

Measurement and Data Analysis for Source Attribution of Ambient Particulate Matter Arsenic and Other Air Toxics Metals in St. Louis

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Motivation

The St. Louis Community Air Project (CAP)

- identified six hazardous air pollutants of concern including arsenic, *however...*
- poor data quality for PM_{2.5} arsenic from speciation network data
- PM₁₀ air toxics metals routinely measured at only one site (1-in-6 day)

Objectives

Community Air Toxics Grant from USEPA

- Phase I

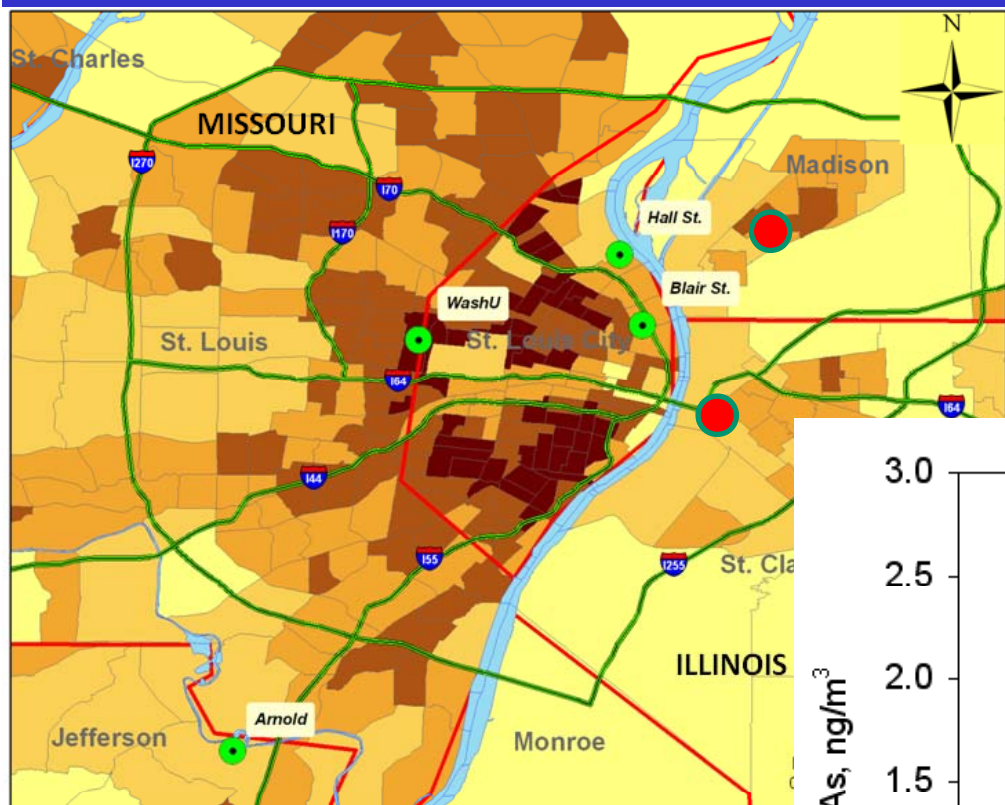
- four site network of HiVol PM₁₀ samplers
- one year at 1-in-3 days
- hot acid extraction and analysis by ICP-MS

- Phase II

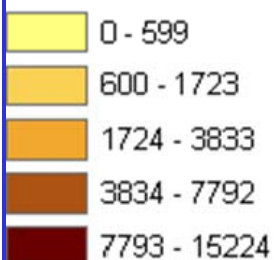
- high(er) time resolution measurements
- six one-month deployments of CES Xact 620
- *Xact performance evaluation
(already shown this week)*

Filter Network Monitoring Sites

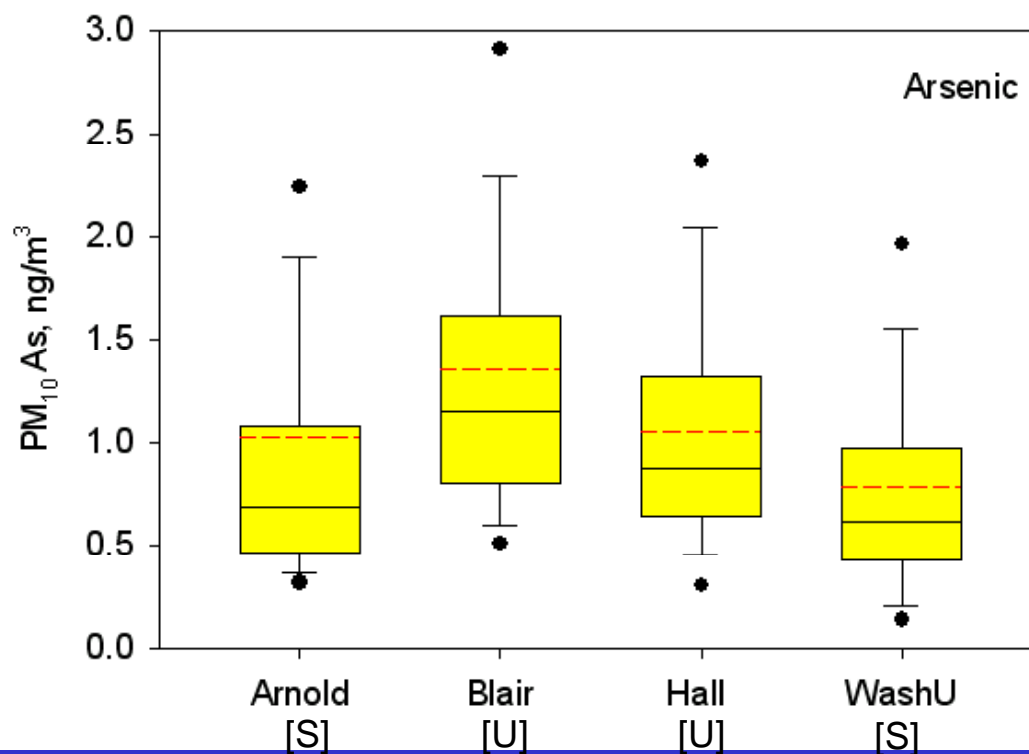
4 × Missouri (1-in-3), 2 × Illinois (1-in-6)



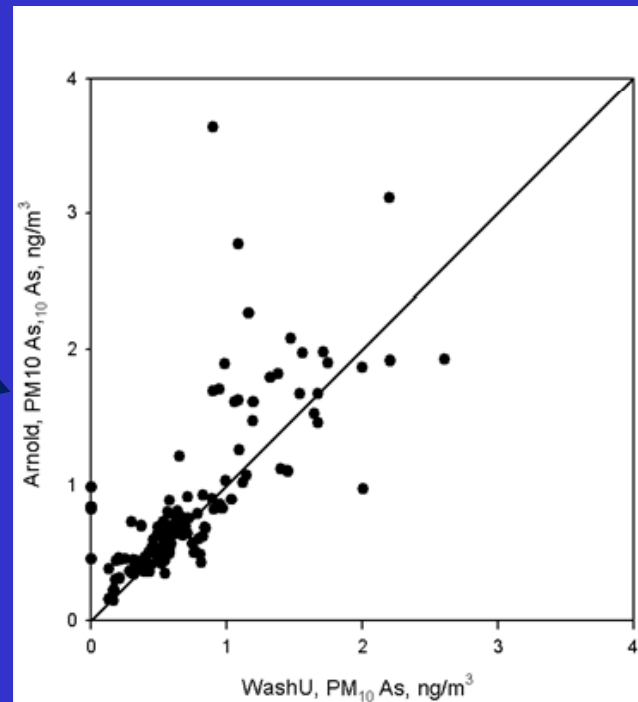
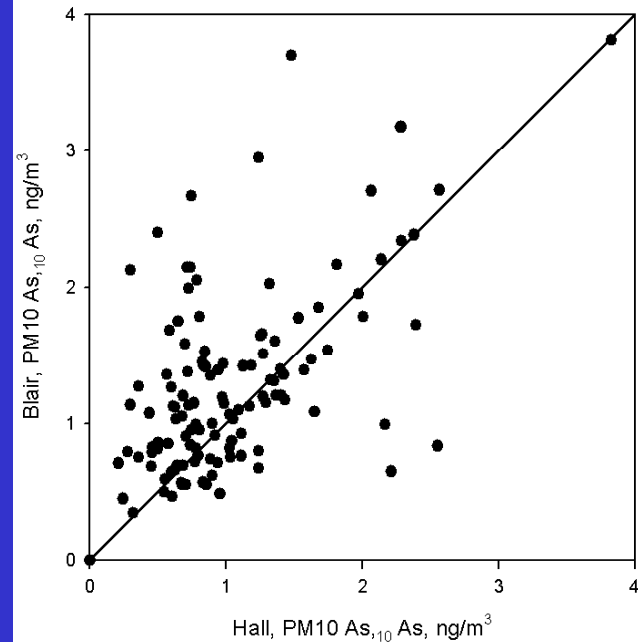
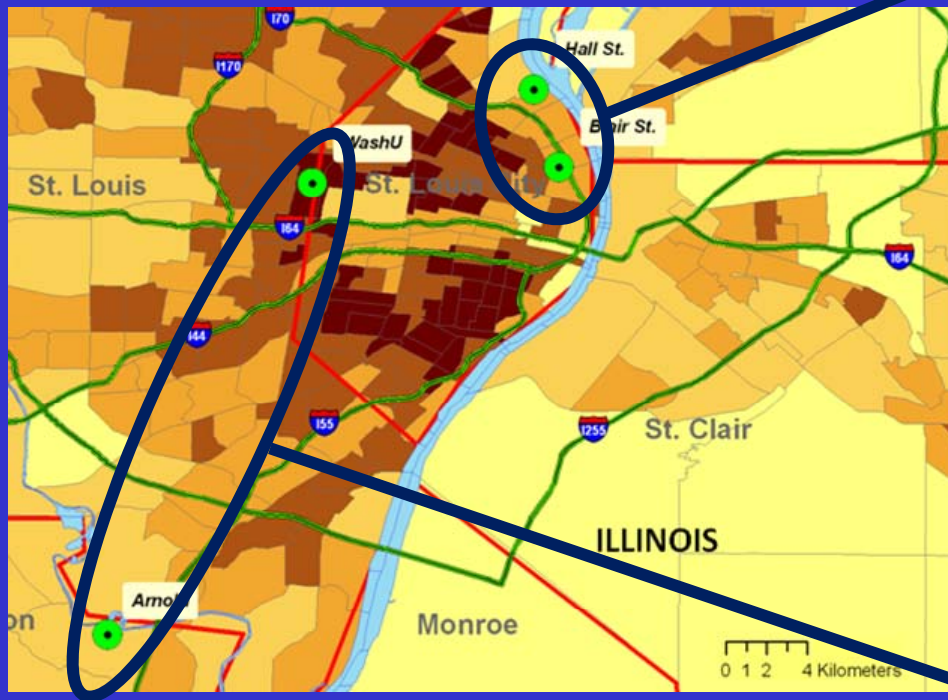
Pop. Density
(#/sq. mile)



