Climatology of PM_{10} Metals in St. Louis from Hourly Data

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From: G. Gordon and W. Keifer (1980) The Delicate Balance: An Energy and the Environment Chemistry Module, Harper & Row, New York.

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Photo: Varun Yadav

Motivation and Objective

- St. Louis has a National Air Toxics Trends Station (NATTS) including 24-hour integrated 1-in-6 day PM_{10} air toxics metals.
- In 2008 a four-site network was operated (same sampling schedule) to place the NATTS measurements in context.
- Missouri Department of Natural Resources (MDNR) now operates a continuous metals monitor at the site
  - Data reported to the USEPA Air Quality System database starting November 2012.
- **Objective:** examine temporal and wind direction patterns in the continuous data towards characterizing the climatology of air toxics metals.

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

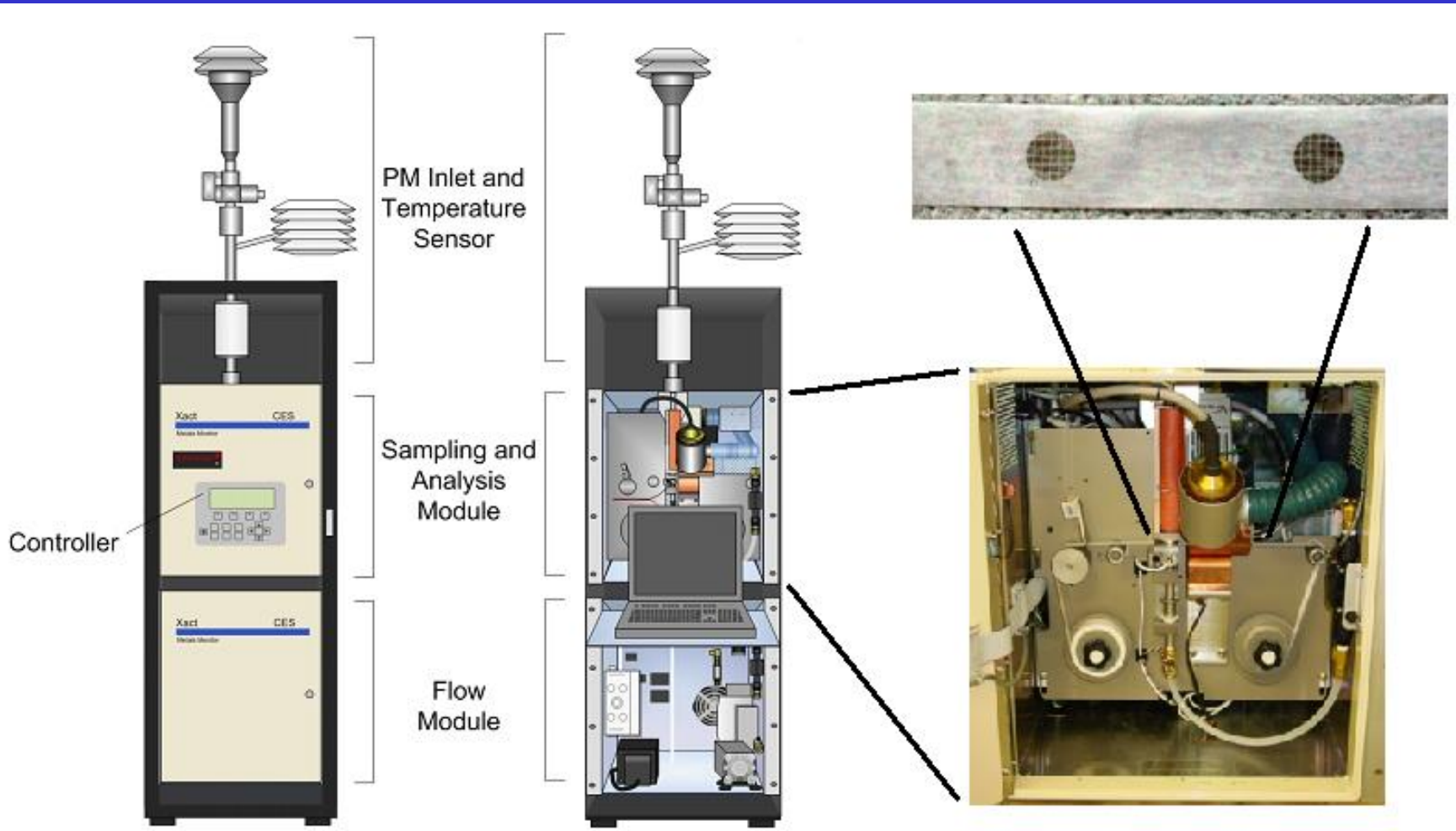
- Single particle mass spectrometry (e.g. TSI ATOFMS)
- Aerosol mass spectrometer (Aerodyne AMS)
  - no refractory elements
- Cooper Environmental Services field XRF analyzer

SEAS Version IV

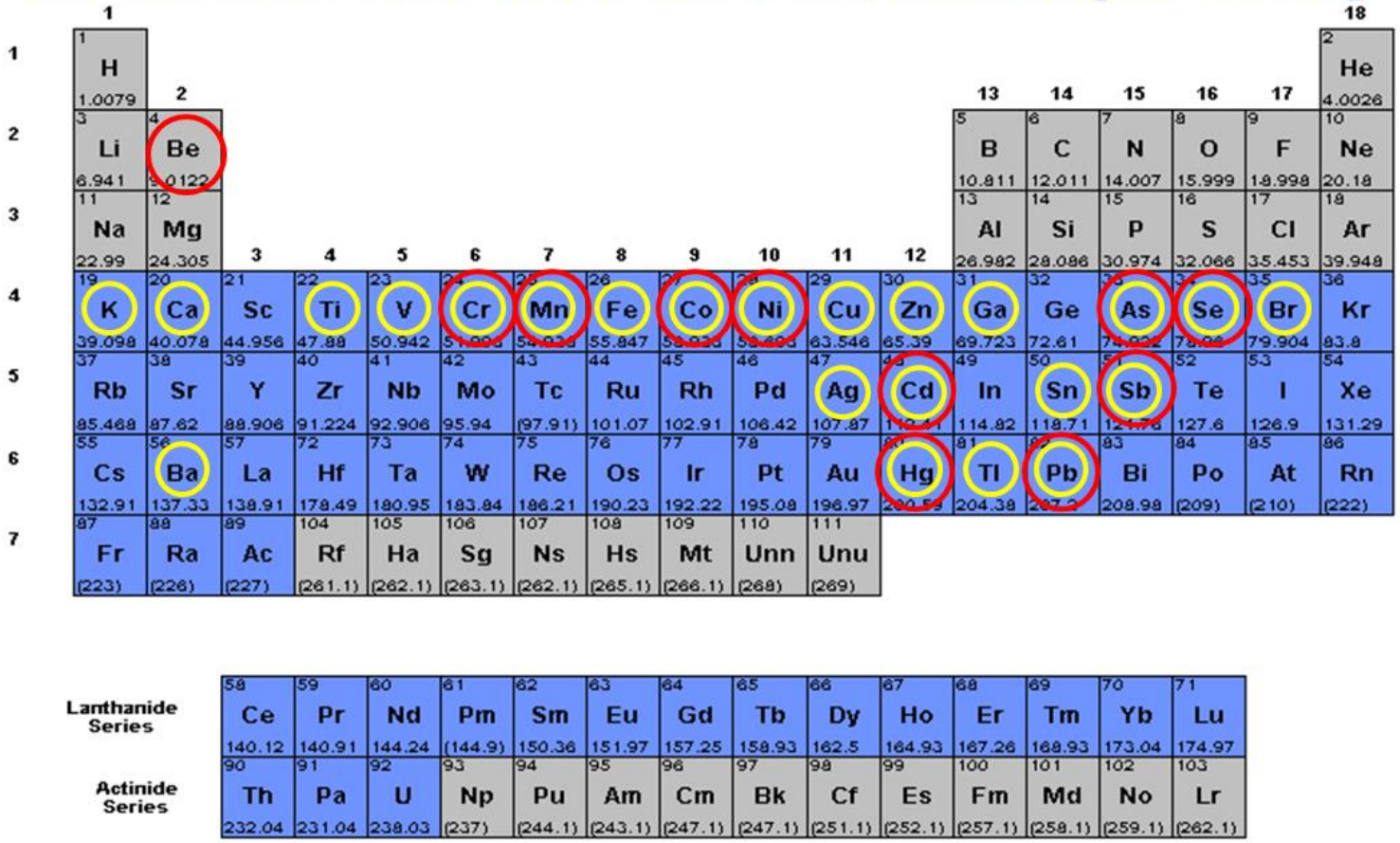
Cooper Environmental Services (CES) Xact

- Xact series
  - I: stack sampling
  - II: fenceline monitoring
  - III: ambient monitoring
- particle collection on a reel-to-reel filter tape
- analysis by XRF
- continuous data series at user-defined time intervals
- this version (Xact 620) optimized for As, Hg, and Pb at low concentrations

Cooper Environmental Services (CES) Xact



ELEMENTS THE XACT CAN MEASURE (IN BLUE)



