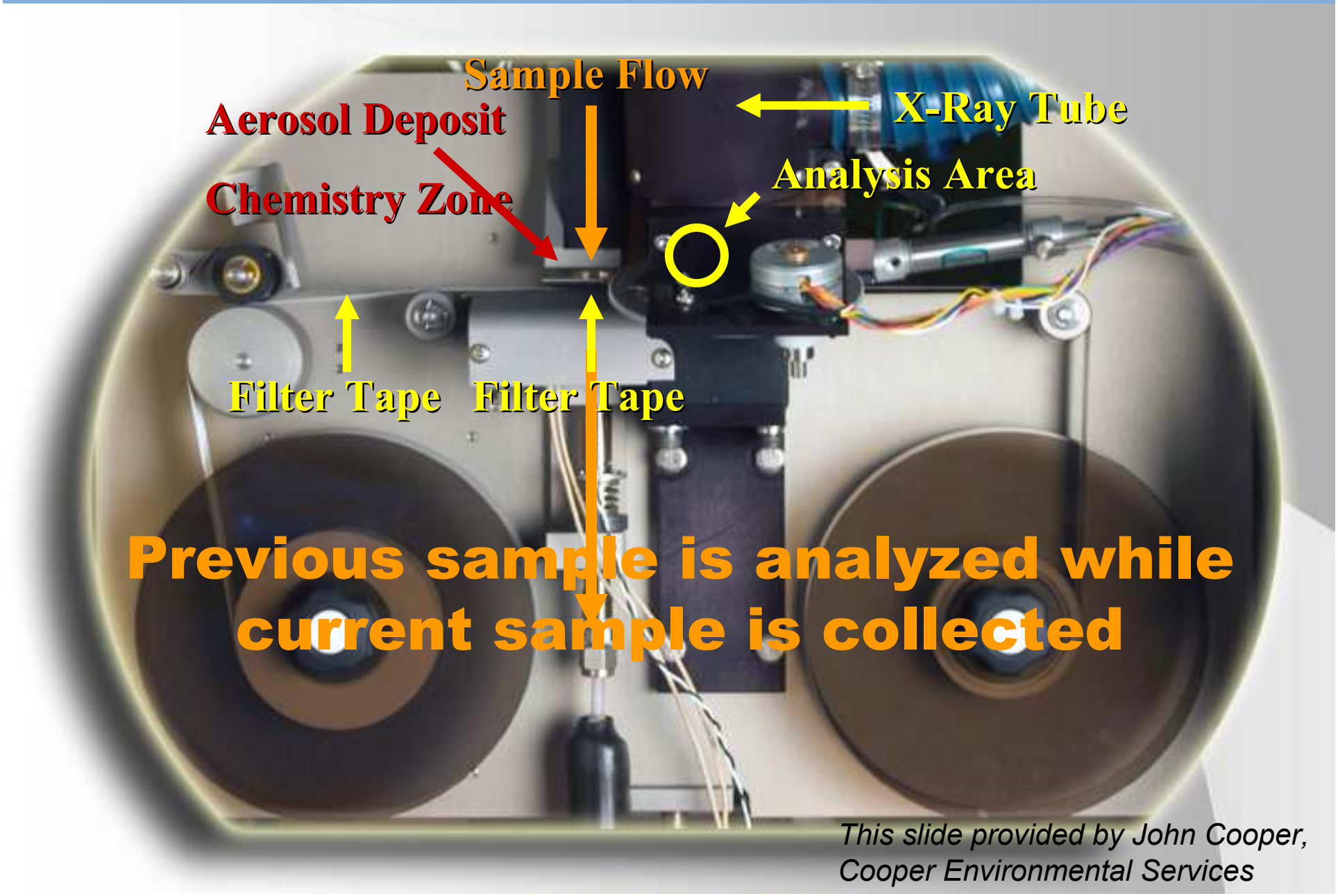
measured by Xact in this study

EPA Air Toxics PM metals

