Field Performance Evaluation of the Cooper Environmental Services Ambient Metals Monitor (Xact 620) for Near-Real Time PM_{10} Metals Monitoring

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High Time Resolution Multi-Metals Measurements

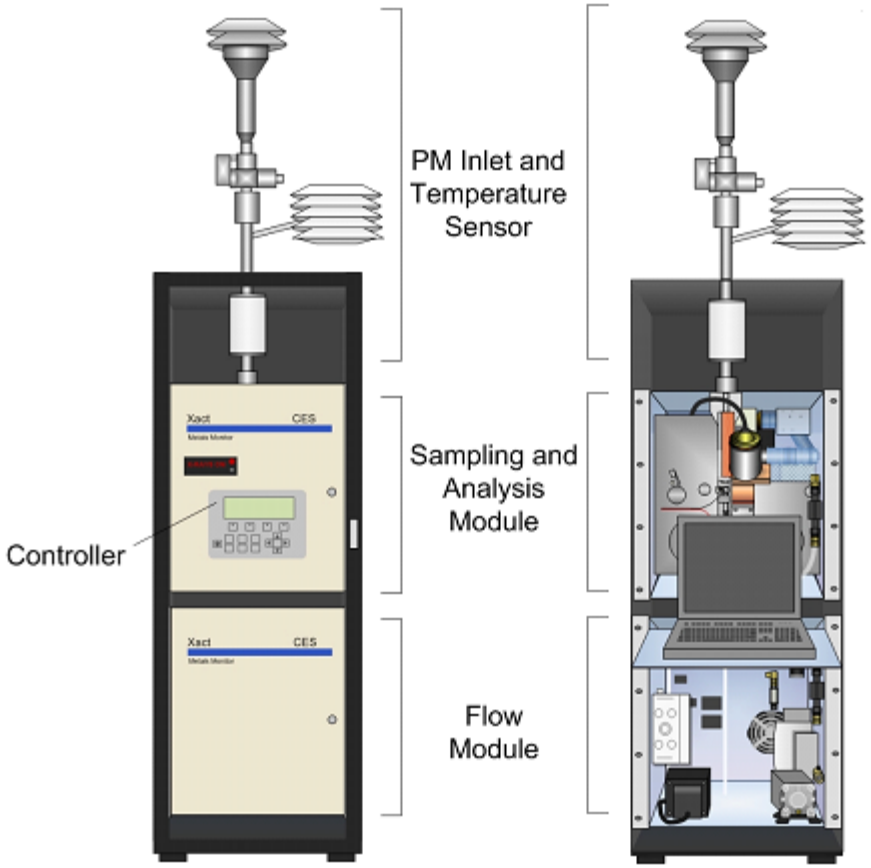
Field sampling, laboratory analysis

- Serial collection of filter samples
- Davis Rotating-drum Unit for Monitoring (DRUM)
- Semicontinuous Elements in Aerosol Sampler (SEAS)

Online, semi-continuous measurements

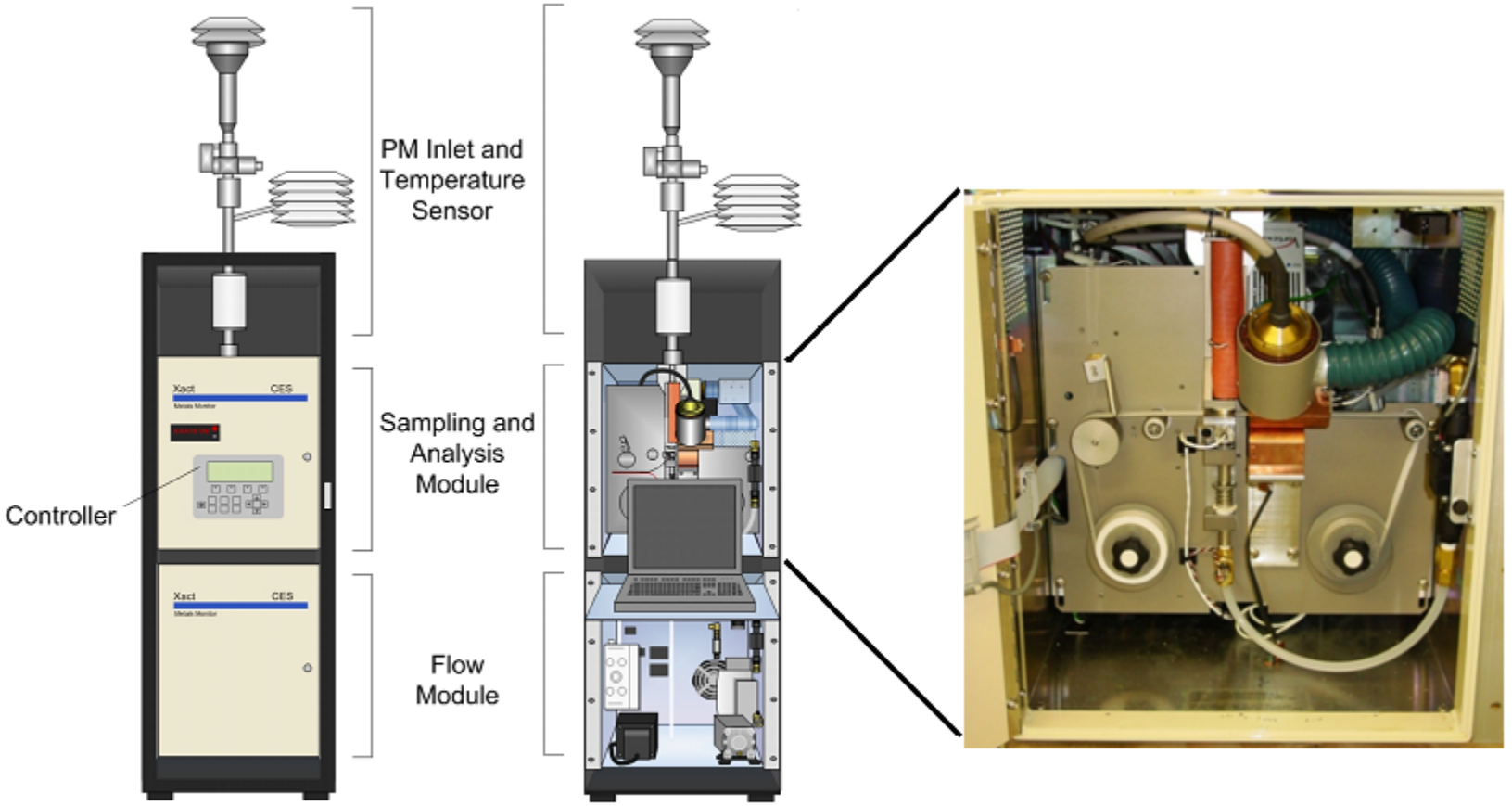
- Single particle mass spectrometry (e.g. TSI ATOFMS)
- Aerosol mass spectrometer (Aerodyne AMS)
  - no refractory elements
- Cooper Environmental Services field XRF analyzer

