Evaluation of Passive Sampling Techniques for Monitoring Roadway and Neighborhood Exposures to Benzene and Other Mobile Source VOCs

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Milwaukee risk assessment studies use the RAIMI (Regional Air Impact Modeling Initiative) technique. Included in the inputs are results for mobile sources modeling. Risk Assessment, planning and modeling staff requested air monitoring to verify modeling results.

Questions

- How accurate are current modeling efforts in predicting ambient benzene concentrations near roadways?
- How quickly is benzene dispersed from the roadways to the adjoining environment ?
- Are benzene exposures in neighborhood environment different from roadway exposure?

Roadway benzene studies
to answer these questions would require:

- multi-site networks,
- small site footprints,
- minimal on-site support,
- accurate long term benzene measurements

Passive sampling techniques would be best able to meet the projects monitoring needs.

Our Assets

- We have an analytical system. The PE Ozone Precursor Analytical System. Available September through May.

- We have experience using passive monitoring badges (3M OVM) and passive canisters.

- Have experience conducting roadway monitoring projects (1995 RFG Study).

- IEPA has used passive samplers.

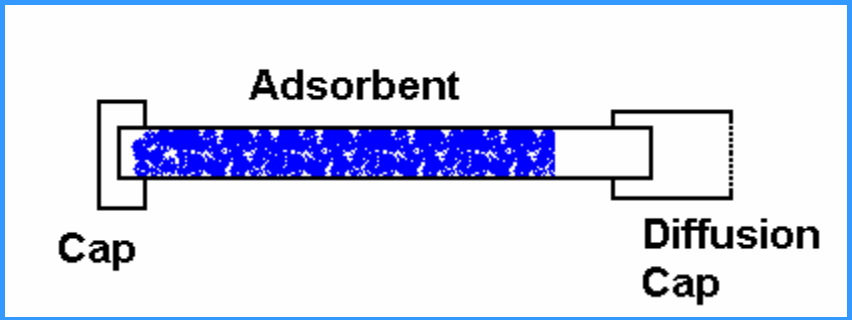
QAPP Goals

Goal 1: Develop in-house analytical methods for passively sampled canisters and adsorbent tubes using existing analytical systems.

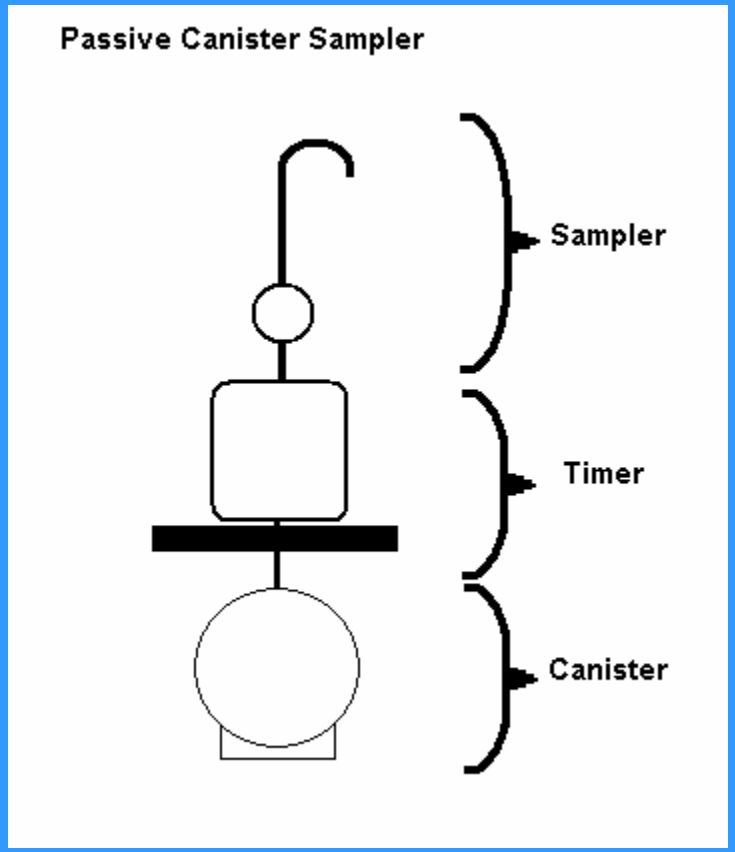
Goal 2: Test the passive sampling systems to establish comparability to existing active sampling systems used by the Wisconsin DNR.

Goal 3: Deploy the passive systems in a field study and use this information to optimize designs to support risk assessment modeling.

Passive Adsorbent Sampler (PAS)



Passive Canister Sampler (PCS)



Passive Sampling

- PCS
  - Commercially available regulators and timers built in-house.
  - 1-hour samples 07:00 Local Time.
- PAS
  - Use commercially available tubes packed with Carbopak B.
  - Weekly samples (typically Wed to Wed).

Canister Samples Analysis

- PAMS Analysis
  - Ozone Precursor Analysis System
  - Two columns (dimethly polysiloxane and aluminum oxide)
  - Standardize with benzene and propane
  - Use 55 compound standard as secondary standard
  - Instrument results ppbC; converted to ug/M3

PAS Analysis

- Use Ozone Precursor Analysis System
- Use PAMS analysis program
  - Single column analysis (100% dimethly polysiloxane)
- Standardize with Benzene
  - Calibration standard trapped on internal trap only
- Use 55 compound standard as secondary standard
- Instrument results ngC; calculated ambient concentration ug/M3

DP-1 (dimethly polysiloxane) Column

Target List

- Critical – Benzene
- Priority - N-hexane, 224-trimethylpentane,
  Toluene, M/P-xylene,
  O-xylene, 123-trimethylbenzene
- Base – Methylcyclopentane, 24-dimethylpentane, Cyclohexane, 2-methylhexane, 23-dimethylpentane, 3-methylhexane, N-heptane, Methylcyclohexane, 234-trimethylpentane, 2-methylheptane, 3-methylheptane, N-octane, Ethylbenzene, Styrene, N-nonane, Isopropylbenzene, N-propylbenzene, M-ethyltoluene, P-ethyltoluene, 135-trimethylbenzene, O-ethyltoluene, 124-trimethylbenzene, N-decane, M-diethylbenzene, P-diethylbenzene, Undecane, Dodecane

Data Evaluation

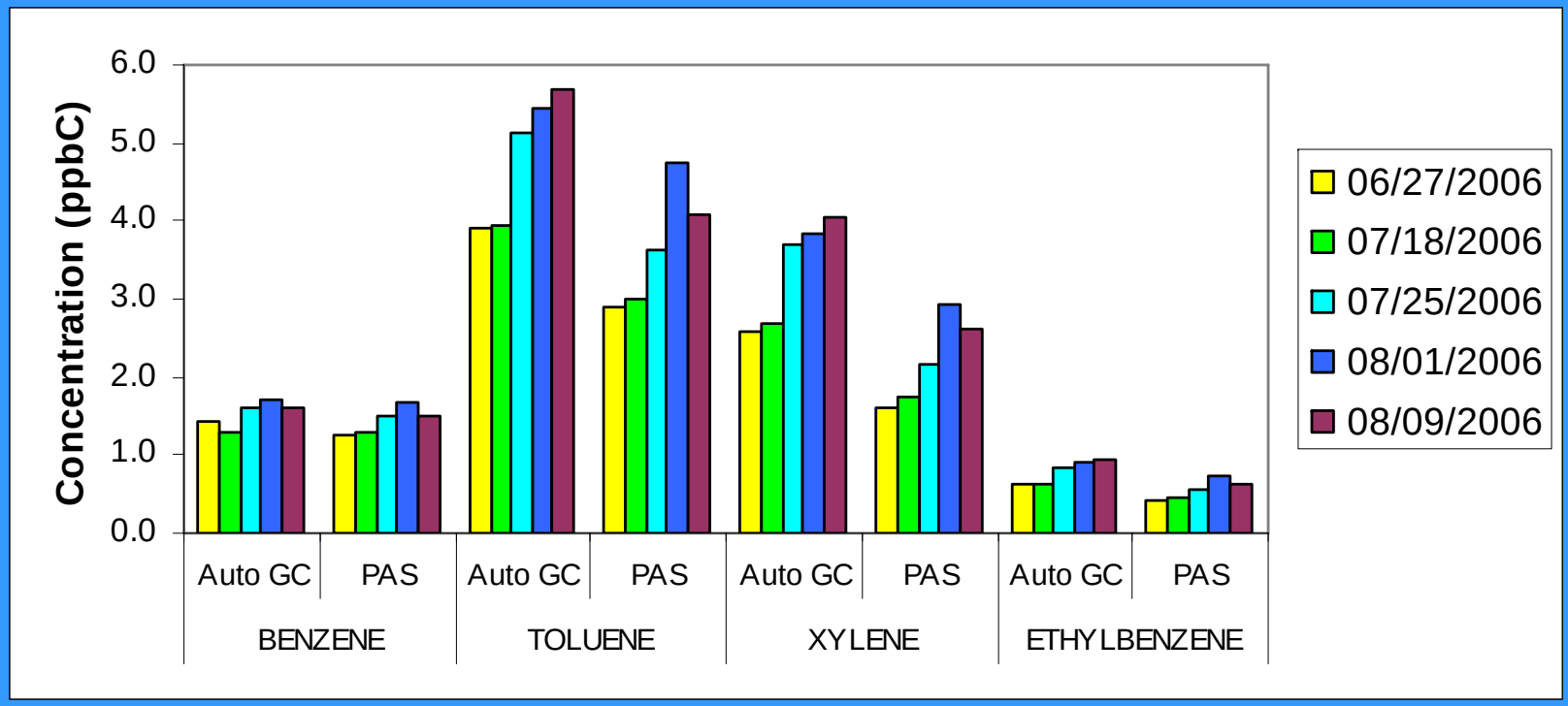
- *Accuracy – as recovery*
- *Background - blanks*
- *Precision as – duplicates*
- *Comparability – to PAMS/UATM*
- *Diffusive Sampling Uptake Rate*

The final compound list includes compound showing good evaluation parameters, and which were commonly detected with measurable concentrations.

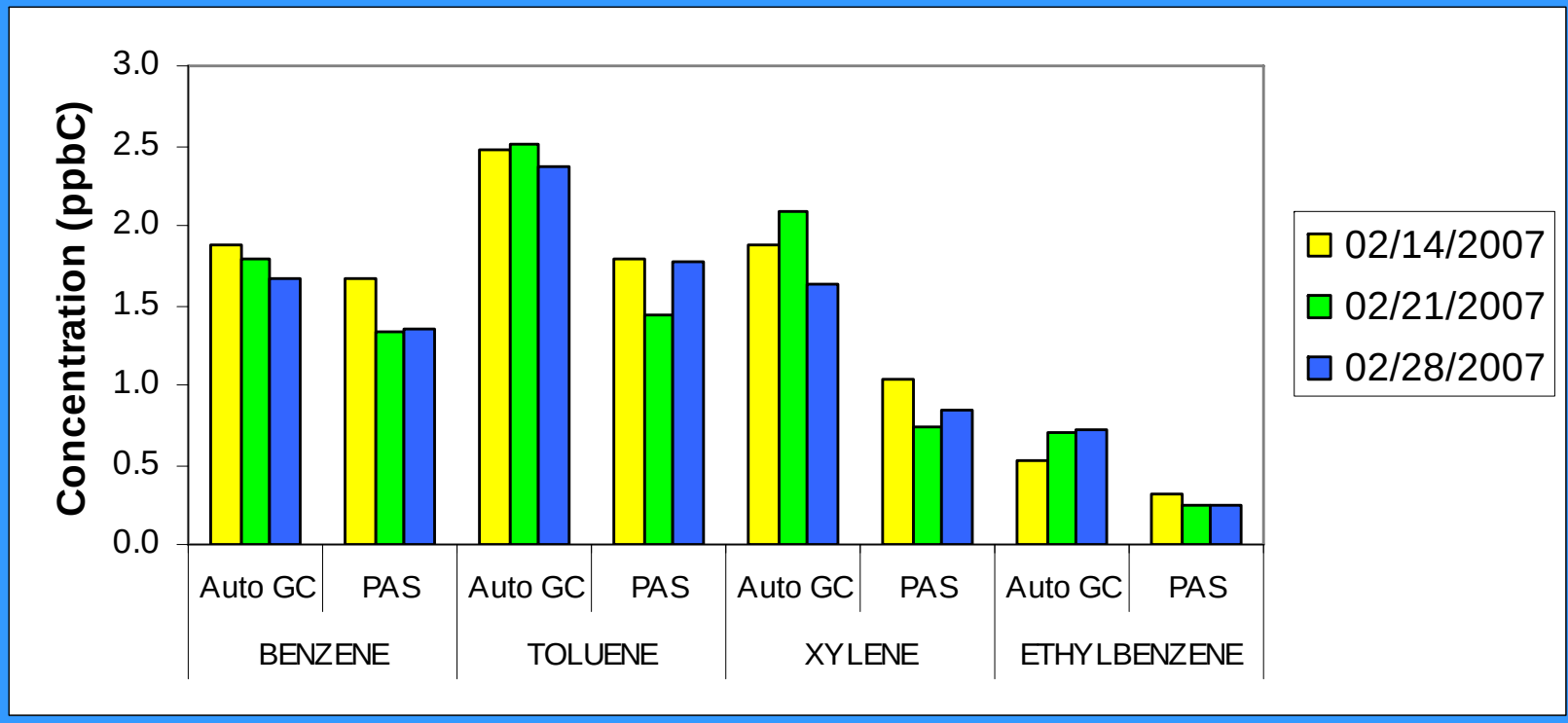
- Benzene – critical
- Toluene
- Ethylbenzene
- Xylene (sum of isomers)
- 224 – Trimethylpentane (224-TMP)

Data Comparability to Established Methods

PAS vs. AutoGC Summary of 2006 Test Samples

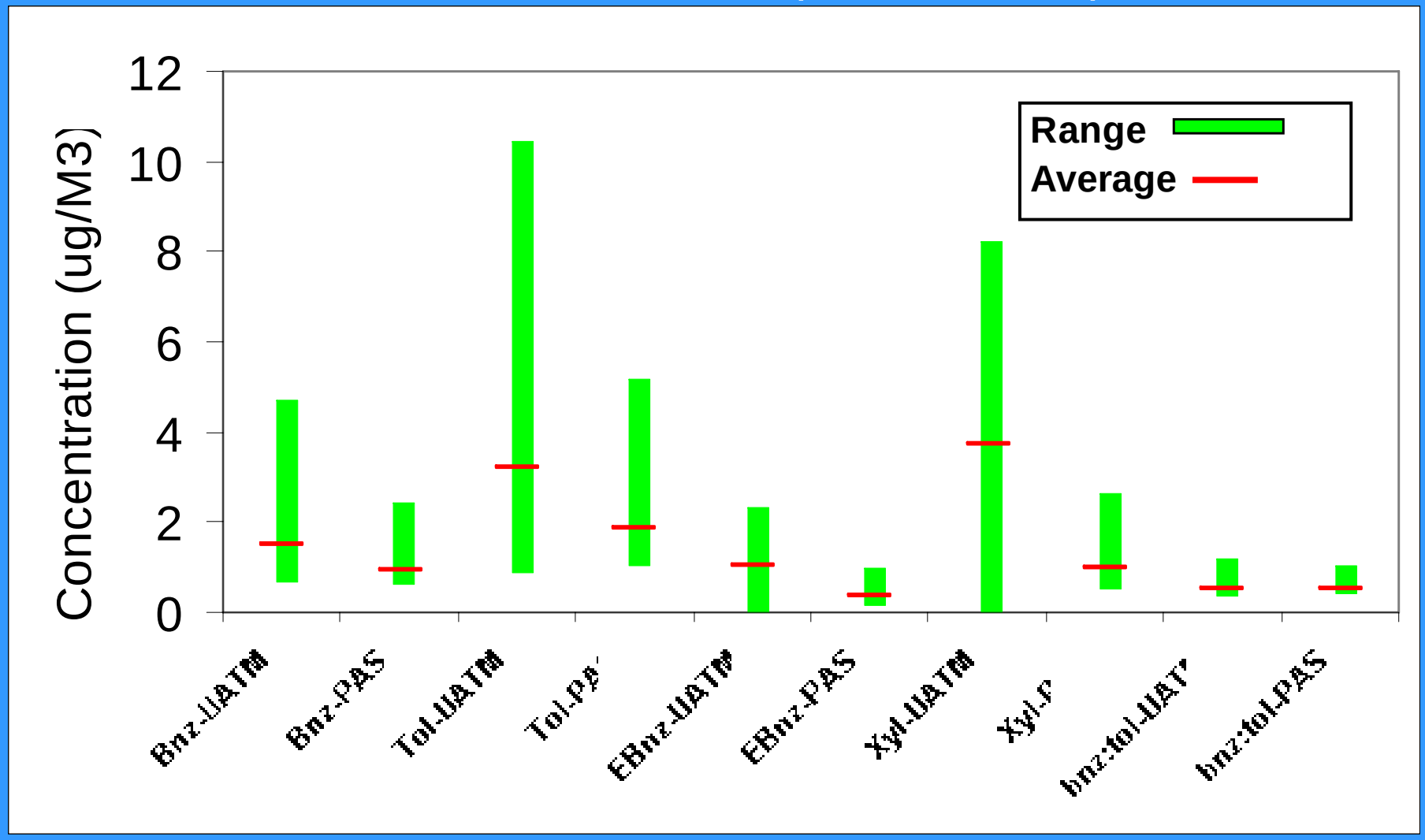


PAS vs. AutoGC Summary of 2007 Test Samples



Summary of Percent Bias PAS v. AutoGC			
Parameter	2006 (n=5)	2007 (n=3)	Overall (n=8)
BENZENE	94.4	81.5	89.5
TOLUENE	75.8	68.1	72.9
ETHYLBENZENE	69.0	43.3	59.4
XYLENE	65.1	47.3	58.5
224-TMP	61.5	46.6	55.9

