Advances in the Monitoring of Hazardous Metals in Urban Areas Using a High Resolution Continuous Ambient System

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<u>Why Metals?</u>

- Global concern of toxic metals – As, Cd, Cr, Pb, Hg, Ni, V, and Zn (*Fang et al., 2010; Lippmann and Chin, 2009; Pope et al., 2009*)
- Arsenic is one of U.S. EPA's top three priority pollutants of concern
- Coal Fire Power Plants are the largest source of As, Se, Hg and Cr
- Metals persist in the environment once released
- Metals do not biodegrade
- Available for re-introduction into the air, water and food chain

Why Measure Metals in Real-Time?

- Locate the sources of pollution within urban areas
- Decreased the cost of monitoring operations by automating the sampling and analysis method into one instrument
- Increased understanding of the industries producing pollution and when they emit it into the air
- Uncover periods of acute concentrations missed by current integrated samplers e.g. Hi Vol TSP and PM 10 FRM
- Characterize back ground concentrations in urban areas to establish baseline levels
- Maximize productivity while maintaining healthy air quality

Xact 620 and 625 Ambient Metals Monitors

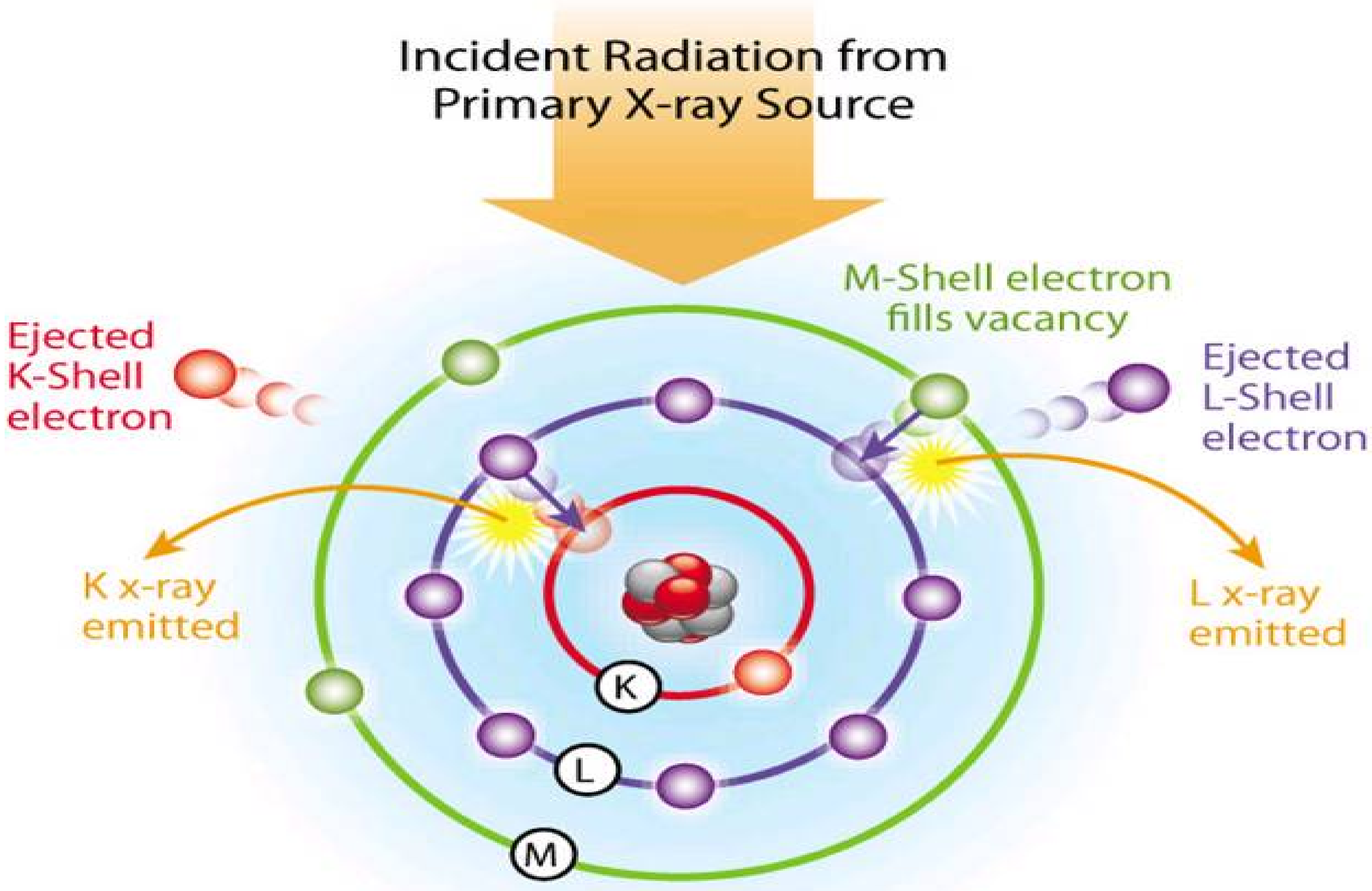
- PM size-selective inlet
- Temperature controlled 19 inch rack
- Heater
- Sampling & Analysis Module
- Operator interface/control panel
- Flow control module

