



Operating Experience with a Near-Real-Time Ambient Airborne Metals Instrument System (Cooper Environmental Systems Xact 620)

National Ambient Air Monitoring Conference, Nashville, Tennessee

November 2-5, 2009



**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.**
- **Missouri DNR and Washington University obtained a Community-Scale Air Toxics grant from EPA to better determine sources of arsenic and other species in St. Louis.**
- **A Cooper Xact 620 was purchased on this grant and operated at multiple sites.**

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

Cooper Environmental Services Xact 620 Ambient Air Toxic Metals Monitor



← PM10 size-selective inlet

← Temperature controlled cabinet

← Heater

← Sampling & Analysis Module

← Operator interface/control panel

← Flow control module

ELEMENTS THE XACT CAN MEASURE (IN BLUE)

| | | | | | | | | | | | | | | | | | | | | | | | |
|---|--------------|--------------|--------------|---------------|---------------|---------------|---------------|---------------|---------------|--------------|--------------|--------------|--------------|--------------|--------------|-------------|--------------|--------------|--------------|-------------|-------------|--------------|--------------|
| 1 | 1 | 2 | | | | | | | | | | | 13 | 14 | 15 | 16 | 17 | 18 | | | | | |
| 1 | H 1.0079 | | | | | | | | | | | | | | | | | He 4.0026 | | | | | |
| 2 | 3 | 4 | | | | | | | | | | | 5 | 6 | 7 | 8 | 9 | 10 | | | | | |
| | Li 6.941 | Be 9.0122 | | | | | | | | | | | | | | | | B 10.811 | C 12.011 | N 14.007 | O 15.999 | F 18.998 | Ne 20.18 |
| 3 | 11 | 12 | | | | | | | | | | | 13 | 14 | 15 | 16 | 17 | 18 | | | | | |
| | Na 22.99 | Mg 24.305 | | | | | | | | | | | | | | | | Al 26.982 | Si 28.086 | P 30.974 | S 32.066 | Cl 35.453 | Ar 39.948 |
| 4 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 | | | | | |
| | K 39.098 | Ca 40.078 | Sc 44.956 | Ti 47.88 | V 50.942 | Cr 51.996 | Mn 54.938 | Fe 55.847 | Co 58.933 | Ni 58.693 | Cu 63.546 | Zn 65.39 | Ga 69.723 | Ge 72.61 | As 74.922 | Se 78.96 | Br 79.904 | Kr 83.8 | | | | | |
| 5 | 37 | 38 | 39 | 40 | 41 | 42 | 43 | 44 | 45 | 46 | 47 | 48 | 49 | 50 | 51 | 52 | 53 | 54 | | | | | |
| | Rb 85.468 | Sr 87.62 | Y 88.906 | Zr 91.224 | Nb 92.906 | Mo 95.94 | Tc (97.91) | Ru 101.07 | Rh 102.91 | Pd 106.42 | Ag 107.87 | Cd 112.41 | In 114.82 | Sn 118.71 | Sb 121.76 | Te 127.6 | I 126.9 | Xe 131.29 | | | | | |
| 6 | 55 | 56 | 57 | 72 | 73 | 74 | 75 | 76 | 77 | 78 | 79 | 80 | 81 | 82 | 83 | 84 | 85 | 86 | | | | | |
| | Cs 132.91 | Ba 137.33 | La 138.91 | Hf 178.49 | Ta 180.95 | W 183.84 | Re 186.21 | Os 190.23 | Ir 192.22 | Pt 195.08 | Au 196.97 | Hg 200.59 | Tl 204.38 | Pb 207.2 | Bi 208.98 | Po (209) | At (210) | Rn (222) | | | | | |
| 7 | 87 | 88 | 89 | 104 | 105 | 106 | 107 | 108 | 109 | 110 | 111 | | | | | | | | | | | | |
| | Fr (223) | Ra (226) | Ac (227) | Rf (261.1) | Ha (262.1) | Sg (263.1) | Ns (262.1) | Hs (265.1) | Mt (266.1) | Unn (268) | Unu (269) | | | | | | | | | | | | |

Lanthanide Series

| | | | | | | | | | | | | | |
|--------|--------|--------|---------|--------|--------|--------|--------|-------|--------|--------|--------|--------|--------|
| 58 | 59 | 60 | 61 | 62 | 63 | 64 | 65 | 66 | 67 | 68 | 69 | 70 | 71 |
| Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |
| 140.12 | 140.91 | 144.24 | (144.9) | 150.36 | 151.97 | 157.25 | 158.93 | 162.5 | 164.93 | 167.26 | 168.93 | 173.04 | 174.97 |

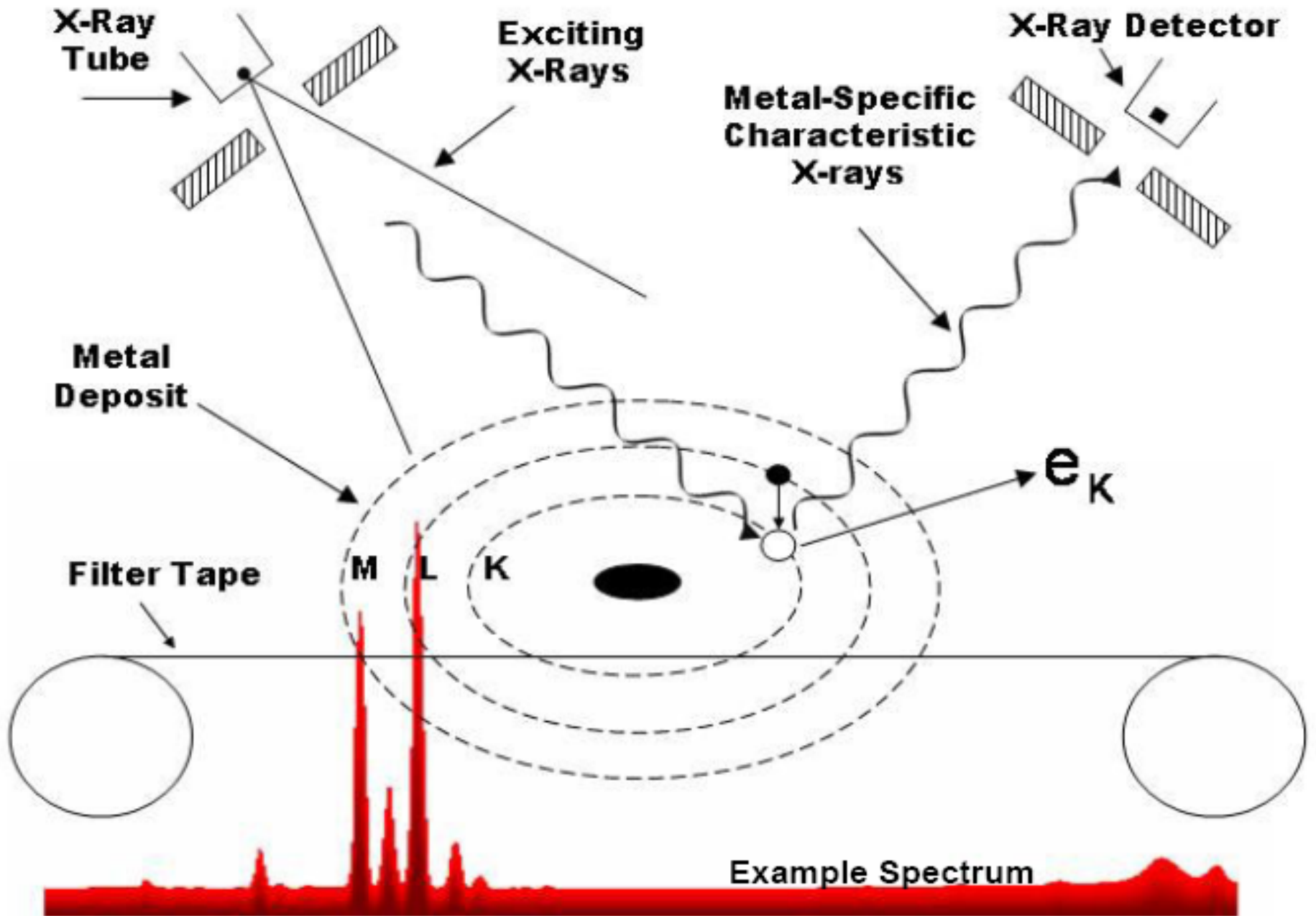
Actinide Series

| | | | | | | | | | | | | | |
|--------|--------|--------|-------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 90 | 91 | 92 | 93 | 94 | 95 | 96 | 97 | 98 | 99 | 100 | 101 | 102 | 103 |
| Th | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No | Lr |
| 232.04 | 231.04 | 238.03 | (237) | (244.1) | (243.1) | (247.1) | (247.1) | (251.1) | (252.1) | (257.1) | (258.1) | (259.1) | (262.1) |

