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

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Acronyms and Abbreviations

AD	Absolute Difference
AQS	Air Quality System
ATMP	Air Toxics Monitoring Program
ATD	Automatic thermal desorption system
AUTOGC	Perkin Elmer Ozone Precursor Analysis System
CFR	Code of Federal Regulations
DP1	capillary gas chromatography column coated with 100% dimethylsiloxane
DRC	dissuasive uptake rate constant
EPA	Environmental Protection Agency
GIS	geographical information systems
GLP	good laboratory practice
HRGC	high resolution (capillary) gas chromatography
LIMS	Laboratory Information Management System
MSA	metropolitan statistical area
PAS	Passive adsorbent sampler
PC	personal computer
PCS	Passive canister sampler
PD	percent difference
PLOT	porous layer open tubular chromatography column
PM	Project Manager
QA/QC	quality assurance/quality control
QA	quality assurance
QAO	quality assurance officer
QAPP	quality assurance project plan
QMP	quality management plan
RAIMI	Regional Air Impact Modeling Initiative
SER	Southeast Region
SOP	standard operating procedure
VMWD	vector mean wind direction
VMWS	vector mean wind speed
WSLH	Wisconsin State Laboratory of Hygiene
WDNR	Wisconsin Department of Natural Resources

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Executive Summary

Air pollution in the urban environment is increasingly indicated as a significant factor affecting the public health. Within urban areas, roadway emissions are thought to be very significant and sometimes the most significant source of air pollution. A number of studies have addressed this issue and have focused on the relationship between exposure and proximity to major roadways. One of the primary risk drivers studied in mobile source emissions is benzene, a common known human carcinogen.

Wisconsin has been evaluating the risks from hazardous air pollutants through the RAIMI (Regional Air Impact Modeling Imitative) technique. These studies, which have focused on Milwaukee, have included modeling of mobile source emissions from the urban interstate highway. Modeling used USEPA Mobile 6.2 to estimate vehicle emissions, USEPA Industrial Source Complex - Short Term 3 Gaussian plum model was used to conduct dispersion modeling, and risk from the dispersion modeling was calculated using the Regional Air Impact Modeling Initiative (RAIMI).

Our monitoring study was designed to address questions raised by Wisconsin's and other attempts to model mobile source emissions. These questions include;

- How accurate are current stationary source and mobile source inventories in predicting ambient benzene concentrations?
- Are major roadways significant sources of benzene?
- How quickly is benzene dispersed from the roadways to the adjoining environment?
- What are benzene exposures in neighborhood environments?

Passive Sampling Technique Evaluation

Roadway benzene studies to answer these questions require multi-site networks, small footprints, methods with minimal on-site support, and methods that provide accurate long-term benzene measurements. Passive sampling techniques were used because these techniques were best able meet the project's monitoring needs.

Using commercially available sampling methods supported with some in-house built equipment we implemented, evaluated, and deployed two passive sampling methods. We used passive adsorbent samplers for week-long measurements and passive canister samplers for short-term peak measurements.

Our evaluation of the passive sampling techniques included standard method evaluation criteria and direct comparisons with our existing PAMS and UATM methods. Our testing of the methods found the following.

- We conclude that the passive adsorbent sampling method generates data comparable to established methods, but note the data is biased low to the established methods.
- From our study of the blank samples we conclude that background weights of target compounds are not significant enough to invalidate the method, but these background weights must be addressed by blank correcting the data.
- We conclude on average the precision of the passive adsorbent sampler is good.
- Finally, we conclude it is necessary to use literature diffusive uptake rate constants to calculate all ambient concentrations.

Field Study Results

Using the passive sampling techniques, we conducted three field studies to examine the relationship between benzene concentrations and distances from heavily trafficked roadways. In our studies, the heavily trafficked roadways were sections of Wisconsin Interstate Highways. Two studies were located across an urban highway and one control study across a rural highway. Our field studies yielded the following five conclusions about benzene near roadways.

- Measured benzene concentrations at all sampling sites for Study 1 were higher than the concentrations predicted by the computer model. The concentrations were confirmed for six of the 10 sites in Study 3. We conclude that the model missed some unknown sources or that the model underestimated the vehicular emissions.
- In all three studies, the measured ambient benzene concentrations were more uniform across transects than suggested by computer modeling. This was confirmed by multiple samples collected over many weeks. We conclude that benzene is diffusing out to a uniform concentration more quickly than predicted by the computer model.
- We observed that average benzene concentrations in the studies showed much greater variability between individual weeks of the study than between individual sites used in the studies. This shows results from individual sites have more in common with results from other sites collected at the same time than they do with results obtained from the same site during different weeks. This supports the second conclusion, that concentrations are more uniform across transects of roadways than predicted.
- We observed that in the urban study peak benzene concentrations were not measured on the interstate highway, but rather on the parallel city roadway to the west of the highway. The observed peak along Milwaukee’s Sixth Street was noted in both Study 1 and Study 3 but was only statistically significant in Study 3. We conclude that urban traffic routes may have significant mobile source emissions even though these routes have less traffic volume.

- Finally, we observed that benzene concentrations at all study sites were higher than the one-in-a-million risk concentration of 0.128 ug/m3. Computer models predict that at distances of 100 to 150 meters from the roadway the benzene concentration drops below the one-in-a-million risk concentration benchmark. We conclude that risks above the one-in-a-million risk concentration benchmark are present at distances up to 600 meters from the heavily trafficked highway.

