

# EVALUATION OF A NEAR REAL TIME METALS MONITOR FOR MEASURING FUGITIVE METAL EMISSIONS

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# Why Measure Metals?

- Significant adverse human health effects
- Developing fetus & children especially susceptible
- Metals represent 8 of US EPA's top 33 pollutants of highest concern
- Arsenic is one of US EPA's top three priority pollutants of concerns
- Global concern for metals – As, Cd, Cr, Pb and Hg - RoHS, WEEE and ELV

•US EPA. Framework for Inorganic Metals Risk Assessment. EPA 120/R-07/001. March 2007.

•US EPA. Health Effects Notebook for Hazardous Air Pollutants. EPA Technology Transfer Network Air Toxics Website. Accessed November 2007.

•Agency for Toxic Substances and Disease Registry. Toxic Substances Portal. Accessed November 2007.

# Why Measure Metals (cont.)?

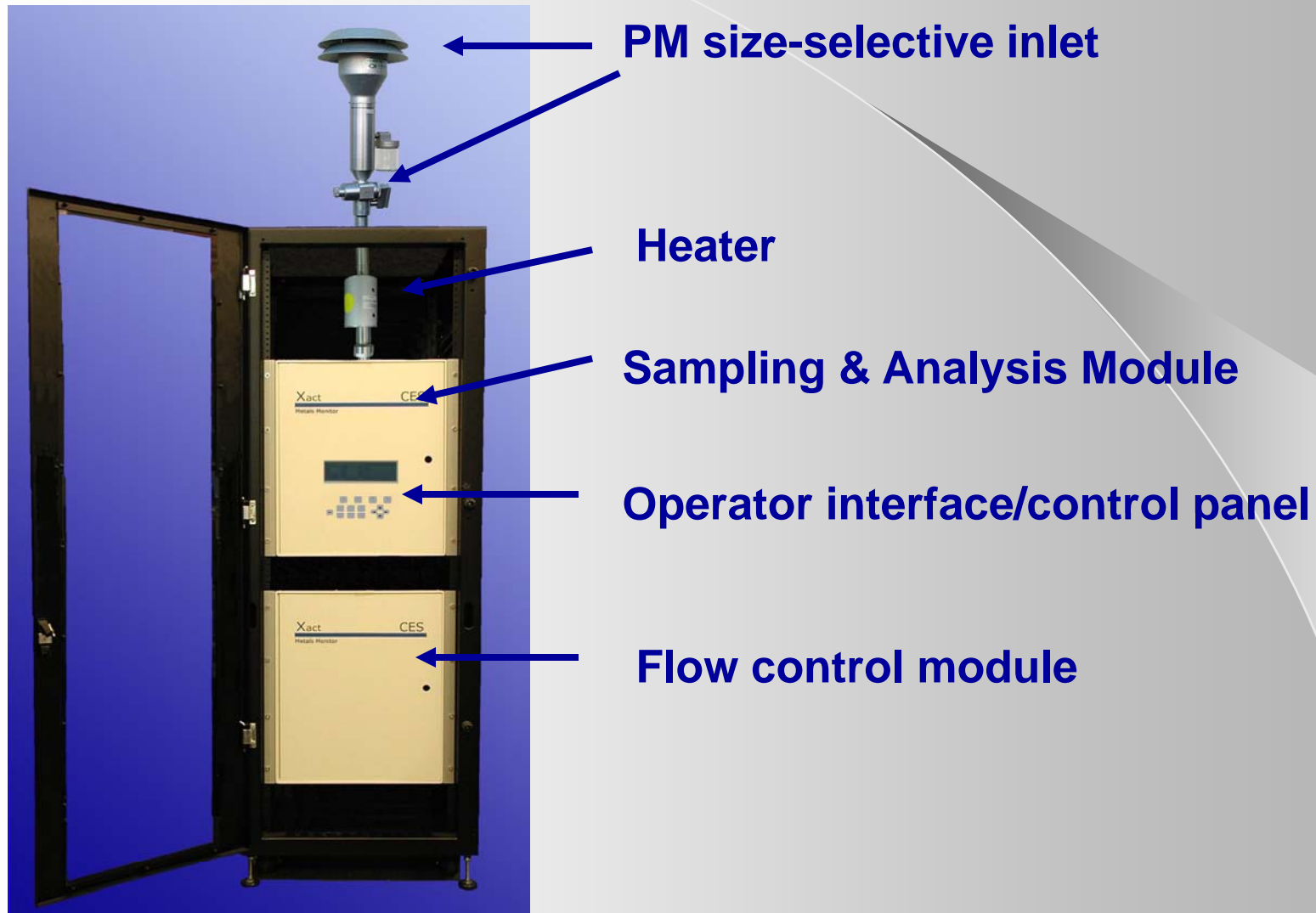
## **Metals Represent Significant Health Concerns**

- **No apparent threshold for blood Pb**
- **Persistent – will not biodegrade**
- **Source Apportionment**

# Why Continuous Real Time Metals Monitors?

- **Improved exposure estimates – time resolution of concentration data**
- **Improved source apportionment**
  - Correlation with wind speed and wind direction
- **Plant feedback to eliminate problem**
- **Identification of hot spots**