Study 1: PAS vs. Canister Samples Collected at Milwaukee SSHC (55-079-0010)



UATM n = 9 : PAS n = 5

QAPP Data Quality Objective

- *The overall data quality objective is to provide a dataset of known quality for use in assessing the benzene concentrations near roadways. The dataset should also be comparable to current fixed site PAMS monitoring within known limits..*

PAS Method Evaluation Summary

- PAS method shows data comparable to established methods, but is biased low.
- PAS results must be blank corrected.
  - Background on tubes, but no evidence of contamination.
  - Used average of prep, trip, field blanks.
- Precision is good on average.
  - Benzene 10.9% dif; toluene 8.3%.
- Need to use literature DRC.
  - Reference values taken from Brown, R.H., J. Environ. Monit., 1999, 1, 115–116

Roadway Monitoring Field Studies

Roadway Study #1

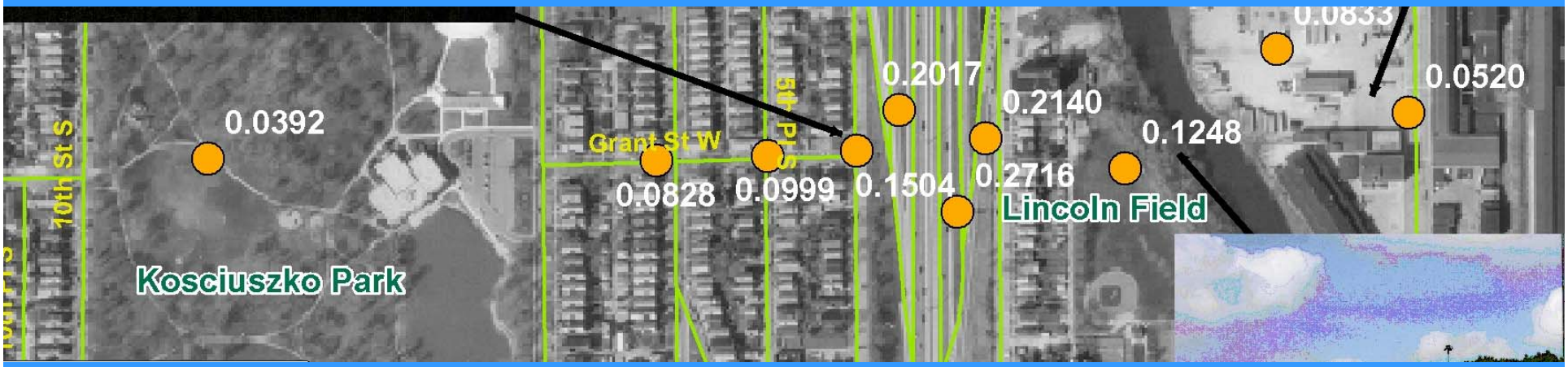
Began: 11/8/2006

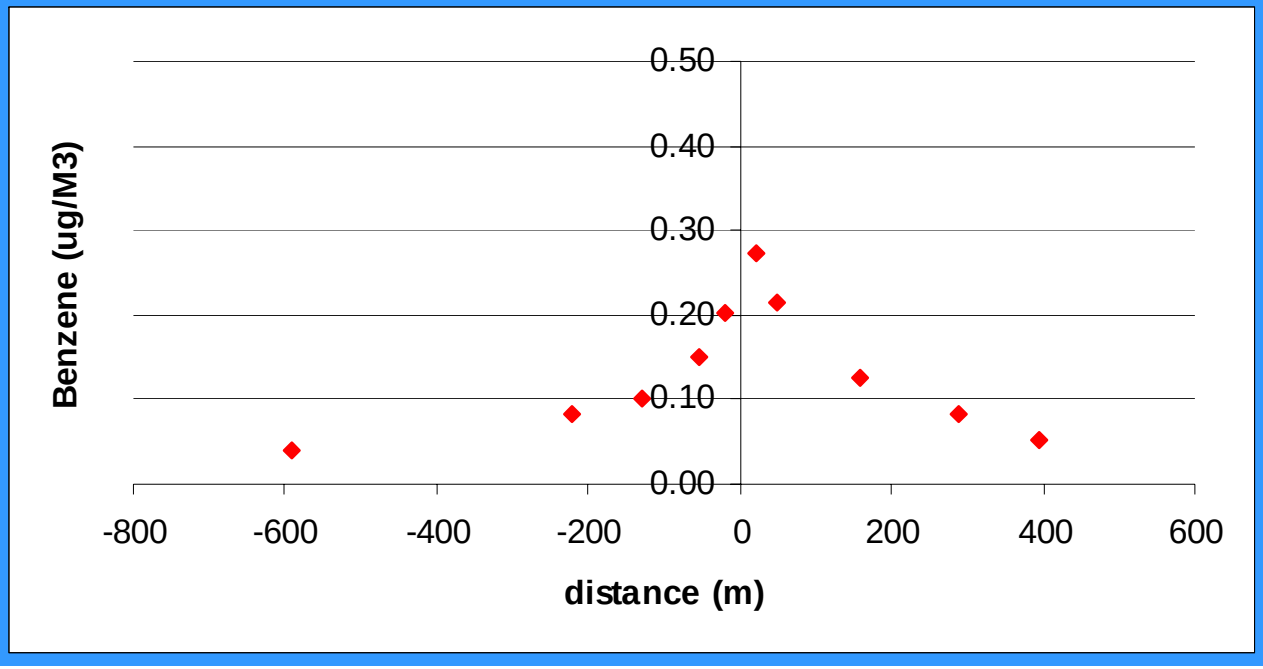
Duration 5 weeks

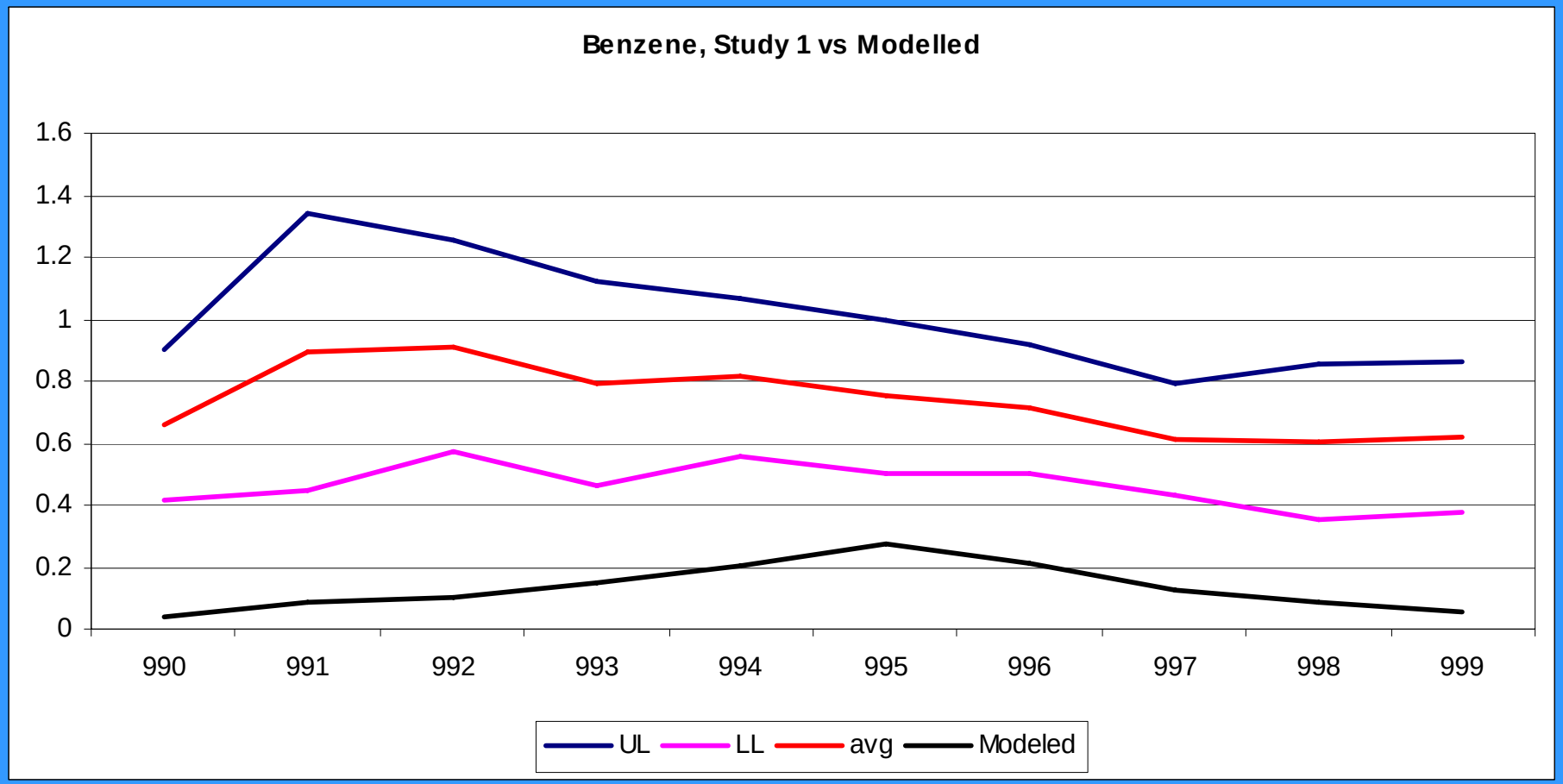
Sites: 10 plus 1 off-area site

Study 1: Monitoring Site 990 and 994

Roadway Modeling Predictions

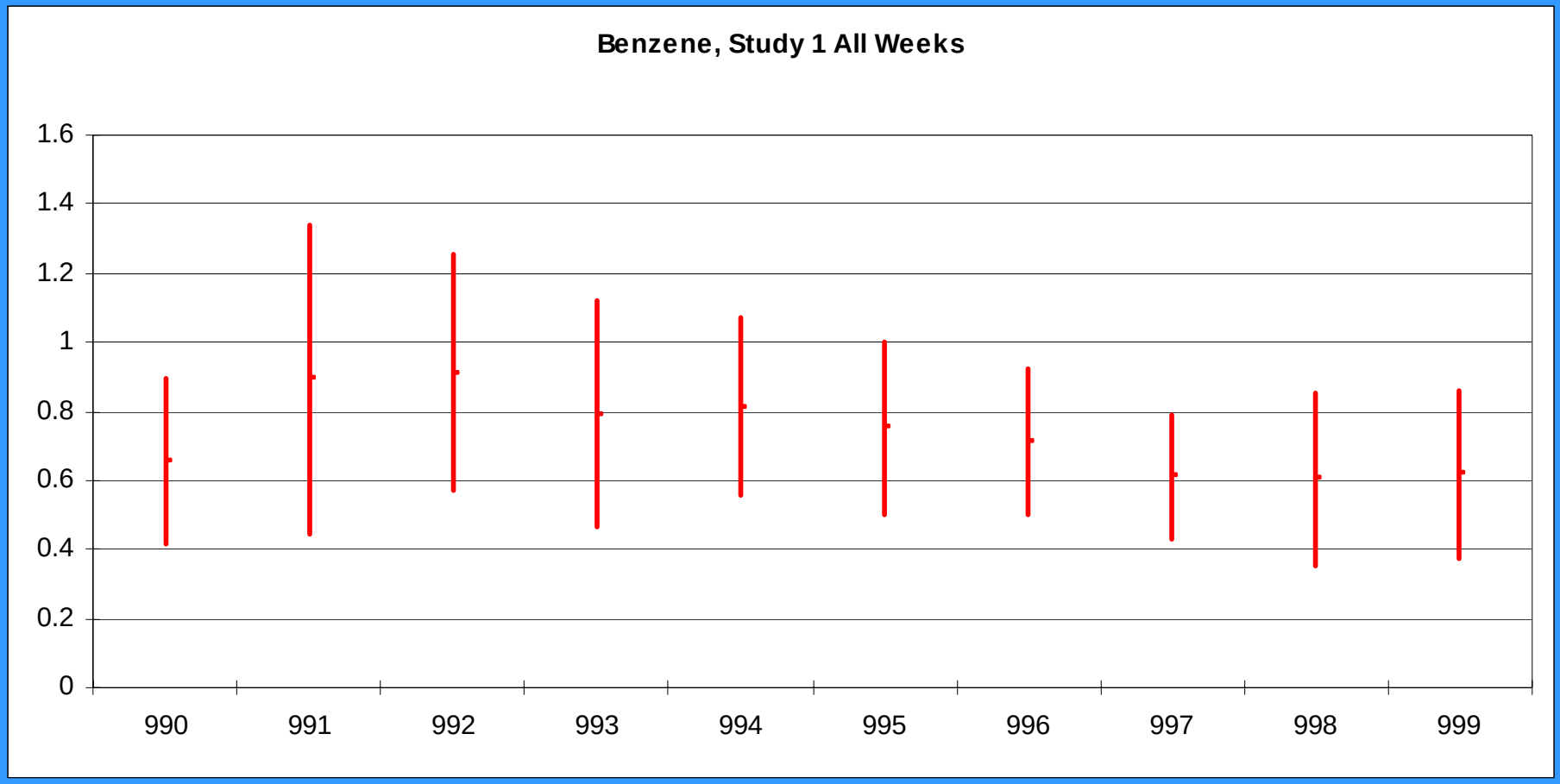






N = 5 samples x 10 sites

Y-axis concentration in ug/M3: X-axis sites are arranged west to east.