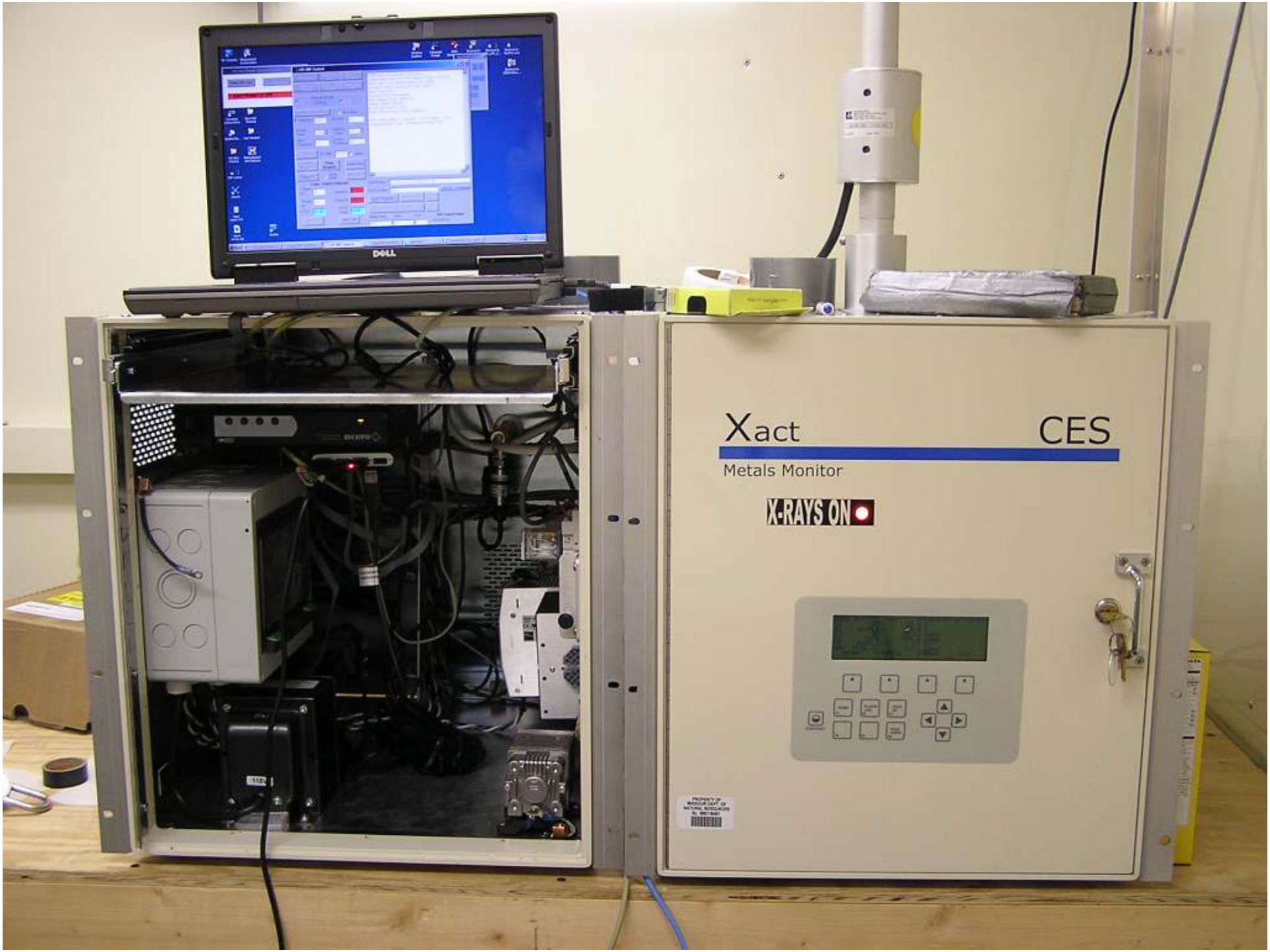
DIAGRAM OF X-RAY FLUORESCENCE TECHNOLOGY