Section 1. Background

1a. Roadway Toxics and Exposure

Air pollution in the urban environment is increasingly indicated as a significant factor affecting public health. Within urban areas, roadway emissions are thought to be very significant and sometimes the most significant source of air pollution. EPA has reported mobile source emissions may account for 50% or more of the cancer risk in urban areas (Federal Register, Vol. 71). Currently much of the work to document health risks is epidemiological. Several studies have shown increased respiratory health problems associated with traffic related air pollutants **(**Morgenstern et. al., 2007, Pierse, et. al., 2006). There are also studies showing relationships between traffic counts and respiratory health effects (Ciccone, et. al.,1998). While there is increasing evidence to suggest links between health effects and mobile source air pollution there is not a firm link between distance from roadway and asthma (Livingstone, et. al.,1996). While questions exist about risks in relation to one's proximity to roadways, it has been shown that exposure to mobile source emissions increases health problems including cardiovascular disease, respiratory diseases and cancers. The amount of roadway emission will likely increase rather than decrease as the Wisconsin DOT has reported both the number of registered vehicles and the number of licensed drivers increases annually.

Significant risk drivers from mobile sources include benzene, which is addressed in this report. Another significant risk driver is fine particulate matter, which can not at this time be adequately addressed by passive monitoring. Benzene is a ubiquitous aromatic hydrocarbon that is present in gasoline and formed in many combustion processes. Benzene is a known human carcinogen and is considered one of the most significant risk drivers in the urban environment. Mobile source emissions make up the major source of benzene in the urban environment (Fruin et.al., 2001). Models show that the exposure from roadways is related to the distance from the roadway (Funk and Lurmann, 2001). Monitoring studies suggest that for mobile source pollutants, like benzene, the outdoor and indoor air concentrations are similar and indicate ambient air is the most important exposure driver (Paynes-Struges et. al., 2004).

Stationary benzene emissions are well qualified and a review of Wisconsin's air emission inventory for the year 2005 shows a total of 45 facilities in Milwaukee reporting a total of more than 30495 pounds of benzene emissions. The majority of these emissions (over 27940 pounds) are accounted for by 12 primary metal industries (foundries and metal casting). Petroleum products terminals, motor manufacturing, pipelines, power generation and wastewater treatment account for the majority of the remaining reported emissions (over 2110 pounds)

While less well quantified, roadway emissions are important because Milwaukee is the location of a major urban interstate roadway, Interstate Highway 94. The Wisconsin Department of Transportation has estimated the daily vehicle miles traveled in Milwaukee County to be $2.07\text{x}10^7$ and the annual average to be $7.56\ \text{x}10^9$ (Wisconsin DOT website), when averaged over 2004 to 2006. Wisconsin has a major construction project underway on the Highway 94's Marquette interchange which will continue until 2008. This construction project, along with the updates to the vehicle fleet, and changing fuel blends can be expected to have significant impact on mobile source roadway emissions in the city.

This project was undertaken because we felt many questions remained about benzene in the urban environment and these questions warranted further study. Our questions include; how accurate are current stationary source and mobile source inventories in predicting ambient benzene concentrations; are major roadways significant sources of benzene; how quickly is benzene dispersed from the roadways to the adjoining environment; and what are benzene exposures in neighborhood environments adjoining roadways?

To better measure ambient concentrations we required a multiple site network. This requires sampling apparatus with both a small footprint and low support overhead. The Wisconsin DNR's passive sampling techniques provided the tools to better understand the sources, transport, and diffusion of benzene from roadways. The passive techniques used here focused on benzene and measured related hydrocarbons to assist in assessing the sources and impact of the benzene.

1b. Wisconsin's RAIMI Study

The Wisconsin DNR, with funding support from EPA, has conducted community scale risk assessment in Milwaukee. The studies were conducted to assess new modeling techniques to better address the public's concern about and interest in the safety of the air we all breathe. The study goal was to look at source inputs for the aggregate effect on air quality and in-turn the risk this posed to the public. The study was conducted in Milwaukee's densely populated urban center. The modeling domain covered an approximate area of 5.9 Km by 4.5 Km with the study boundary marked by the roadways and geographical features listed below.

RAIMI Modeling Domain
West Boundary – 35th Street
North Boundary – Wisconsin Ave
South Boundary – Lincoln Ave
East Boundary – Lake Michigan

Included with this domain is a large segment of Milwaukee urban interstate highway. The primary target compound for the study was benzene a known human carcinogen. Benzene was of interest because concentrations were predicted to be high; the compound is ubiquitous and originates from point, area, and mobile sources; and because of existing monitoring data for benzene inside the domain.

Monitoring data came from the Wisconsin DNR's multi-parameter air monitoring site at the Sixteenth Street Health Center site. Located near the center of the modeling domain, this monitoring site measures ambient ozone, particulates and air toxics.

Roadway emission data, the modeling tools, the techniques used and the graphical display of the data is summarized in the following. GIS data layers for roadway links containing data on 2003 annual average daily traffic counts for various roadway types were obtained from Wisconsin DOT. Emission rates in grams per vehicle mile for each roadway type were developed using the USEPA Mobile 6.2 model. Roadways were modeled as point sources spaced every 25 meters in the dispersion model. The EPA Industrial Source Complex - Short Term 3 Gaussian plum model was used to conduct the dispersion modeling that predicted annual concentrations of benzene. Risk from the dispersion modeling was calculated using the Regional Air Impact Modeling Initiative (RAIMI). The risk assessment was done within the RAIMI modeling system using the EPA Human Health Risk Assessment Protocol procedures and standard default health benchmarks. Health benchmarks used were the unit risk factors for carcinogens. The results of the analysis are put into a GIS point layer and are then seen graphically as a GIS map.

The modeling estimated annual average concentrations over the course of 5 years of hourly meteorological data used for the model simulation. It did not estimate concentrations for any shorter periods of time than for an annual average. The concentration data and risks represent a long term average exposure to the modeled chemicals and sources. Because the traffic data used was from 2003, the RAIMI results could be considered a representation of average annual exposures due to 2003 traffic volumes from roadway emission sources.

While the modeling effort was able to identify significant sources of risk within the domain, the study also raised questions about the data's validity. Benzene concentrations predicted by the model were two orders of magnitude smaller that concentration measured at the Sixteenth Street Health center. We believe that mobile source emissions may be underestimated and this contributes significantly to the modeled benzene shortfall.