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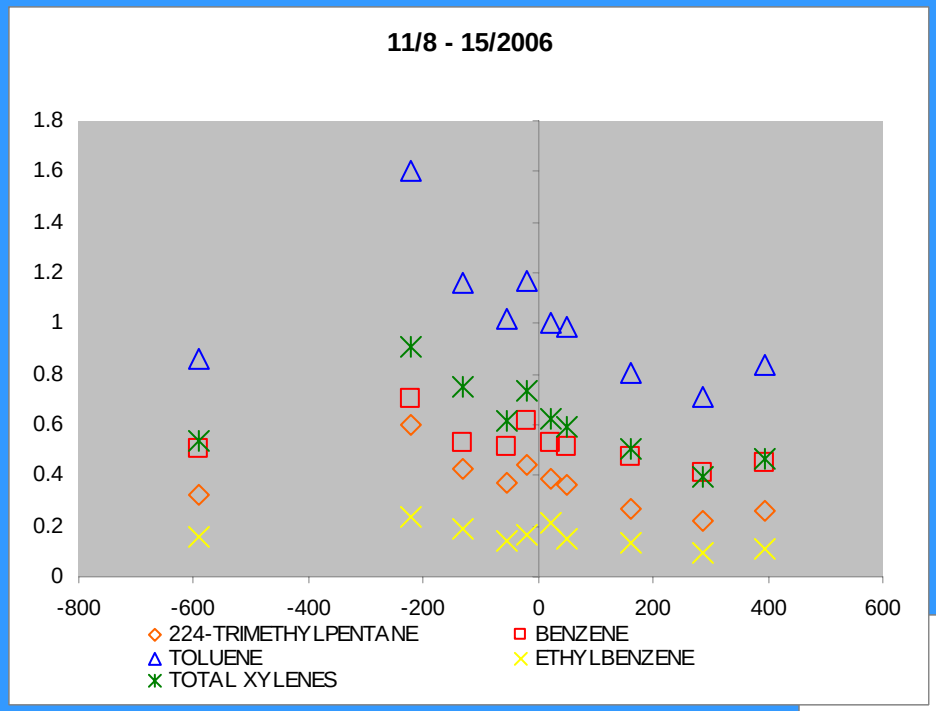
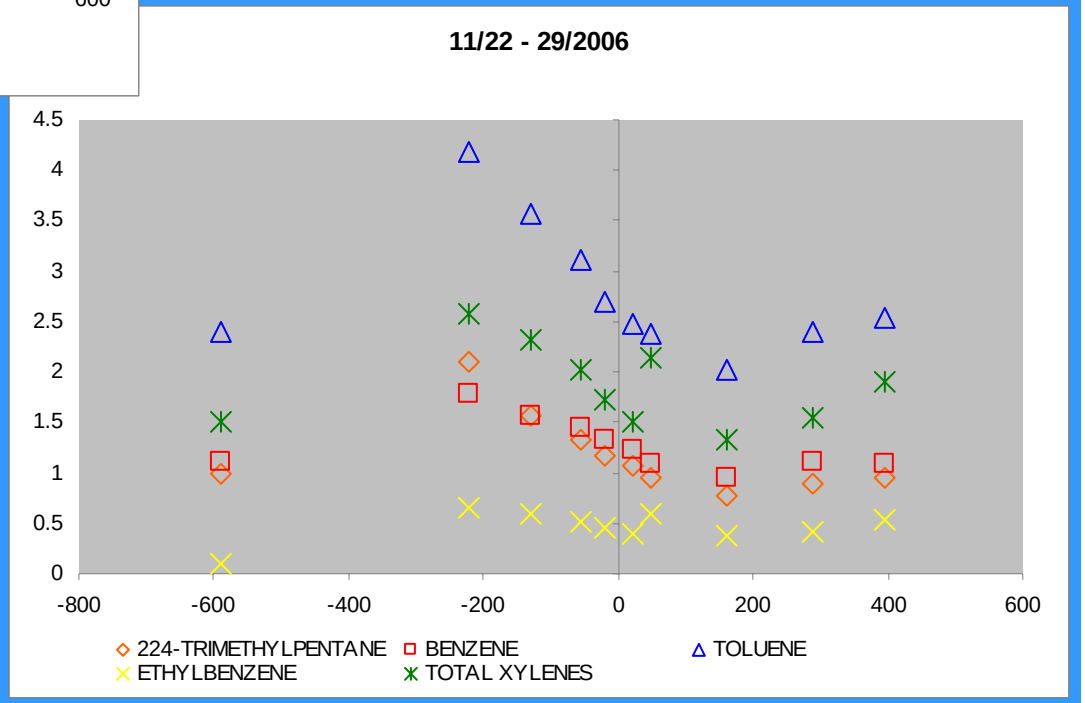
Y-axis concentration in ug/M3: X-axis sites are arranged west to east.

Study 1 Week 1



Study 1 Week 3

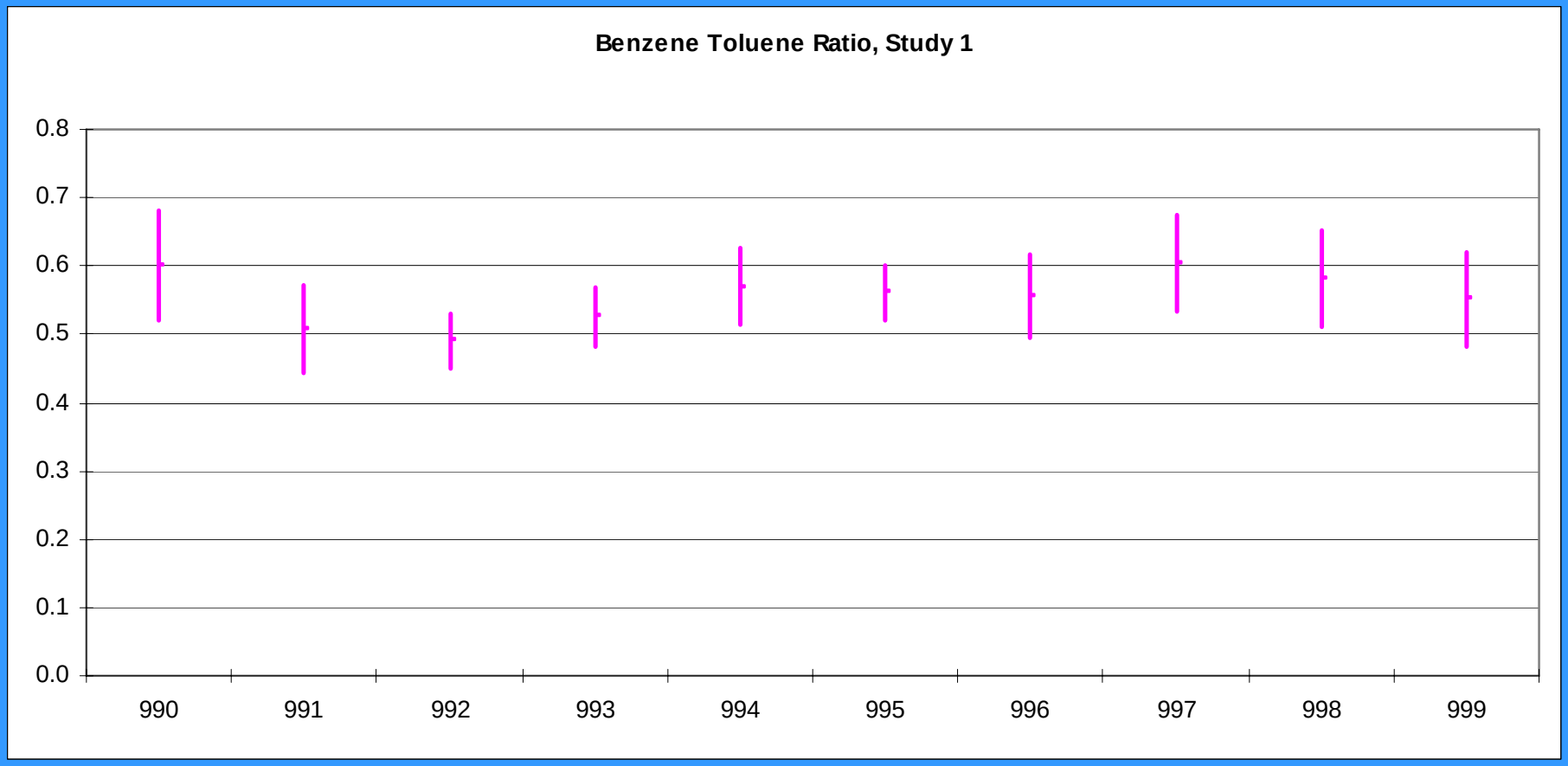


Graph Notes:

X axis units are meters

Y axis units are ug/M3

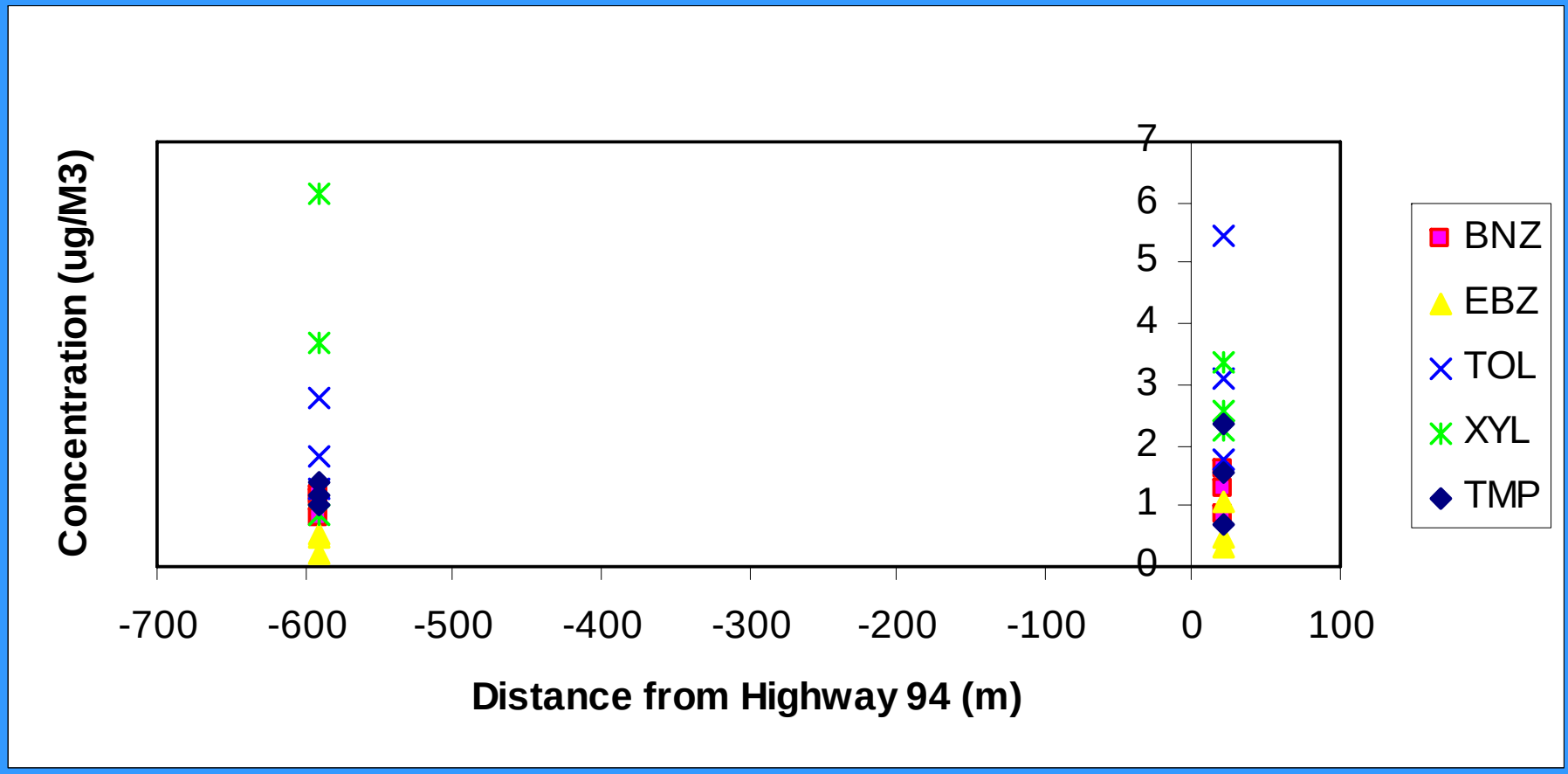
t-Test: Two-Sample Assuming Equal Variances									
Study 1	critical 2 tail = 2.306				df =8				
Benzene	*991*	*992*	*993*	*994*	*995*	*996*	*997*	*998*	*999*
990	-0.910	-1.200	-0.650	-0.862	-0.535	-0.338	0.296	0.295	0.222
991		-0.067	0.354	0.307	0.543	0.719	1.145	1.101	1.058
992			0.496	0.460	0.750	0.984	1.536	1.426	1.380
993				-0.092	0.196	0.405	0.947	0.889	0.835
994					0.334	0.593	1.257	1.131	1.075
995						0.238	0.899	0.816	0.753
996							0.718	0.645	0.575
997								0.046	-0.042
998									-0.077



N = 5 samples x 10 sites

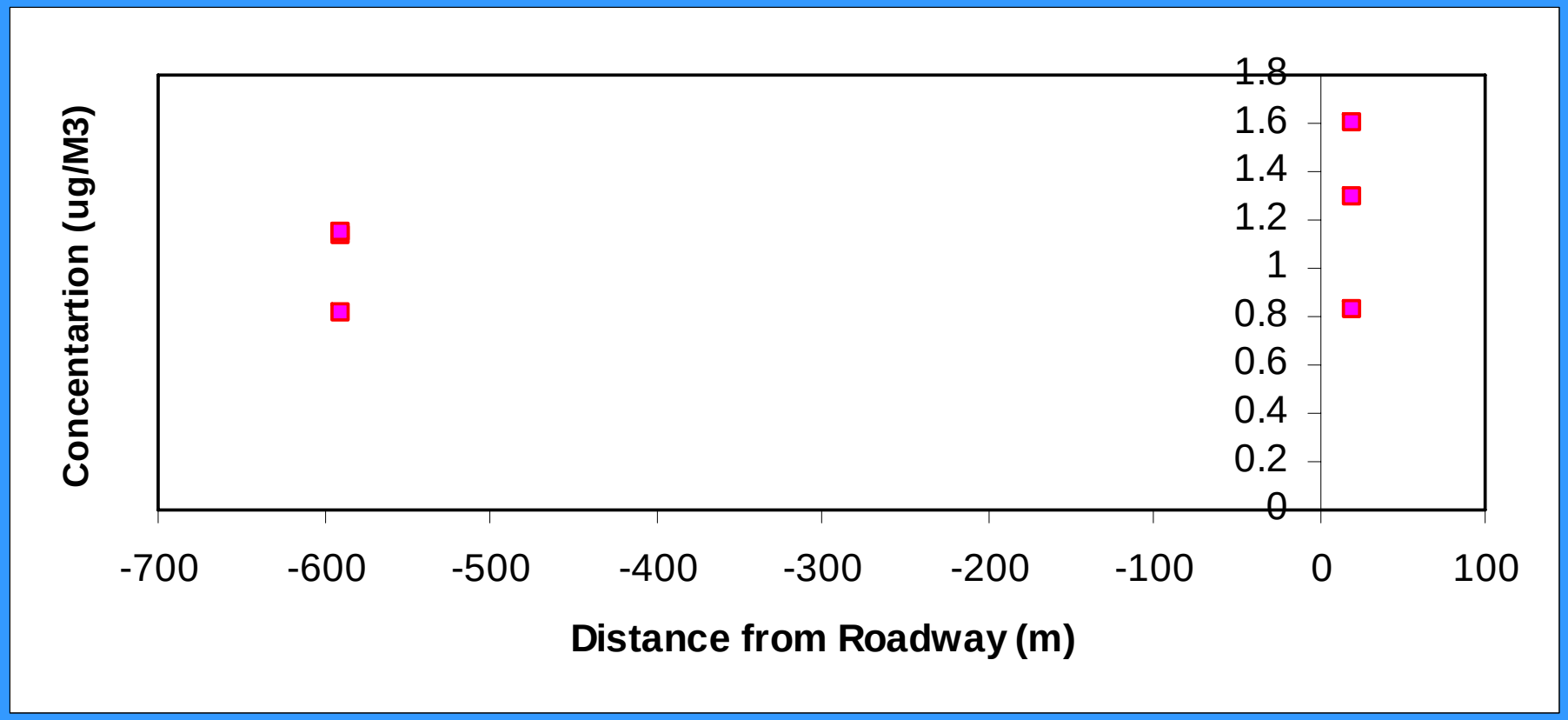
Y-axis concentration ratio: X-axis sites are arranged west to east.