Xact Sampling and Analysis

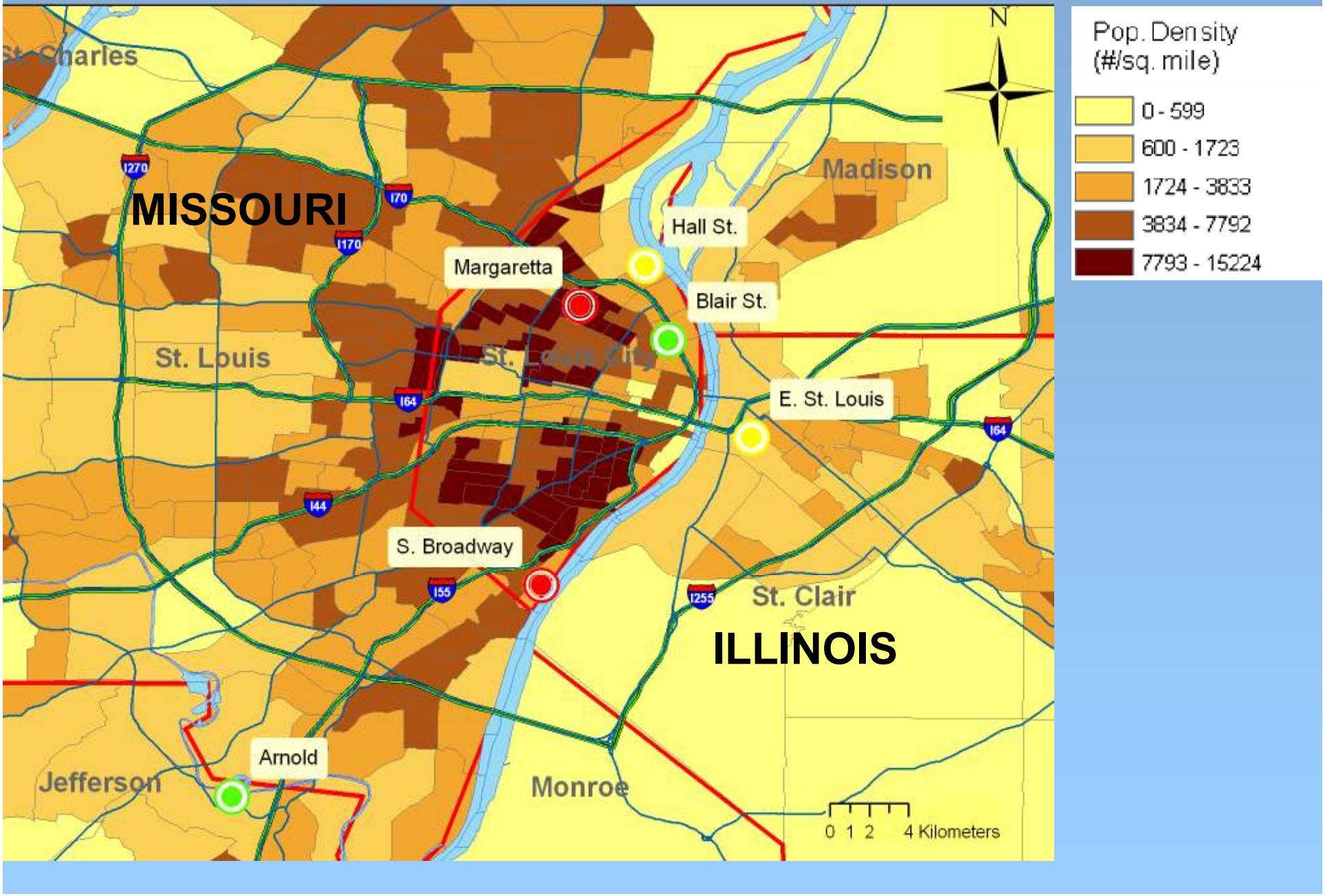


This slide provided by John Cooper, Cooper Environmental Services


DELL
Xact
CES
Metals Monitor
X-RAYS ON


CES
Model: Xact 620
Serial Number: 1120608

Phase II Xact Monitoring Sites



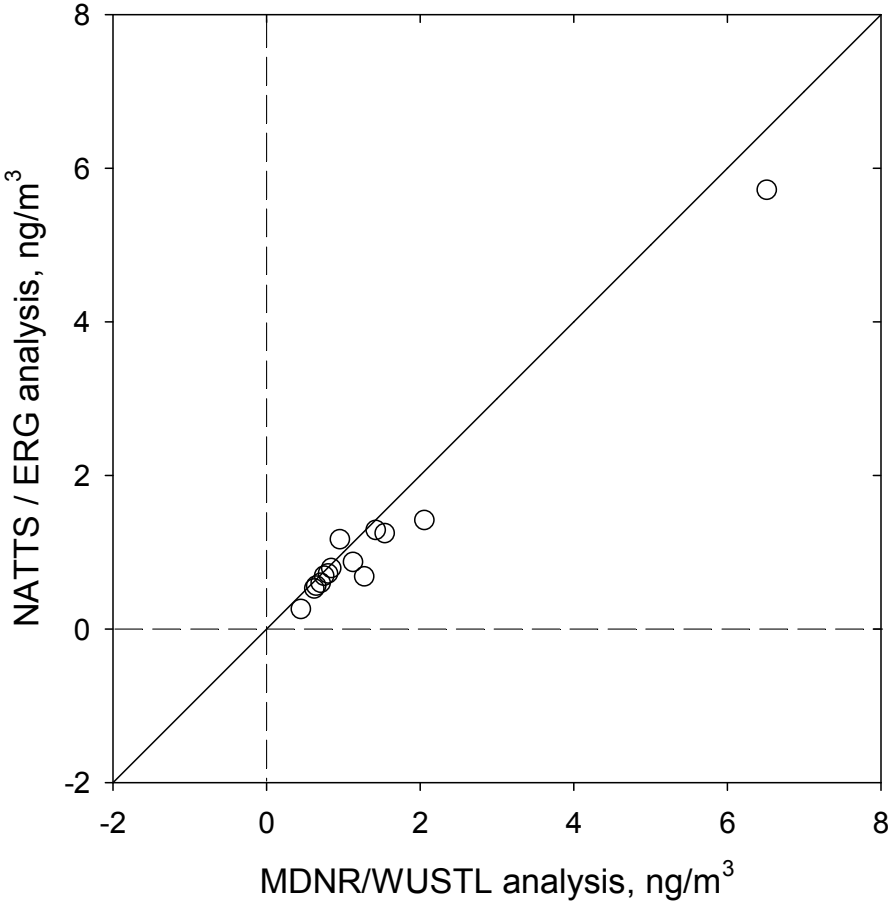
Blair St.