# Xact 620 Ambient Metals Monitor





## ELEMENTS THE XACT CAN MEASURE (IN BLUE)

Xact 620 Optimized for  
Remote Measurement of

As, Se, Hg & Pb

Xact 620 Optimized for Remote Measurement of As, Se, Hg & Pb																		
1	1	2											13	14	15	16	17	18
1	H																	He
	1.0079																	4.0026
2	3	4											5	6	7	8	9	10
	Li	Be											B	C	N	O	F	Ne
	6.941	9.0122											10.811	12.011	14.007	15.999	18.998	20.18
3	11	12											13	14	15	16	17	18
	Na	Mg											Al	Si	P	S	Cl	Ar
	22.99	24.305											26.982	28.086	30.974	32.066	35.453	39.948
4	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
	39.098	40.078	44.956	47.88	50.942	51.996	54.938	55.847	58.933	58.693	63.546	65.39	69.723	72.61	74.922	78.96	79.904	83.8
5	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
	85.468	87.62	88.906	91.224	92.906	95.94	(97.91)	101.07	102.91	106.42	107.87	112.41	114.82	118.71	121.76	127.6	126.9	131.29
6	55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
	132.91	137.33	138.91	178.49	180.95	183.84	186.21	190.23	192.22	195.08	196.97	200.59	204.38	207.2	208.98	(209)	(210)	(222)
7	87	88	89	104	105	106	107	108	109	110	111							
	Fr	Ra	Ac	Rf	Ha	Sg	Ns	Hs	Mt	Unn	Unu							
	(223)	(226)	(227)	(261.1)	(262.1)	(263.1)	(262.1)	(265.1)	(266.1)	(268)	(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

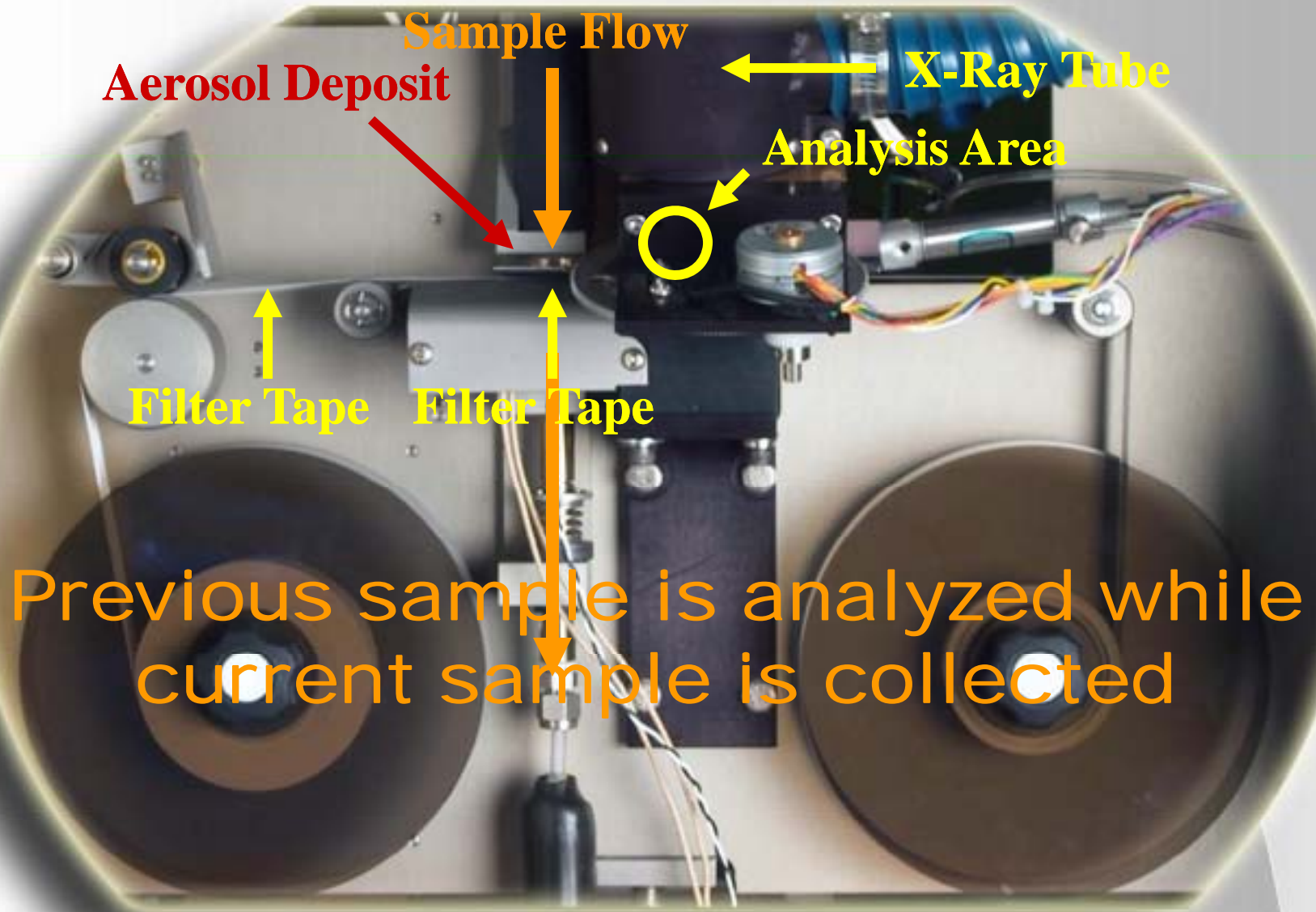
Actinide Series

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

# XACT SAMPLING AND ANALYSIS



# Performance Evaluation

- 1. Minimum Detection Limit Determination**
- 2. Precision – Comparison of Two Xacts Side by Side**
- 3. Comparison with Federal Reference Method (FRM) Sampling followed by XRF Analysis (IO 3.3)<sup>a</sup>**