Study 1: Passive Canister Results by Site and Compound

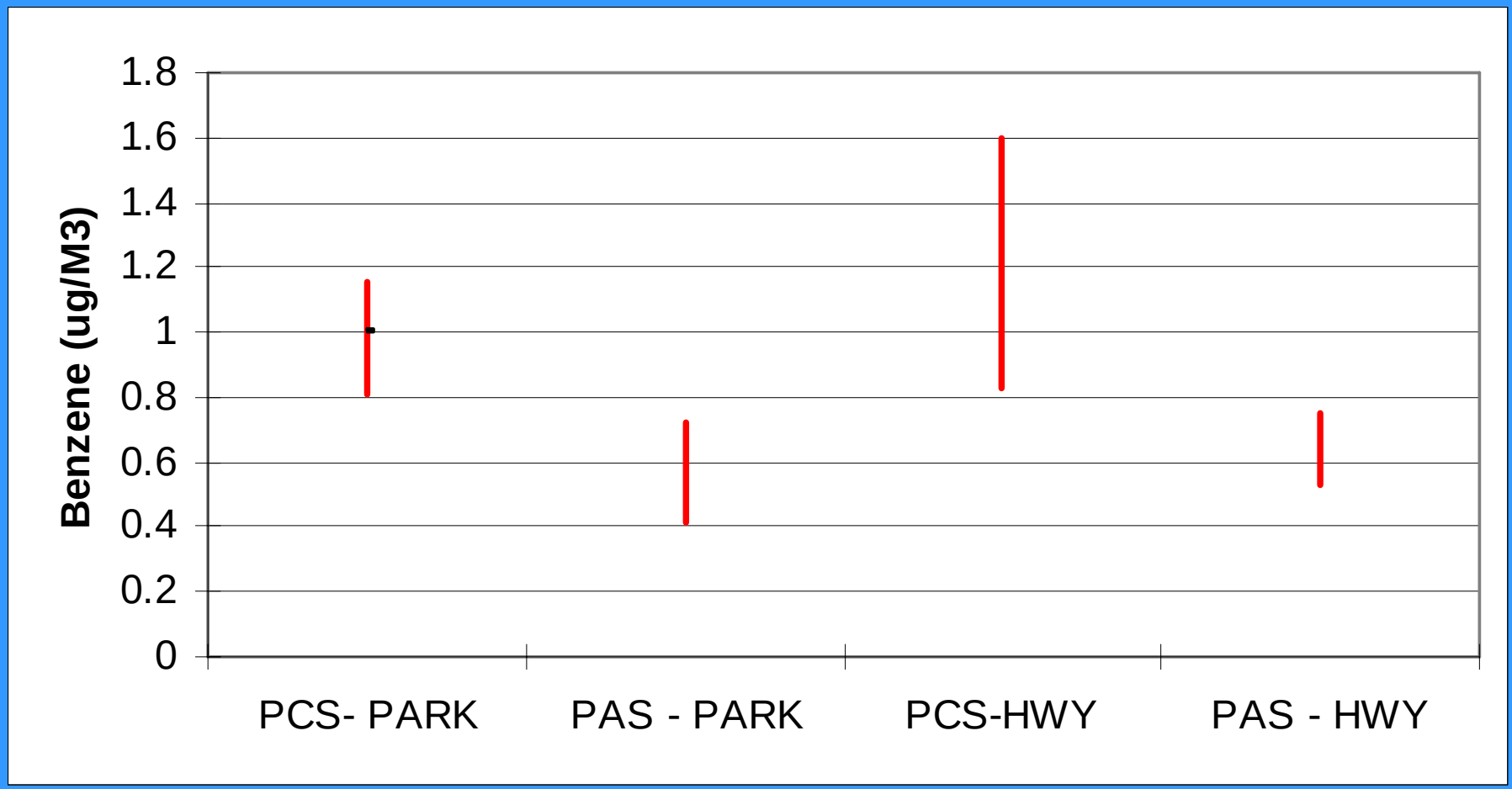


Sample Pairs = 7 ; N = 3 valid samples x 2 sites

Study 1: Passive Canister Results for Benzene by Site



Study 1: Comparison of Benzene Data Ranges of the Passive Methods



N(PAS) =3 ; N(PCS)=5

Project Advisory Group Met January 30, 2007

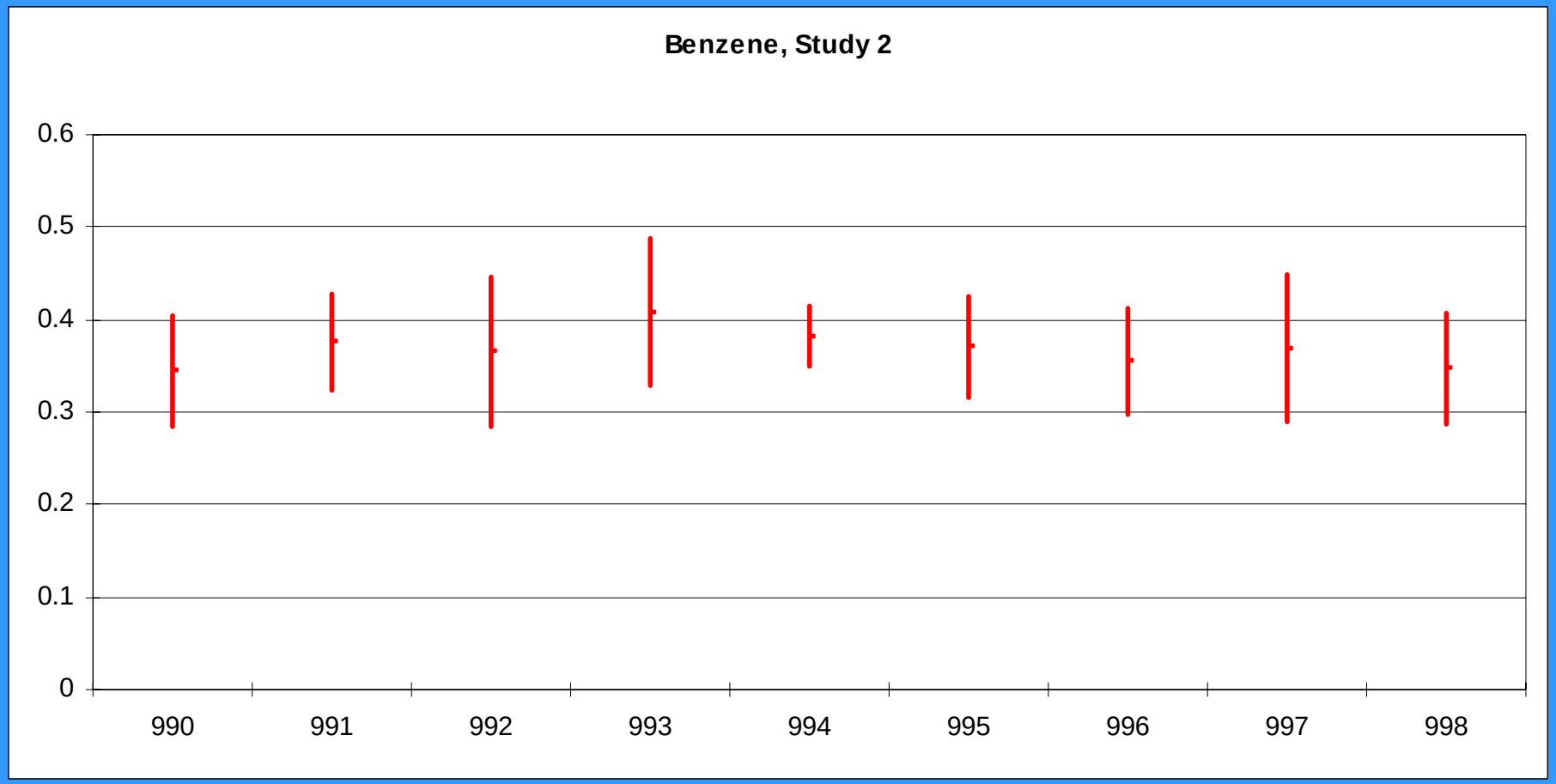
- Purpose to review results for Study 1 and make recommendations for additional monitoring.
  - Benzene concentrations were greater than modeling predicted.
  - No benzene gradient seen.
- Possible explanations
  - Benzene diffuses to a uniform concentration more quickly than predicted.
  - Contributions from minor side roads are significant.
- Recommendations
  - monitoring study at isolated site
  - confirm Study 1 results

Roadway Study #2

Began 3/14/2007

Duration 4 weeks

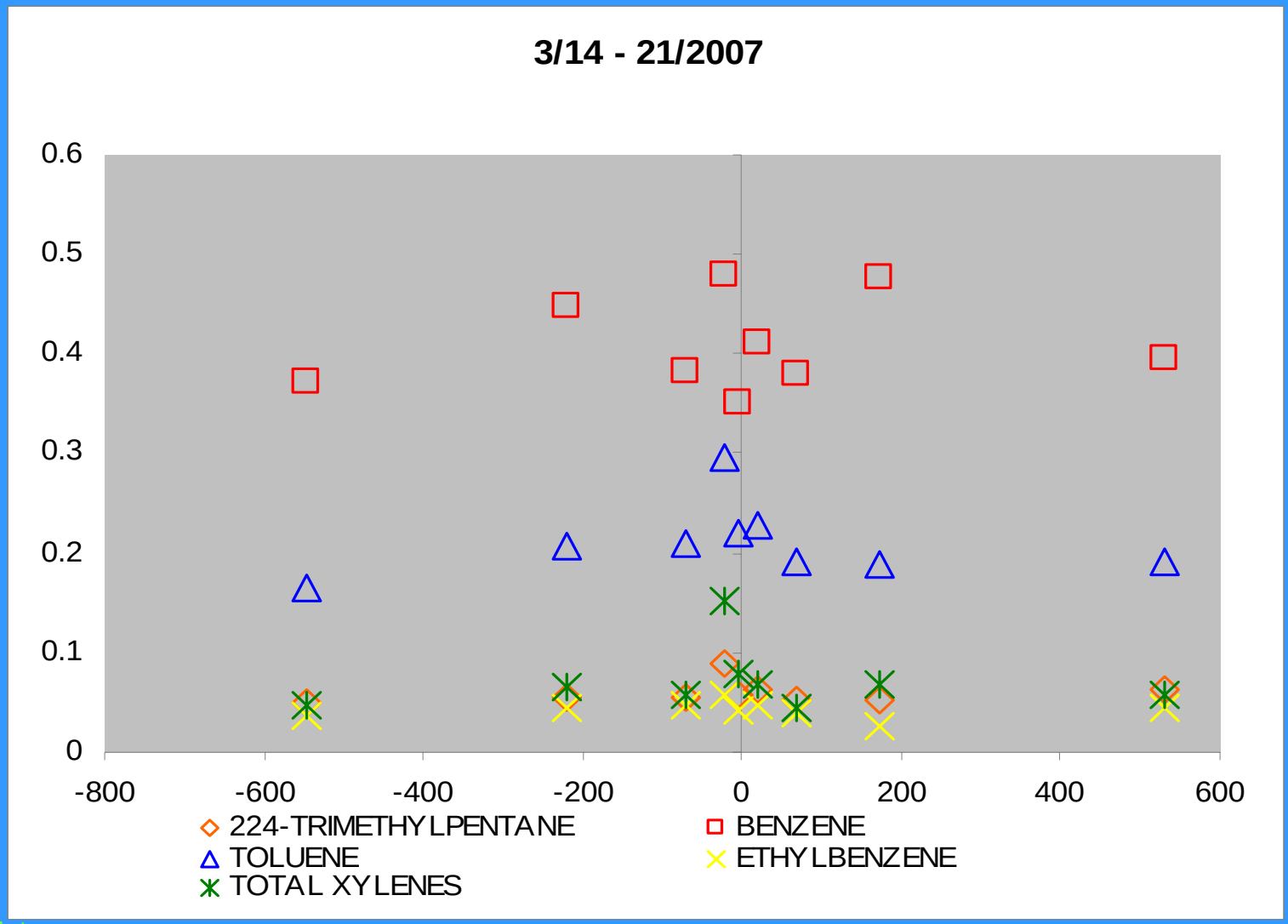
Sites: 9



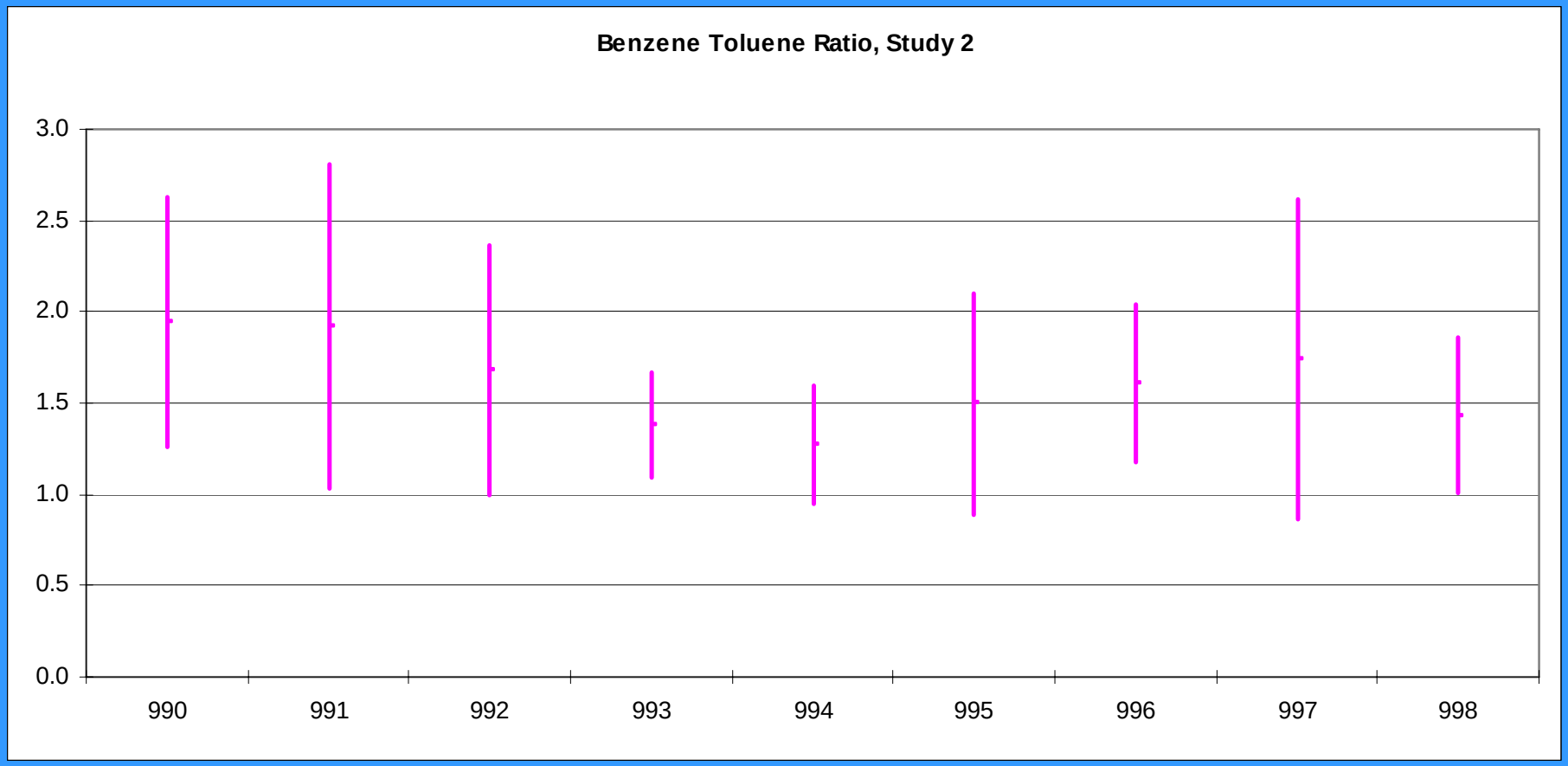
N = 4 samples x 9 sites

Y-axis concentration in ug/M3: X-axis sites are arranged south to north.