Cooper Environmental Services (CES) Xact 620

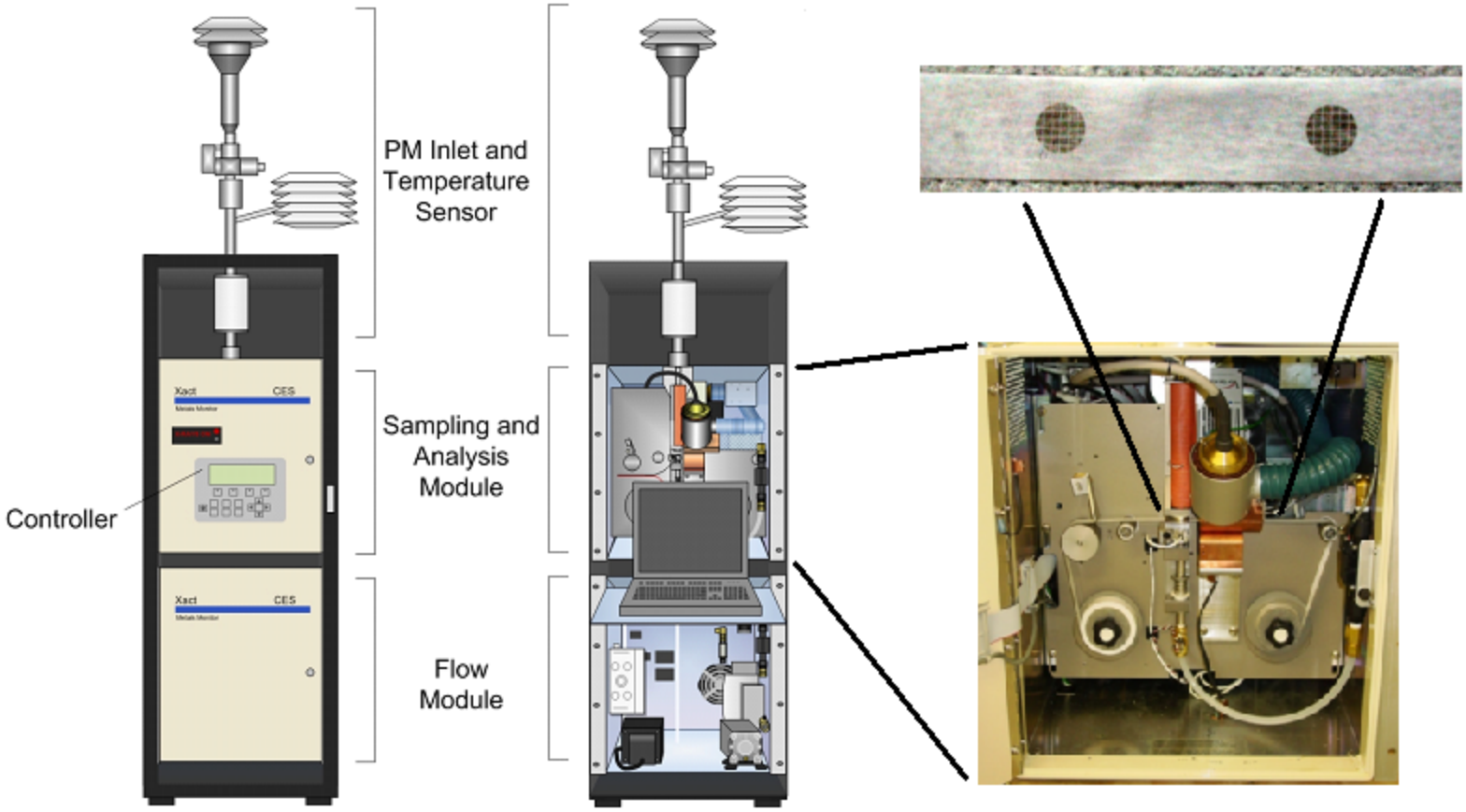


- Xact series
  - I: Stack Sampling
  - II: Fenceline Monitoring
  - III: Ambient Monitoring

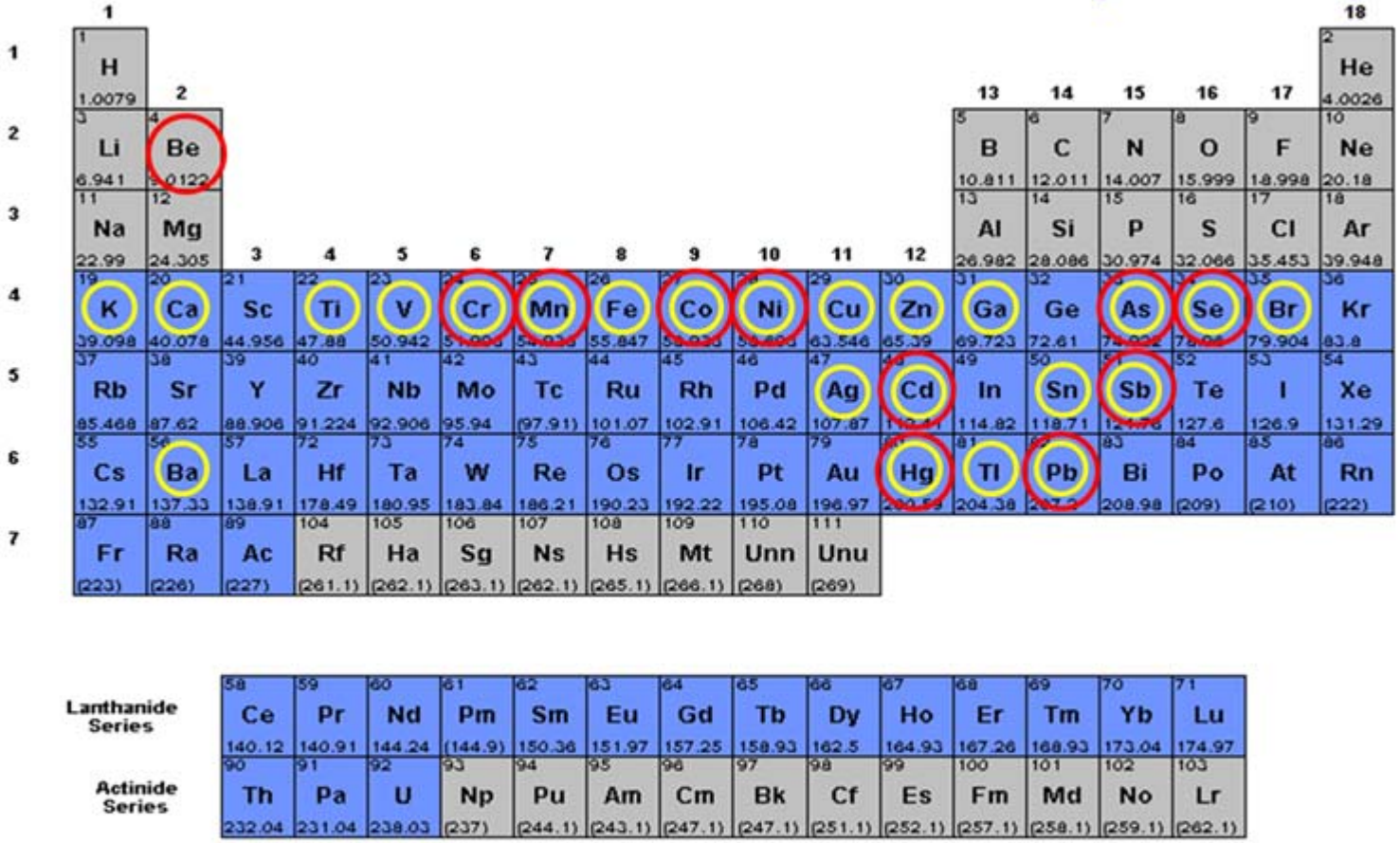
Cooper Environmental Services (CES) Xact 620