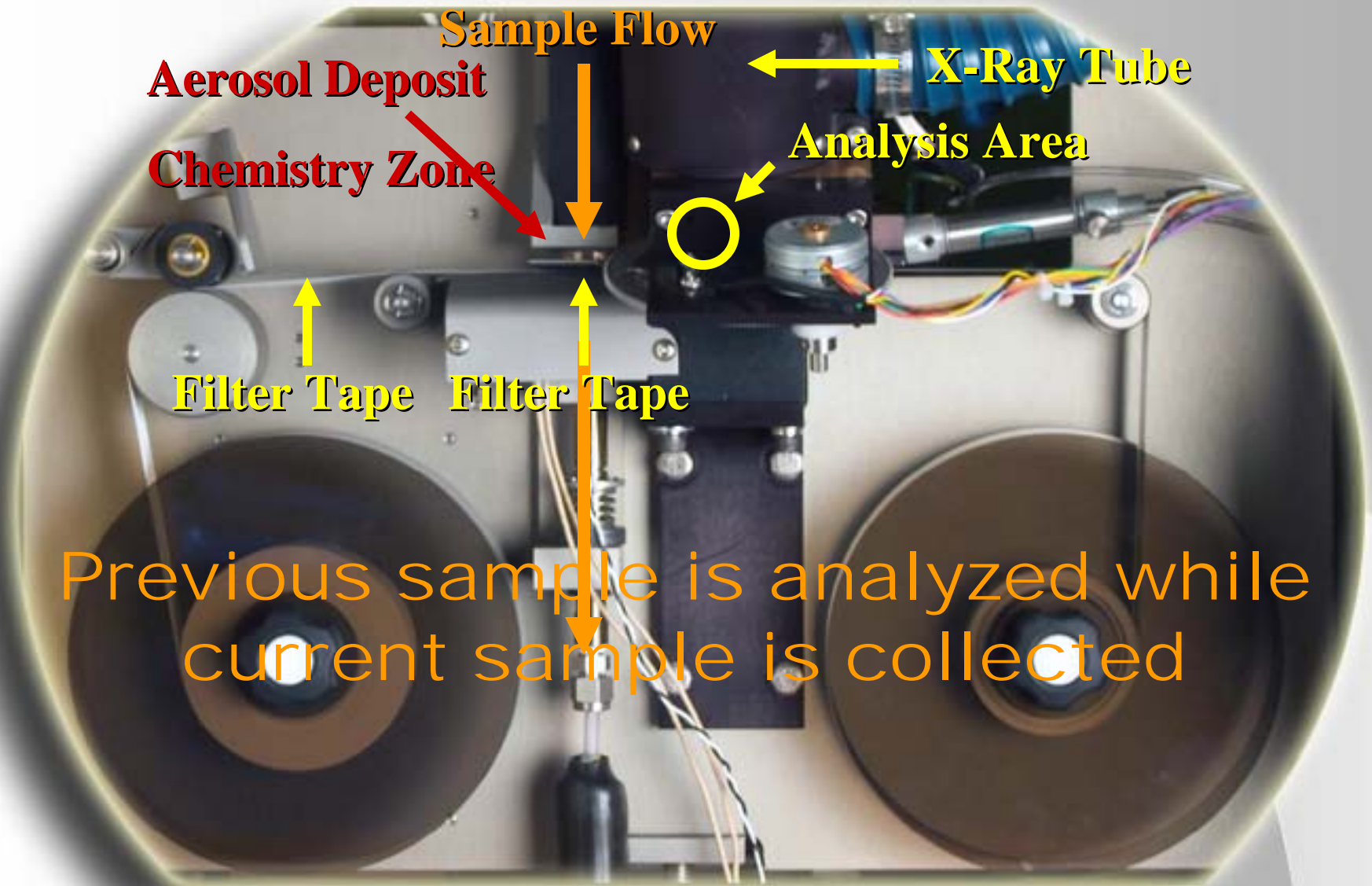
 measured by Xact in this study

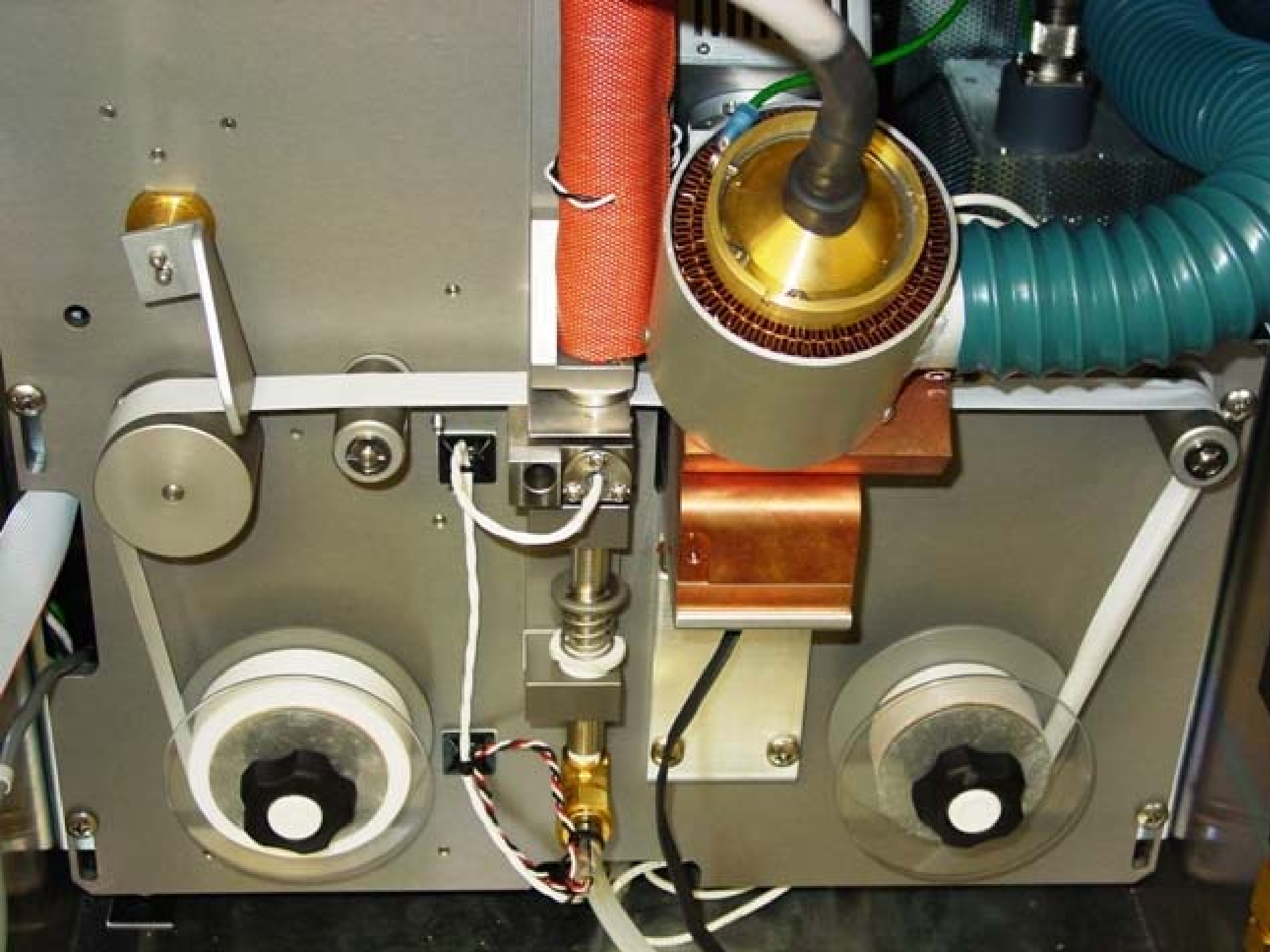
 EPA Air Toxics PM metals

DIAGRAM OF X-RAY FLUORESCENCE TECHNOLOGY



Xact Sampling and Analysis





Xact Tape Deposits



Deposit Area 0.747 cm^2



Xact

CES

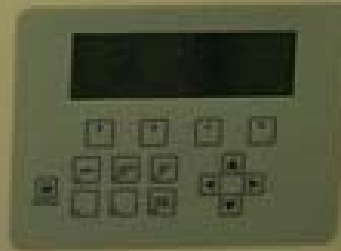
Metals Monitor



Xact

CES

Metals Monitor

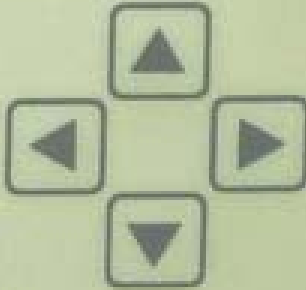


Model: Xact CES
Serial: 123456789
Date: 12/12/2011

Xact 620 14-OCT-09 09:49:17
01 AT 8.9 C
02 SAMPLE 24.3 C
03 BP 751.6 mmHg
04 TAPE 744.9 mmHg
05 SAMPLE 54 %
06 FLOW 25 0.0 slpm
SETUP OPERATE STATUS TEST



CONTRAST



Remote Control

My Computer 08_02_200...

Windows Explorer Command Prompt 8832 Ethernet.bt Shortcut to Xact.exe Shortcut to CES_XRF_C...

CES Xact Power Control Program

Power OFF Xact Power ON Xact

Xact Power is ON

Symantec pcAnywhere New Xact Terminal

UpdateCloc... Xact Terminal

MO DEQ Patches Malwarebytes' Anti-Malware

CES XRF Control

XRS-FP

state report.TXT

latest server.cfg System

CES XRF Control

Reset Vortex Query Vortex Status Query VTX Connection

Query Vortex Firmware Query Baseline Parameters Initialize Vortex DPP

Live Time Preset Mode Setting Real Time

Set Parameters Auto Current

- Channels 2048 Bin Size 20

Preset Time 14400 Peaking Time 1.0

Slow Threshold 0 Energy Threshold 650

Energy Cal ADC Gain = 35261 LogFile ?

Start Acquire Stop Acquire Enable Debug

Status ? Debug Display **ABORT !**

X-RAY POWER CONTROL

Target KV 49 Actual KV 48.94

Target uA 510 Actual uA 992.27

24VDC 23.47 HYPs Temp 60.83

XRAY ON XRAY OFF

14400 Second Acquisition in Progress
 Acquire Start Time = 12:00:42 Elapsed Time = 00:51:10
 Real Time = 1200.00 Accum Real Time = 2400.00
 LiveTime = 979.36 Accum Live Time = 1958.93
 Dead Time = 18.23
 Acq Nn 2 Of 12 Completed
 High Voltage Power = 48.93 W
 Beam Current = 992.27
 UC 24 Volt Source = 23.48
 HYPs Temperature = 60.8 Degrees C

XRF Control Status = Acquiring HVPS Status = True
 Acquiring State = True Multi-Acquire Flag = True

Last Error Msg [None as of 10/28/2009 11:59 56 AM]

Last Ecal Status [Eca OK !! 10/28/2009 12:03:27 AM XRS-FP --> Analyze]

Exit Program Set ADC Gain Set Status

Emergency XRAY OFF ! Load File

Modbus Read Write Error **XRF Control Status**

1188050 683 0 Acquiring

XRF Control Initialization file parameter description

XRF Control version 14.1 and higher use an initialization file to set the control panel and parameter settings. The user must create the initialization file before the program can be installed. The user must create the initialization file before the program can be installed. The user must create the initialization file before the program can be installed.







SpectraX File View Process Setup Help

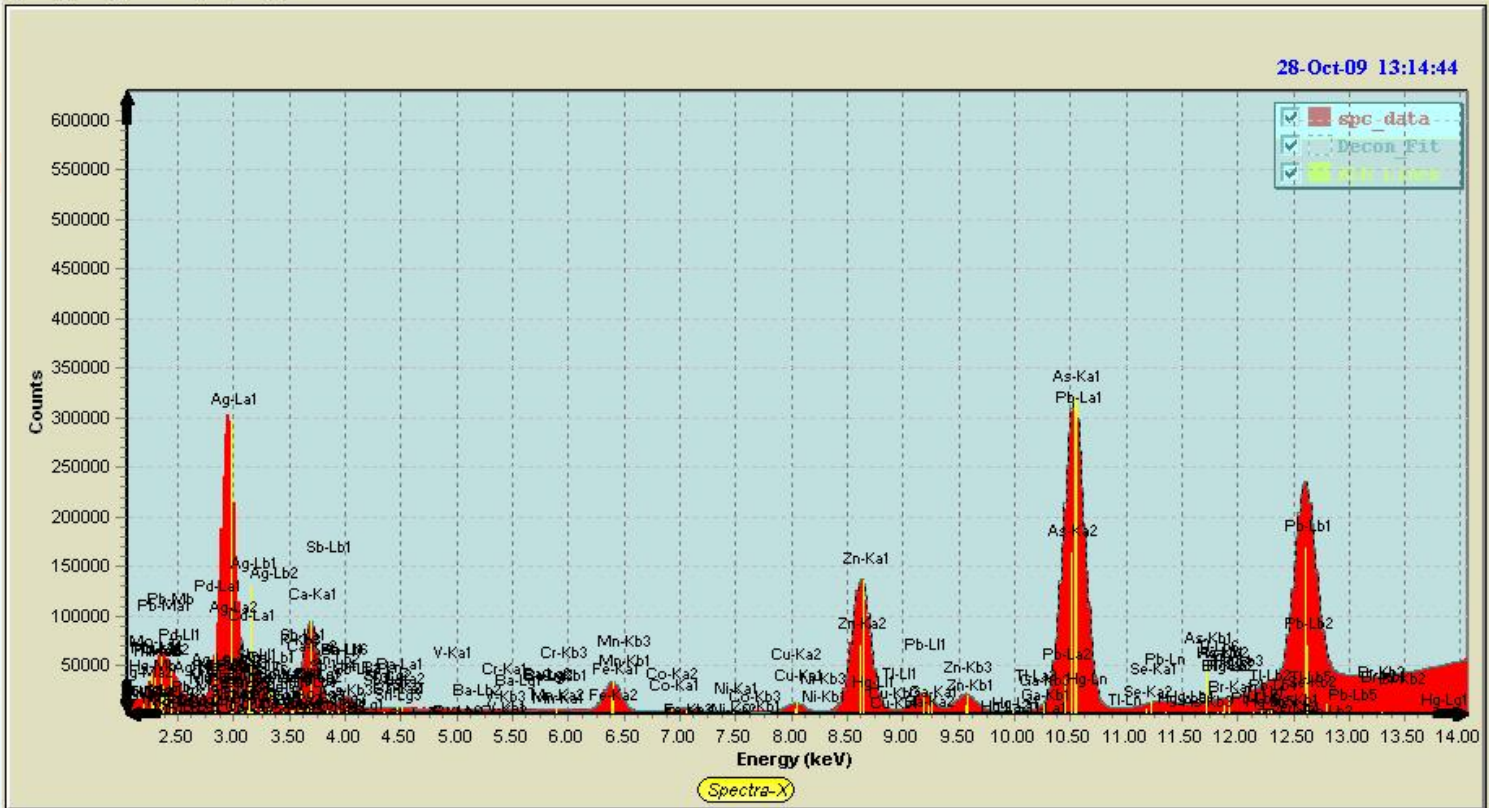


Chart Tools

Zoom In Zoom Out

KLM Markers

25 | Pb | Add | Clear

Shortcut to act.exe

Shortcut to CES_XRF_C...

Shortcut to XactPwr.exe

Shortcut to CESArchive...

--- Analyze()

SpectraX Controls

Navigation buttons: Home, Back, Forward, Stop, etc.