measured by Xact in this study

EPA Air Toxics PM metals

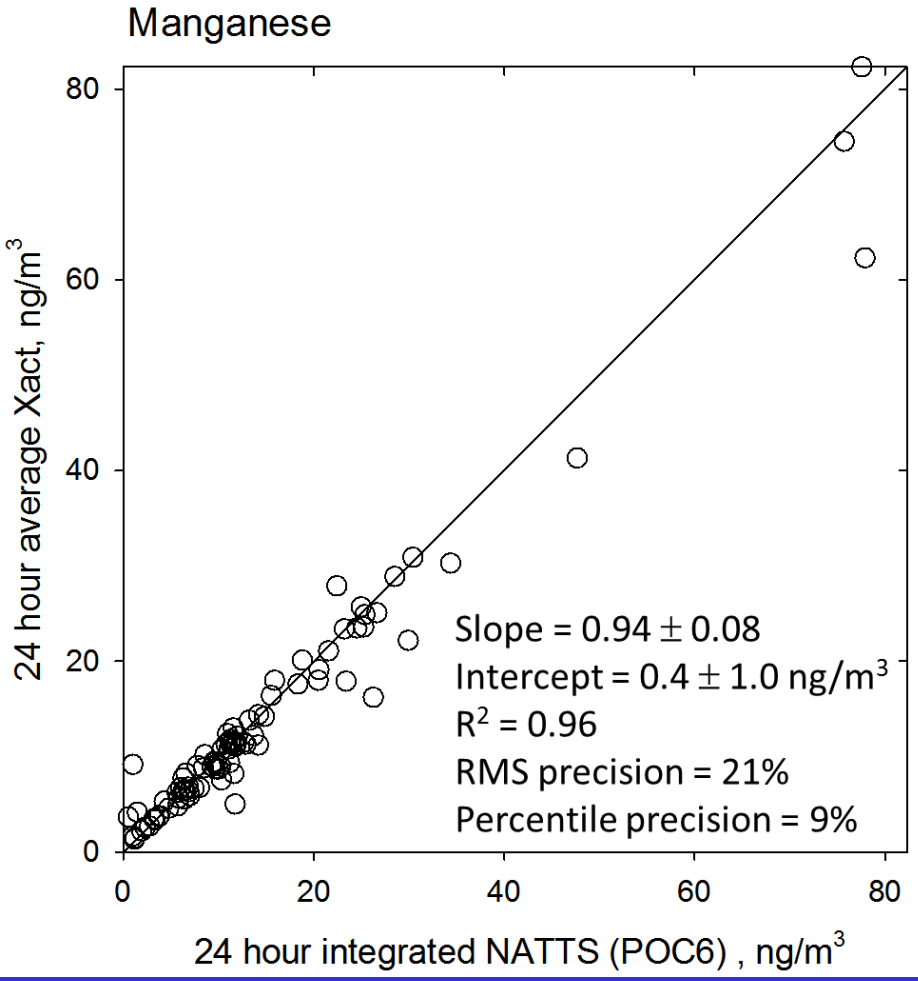
Measurements

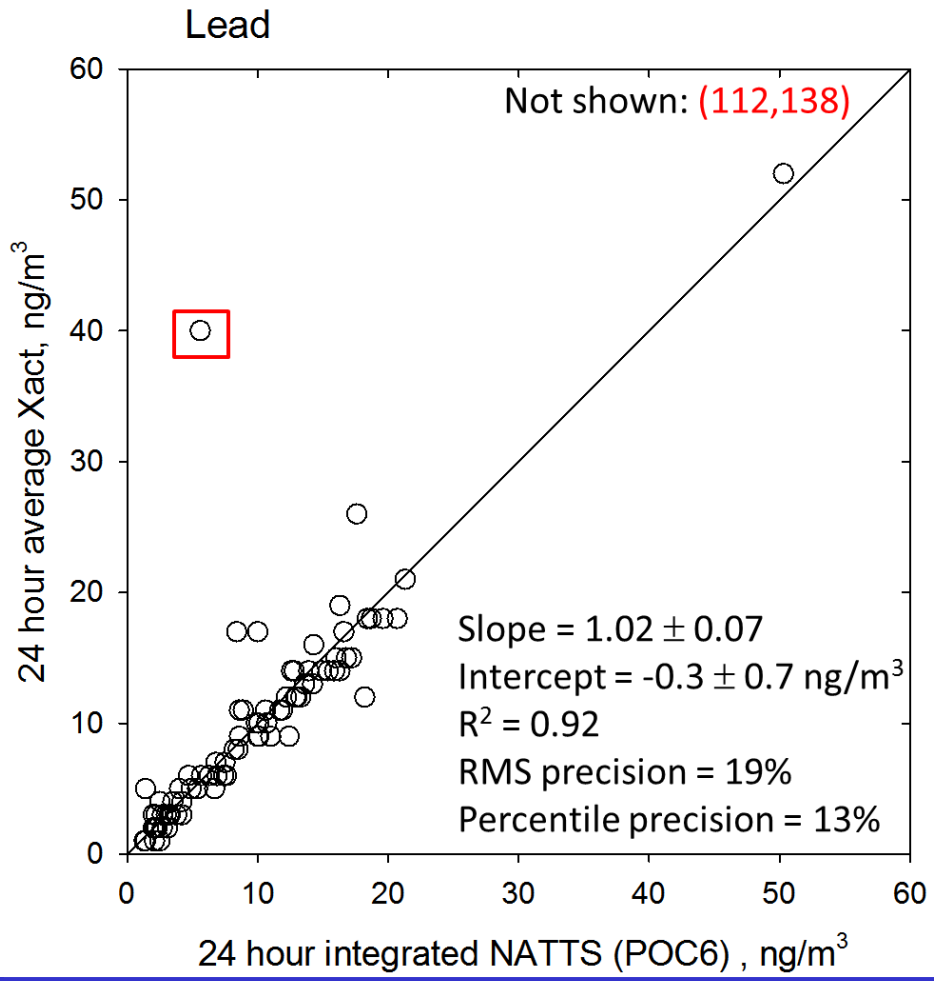
- Blair Street (City of St. Louis, Missouri) NCore site.
- NATTS samples
  - Teflon filters with low-volume (16.7 LPM) sampler
  - Analysis by the Eastern Research Group (ERG) using sample digestion followed by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS)
- Continuous (1-hour) PM_{10} metals
  - Cooper Environmental Services (CES) Xact 620.
  - Predecessor to the current Model 625i.
- This study used data collected from November 2012 through August 2014
  - Data completeness was 78% (12,526 valid hours out of 15,960 total hours)

Xact vs. NATTS Comparisons

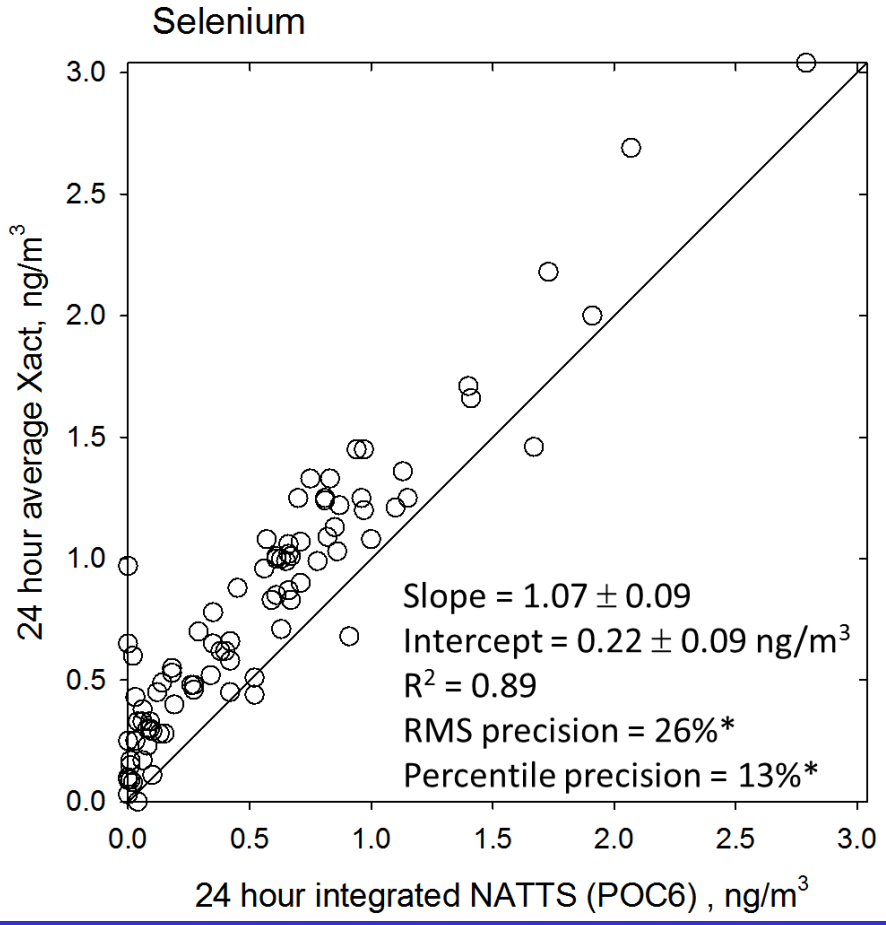
- Daily-average Xact data calculated for days with at least 21 hours of valid data.
  - Daily data completeness was 75% (449 valid days out of 554 total days)
- Focus on the four elements featured in the 2008 four-site study (Yadav and Turner, 2014)… Se, As, Mn and Pb
  - Regression statistics from reduced major axis (RMA) regression with bootstrapped 95% confidence intervals.
  - Root-Mean-Square (RMS) and percentile precisions including data with concentrations >3×MDL

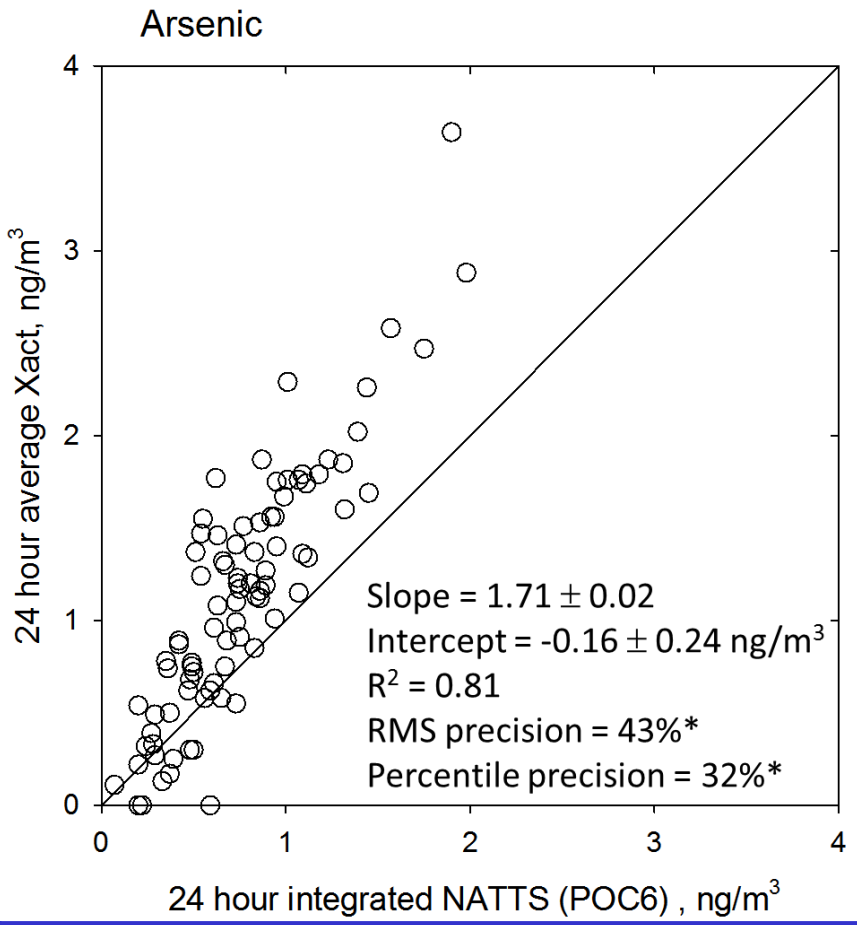
Xact vs. NATTS Comparisons





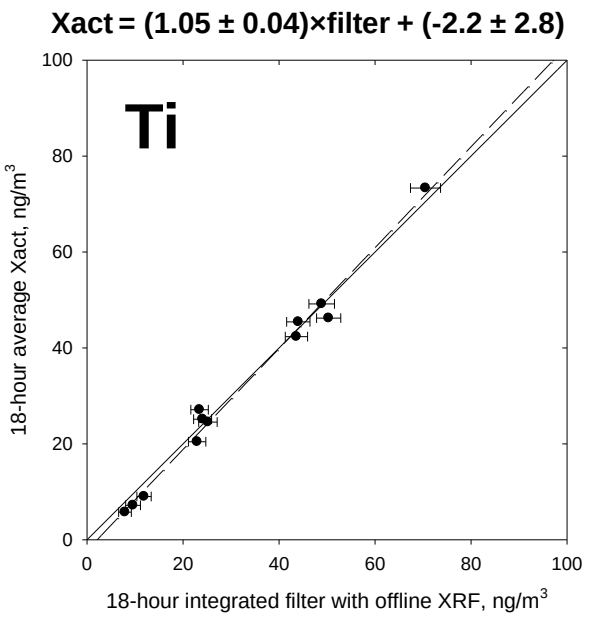
Xact vs. NATTS Comparisons

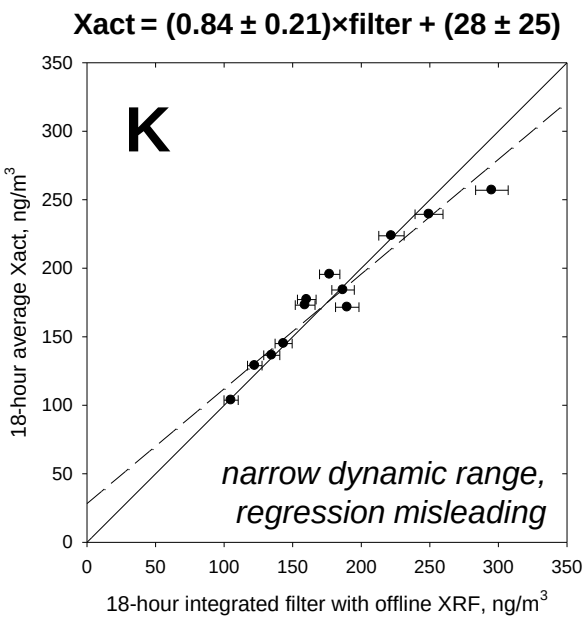


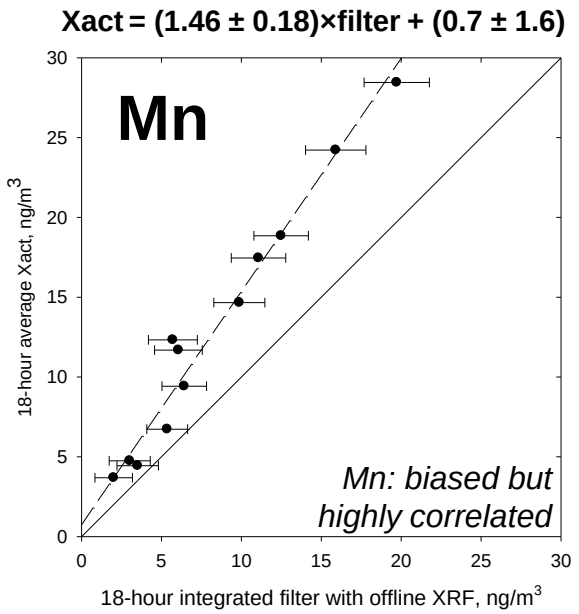


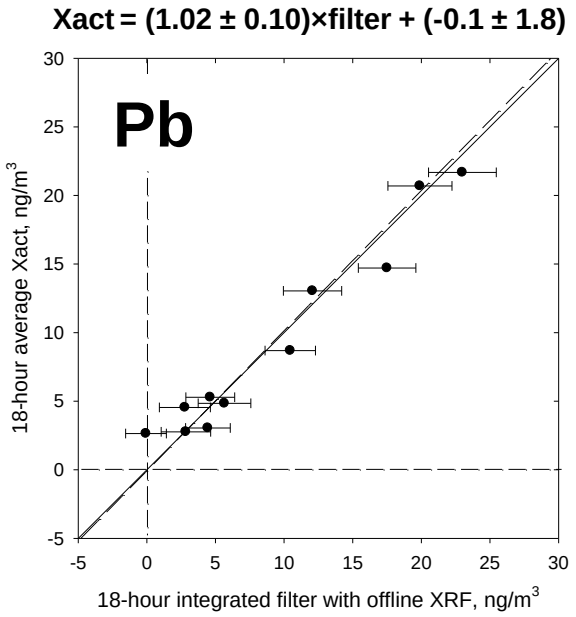
- High correlation between the methods
- Precision estimates are influenced by the bias