Cooper Environmental Services (CES) Xact 620



ELEMENTS THE XACT CAN MEASURE (IN BLUE)



measured by Xact in this study

EPA Air Toxics PM metals

Xact Performance Evaluation

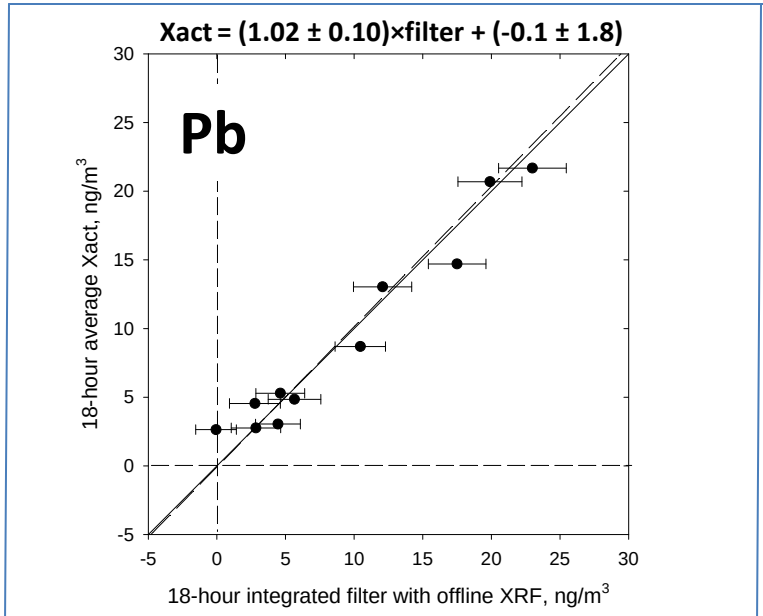
LowVol PM_{10} (FRM) / Teflon filter

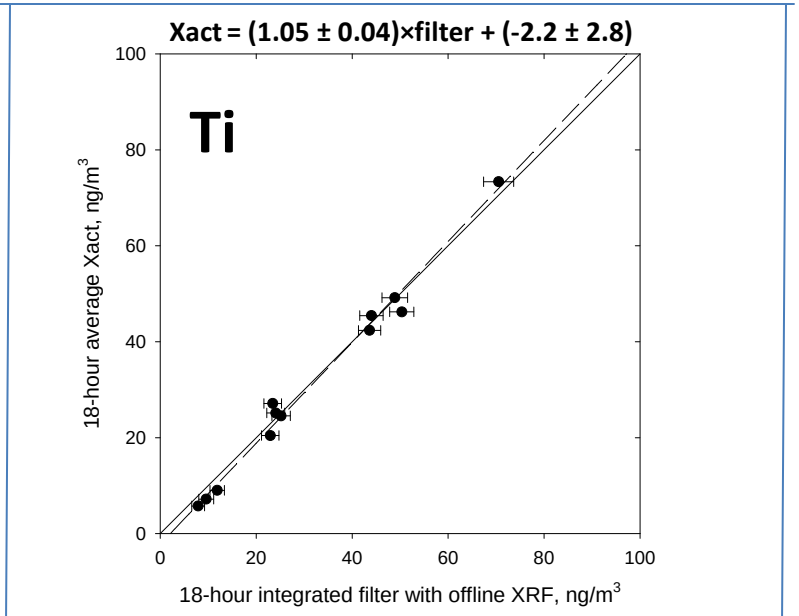
XRF: Ca, Fe, K, Mn, Pb, Ti…

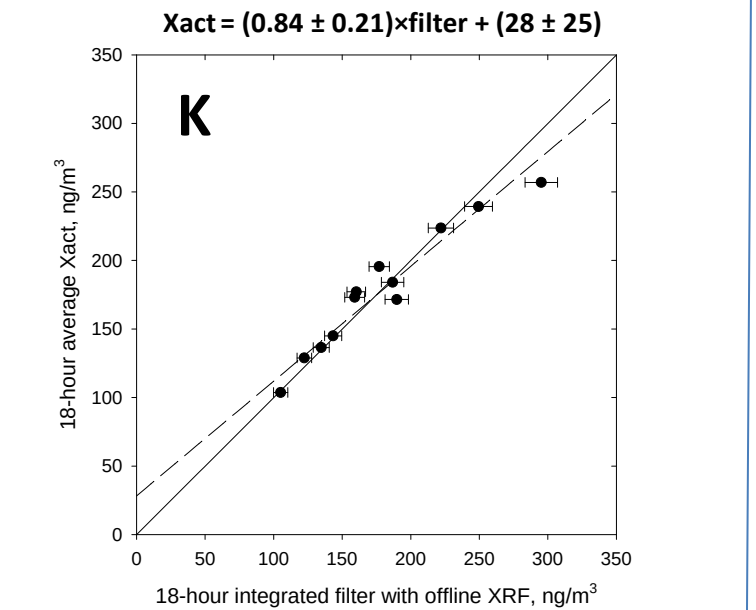
HiVol PM_{10} / quartz filter
NATTS digestion protocol