AutoVS

Log

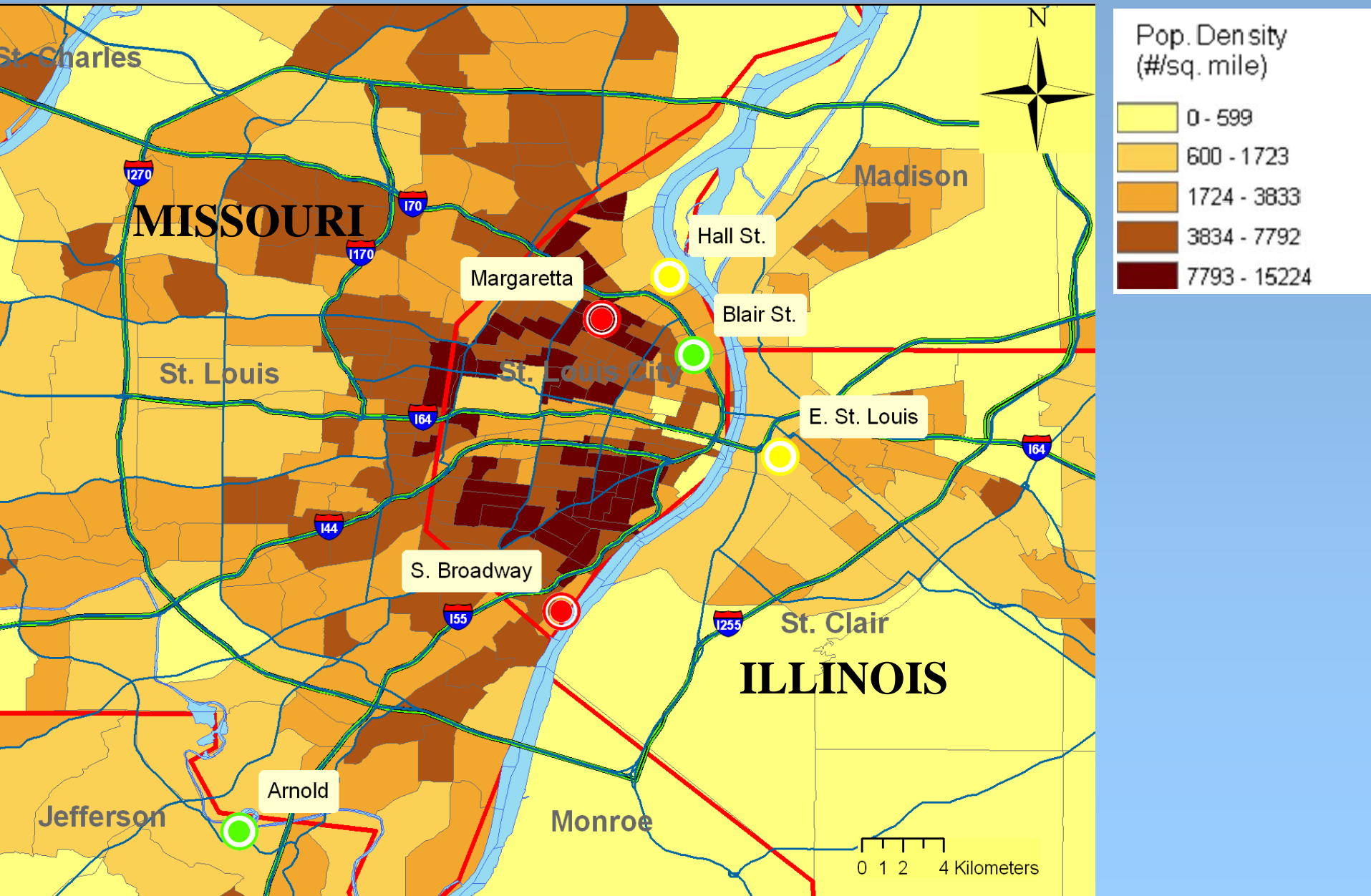
24 VDC **23.48** HVPS Temp **60.10** Emergency XRAY OFF!

XRAY ON XRAY OFF Load File

Modbus Read Write Error **XRF Control Status**

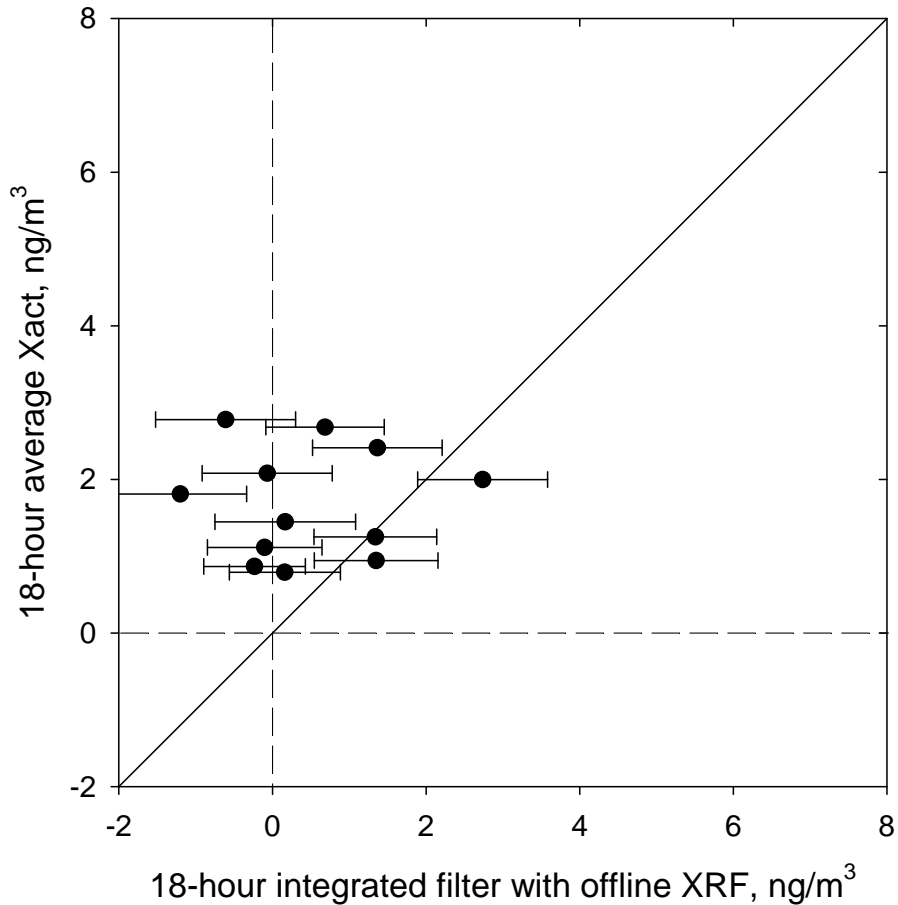
1188349 685 0 Acquiring

Phase II Xact Monitoring Sites

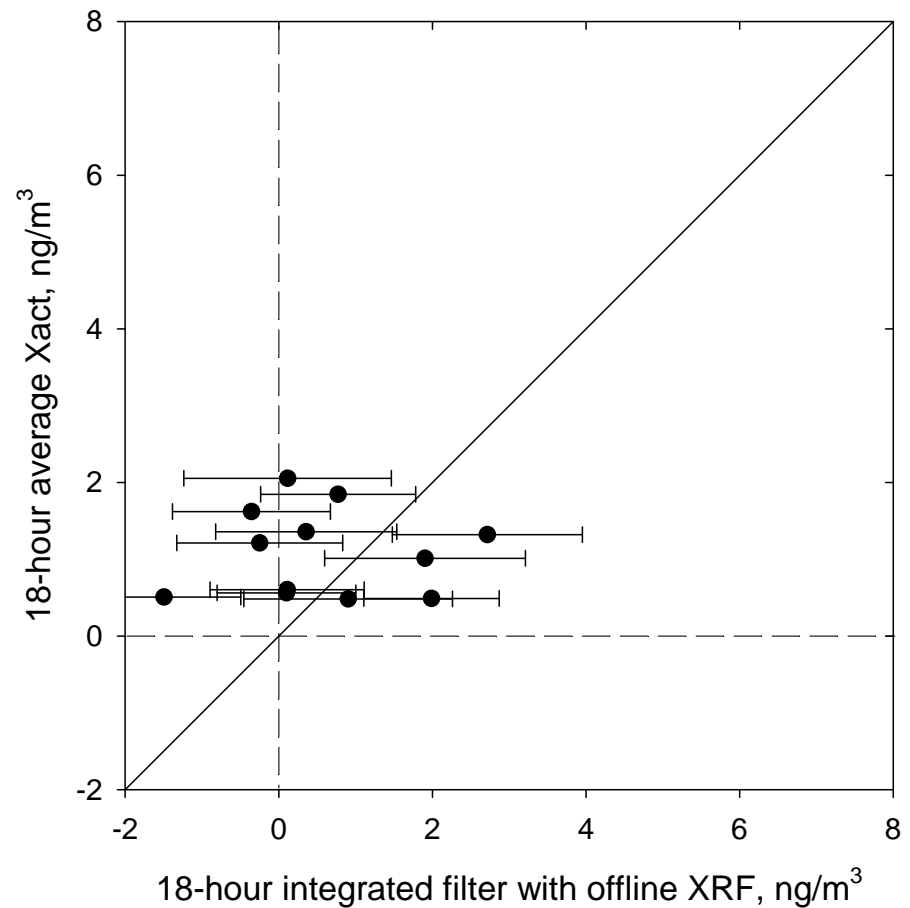


Xact vs. LowVol PM₁₀ FRM / XRF

Selenium



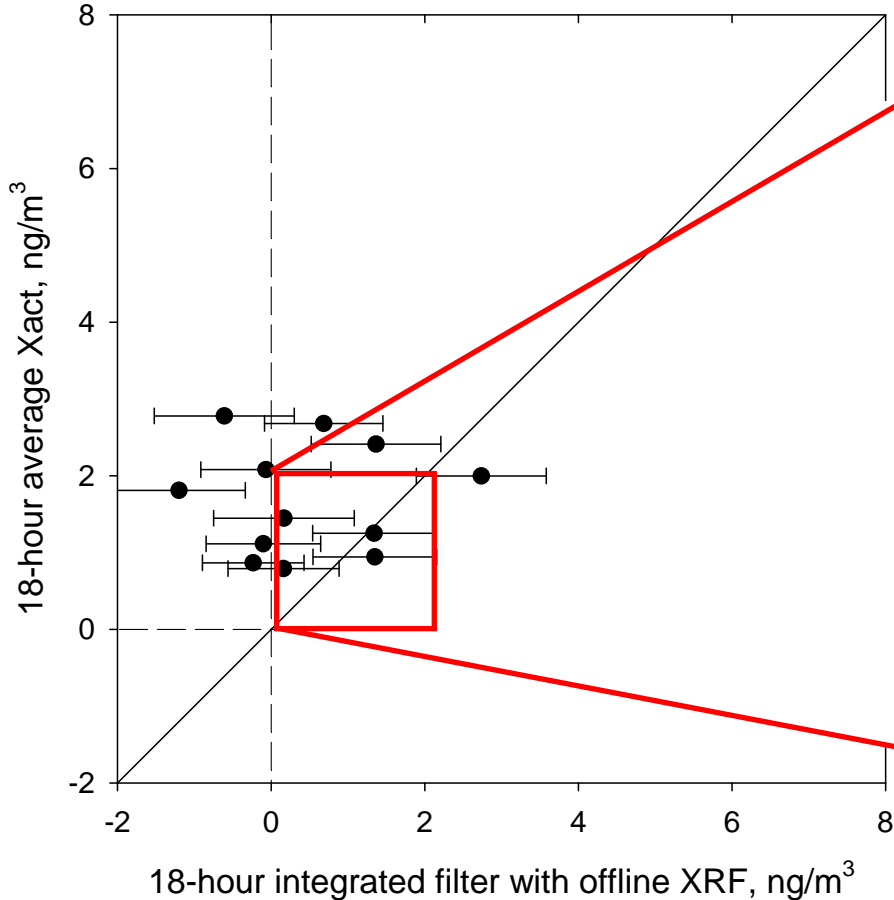
Arsenic



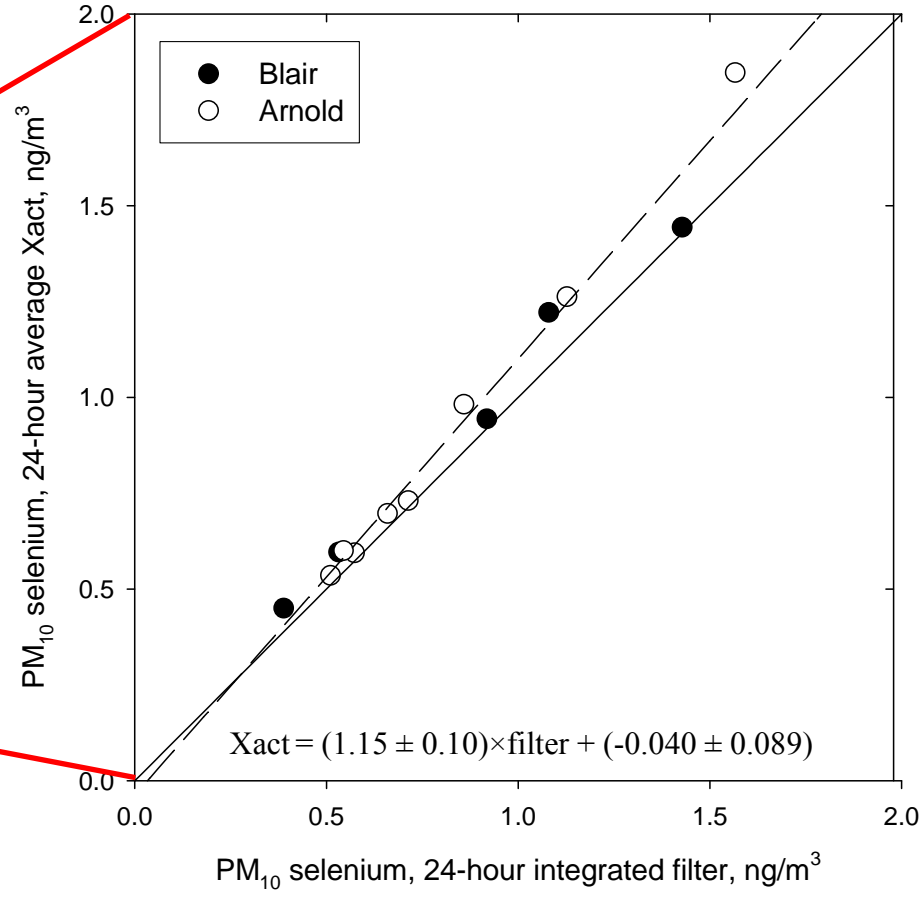
Se and As: pushing the detection limit of the lab-based XRF. need to compare the Xact to ICP-MS (next slide)...