a. EPA Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air. June, 1999. Compendium Method IO-3.3 Determination of Metals in Ambient Particulate Matter Using X-Ray Fluorescence (XRF) Spectroscopy.



# Minimum Detection Limit Determination

- Laboratory Evaluation
- Calculated from Spectrum of Blank Sample (95 % Confidence Interference Free)
  - Standard method used to calculate MDL for XRF
  - Used to calculate Detection limits given in IO 3.3

$$C_{MDL} = 3.29 \frac{\sqrt{RtI}}{StI}$$

- Empirically Determined - 66 Blank Samples
  - Replaced PM inlet with Hi-vol filter to remove PM
  - Operated the unit in 1 hour mode
  - 95% confidence MDL – means 95% of samples fell below stated concentration level

# Xact 620 Minimum Detection Limits

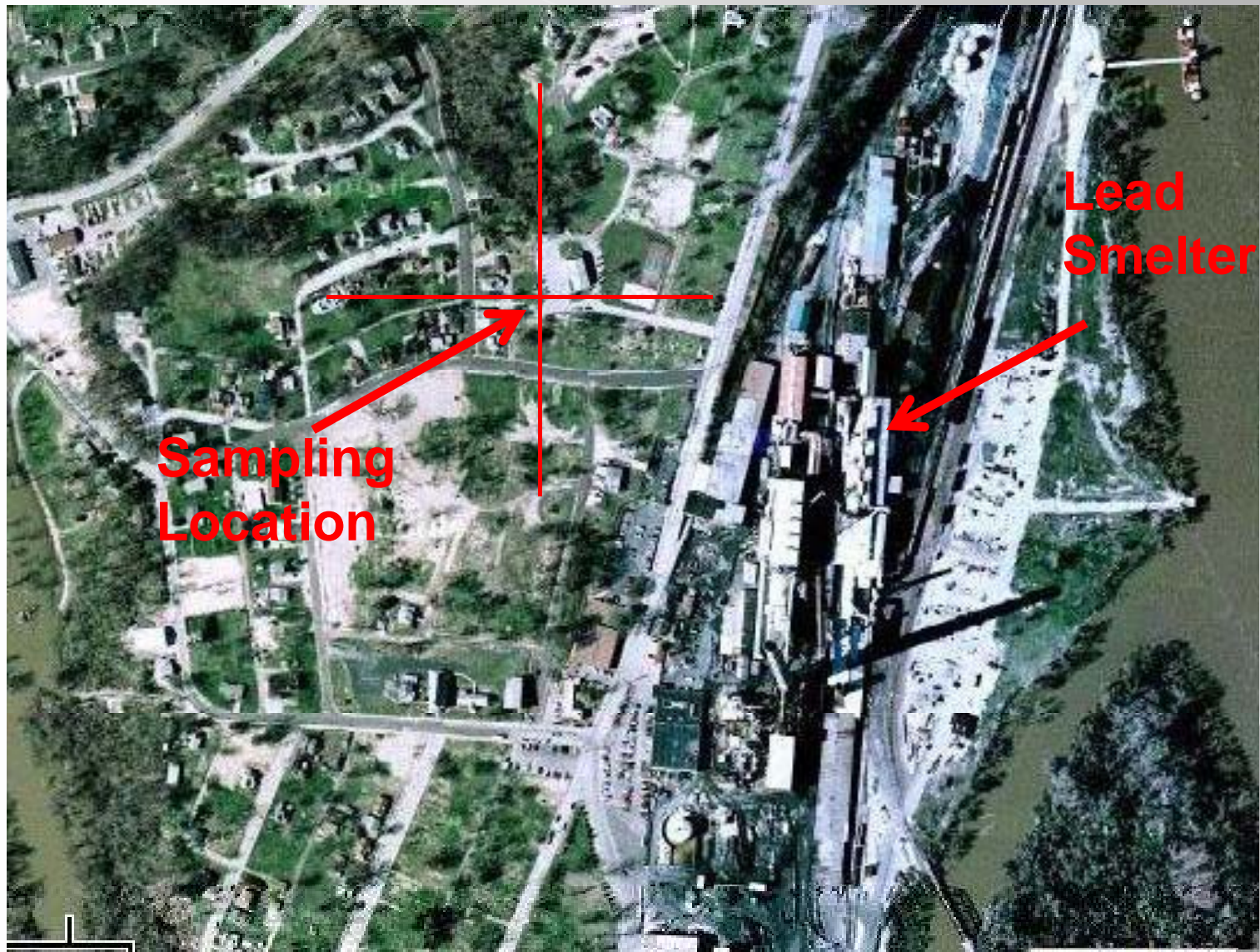
Element	1-hour Xact 620		24-hour FRM/IO3.3
	66 Blank Measurements	Calculated	Calculated
K	0.00	1.89	4.40
Ca	2.66	0.75	6.30
Ti	0.73	0.41	11.82
V	0.26	0.32	3.70
Cr	0.57	0.25	2.09
Mn	0.31	0.16	0.56
Fe	2.82	0.19	0.49
Co	0.21	0.11	0.28
Ni	0.15	0.08	0.42
Cu	0.15	0.15	0.49
Zn	0.21	0.10	0.70
Ga	0.08	0.06	1.12
As	0.08	0.06	0.56
Se	0.00	0.07	0.49
Ag	2.09	1.91	14.00
Cd	0.00	3.15	15.40
Sn	1.11	5.92	21.36
Sb	1.81	1.55	21.98
Ba	1.55	0.92	36.27
Hg	0.00	0.10	1.05
Tl	0.07	0.11	1.05
Pb	0.00	0.12	1.05

