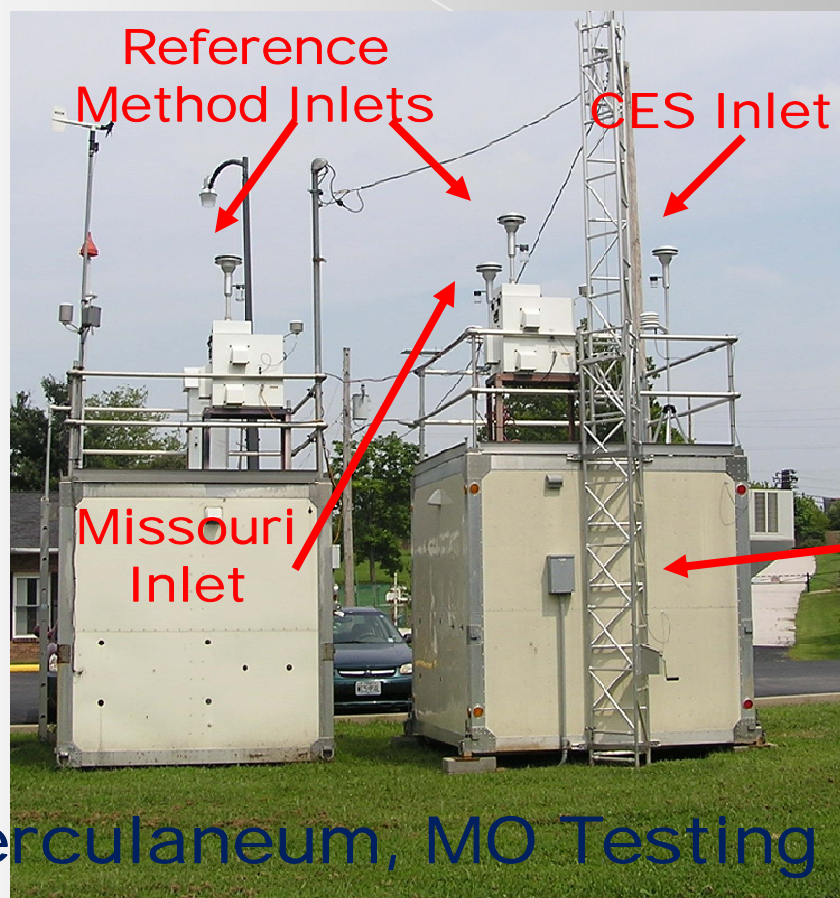


Field Validation of a Near Real Time Multi-Metals Fence Line Monitor

**Xact 620 Ambient
Metals Monitor**



Herculaneum, MO Testing Site

**John Cooper & Krag Petterson
Cooper Environmental Services LLC**

**Dan Bivins
U. S. EPA OAQPA**

February 10, 2010

Participants & Activities

- **State of Missouri – St. Louis & Herculaneum**
 - Missouri Xact, Sheds, FRM, On-site staffing
 - Jim Brunnert, Jerry Downs, Celeste Koon, Dustin Kuebler, Robert Nilges, Terry Rowles, Will Wetherell
- **Washington University – St. Louis Jay Turner**
 - Hi-Vol plus ICP/MS, FRM/EPA XRF, St. Louis data interpretation
 - Jay Turner, Stephen Feinberg, Varun Yadav
- **CES/Mactec/EPA team - Herclaneum**
 - CES Xact, FRM XRF, planning and data interpretation
 - Mactec: Art Warner
 - EPA OAQPS: Dan Bivins
 - CES: Troy Pettinger, Mike Nakanishi, Douglas Barth, Paul Ginochio

Outline

- Introduction
- Operation and performance
- Quality control and assurance
- Validation criteria and results
- Validation summary
- What's next?
- Key Conclusions:
 - No reference methods exist for comparison; but
 - Xact 620 multi-metals monitor yields better, more useful PM₁₀ lead measurements with one-hour samples than current PM₁₀ FRM samplers with laboratory XRF analysis of 24-hour samples.

General Project Objectives

Develop monitoring and modeling technology to support:

- Programs to regulate fugitive metal emissions
- **Pb** & PM NAAQS SIPs
- Public right to know programs
- Environmental justice
- Enforceable local ambient air quality limits

Phase III: Field Validation Accuracy and Precision

EPA Phased Approach

- **2006/7: Phase I – Demonstrated feasibility of CEMS to ambient monitoring**
- **2007/8: Phase II – Demonstrated field deployable feasibility**
- **2009: Phase III - Field validation of accuracy and precision**
- **2010: Phase IV- Development of FLM certification procedures and protocols for applying technology for permitting and compliance demonstration**

2009 Phase III:Field Validation – Two Independent Programs

- **Missouri Xact – St. Louis, MO**
- **CES and Missouri Xacts – Herculaneum, MO**

Why Multi-Metals FLM?

Metals

- Eight of EPA's 33 highest concern pollutants
- Persistent
- Under reported
- No apparent threshold for blood Pb
- What is the threshold for As, Cd, Sb, etc.

Fugitive/Area/Low Elevation Emissions

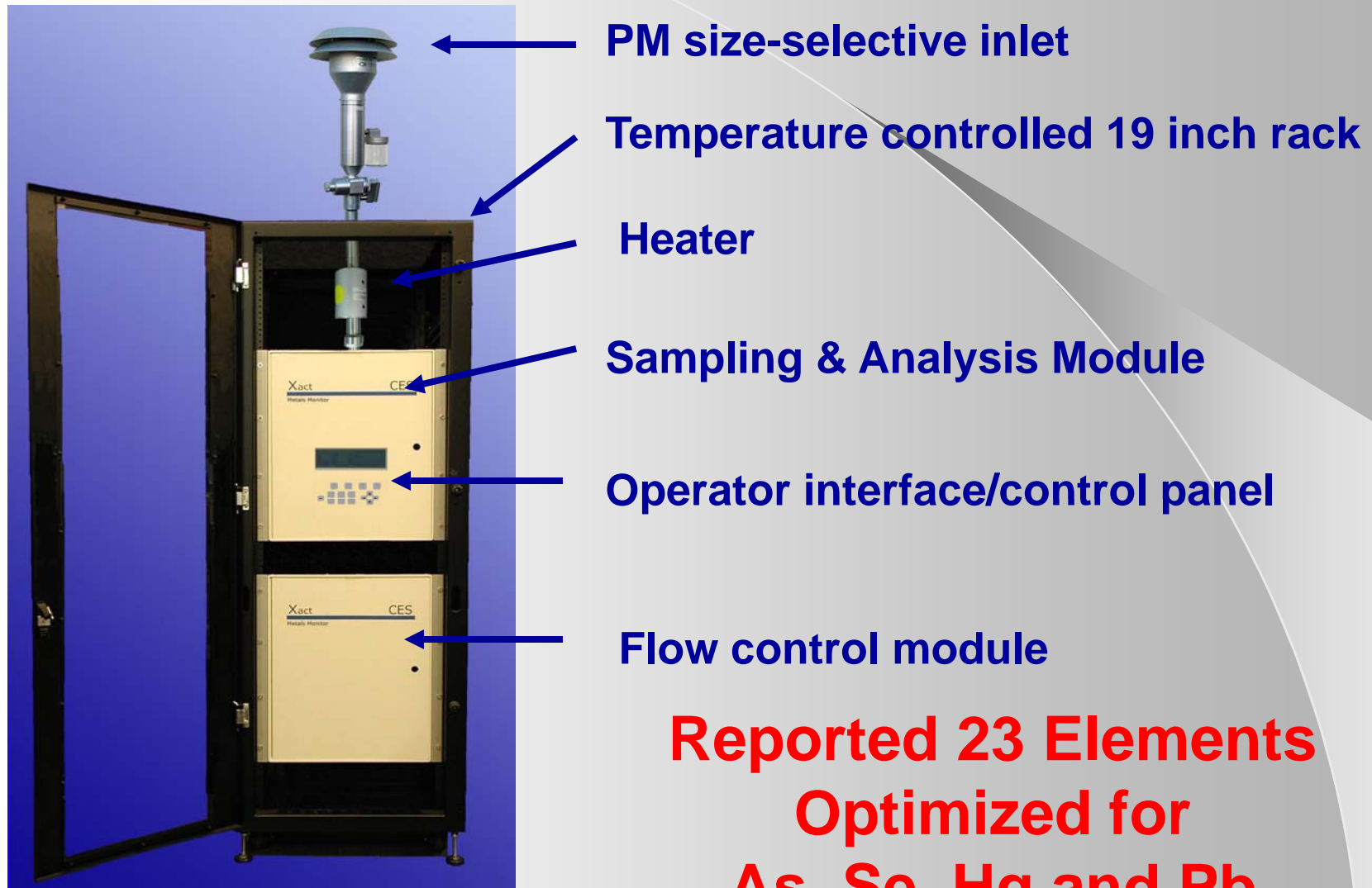
- Can dominate local exposure
- Infrequent/difficult measurements
- High uncertainty