Selenium: Xact vs. Filter-Based Measurements

Xact vs. LowVol filter / lab XRF



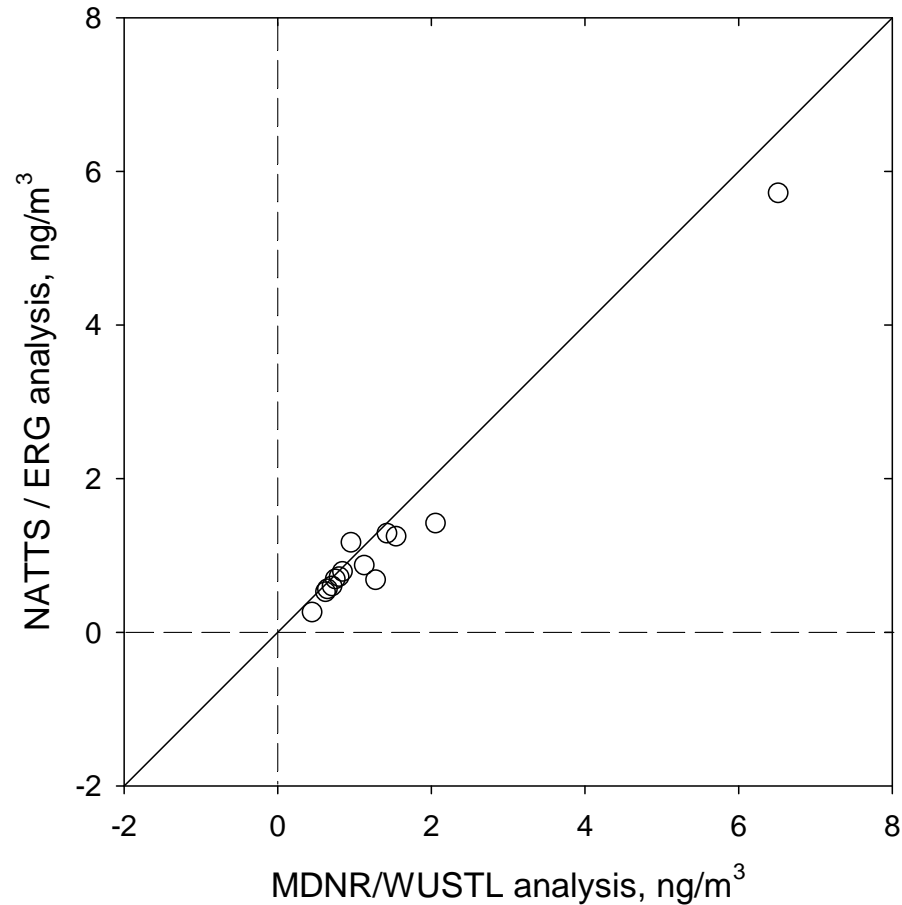
Xact vs. HiVol filter / lab ICP-MS



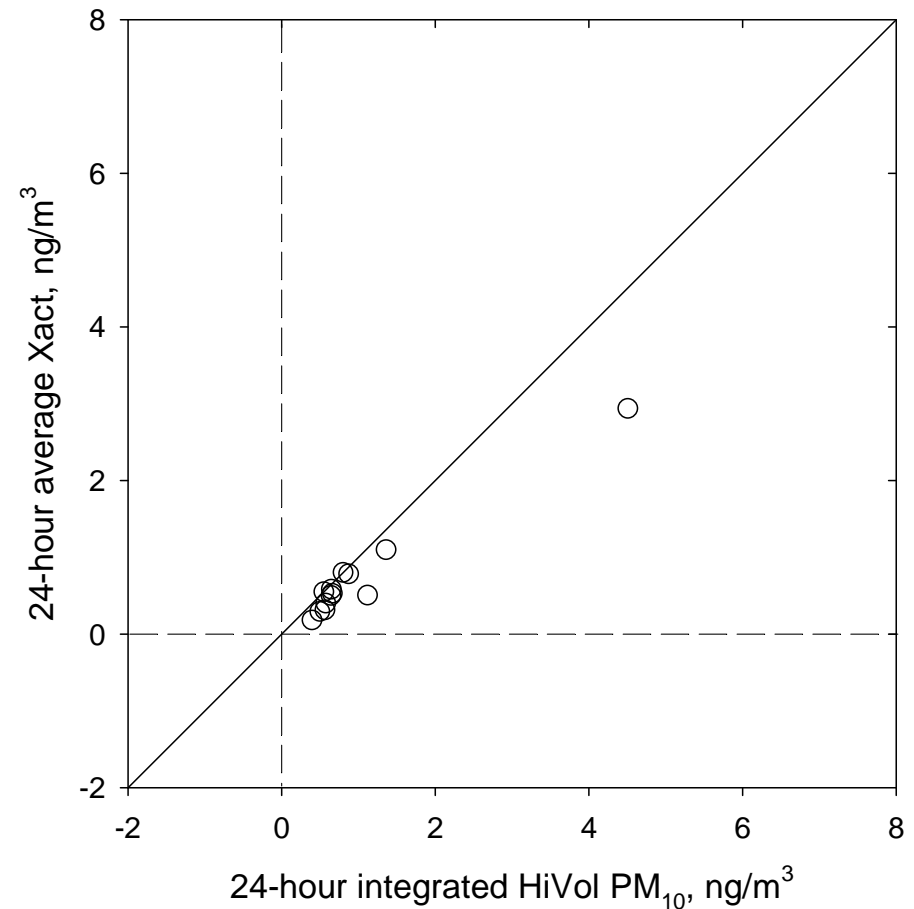
Se: favorable comparison between Xact and PM₁₀ HiVol samples with analysis by ICP-MS

Arsenic – Methods Comparisons

Collocated HiVol Samplers
Blair site, 4th Quarter 2008



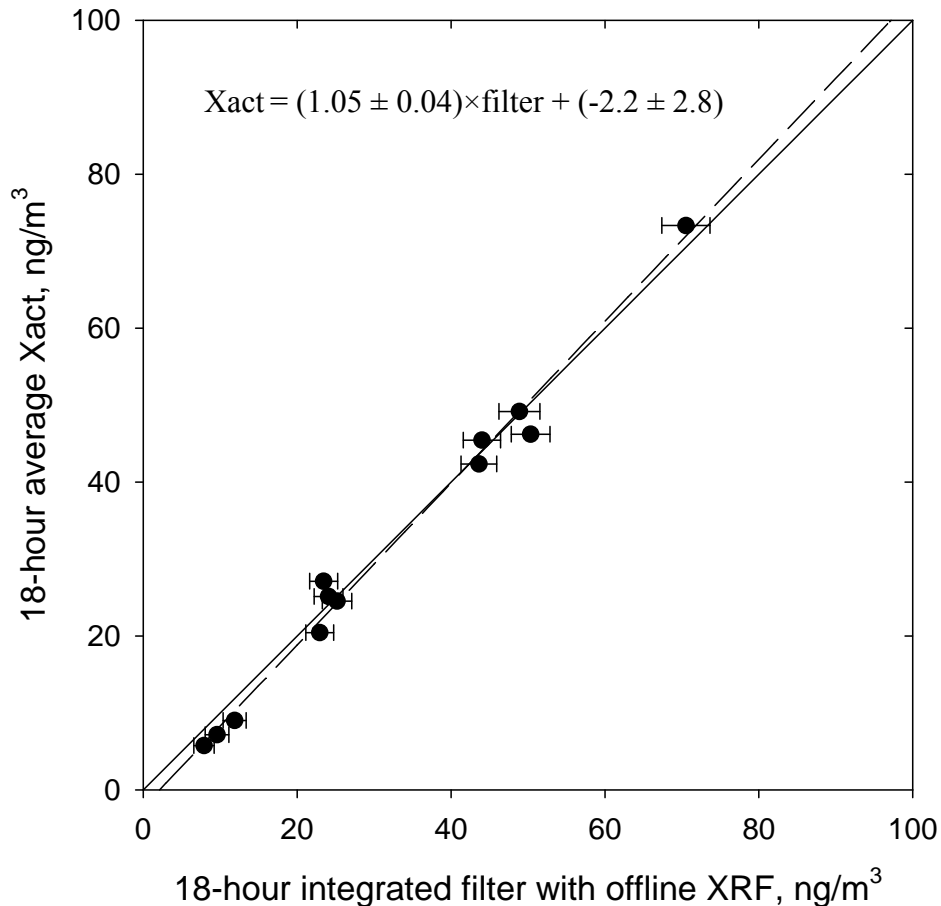
Xact vs. WUSTL HiVol
Dec 2008 / Jan 2009



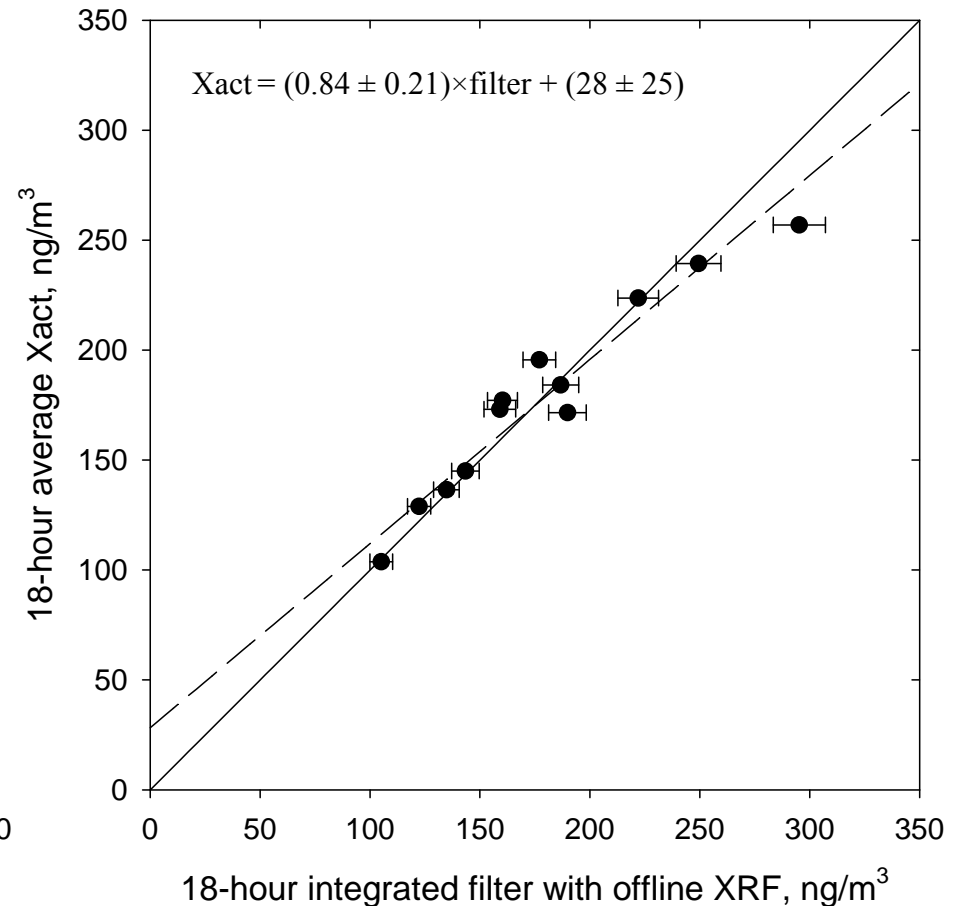
As: favorable comparison between Xact and PM₁₀ HiVol samples with analysis by ICP-MS.