Reports 23 elements per sample

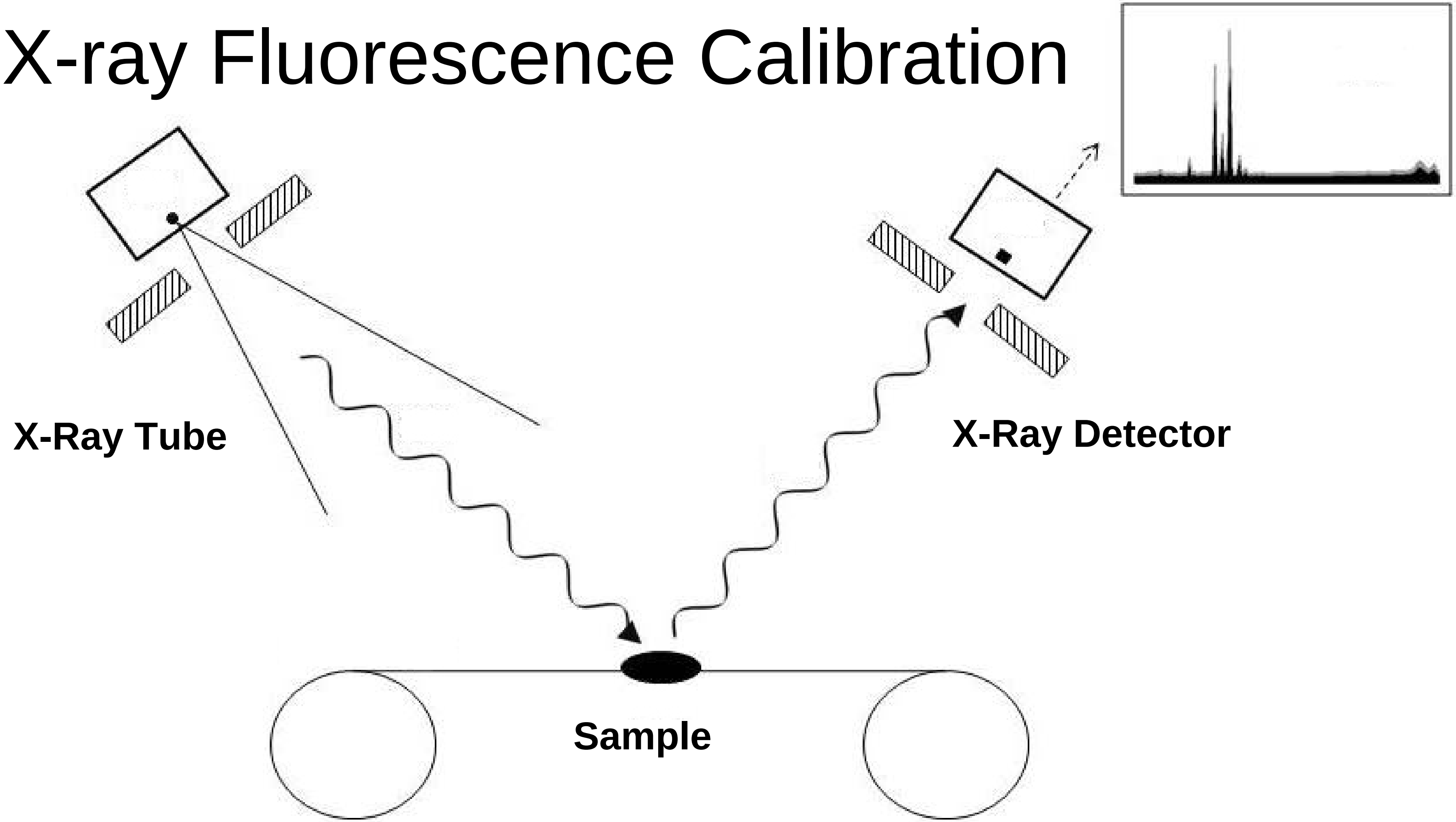
About 180,000 results per year when monitoring every hour

ELEMENTS THE XACT CAN MEASURE (IN BLUE)

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H 1.0079																	2 He 4.0026
2	3 Li 6.941	4 Be 9.0122											5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.305											13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.066	17 Cl 35.453	18 Ar 39.948
4	19 K 39.098	20 Ca 40.078	21 Sc 44.956	22 Ti 47.88	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.693	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.8
5	37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.94	43 Tc (97.91)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.6	53 I 126.9	54 Xe 131.29
6	55 Cs 132.91	56 Ba 137.33	57 La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261.1)	105 Ha (262.1)	106 Sg (263.1)	107 Ns (262.1)	108 Hs (265.1)	109 Mt (266.1)	110 Unn (269)	111 Unu (269)							
Lanthanide Series			58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (144.9)	62 Sm 150.36	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.5	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97		
Actinide Series			90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np (237)	94 Pu (244.1)	95 Am (243.1)	96 Cm (247.1)	97 Bk (247.1)	98 Cf (251.1)	99 Es (252.1)	100 Fm (257.1)	101 Md (258.1)	102 No (259.1)	103 Lr (262.1)		


Incident Radiation from
Primary X-ray Source
M-Shell electron
fills vacancy
Ejected
K-Shell
electron
Ejected
L-Shell
electron
K x-ray
emitted
L x-ray
emitted
K
L
M