U = Urban
S = Suburban

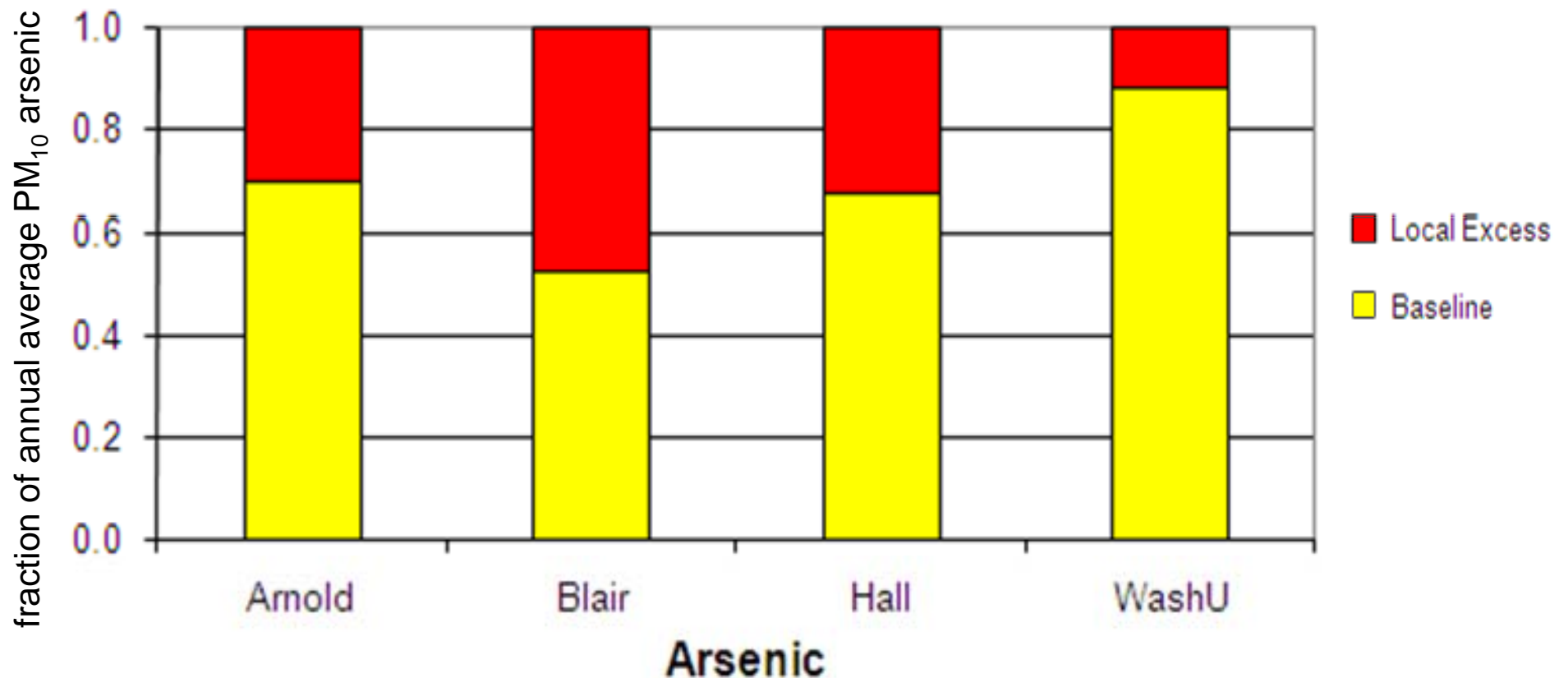


Intersite Variability



variability (proximate urban sites)
>
variability (distance suburban sites)

Baseline and Excess Contributions to PM₁₀ Arsenic

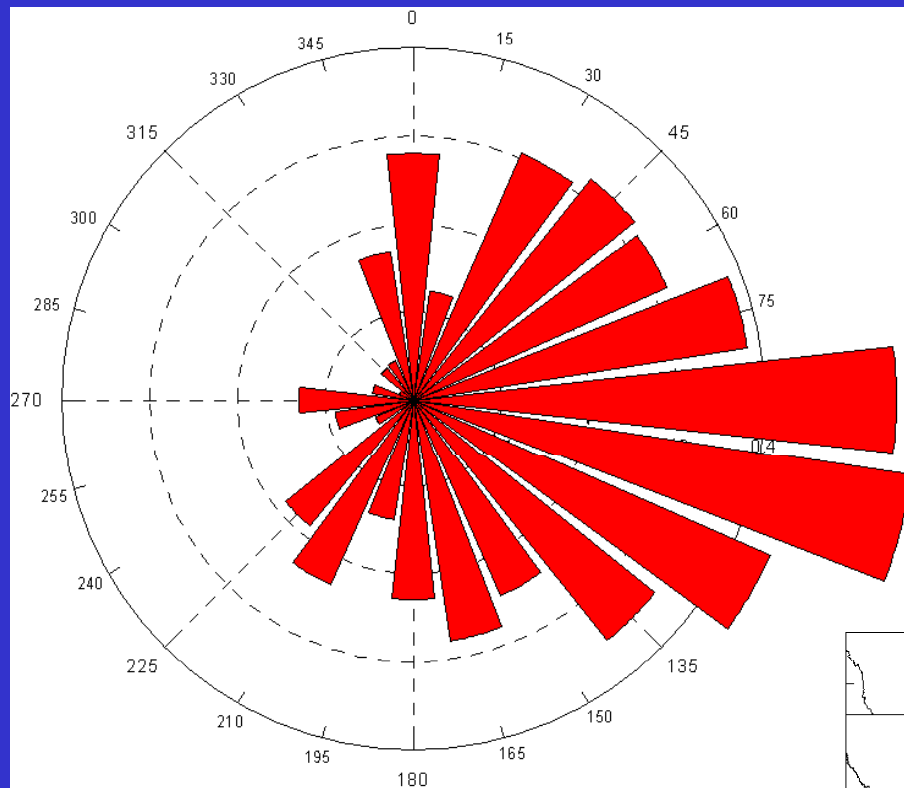


Baseline = regionally transported?

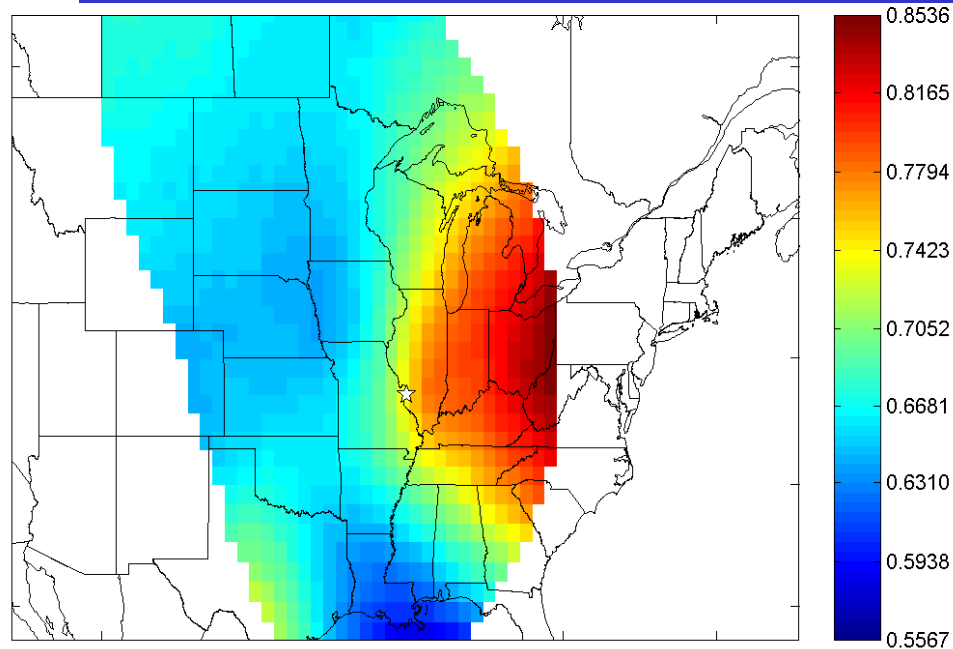
Excess = locally emitted?

Baseline PM₁₀ Arsenic

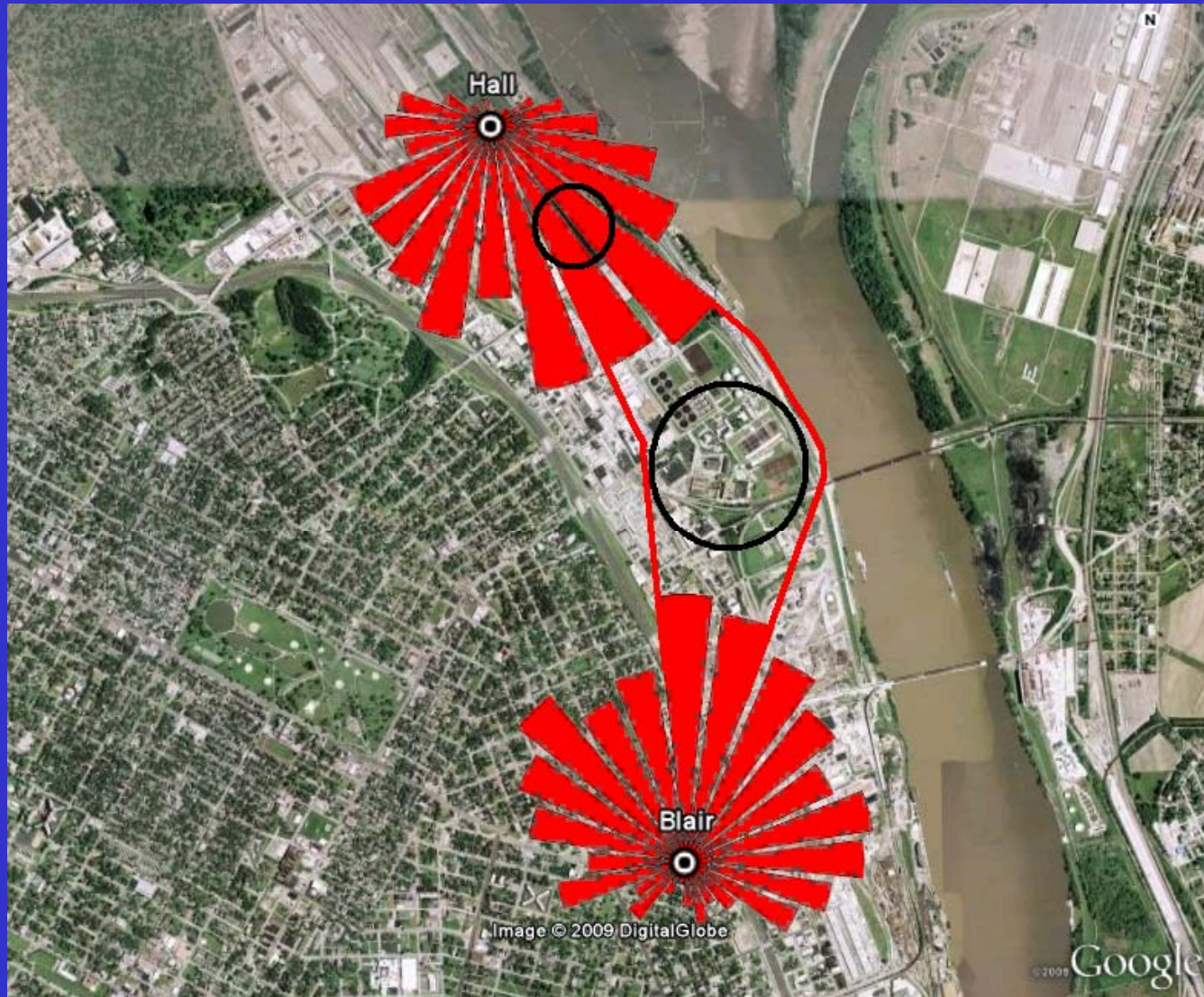
conditional probability function (CPF)
(24-hour As, hourly winds)



quantitative transport bias analysis
(QTBA)
(24-hour As, 3-day back trajectories)