Herculaneum

Arsenic – Methods Comparisons

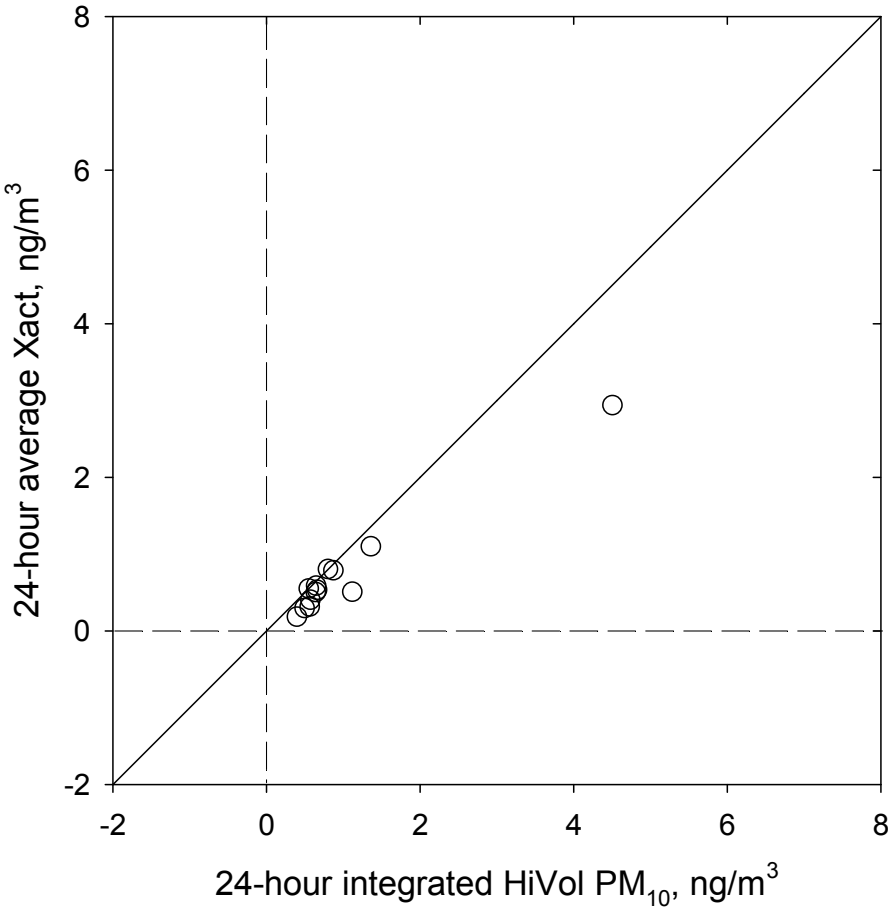
Collocated HiVol Samplers

Blair site, 4th Quarter 2008



Xact vs. WUSTL HiVol