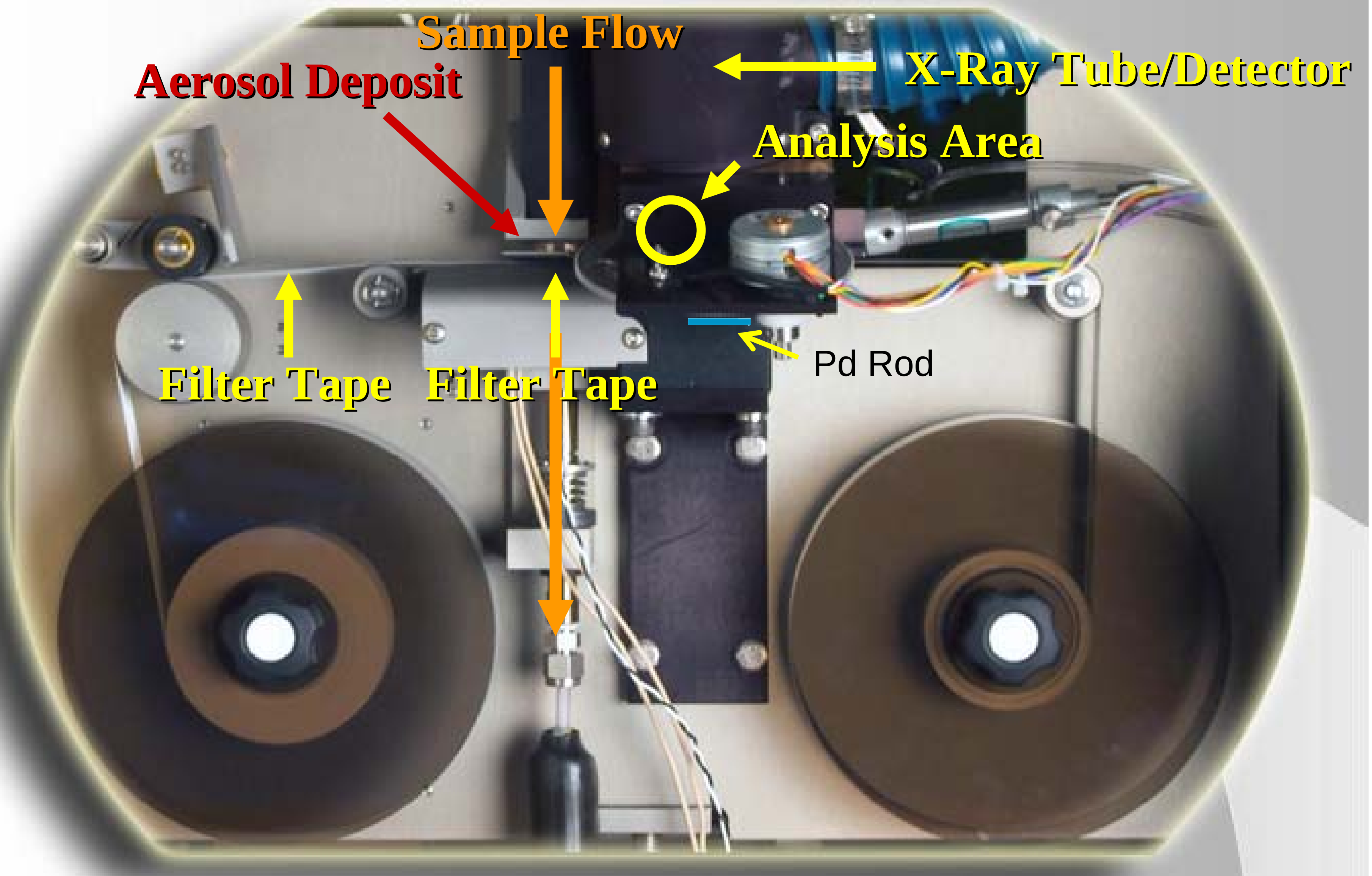
X-ray Fluorescence Calibration



$$\frac{I_x}{C_x} = \frac{I_s}{C_s}$$

$$C_x = \frac{I_x}{I_s} C_s$$

XACT METALS MONITOR SAMPLING AND ANALYSIS MODULE



Quality Assurance and Control

1. Every Sample

- Pd Rod calibration error check
- Pressure gauge leak check

2. Daily Automatic QA

- XRF calibration error check
- Flow calibration check
- Zero level check

NIST Traceable Thin Film Standards

3. Required Maintenance

- 8 hours labor per month
- 1 X-ray tube per year
- 1 roll of sample tape every two weeks

Comparison of CES Xact 625 Detection Limits (pg/m^3)[a]
For Ambient Monitoring Applications