Wisconsin's risk assessment study was not able to fully evaluate the risk effects of mobile sources in the study domain. The study did identify mobile sources as significant and worthy of further study. In the draft final report the authors noted a need to improve tools used for mobile source modeling. The purpose of our roadway monitoring study was to validate current modeling assumptions and to guide model improvements

1c. Rationale Supporting the Study's Proposed Methodology

The Wisconsin DNR staff have previous experience monitoring vehicle emissions near roadways. This experience includes a 1995 roadway monitoring study (Allen, Grande and Foley, 1996) of reformulated gasoline compounds which would provide experience and background knowledge. The Reformulated Gasoline monitoring project included air sampling near roadways as well as sampling personal exposure during vehicle refueling. This successful project relied on active sampling techniques that require power generators and on-site monitoring crews. The RFG study employed a total of six staff in two teams that worked to collect samples. Samples were then analyzed at a laboratory in the State of Oregon. The gas chromatographic analysis measured two ethers, ethanol, and other hydrocarbons. The 1995 study was resource intensive and the level of effort required for the earlier study could not be duplicated in the planned monitoring project. We would need samplers that required less operator oversight and lower analysis costs.

To meet the projects needs for multiple, low operating overhead samplers our project relied on passive air monitors. The development and testing of passive monitors for monitoring concentration of benzene and other aromatic hydrocarbons has been reported by Brown, et. al. (1981). In a later paper, Brown et. al.(1999) discussed the use of these passive sampler for mobile source related pollutants, including benzene, toluene, and xylenes. In past monitoring efforts Wisconsin DNR staff have used badge type passive samplers including the 3M OVM monitor. These devices are usually exposed at monitoring sites for a month long period of time.

For this project we used commercially available diffusion tubes designed for analysis on a Perkin-Elmer gas chromatographic system. Our gas chromatographic analysis system is in use at Wisconsin's Milwaukee PAMS site. Used for PAMS monitoring, the gas chromatographic system is operated during the peak ozone months, June through August. Our project made use of the system by conducting analyses of the passive samples before June and after August. Current analysis parameters provided an analytical base for the passive sample analysis and development time for the method was minimal.

Wisconsin DNR's current methodologies and methods have been proven in the Photochemical Assessment Monitoring Station (PAMS) and Urban Air Toxic Monitoring (UATM) projects. These current methodologies provided the benchmarks for evaluation of the passive technologies. Currently, pressurized whole air samples in passivated canisters are analyzed at the Wisconsin State Laboratory of Hygiene. The Wisconsin State Laboratory of Hygiene has analyzed PAMS and UATM monitoring samples for the Wisconsin DNR since 1994. Hourly benzene values are collected at the Type 2 PAMS site using a Perkin-Elmer Ozone Precursor analyzer (AutoGC). This unit has been in operation in Wisconsin since 1999.

Section 2. Study Methodology

2a. Sampling Techniques

Our study utilized two air sampling methods, the first, passive adsorbent sampling tubes (PAS) and the second, passive canister sampling (PCS). The media used for each of these methods were analyzed using with high resolution gas chromatography (HRGC). PAS were used to collect long term air samples, of one week's duration. Canister samplers were used to collect shorter 1-hour samples.

Passive Adsorbent Samplers collect pollutants through a gradient diffusion process, and are sometime called diffusive samplers. - Detailed description of the gradient diffusion techniques can be found in Brown (1981). The samplers were commercial tubes supplied by Perkin Elmer. The tubes were constructed of stainless steel tubing 89 mm in length with and internal diameter of 6 mm. During sampling the one Teflon cap is replaced with a cap with a permeable membrane. The inlet ends of the tubes have a 15 mm space to allow for a concentration gradient between a membrane and the adsorbent surface. When not in use sampling the tubes are capped with two Teflon caps.

Capped tubes were stored in glass culture tubes and placed in a freezer below 0 degree C. Initial tests of the PAS used Chromosorb 101 as an adsorbent, but we were unable to clean the tubes sufficiently well for the project application. A second adsorbent, Carbopack B, was shown to have a much lower background after cleaning. Even with the low background, the tubes did have a residual peak that was either benzene or an unknown compound that co-eluted with benzene. The residual peak area was much less than the area for ambient benzene. Background benzene and other background concentrations are discussed in Section 3b of this report. Background corrections are discussed in Section 4b1.

Figure 2-1: Photo of passive adsorbent sampler tube. Teflon cap (white) on one end and the diffusion cap (gold) on the opposite end.

In the field studies, the adsorbent tubes were placed on existing light, signal, or power poles. Shown in Figure 2-2, an 18 inch PVC stand-off, held a cone shaped shield, and adsorbent tubes were mounted under the shield. Stand offs were placed at an approximate height of 10 feet from the base of the pole. A total of eleven sites were used on Field Study 1, nine sites for Field Study 2, and 9 sites for Field Study 3. Two additional sites planned for Field Study 3 were dropped due to repeated acts of vandalism. Listings of the sites for the field studies are provided with the results discussion in Tables 4-2, -6, & -9.