- General Agreement between calculated and empirical detection limits
  - Fe and Ca are exceptions
- Xact 1 hour detection limits are generally lower than 24-hour FRM/IO 3.3 Detection Limits
- All these MDL's are Interference Free

# Field Deployment - Summary

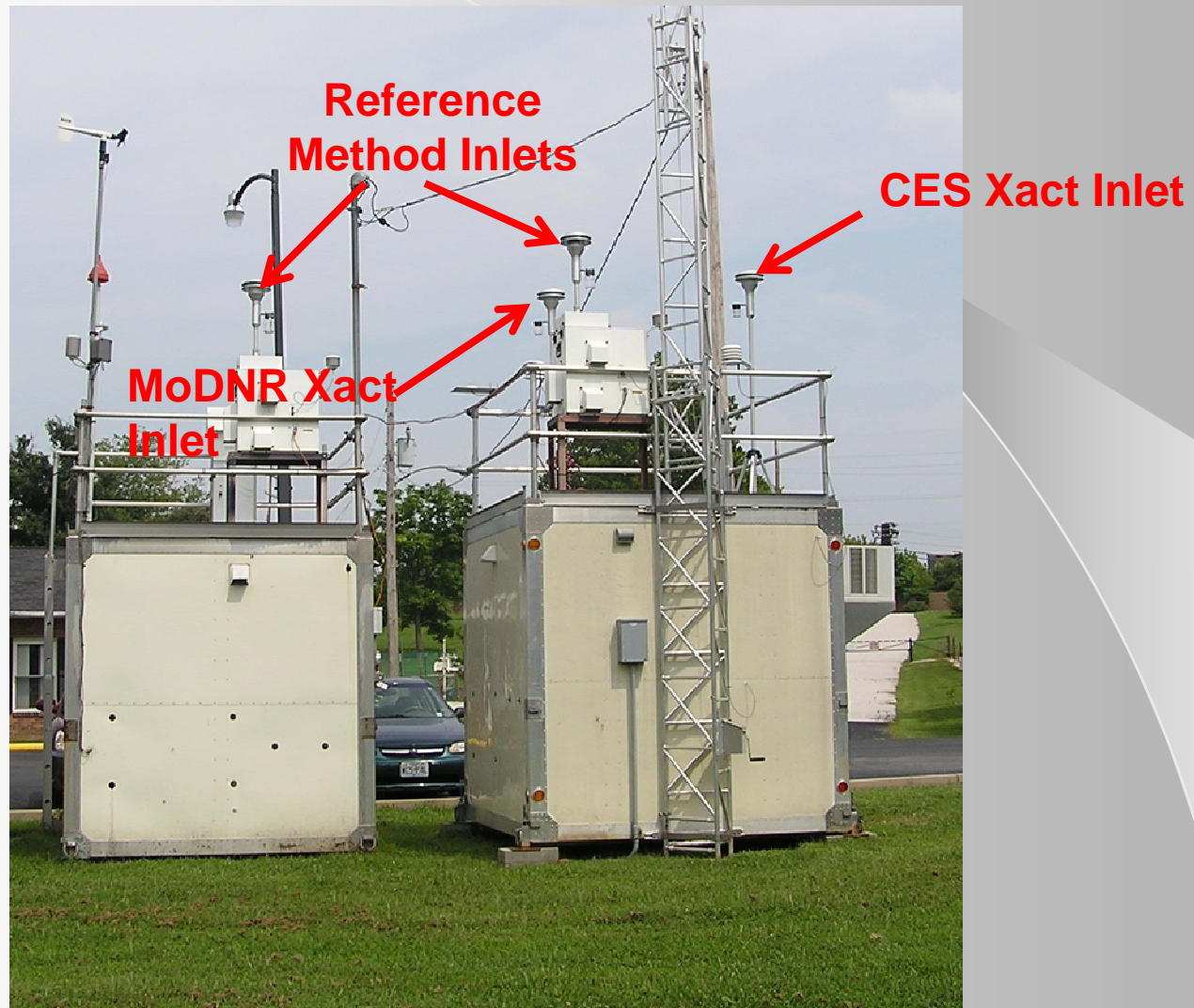
- **Two Xact 620s**
- **Two Reference Method Samplers (R & P 2025)**
- **Near Fence Line of a Primary Lead Smelter (Herculaneum, Missouri)**
- **25 days of Run time**
- **605 hourly data points on each Xact**
- **23 elements reported per Xact**
- **Over 27,000 individual hourly concentration data points**