System	Element	EPA IO 3.3[b]	Xact 625A	Xact 625A	Xact 625A	Xact 625A
Sampling Time (minutes)		1,440	240	60	30	15
Sampling flow (lpm)		16.7	16.7	16.7	16.7	16.7
Vol. Sampled (m^3)		24.00	4.00	1.00	0.50	0.25
Filter		37 mm PTFE	PTFE Tape	PTFE Tape	PTFE Tape	PTFE Tape
Filter density (mg/cm^2)		0.5	2	2	2	2
Detector[a]		Si(Li)	SDD	SDD	SDD	SDD
Tube Anode[a]		Rh	Rh	Rh	Rh	Rh
Tube power (Watts)		50	50	50	50	50
No. Excitation Conditions		5	2	2	2	2
Detection Limits						
1	Si	1,000				
2	Cl	1,000				
3	K	2,000				
4	Ca	3,000				
5	Ti	5,000				
6	V	2,000	80	640	2,560	5,120
7	Cr	900	72	576	2,304	4,608
8	Mn	200	72	576	2,304	4,608
9	Fe	200	64	512	2,048	4,096
10	Co	100	64	512	2,048	4,096
11	Ni	200	64	512	2,048	4,096
12	Cu	200	56	448	1,792	3,584
13	Zn	300	48	384	1,536	3,072
14	Ga	500	40	320	1,280	2,560
15	As	200	32	256	1,024	2,048
16	Se	200	32	256	1,024	2,048
17	Br	200	40	320	1,280	2,560
18	Rb	200	72	576	2,304	4,608
21	Ag	6,000	400	3,200	12,800	25,600
22	Cd	7,000	880	7,040	28,160	56,320
23	Sn	9,000	1,200	9,600	38,400	76,800
24	Sb	9,000	1,280	10,240	40,960	81,920
26	Ba	16,000	1,600	12,800	51,200	102,400
28	Hg	400	40	320	1,280	2,560
29	Tl		40	320	1,280	2,560
30	Pb	400	40	320	1,280	2,560

a Interference-free, one sigma

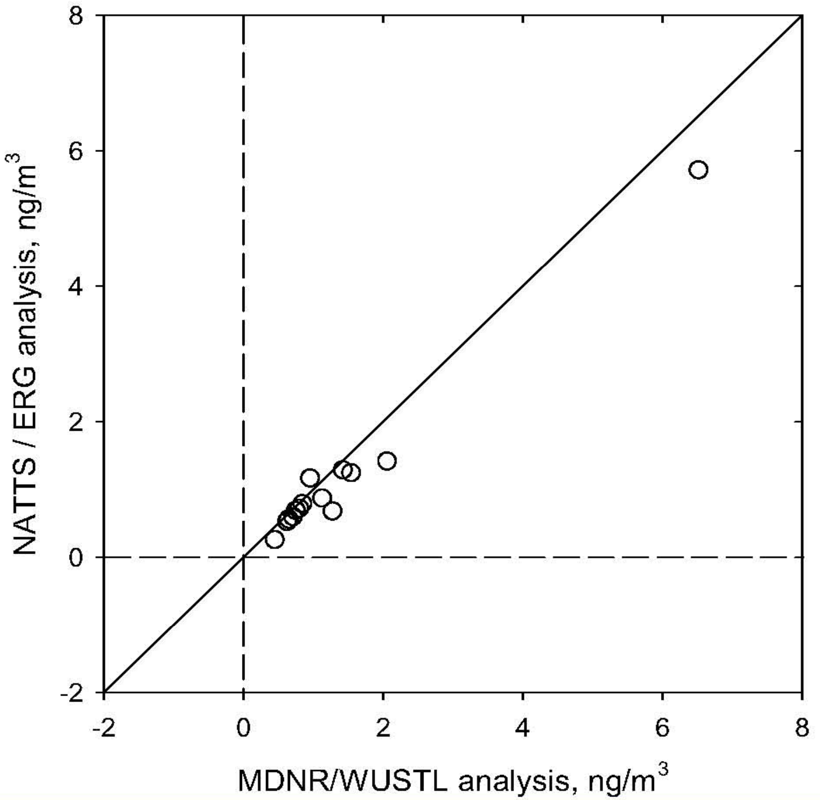
b EPA Compendium Method IO-3.3 – EPA Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air, EPA/625/R-96/010a, Table 2, page 3.3-16

