



# Semi-continuous metals monitoring in Ohio industrial communities

Motria Caudill, PhD  
USEPA Region 5

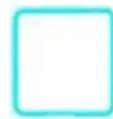


# Why are we interested in new metals monitoring techniques in Region 5?

- 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

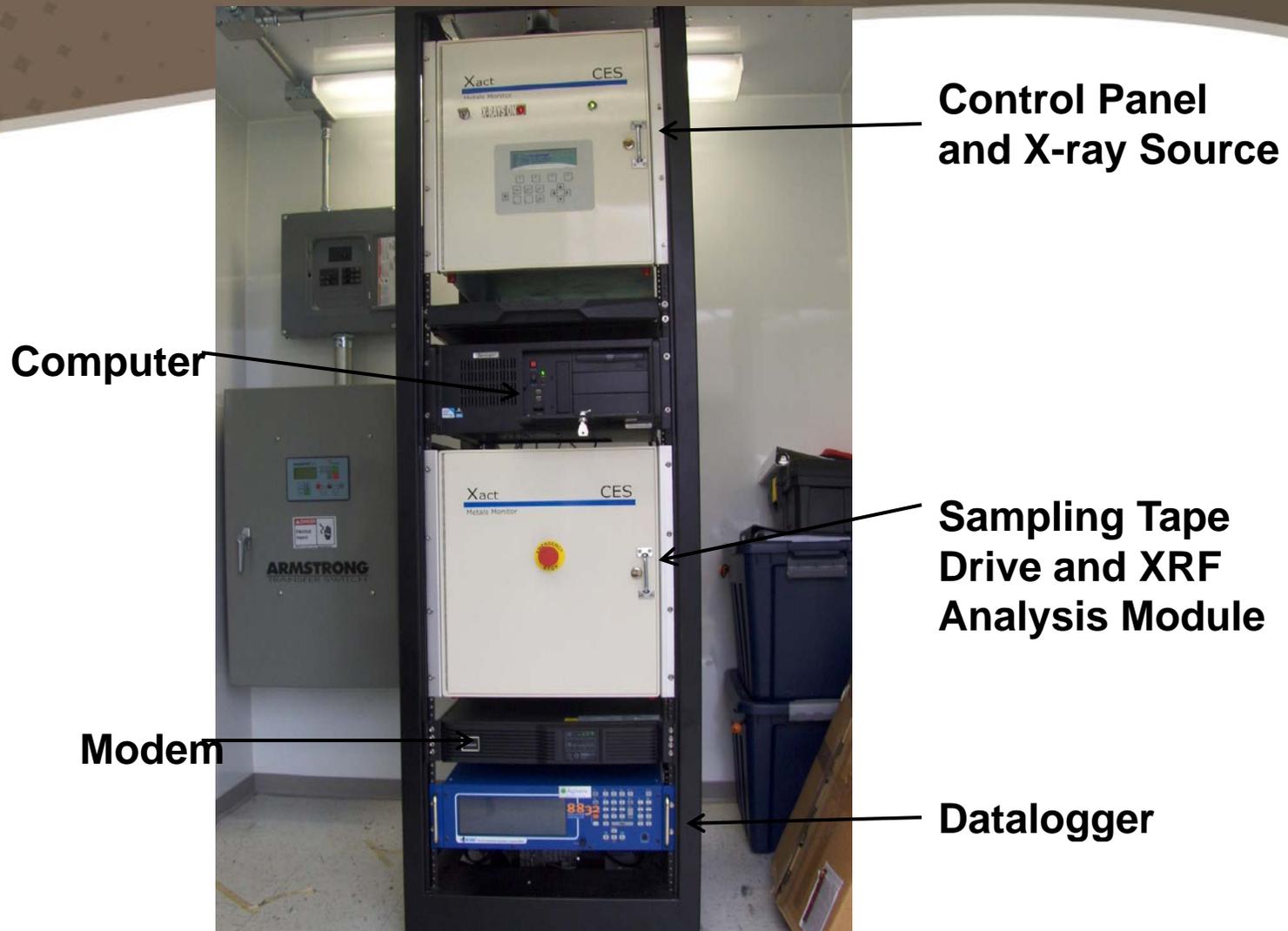
- 24-hour integrated sample
- Weeks lag time for lab results
- Good for chronic exposure and long term studies