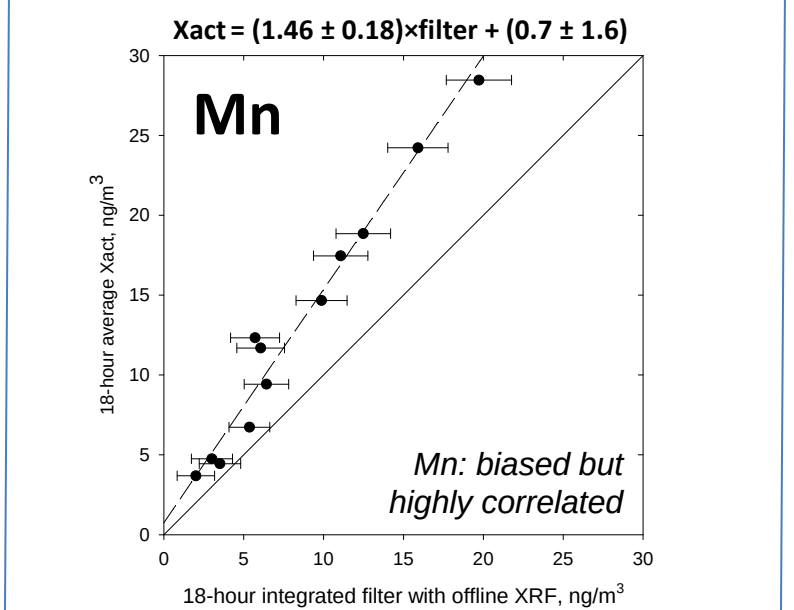
ICP-MS: As, Pb, Se…

Xact vs. LowVol PM10 FRM / XRF

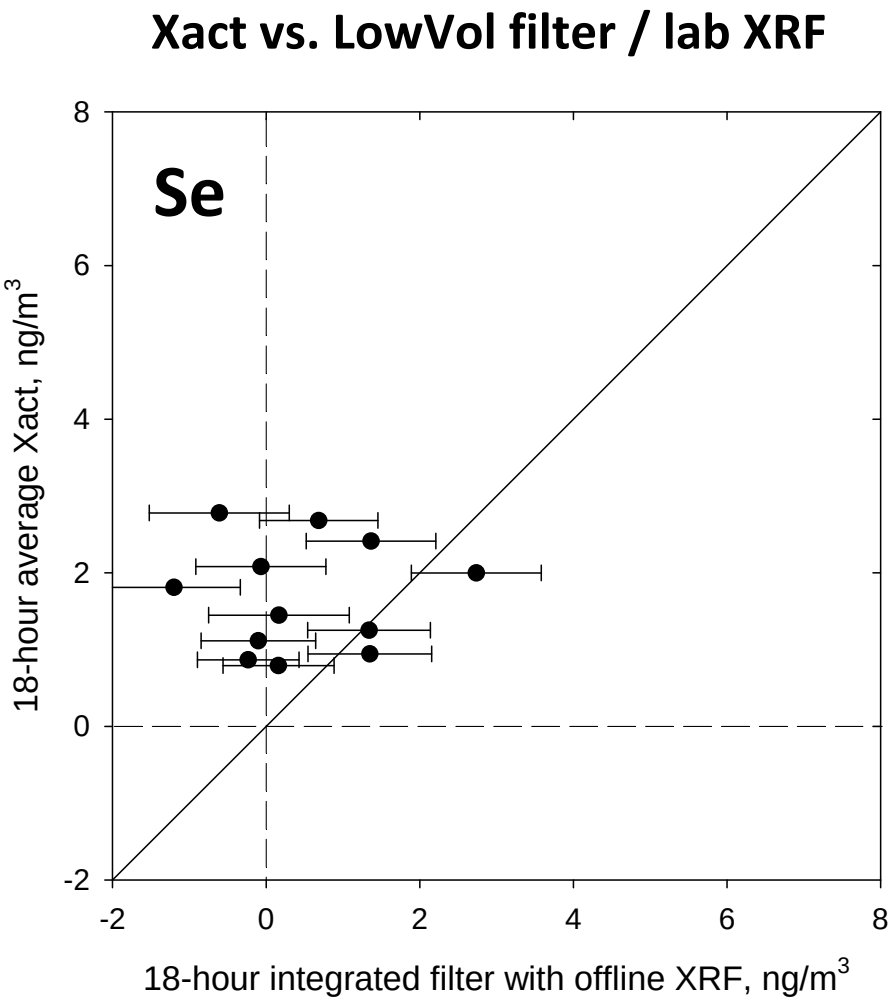




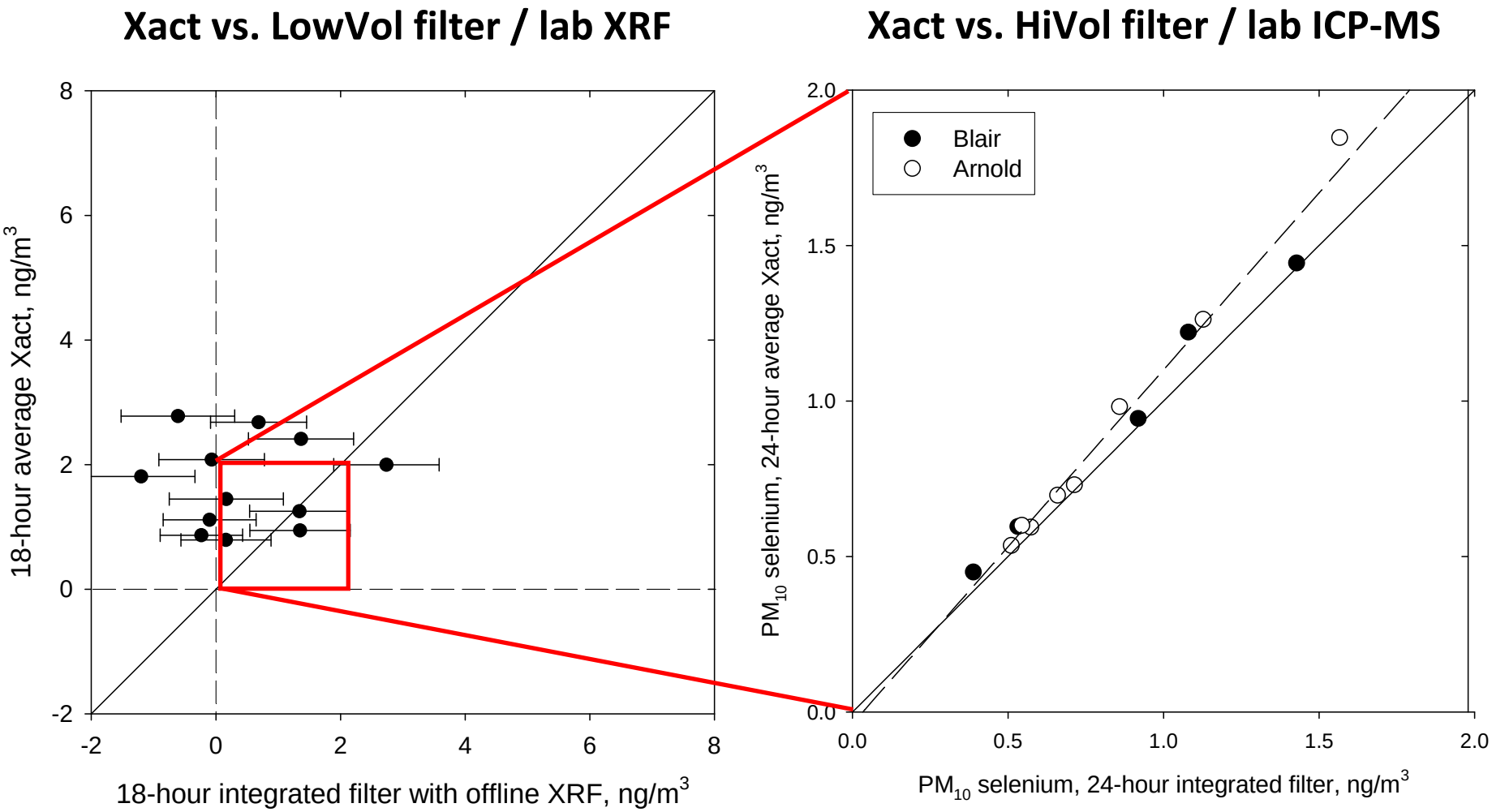




Xact vs. LowVol PM10 FRM / XRF



Selenium: Xact vs. Filter-Based Measurements



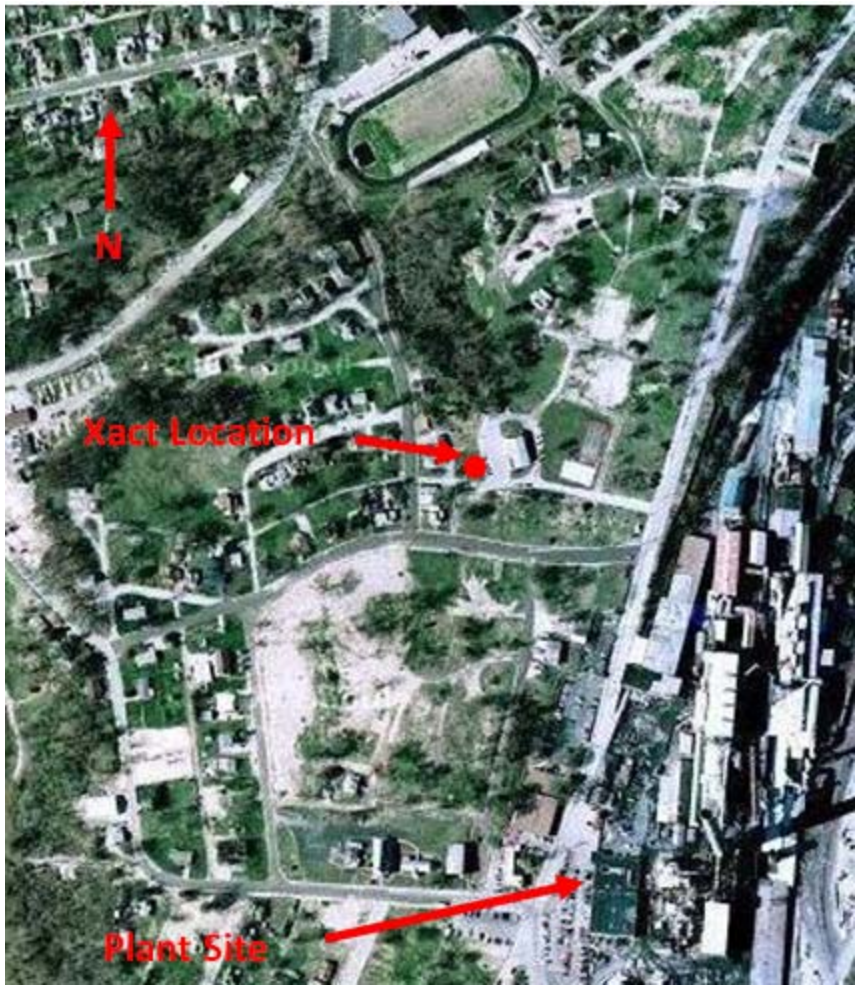
Se: favorable comparison between Xact and PM_{10} HiVol samples with analysis by ICP-MS

Collocated Study - Opportunities

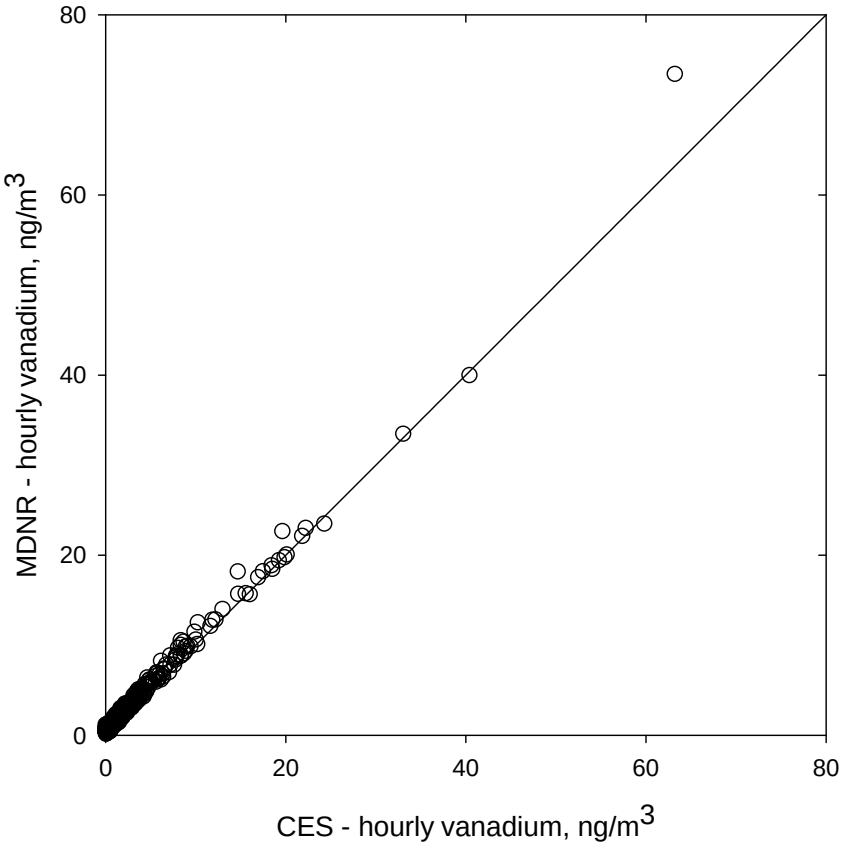
- One month of collocated Xact data collected near the Doe Run primary lead smelter in Herculaneum, MO
- Examine collocated precision and practicable detection limits for various metals
- Uncertainties for source apportionment modeling (CMB, PMF)
- Missouri DNR instrument optimized for As, Hg, and Pb at remote areas

Collocated Study - Challenges

- High concentrations of lead and other elements observed
- Spectral interferences by lead and/or other elements in the plumes
- Removal of instrument-to-instrument bias for collocated precision



Collocated XACT – Vanadium (N=606)