## Field Deployment - Location





# Field Deployment - Samplers





# Xact Precision

- Percent Difference Used as an Indicator
  - Non-detects and concentrations less than the limit of Quantitation (approximately three times the minimum detection limit) removed from calculation
- Least squares linear regression also used as an indicator of Precision
- Precision also calculated for FRM IO 3.3

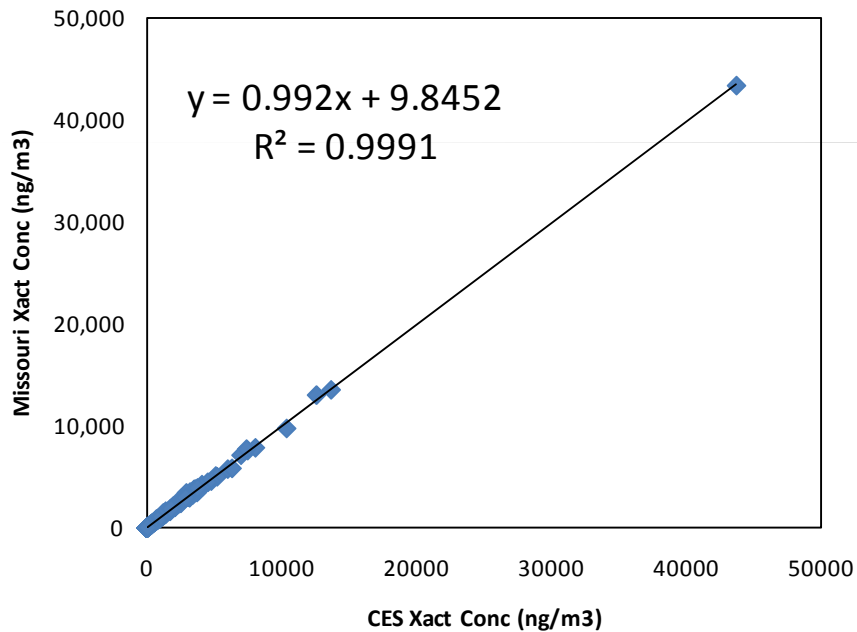
# Precision – Percent Difference

Element	Xact				FRM Daily Average Precision	
	Hourly		Daily Average		N	% Difference
	N	% Difference	N	% Difference		
Ca	605	5.9%	25	2.2%	21	5.0%
Fe	605	5.0%	25	1.5%	21	5.0%
Cu	605	13.6%	25	7.4%	21	8.8%
Zn	605	7.9%	25	3.9%	21	5.7%
Pb	587	20.2%	25	4.7%	20	10.4%

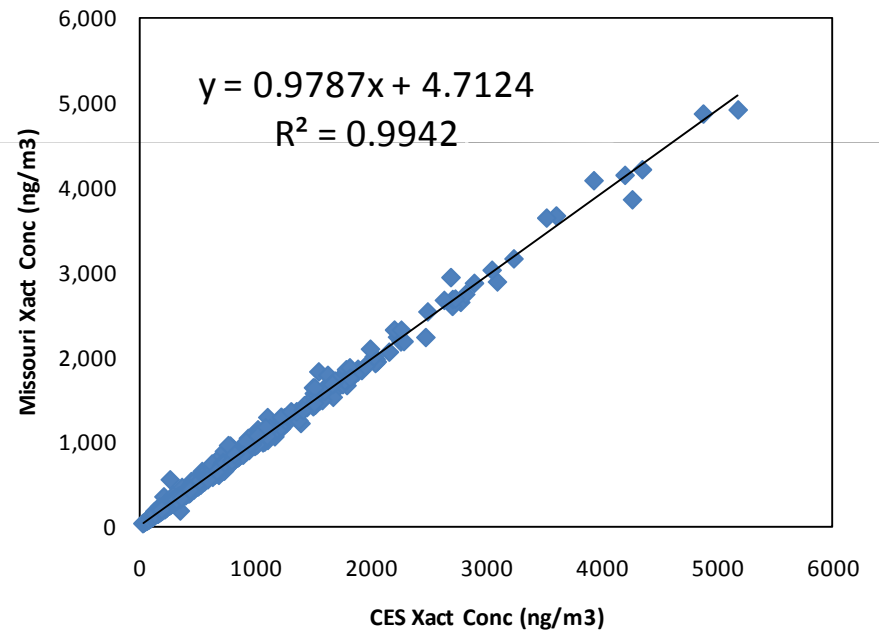
- Precision of hourly Xact measurement similar to that of 24 hour FRM sampling with XRF analysis
- Precision of Xact daily average is generally better than that for FRM sampling with XRF analysis
- Xact Precision results include **two** samplers and **two** analyzers
- FRM Precision results include **two** samplers and **one** analyzer