c CES analyzed filters as part of US EPA PM2.5 speciation program - 2002

Arsenic – Methods Comparisons

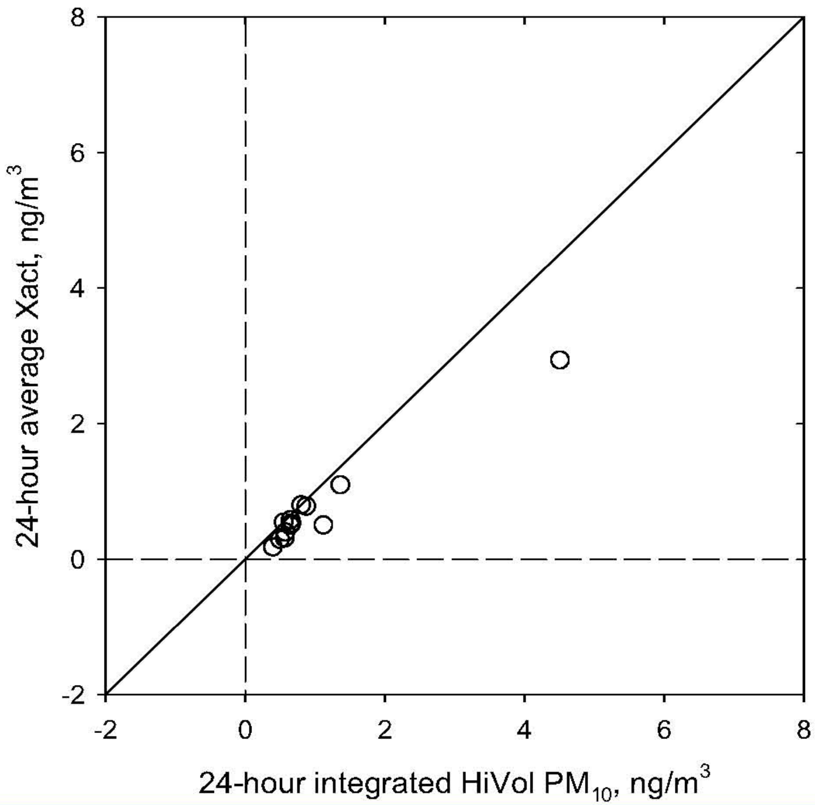
Collocated HiVol Samplers

Blair site, 4th Quarter 2008

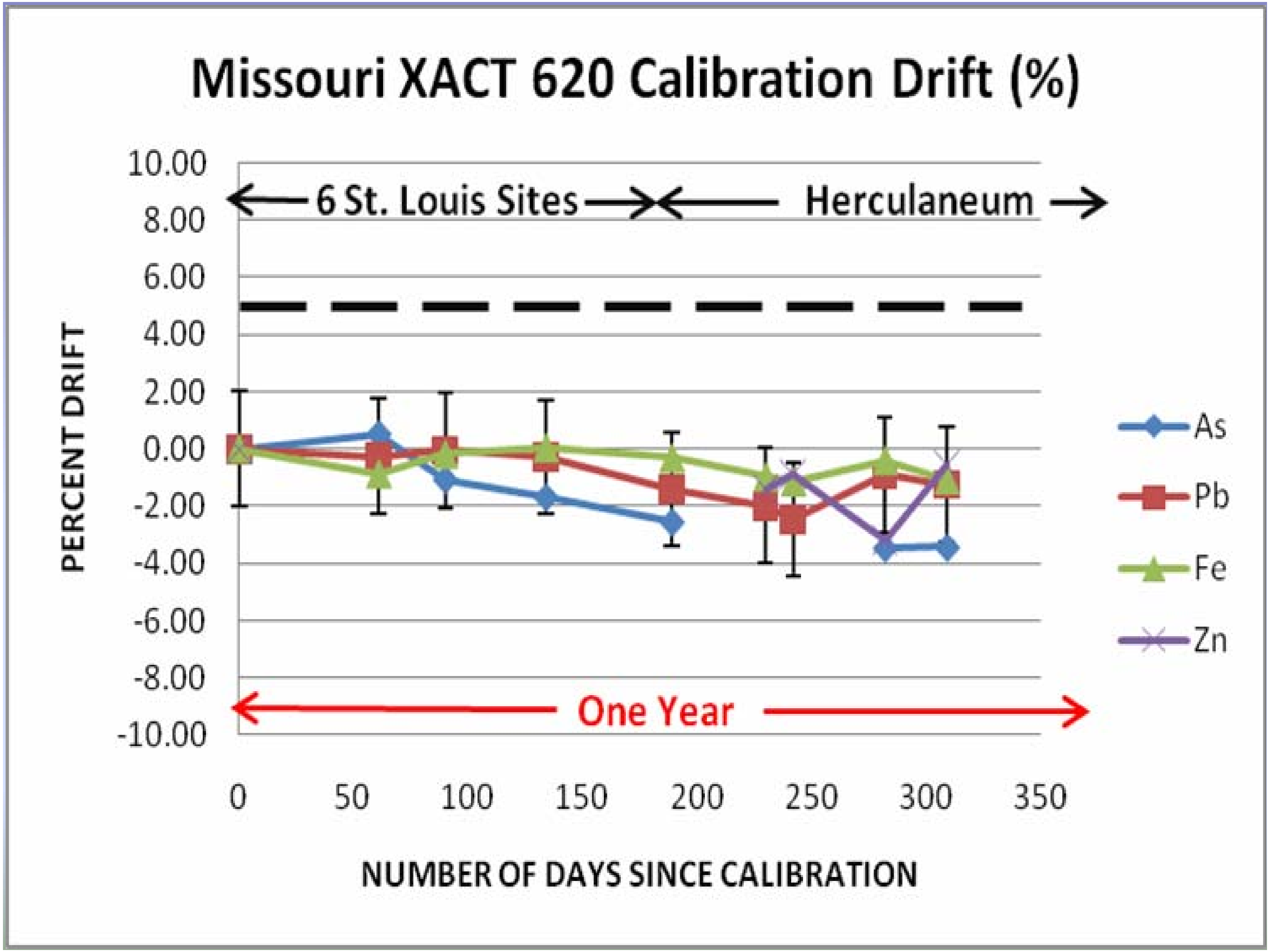


Xact vs. WUSTL HiVol

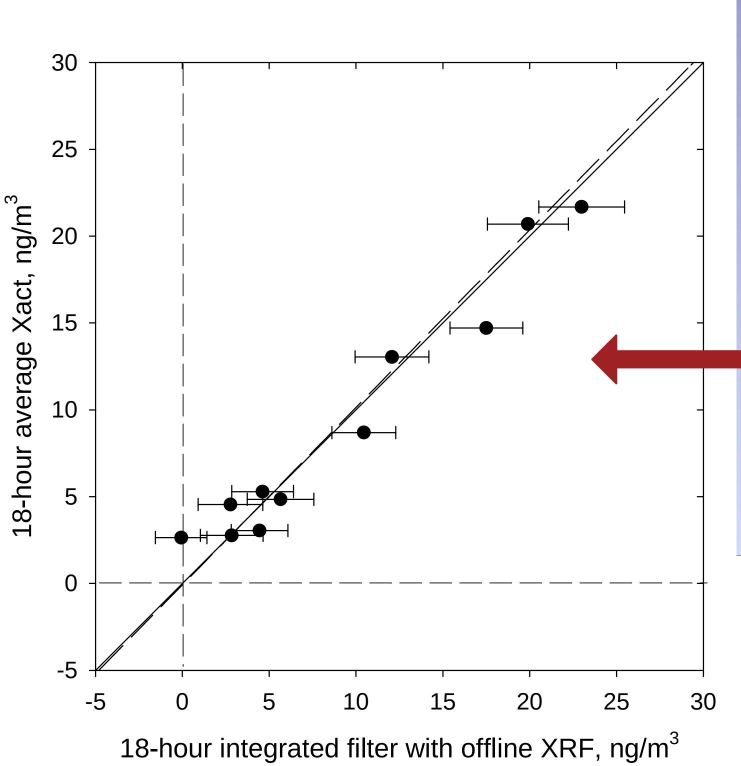
Dec 2008 / Jan 2009



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


Missouri XACT 620 Calibration Drift (%)
6 St. Louis Sites
Herculaneum
One Year
PERCENT DRIFT
10.00
8.00
6.00
4.00
2.00
0.00
-2.00
-4.00
-6.00
-8.00
-10.00
0
50
100
150
200
250
300
350
NUMBER OF DAYS SINCE CALIBRATION
As
Pb
Fe
Zn