Study 2 Week 1



Graph Notes:
X axis units are meters
Y axis units are ug/M3



N = 4 samples x 9 sites

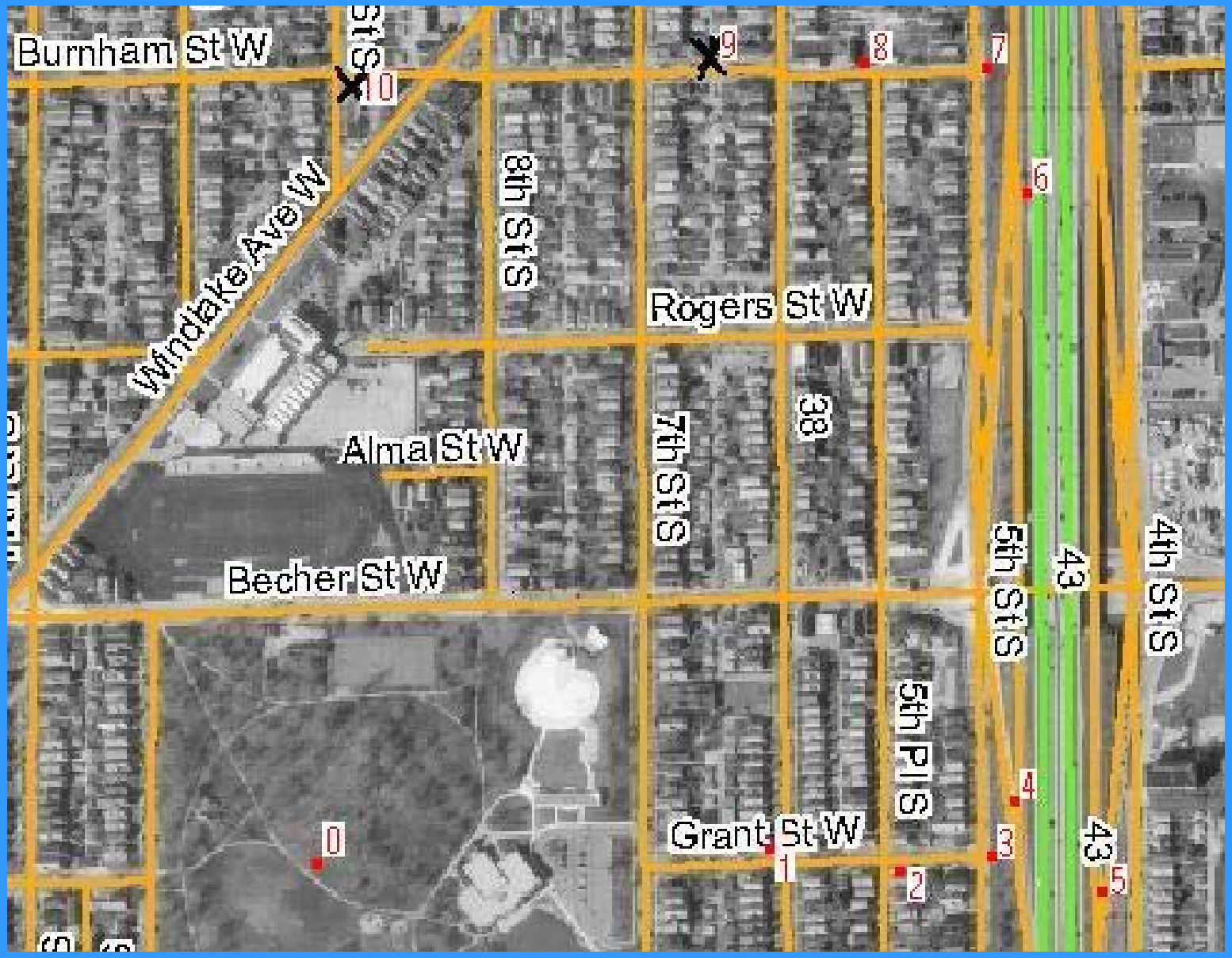
Y-axis concentration ratio: X-axis sites are arranged south to north.

t-Test: Two-Sample Assuming Equal Variances								
Study 2	critical 2 tail = 2.447				df =6			
Benzene	*991*	*992*	*993*	*994*	*995*	*996*	*997*	*998*
990	-0.753	-0.402	-1.229	-1.064	-0.617	-0.251	-0.462	-0.053
991		0.203	-0.654	-0.198	0.140	0.506	0.149	0.695
992			-0.723	-0.365	-0.094	0.199	-0.048	0.356
993				0.583	0.760	1.038	0.682	1.183
994					0.364	0.786	0.309	0.995
995						0.368	0.038	0.560
996							-0.257	0.196
997								0.416

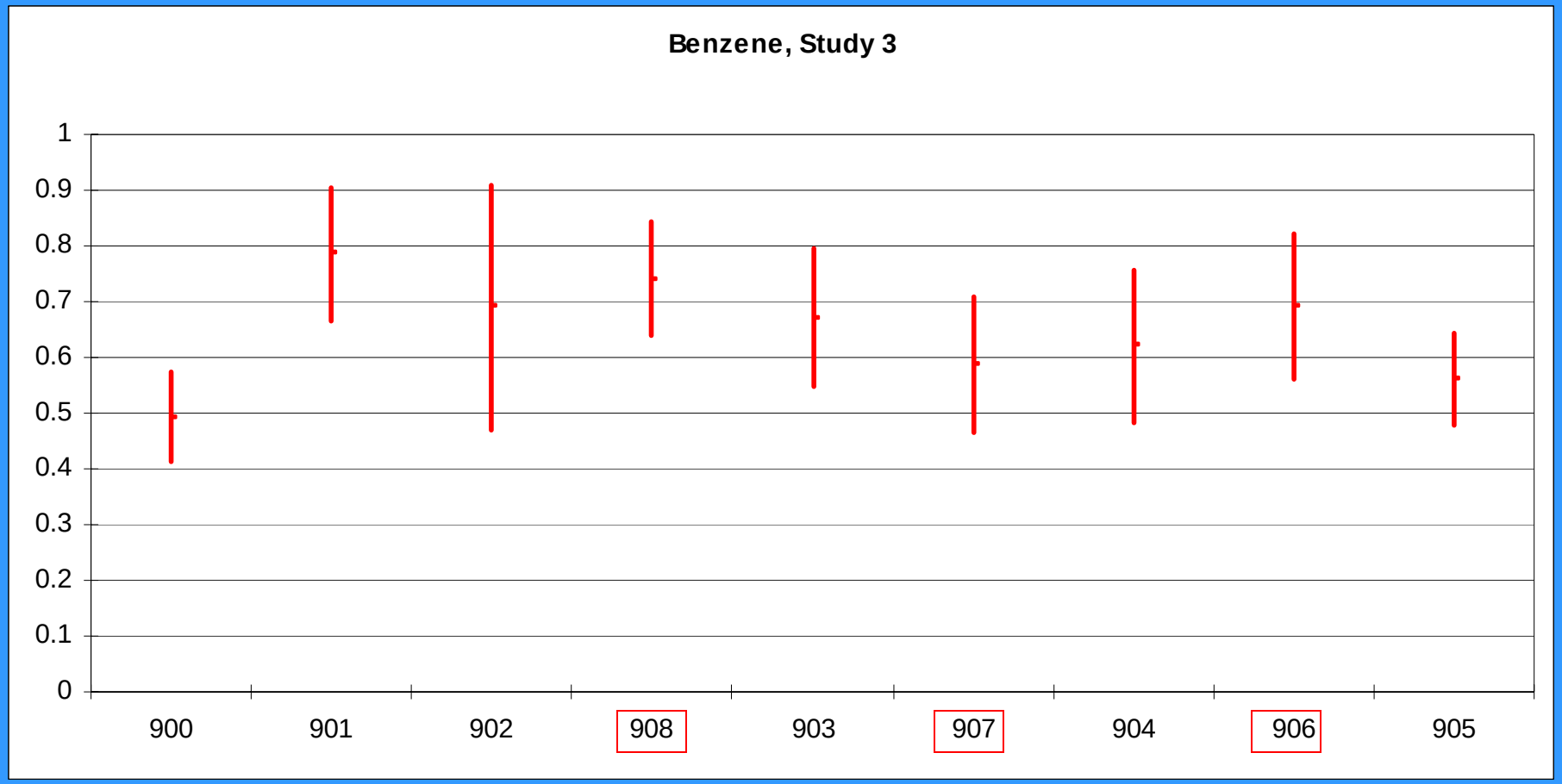
Study 2 Observations

- Benzene gradient not seen.
  - Minimal side road contributions
  - Implies benzene diffusion greater than model predicted.
- Benzene:toluene ratio is the inverse of urban ratio.

Roadway Study #3

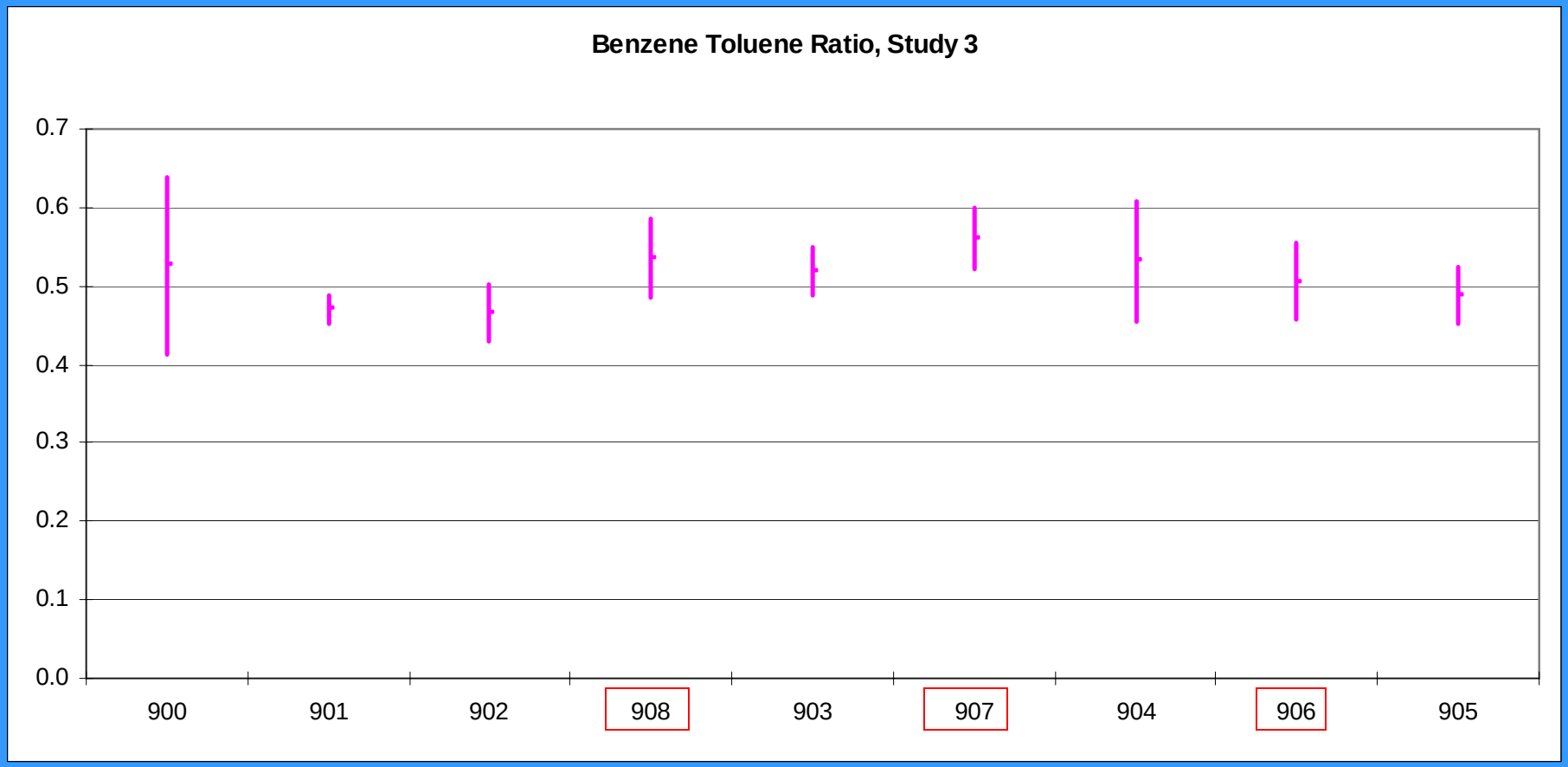


Began: 4/18/2007 Duration: 4 weeks Sites: 11 planned (9 actual)



N = 4 samples x 9 sites

Y-axis concentration in ug/M3: X-axis sites are arranged west to east.



N = 4 samples x 9 sites

Y-axis concentration ratio: X-axis sites are arranged west to east.

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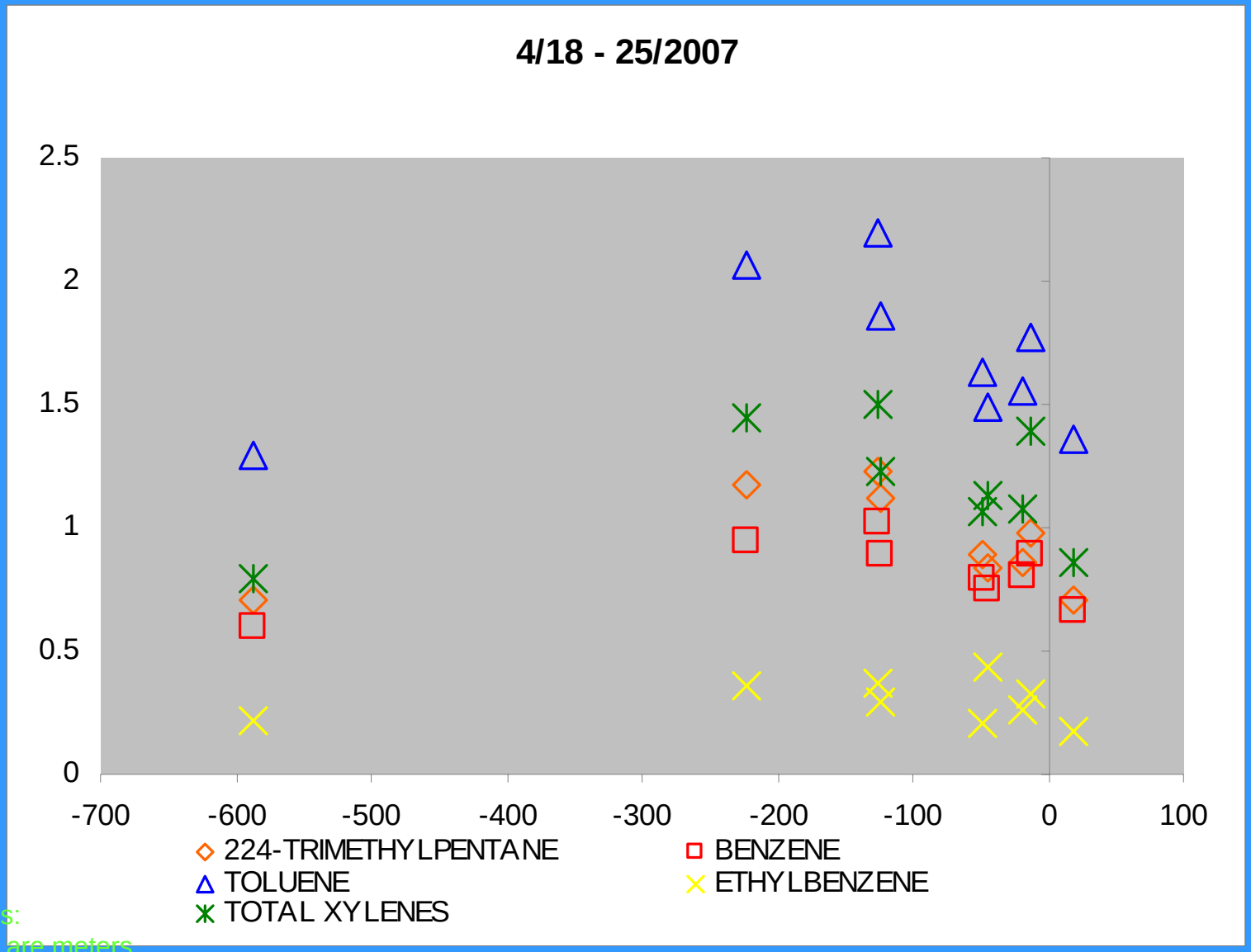
Study 3, Week 1