Improved Airshed Management

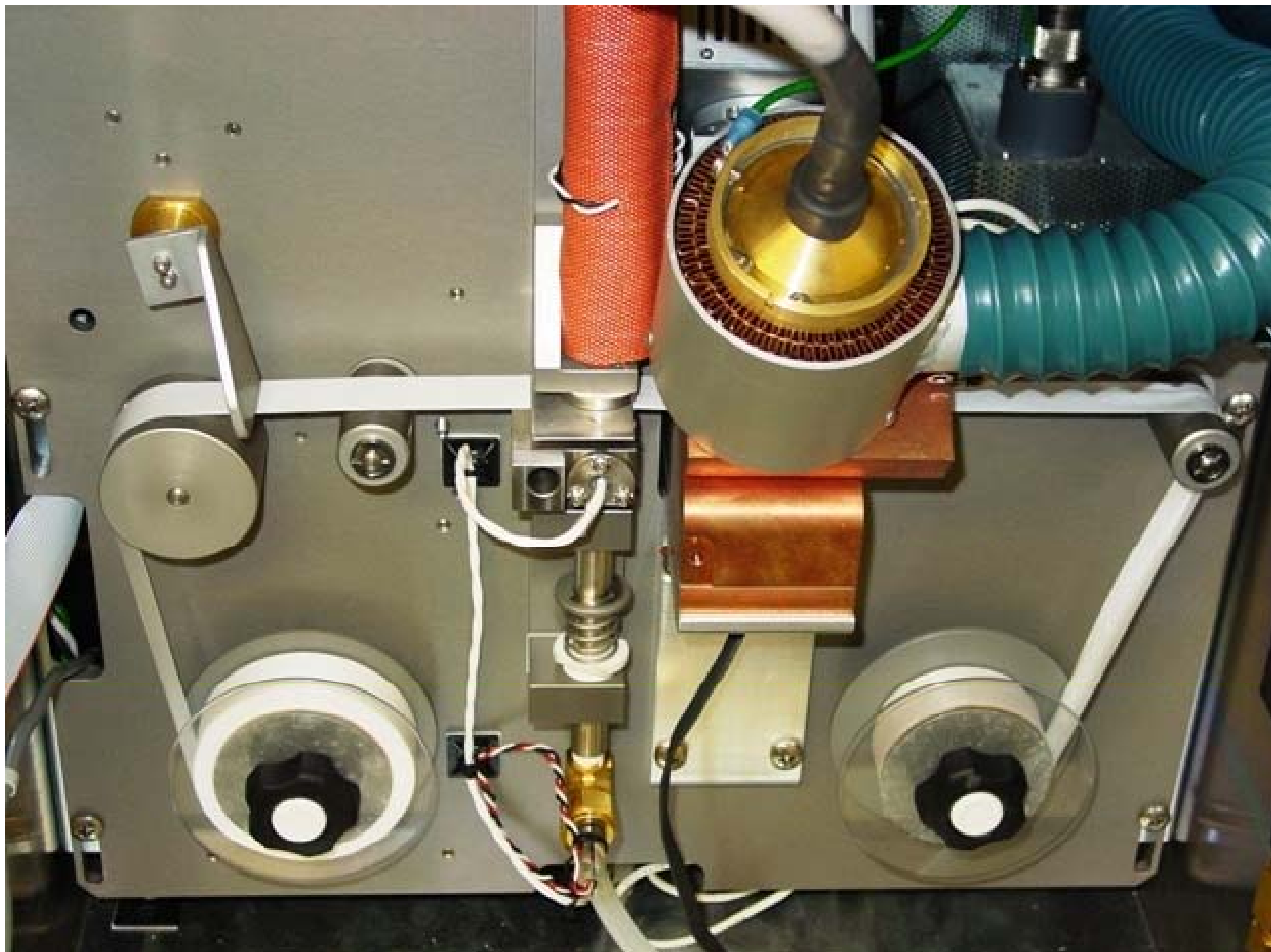
- Rapid plant feedback to eliminate problem
- Improved source apportionment
- Protect public health

Operation and Performance

Xact 620 Ambient Metals Monitor



**Reported 23 Elements
Optimized for
As, Se, Hg and Pb**



Xact Tape Deposits

A photograph of a white Xact Tape strip, which is a type of tape used for measuring surface area. The tape has three circular deposits of a dark, textured material. A yellow arrow points to the leftmost deposit. The background is a light-colored, textured surface.

Deposit Area Used = 0.747 cm^2

Corrected Deposit Area = 0.707 cm^2 (6%)

Determined with actual Herculanum deposits

XACT 620 Demonstrated Detection Limits (pg/m³)

4 hour sampling and analysis times

1 pg Hg vapor/m³ = 0.0001 PPTV

<u>Element</u>	<u>Xact 620</u>	<u>IO-3.3</u>	<u>PM2.5 Median</u>
As	4	240	269
Cd	110	1,200	440
Cr	9	400	478
Hg	5	450	503
Pb	5	450	1,309

Other elements: Ca, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Ag,
Sb, Sn, Ba, Tl

**DL function of time to -1.5 power; i.e. 1 hour DL
= 8 times 4 hour DL**

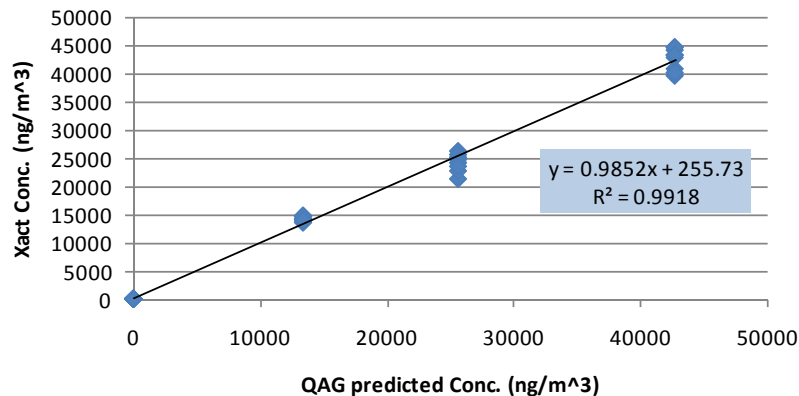
Quality

Assurance

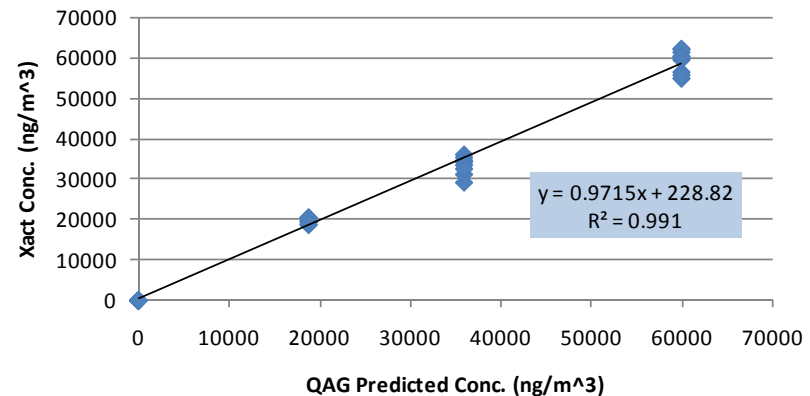
CES Xact Laboratory QAG Audit

Xact challenged with independently generated QAG
aerosol traceable to NIST standards

