


Semi-continuous metals monitoring in Ohio industrial communities

Motria Caudill, PhD
USEPA Region 5



Why are we interested in new metals monitoring techniques in Region 5?

- Industrial Midwest disproportionately impacted by metallurgic industry
 - 29 NAAQS source-oriented lead monitors.
 - Multiple communities with elevated neurologic noncancer risk from manganese.
- Emissions inventories are imperfect and incomplete.
- Ambient monitoring can be very time- and resource-intensive.



Existing technology vs. new



Traditional filter-based

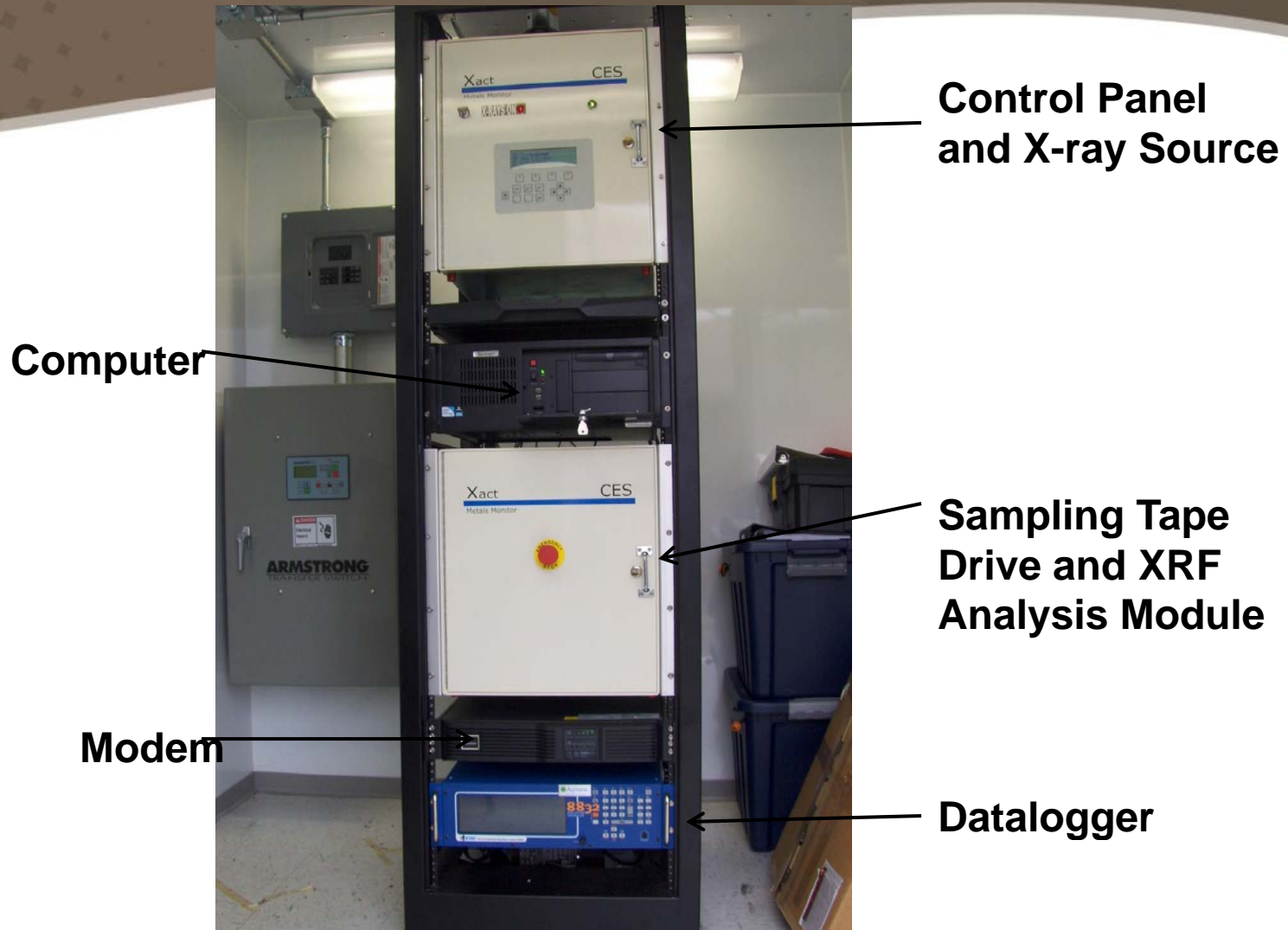
- 24-hour integrated sample
- Weeks lag time for lab results
- Good for chronic exposure and long term studies