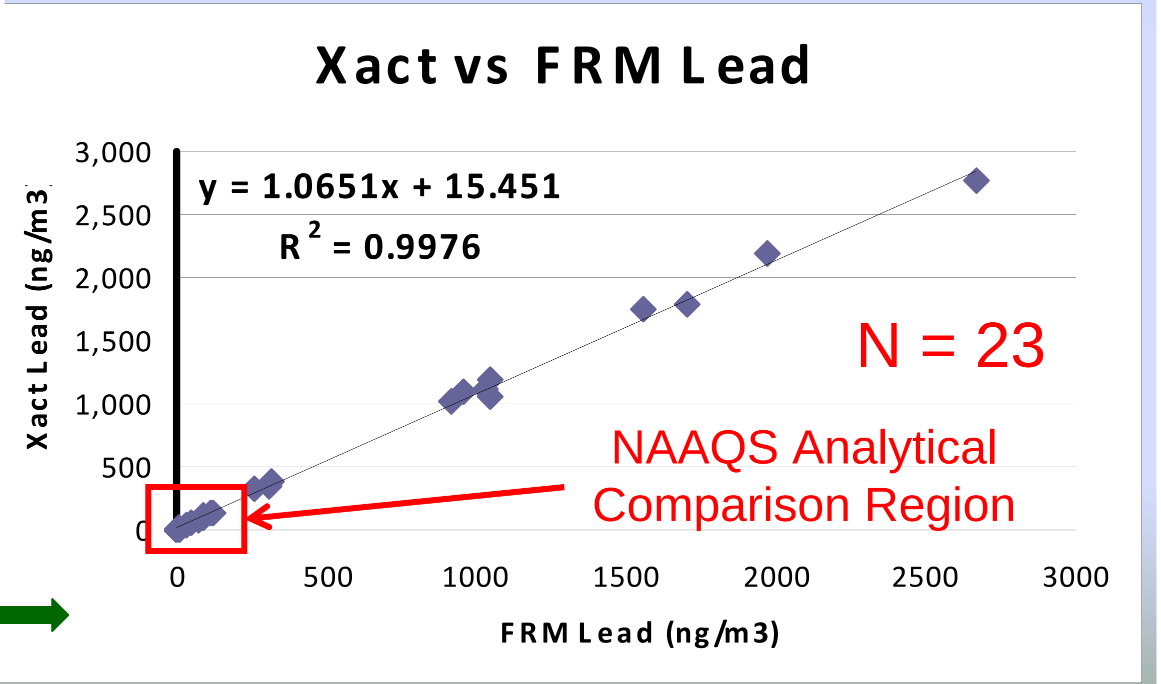
Lead Accuracy Linear Regression



St. Louis, MO

Xact = 1.02 FRM + -0.1

Low Concentrations

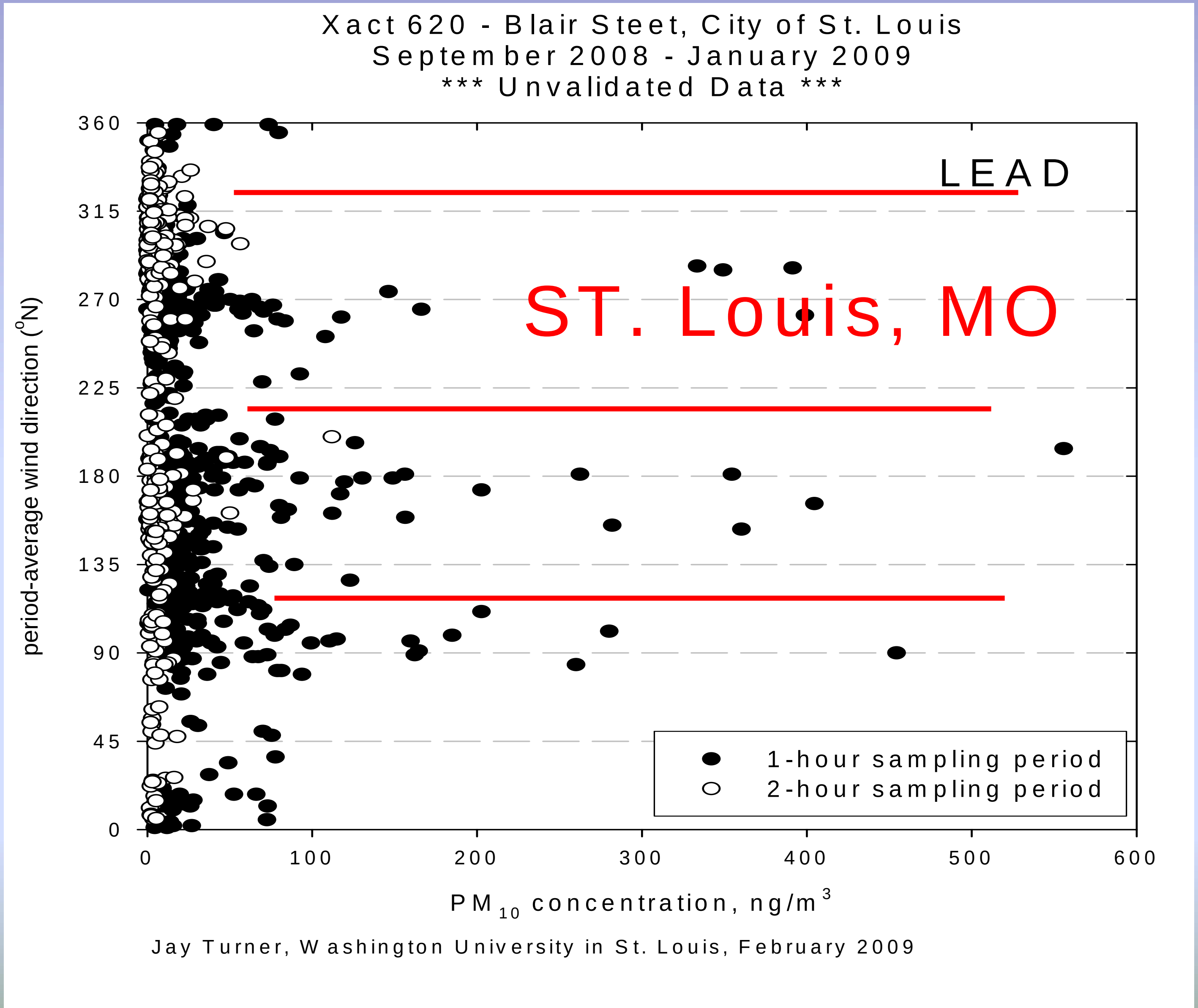


Herculaneum, MO

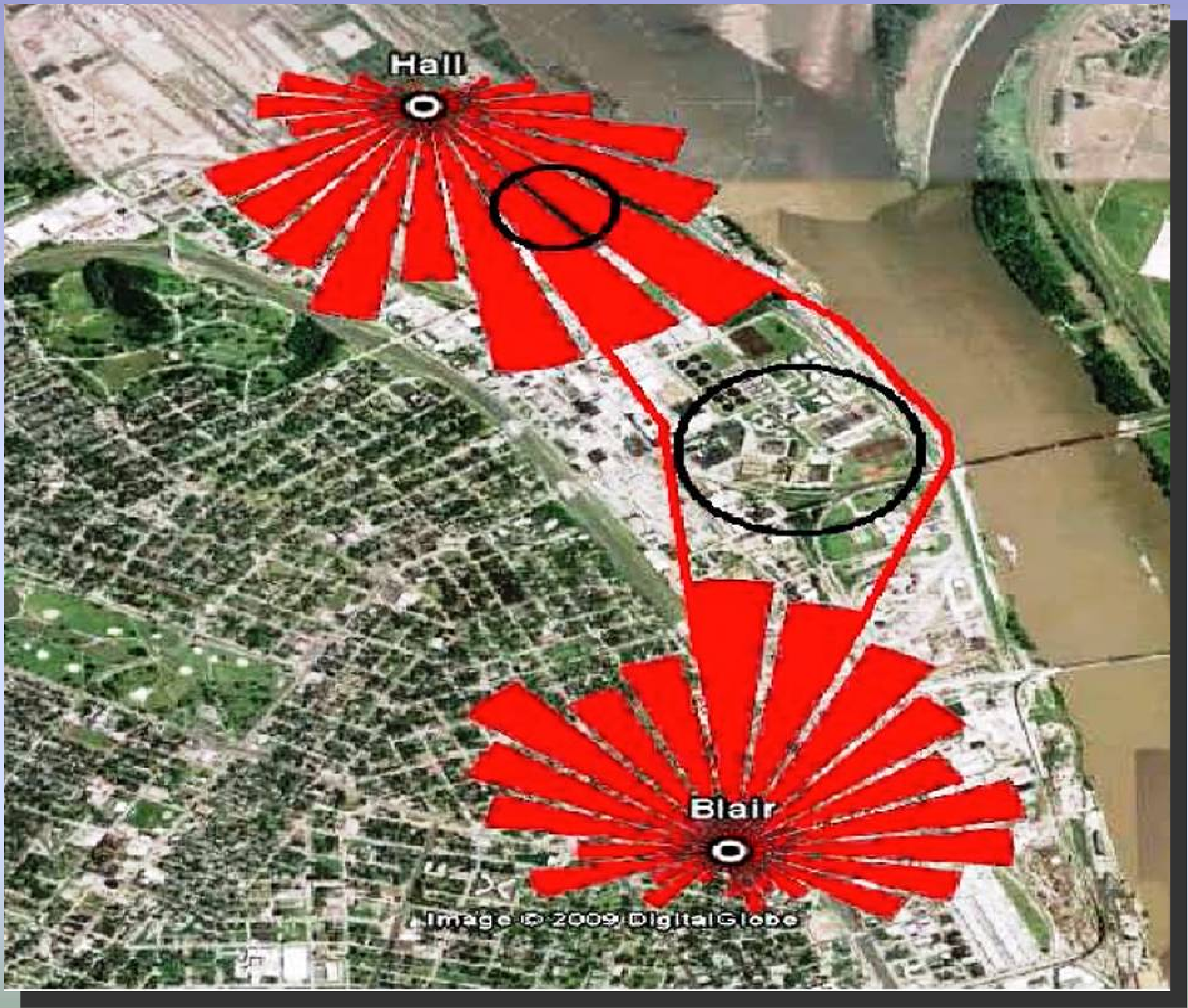
Xact = 1.07 FRM + 15