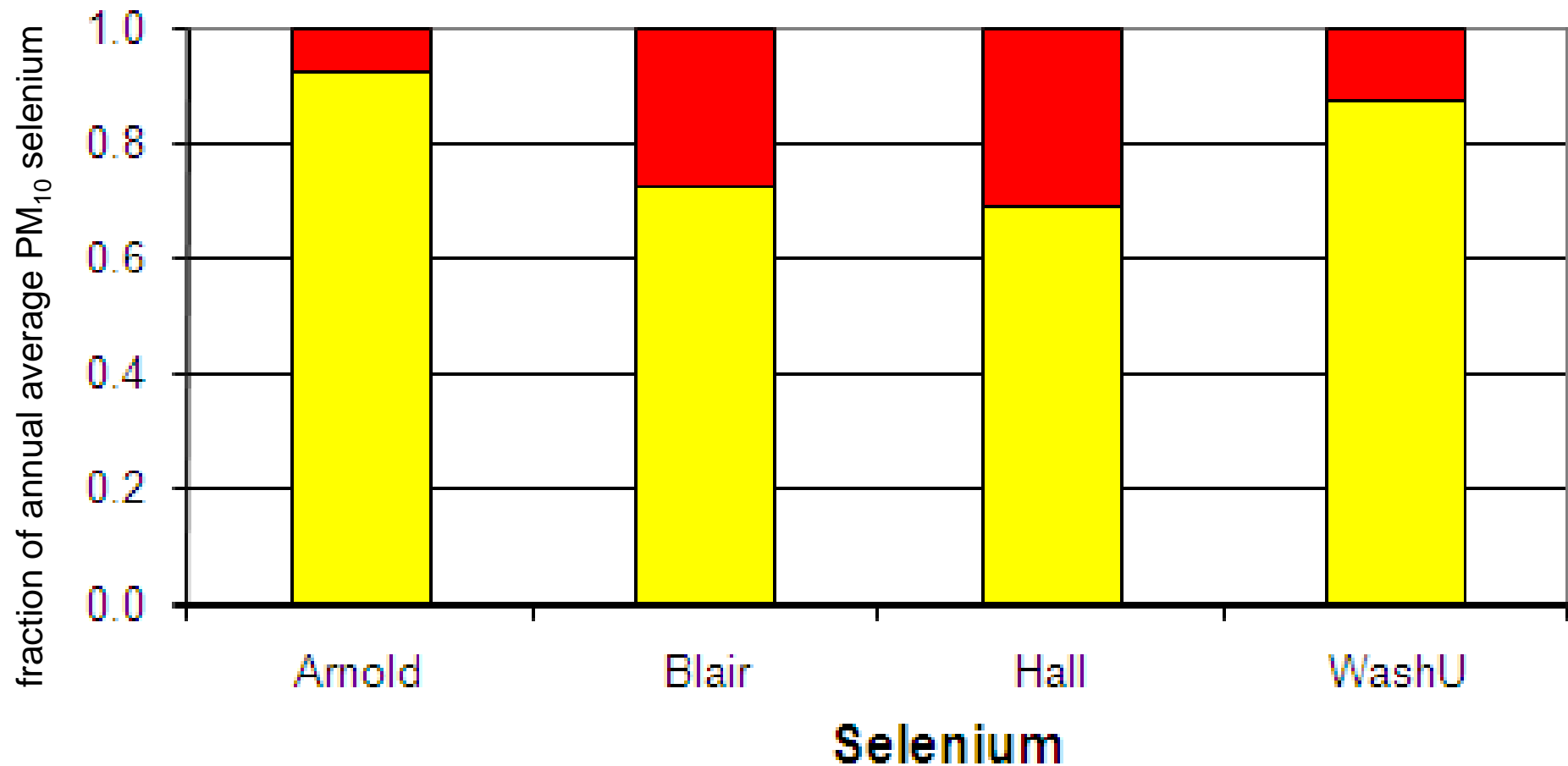


Excess PM_{10} Arsenic at Urban Sites



conditional probability function plots (24-hour As, hourly winds)

Baseline and Excess Contributions to PM_{10} Selenium



Cooper Environmental Services (CES) Xact 620

- particle collection on a filter tape
- analysis by x-ray fluorescence (XRF)
- continuous data time series at user-defined intervals
- Missouri DNR instrument optimized for As, Hg, and Pb at remote areas



ELEMENTS THE XACT CAN MEASURE (IN BLUE)

1	1	2											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 (268)	111 Unu (269)								

Lanthanide Series

58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce 140.12	Pr 140.91	Nd 144.24	Pm (144.9)	Sm 150.36	Eu 151.97	Gd 157.25	Tb 158.93	Dy 162.5	Ho 164.93	Er 167.26	Tm 168.93	Yb 173.04	Lu 174.97

Actinide Series

90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th 232.04	Pa 231.04	U 238.03	Np (237)	Pu (244.1)	Am (243.1)	Cm (247.1)	Bk (247.1)	Cf (251.1)	Es (252.1)	Fm (257.1)	Md (258.1)	No (259.1)	Lr (262.1)

○ measured by Xact in this study

○ EPA Air Toxics PM metals

Xact Performance Evaluation

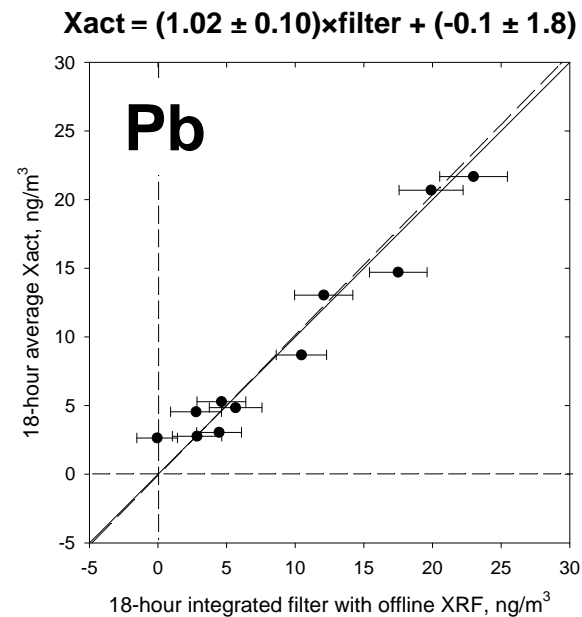
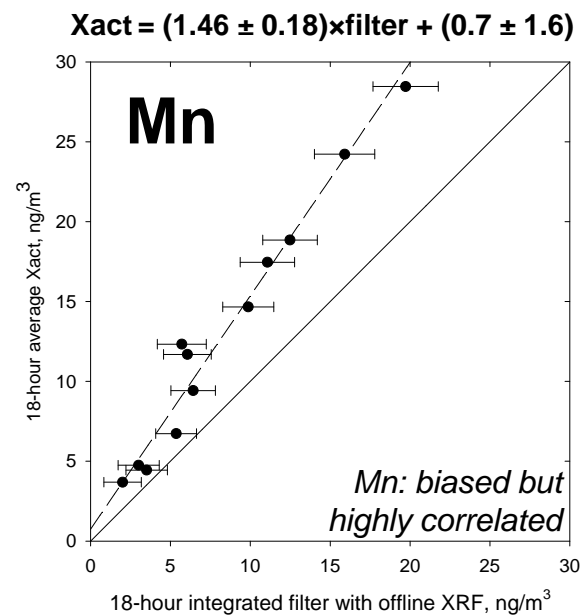
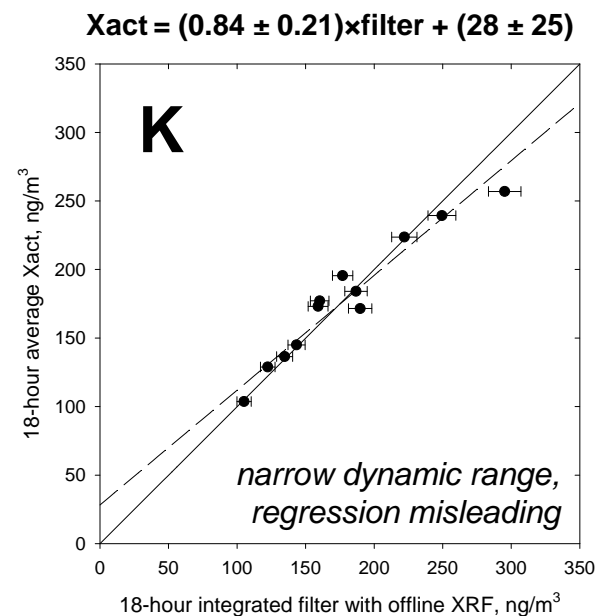
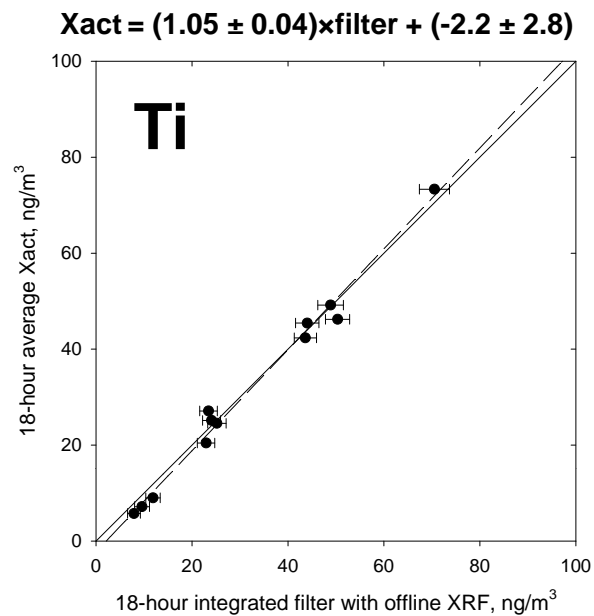


HiVol PM₁₀ / quartz filter,
NATTS digestion protocol
ICP-MS: As, Pb, Se...