New generation semi-continuous

- 1-hour integrated sample
- Near real-time metals data via built-in analytical instrument
- Can evaluate short-term peak exposures to toxics
- Match data to hourly wind direction to help ID sources
- Quick decision making allows for earlier risk reduction

Pall Corp. Xact 625 Fence-line Monitor



Xact Tape Deposits




Deposit Area Used = 0.75 cm^2

Elements detected by Xact 625

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	**	104 Rf	105 Ha	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Uub	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo
* Lanthanide Series			57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
** Actinide Series			89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

What's missing:

- Beryllium. All other HAP metals can be measured.
- Certain tracers for soil (Si, Al) and sea salt (Na, Cl).



2011 field test in East Liverpool & Marietta, OH

- Key deliverables:
 - Environmental Technology Verification (ETV) testing of semi-continuous monitor
 - Valuable site-specific data and interpretation for two communities with Mn issue as identified by Ohio EPA, confirmed by USEPA in School Air Toxics effort



Cast of characters

- **EPA-R5** funded testing via **EPA-ORD's** Advanced Monitoring Systems Center ETV program
- **Cooper Environmental Services (CES)** created Xact 625
- **EPA/OAQPS** acquired Xact 625, PM₁₀ sampler, & trailer
- CES sold rights to the Xact 625 to **Pall Corporation**
- **Ohio EPA** provided site operation (trained by Pall)
- **EPA/OAQPS** provided contractor support:
 - **AMEC** - transport, setup, and maintenance of Xact 625
 - **ERG** – PM₁₀ reference sample analysis by ICP-MS
- **Battelle Memorial Institute** prepared and completed peer reviewed test plan, organized communication among parties, analyzed data, and prepared ETV report
- **EPA-R5** to perform additional data analysis (incl. receptor modeling) and draft School Air Toxics follow-up report