Xact vs. LowVol PM₁₀ FRM / XRF

Titanium

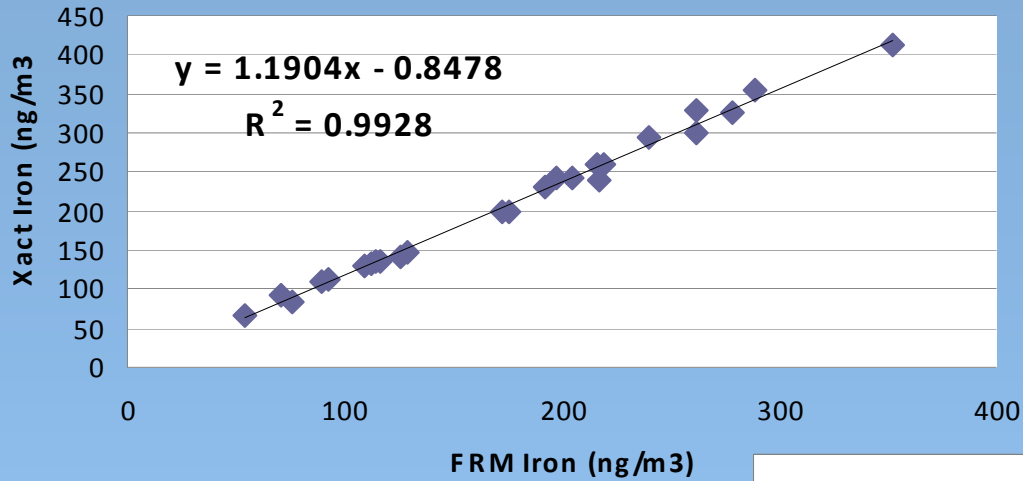


Potassium

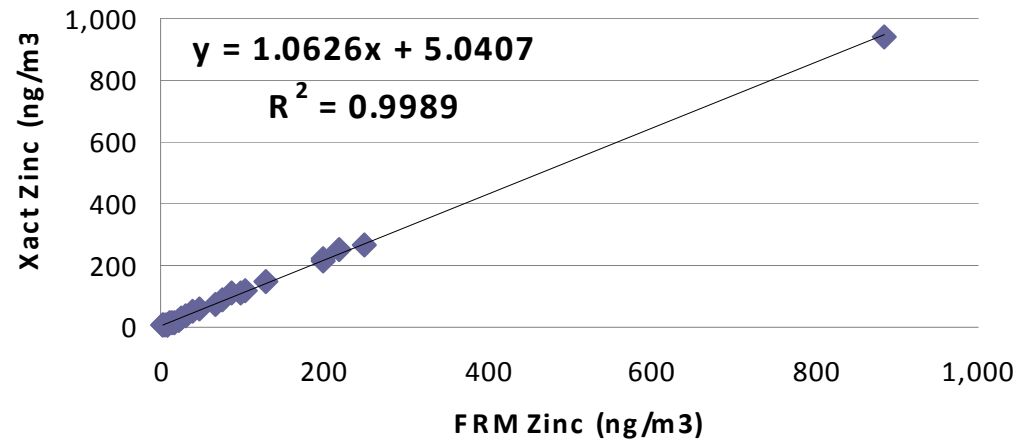


Herculaneum, MO

Xact vs FRM Iron

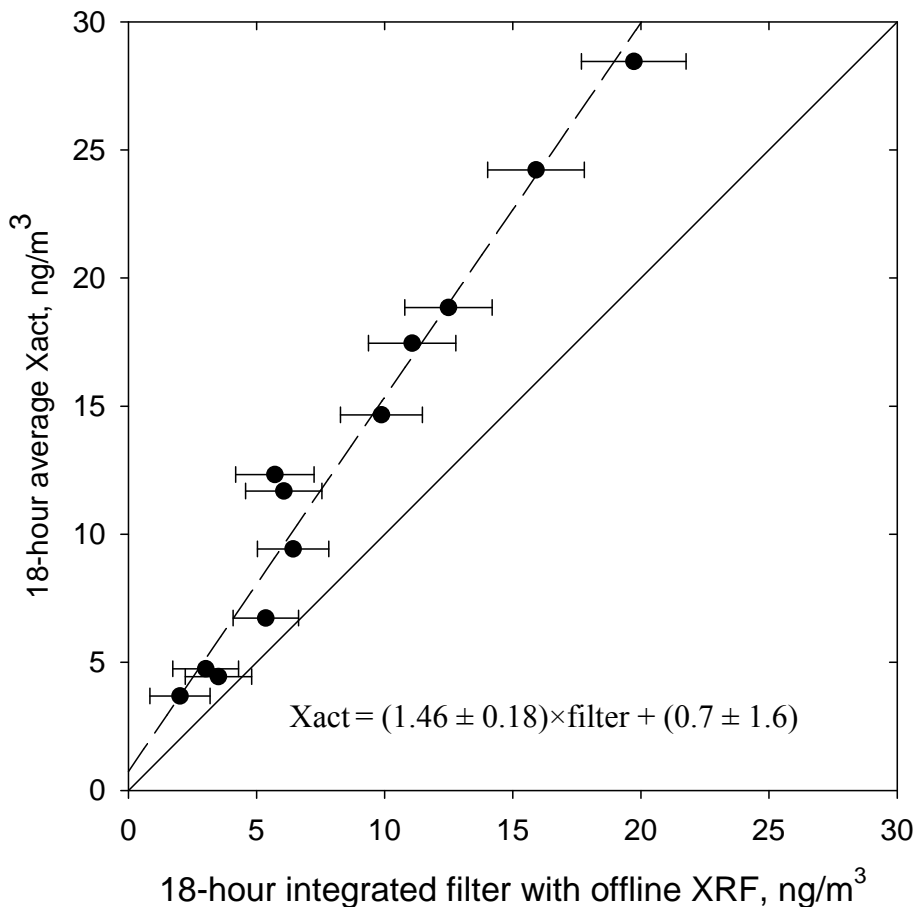


Xact vs FRM Zinc

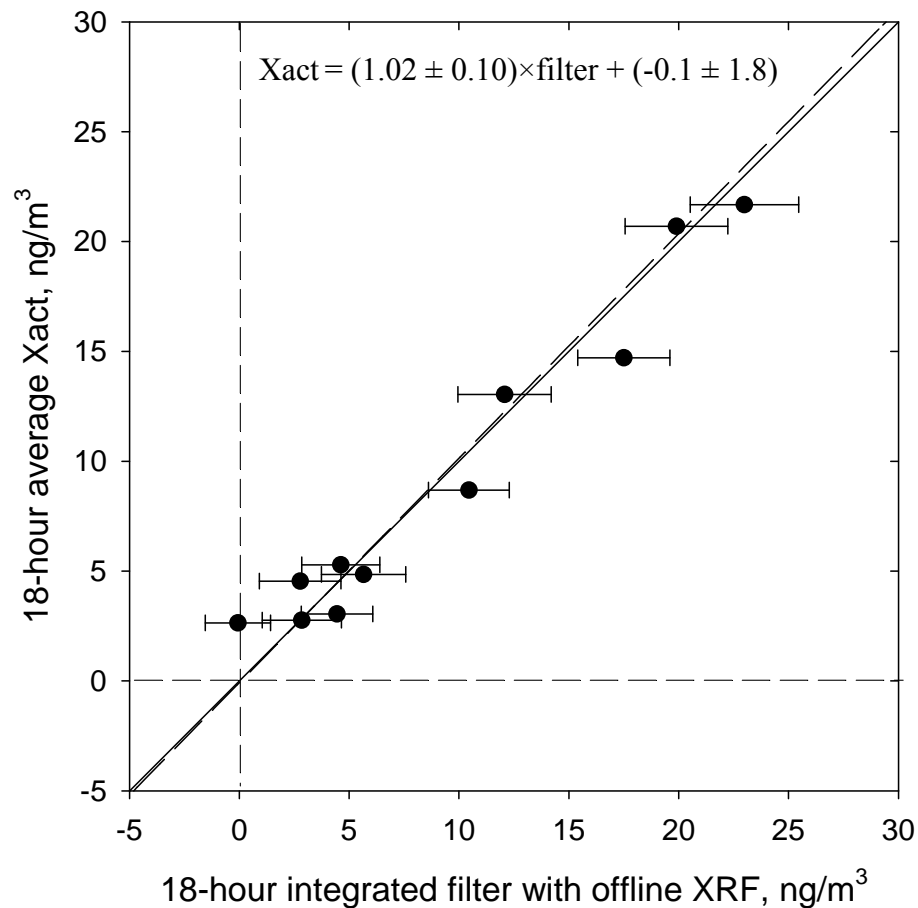


Xact vs. LowVol PM₁₀ FRM / XRF

Manganese



Lead

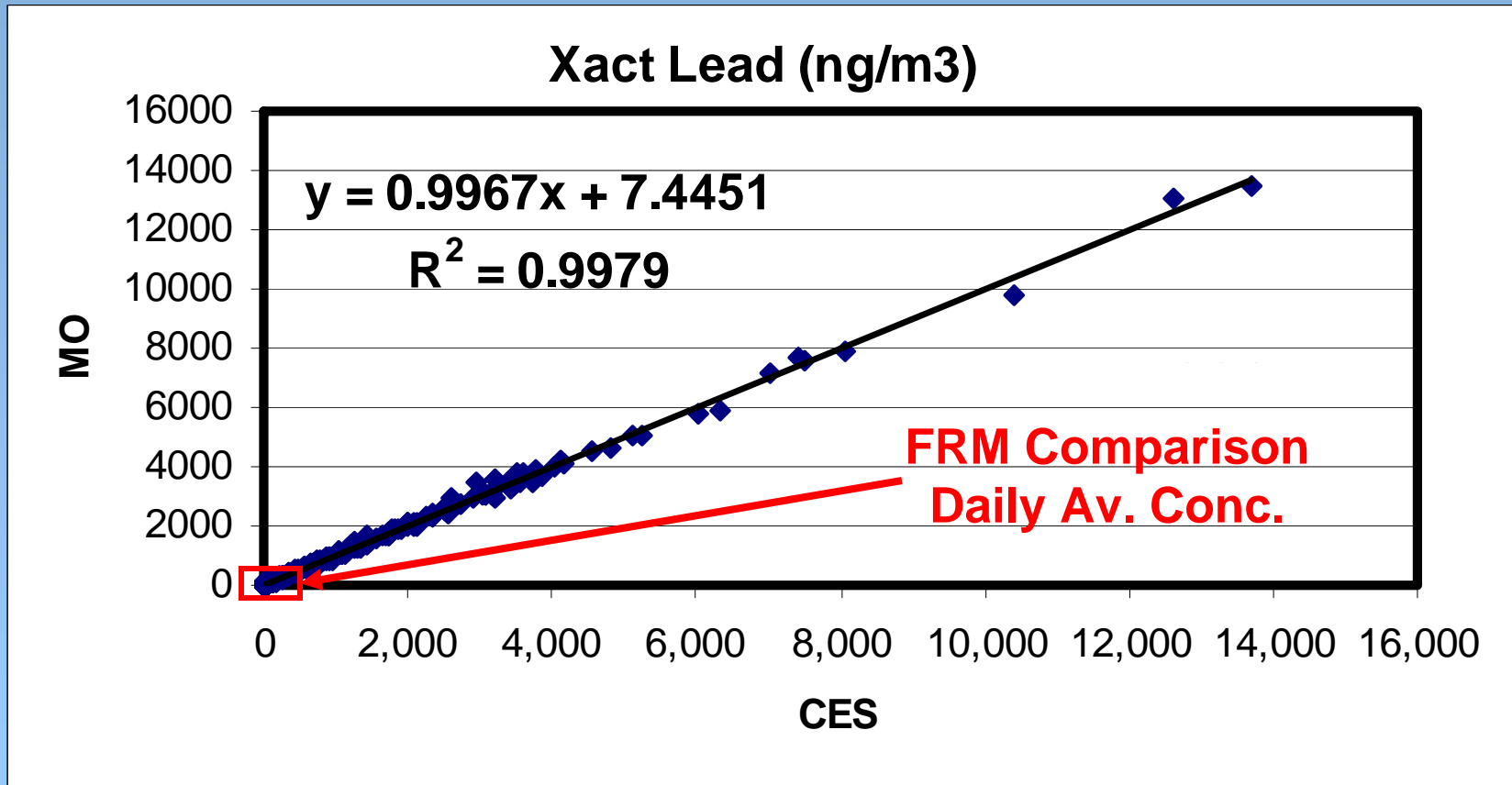