## 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 =  $0.75 \text{ cm}^2$

# Elements detected by Xact 625

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

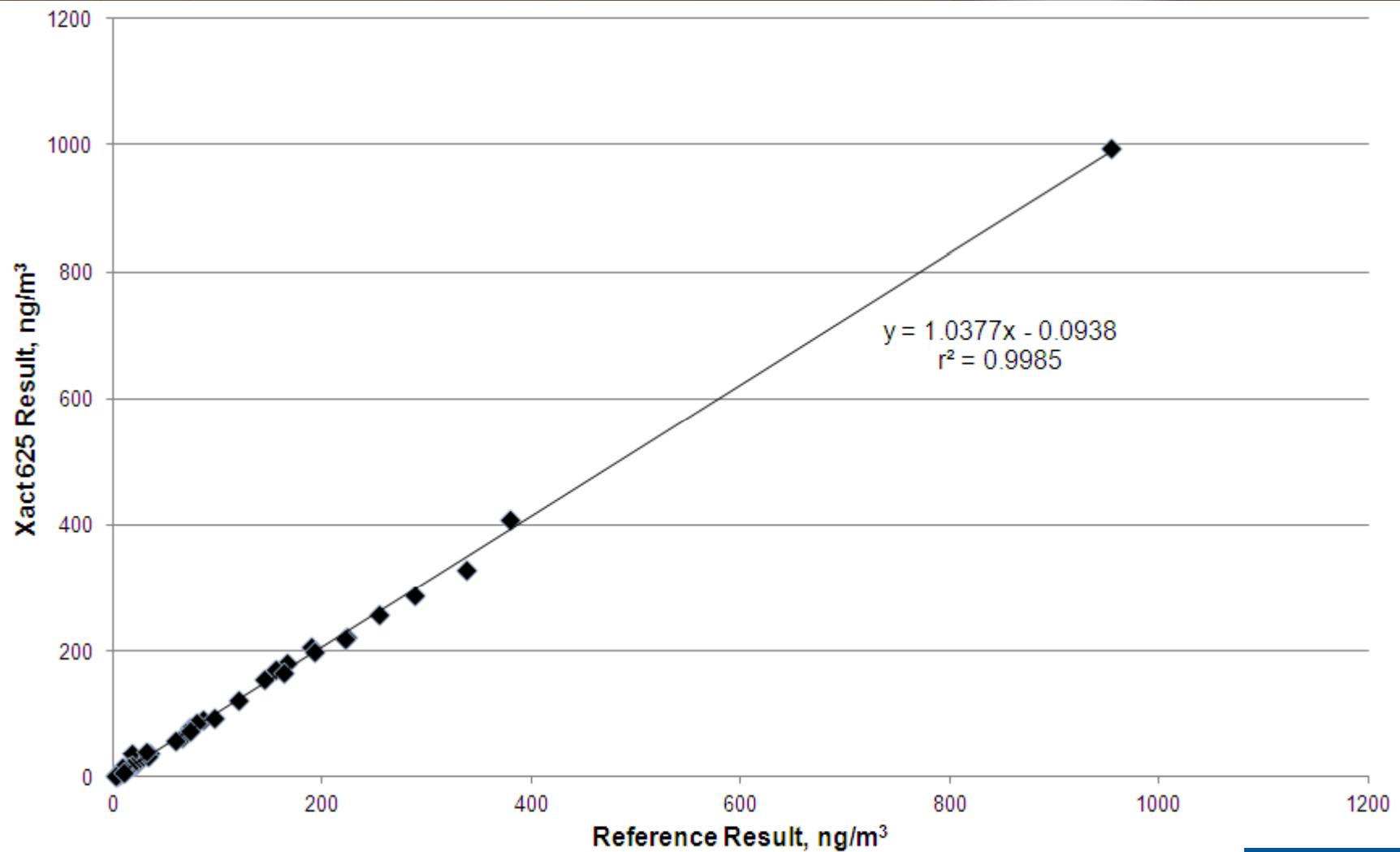




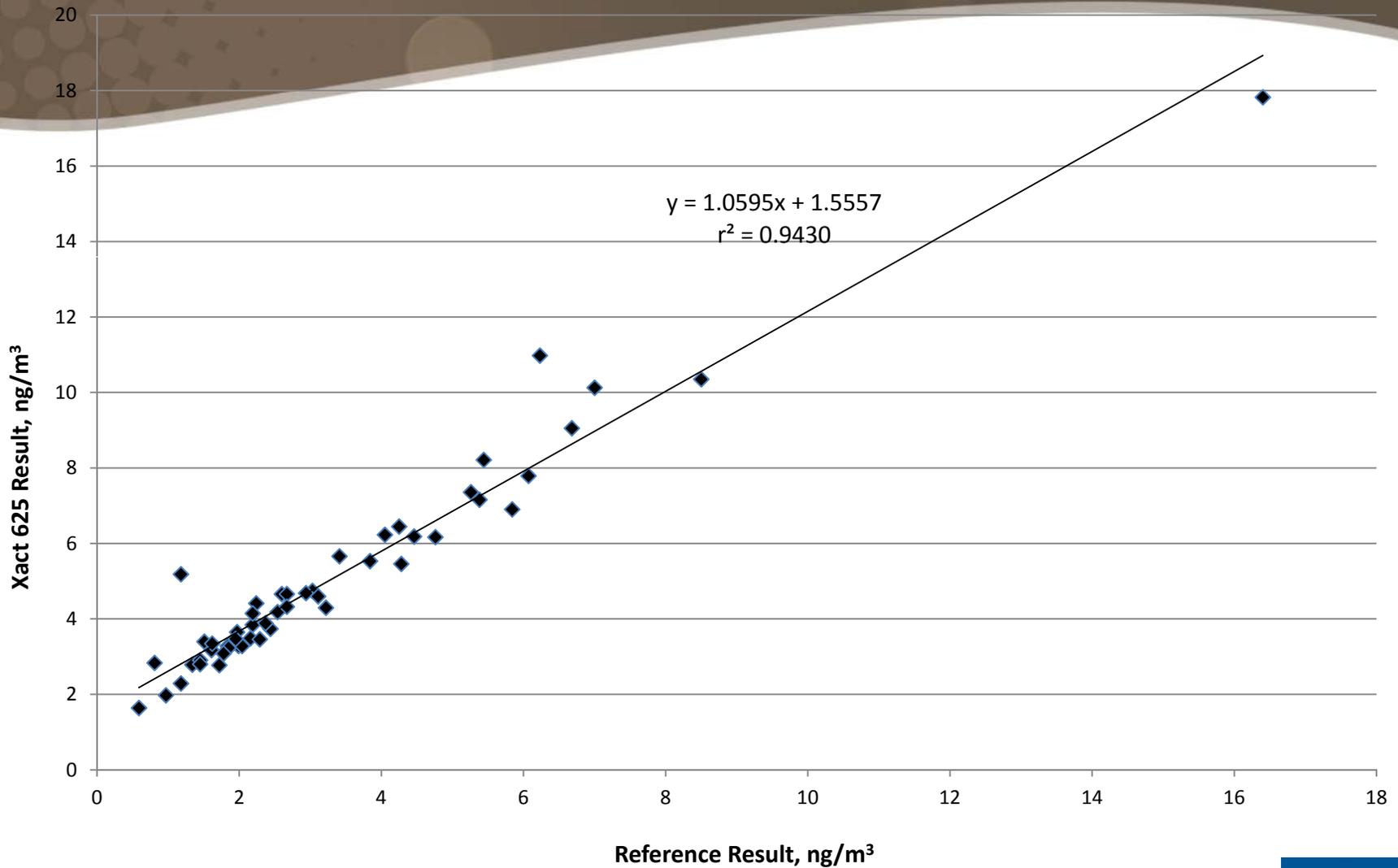
# ETV performance parameters

- 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

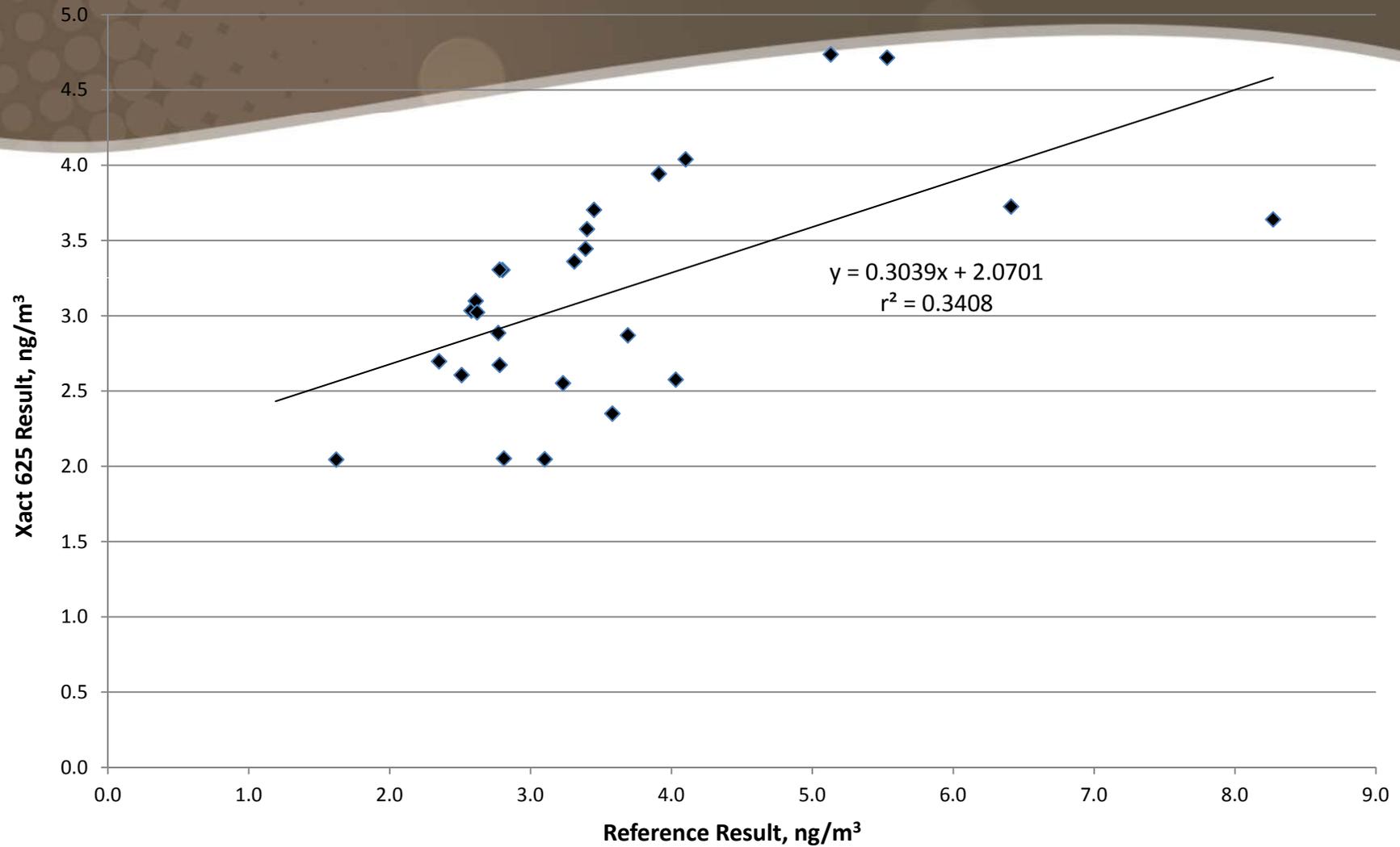