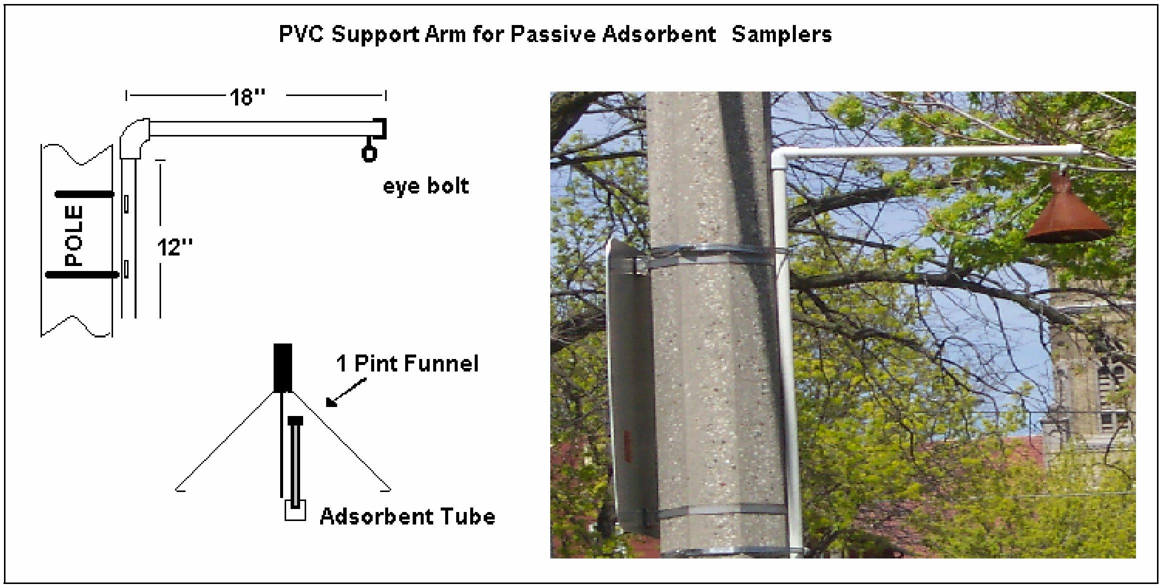


Figure 2-2: Diagram and photo of the support arm used to suspend the PAS.

Whole air samples were collected in canisters for short term 1-hour samples. The canisters were cleaned and evacuated at the Wisconsin State Laboratory of Hygiene. The canister field sampling apparatus, show in Figure 2-3, consisted of a commercially purchased Entech passive sampler and a timer unit built in-house. Component parts of the system are provided in Table 2-1. Sampling canisters were deployed a day before sampling with the timer set to open the canisters at 07:00 local time the following day. Once opened, the Entech passive sampler regulated flow to collect a 1-hour sample. After sampling the timer sealed the canister. At our analysis laboratory, the canisters were measured for initial pressure, approximately 1 atmosphere. Using a zero gas, the canister was then pressurized to approximately 1.5 atmospheres to allow analysis on the Perkin Elmer system.

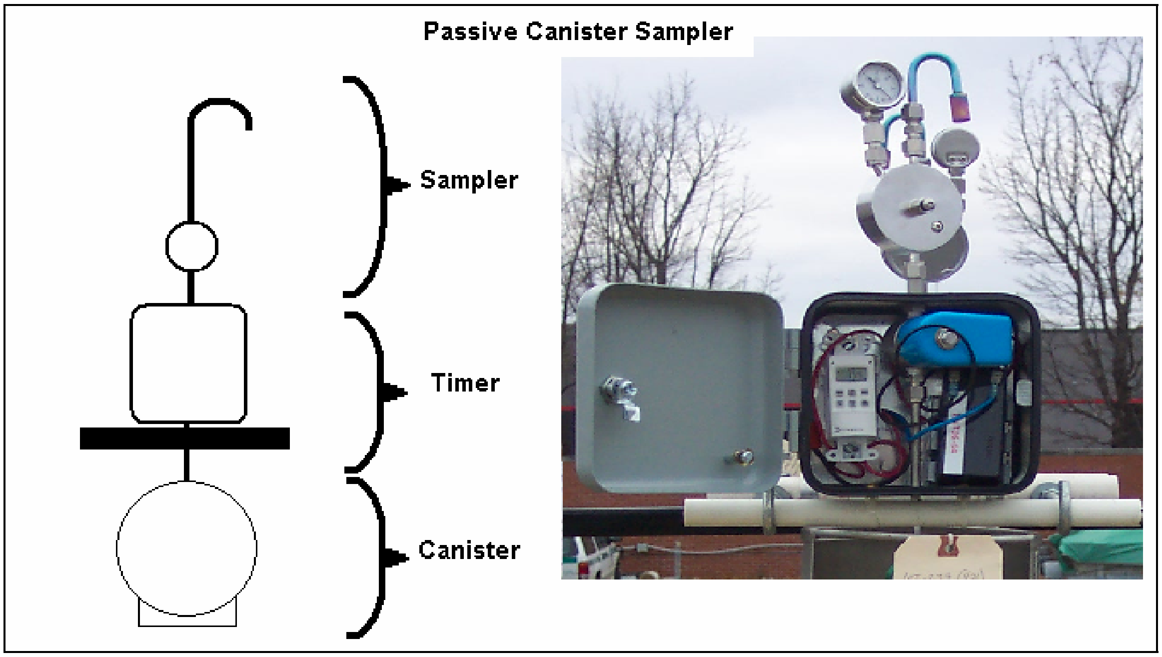


Figure 2-3: Diagram and photo of the PCS used in the project.

Table 2-1: Components Of Wisconsin’s Passive Canister Sampling Apparatus	
Valve	A Parker Skinner solenoid valve (Parker Hannifin) commercial valve was used (part number (71215SN1MN00A0J611C1). The valve used 1/8” NPT fitting, was normally closed, and used a low power Fluxtron coil that required on 12 V DC for activation.
Sampler/Regulator	Entech Instruments, 2207 Agate Ct.,Simi Valley, CA 93065 supplied the passive sampler used for canister sampling. The CS1200E model canister samplers are compatible with the 1/4" connector found on Wisconsin’s 6L canisters. The samplers were purchased with the regulators’ flow set to fill the canister in one hour.
Timer	Timing was accomplished using Intermatic switches,(Intermatic, Inc.Intermatic Plaza,Spring Grove, IL 60081). This small battery operated timer can be set for up to seven days in advance. The unit used was the “Heavy-Duty Digital 7-Day Wall Switch Timer SS7C”
Power Source	Power was supplied by a small rechargeable 12V 750 mA lead acid battery