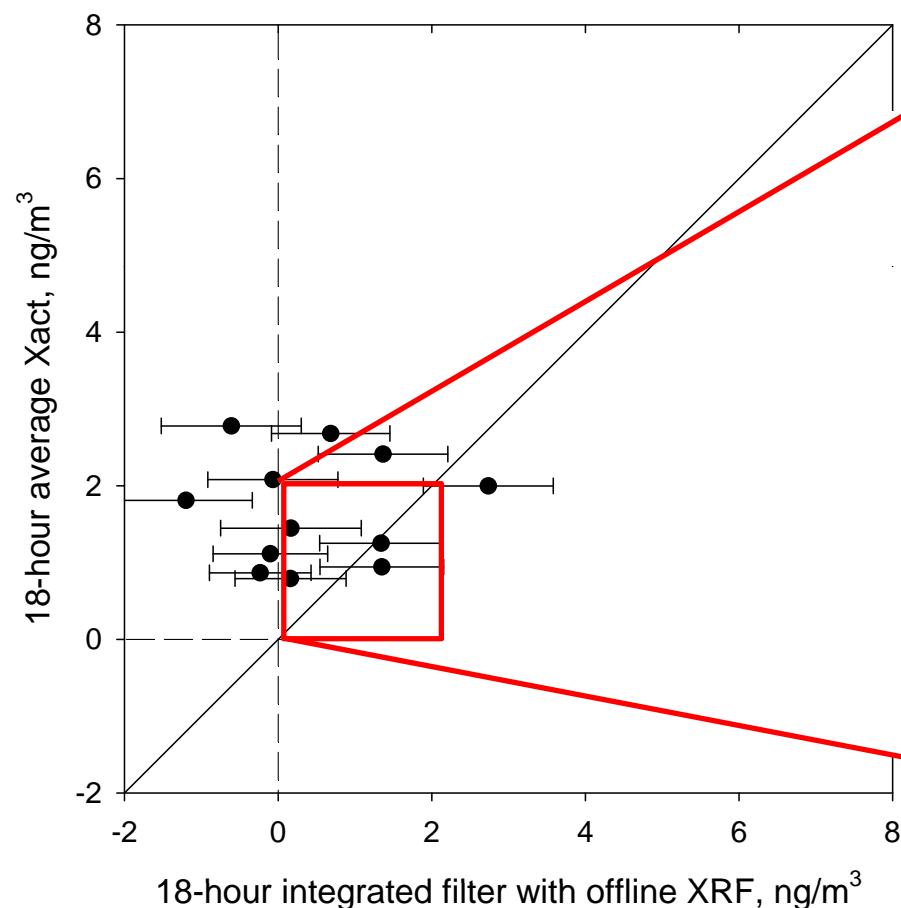
LowVol PM₁₀ (FRM) / Teflon filter
XRF: Ca, Fe, K, Mn, Pb, Ti...

Xact vs. LowVol PM₁₀ FRM / XRF

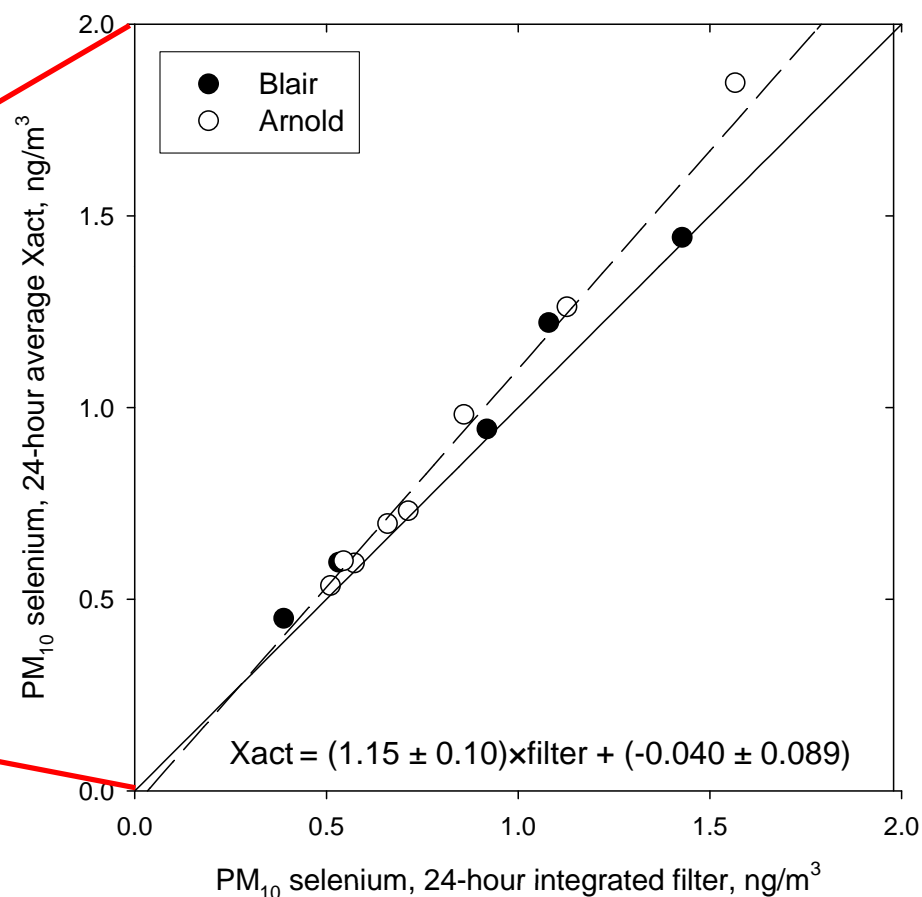


Selenium: Xact vs. Filter-Based Measurements

Xact vs. LowVol filter / lab XRF



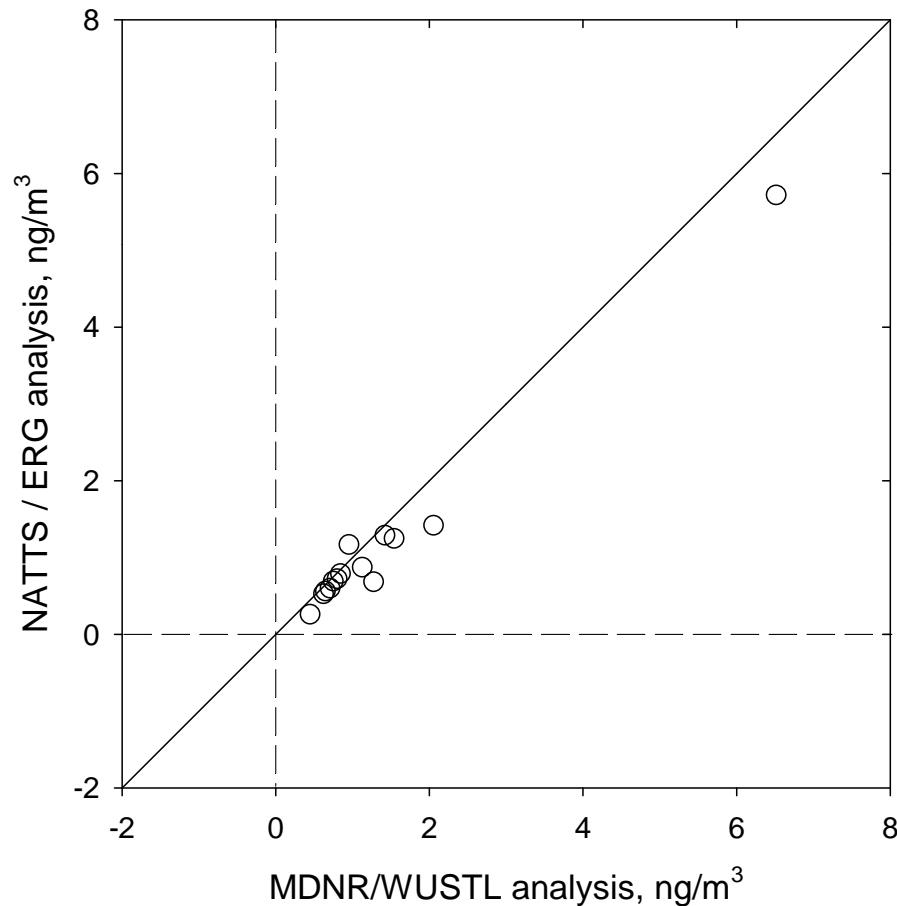
Xact vs. HiVol filter / lab ICP-MS



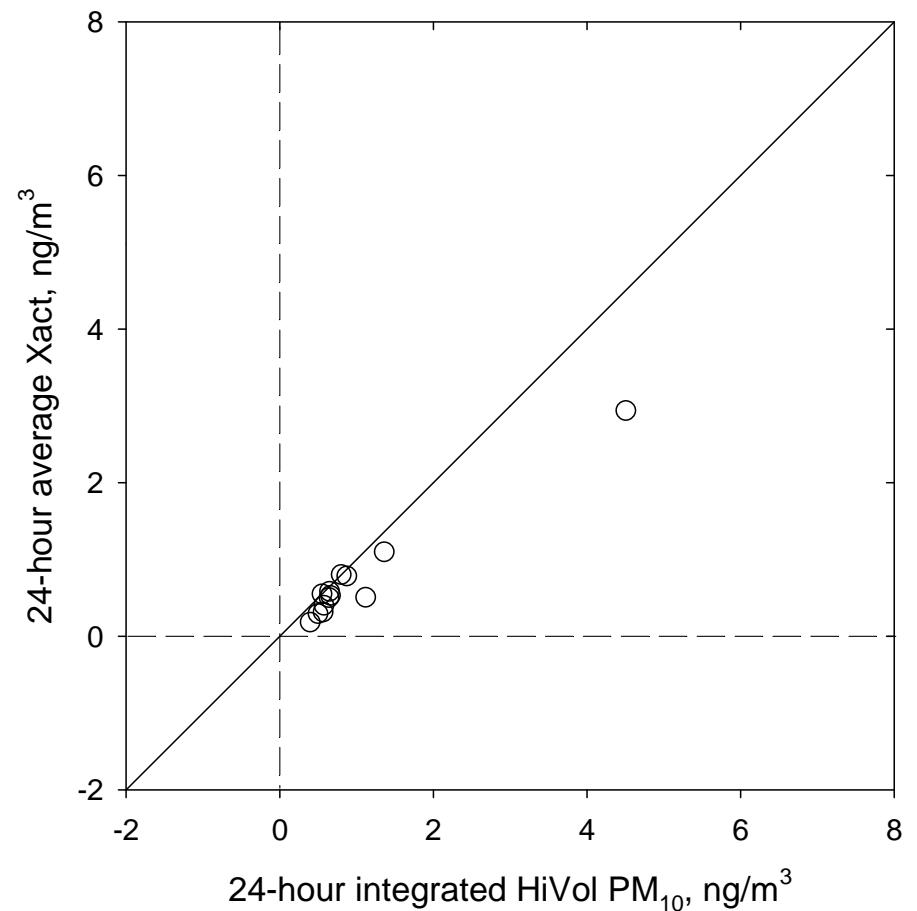
Se: favorable comparison between Xact and PM₁₀ HiVol samples with analysis by ICP-MS