Fe Linearity Comparison



Zn Linearity Comparison

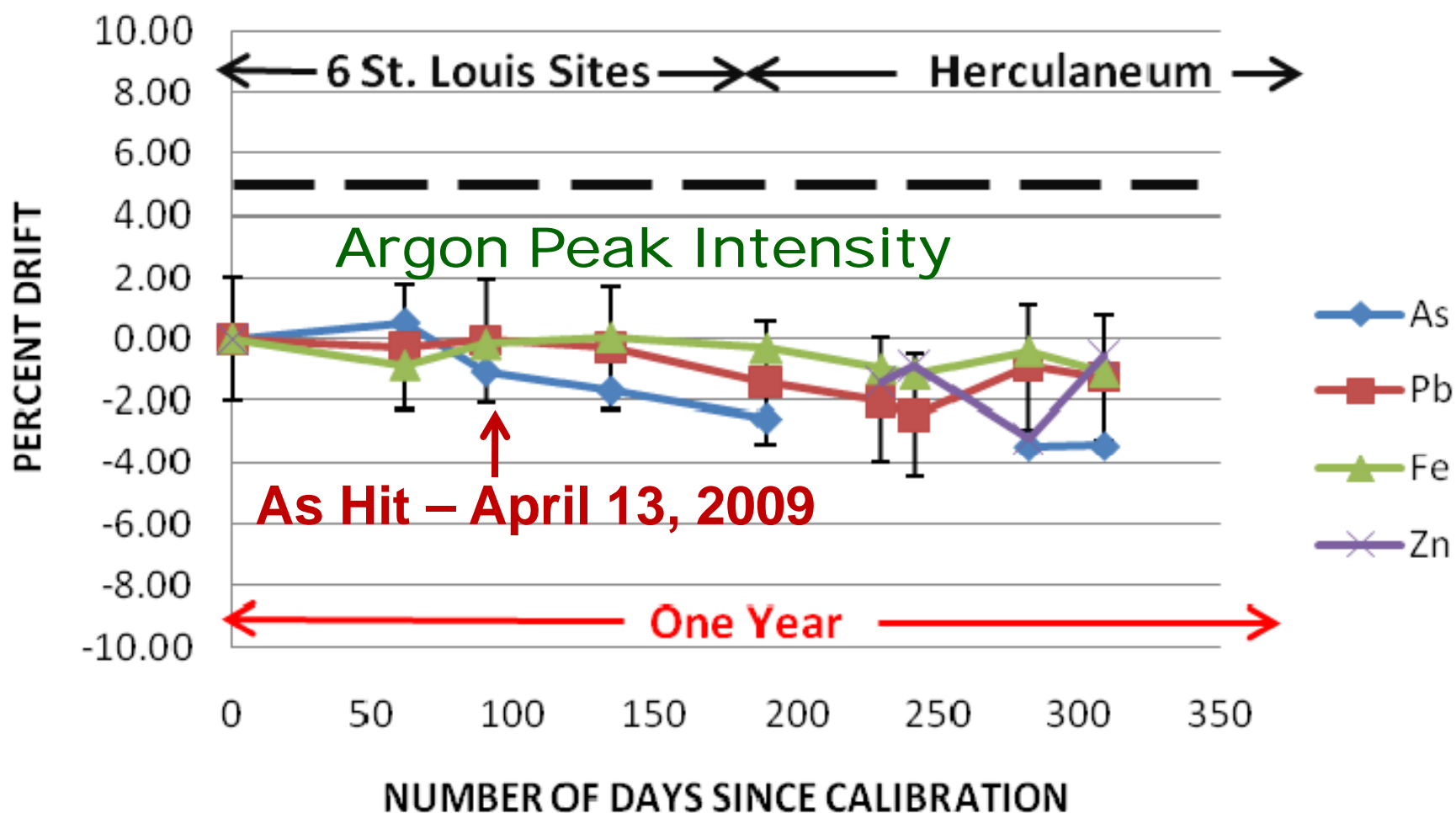


“Round Robin” Analytical comparison Between CES and EPA IO 3.3 XRF

- **About 50% of FRM filters analyzed by CES sent to EPA**
- **High lead filters selected for comparison**
- **Percent difference $[(\text{EPA}-\text{CES})/\text{Ave.}]*100\%$**

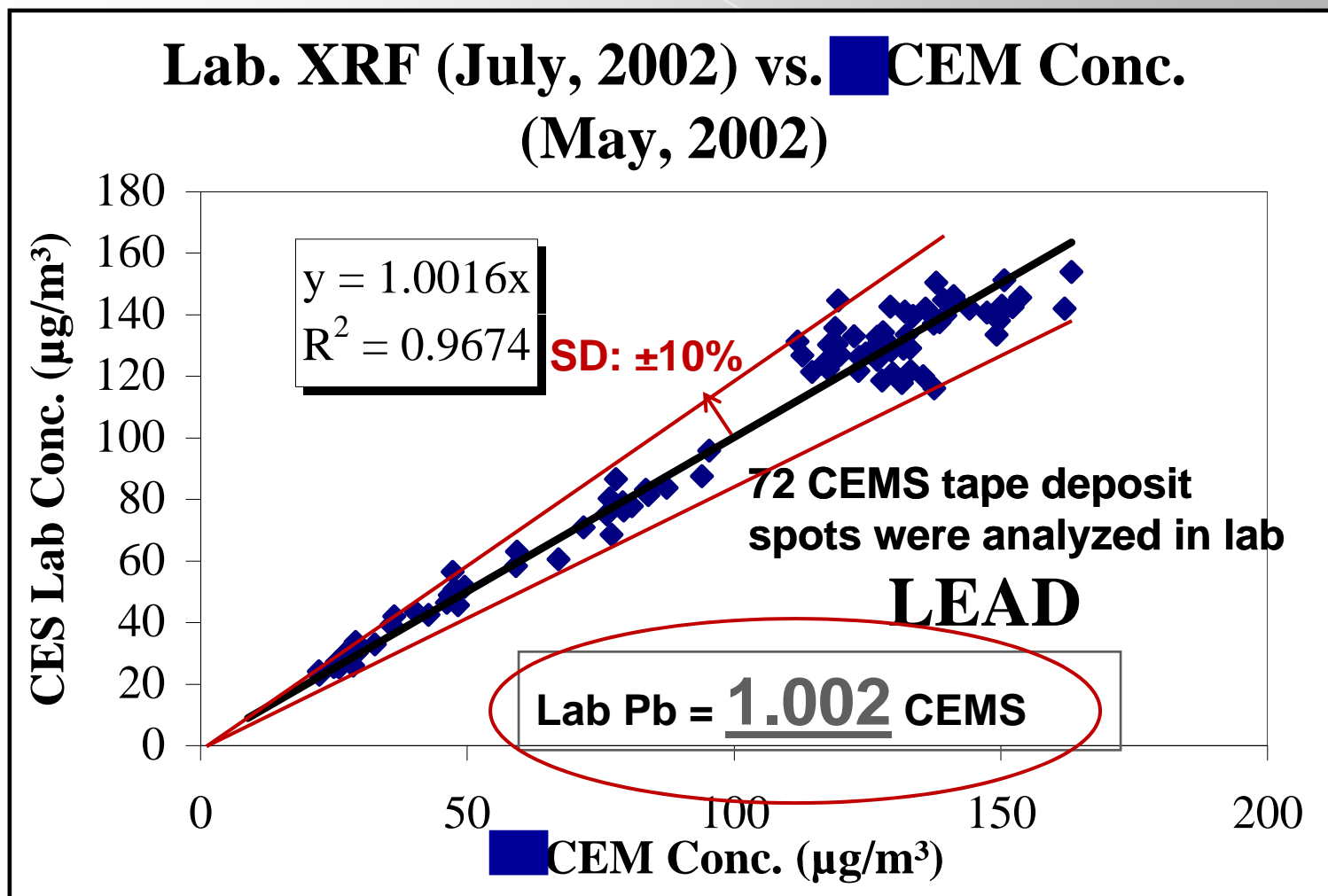
<u>Lead Concentration Range</u>	<u>N</u>	<u>Average % Diff.</u>
● All high Pb filters	23	-0.4%
● NAAQS (45 to 375 ng/m³)	13	1.7%

Missouri XACT 620 Calibration Drift (%)



INDEPENDENT VERIFICATION

Lab. Analysis of Tape Deposit Spots



Monitoring Sites

St. Louis, Missouri – Six
Herculaneum, Missouri - One

St. Louis Xact Testing

Washington University and State of Missouri



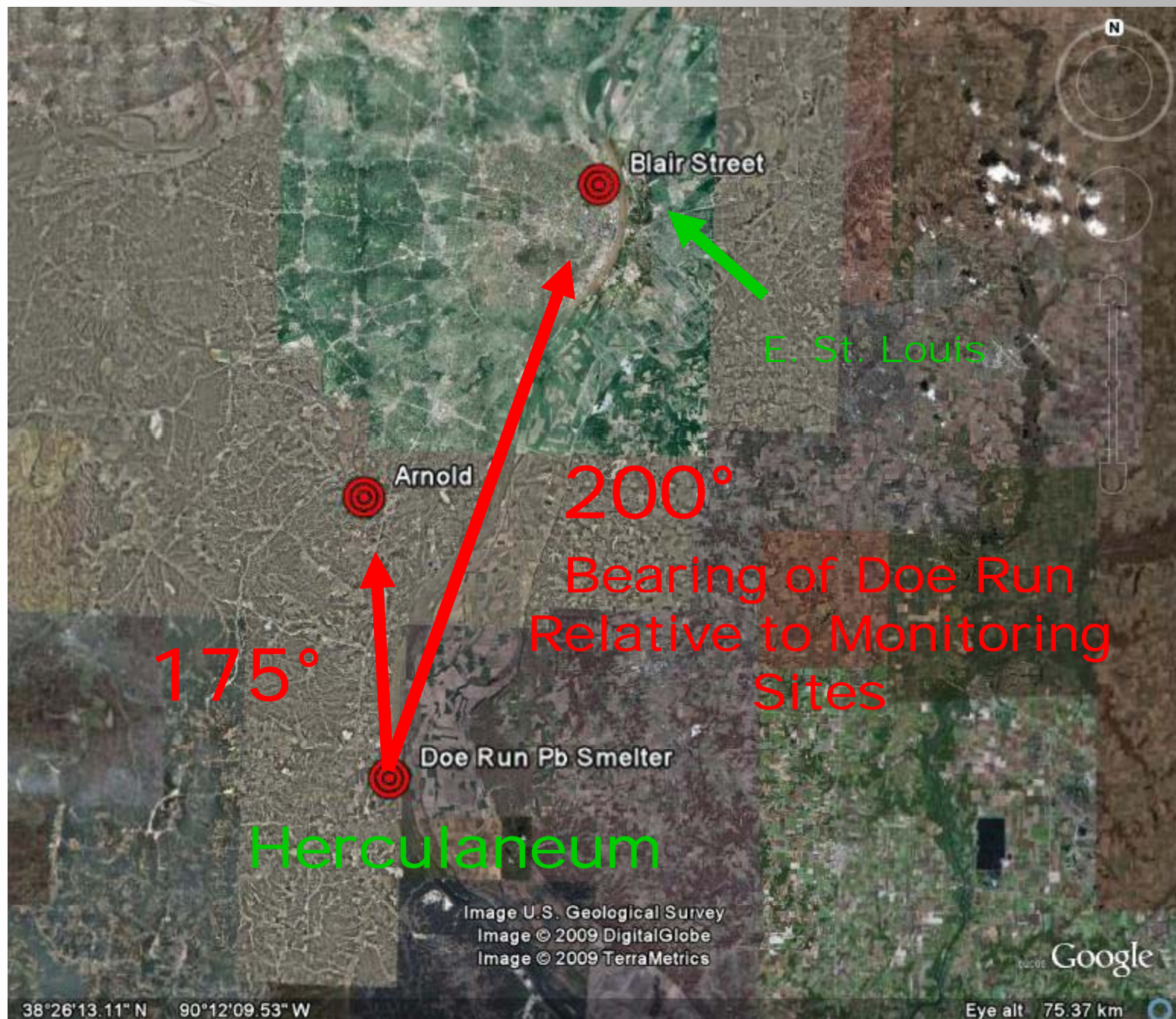
**HiVol PM₁₀ /quartz
filter, NATTS
digestion protocol
ICP-MS: As, Pb, Se...**