EPA-OAQPS trailer

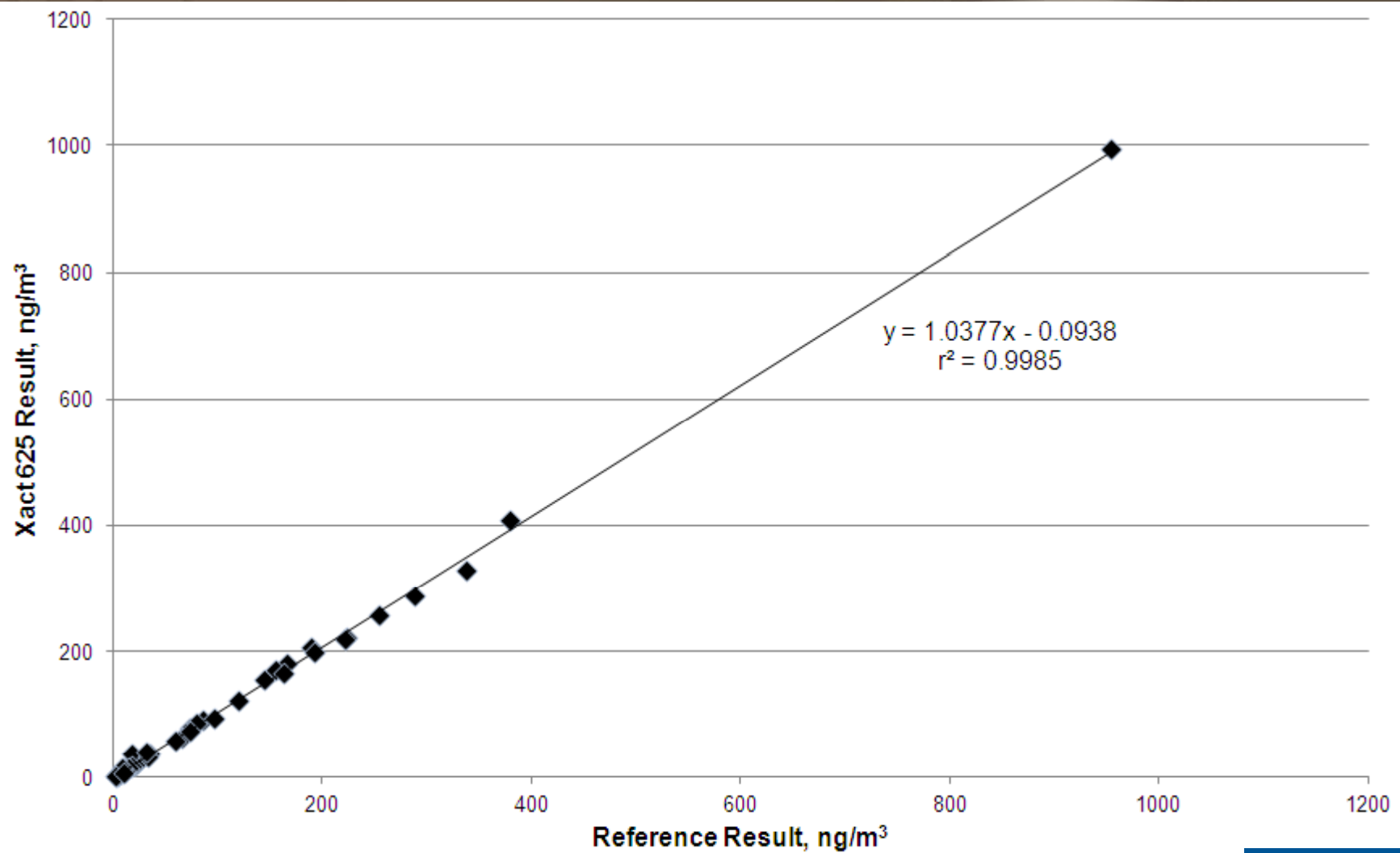




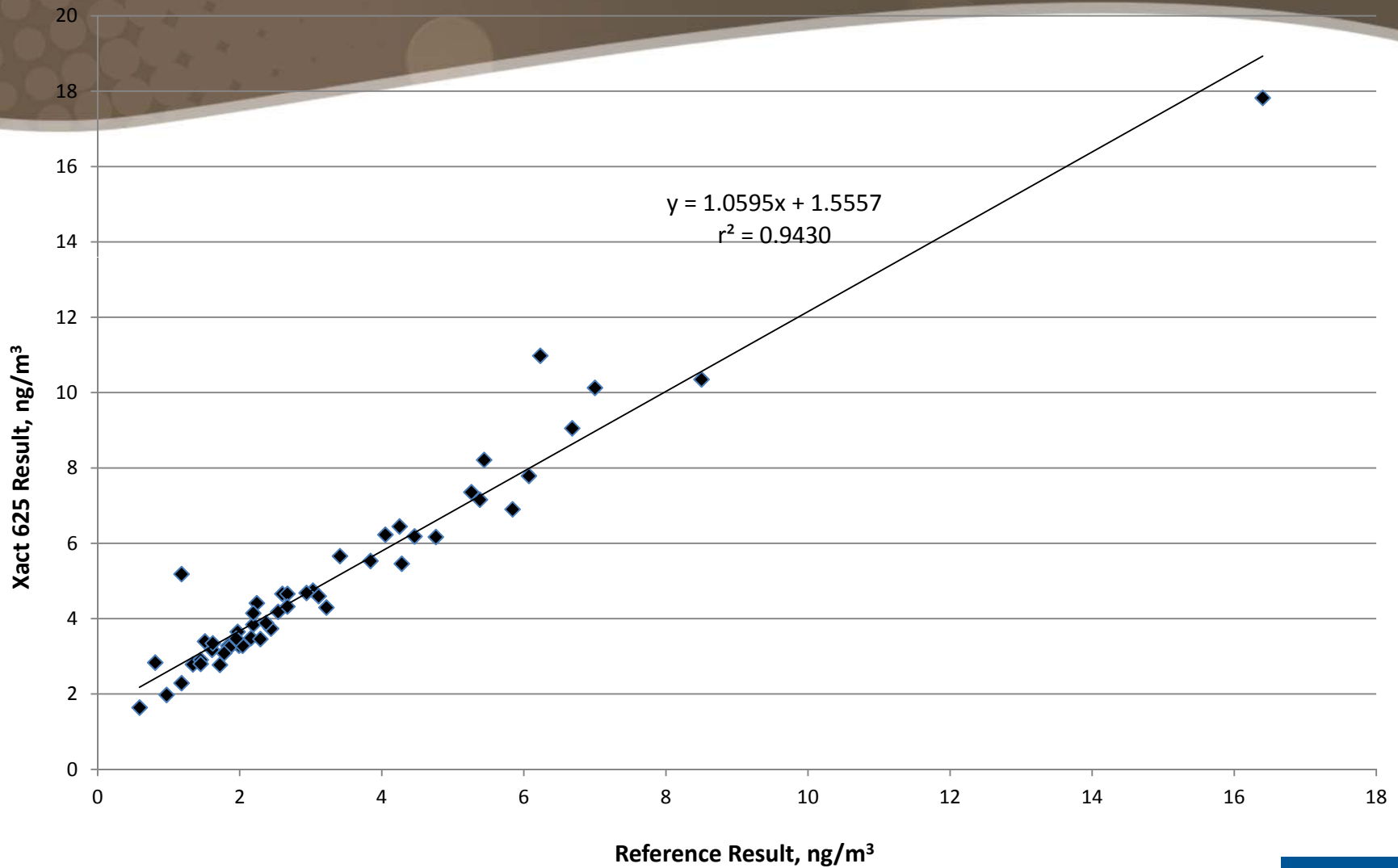
ETV performance parameters

- Comparability
 - Slope and intercept of linear regression between XRF and reference method
- Correlation
 - Coefficient of determination (r^2)
- Bias
 - Percent difference between samples
- Data completeness
- Operational factors (ease of use, maintenance, repair, cost, etc.)
- **Draft** report currently under review