Xact (*y-axis*) vs. LowVol PM_{10} FRM & XRF (*x-axis*)

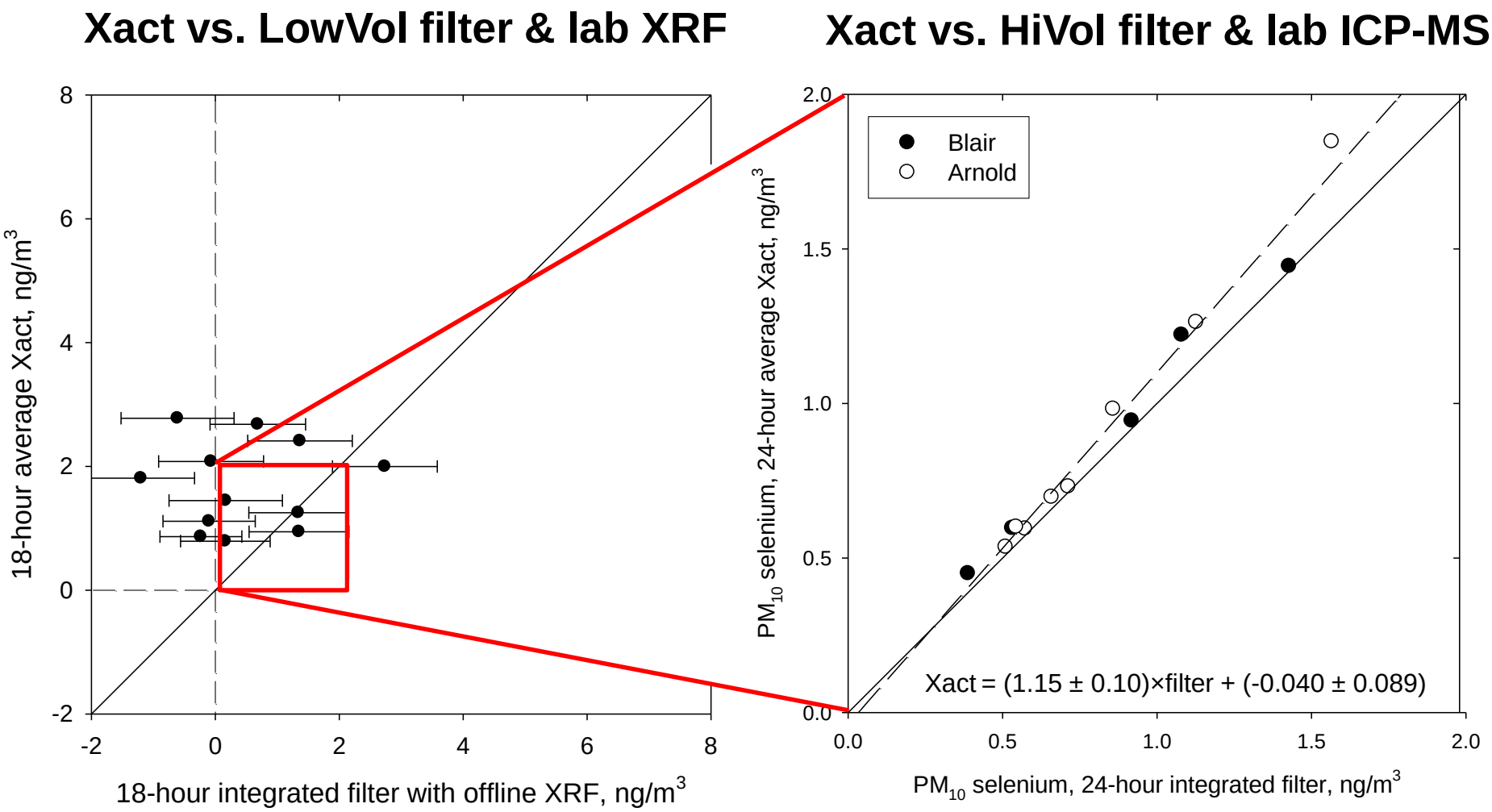








Selenium: Xact vs. Filter-Based Measurements

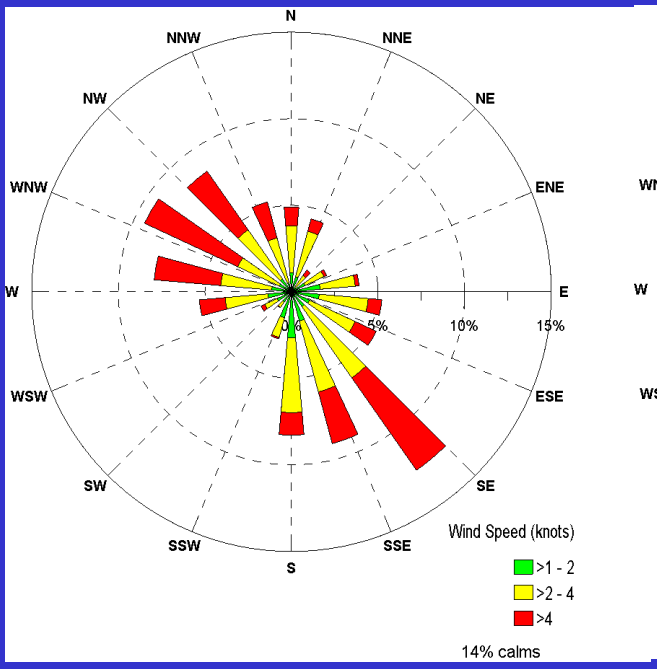


Selenium: favorable comparison between Xact and PM_{10} HiVol samples with analysis by ICP-MS

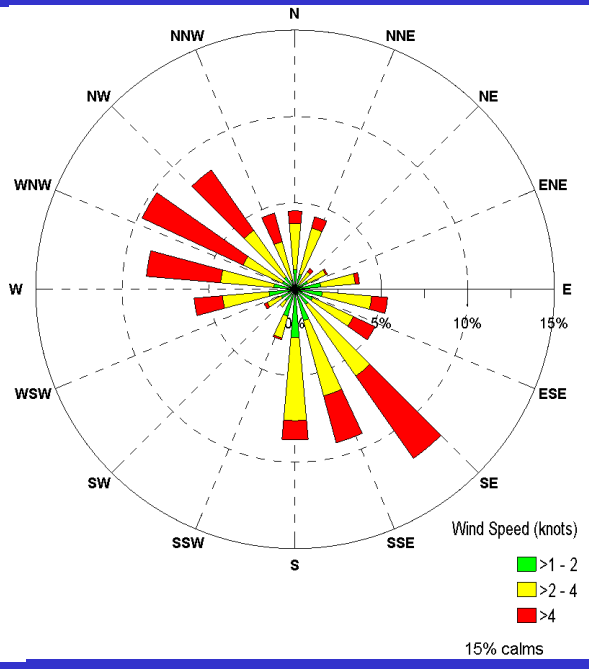

MISSOURI
Mississippi River
MDNR - Blair
Downtown
City of St. Louis
2 km
ILLINOIS

Blair Street (City of St. Louis) Hourly 10m Winds matched to Hours with Valid Xact Data November 2012 – August 2014