High Concentrations

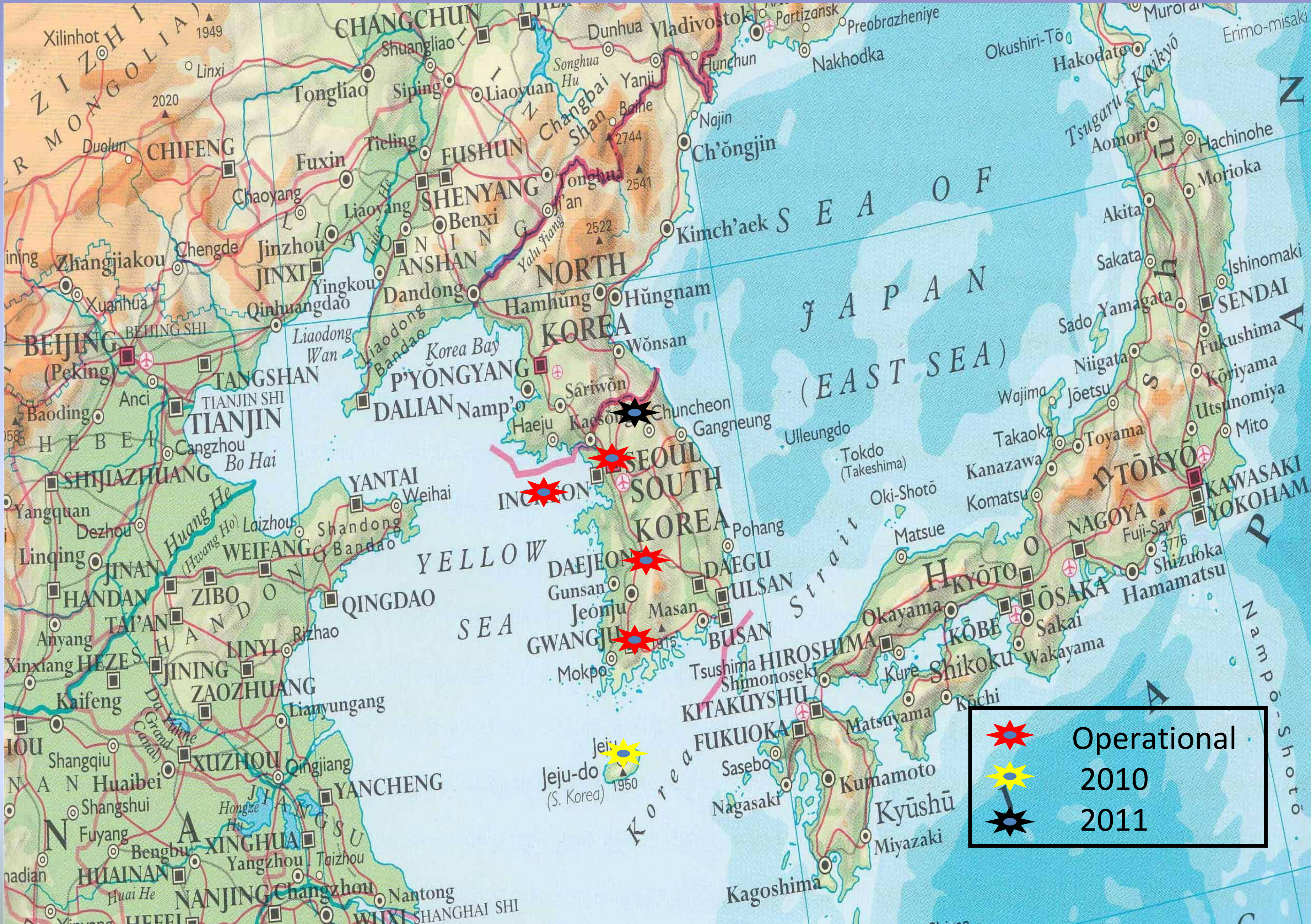
Our Xact 620 in the St. Louis metro area has collected some interesting data as well. This plot shows the possibility that the Xact is detecting three distinct lead sources.



Wind Speed and Direction are Utilized to Determine Origin of Pollution



Korea National Institute of Environmental Research Monitoring Sites



Thank you for your time

I would be happy to answer any questions

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