# Manganese regression



# Lead regression



# Copper regression



# Regression summary

| <b>Metal</b> | <b>Number of Data Points</b> | <b>Slope</b> | <b>Intercept (ng/m<sup>3</sup>)</b> | <b>Coefficient of Determination (r<sup>2</sup>)</b> |
|--------------|------------------------------|--------------|-------------------------------------|---|
| Ca           | 47                           | <b>0.822</b> | <b>-30.64</b>                       | 0.979   |
| Cu           | 26                           | <b>0.304</b> | <b>2.07</b>                         | 0.341   |
| Mn           | 48                           | <b>1.038</b> | -0.094                              | 0.999   |
| Pb           | 52                           | 1.060        | <b>1.56</b>                         | 0.943   |
| Se           | 25                           | 0.986        | 0.012                               | 0.926   |
| Zn           | 53                           | 0.971        | <b>-3.01</b>                        | 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



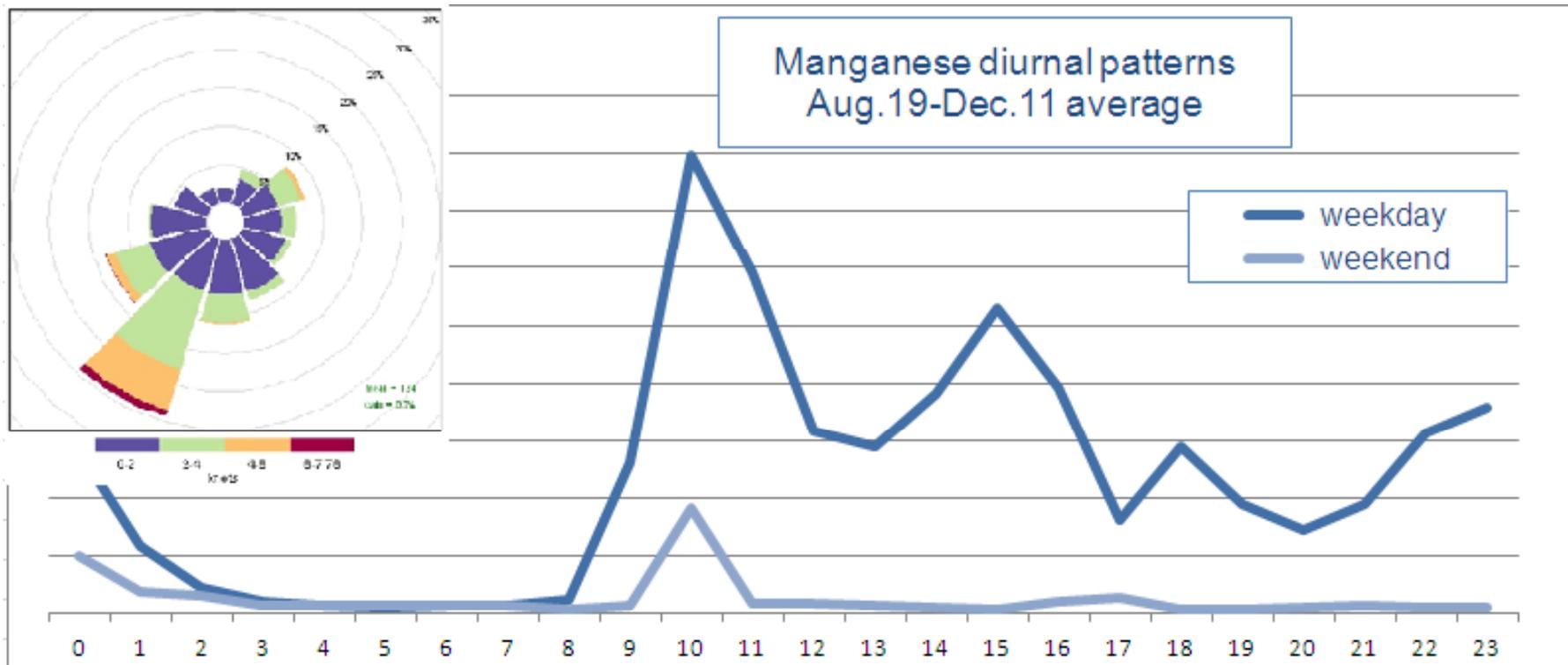
# EPA Region 5 data analysis

- 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.