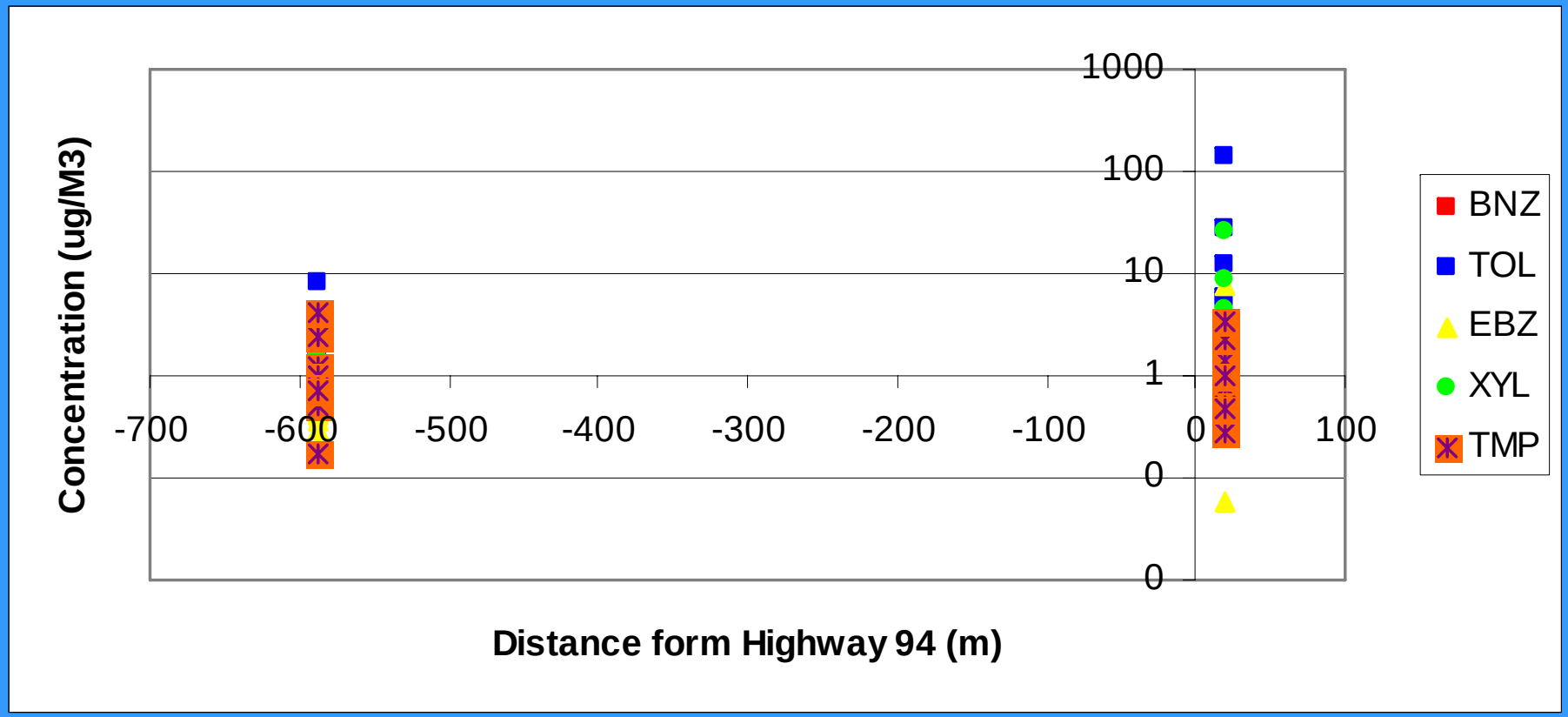
Graph Notes:
X axis units are meters
Y axis units are ug/M3

t-Test: Two-Sample Assuming Equal Variances

Study 3	critical 2 tail = 2.447					df =6			
Benzene	*900*	*901*	*902*	*908*	*903*	*907*	*904*	*906*	*905*
900		**-3.994**	-1.642	**-3.755**	-2.391	-1.253	-1.571	**-2.534**	-1.180
901			0.753	0.566	1.305	2.281	1.785	1.060	**3.010**
902				-0.411	0.140	0.801	0.524	-0.005	1.060
908					0.845	1.894	1.381	0.596	**2.660**
903						0.961	0.548	-0.204	1.446
907							-0.359	-1.138	0.322
904								-0.727	0.709
906									1.626

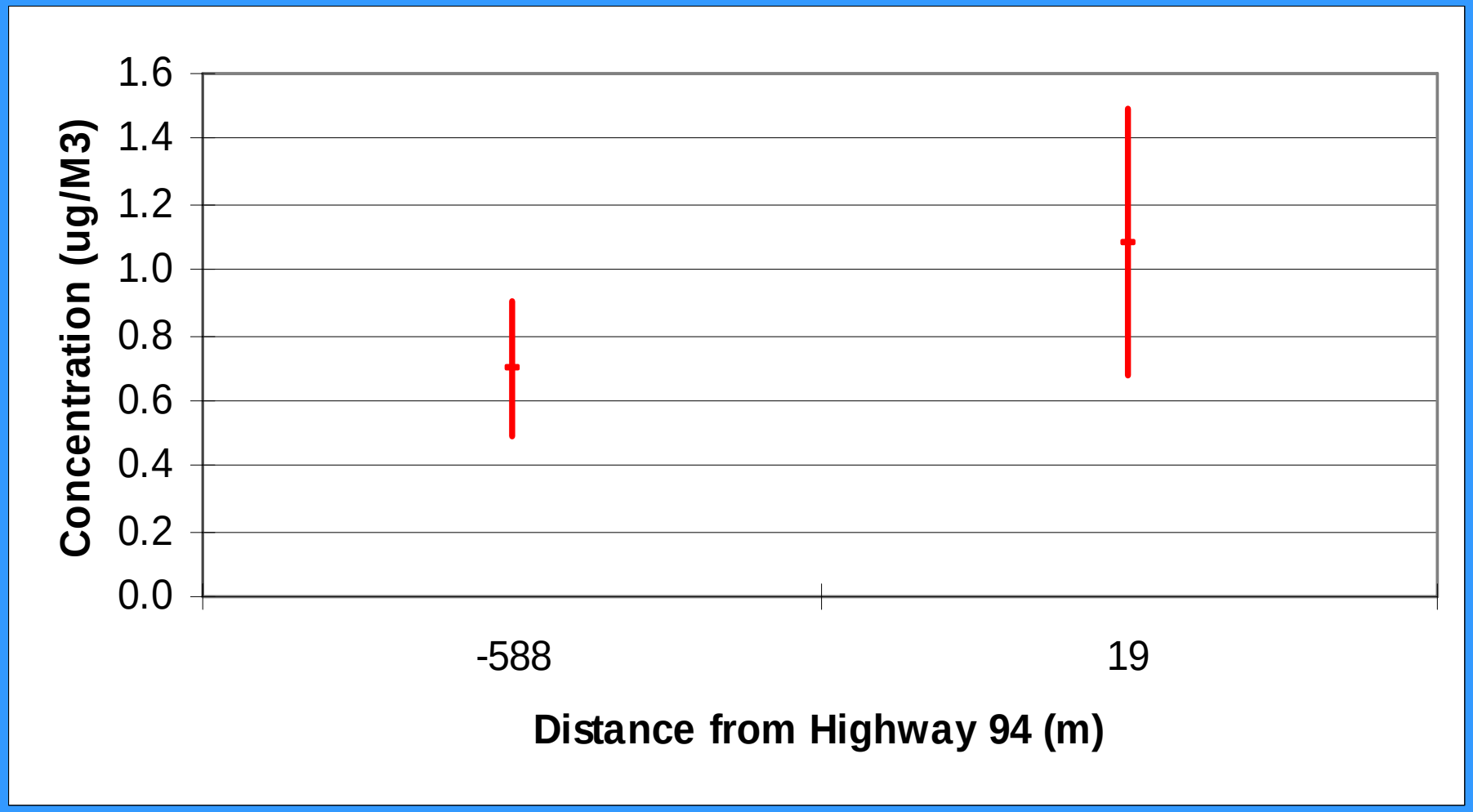
Study 3 Passive Canister Results

by Site and Compound



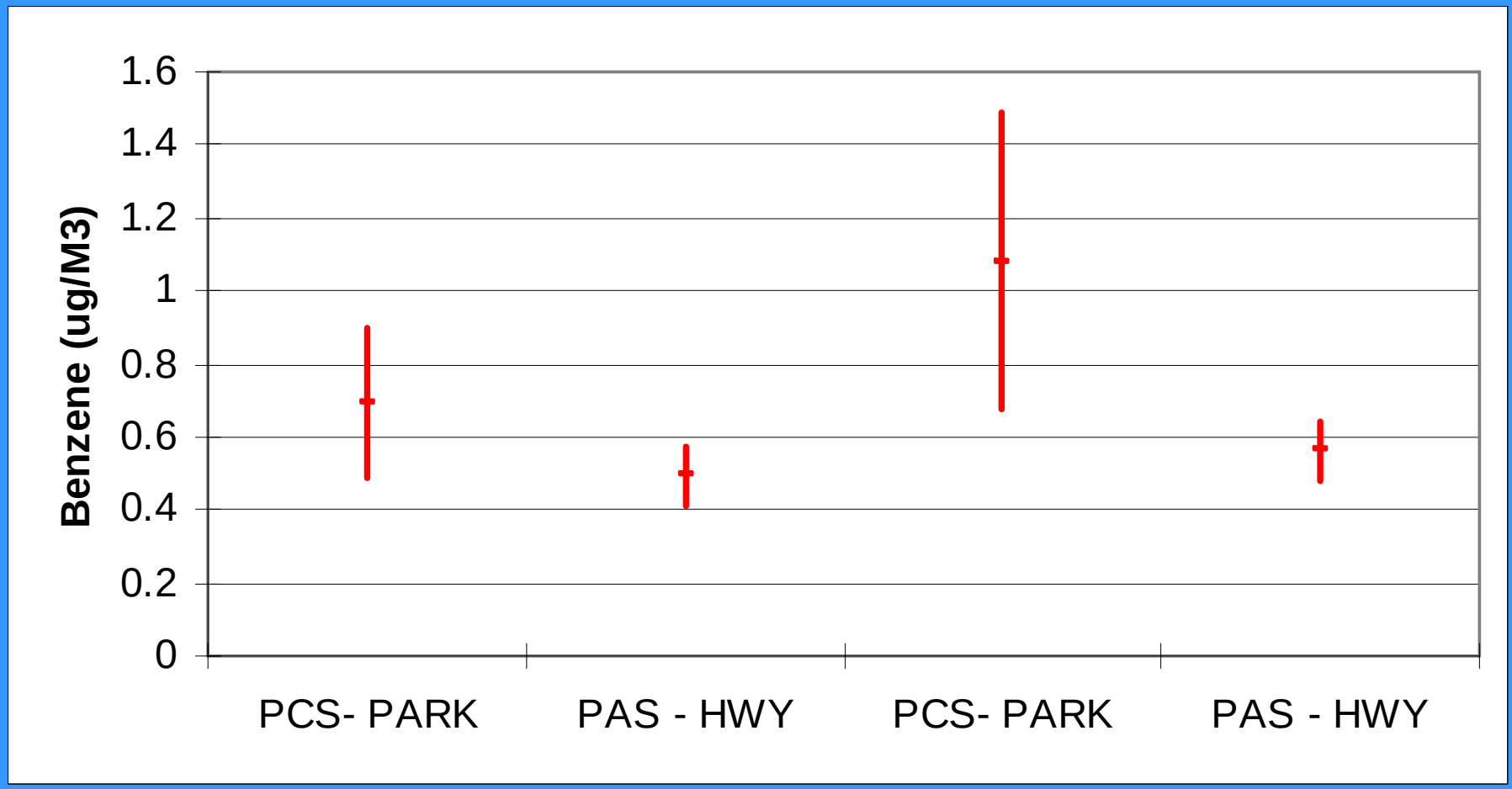
Collected 13 canister pairs, 10 pairs were valid.

Study 3: 1 Hour Canister Samples Average Benzene with 95% Confidence Intervals



COMPONENT SUMMARY REPORT FROM ANALYSIS STUDY #3 CANISTERS						
		BENZENE (ugM3)	TOLUENE (ugM3)	ETHYL-BENZENE (ugM3)	XYLENE (ugM3)	224 TMP (ugM3)
Park	Mean	0.700	2.380	0.490	0.880	1.200
	StDev	0.333	2.198	0.184	0.495	1.184
Roadway	Mean	1.080	20.110	1.540	2.880	1.470
	StDev	0.657	43.626	2.281	3.829	1.031
t- Statistic		-1.913	-1.270	-1.433	-1.680	-0.559
t-critcal		1.833	1.833	1.833	1.833	1.833

Study 3: Comparison of Benzene 95% Confidence Intervals for the Passive Methods



N(PAS) =10 ; N(PCS)= 4

Weekly Data Comparisons

Study 1	tcritical =2.101		df =18	
Benzene	*11/15/2006*	*11/22/2006*	*11/29/2006*	*12/6/2006*
11/8/2006	**-5.287**	**-8.659**	-0.290	**-2.262**
11/15/2006		**-6.108**	**3.939**	**3.027**
11/22/2006			**8.017**	**7.602**
11/29/2006				-1.490
Study 2	tcritical =2.120		df =16	
Benzene	*3/21/2007*	*3/28/2007*	*4/4/2007*	
3/14/2007	**2.204**	0.869	**4.531**	
3/21/2007		-1.143	2.113	
3/28/2007			**3.151**	
Study 3	tcritical =2.120		df =16	
BENZENE	*4/25/2007*	*5/2/2007*	*5/9/2007*	
4/18/2007	**3.401**	**3.780**	**4.872**	
4/25/2007		0.966	**2.311**	
5/2/2007			1.093	

Overall Observations

- Measured higher benzene concentrations than modeled
  - unknown sources or underestimation of vehicular contribution?
- Benzene concentrations were more uniform across transect than suggested by model.
  - implying quicker diffusion than expected
- Much greater variability seen between weeks than between sites.
- Urban peak benzene concentrations were observed off interstate highway.
  - implying adjacent roadway may have significant impacts

Review of Goals

Goal 1: Develop in-house analytical methods for passively sampled canisters and adsorbent tubes using existing analytical systems.

Goal 2: Test the passive sampling systems to establish comparability to existing active sampling systems used by the Wisconsin DNR.

Goal 3: Deploy the passive systems in a field study and use this information to optimize designs to support risk assessment modeling.