# Precision – Regression Analysis

**Lead**



**Calcium**



## Comparison With FRM/IO 3.3

- FRM /IO 3.3 – 24 hour sample on Teflon Filter followed by XRF Analysis
- XRF Analysis Performed by CES
- QA of XRF Analysis Performed by USEPA ORD
- Xact 24 hour average calculated by averaging 24, 1 hour samples
- Daily average Xact (average of two units) plotted against daily average FRM/IO 3.3 (average of two samplers when both where available)
- All data included

## XRF Analysis "Round Robin" Comparison (CES and EPA)

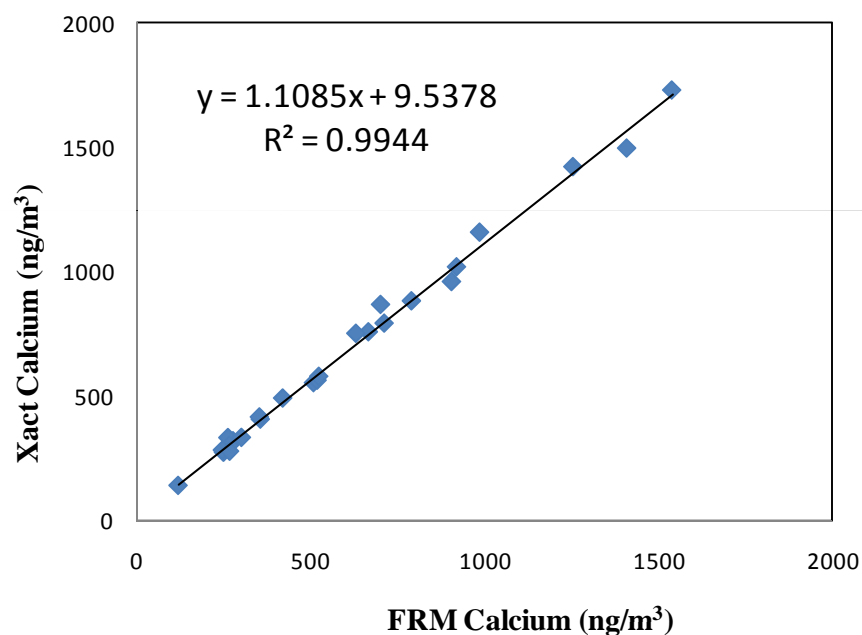
Element	N	Average Percent Difference
Calcium (Ca)	23	- 0.41
Iron (Fe)	23	0.92
Copper (Cu)	8	8.66
Zinc (Zn)	23	- 1.48
Lead (Pb)	23	-0.42