**Continuous
Sampling and
Analysis**

**Xact LV PM₁₀/PTFE filter tape
XRF: K, Ca, Fe, etc.**



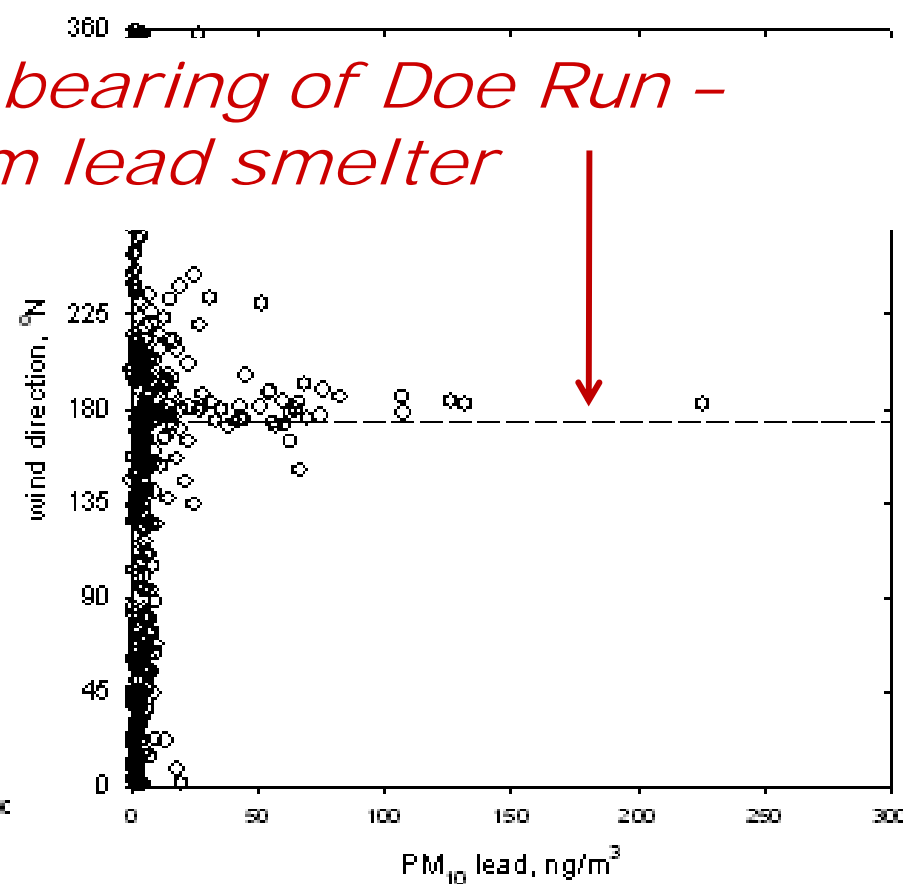
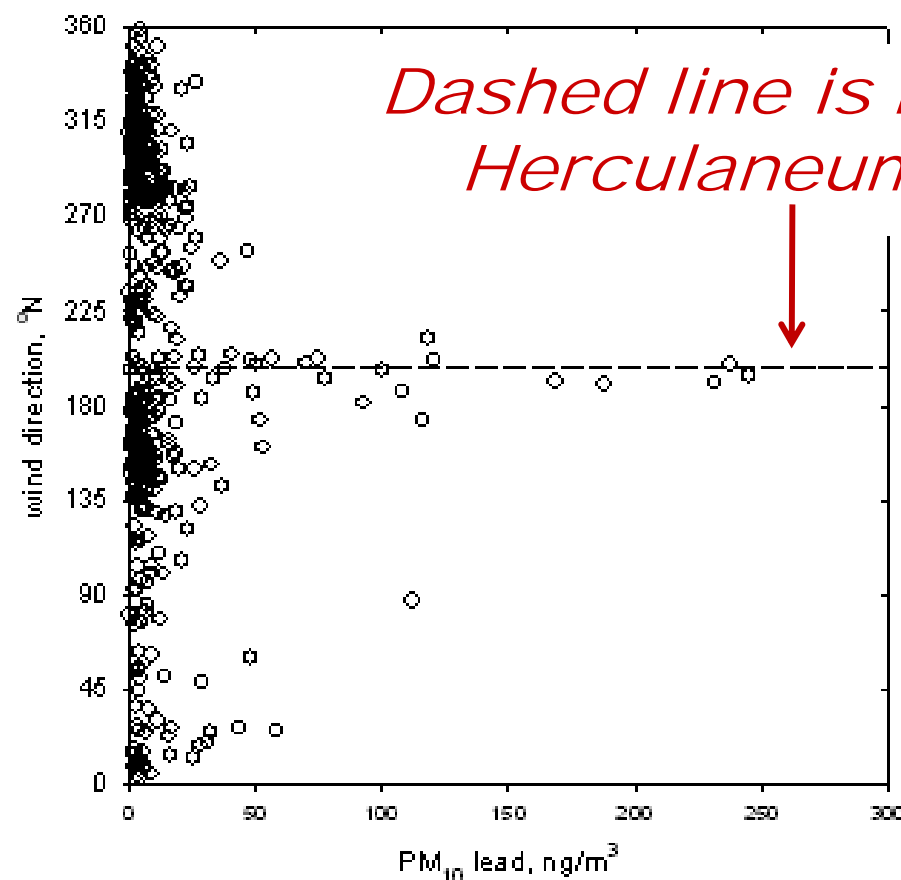
**LowVol PM₁₀ (FRM) / Teflon filter
EPA XRF: Ca, Fe, K, Mn, Pb, Ti...**



PM₁₀ Lead by Xact (2-hour resolution)