Mn: biased but highly correlated

Herculaneum

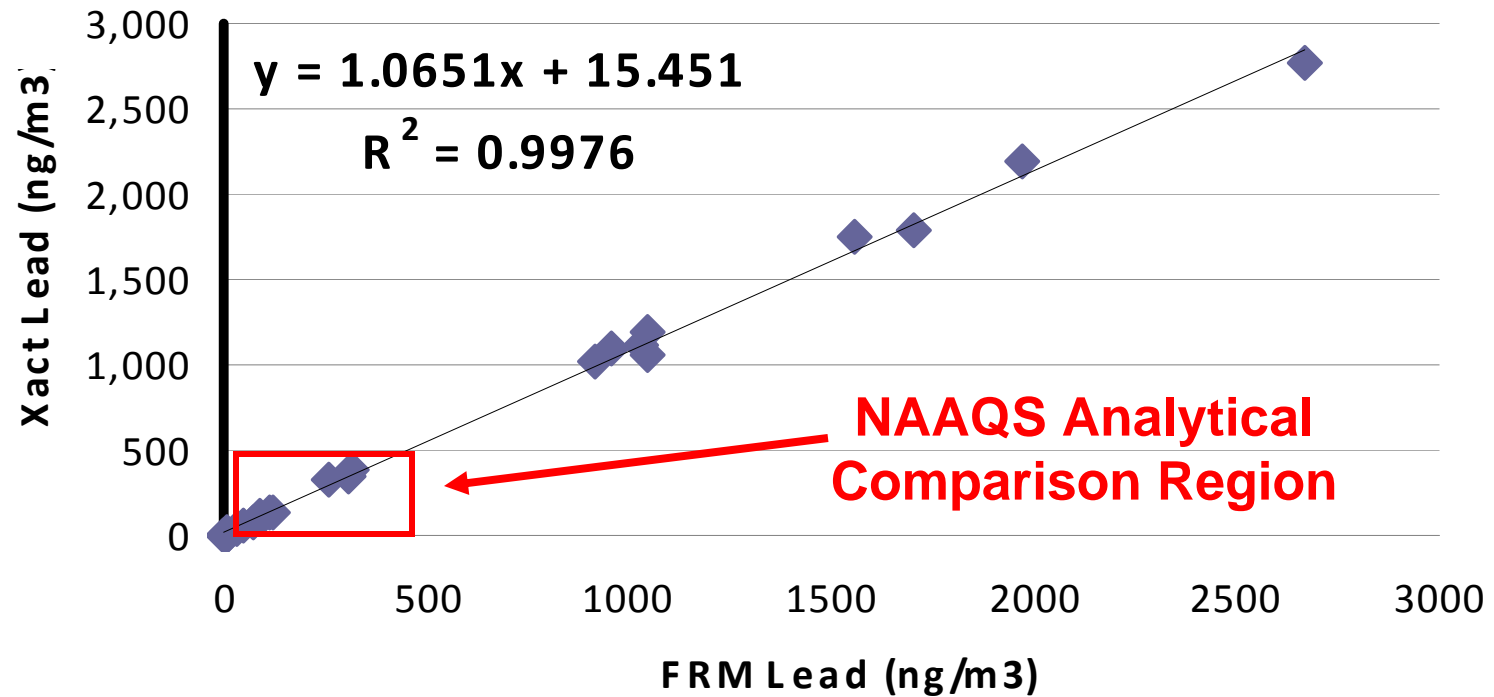


Minus High Concentration Data Point Herculaneum MO

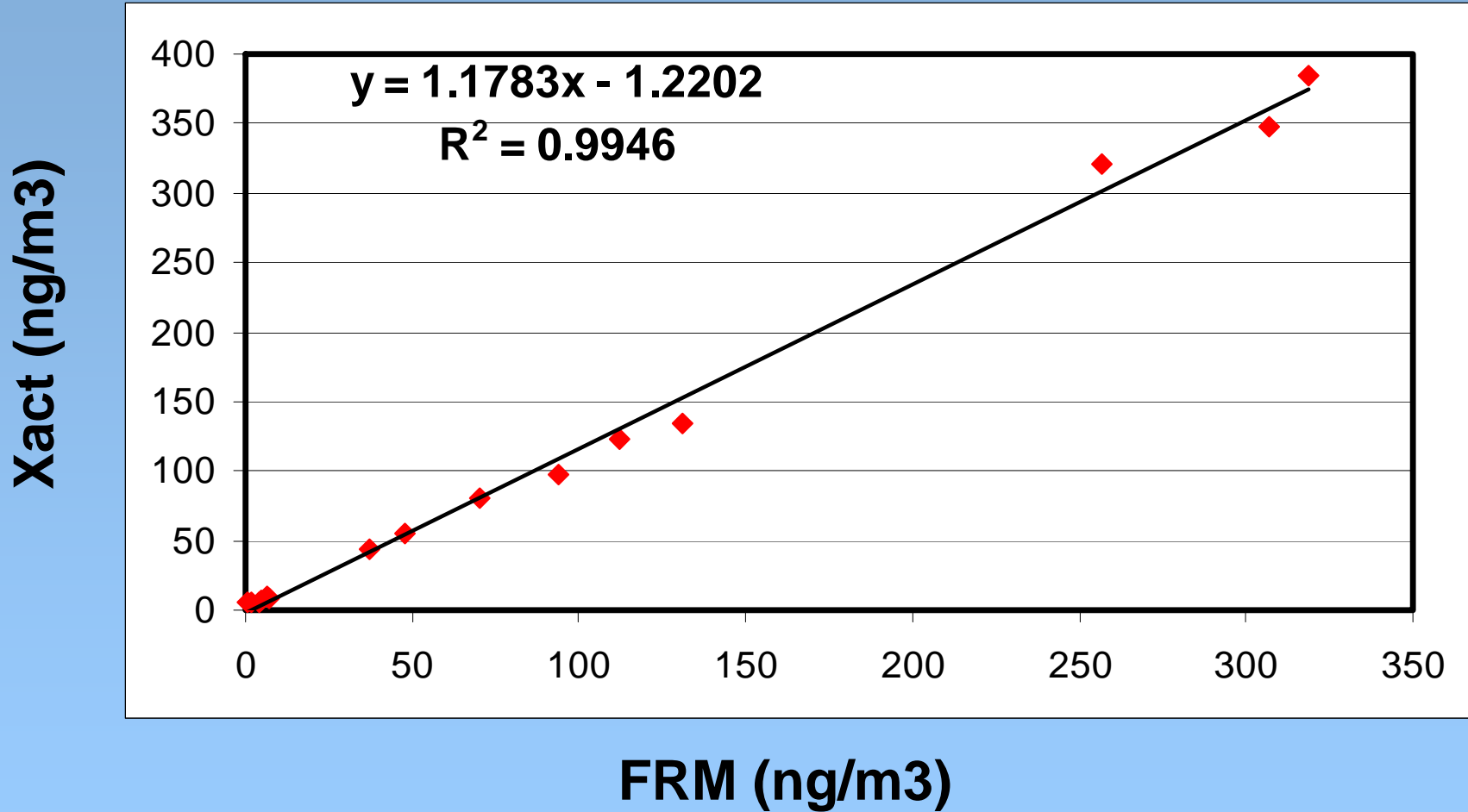


Herculaneum, MO Lead

Xact vs FRM Lead

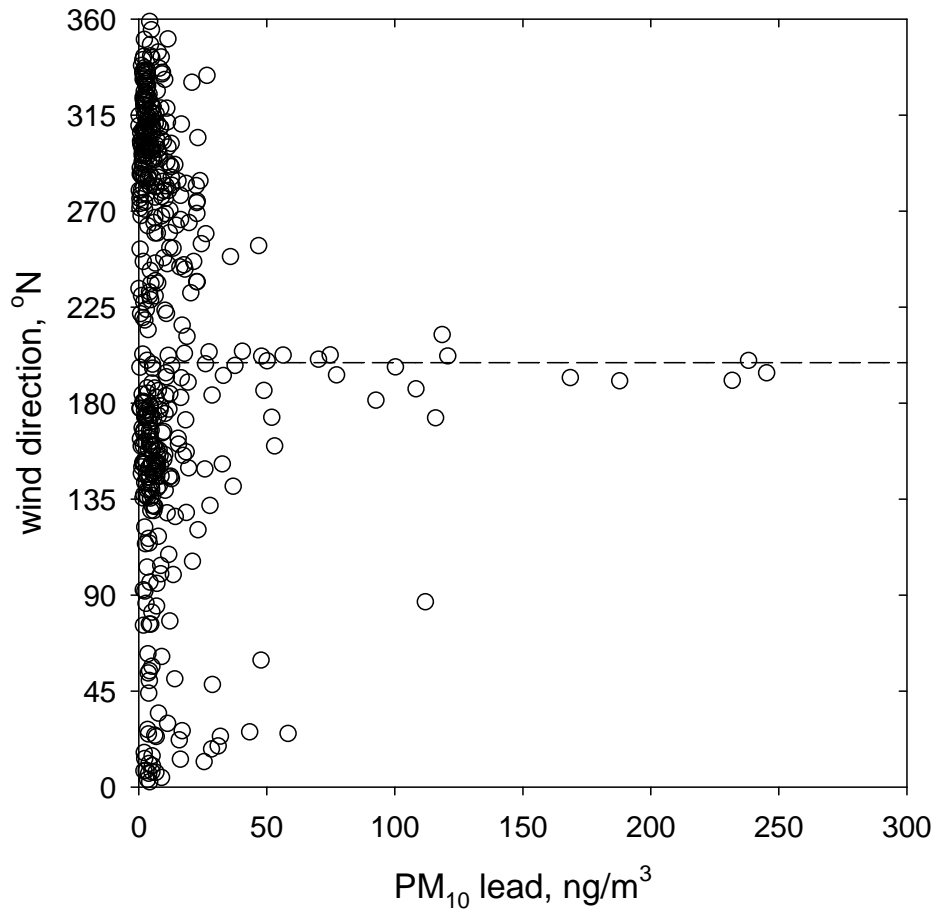


FRM v. Xact Lead Comparison

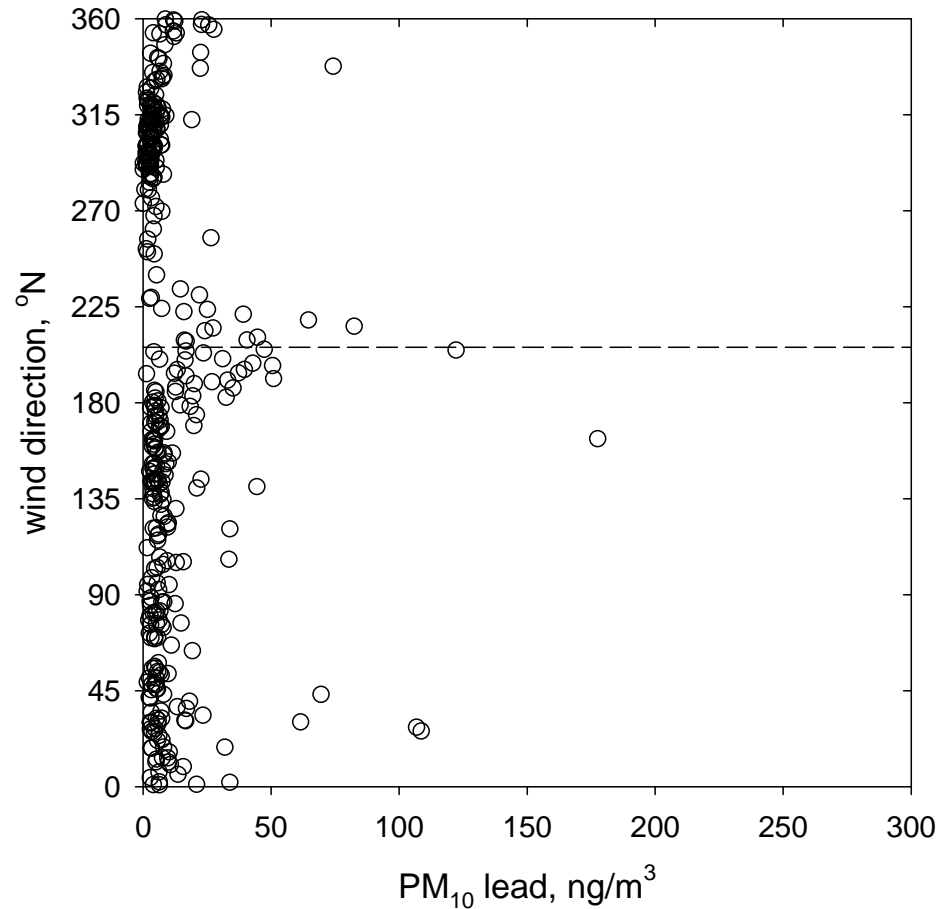


PM₁₀ Lead by Xact (2-hour resolution)