Canister samplers were also mounted on poles using a bracket. Canister samples were typically placed 24 hours prior to sampling and usually picked up within 8 hours of sampling. Canister samples were collected during field studies 1 and 3 in Milwaukee and were collected from two locations. The first PCS was collocated with the PAS site 990 located in Kosciuszko Park. The second PCS was collocated with the PAS sampling site 995, placed on the northbound exit for Highway 94

2b. Gas Chromatographic Analysis

After sampling, the exposed tubes were analyzed with a combination of thermal desorption, gas chromatography, and flame ionization detection. Exposed sampling tubes are placed in the carousel of the automated thermal desorber (ATD). Tubes move into the analysis position, the end caps are removed and the tubes sealed in the unit. An oven block then moves around the tubes, heating them while the helium carrier gas moves through the tubes. Compounds are released and then trapped on an internal multisorbent trap. In the next step, the internal trap is heated and the compounds passed to the gas chromatographic column. Compounds are separated on the gas chromatographic column and finally pass into the flame ionization detector. The response of the flame ionization detector is proportional to the number of carbon atoms in each compound in the sample. The analytical system is standardized using a known standard gas of propane and benzene in nitrogen. For our application only the benzene was used in standardization.

The analytical system was standardized using a propane and benzene gas trapped only on the analytical trap. The 75 ppbC standard was sampled for 40 minutes at a flow rate of 15 ml/min. A total of 0.6 liter of gas was trapped and the amount of benzene mass in the system is calculated as follows:

$$\text{mass} = 75 \text{ ppbC} * 0.6 \text{ liter} = 75 \text{ nl/L} * 0.6 \text{ L}$$

mass = 45 nlC * 1 mole/24.45 nl * 78 ngC/mole

mass = 143.6 ngC

A system response factor was then calculated as:

RF = Peak Area Benzene/ 143.6 ngC

{this is redundant, already present in sampling section above}

When analyzing canisters, the analysis system consisted of automated thermal desorption unit, gas chromatography on dual columns, and two flame ionization detectors. The gas sample taken from the canister was trapped directly on the multisorbent analytical trap of the ATD. The analytical trap was then heated and the compound passed to the first analytical column. During the initial minutes of the analysis, the output of column one was passed to the second column for the analysis of light hydrocarbons. After approximately 9 minutes the output of the first column was shifted to the FID. The system's analytical columns include a dimethlypolysiloxane
column (DP-1) for C6 to C12 hydrocarbons and an Al2O3 column for the analysis of lighter hydrocarbons.

The analytical system was standardized using a propane and benzene gas trapped only on the analytical trap. The 30 ppbC propane standard and the 75 ppbC benzene standard were sampled for 40 minutes at a flow rate of 15 ml/min. All canister samples were also trapped for 40 minutes and the response factors were calculated as

Propane RF = Area Propane / 30 ppbC

Benzene RF = Area Benzene / 75 ppbC

Section 3. Evaluation of the Passive Sampling Methods

3a. Performance of the Two Study Methods

The PAS or adsorbent tubes were simple to prepare for sampling, to deploy in the field, to retrieve, and to analyze. Over the course of three field studies , we experienced very few problems with the tube samples. Two problems that did arise with the study resulting in lost data. The first is the loss of two samplers due to vandalism. Because of this vandalism , we were unable to use two of eleven planned monitoring sites in Field Study 3. The second problem was a detector noise problem that developed on one of two FIDs used on the gas chromatograph. The problem began during the second field study and compromised some data. The problem continued but we were able to compensate and recovered most of the data in Field Study 3.

Canister samplers were more complicated and thus prone to operational problems. Many of these problems appeared in the first field study , resulting in a very low completion percentage (43%). In many cases we were successful in getting one canister to operate but had a failure on the paired sample. By Study 3, staff were more familiar with the systems and our completion rate showed significant improvement (77%).

3b. Study Blank Samples

We examined four types of blanks in this study. One blank was associated with the analysis process and the other three types of blanks are used to assess field study samples. A description of the blanks follows.

Run Blanks – Analytical runs include standards captured on unexposed tubes. In addition , a randomly selected unexposed tube is analyzed as a run blank for each analytical run.

Process Blanks – Process blanks are cleaned tubes that are held in the study's freezer during the time that other tubes are exposed. The process blank is used to show that the tubes are cleaned and that no contamination has occurred between the time the tubes were cleaned and when they were analyzed. The process blank is analyzed with the sampling tubes in each analytical run.

Trip Blanks – Trip blanks travel to the field site with the samples for deployment and retrieval. While the sampling tubes are exposed the trip blank is stored in the study freezer. The trip blank is included to show if any contamination occurs during the transport of the sampling tubes. The trip blank is analyzed with the sampling tubes in the analytical run.

Field Blanks – Field blanks travel to the field site with the samples for deployment and retrieval. The field blank is uncapped and fitted with a diffusion cap for a period of approximately five minutes, usually during one of the sampling tube deployments. While the sampling tubes are exposed the field blank is stored in the study freezer. The field blank is included to show what contamination might occur during handling of the sampling tubes during deployment and retrieval of the sampling tubes. The field blank is analyzed with the sampling tubes in the analytical run.

Blank data has no exposure time and data is evaluated as the weight of carbon per tube (ngC). Blanks were analyzed by type and across all 13 weeks of study. Data was analyzed by parameter for the number of detects, the average and maximum weight per tube, and the standard deviation of the blanks. Summary data is provided in Table 3-1. Benzene is the critical compound for our study and data shows that benzene or a co-eluting compound is the on average the highest compound on the blanked tubes. The benzene peak is present and is consistent across the blanks with average values ranging from 3.694 to 4.198 ngC. This is well below the weights of benzene detected on the exposed tubes. We chose to address the presence of a detectable benzene peak by blank correcting all ambient data. Data blank correction is addressed in Section 4b1 of this report characterizing ambient data.

Other compounds addressed in this report showed varying weights on the blanks. The highest compounds are the xylenes with maximum weights over 10 ngC. Xylenes , which are the sum of the m/p xylene peak and the o-xylene peak, also show a higher variability, as expressed by the standard deviation.