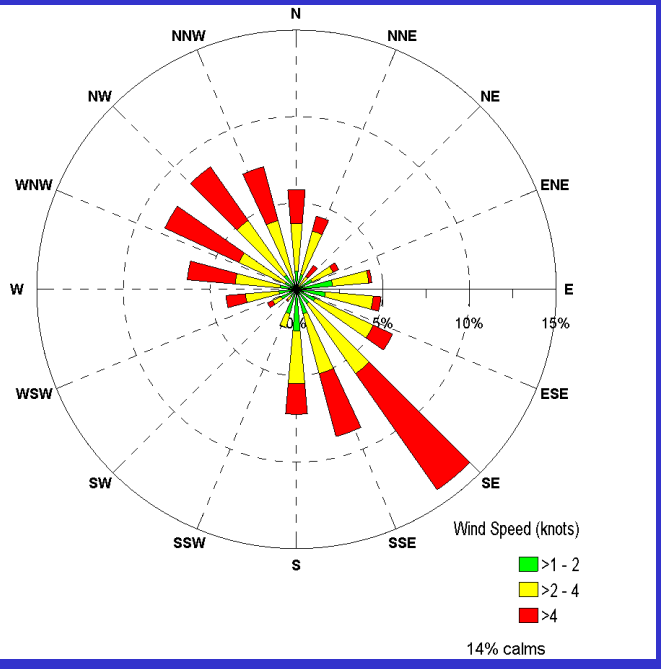
All Days



Weekdays

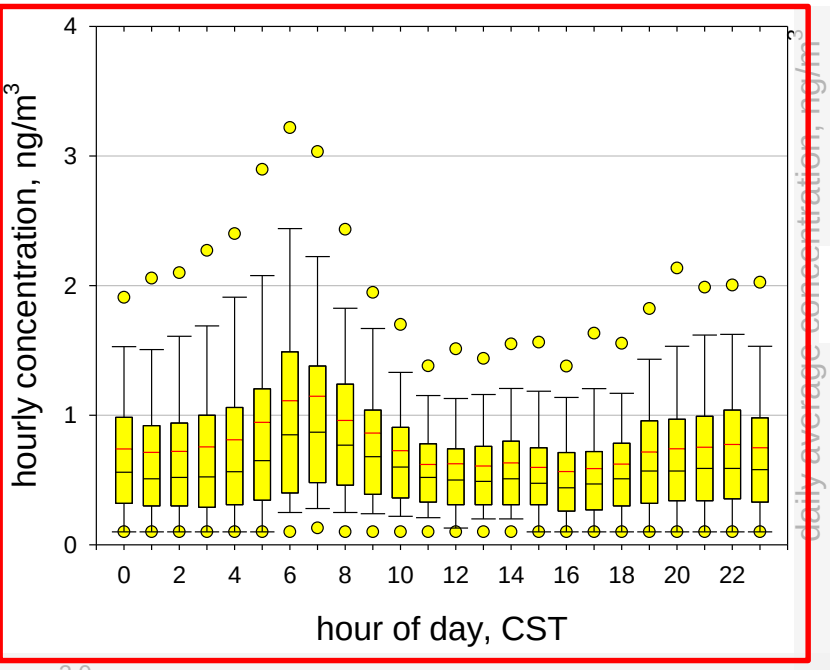


Weekends

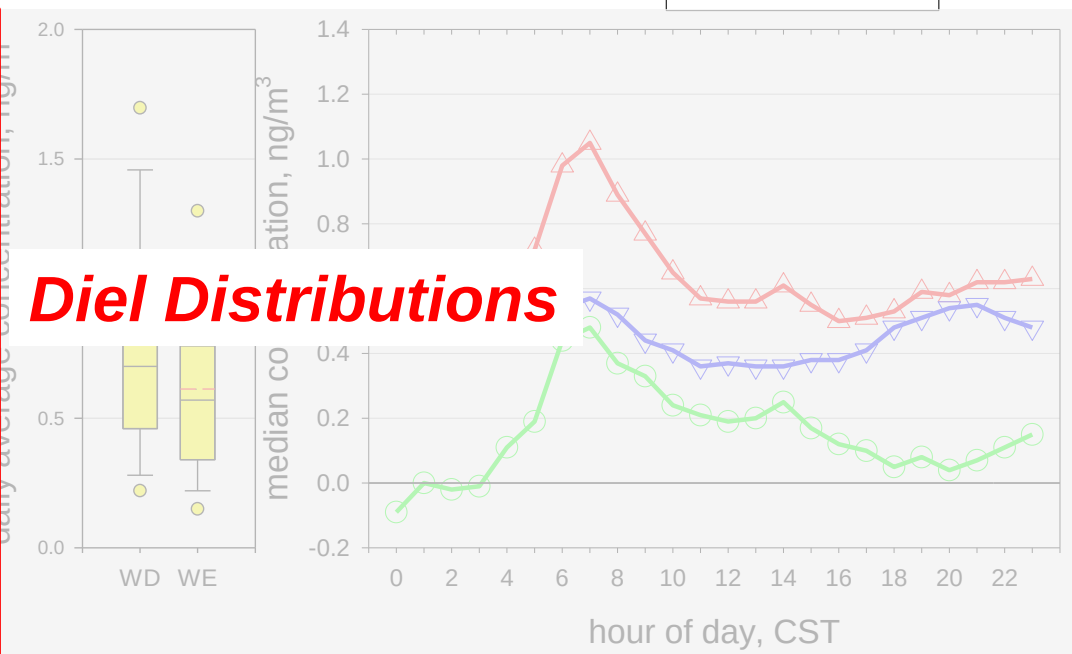


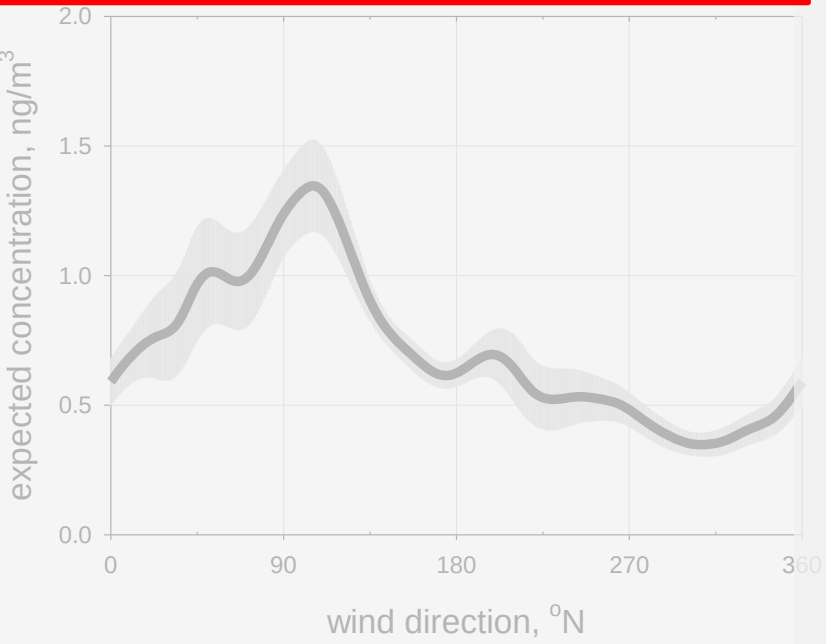
BC

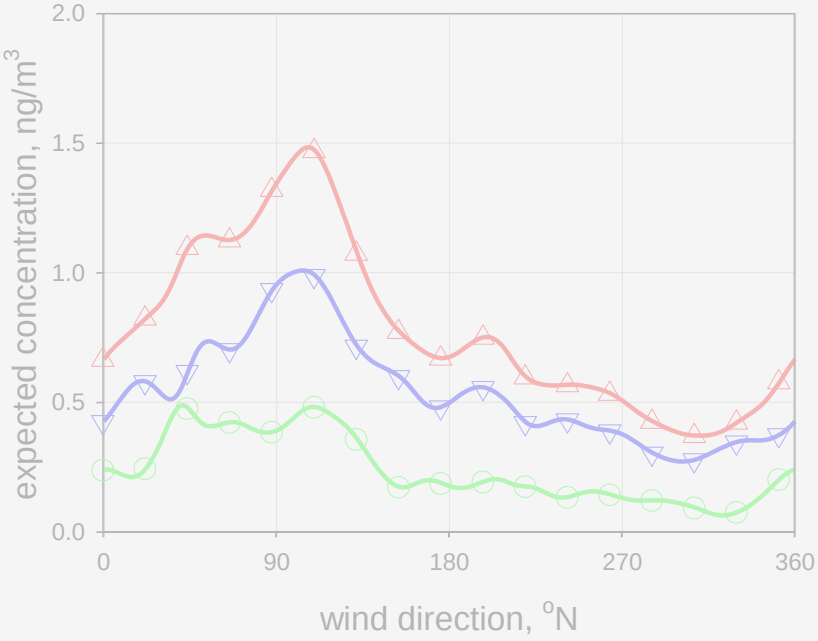
DATA DASHBOARDS



Diel Distributions







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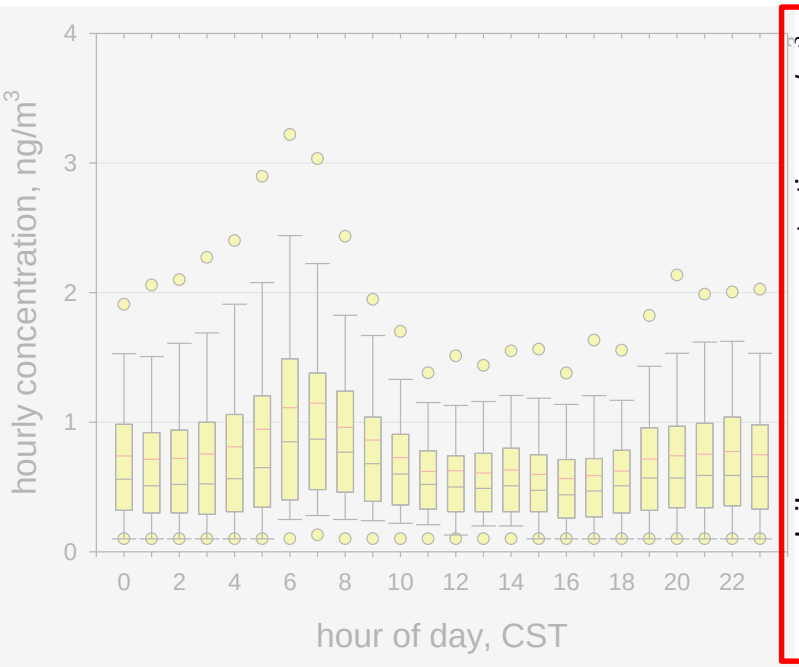
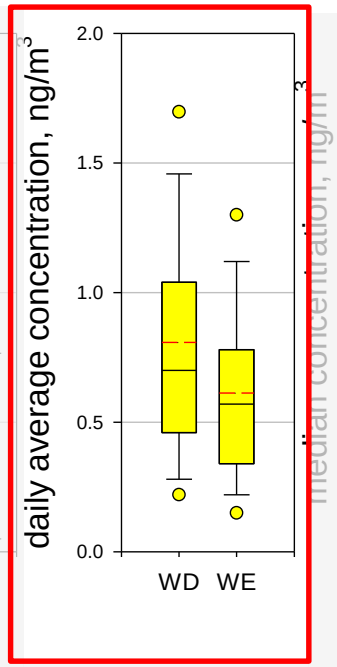
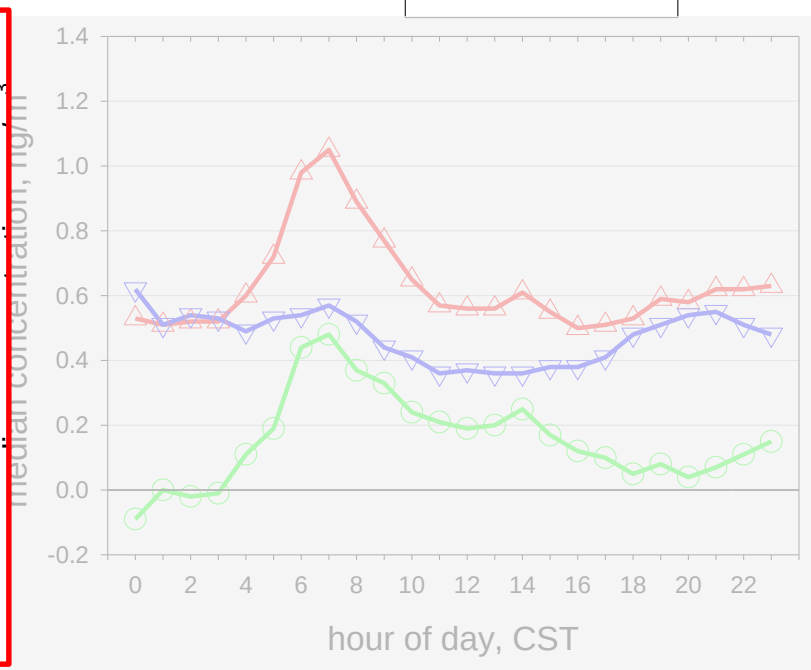
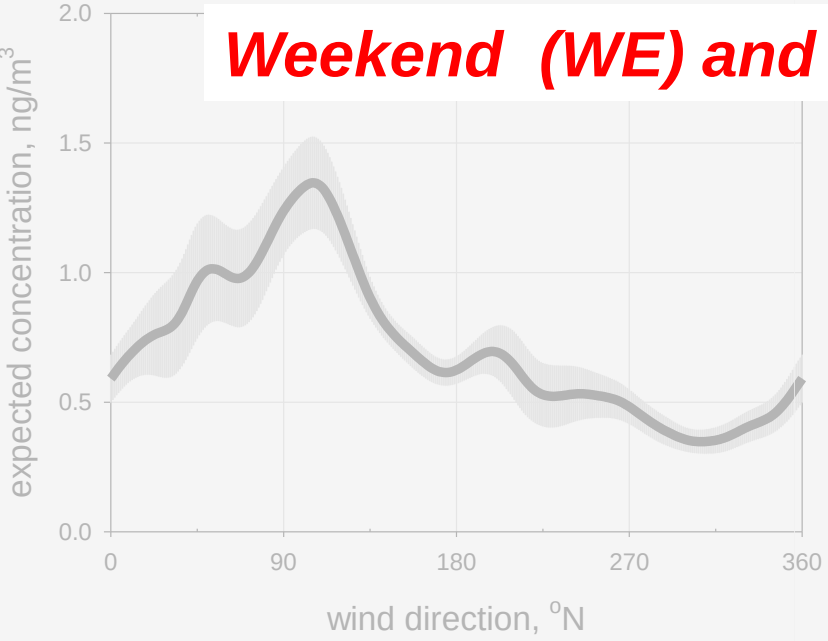
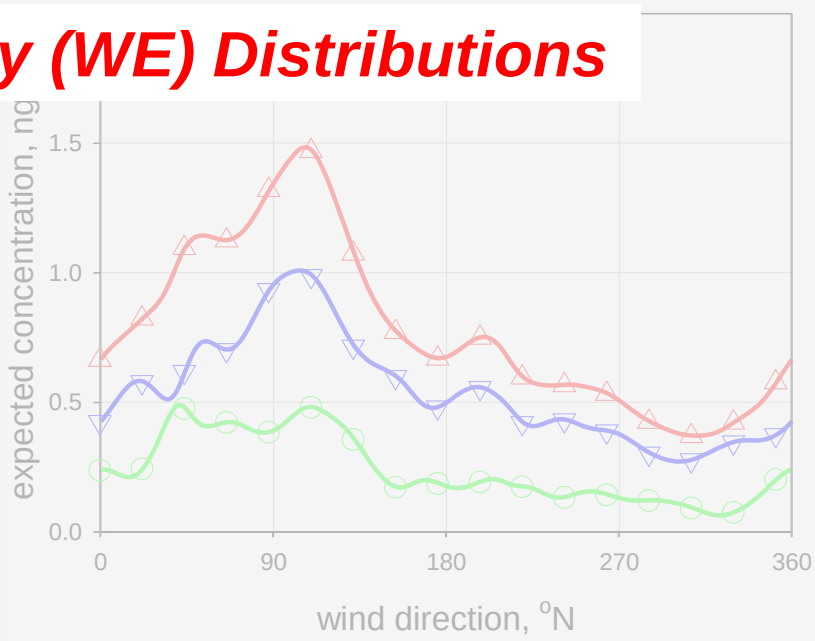