**Excellent Agreement Between CES' and EPA's XRF Analysis**

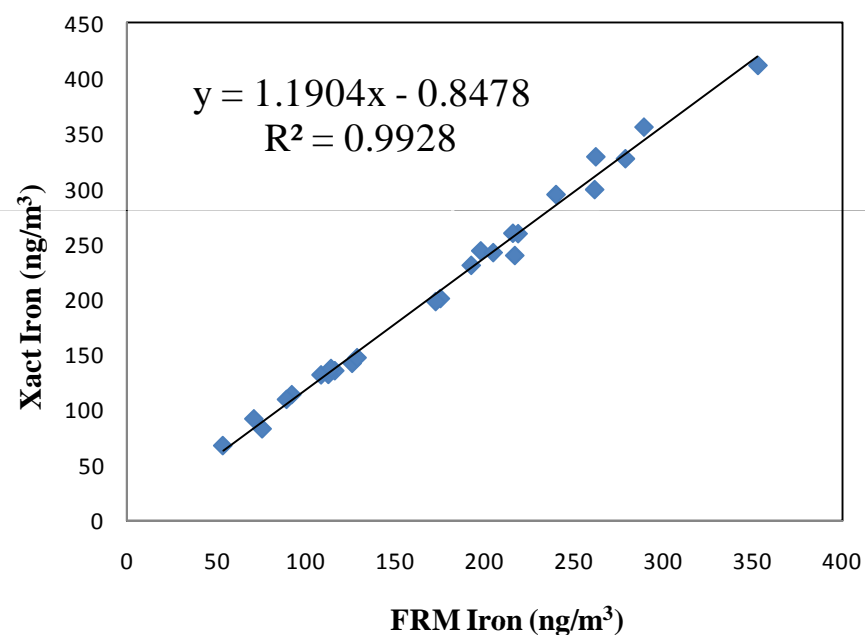


# Xact 620 and FRM/IO 3.3 Comparison

## Calcium

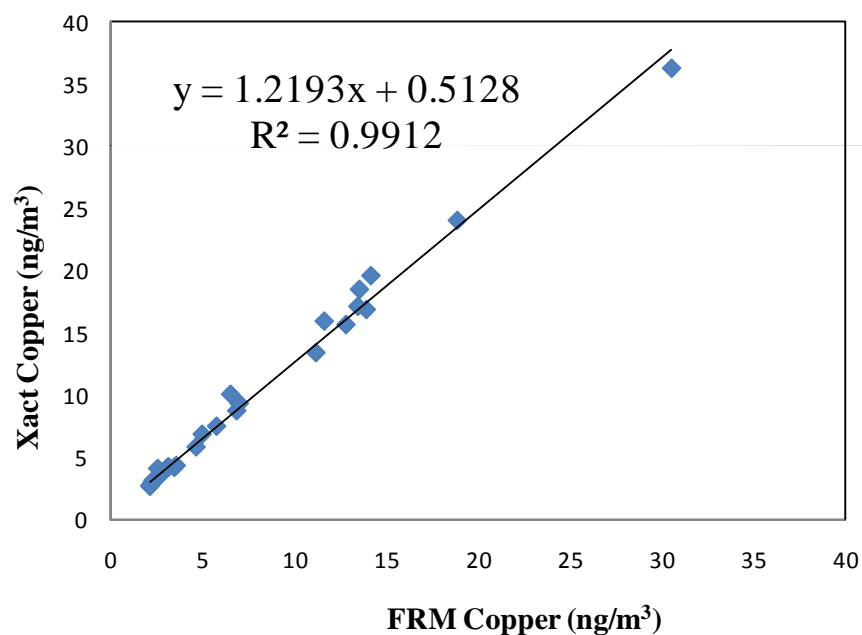


## Iron

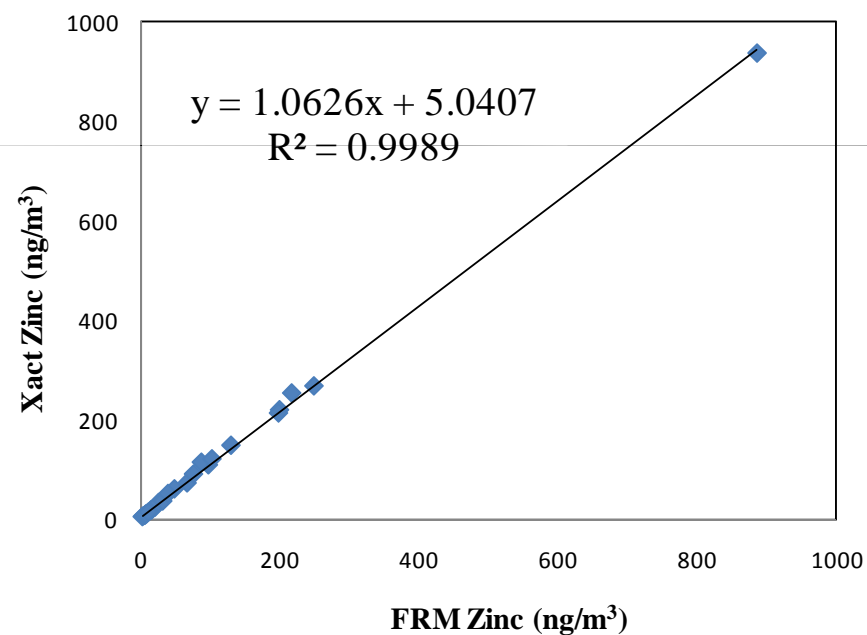


# Xact 620 and FRM/IO 3.3 Comparison

## Copper

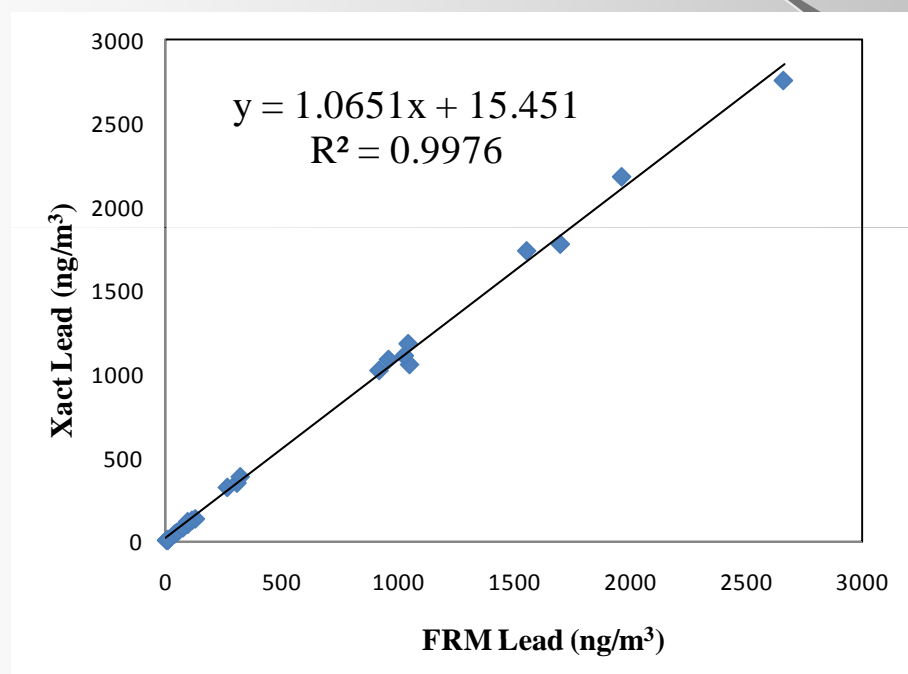


## Zinc



# Xact 620 and FRM/IO 3.3 Comparison

## Lead





# Post Field Test Work – Deposition Size Measurements

## Xact Tape Deposits

Deposit Area Used =  $0.747 \text{ cm}^2$

Corrected Deposit Area =  $0.707 \text{ cm}^2$  (6%)  
Determined with actual Herculanum deposits