Arsenic – Methods Comparisons

Collocated HiVol Samplers
Blair site, 4th Quarter 2008



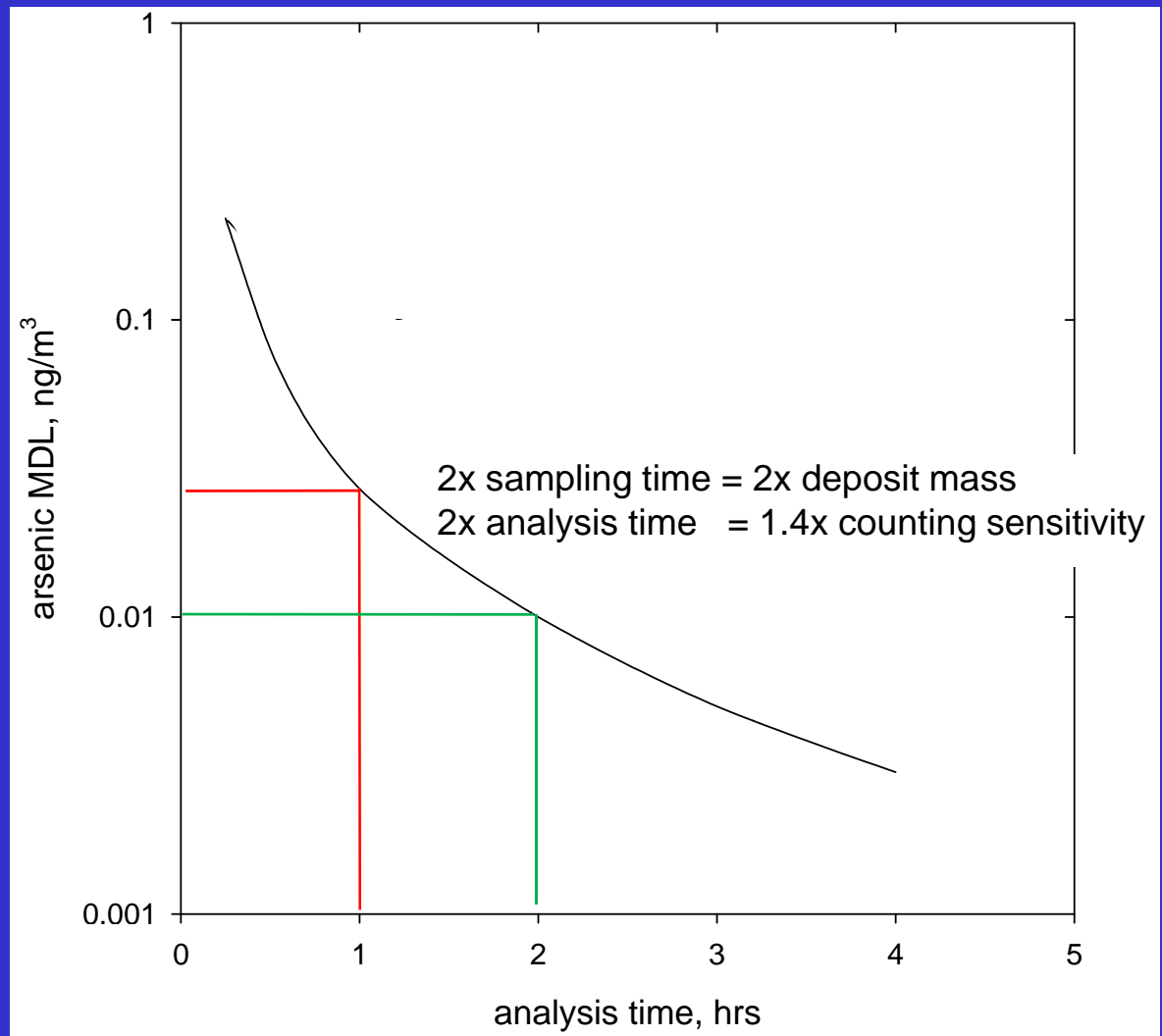
Xact vs. WUSTL HiVol
Dec 2008 / Jan 2009



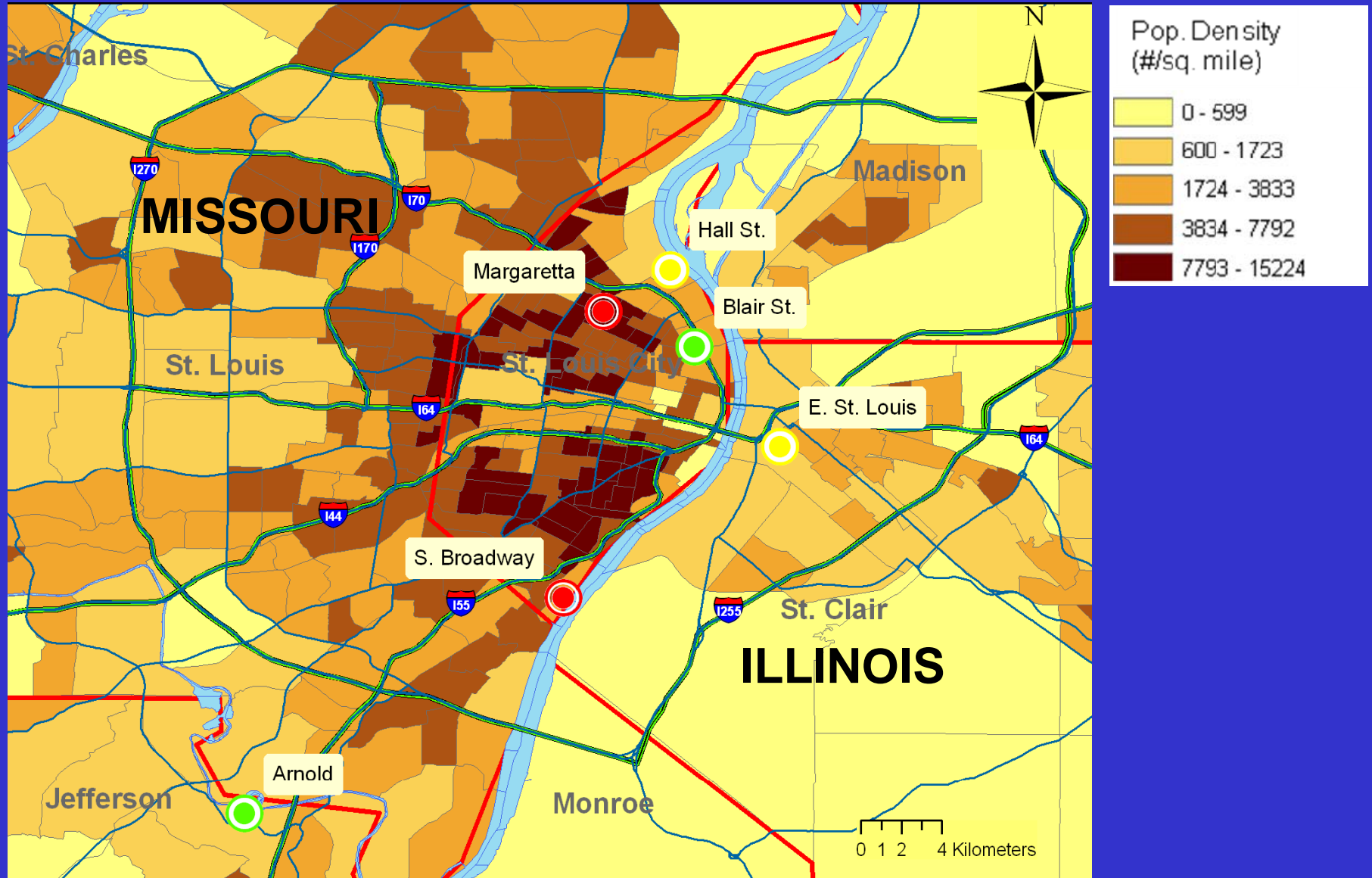
As: favorable comparison between Xact and PM₁₀ HiVol samples with analysis by ICP-MS.

Optimizing the Sampling Time Interval

- depends on study objectives!
- trade-offs between time resolution and frequency above MDL
- Blair Street (STL)
 - 1-hour: 56% > MDL
 - 2-hour: 86% > MDL