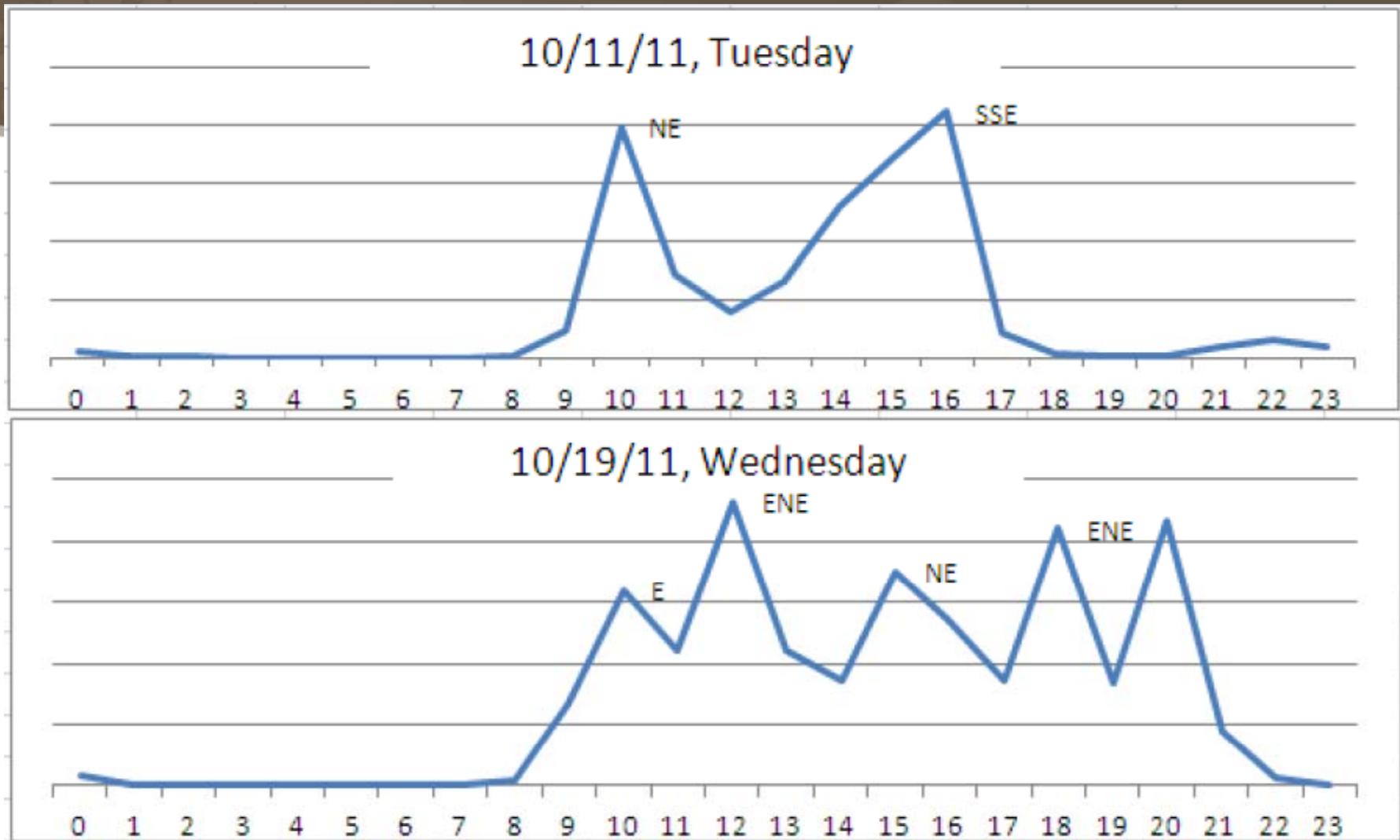
# E. Liverpool - pollution rose @fenceline



# 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.