Data Evaluation
(Extented Review)

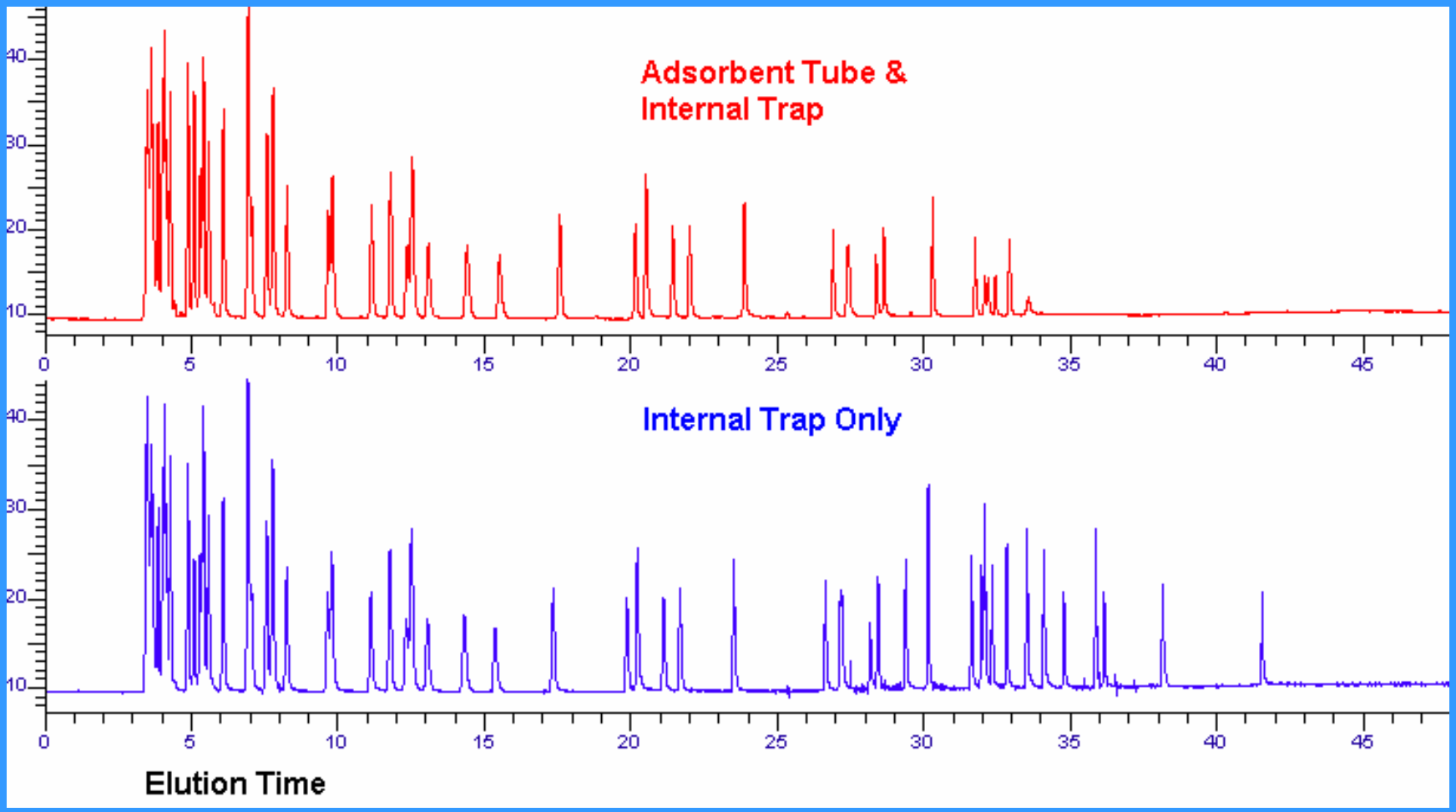
- *Accuracy – as recovery*
- *Background - blanks*
- *Precision as – duplicates*
- *Comparability – to PAMS/UATM*
- *Diffusive Sampling Uptake Rate*

The final compound list includes compound showing good evaluation parameters, and which were commonly detected with measurable concentrations.

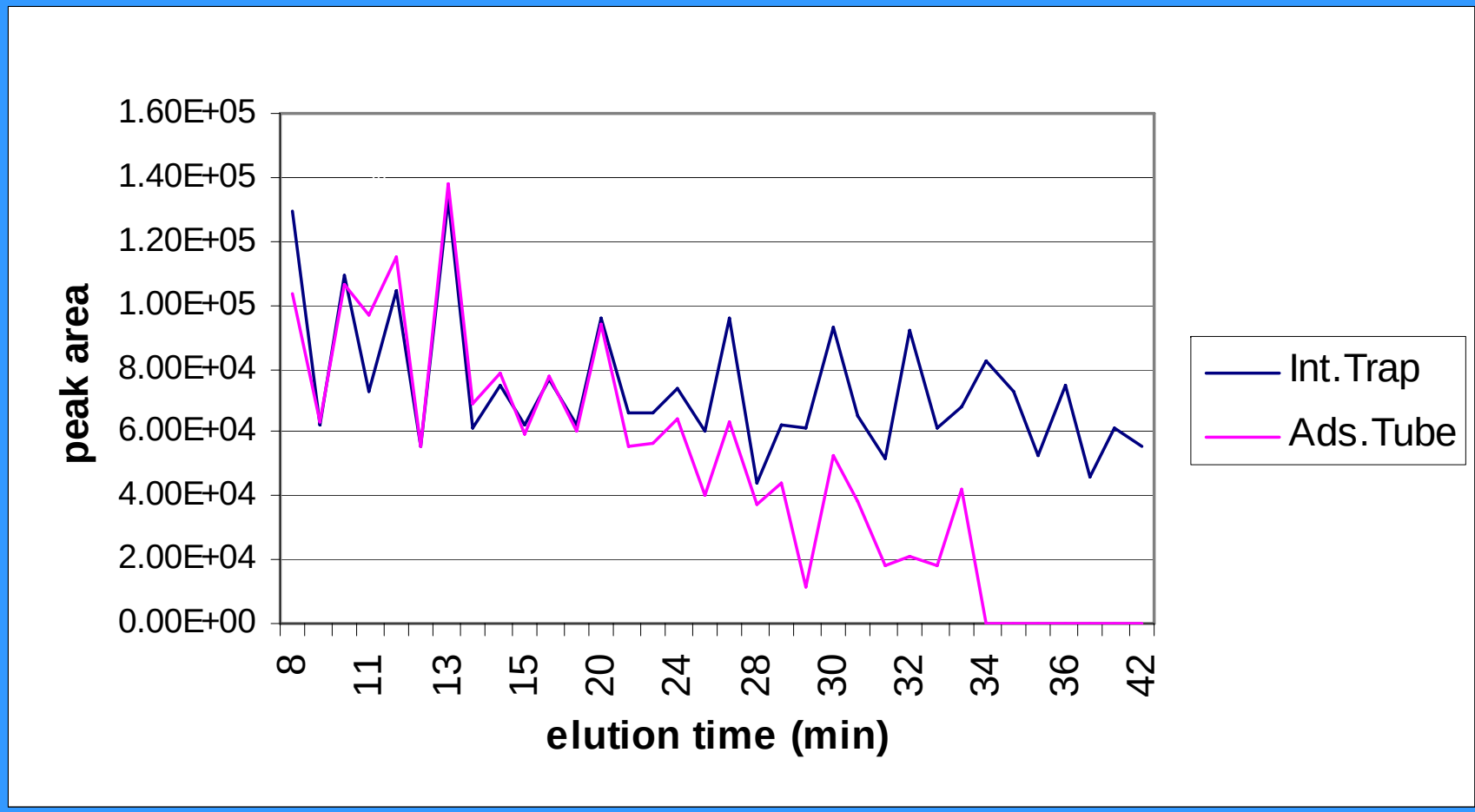
- Benzene – critical
- Toluene
- Ethylbenzene
- Xylene (sum of isomers)
- 224 – Trimethylpentane (224-TMP)

Recovery

55 Compound Standard



Recovery by Elution Time



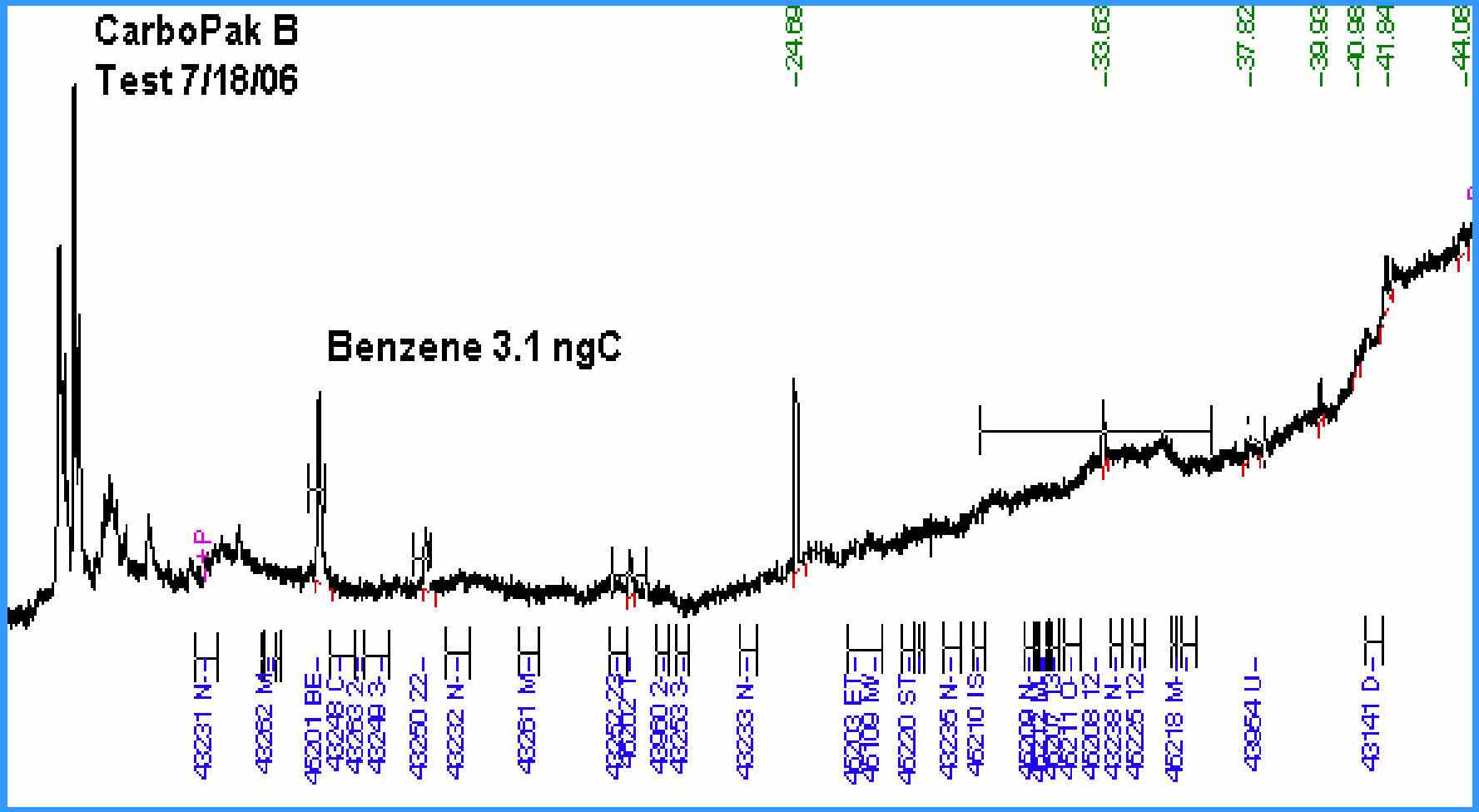
Recovery by Compound

	Target	Average	% Diff
BENZENE	61	76	24.6%
TOLUENE	95	73	-23.2%
ETHYLBENZENE	68	32	-52.9%
M/P-XYLENE	107	44	-58.9%
O-XYLENE	65	33	-49.2%
224-TMP	92	62	-32.6%

n = 13

Background –

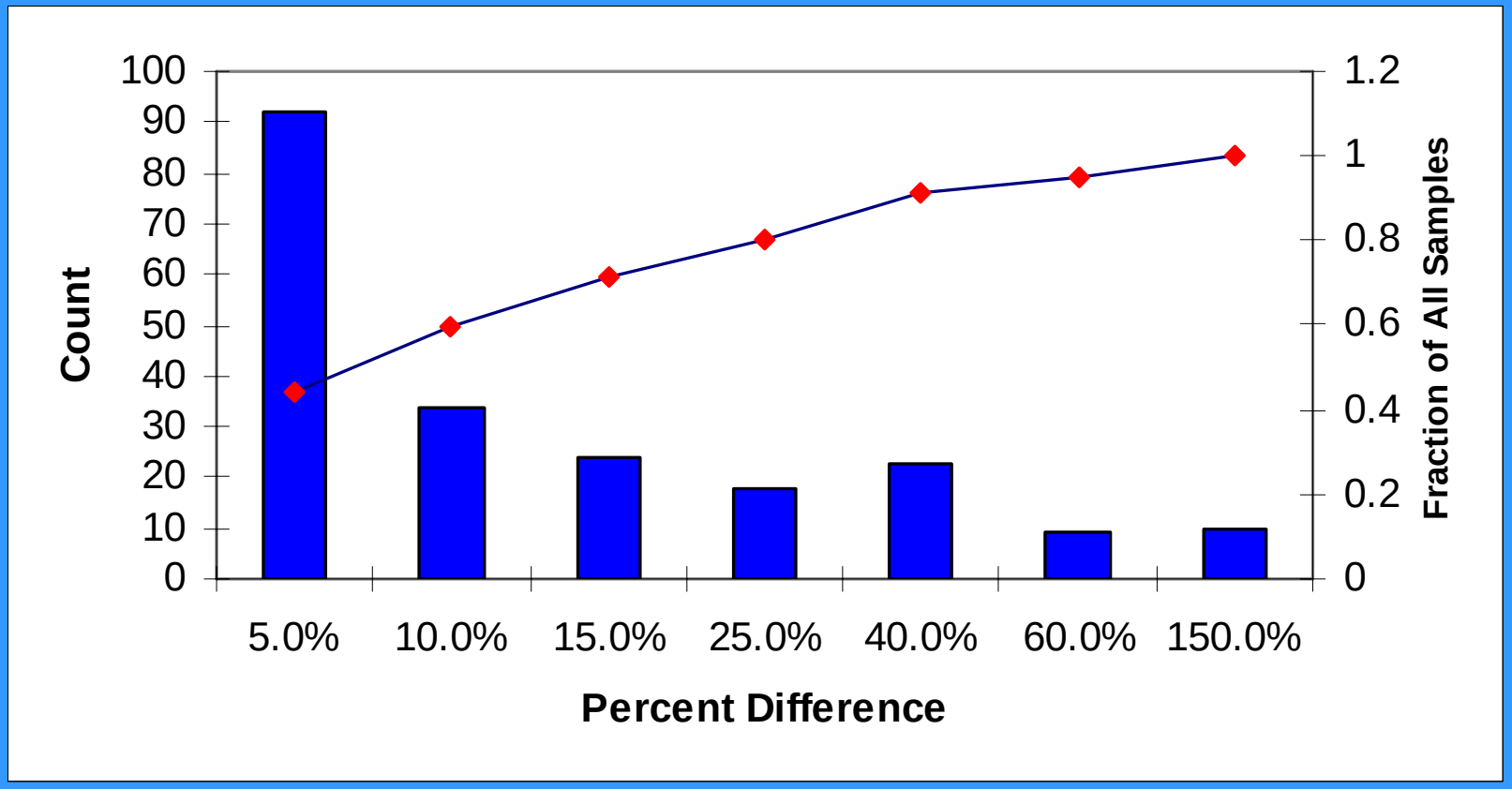
Sample Blank Chromatogram



Blank Backgrounds

	Average Weight /Tube (ng)			
	Run	Prep	Trip	Field
Compound \ N	16	13	13	13
Benzene	4.20	4.07	4.73	3.69
Toluene	1.96	2.61	3.31	2.24
Ethylbenzene	0.19	0.45	0.90	0.53
Xylene	0.60	1.51	3.34	3.10
224-trimethylpentane	1.18	1.66	1.64	1.13