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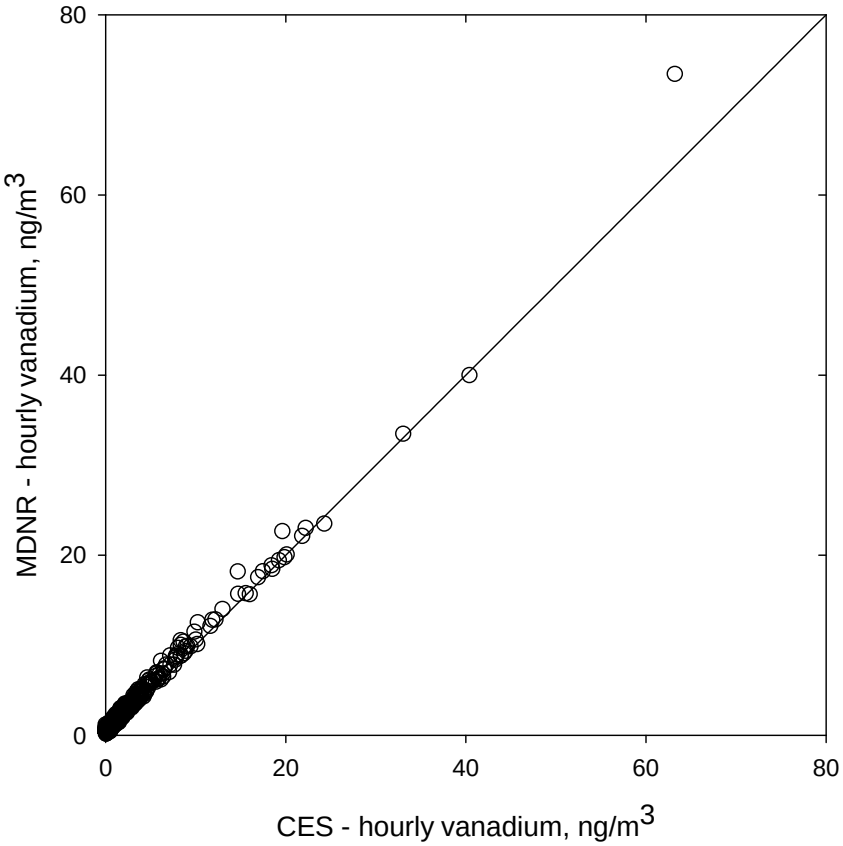
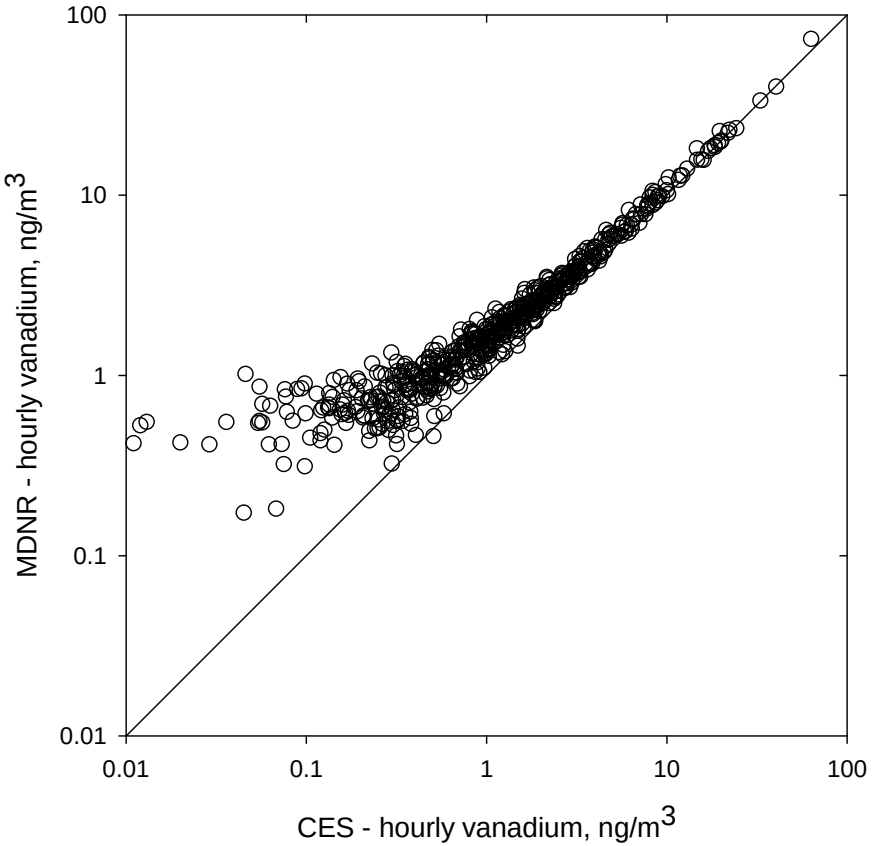


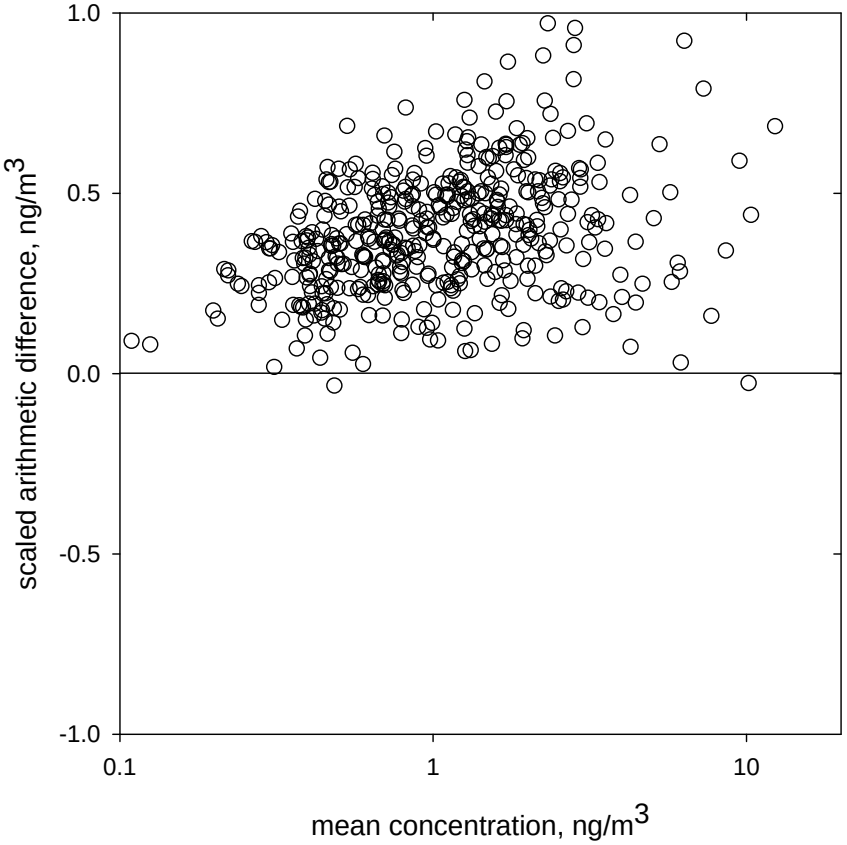


- Instrument-to-instrument Bias highlighted
- Similar trends seen for Cr, Mn, Ni and Ba