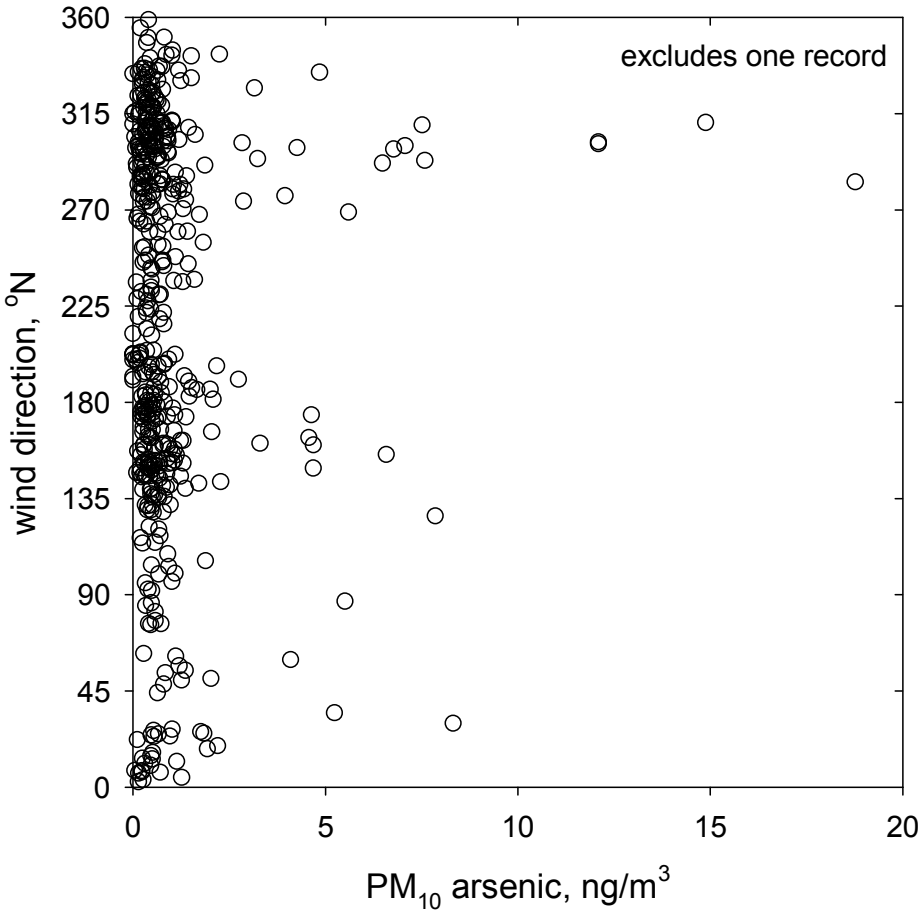
Dec 2008 / Jan 2009



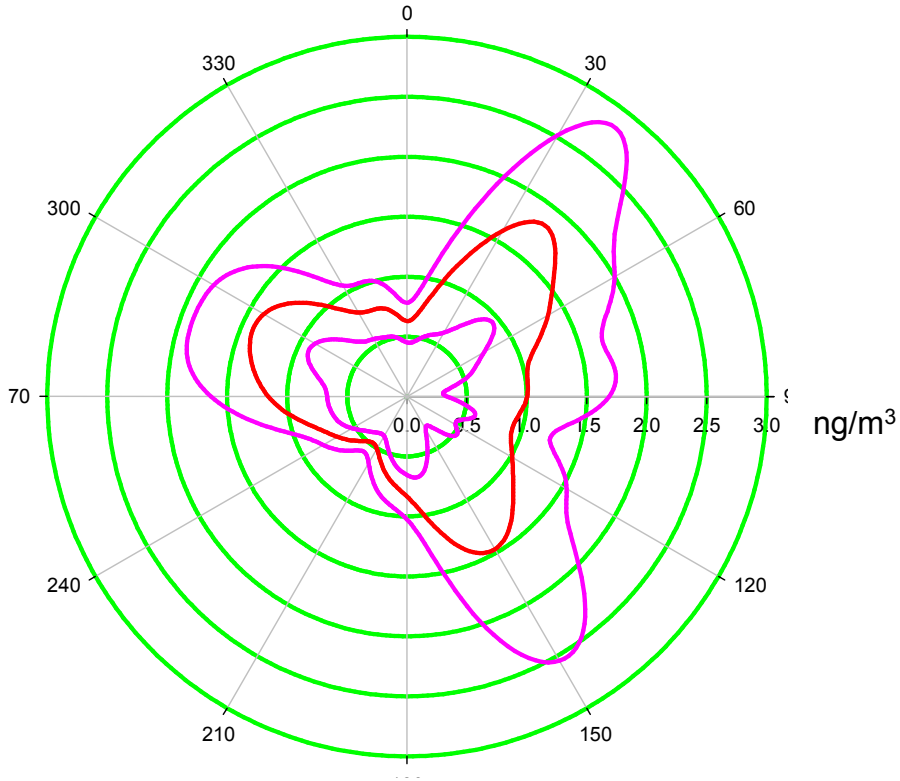
As: favorable comparison between Xact and PM_{10} HiVol samples with analysis by ICP-MS.