Weekend (WE) and Weekday (WE) Distributions





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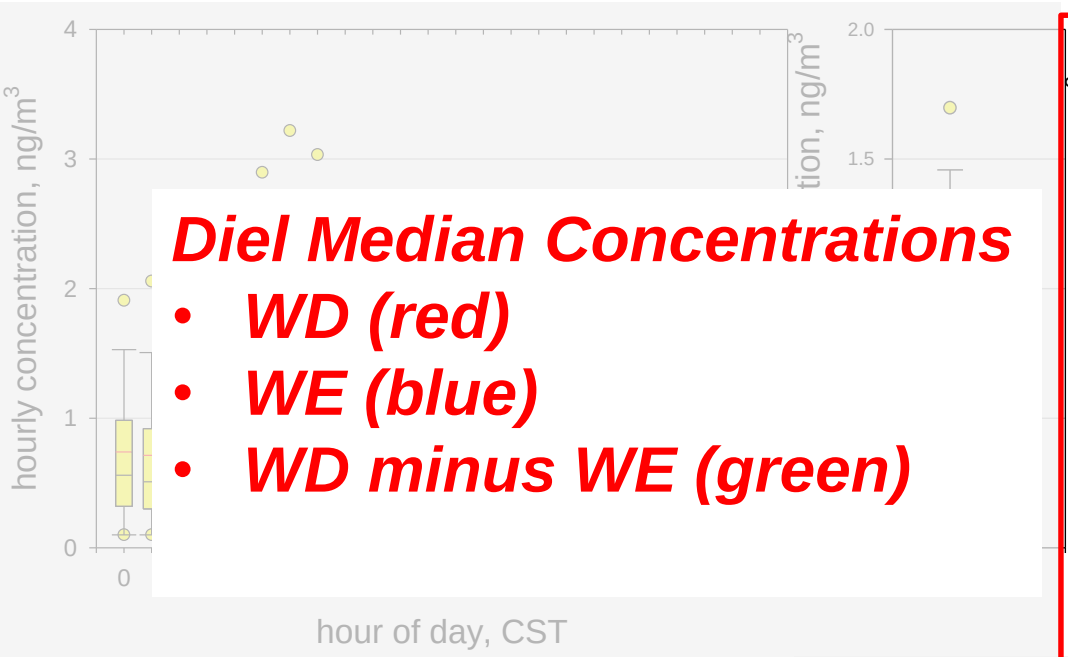
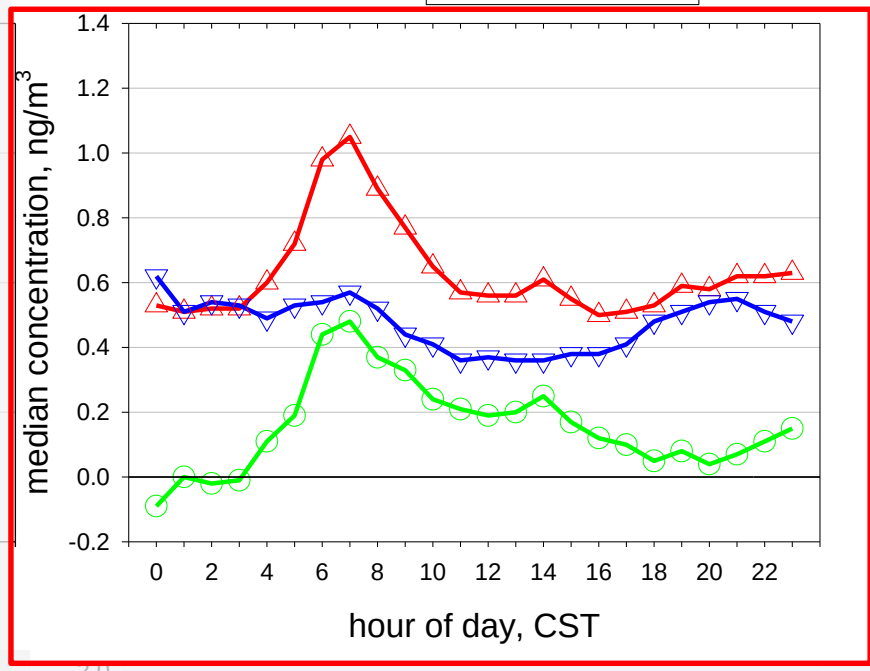
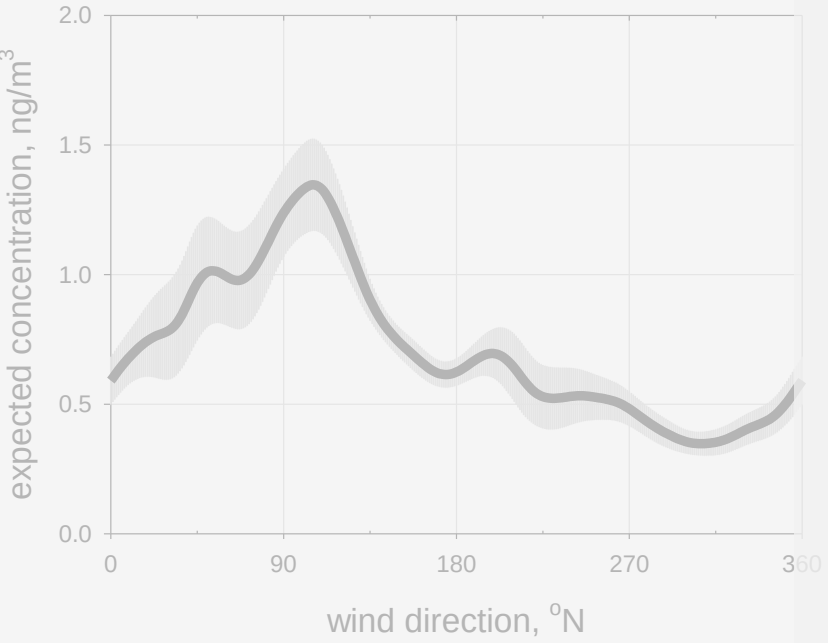
DATA DASHBOARDS

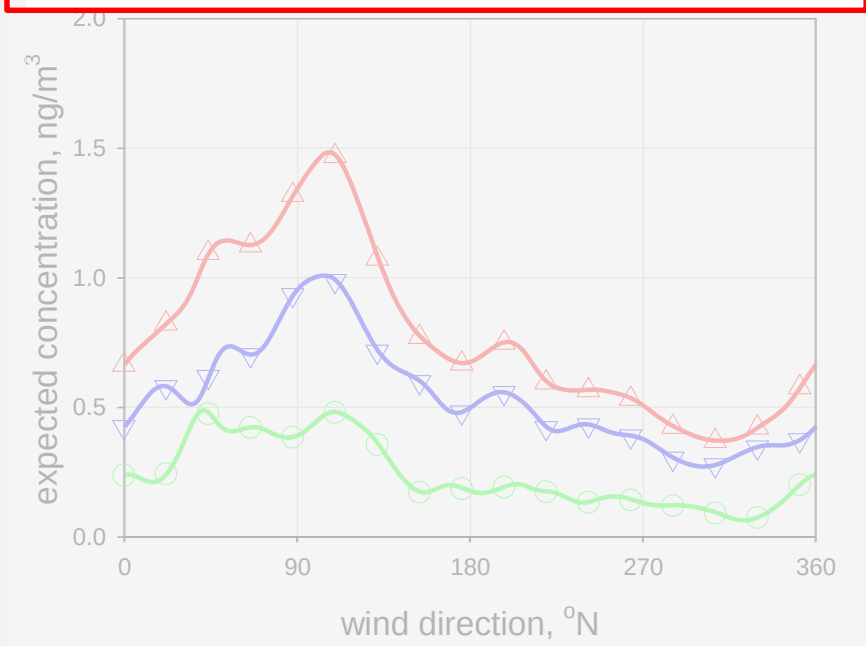


Diel Median Concentrations

- *WD (red)*
- *WE (blue)*
- *WD minus WE (green)*







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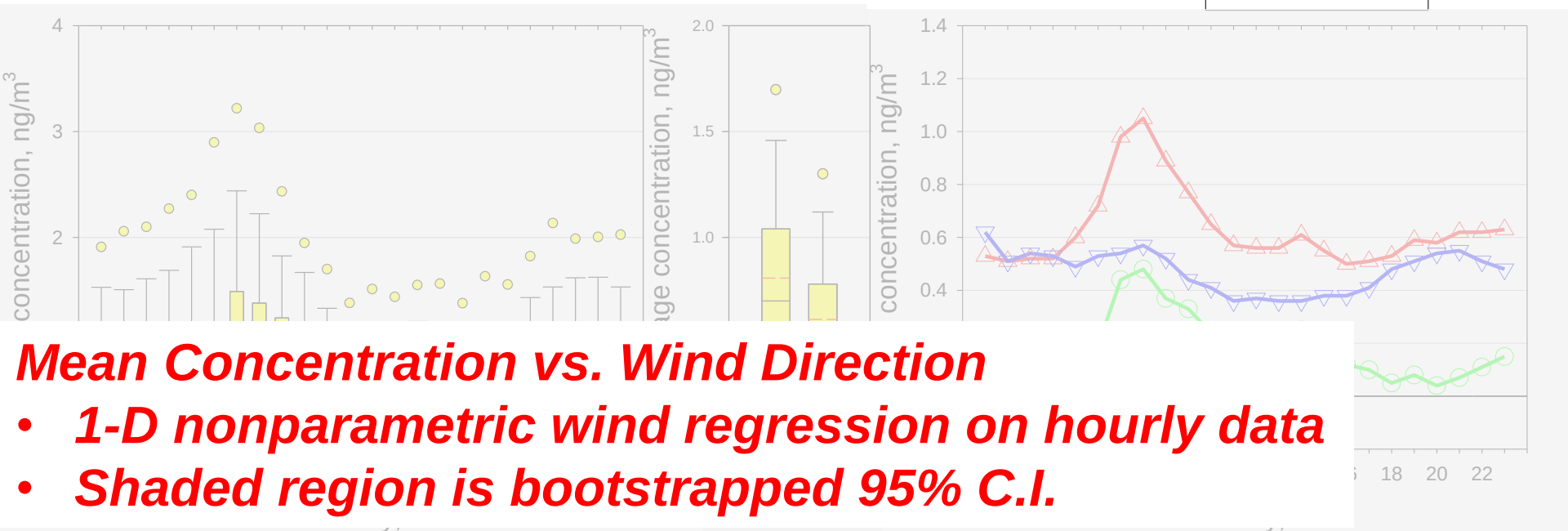
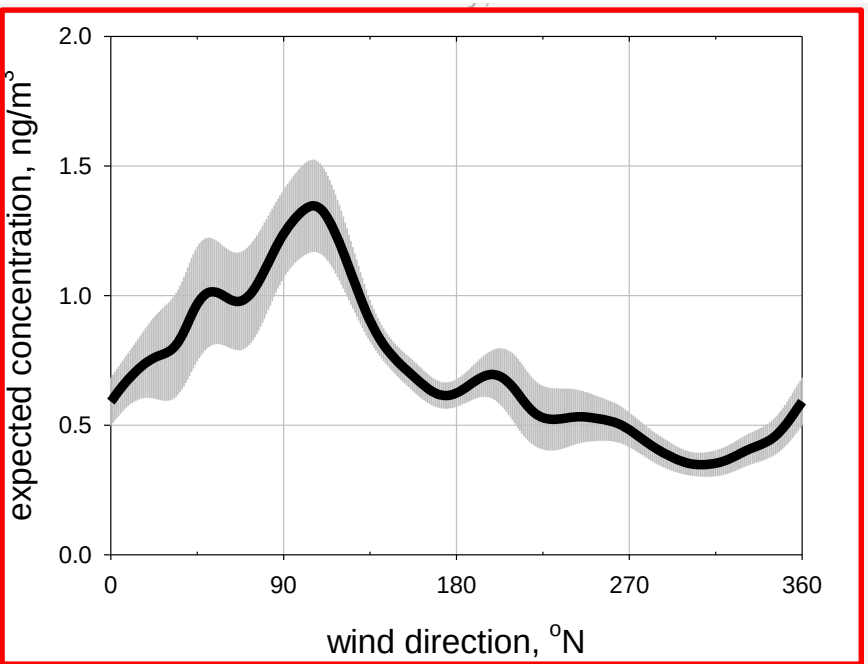
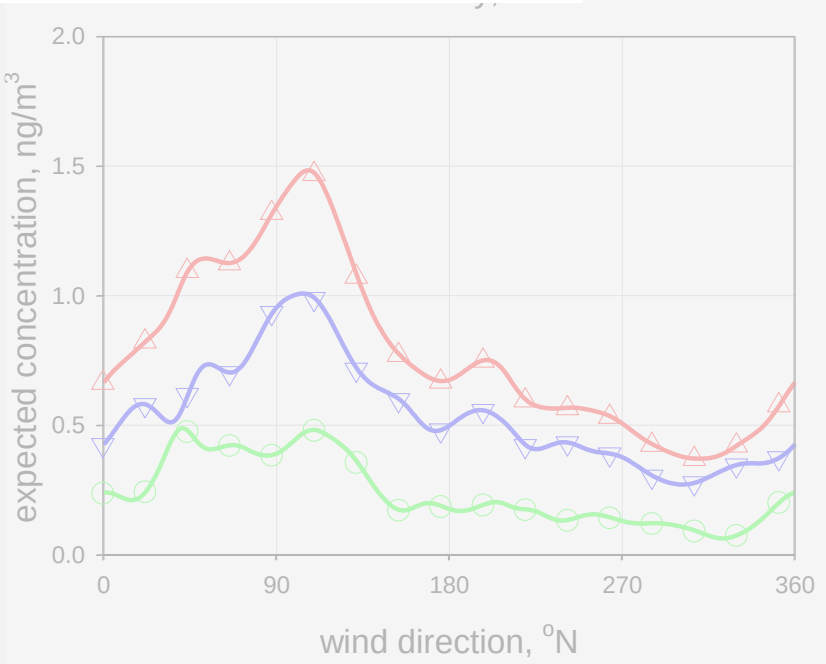
DATA DASHBOARDS