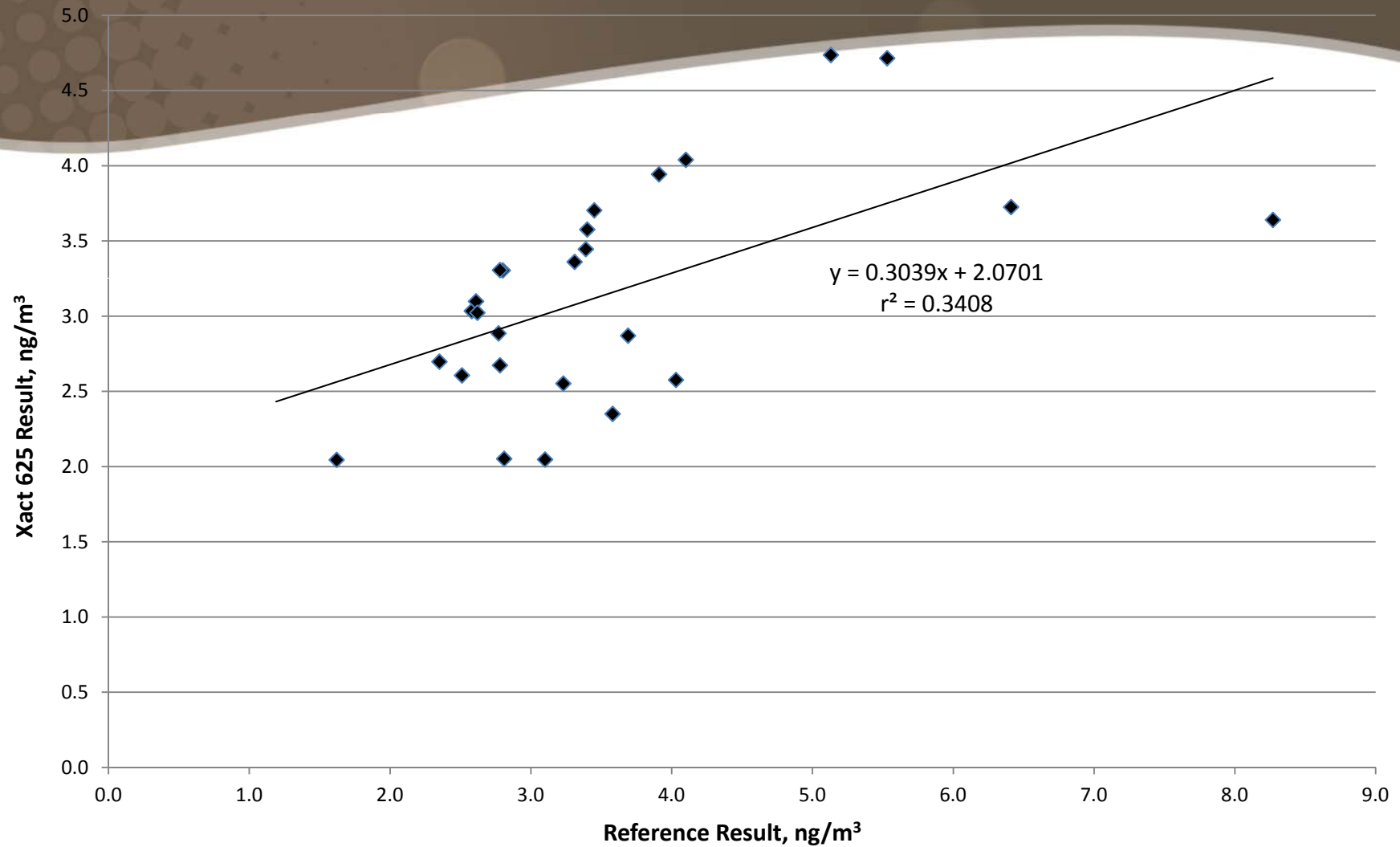
Manganese regression



Lead regression



Copper regression



Regression summary

Metal	Number of Data Points	Slope	Intercept (ng/m³)	Coefficient of Determination (r²)
Ca	47	0.822	-30.64	0.979
Cu	26	0.304	2.07	0.341
Mn	48	1.038	-0.094	0.999
Pb	52	1.060	1.56	0.943
Se	25	0.986	0.012	0.926
Zn	53	0.971	-3.01	0.988


Bias summary

Metal	Number of Data Points	Bias (%)		
		Mean	Median	Range
Ca	47	-31.3	-31.0	-57.0 to -9.8
Cu	26	-5.6	1.2	-56.0 to 26.2
Mn	48	1.12	-0.6	-33.3 to 103
Pb	52	74.8	61.9	8.7 to 339
Se	25	-0.7	-1.3	-15.9 to 17.7
Zn	53	-20.5	-17.9	-59.3 to 27.6



Operational factors

- Minimal operator attention required – changed filter tape ~every 2 weeks
- Readily understandable data files that include flow, T, P, internal diagnostics, and QC checks
- QC checks showed stable operation
- Purchase price \$180,000