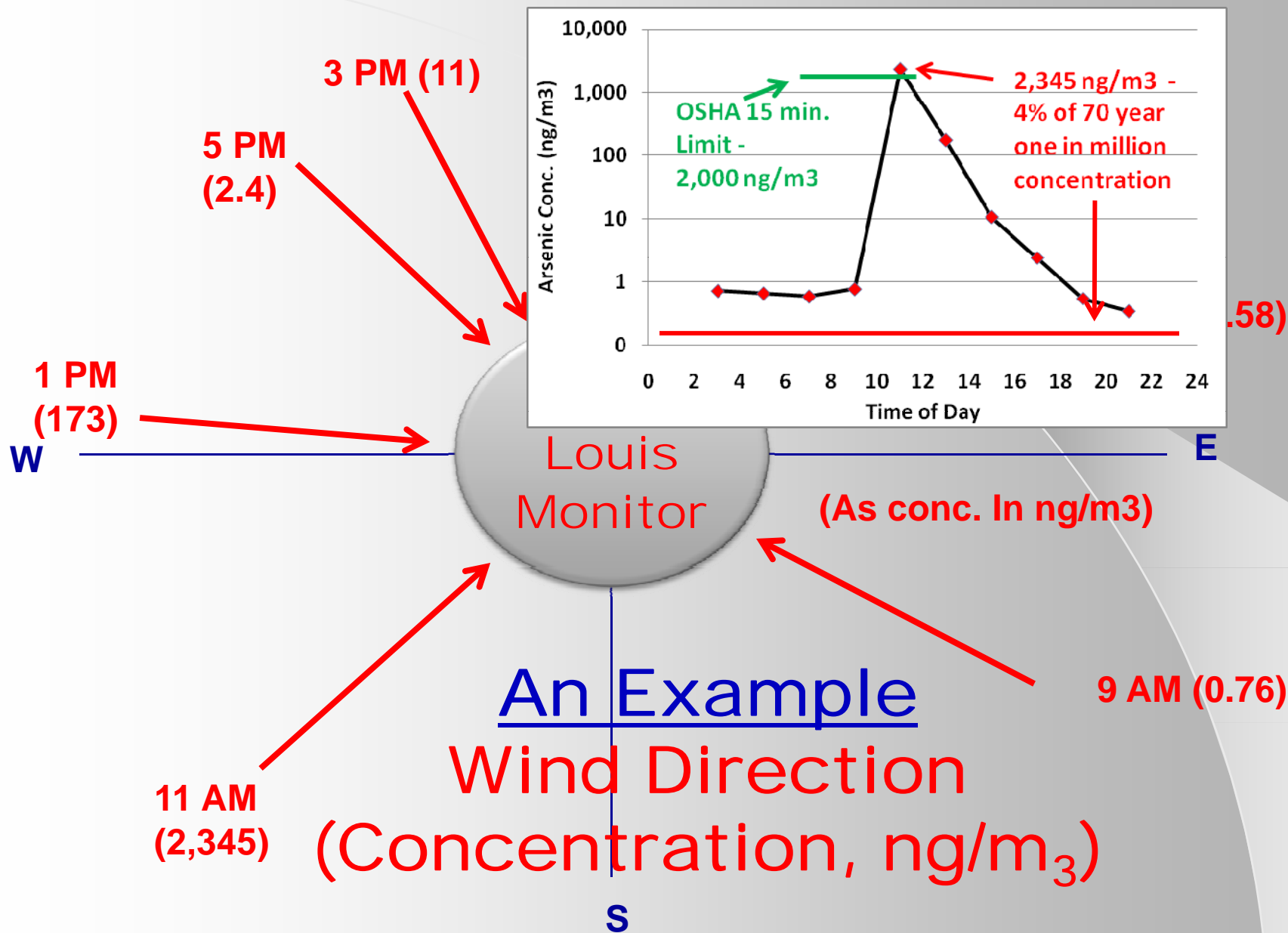
BLAIR

ARNOLD

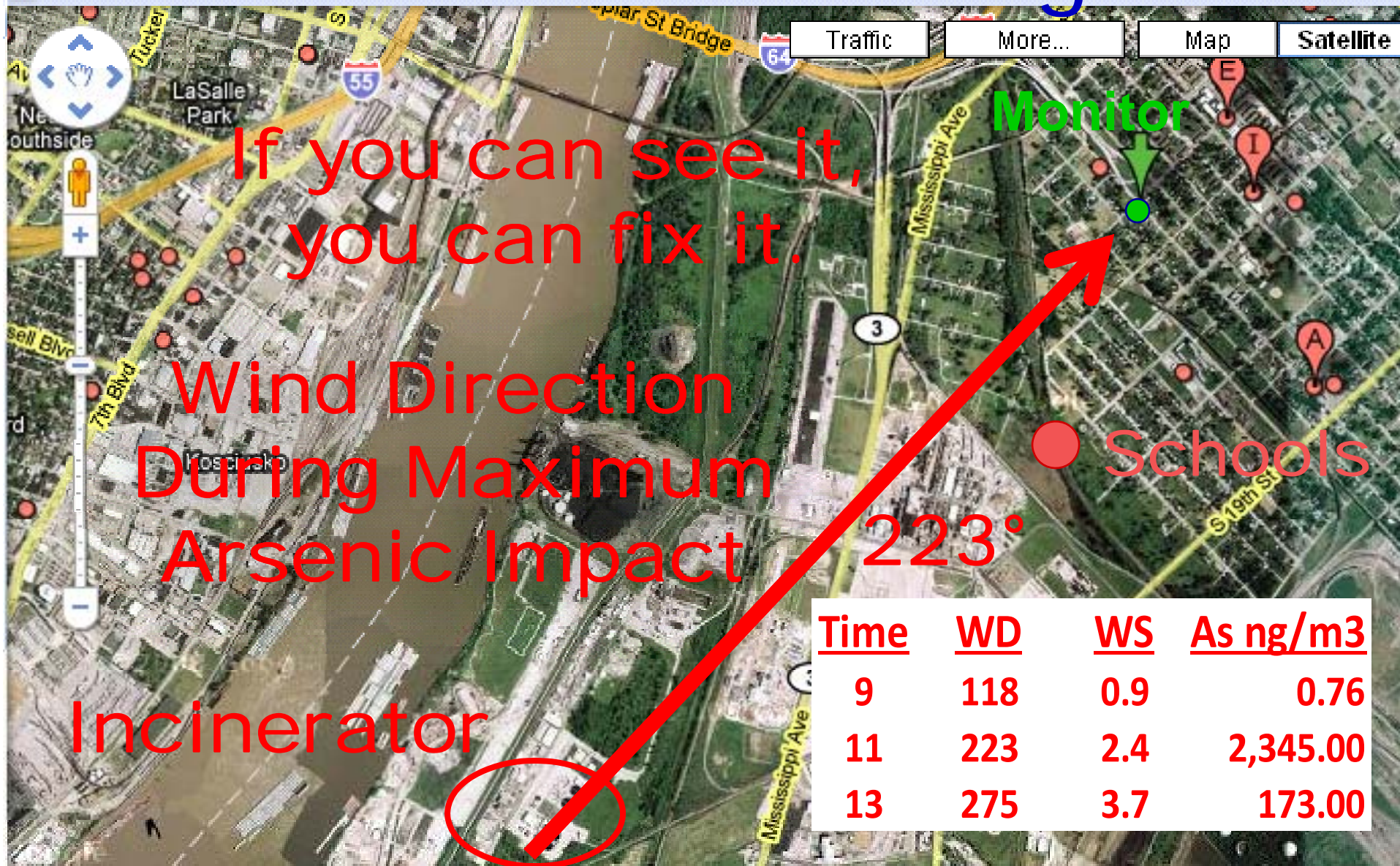


J. Turner, Washington University

Cooper Environmental Services

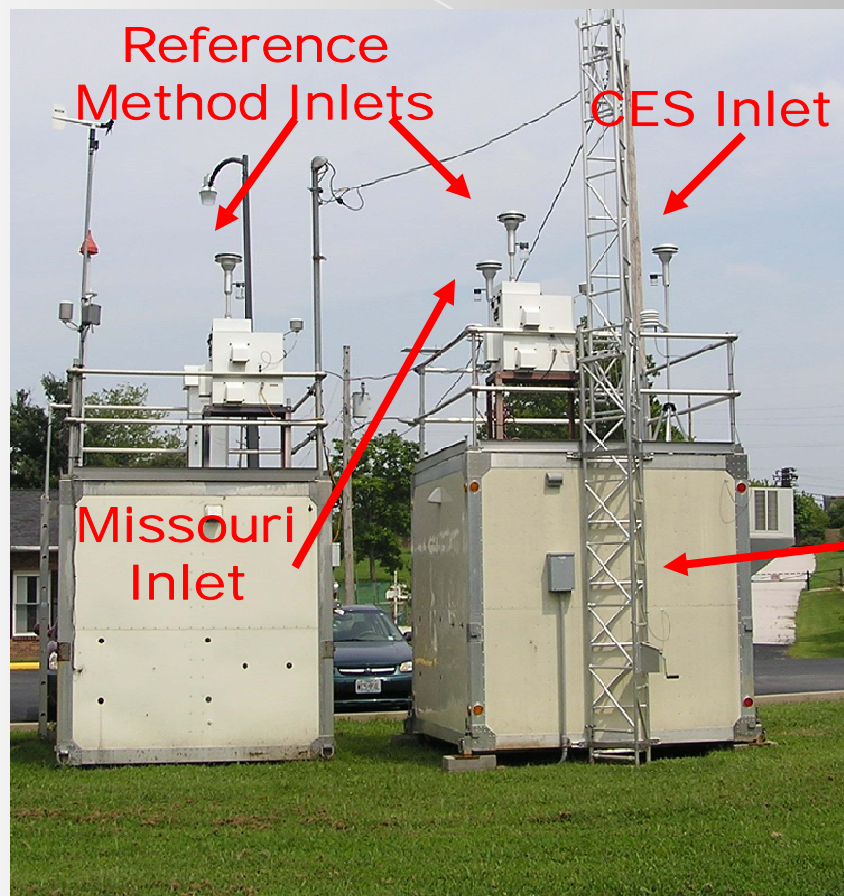


E. St. Louis Monitoring Site



Herculaneum Monitoring Site

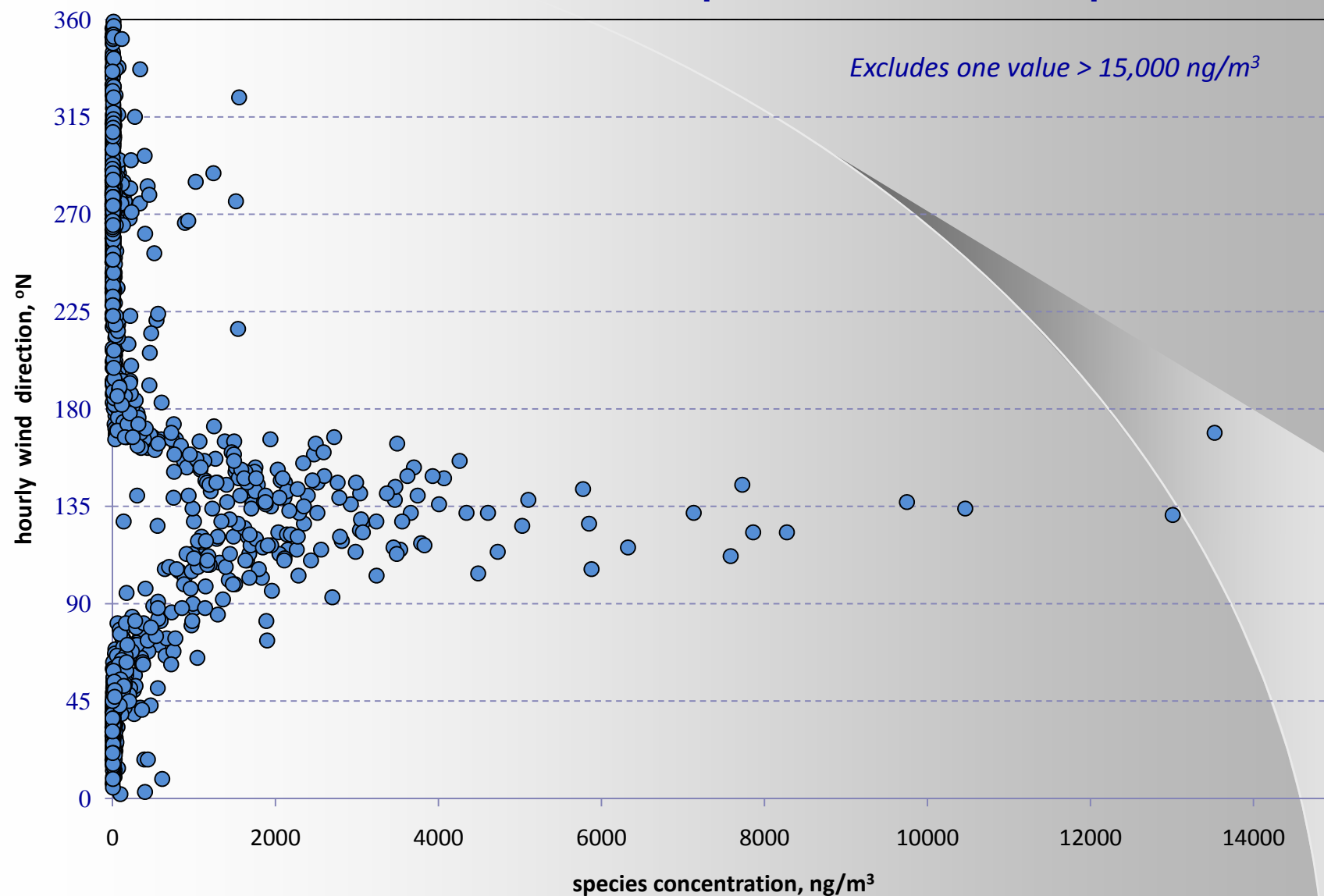
**Xact 620 Ambient
Metals Monitor**





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

Excludes hours with wind speeds less than 0.5 mph



W. Wetherell, St. of MO

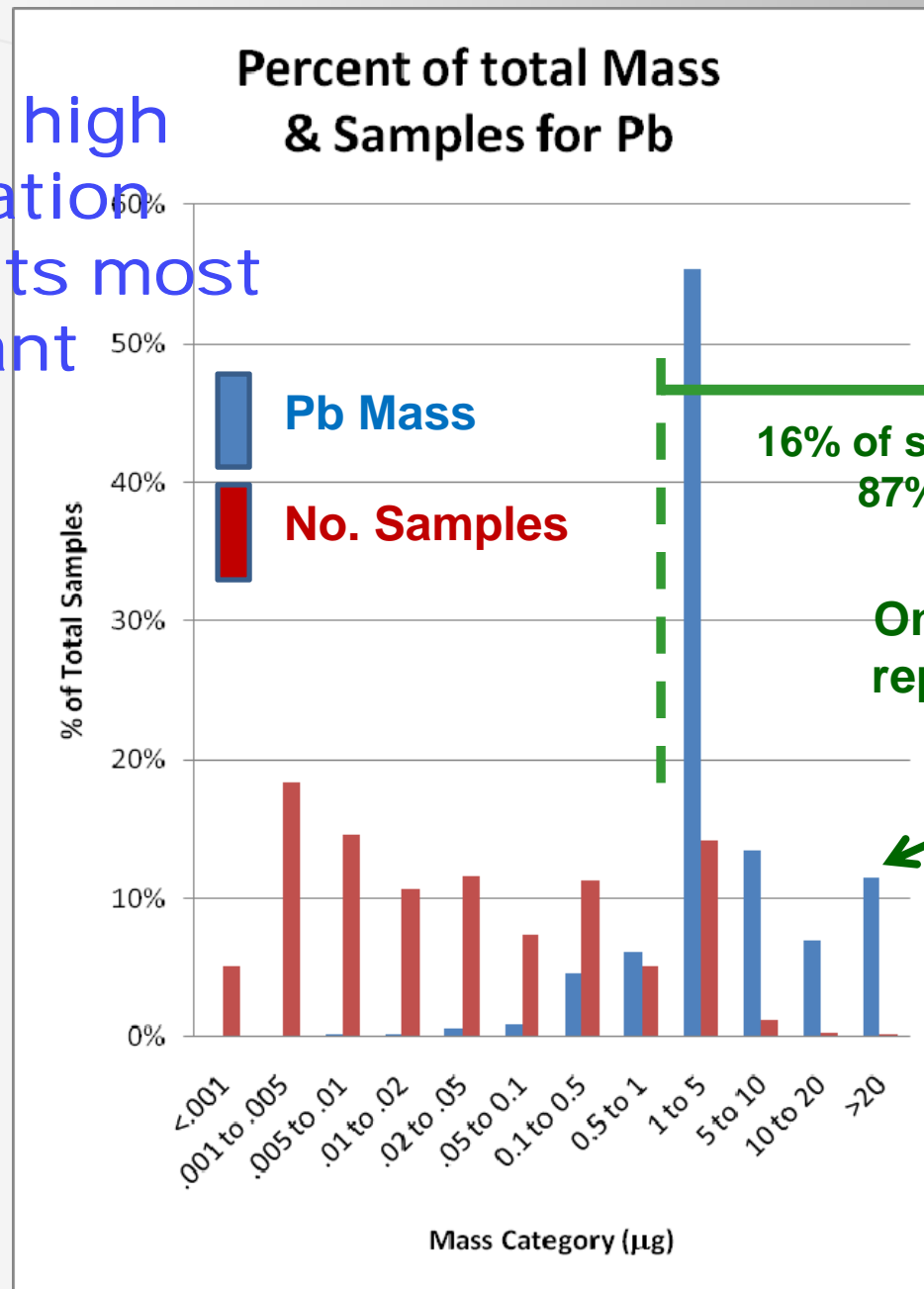
New Method/Instrumentation Validation and Certification Steps

- 1. New Method/Instrument Validation**
- 2. New Site Installation:**
 - Initial Certification**
 - On-going Quality Assurance**
 - Accuracy and uncertainty traceability**

Validation