BLAIR



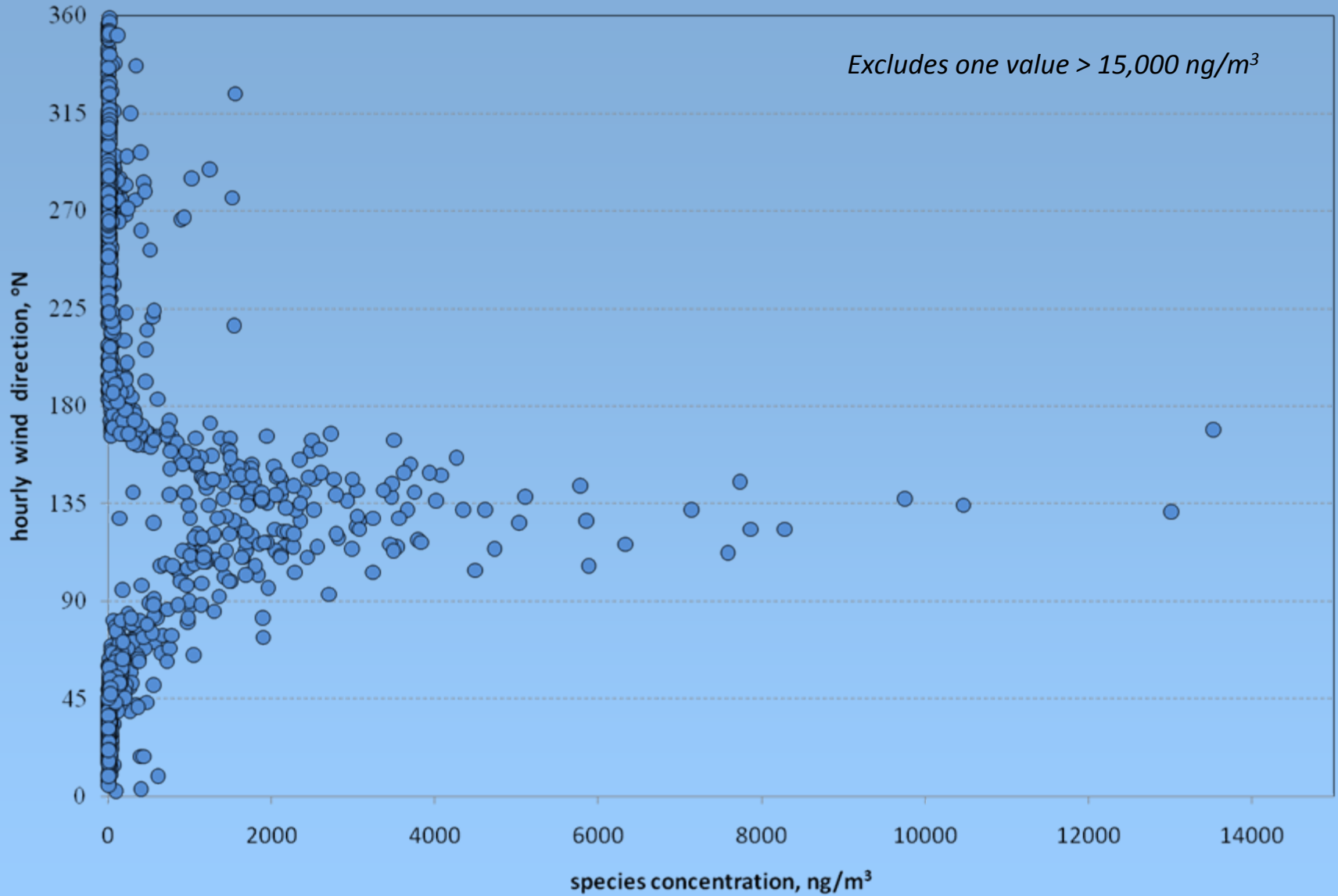
ARNOLD

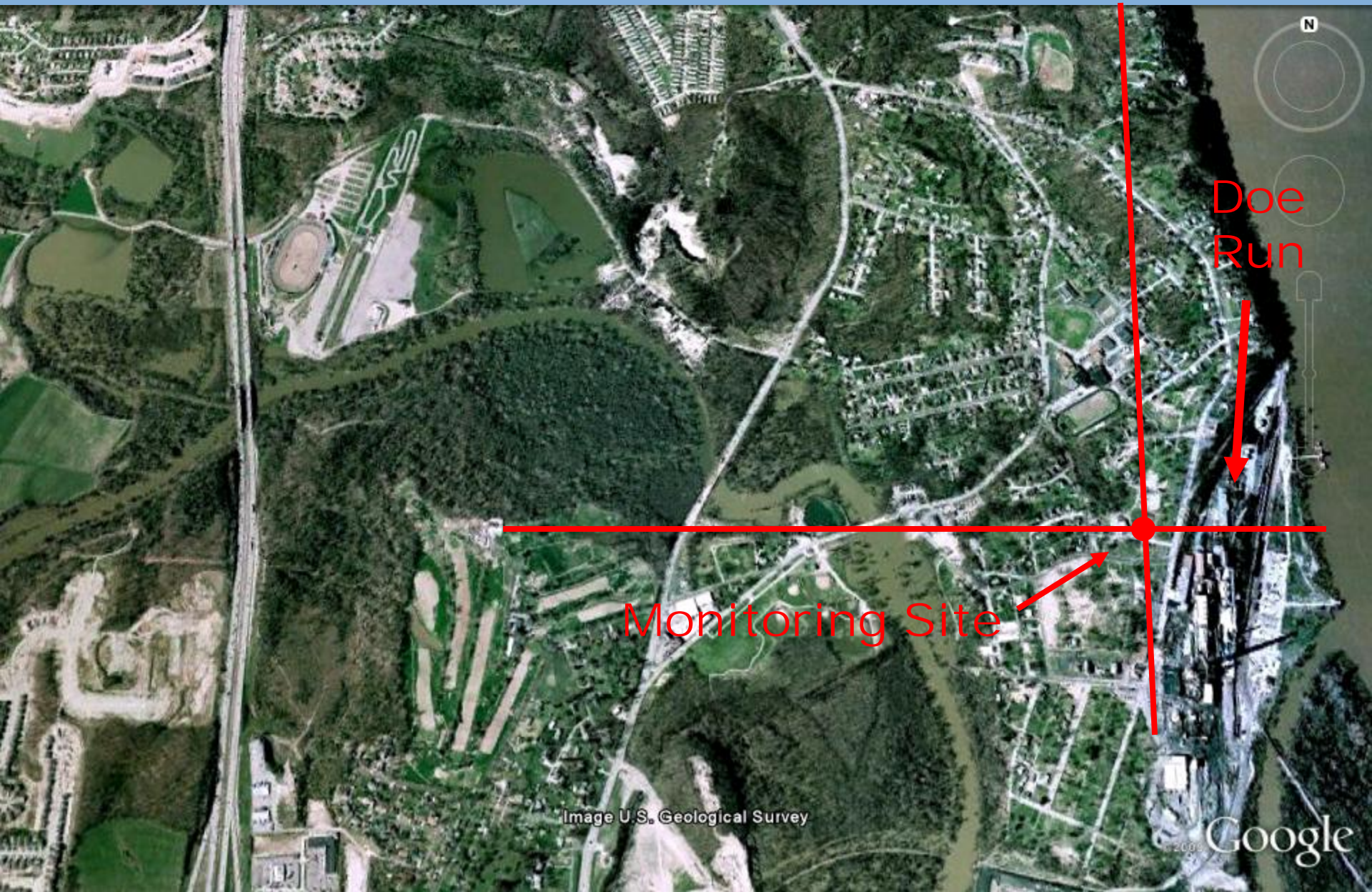


Dashed line is bearing of Doe Run – Herculaneum lead smelter

Hourly PM₁₀ Lead, Herculaneum Main Street Site, 8/8/09 – 10/10/09

Excludes hours with wind speeds less than 0.5 mph



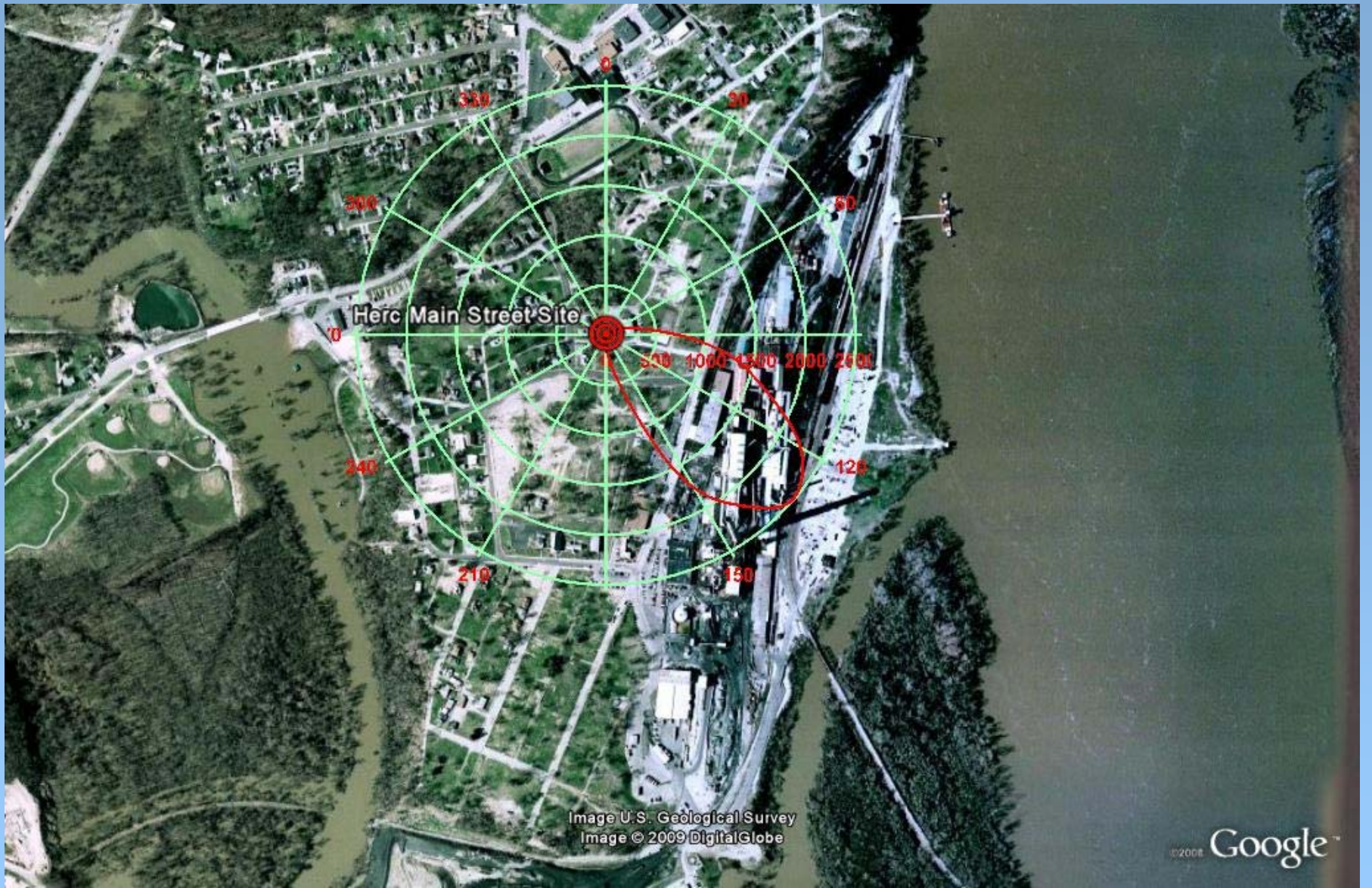


Doe Run

Monitoring Site

Image U.S. Geological Survey

Google



Herc Main Street Site

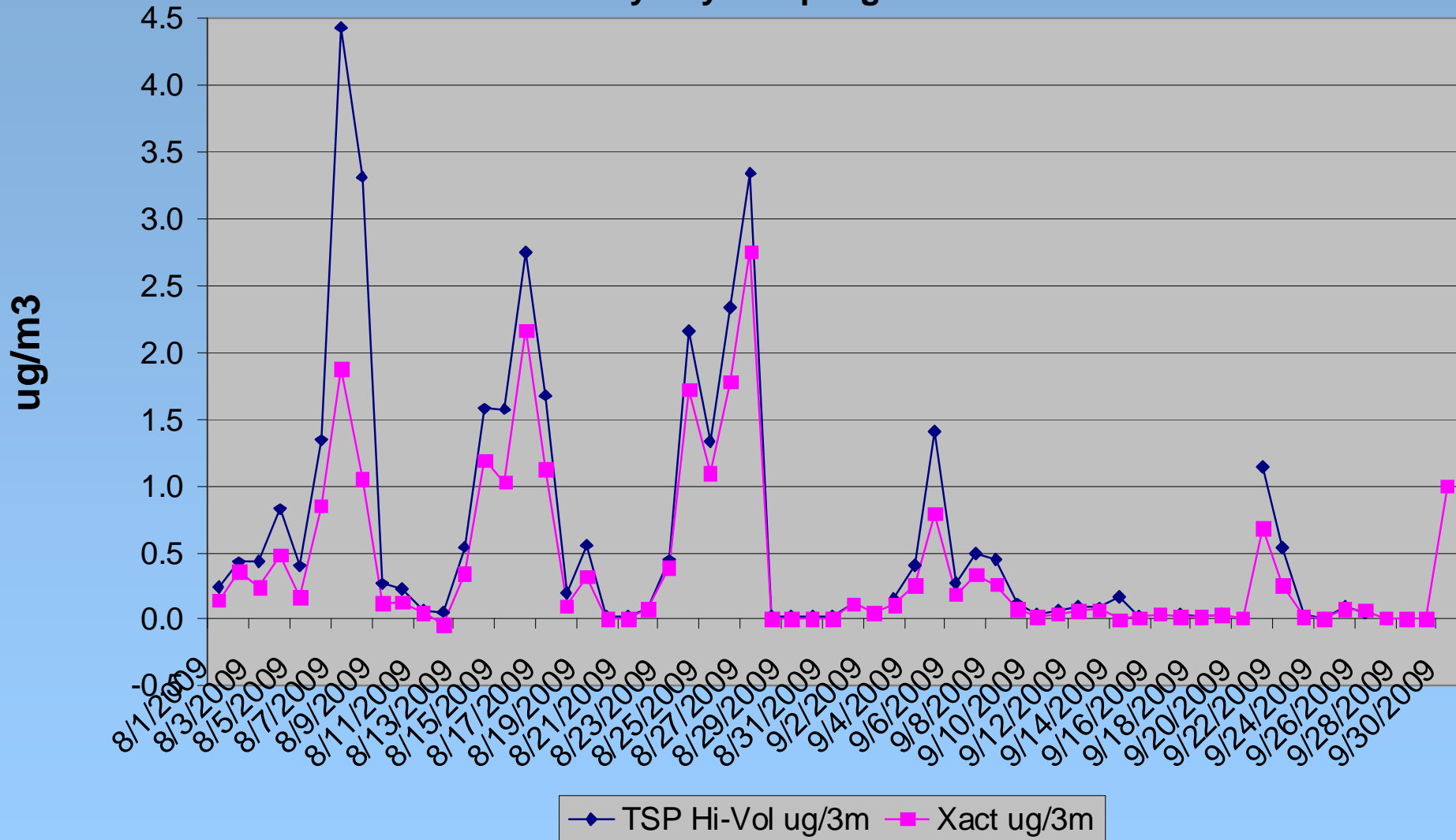
Image U.S. Geological Survey
Image © 2009 DigitalGlobe