Table 3-1: Roadway Study Passive Adsorbent Blanks

Compound	N	Detects	Average (ngC)	Max (ngC)	SD
Analytical Run Blanks					
224-Trimethylpentane	16	15	1.177	5.160	1.153
Benzene	16	16	4.198	7.877	2.069
Ethylbenzene	16	5	0.187	2.167	0.540
Xylene	16	8	0.602	3.868	1.074
Toluene	16	15	1.955	5.197	1.314
Prep Blanks					
224-Trimethylpentane	13	13	1.656	3.789	1.085
Benzene	13	13	4.066	9.630	2.029
Ethylbenzene	13	12	0.454	1.112	0.316
Xylene	13	13	1.507	3.518	1.133
Toluene	13	13	2.612	6.020	1.216
Trip Blanks					
224-Trimethylpentane	13	12	1.636	2.757	0.660
Benzene	13	13	4.735	8.691	2.158
Ethylbenzene	13	12	0.895	4.375	1.109
Xylene	13	13	3.339	12.647	3.592
Toluene	13	13	3.306	6.156	1.542
Field Blanks					
224-Trimethylpentane	13	12	1.127	2.128	0.612
Benzene	13	13	3.694	6.100	1.114
Ethylbenzene	13	10	0.534	1.886	0.532
Xylene	13	11	3.096	14.020	4.505
Toluene	13	13	2.243	3.570	1.075

We see only a random pattern between the benzene and toluene concentrations when graphed, in Figures 3-1a,b,&c. We would expect to see a linkage between benzene and toluene were the tubes contained by some action of the operators. This linkage should occur as both benzene and toluene are present in the ambient air and the project vehicle used to transport the tubes. We suspect that the blank values are residual compounds on the tubes after cleaning. We also note that blanks were high for Study 1/Week 4. Week 4 followed the week with the highest ambient concentrations noted during the Study 1.

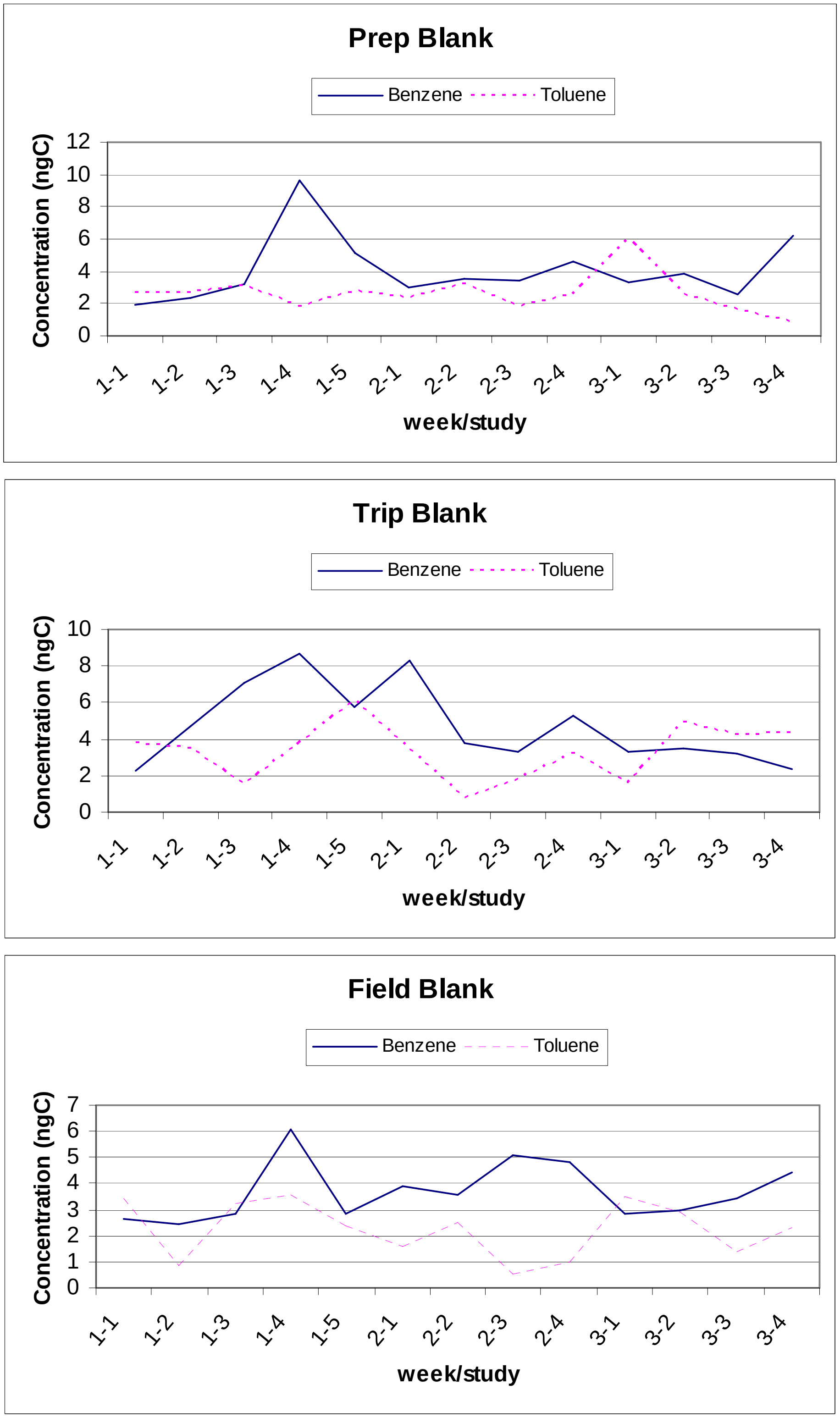


Figure 3-1a,b, and c. These graphs show the variability of the prep, trip and field blanks throughout the project's 3 field studies.