- **No validation procedures for near-real time multi-metal ambient direct reading monitors**
- **Used following as guides to develop validation criteria and requirements:**
 - **EPA Method 301 for alternative stack emission methods**
Weighted most heavily because of need to enforce
 - **EPA NAAQS Pb requirements for analytical methods**
Weighted least because only applicable to analytical methods and suffers from ill-defined conditions

Validity of high
concentration
measurements most
important



16% of samples represent
87% of Pb Mass

One 1-hour sample
represents >11% of
Pb mass

Validation Results

Precision

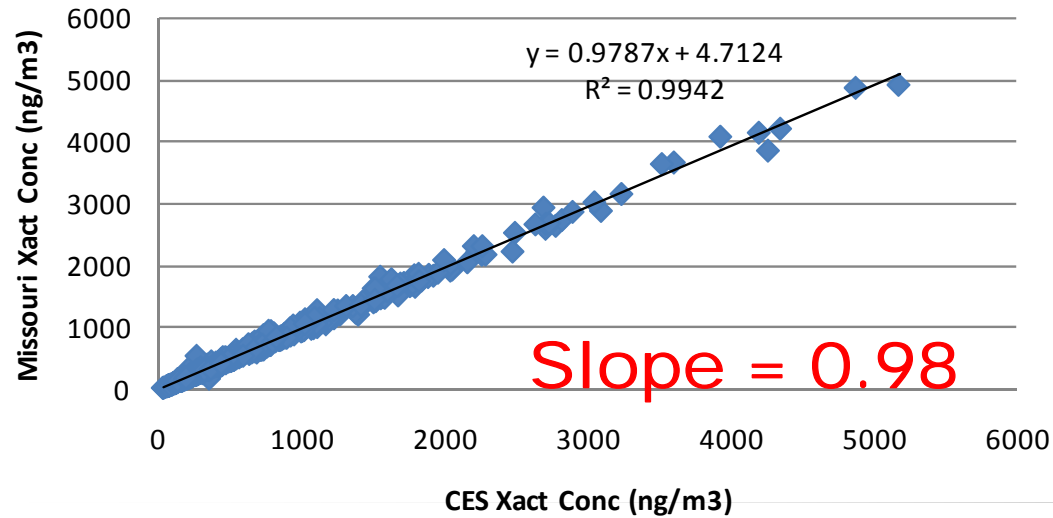
Four Measures of Precision

- Linear regression
- Average percent difference
- Method 301 F-test criteria
- NAAQS Lead analytical FEM precision criterion