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

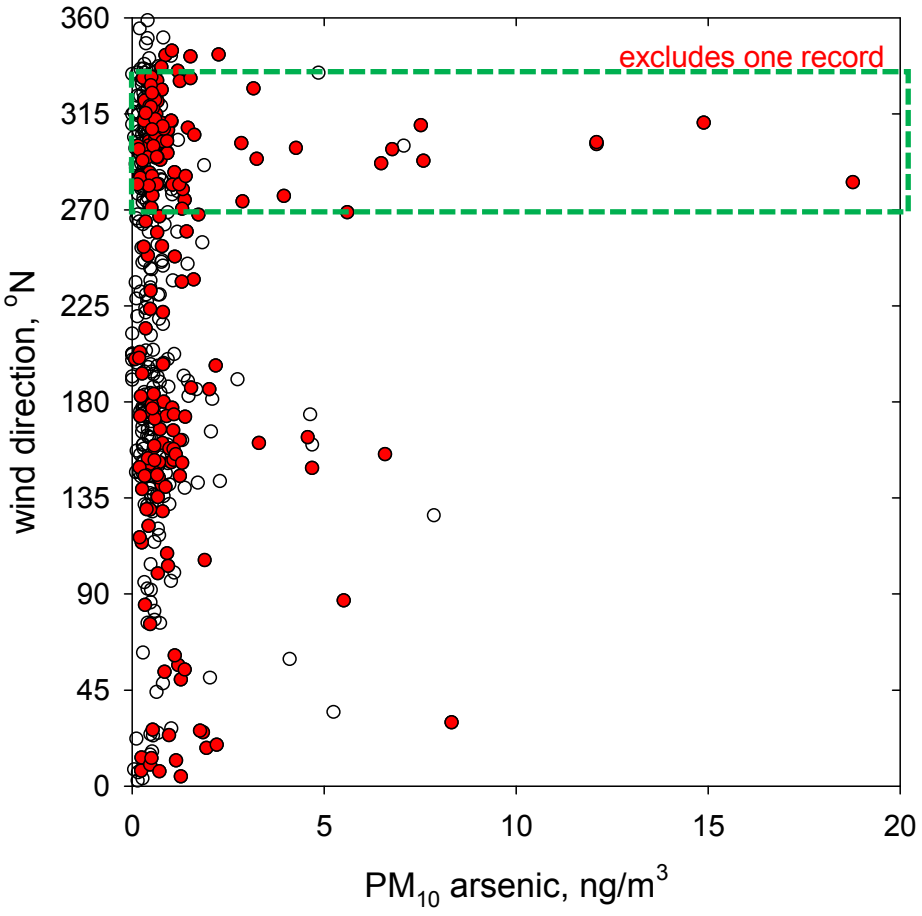
wind direction vs. concentration

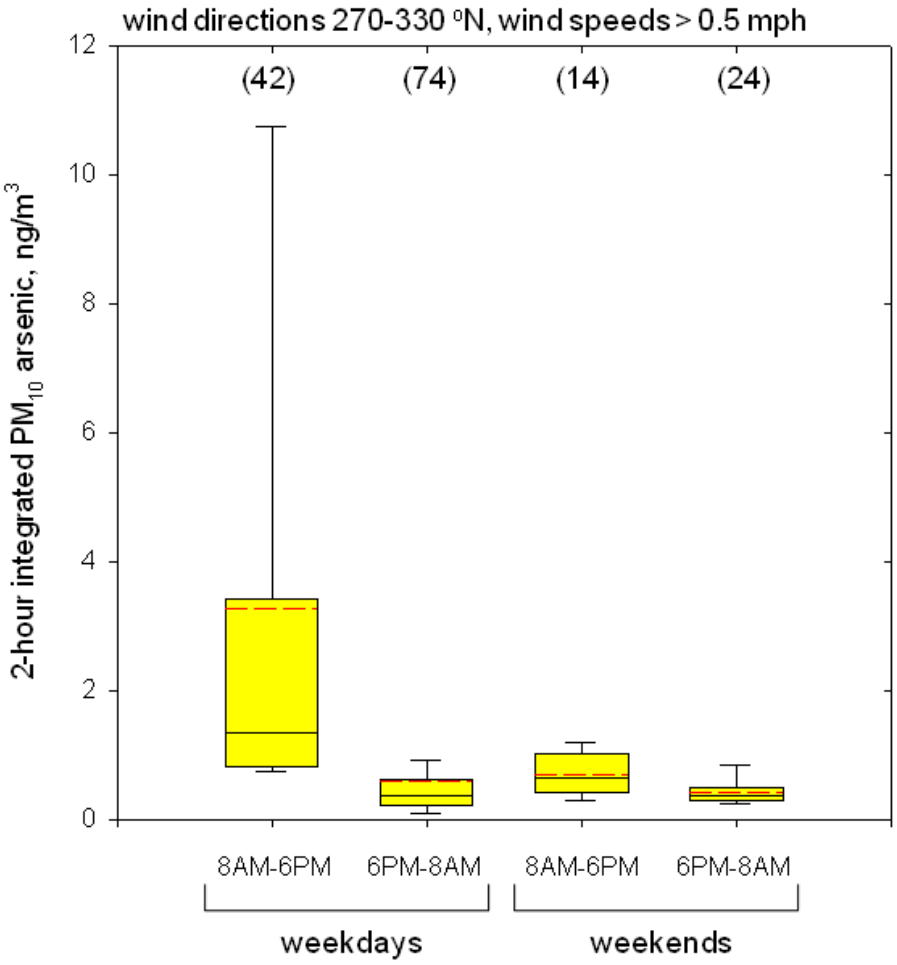


nonparametric wind regression