Duplicate Sample Summary

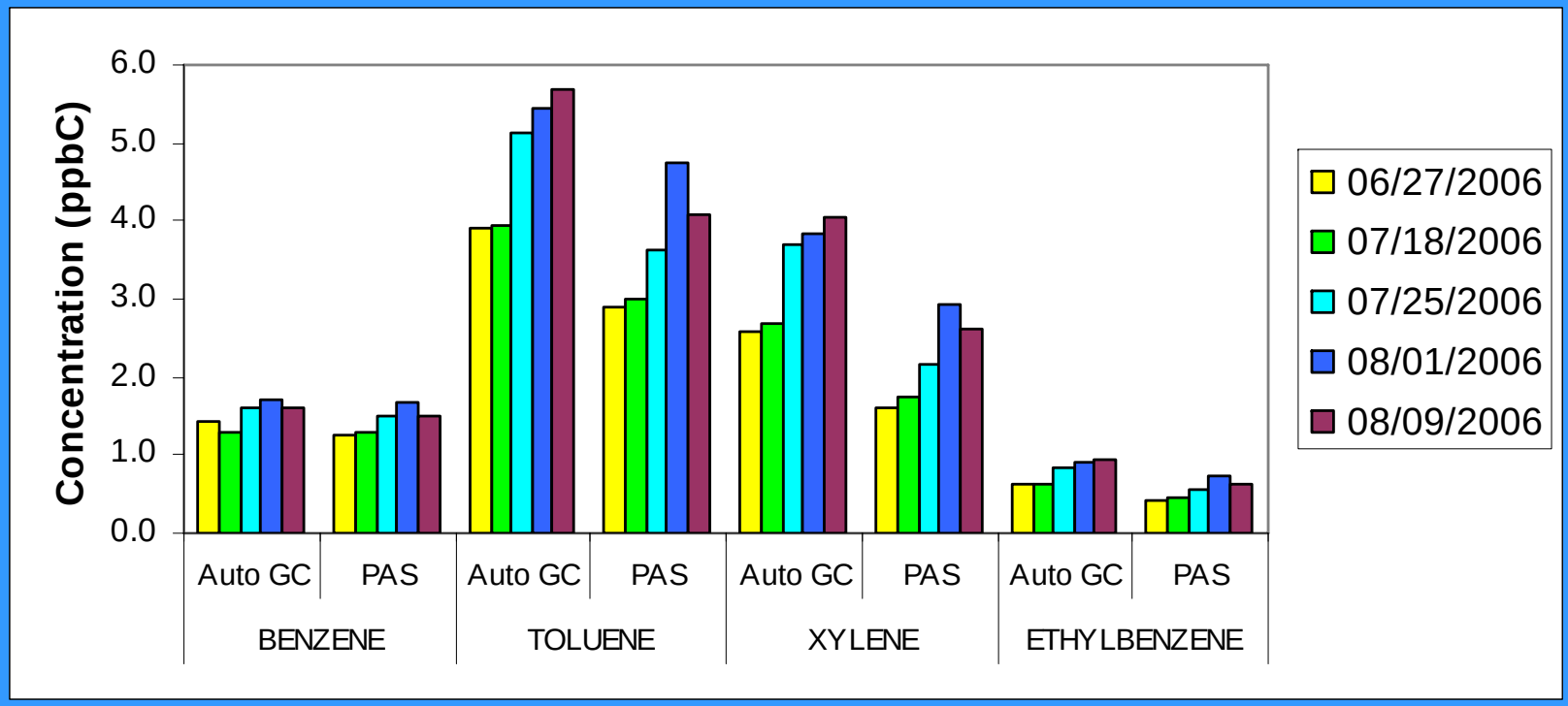


Summary of Duplicate Precision by Compound		
Compound	Average %Diff	Maximum % Diff
Benzene	10.9%	51.9%
Ethylbenzene	34.8%	138.8%
Toluene	8.3%	43.2%
m/p-Xylene	11.8%	81.1%
o-Xylene	15.1%	93.3%
2,2,4- TMP	9.9%	70.2%

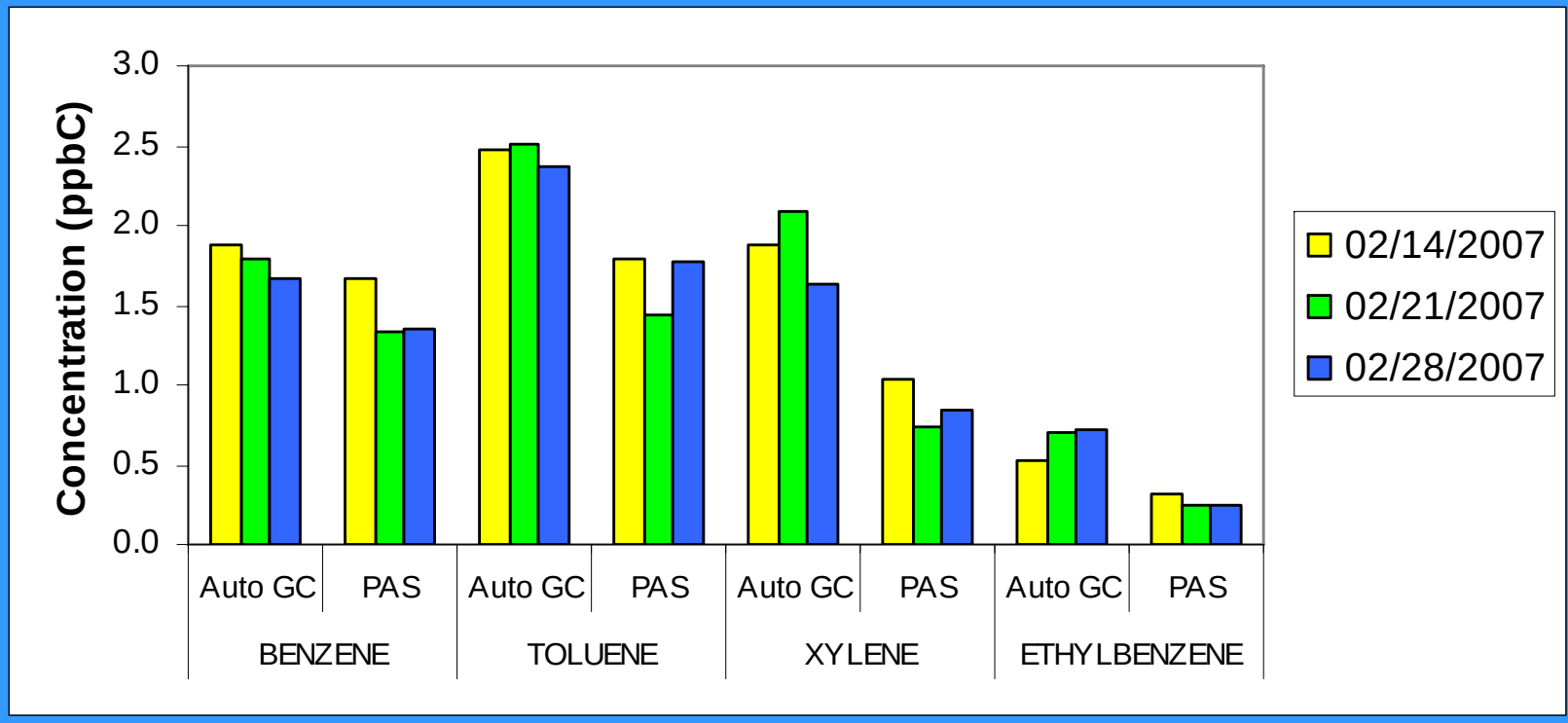
n = 26

Data Comparability to Established Methods

PAS vs. AutoGC Summary of 2006 Test Samples

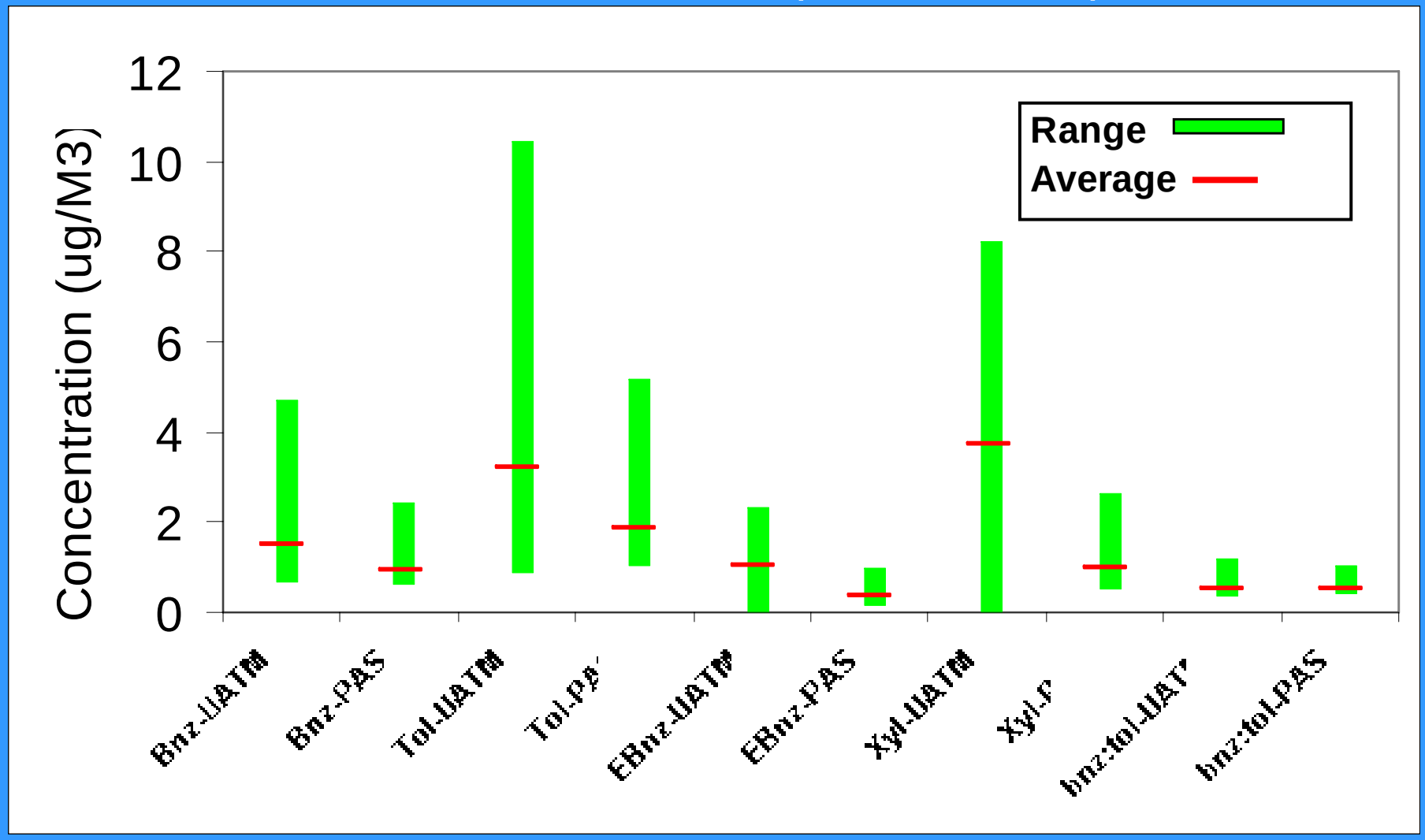


PAS vs. AutoGC Summary of 2007 Test Samples



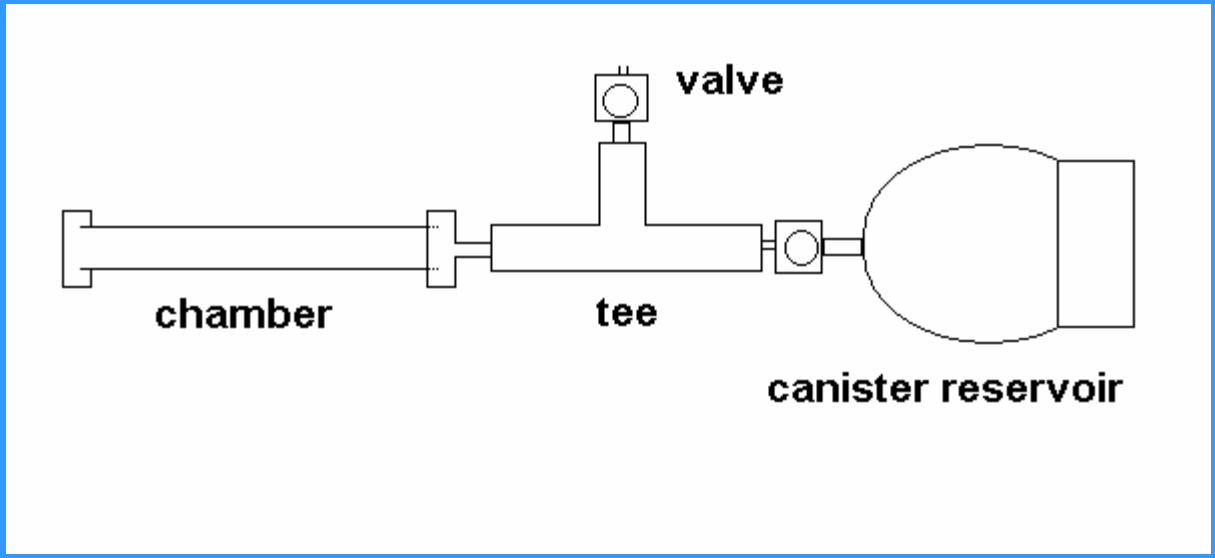
Summary of Bias PAS v. AutoGC			
Parameter	2006 (n=5)	2007 (n=3)	Overall (n=8)
BENZENE	94.4	81.5	89.5
TOLUENE	75.8	68.1	72.9
ETHYLBENZENE	69.0	43.3	59.4
XYLENE	65.1	47.3	58.5
224-TMP	61.5	46.6	55.9

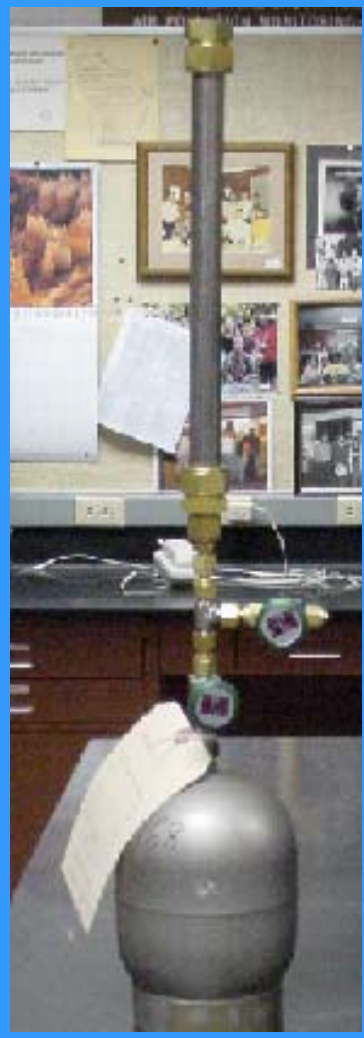
Study 1: PAS vs. Canister Samples Collected at Milwaukee SSHC (55-079-0010)



UATM n = 9 : PAS n = 5

Diffusion Uptake Test Chamber





Experimental Diffusive Update Rate Constant (DRC)

Exposure Time (hours)	Study 1	Study 2	Study 3	Study 4	Reference Diffusive Rate Constant
	24	24	168	168	
Compound	Calculated DRC				
Benzene	0.35	1.18	0.20	0.19	2.14
Toluene	0.30	0.70	0.16	0.15	2.16
Xylene	0.22	0.31	0.14	0.11	2.37

Reference DRC values taken from

Brown, R.H., J. Environ. Monit., 1999, 1, 115–116

QAPP Data Quality Objective

- *The overall data quality objective is to provide a dataset of known quality for use in assessing the benzene concentrations near roadways. The dataset should also be comparable to current fixed site PAMS monitoring within known limits..*

PAS Method Evaluation Summary

- PAS method shows data comparable to established methods, but is biased low.
- PAS results must be blank corrected.
  - Background on tubes, but no evidence of contamination.
  - Used average of prep, trip, field blanks.
- Precision is good on average.
  - Benzene 10.9% dif; toluene 8.3%.
- Need to use literature DRC.
  - Reference values taken from Brown, R.H., J. Environ. Monit., 1999, 1, 115–116