Finally we did not analyze for detection limits in this study. An MDL study was unnecessary because the critical compound, benzene, was detected in measurable amounts in all samples. To address the MDL, we used as a simple measure of the limits of detection the values of three standard deviations of the baseline. Applying this statistic to the analytical blank detection limits are estimated in Table 3-2. The information in the table is provided as a tool to assist the reader in assessing ambient data and should not be taken as equivalent to the more robust detection required when assessing data with a higher percentage of censored data.

Table 3-2: Detection Limits Expressed as 3 SD

Compound	Estimated DL (ngC)	Estimated DL (ug/m3) {168 hour exposure}	Estimated LOQ (ug/m3) {168 hour exposure}
224-trimethylpentane	3.5	0.02	0.06
Benzene	6.2	0.05	0.14
Toluene	3.9	0.03	0.10
Ethylbenzene	1.6	0.02	0.06
Xylenes	3.2	0.06	0.18

3c. Compound Recovery from Carbopak B.

We selected Carbopak B as the adsorbent for passive sampling based on the low background found on the tubes when thermally cleaned. Carbopak B, however, showed varying recovery for the target compounds selected for this monitoring project. We made analytical runs of our 55 compound PAMS standard trapping the compounds on the internal trap and on the adsorbent tubes followed by the internal trap. An overlay of two chromatograms made during two May 2007 analytical runs is shown in Figure 3-2 below.

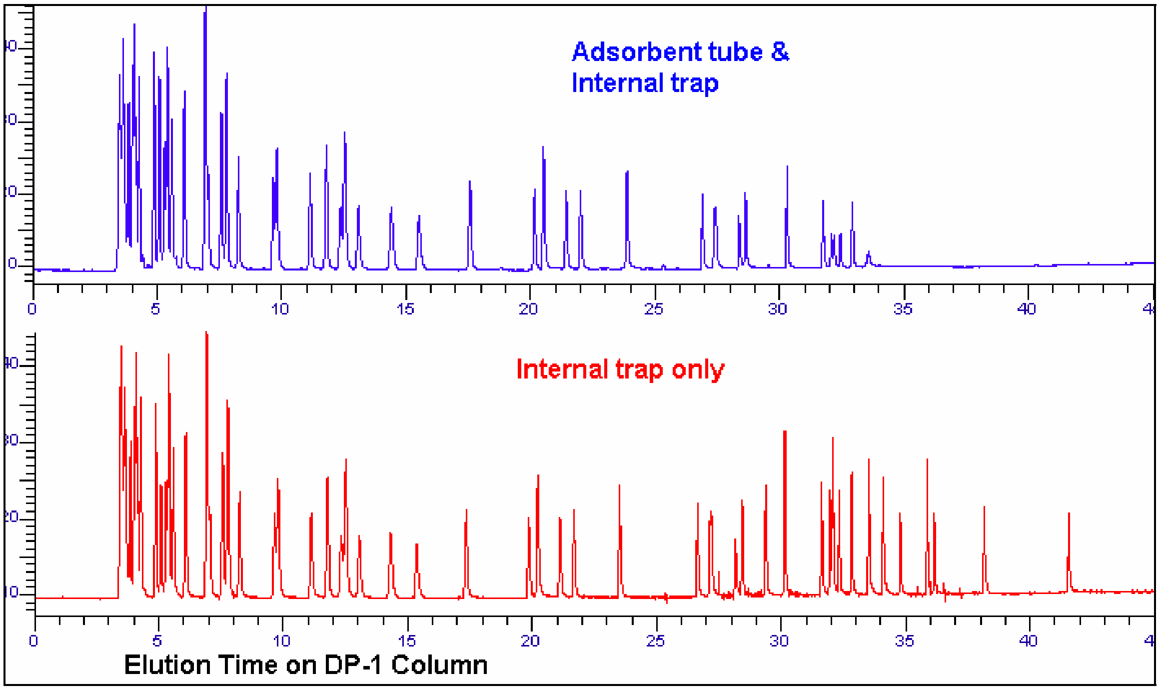


Figure 3 - 2 Overlaid chromatograms of Wisconsin’s 55 compounds PAMS standard trapped directly on the ATDs internal trap and trapped on CarboPak B and the internal trap.

The chromatogram shows the light hydrocarbons bunched early on the DP-1 column, followed by the heavier C6 compounds which are well separated . Later in the chromatogram, starting about C9, we see a distinct fall off of the compound recovery. This suggests either the compounds are not well trapped on the Carbopak B, or they are trapped but can not be recovered by the thermal program used in the study. This is also shown in Figure 3-3, where the detector response is compared to the elution time on the analytical run. We see that at 28 minutes, as we are eluting C8 compounds, the response for the adsorbent tube/internal trap run begins to drop and to show increasingly larger differences with compounds trapped directly on the internal trap.

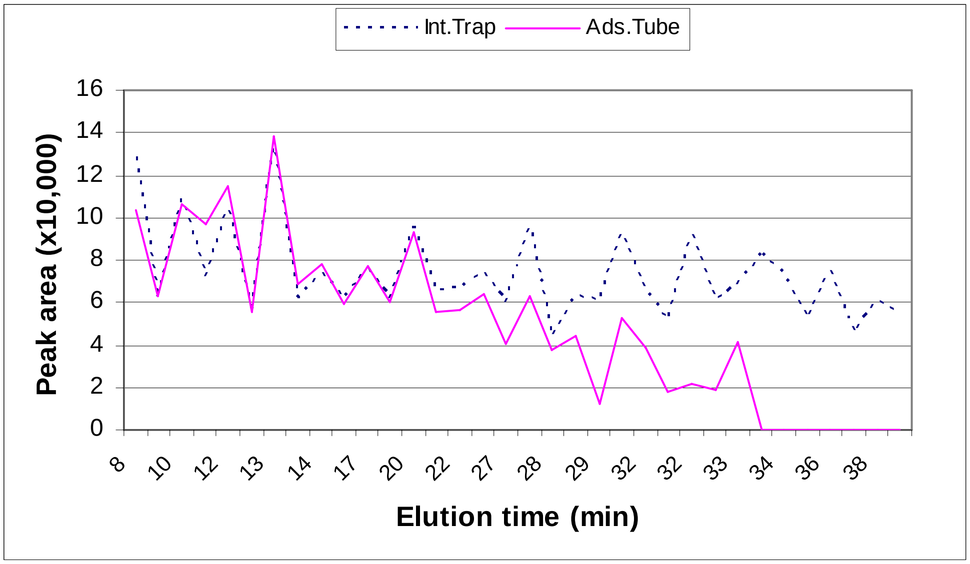


Figure 3-3: Graph comparing compound elution time with of peak area for the 55 compound standard. Peak areas drop for compounds eluting later on the DP-1 column.