Mean Concentration vs. Wind Direction

- *1-D nonparametric wind regression on hourly data*
- *Shaded region is bootstrapped 95% C.I.*





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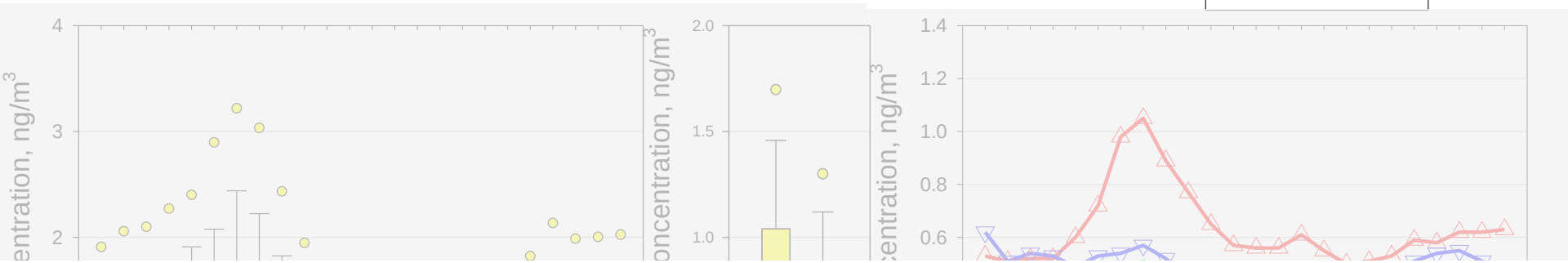
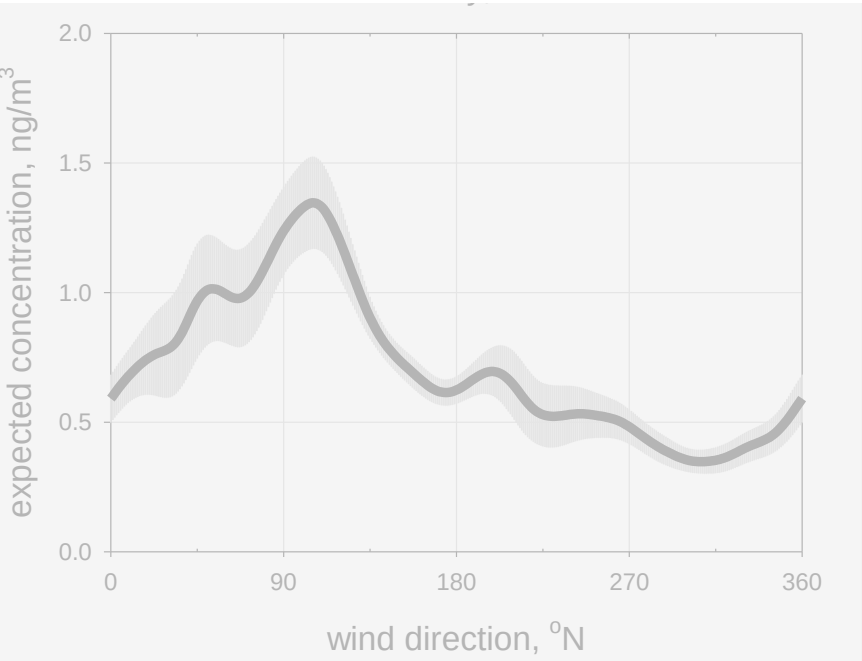
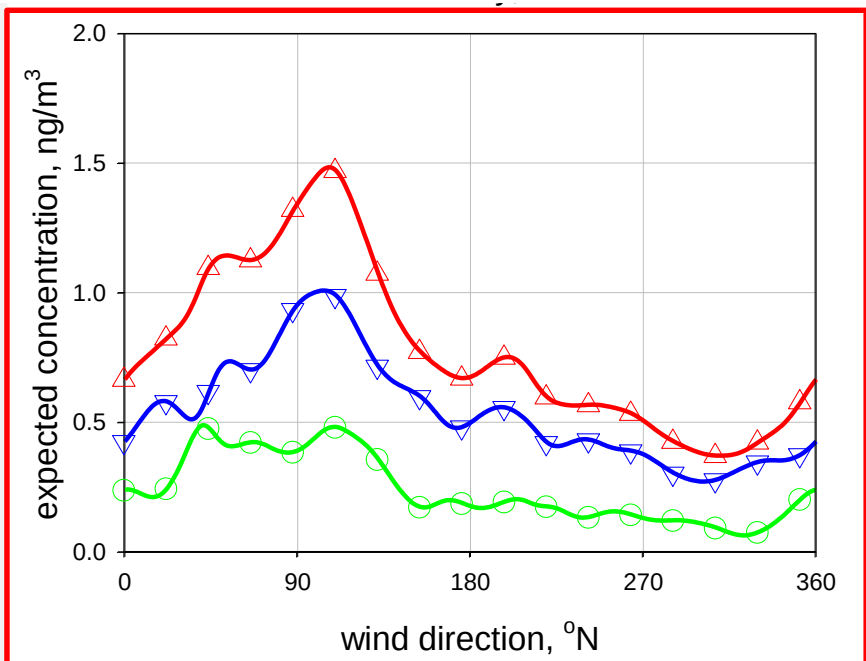
DATA DASHBOARDS



Mean Concentration vs. Wind Direction

- *1-D nonparametric wind regression on hourly data stratified by weekdays (red) and weekends (blue)*
- *Weekdays minus weekends (green)*