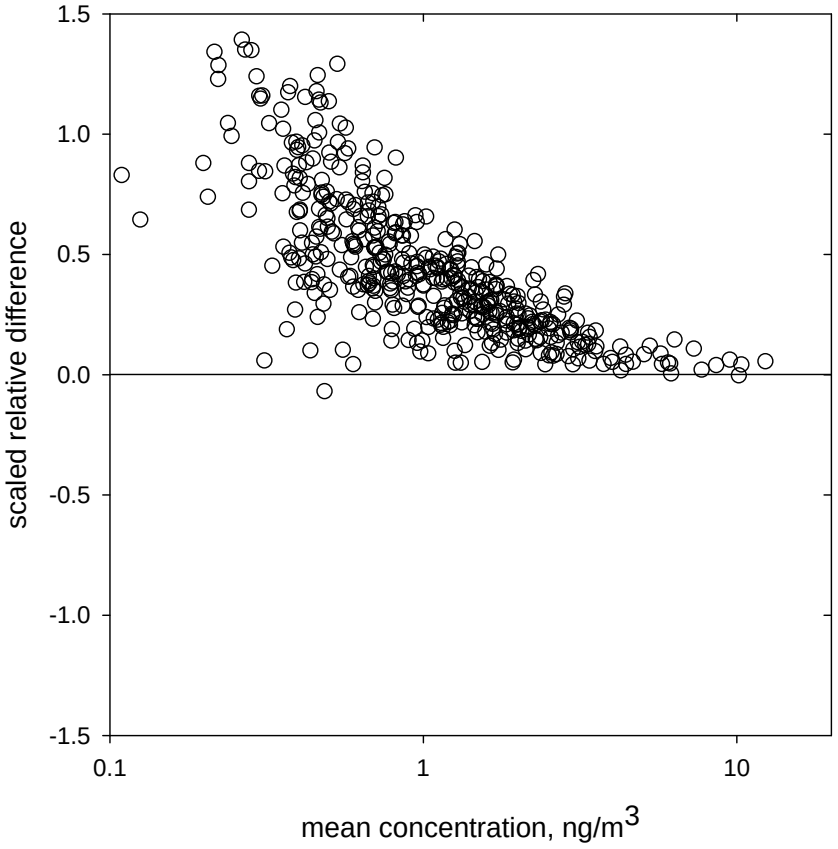
Collocated XACT – Vanadium

- Removed records with zero V concentration
- Removed records for top 25th percentile Pb

scaled arithmetic difference



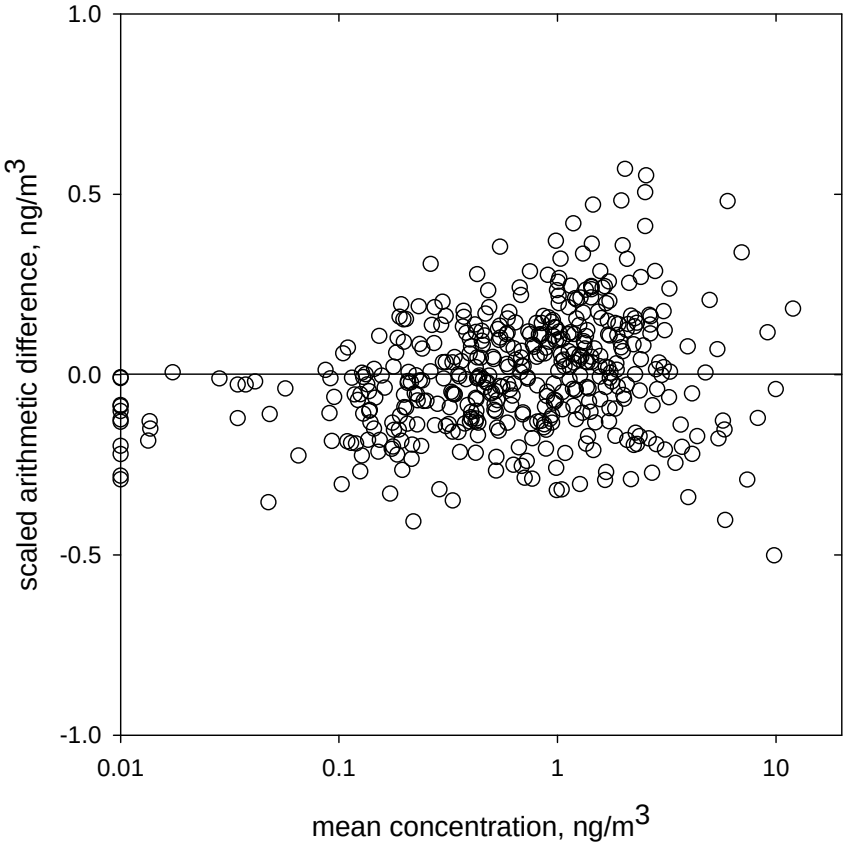
scaled relative difference



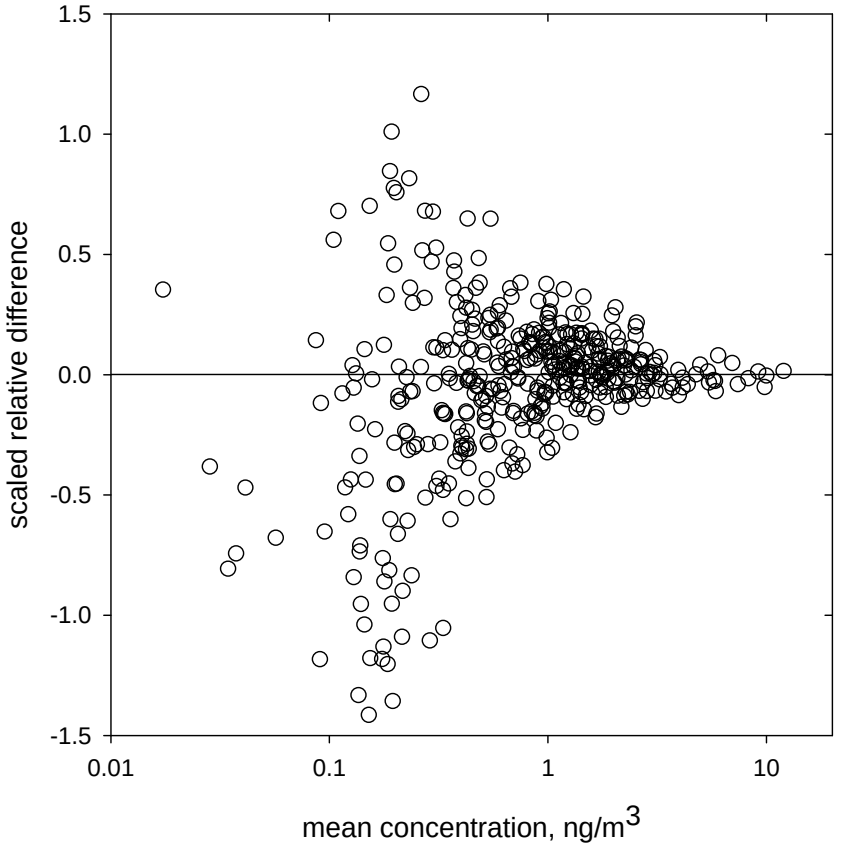
- Collocated precision = 0.42ng/m^3 (29%)