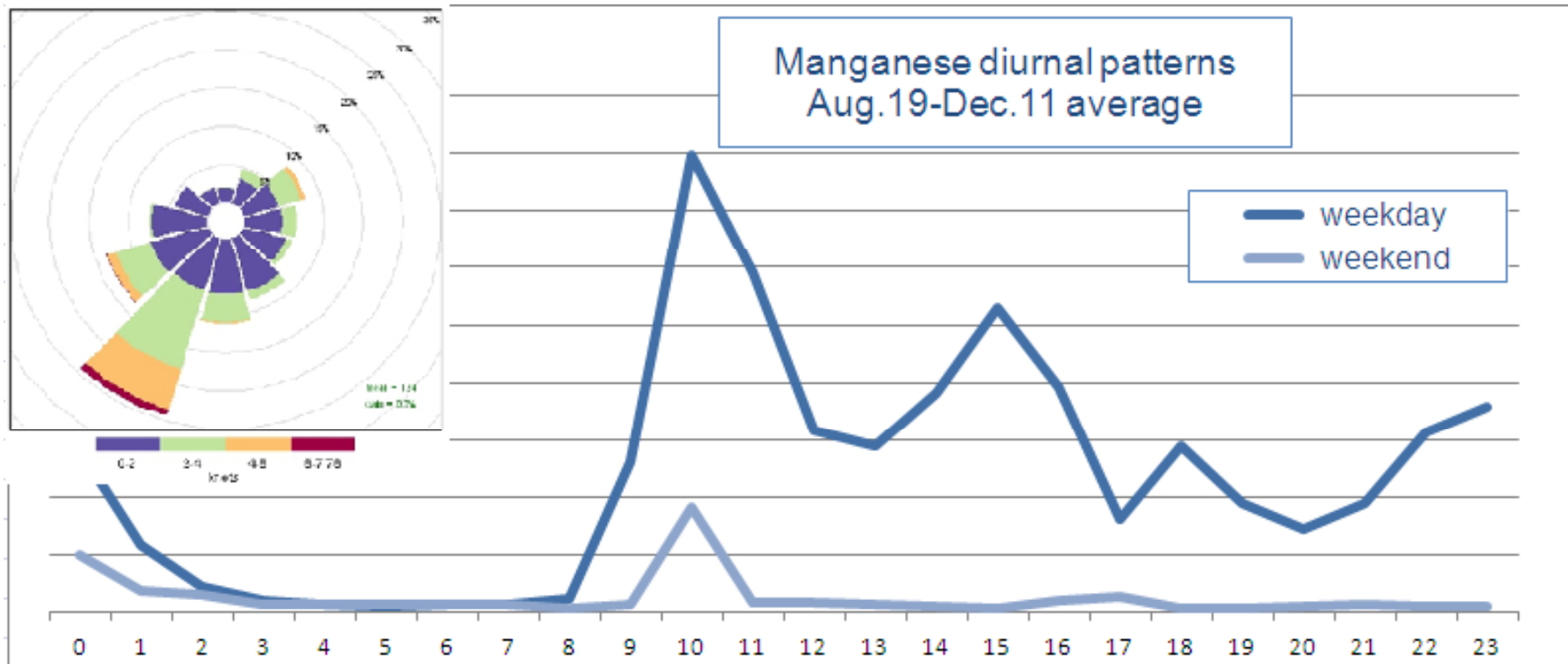
EPA Region 5 data analysis

- East Liverpool dataset failed QA checks due to T&P sensor malfunction, not an Xact issue.
 - Data cannot be validated or used quantitatively
 - However, some qualitative assessment of temporal patterns would be helpful to ongoing Ohio EPA enforcement case
- Marietta dataset was used by Battelle for ETV and will be evaluated by EPA-R5 in School Air Toxics follow-up report.