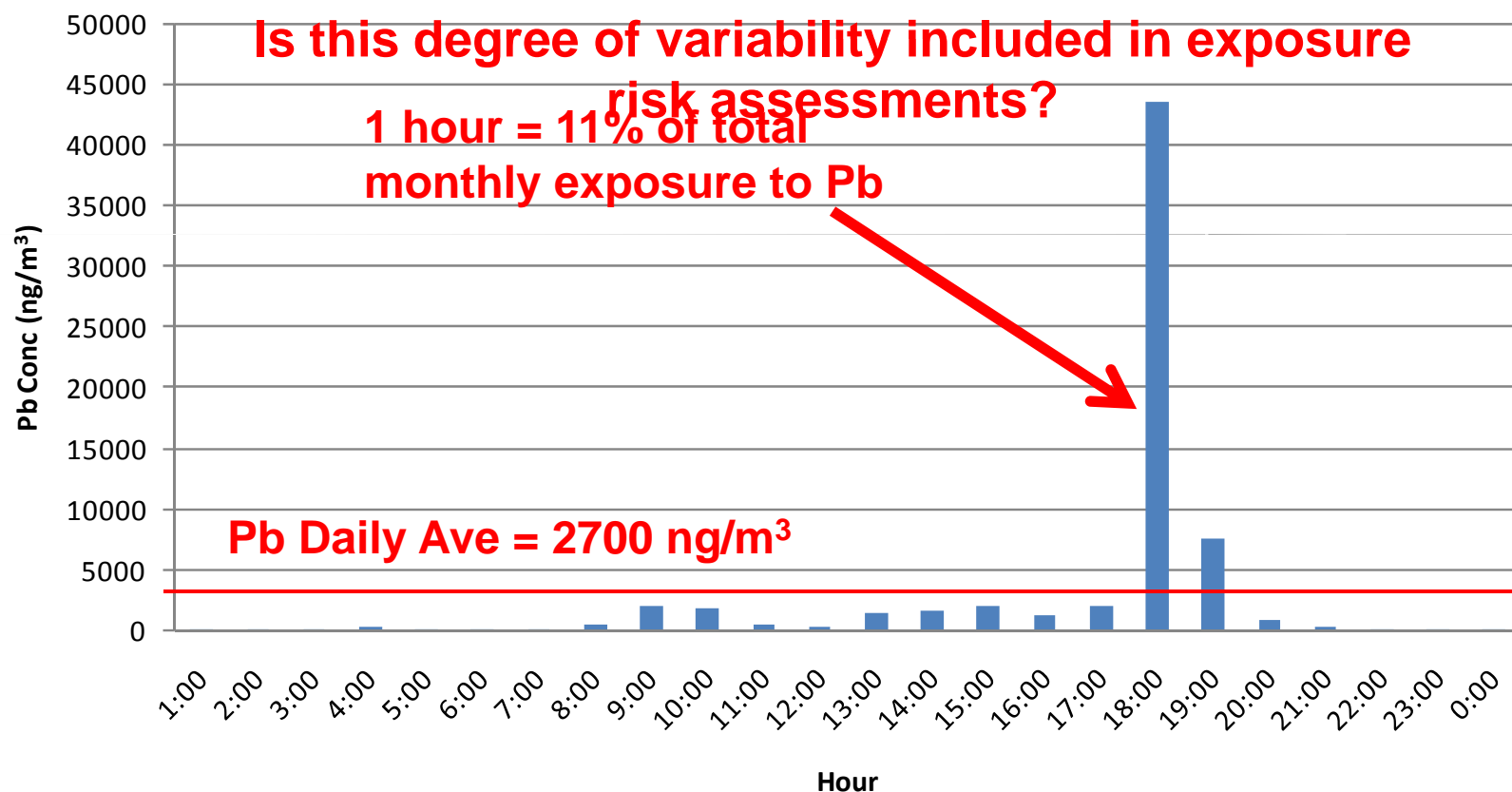
# Conclusions

- **1 hour Minimum Detection Limits Are as good or better than those achieved using 24 hour FRM Sampling and Laboratory XRF Analysis**
- **Precision – Xact 620 Exhibits Excellent Precision**
  - 1 hour precision is as good as 24 hour sampling and analysis
  - Precision of 24 hour average is better than FRM/XRF
- **Comparability – Agrees well with FRM/XRF analysis particularly for those metals present at concentrations well above MDL**



# WHAT YOU MISS WITH 24 HOUR AVERAGES

## Hourly Lead Concentrations 8/27/2010



## Further Work

- Further Data Analysis – Jay Turner
- Analysis of Filter samples by ICP-MS

# Acknowledgements

- Jim Brunnert, Celeste Koon – Missouri Department of Natural Resources
- Terri Conner, Bob Willis – USEPA Office of Research and Development
- US EPA Office of Air Quality Planning and Standards
- MACTEC Federal Programs

# QUESTIONS

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