Collocated XACT – Vanadium

scaled arithmetic difference



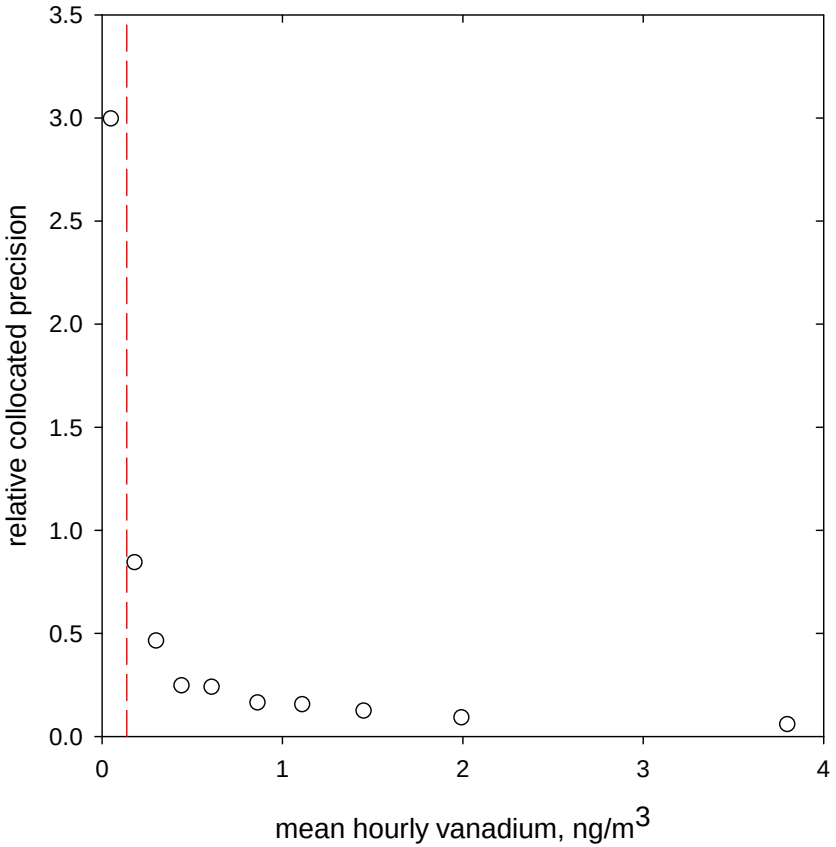
scaled relative difference



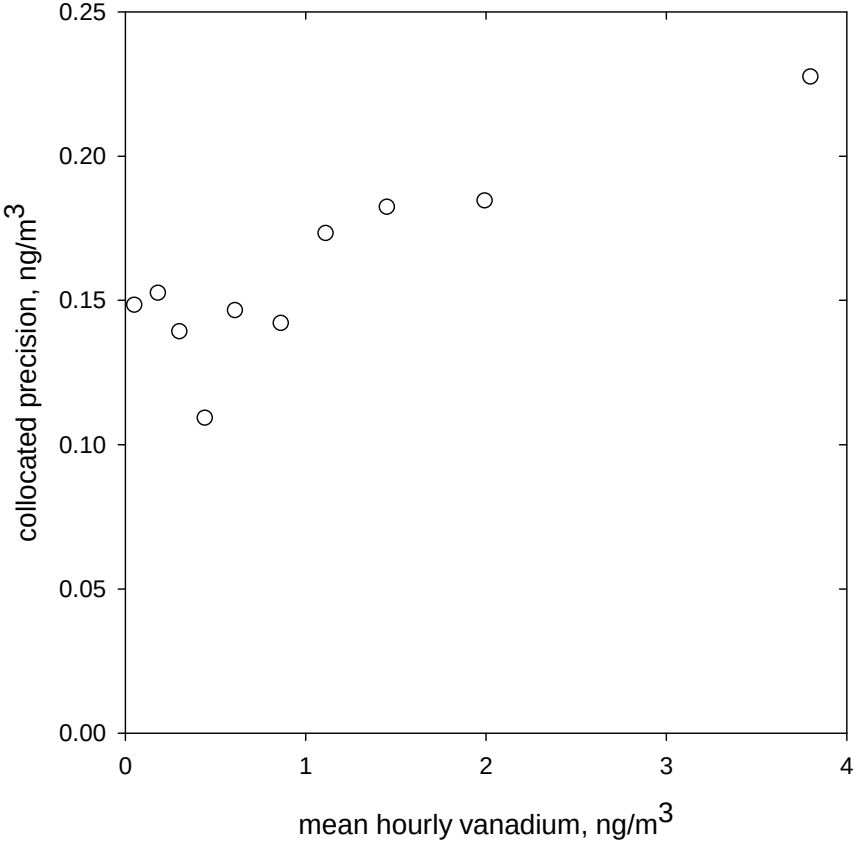
- Regression-adjusted MDNR data
- Collocated precision = 0.17 ng/m^3 (14%)

Collocated XACT – Vanadium

relative collo precision



absolute collo precision



- Binned collocated precision (33 records/bin)

Summary

- V, As, Ba, Cd, Cr, Mn, Ni, Se, Ti, Zn
  - Relative precision better than 10% at higher concentrations (exception Cd)
  - Practicable MDL greater than reported MDL
  - No data near MDL for As, Se, Ti, Zn
- Ca, Fe, K
  - Data range well over MDL
    (e.g. 5^{th} percentile Ca>300*MDL)
  - Relative precision better than 10% over entire data range
- Co, Hg, Sn, Sb
  - Removal of high Pb, leaves no trend in lower concentration data

Next steps ...

- XRF analysis of additional lowvol filters
- ICP analysis of lowvol filters
- Examine spectral interference due to lead on other elements
- Analysis of covariance of error

Acknowledgements

- Missouri Department of Natural Resources
  - Jim Brunnert, Celeste Koon, Will Wetherell
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- U.S. EPA / Region VII
  - Gwen Yoshimura
- Washington University
  - Stephen Feinberg, Victoria Martin

Xact 620 Minimum Detection Limits (ng/m3)

Element	Atomic No.	4 hour	3 hour	2 hour	1 hour	30 min.	15 min.
Si	14	0.018	0.028	0.051	0.144	0.41	1.15
K	19	0.101	0.156	0.287	0.811	2.29	6.49
Ca	20	0.040	0.062	0.113	0.321	0.91	2.56
Ti	22	0.022	0.034	0.063	0.177	0.50	1.42
V	23	0.017	0.026	0.048	0.137	0.39	1.10
Cr	24	0.014	0.021	0.039	0.109	0.31	0.87
Mn	25	0.008	0.013	0.024	0.067	0.19	0.54
Fe	26	0.010	0.015	0.028	0.080	0.23	0.64
Co	27	0.006	0.009	0.017	0.047	0.13	0.37
Ni	28	0.004	0.007	0.013	0.035	0.10	0.28
Cu	29	0.008	0.012	0.023	0.064	0.18	0.51
Zn	30	0.005	0.008	0.015	0.043	0.12	0.35
Ga	31	0.003	0.005	0.008	0.024	0.07	0.19
As	33	0.003	0.005	0.010	0.027	0.08	0.22
Se	34	0.004	0.006	0.011	0.032	0.09	0.26
Pd	46	0.070	0.108	0.198	0.560	1.58	4.48
Ag	47	0.103	0.158	0.290	0.821	2.32	6.57
Cd	48	0.169	0.260	0.479	1.353	3.83	10.83
Sn	50	0.318	0.489	0.899	2.543	7.19	20.35
Sb	51	0.083	0.128	0.235	0.665	1.88	5.32
Ba	56	0.050	0.076	0.140	0.397	1.12	3.18
Pt	78	0.006	0.009	0.017	0.048	0.14	0.39
Au	79	0.006	0.009	0.017	0.048	0.14	0.38
Hg	80	0.005	0.008	0.015	0.043	0.12	0.35
Tl	81	0.006	0.009	0.016	0.046	0.13	0.37
Pb	82	0.007	0.010	0.019	0.053	0.15	0.43
Bi	83	0.007	0.011	0.019	0.055	0.16	0.44

[a]Based on US EPA IO Method 3.3 one sigma interference free.

Optimizing Sampling Time Interval