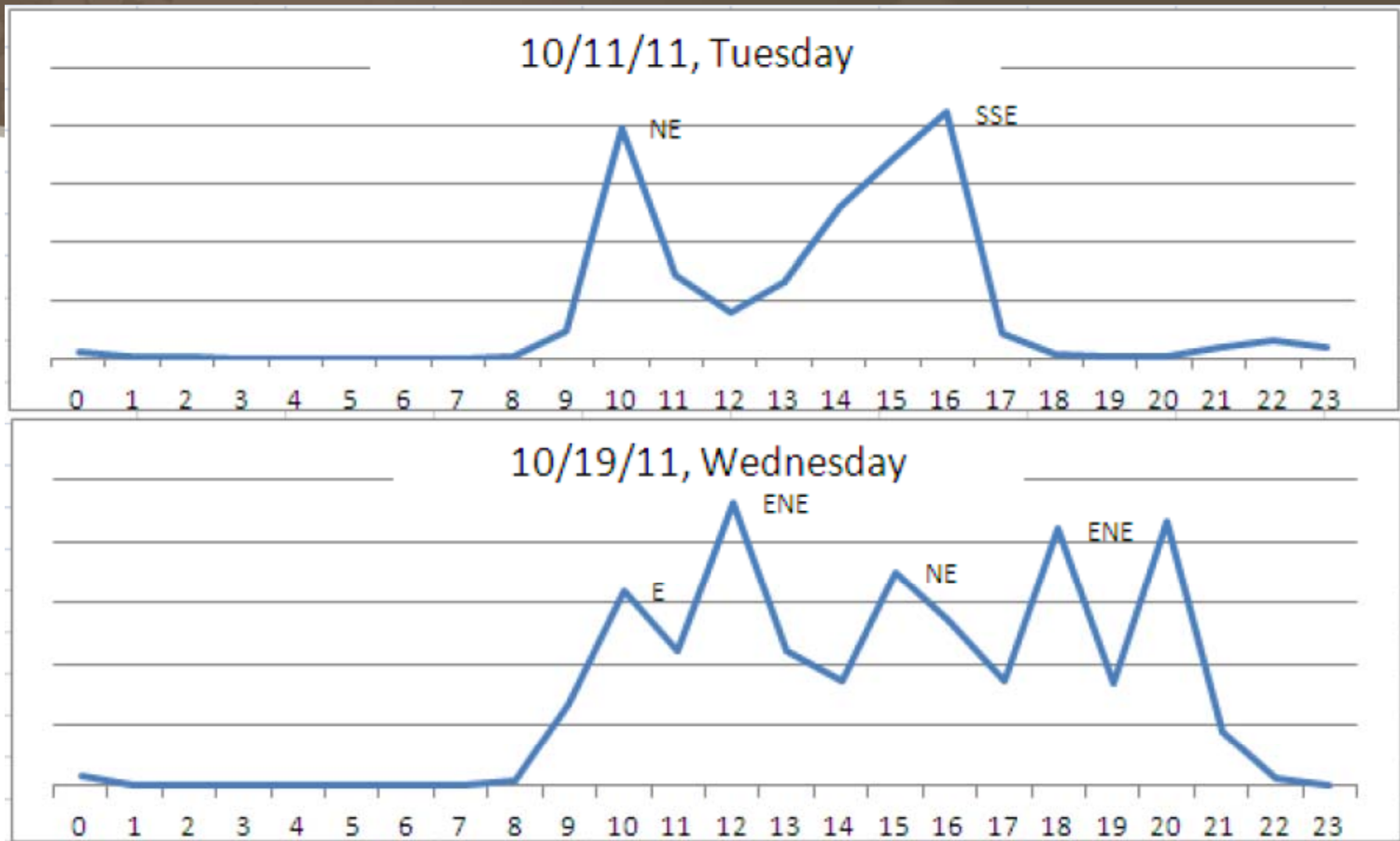
E. Liverpool - pollution rose @fenceline



E. Liverpool – weekday vs. weekend diurnal pattern further implicates source



E. Liverpool – select peak Mn dates





Next steps

- EPA-R5 to draft School Air Toxics follow-up reports for East Liverpool and Marietta, using Xact and filter-based data.
- R5 will perform receptor modeling on Xact dataset using Positive Matrix Factorization (PMF).
- R5 aims to acquire our own Xact to investigate Pb & Mn impacts.