Notes on precision measurements

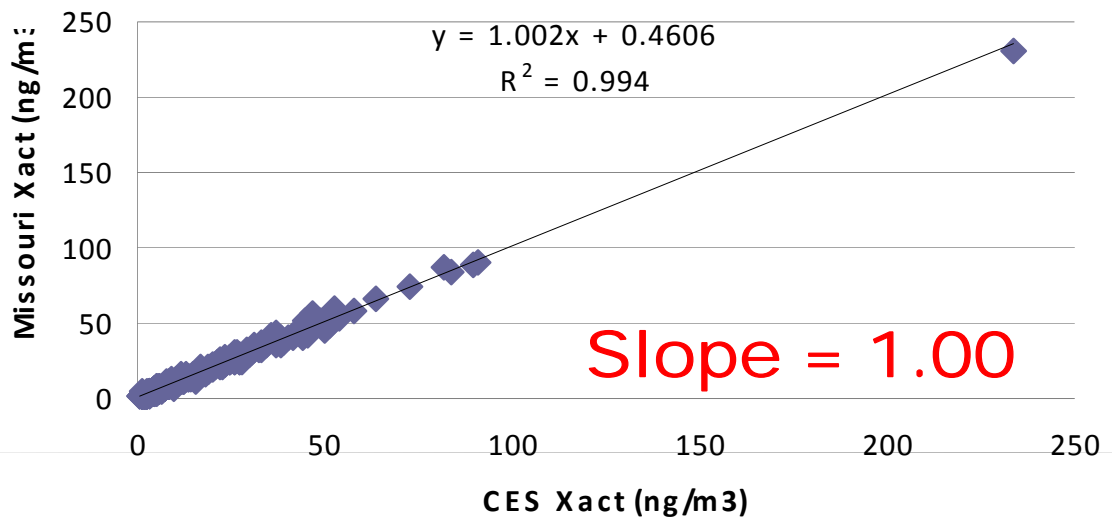
- Xact Precision: Two Xact 620s - two samplers and two analyzers
- FRM Precision: Two FRM samplers and one analyzer

Calcium



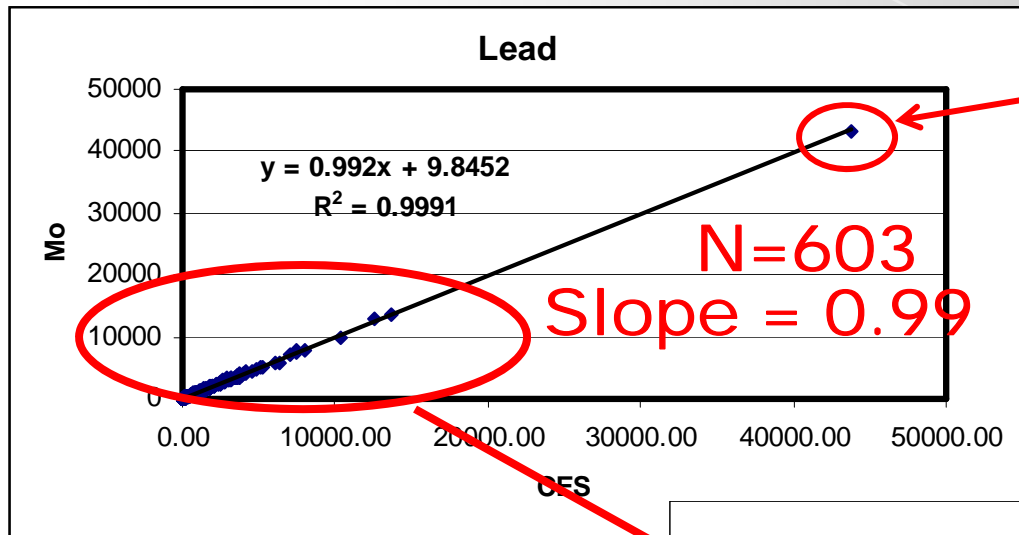
Xact Precision
Missouri versus CES
Xact 620s
N = 603

Copper



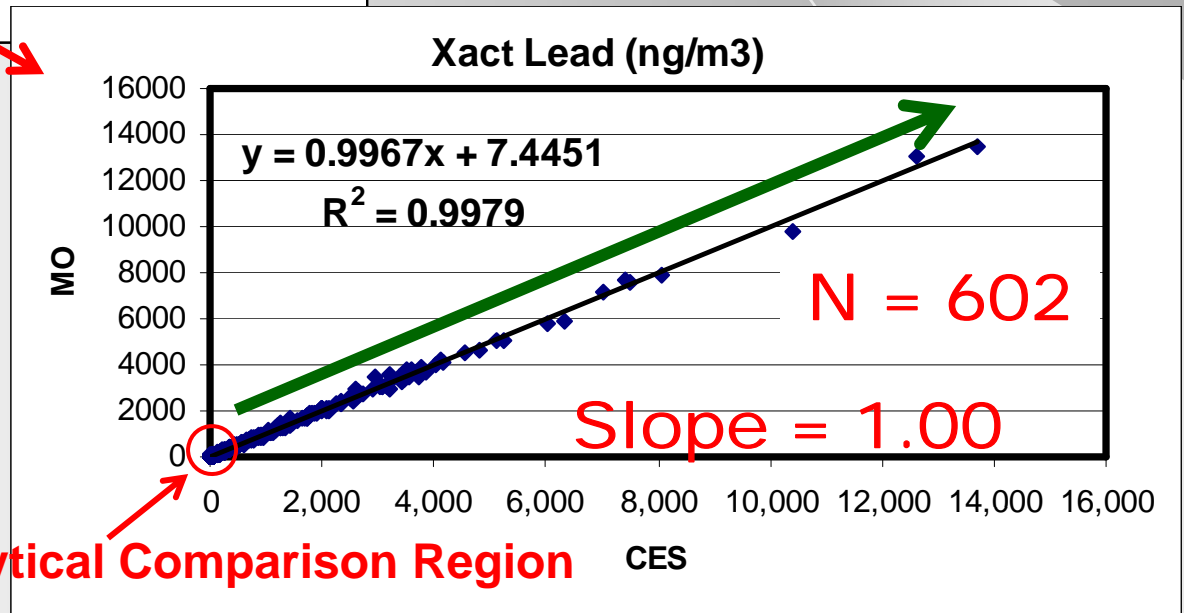
Lead Precision

Linearity – Herculanum, MO



This one, 1-hour data point represents 40% of monthly average Pb NAAQS (60 ng/m³)

Focus of precision quality indicator should be on high concentration measurements



NAAQS 24-hour Average Analytical Comparison Region

Precision

Method 301 F-test Criteria

-requires equal or better precision than FRM-

- Xact statistically equal or better than FRM/IO 3.3

- | | | |
|------|-----------|----|
| – Ca | Ti | V |
| – Mn | Fe | Co |
| – Ni | Cu | Zn |
| – Ga | As | Se |
| – Br | <u>Pb</u> | |