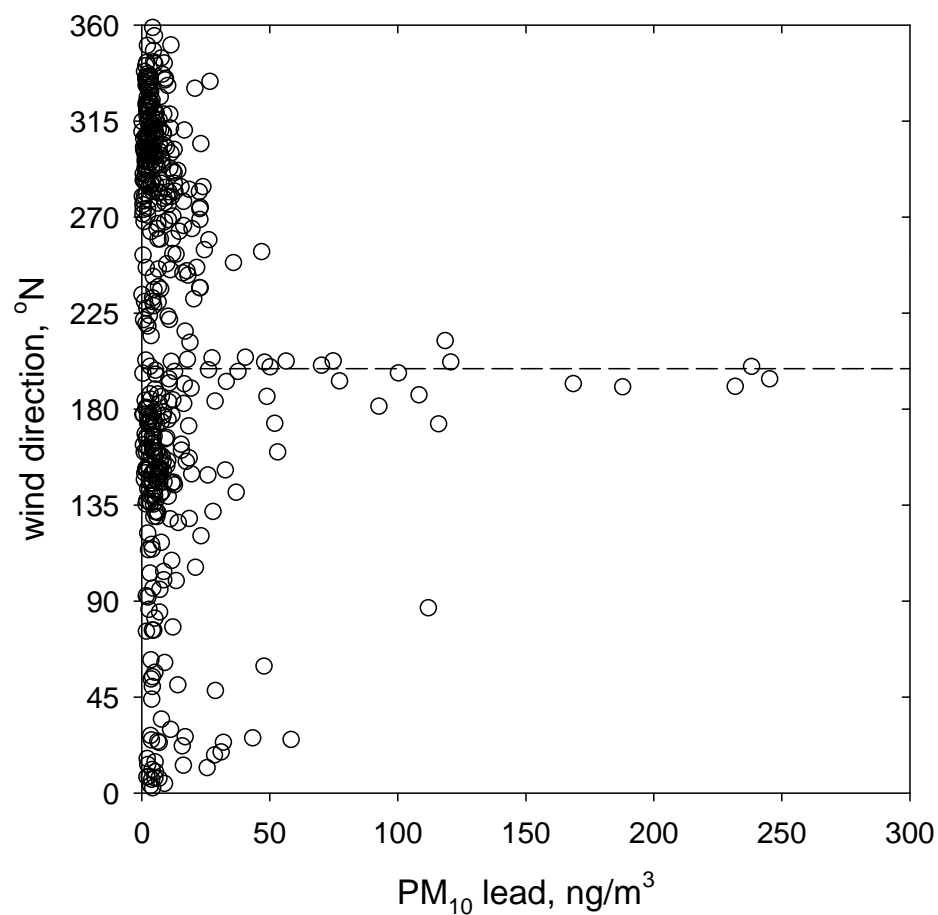


Xact Monitoring Sites

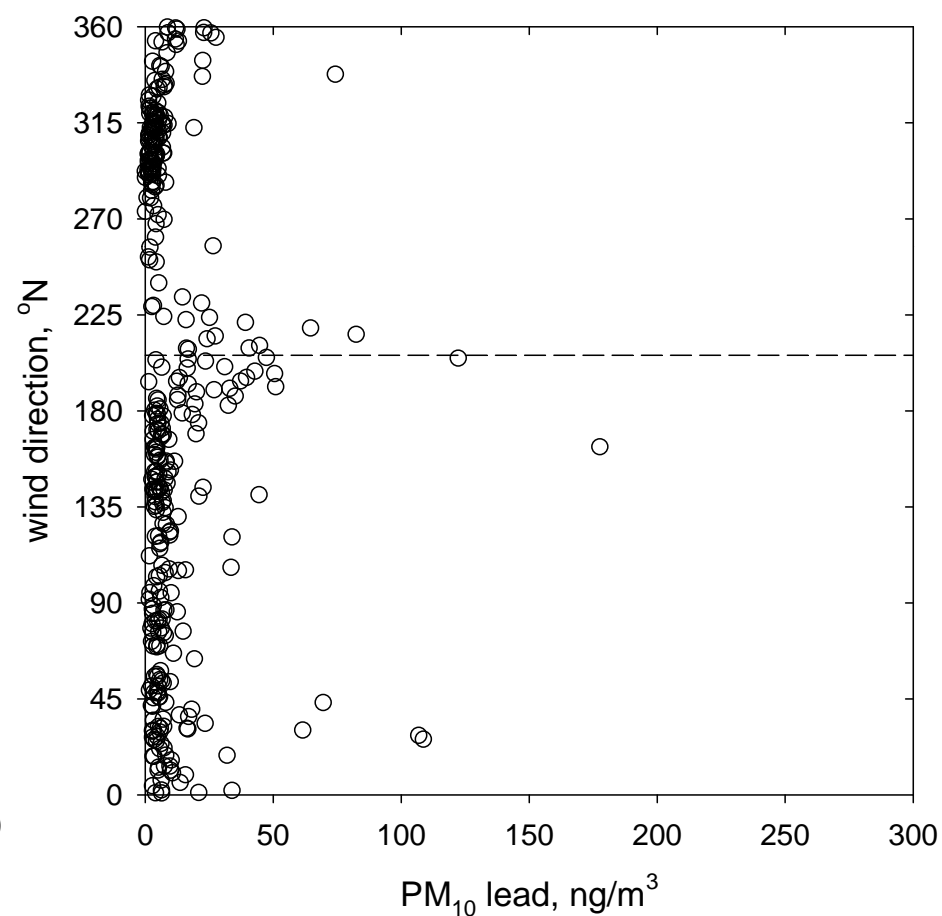


PM₁₀ Lead by Xact (2-hour resolution)

BLAIR



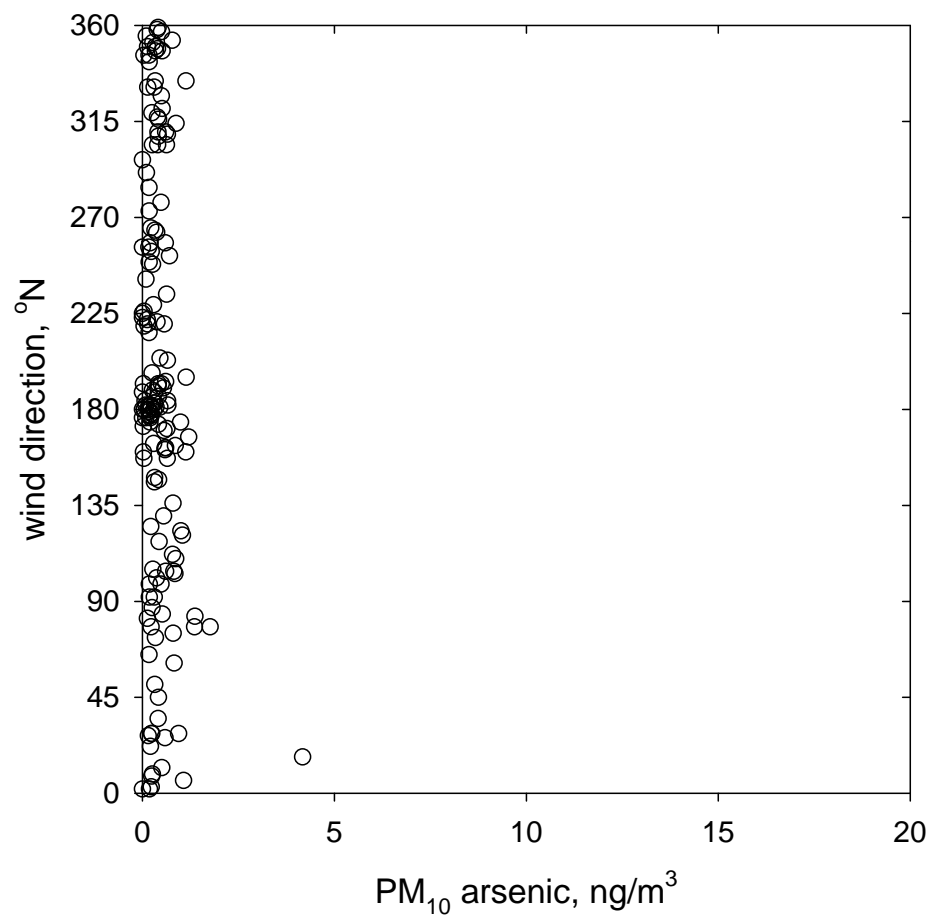
ARNOLD



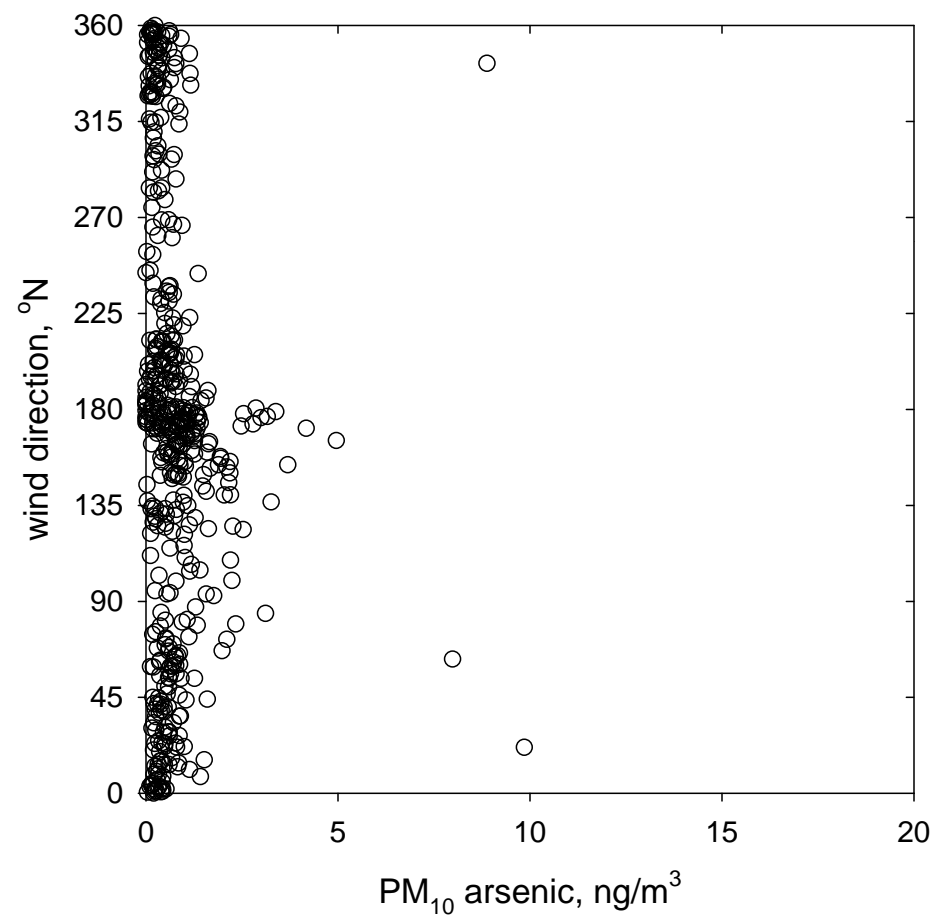
Dashed line is bearing of Doe Run – Herculaneum lead smelter

PM₁₀ Arsenic by Xact (2-hour resolution)