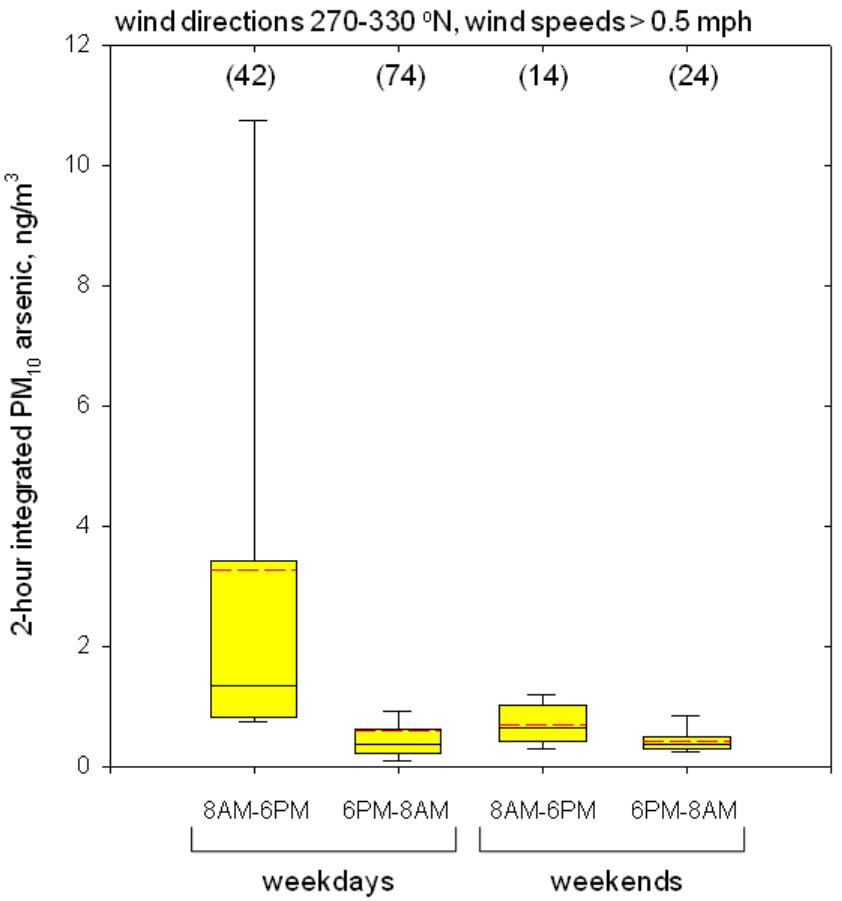
PM_{10} Arsenic at Blair for Winds from Northwest





red markers = 8 AM – 6PM weekdays

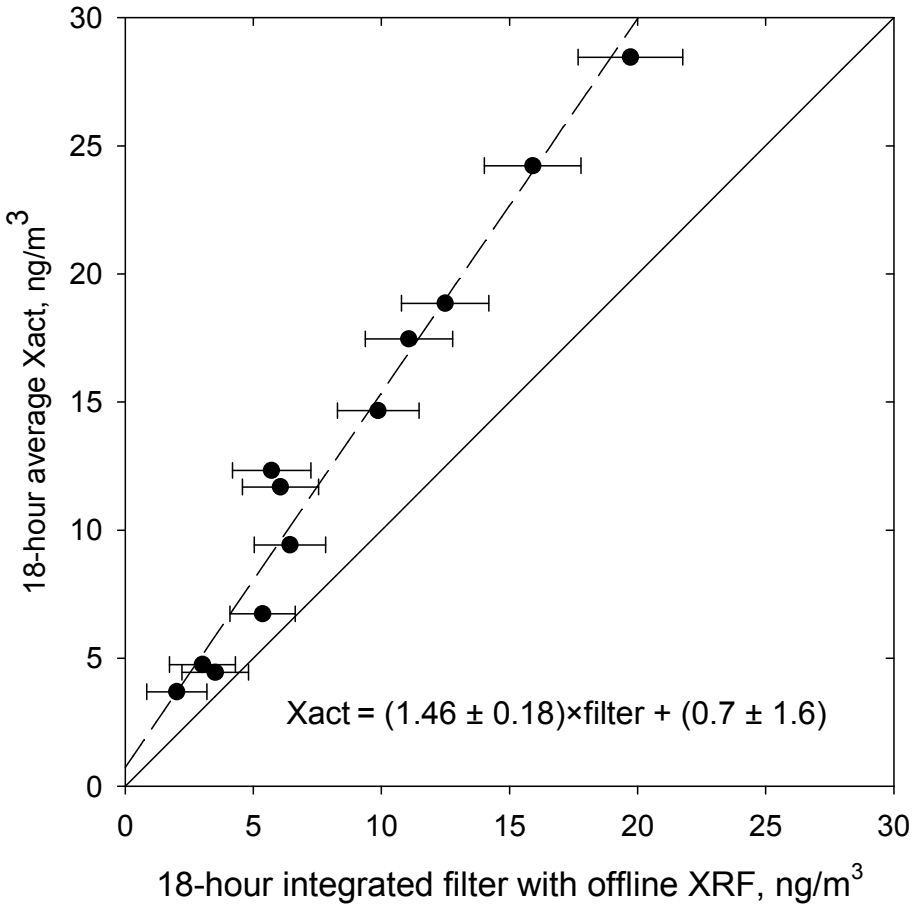
PM_{10} Arsenic at Blair for Winds from Northwest