- Statistically less than FRM

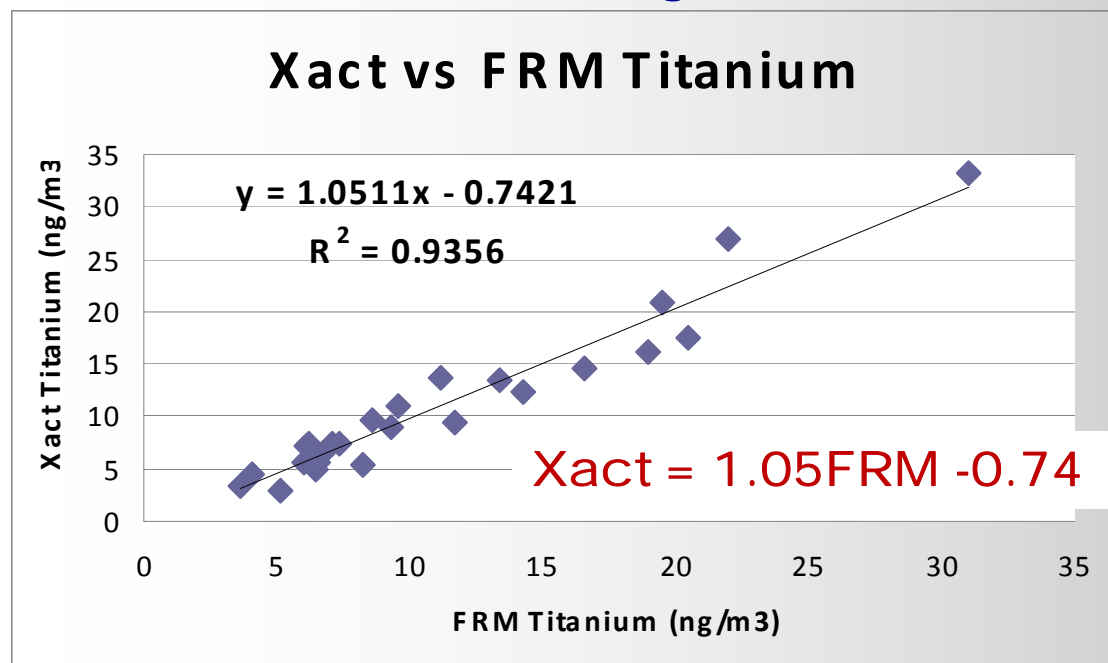
- | | | |
|------|-------|----|
| – K | Cr(2) | Cd |
| – Ba | | |

Accuracy

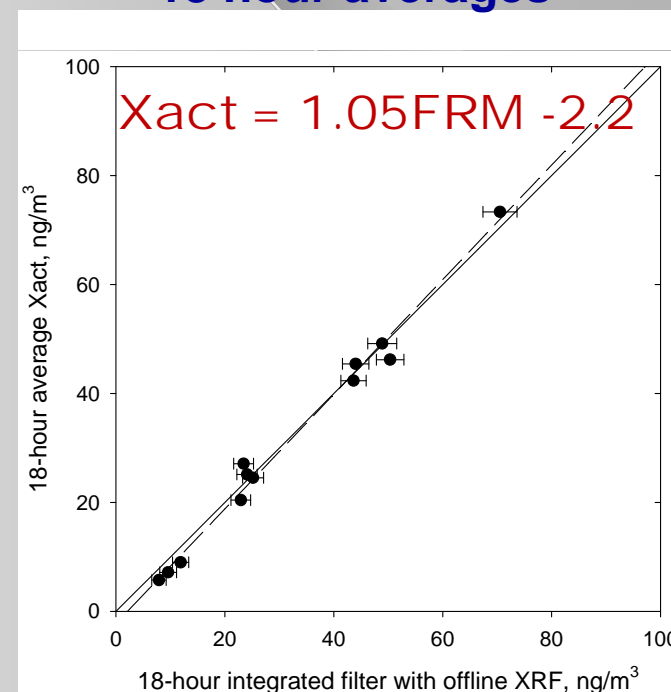
Linear Regression

Ti Example - Xact v. FRM

Herculaneum
24 hour averages



St. Louis
18 hour averages



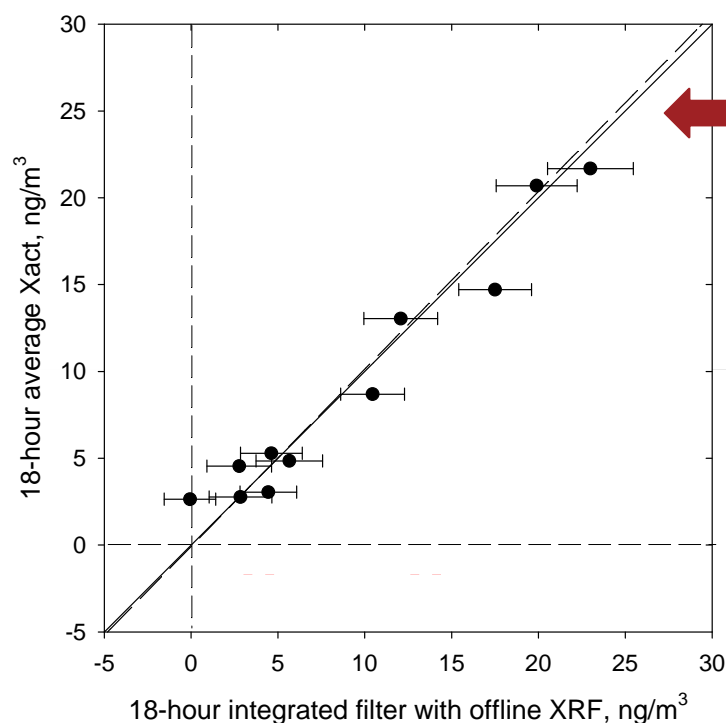
Lead Accuracy Linear Regression

St. Louis, MO

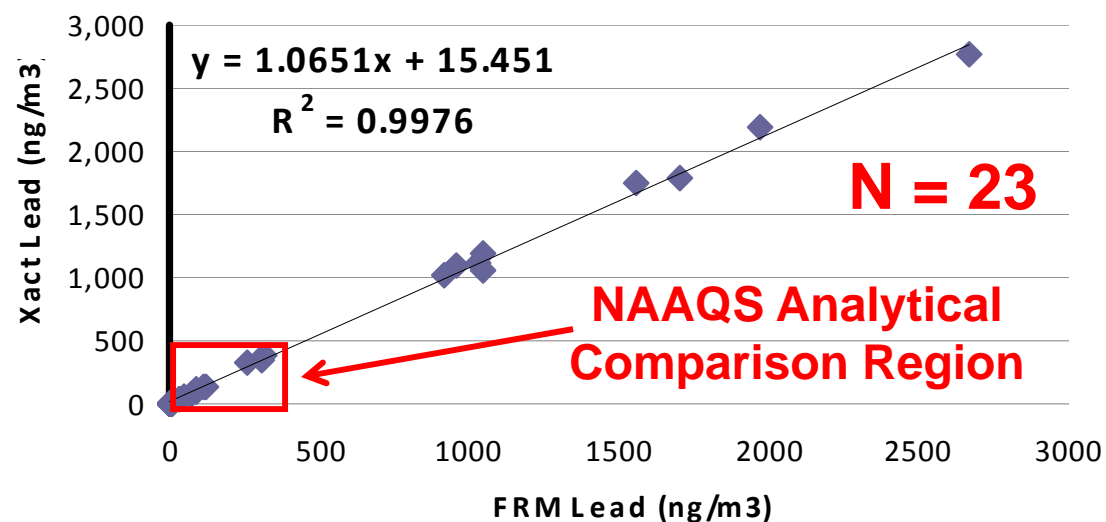
$X_{act} = \underline{1.02}FRM + -0.1$
Low Concentrations

Herculaneum, MO

$X_{act} = \underline{1.07}FRM + 15$
High Concentrations



Xact vs FRM Lead



Robust Technology

- **Demonstrated accuracy over range of conditions**
 - Urban center – incinerator, CFPP, steel, etc.
 - Rural - lead smelter
- **Operating in four countries**
 - Four in Korea
 - Two in Canada
 - One in Australia
 - One in US
- **Stable over a period of about a year**
- **Linear over six orders of magnitude**

Utility and Applicability

Invaluable asset: correlating concentrations with short-term wind speed and direction measurements

Validation Summary

-PM₁₀ Lead-

<u>Validation Parameter</u>	<u>Value</u>	<u>Better than FRM/3.3?^a</u>
•Up time	99%	Yes
•Stability	<4%/yr.	= or better
•Detection limit	<0.01 ng/m ³	Yes
•Quant. Conc. Range	0.1 to 250,000 ng/m ³	= or better
•Precision		Yes
•Pb NAAQS	3%	Yes
•Average % difference	5%	Yes
•Linearity/slope (two Xacts)	1.00	Yes
•M301 F test	-	Yes
•Accuracy		Yes
•Pb NAAQS (5 days req.)	passed 5 days	Yes
•Method 301	No Correction Req.	Passed
•Linear Regression	Slope:1.07	= or better
•Robustness	Urban/rural/industry	= or better
•Utility/applications	time/DL/Appportionment	Yes

a. 24-hour FRM sample with IO 3.3 laboratory analysis

NR: Not defined

Conclusions

- There are no other near real time, direct reading multi-metals ambient monitors available for comparison
- These tests clearly demonstrated the validity of the Xact 620, particularly for measuring PM₁₀ lead.
- The Xact 620 with one hour sampling produced equal to or better PM₁₀ lead measurements than can be made with a 24-hour sample collected with a PM₁₀ FRM sampler and laboratory XRF analysis.
- These tests have demonstrated the high airshed management value of being able to correlate high-sensitive metals measurements to short-time variability in wind direction and speed.
- These monitors can be made and are currently being use in four countries
- This technology is ready for permitting and enforcement applications.

Where do we go from here?

- **Define FLM acceptance protocols**
 - Validation procedures and acceptance criteria
 - Initial certification requirements
 - On-going QA requirements
- **Define permitting and enforcement application procedures**
- **Integrate apportionment and emission models**

QUESTIONS

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or

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