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Herculaneum Airborne Lead Concentration

August and September 2009

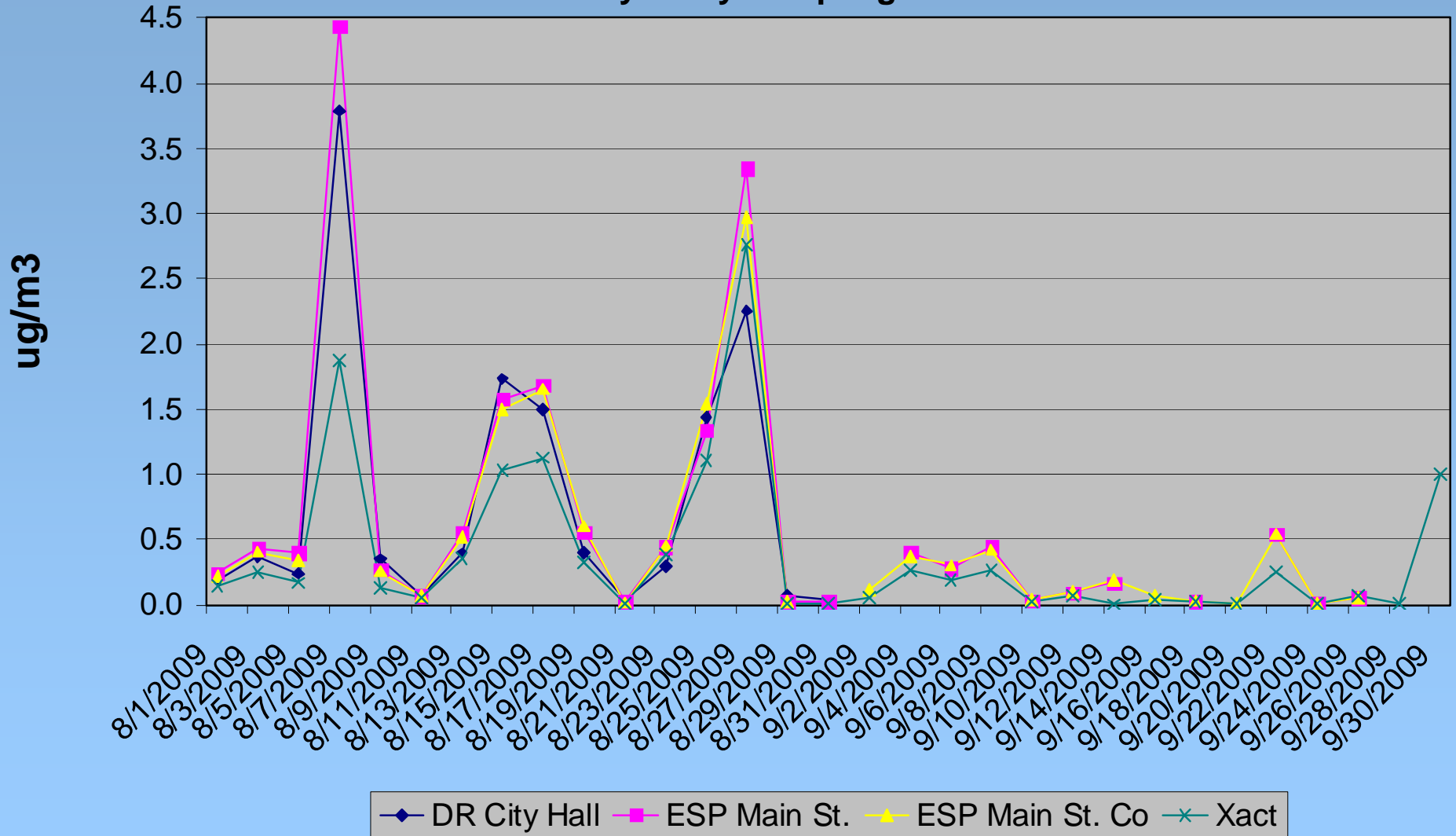
Every Day Sampling



Herculaneum Airborne Lead Concentration

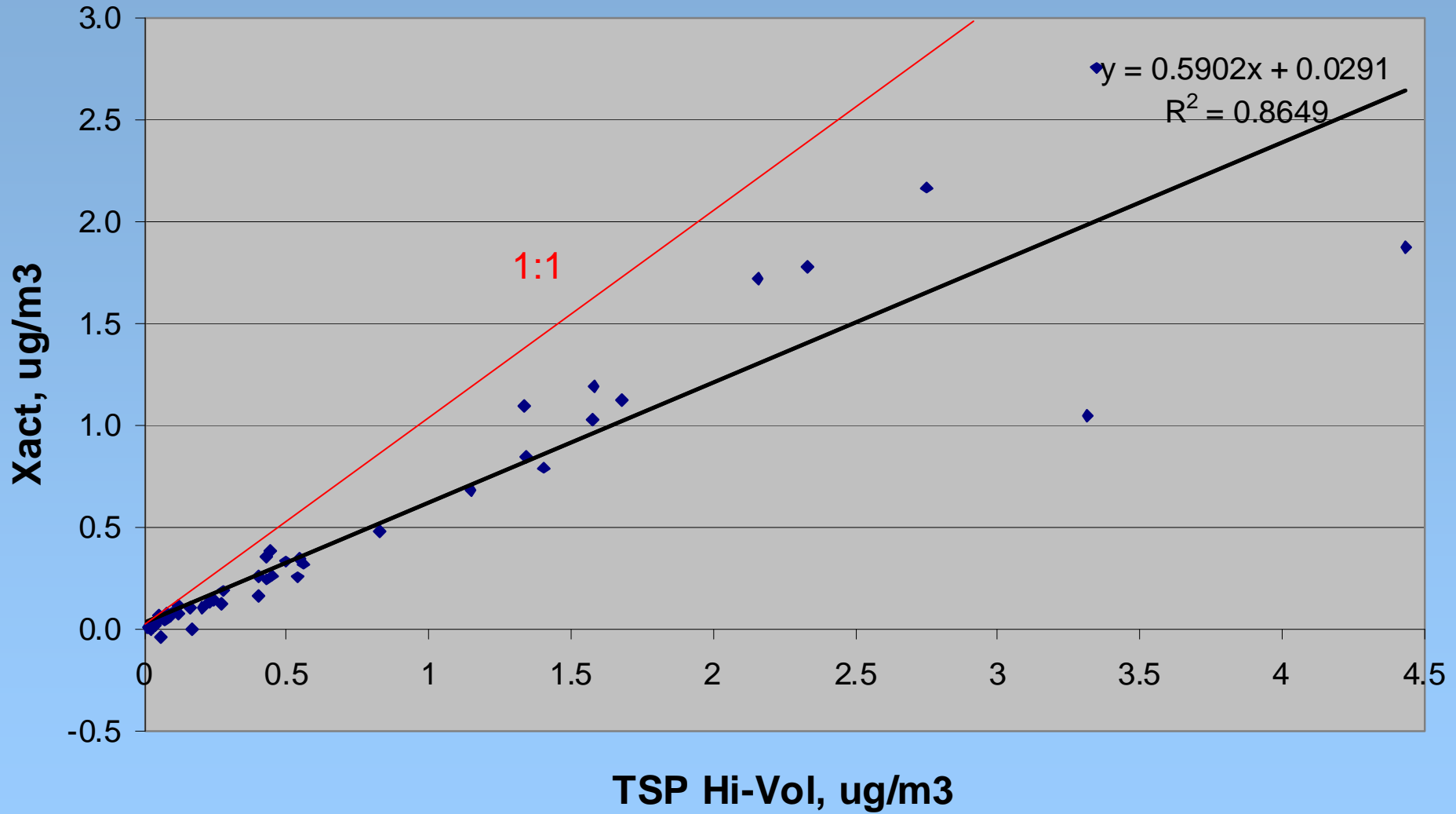
August and September 2009

Every 3 Day Sampling



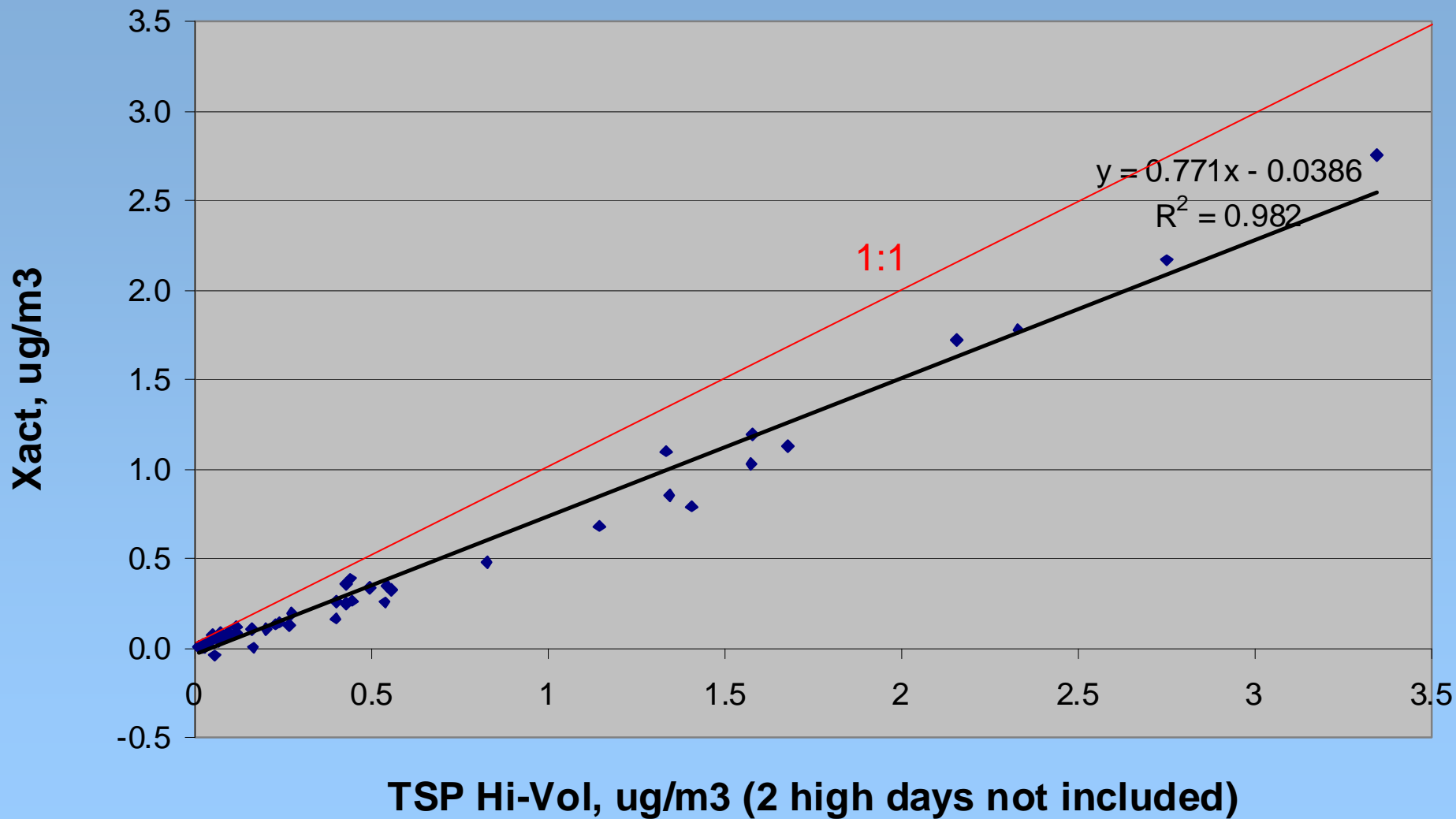
Herculaneum Airborne Lead Concentration

August and September 2009



Herculaneum Airborne Lead Concentration

August and September 2009



Conclusions

- Maintenance and operation of the Xact is comparable to that of other air monitoring instruments. The Xact has operated reliably following initial problems addressed by software and firmware upgrades.
- Xact airborne metallic species results compare well with both low volume and high volume filter sample analysis results.
- Xact results demonstrate the utility of time-dependent measurement for source attribution.

Acknowledgements

- **Missouri Department of Natural Resources**
 - Jim Brunnert, Jerry Downs, Celeste Koon, Dustin Kuebler, Robert Nilges, Terry Rowles, Will Wetherell
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- **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)