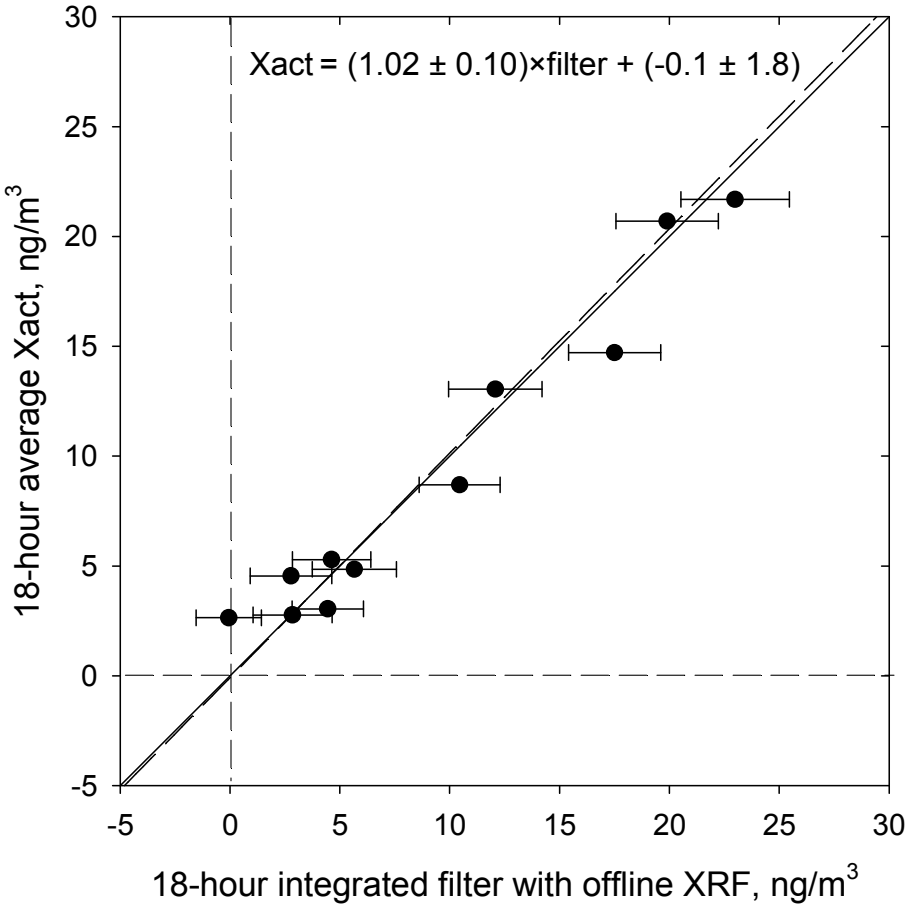
Emission source zone of influence?
Monitor zone of representation?

Xact vs. LowVol PM_{10} FRM / XRF

Manganese



Lead



Mn: biased but highly correlated

The Next Steps

- Analysis of data from other Xact deployments
  - Expanded performance evaluation
  - Analysis by XRF and ICP-MS of additional low-volume PM_{10} FRM samples
  - Collocated Xact measurements (MDNR and CES) at Herculaneum, August 2009; crucial precision data for receptor modeling
- Receptor modeling of the data sets
- Report preparation

Acknowledgements

- **Missouri Department of Natural Resources**
  - Jim Brunnert, Jerry Downs, Celeste Koon, Dustin Kuebler, Robert Nilges, Terry Rowles, Will Wetherell
- **Washington University**
  - Stephen Feinberg, Jay Turner, Varun Yadav
- **Cooper Environmental Services**
  - John Cooper, Krag Petterson
- **City of St. Louis Air Pollution Control**
  - Joe Gallagher, Don Simpson, Tom Wiese
- **U.S. EPA / Office of Air Quality Planning and Standards**
  - Mike Jones
- **U.S. EPA / Region VII**
  - Gwen Yoshimura
- **U.S. EPA / Office of Research and Development**
  - Teri Conner, Gary Norris, Bob Willis

Online Current Data

- **http://www.dnr.mo.gov/env/esp/aqm/allguide.htm**

  (Click on "Current Air Pollution Data Report" at mid-page, scroll down to St. Louis Metals Data)