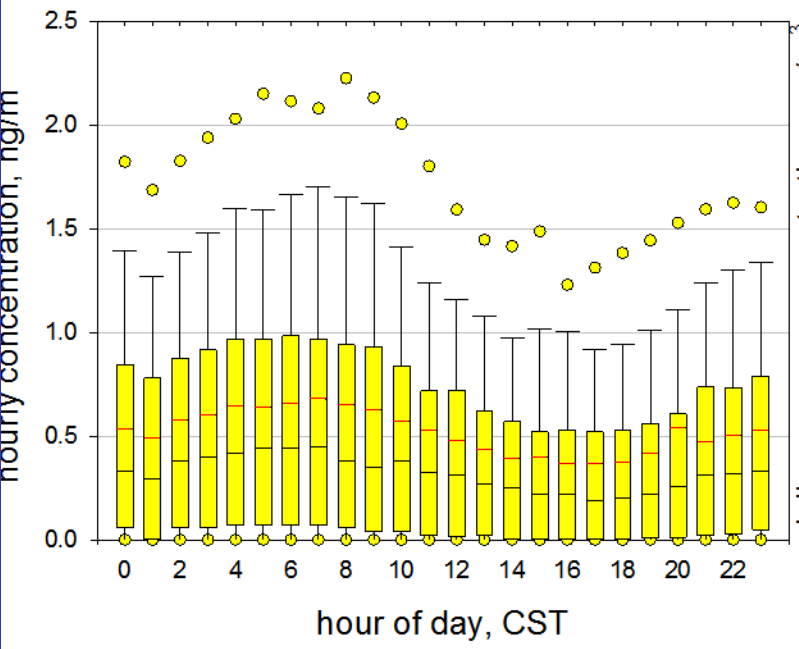


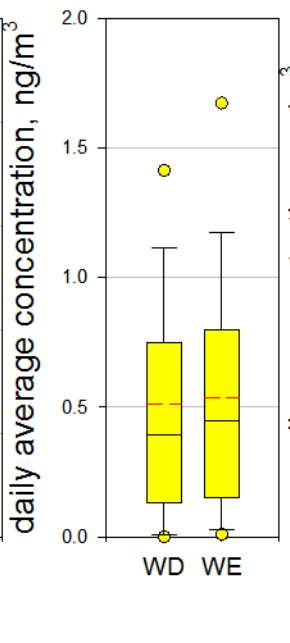


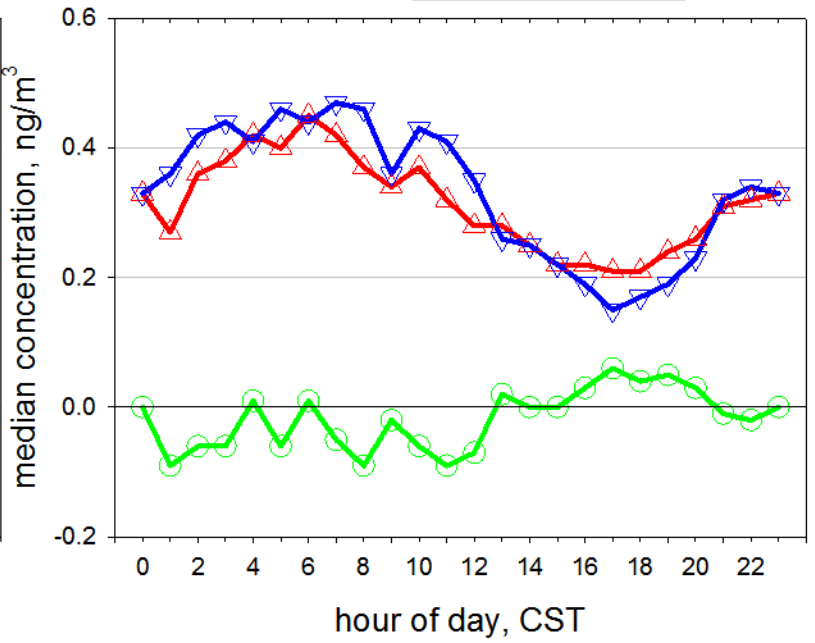
Aethalometer Black Carbon

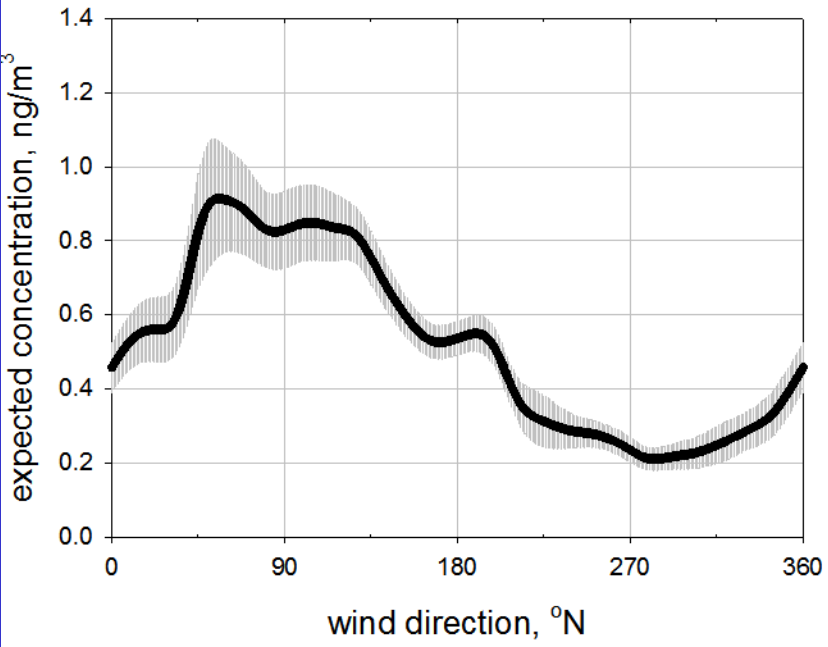
- **Not an air toxics metal but shown for contrast**
- Concentrations greater on weekdays compared to weekends, but only during the daytime hours
- Strong morning rush hour peak
- Emission source region predominantly to the east, consistent with industrial riverfront and a local north-south running interstate
- Concentrations higher on WD compared to WE for all wind directions

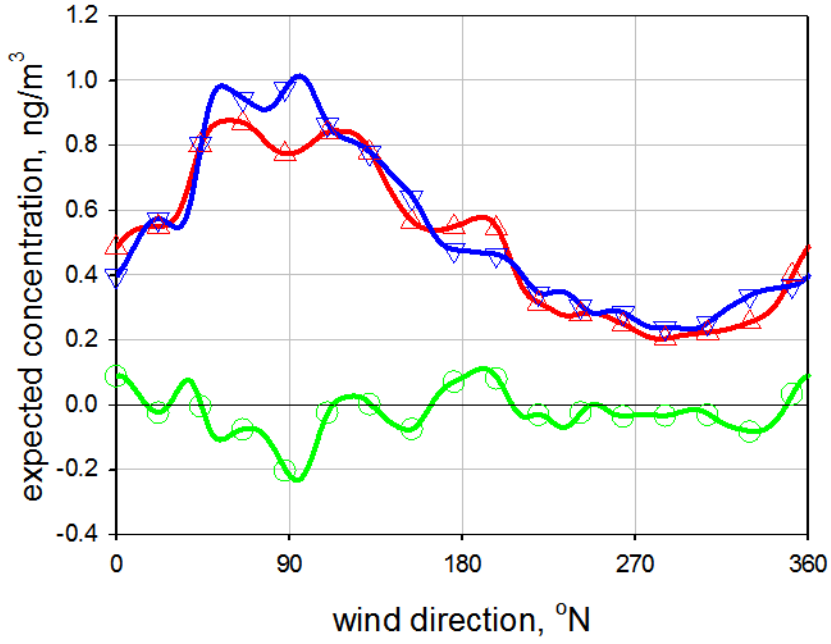
Selenium


hourly concentration, ng/m3
2.5
2.0
1.5
1.0
0.5
0.0
0 2 4 6 8 10 12 14 16 18 20 22
hour of day, CST


daily average concentration, ng/m3
2.0
1.5
1.0
0.5
0.0
WD WE


weekdays (WD)
weekends (WE)
WD minus WE
median concentration, ng/m3
0.6
0.4
0.2
0.0
-0.2
0 2 4 6 8 10 12 14 16 18 20 22
hour of day, CST

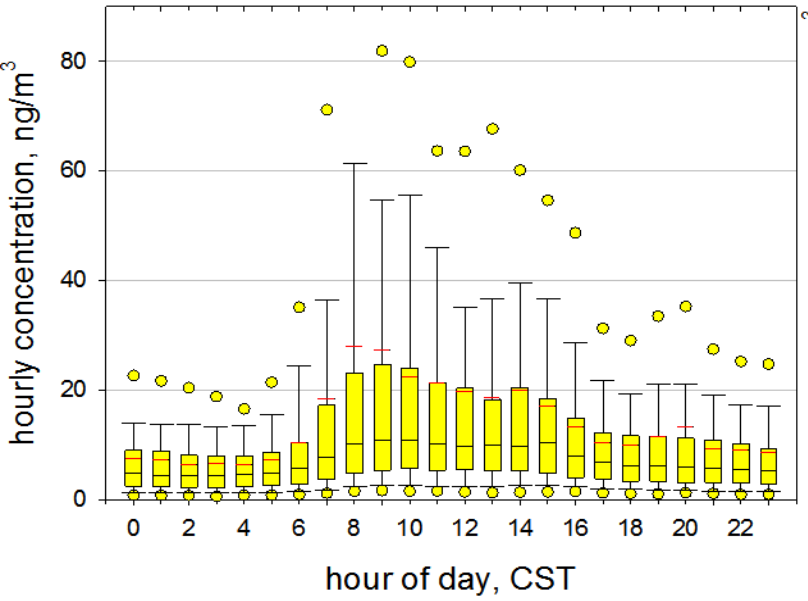

expected concentration, ng/m3
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0 90 180 270 360
wind direction, °N

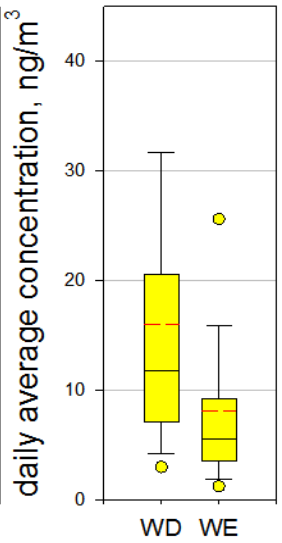

expected concentration, ng/m3
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
0 90 180 270 360
wind direction, °N

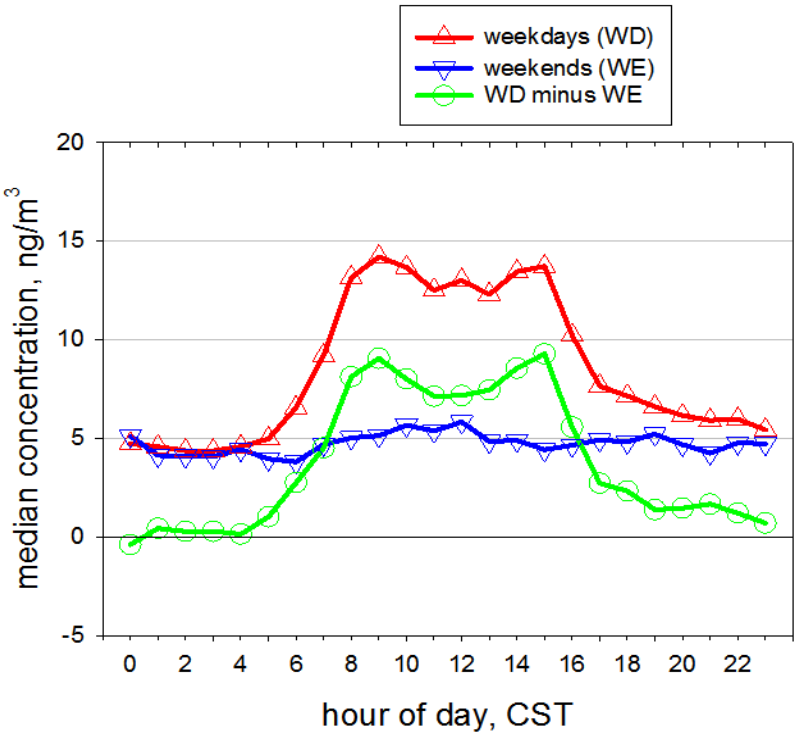
Selenium

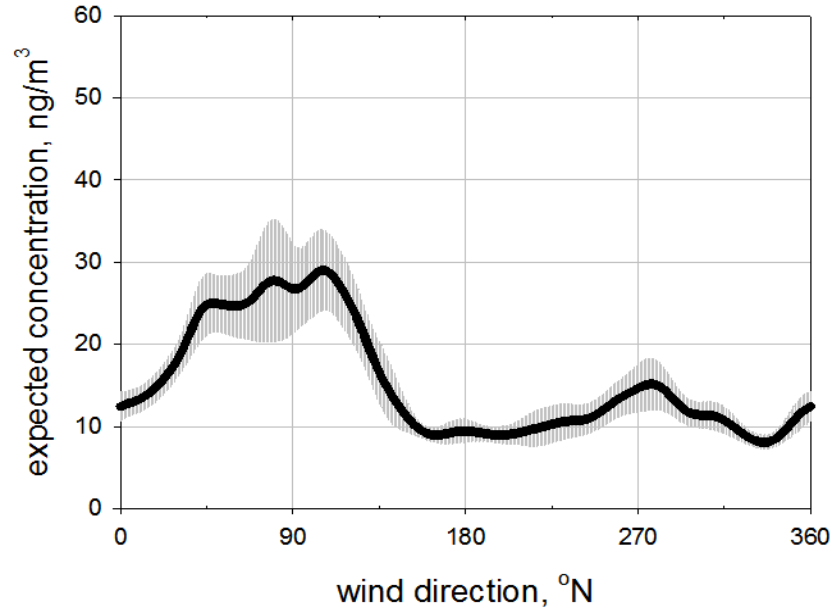
- Maximum concentrations at night and early morning
- No weekday/weekend differences
- Highest concentrations for surface winds from the east
  - Dominated by regional source contributions, consistent with finding of Yadav and Turner (2014) four-site analysis
- Emission source region to the east confirmed using Potential Source Contribution Function (PSCF) analysis
- Similar behavior for As
  - Small excess on weekdays during the midday hours

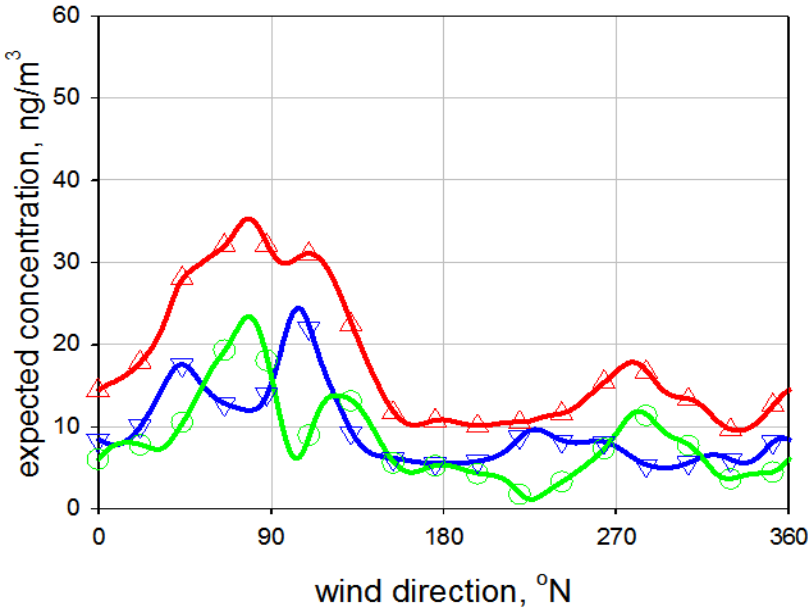
Manganese


hourly concentration, ng/m3
hour of day, CST


daily average concentration, ng/m3
WD
WE


weekdays (WD)
weekends (WE)
WD minus WE
median concentration, ng/m3
hour of day, CST