S. BROADWAY

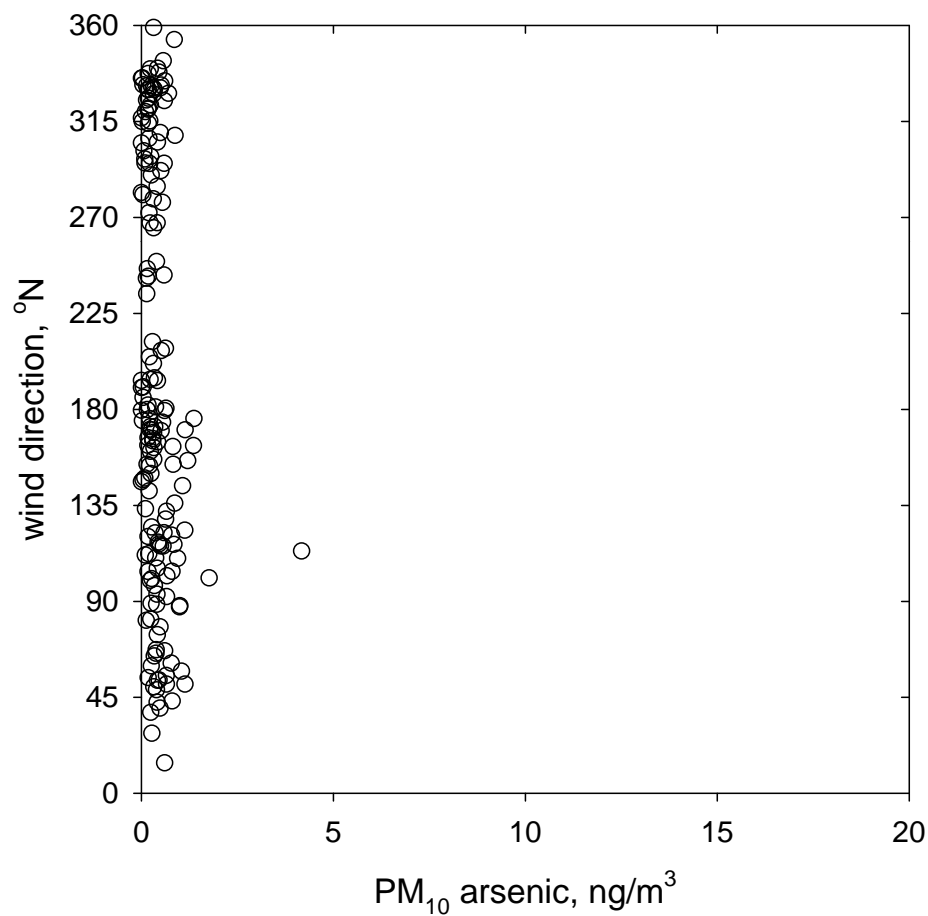


ARNOLD

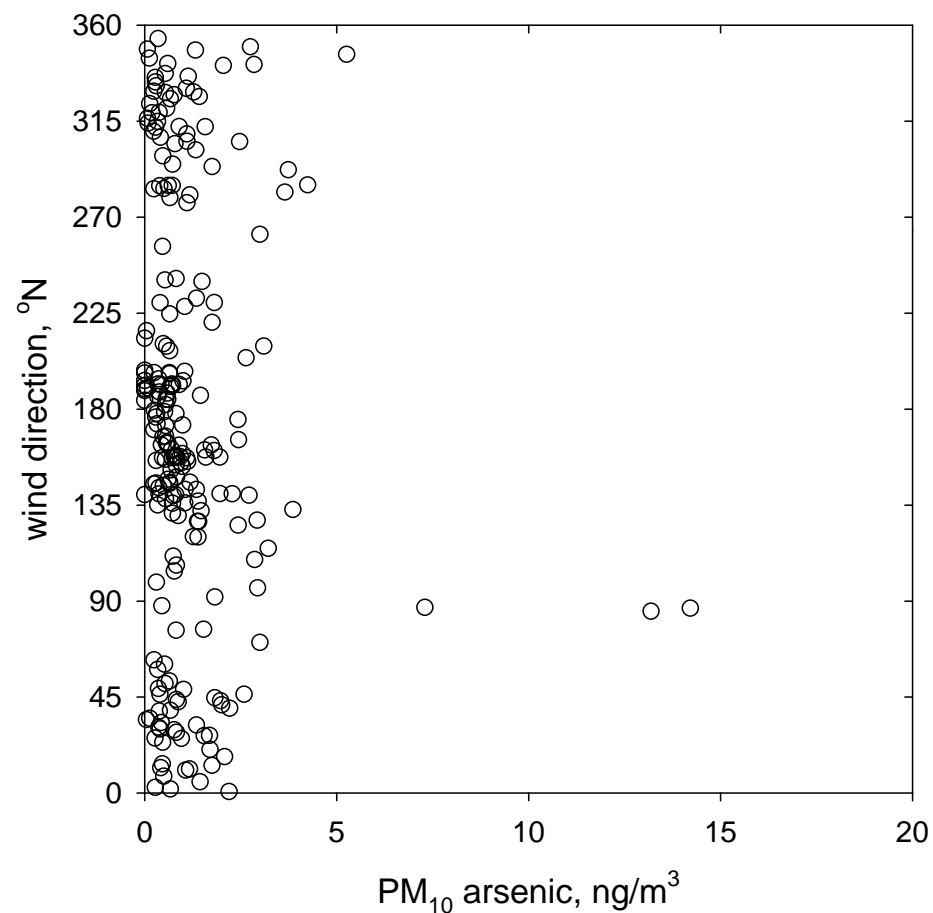


PM₁₀ Arsenic by Xact (2-hour resolution)

MARGARETTA

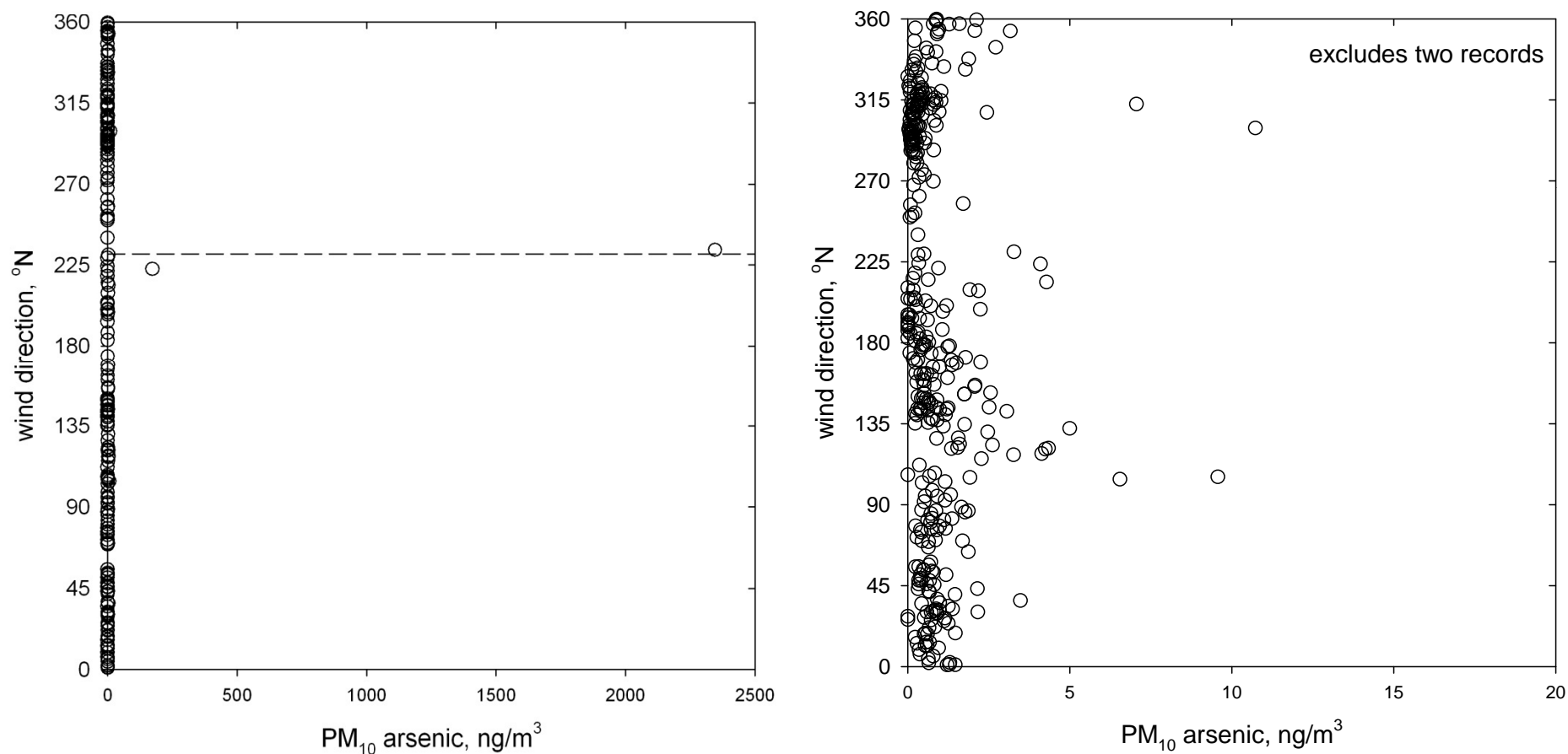


HALL



PM₁₀ Arsenic by Xact (2-hour resolution)

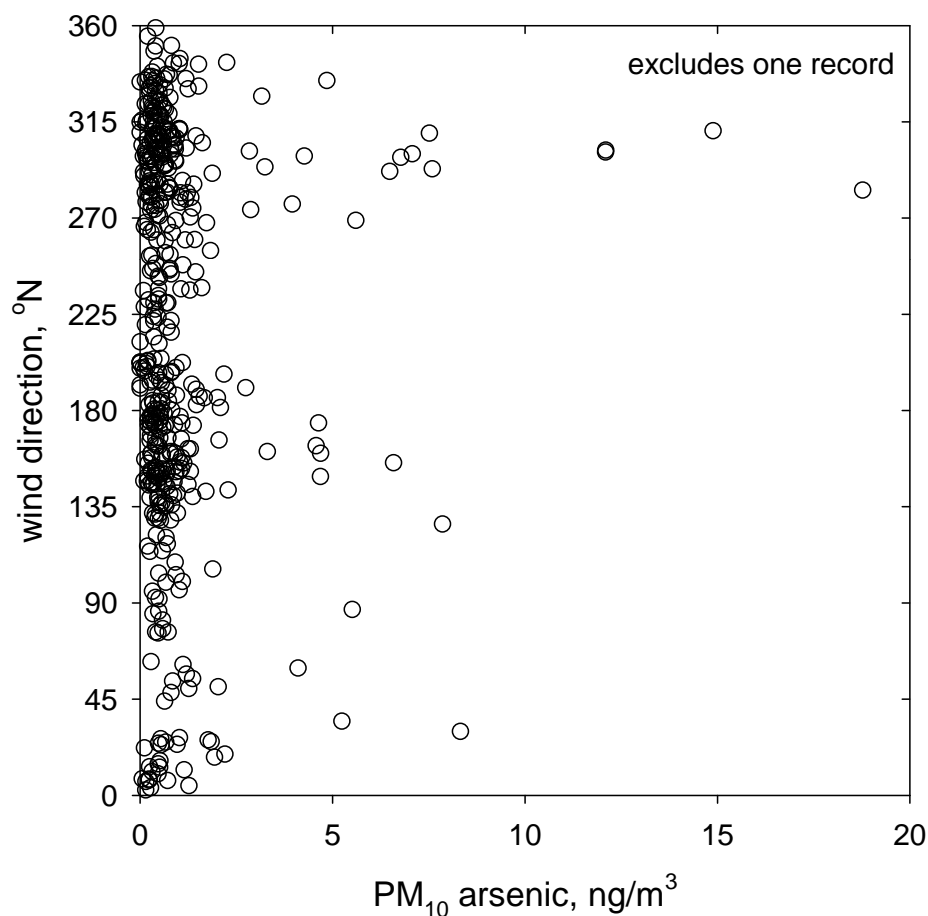
EAST ST. LOUIS



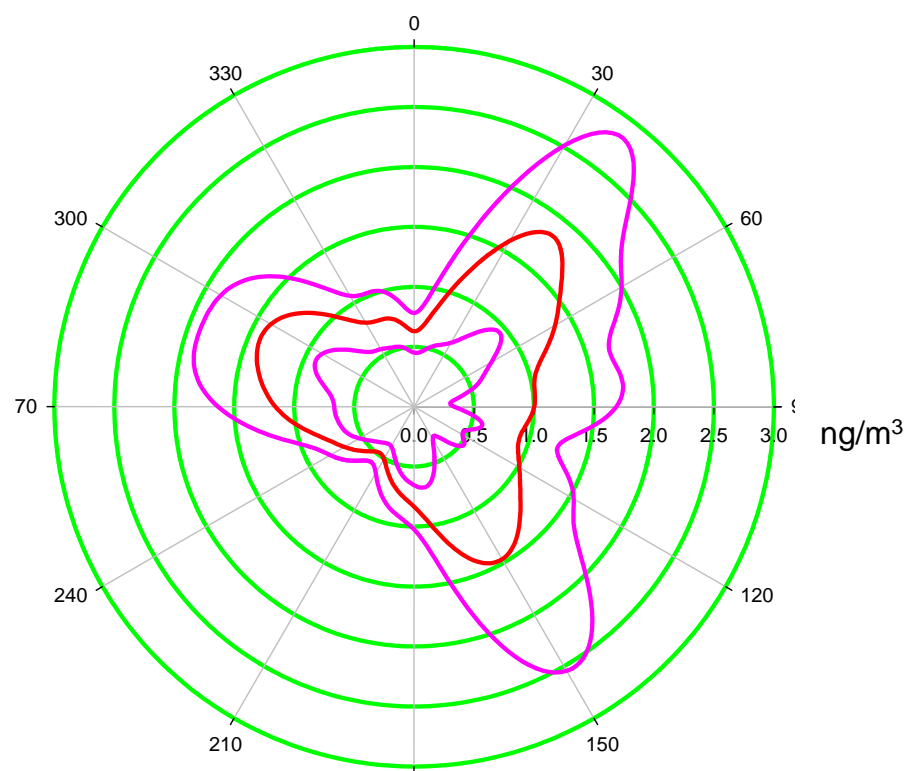
2-hour spike exceeding 2.5 $\mu\text{g}/\text{m}^3$ arsenic!