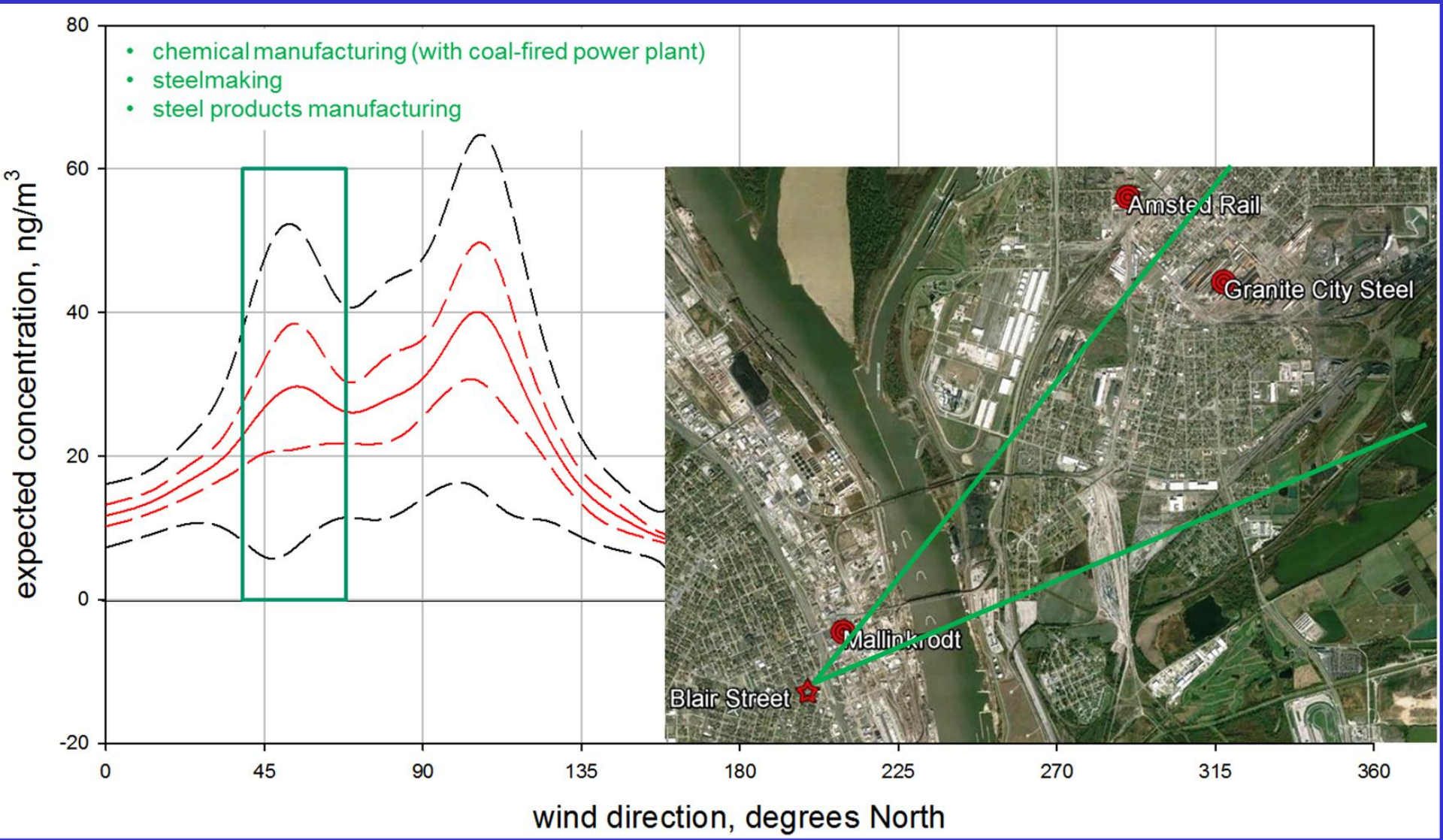

expected concentration, ng/m3
wind direction, °N


expected concentration, ng/m3
wind direction, °N

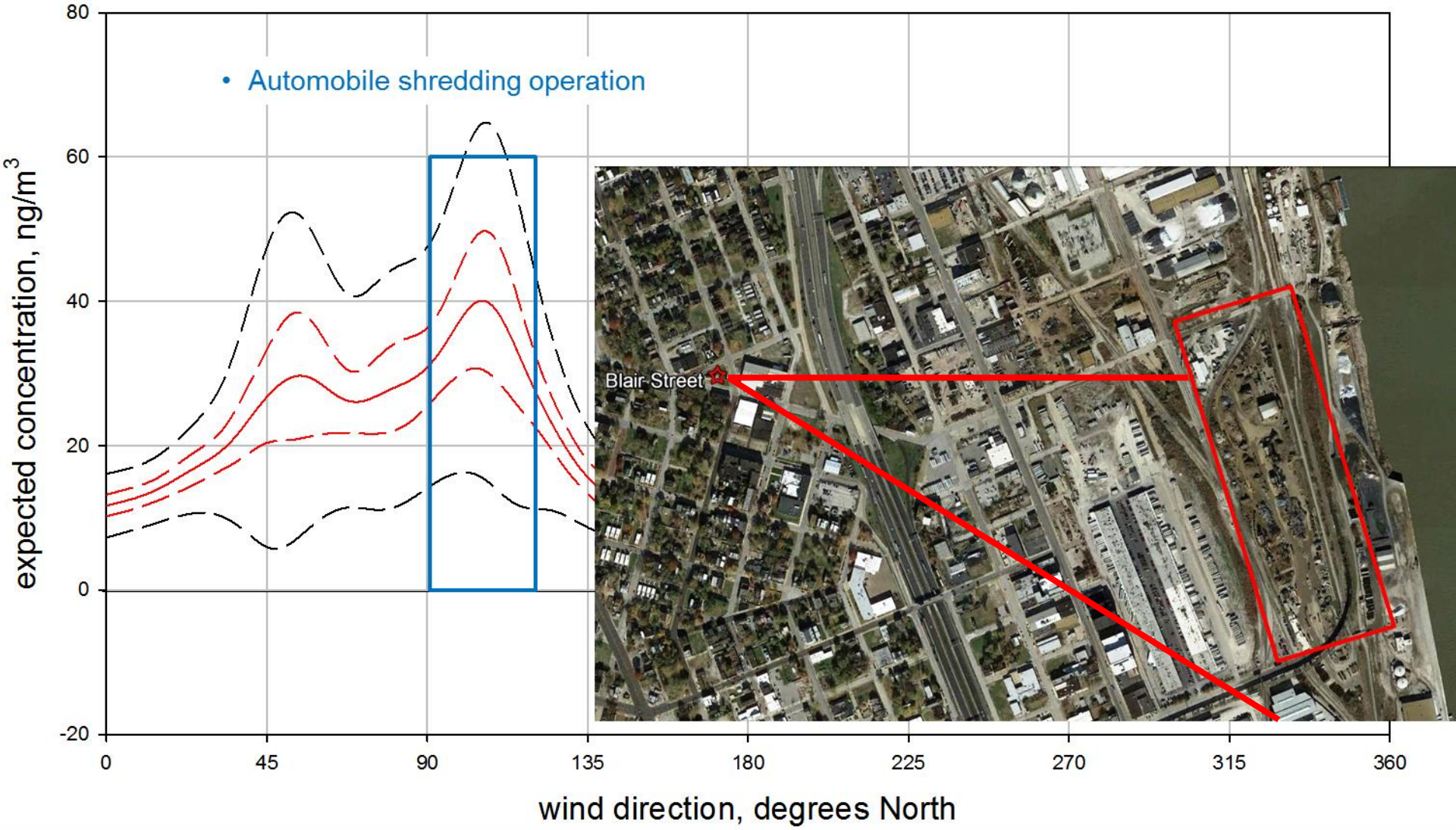
Manganese

- Maximum concentrations during daytime hours
- Concentrations greater on weekdays compared to weekends, but only during the daytime hours
- Significant weekday/weekend differences
- Emission source region to the east
  - Significant contributions from local sources, consistent with finding of Yadav and Turner (2014) four-site analysis which could not locate the source regions
- Several other elements show grossly similar patterns, e.g. Ca and Fe

Mn – 2013 data only



Mn – 2013 data only

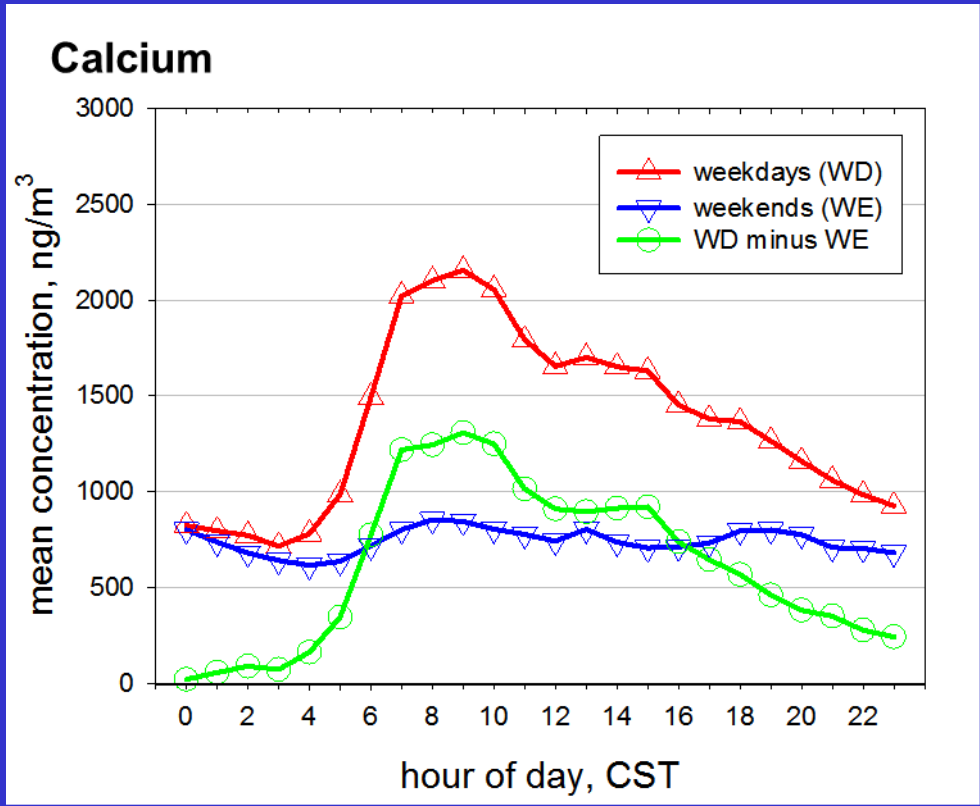


Summary

- Xact measurements provide high quality data for several elements
  - In some cases biased compared to filter methods yet often still highly correlated
- At the Blair Street station, for several species (e.g. As, Cs, Fe, Mn, Se)…
  - All-data wind direction profiles are quite similar
  - Diel profiles, weekday/weekend differences, and weekday/weekend stratified wind direction profiles demonstrate large differences in the underlying emission sources and their contributions
- Results from temporal analysis of high time resolution data (this work) consistent with spatial analysis of a four-site filter-based network (Yadav and Turner, 2014).

Next Steps

- Expand pollutants
  - Fourteen Xact PM_{10} elements
  - Four other species (BC, OC, EC, CO)
  - Maybe more Xact PM_{10} elements, other species (e.g., nitrogen oxides)
- Update the data set
  - This analysis through August 2014
  - Data now available through December 2015
- Quantitative Analysis…
  - e.g., weekday excess Ca is 47% of total
  - Similar analysis for wind direction data



Acknowledgements

- Missouri Department of Natural Resources
  - Jerry Downs, Will Wetherell
- Cooper Environmental Services, CES
  - John Cooper and Krag Petterson
- Varun Yadav
  - Formerly with Washington Univ. in St. Louis
  - Now with CES