PM₁₀ Arsenic at Blair by Xact (2-hour resolution)

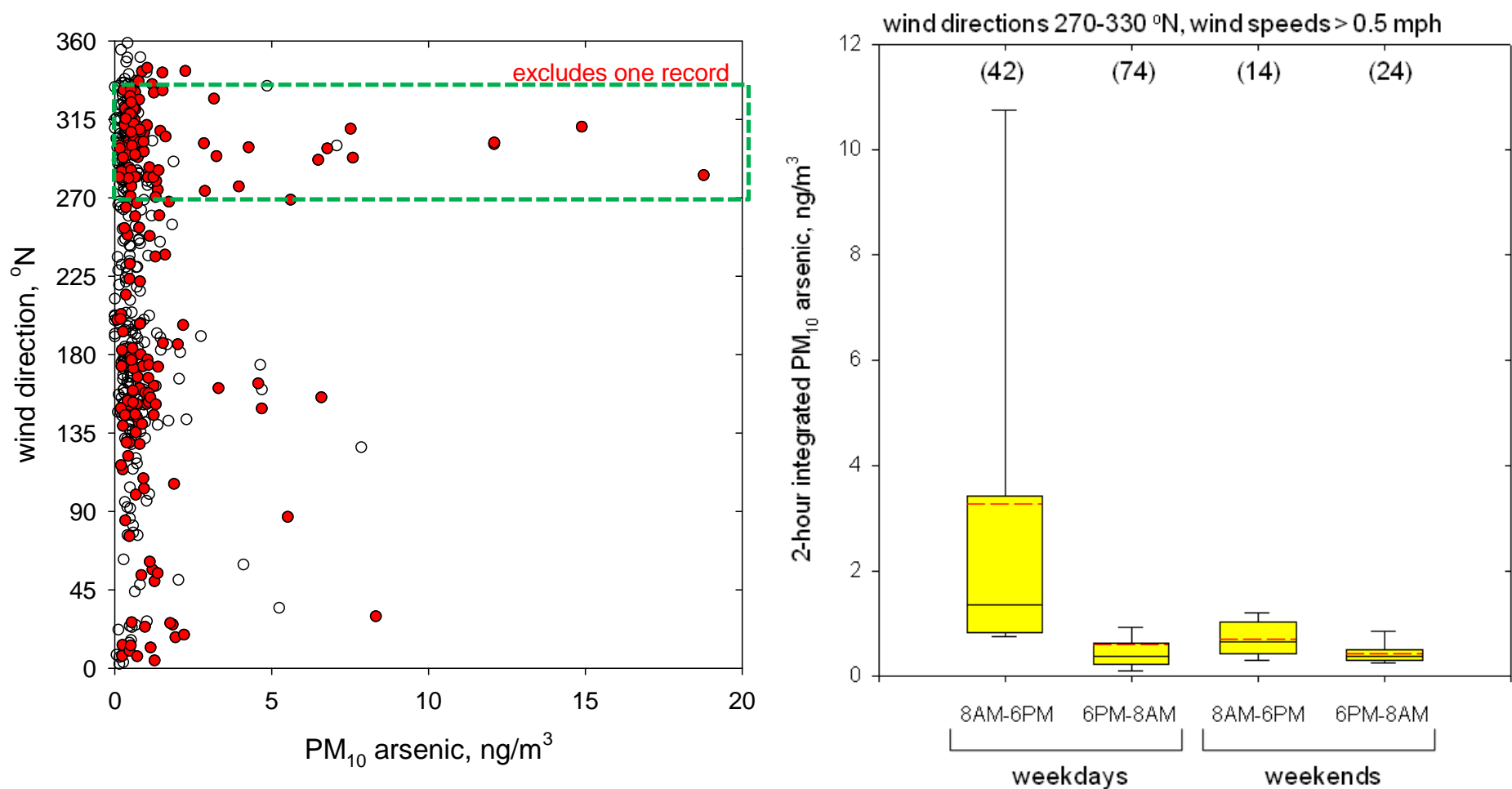
wind direction vs. concentration



nonparametric wind regression



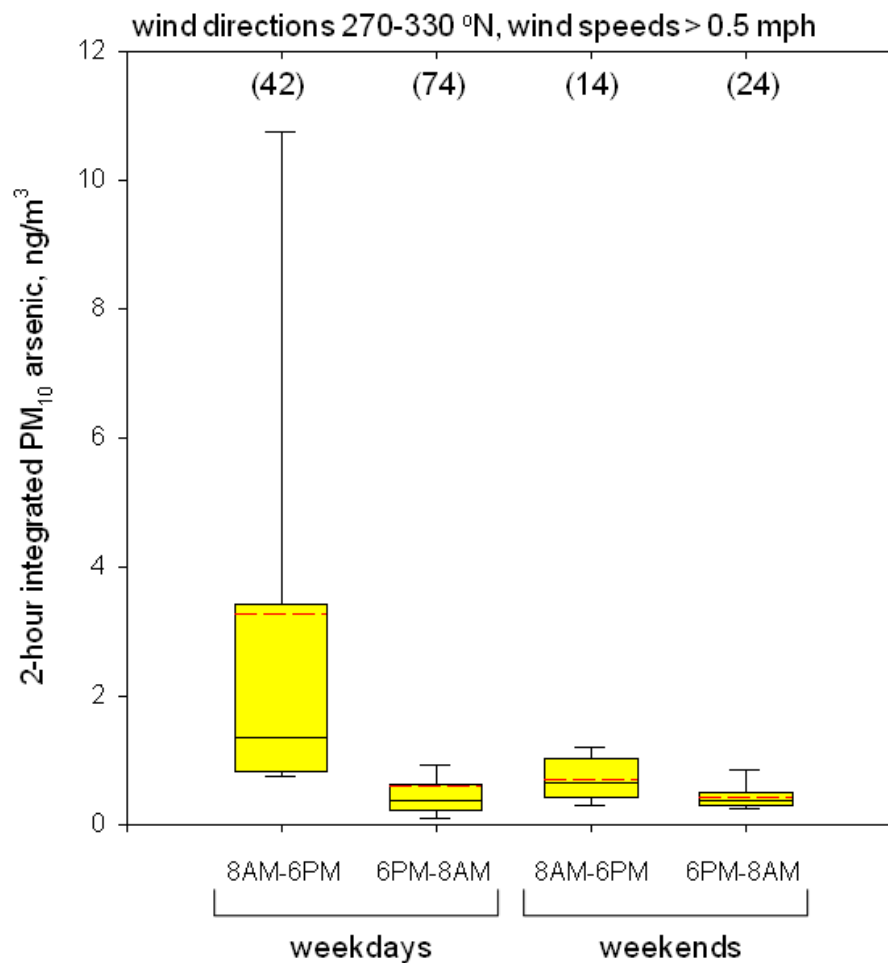
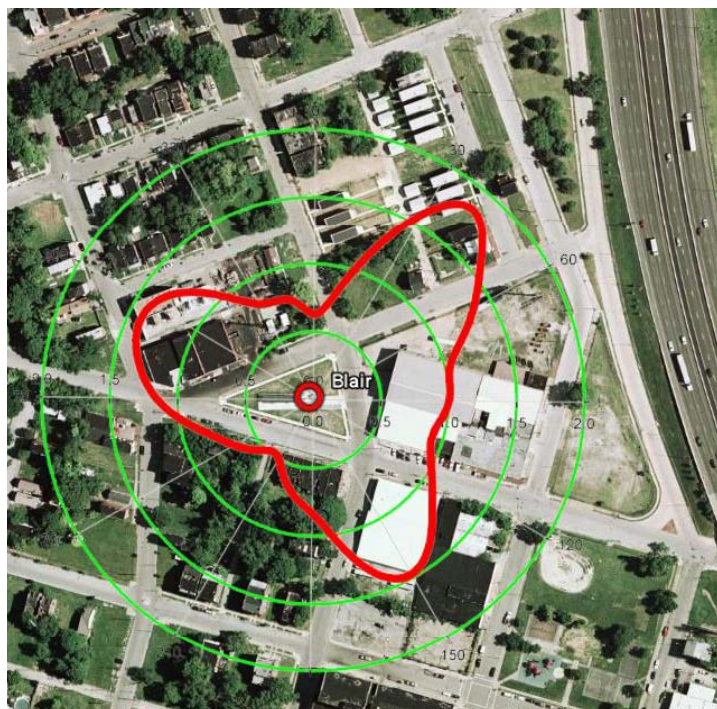
PM₁₀ Arsenic at Blair for Winds from Northwest



red markers = 8 AM – 6PM weekdays

PM₁₀ Arsenic at Blair for Winds from Northwest

nonparametric wind regression



likely microscale impacts

Summary

- Observed urban-scale spatial gradients in PM_{10} arsenic not captured in the emissions inventory
 - Regional transport from the eastern U.S.
 - Local sources along industrial riverfront
 - Microscale impacts at the Blair Street NATTS site
- CES Xact 620 for automated ambient PM elemental analysis
 - Very promising, based on initial performance evaluation
 - Identify intermittent sources not detected by time-integrated measurements
 - How long to stay at a site? “information content” of plumes, separating local from regional contributions?

The Next Steps

- Collocated Xact measurements (MDNR and CES)
 - Herculaneum, August 2009... **done**
 - Measurement precision, crucial data for receptor modeling
- Receptor modeling of the data sets
- Additional Xact deployments
 - Currently near lead smelter in Herculaneum (source profile)
- Expanded performance evaluation
 - Forty additional low-volume PM₁₀ FRM samples, analysis by XRF and ICP-MS

Acknowledgements

- Missouri Department of Natural Resources
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 - Mike Jones
- U.S. EPA / Region VII
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- Washington University
 - Stephen Feinberg