This pattern showing decreased area for later eluting compound is confirmed in the compound recovery of the 55 compounds shown in Table 3.3.

Table 3-3: Compound Recovery Data for Multi-component standards run trapped on Carbopak B.

	Expected	Average	% Diff	Recovery
N-Hexane	72	80	11.1%	111.1%
Methylcyclopentane	58	50	-13.8%	86.2%
24-Dimethylpentane	106	84	-20.8%	79.2%
Benzene	61	76	24.6%	124.6%
Cyclohexane	91	88	-3.3%	96.7%
2-Methylhexane	64	44	-31.3%	68.8%
3-Methylhexane	66	52	-21.2%	78.8%
224-Trimethylpentane	92	62	-32.6%	67.4%
N-Heptane	66	48	-27.3%	72.7%
Methylcyclohexane	80	62	-22.5%	77.5%
234-Trimethylpentane	73	48	-34.2%	65.8%
Toluene	95	73	-23.2%	76.8%
2-Methylheptane	76	46	-39.5%	60.5%
3-Methylheptane	76	48	-36.8%	63.2%
N-Octane	90	52	-42.2%	57.8%
Ethylbenzene	68	32	-52.9%	47.1%
M/P-Xylene	107	44	-58.9%	41.1%
Styrene	77	26	-66.2%	33.8%
O-Xylene	65	33	-49.2%	50.8%
N-Nonane	82	8	-90.2%	9.8%
Isopropylbenzene	121	42	-65.3%	34.7%
N-Propylbenzene	88	27	-69.3%	30.7%
M-Ethyltoluene	14.3%	77	11	-85.7%
P-Ethyltoluene	9.9%	121	12	-90.1%
135-Trimethylbenzene	16.2%	74	12	-83.8%
O-Ethyltoluene	30.7%	88	27	-69.3%

As a result of this information, we have modified our target compounds shown in Table 3-4. Note that Benzene was included, as were 5 of 6 priority compounds (although we acknowledge decreasing recovery for the xylenes. Many of the base compounds (13 of 27) were of heavier weights, and showed poor recovery.

TABLE 3-4: Roadway Study Modified Target List		
Critical	Priority	Base
Benzene	N-Hexane	Methylcyclopentane
	224-Trimethylpentane	24-Dimethylpentane
	Toluene	Cyclohexane
	M/P-Xylene	2-Methylhexane
	O-Xylene	23-Dimethylpentane
	~~123-Trimethylbenzene~~	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~~

The data in the remainder of this report is limited to the six compounds printed in bold type in Table 3-4. These are compounds that showed acceptable recovery. These six compounds were also commonly detected and provided enough data to evaluate method performance.

3d. Sampling and Analysis Precision

The precision of sampling and analysis for the passive adsorbent sampler tubes was determined from results of duplicate sampling. Duplicate sampling was conducted by placing and exposing paired sampling tubes concurrently, at a single sampling location. Following exposure the sampling tubes were analyzed and the results evaluated. Test sampling for comparison to the AutoGC were conducted at the Milwaukee PAMS monitoring site. Most test samples we collected at the PAMS site were collected in multiple samples for analysis and comparison. In our three field studies we collected duplicate samples each week at two sites. For Studies 1 and 3 the duplicate samples were collected at the Kosciuszko Park site and at the northbound Highway 94 exit site. During Study 2, duplicates were collected at the southern most site of the transect and at the Highway 94 median site. In all three studies we chose one sampling site on the roadway and one site well removed from the roadway for duplicate sampling.

The analysis of the adsorbent tubes is destructive in that the sample is completely removed from the sampling tubes and only one analysis is possible. Precision is therefore assessed for the combination of both sampling and analysis. Conversion from analysis weight per tube to the ambient concentration requires the compound weight, the exposure time and a constant. Because duplicate tubes were exposed for the same length of time the exposure time was constant and we chose to evaluate precision using the compound weight as determine directly from the analysis weight. Our evaluation looked at data from the three field studies, as well as evaluation studies at the Milwaukee PAMS site. A total of 35 sample pairs were evaluated for six compounds, for a total of 210 data pairs. All precision data reported here is for six study compounds, with m,p-xylene and o-xylene treated separately. Figure 3-4, 3-5, & 3-6 show precision data assessed overall without regard to compound. Table 3-5 shows precision evaluated by compound and includes the average and maximum percent difference.

The average difference was evaluated as the absolute difference in weight over the average weight. Overall precision for the project was good. Figure 3-4 shows that 80% of the sample pairs showed a percent difference of 25% or less. When examined by study and week (Figure 3-5), we see that Study 2 has highest average percentage difference. Study 2 also showed the lowest weight captured on the adsorbent tubes and this may be the influencing factor. Table 3-5 looks at individual compounds differences. We found that 5 of 6 compounds had good average precision with 4 of 6 under 15%. Our critical compound, Benzene, showed good precision. While the data is good, the maximum difference shows that individual differences can be a problem. Looking at the differences in relation to individual weeks and based on sites suggest that the largest differences are seen in Study 2. Average differences by sites (shown in Figure 3-6) suggests that remote sites show larger differences, but not consistently, as the last study showed equivalent differences at the sites.

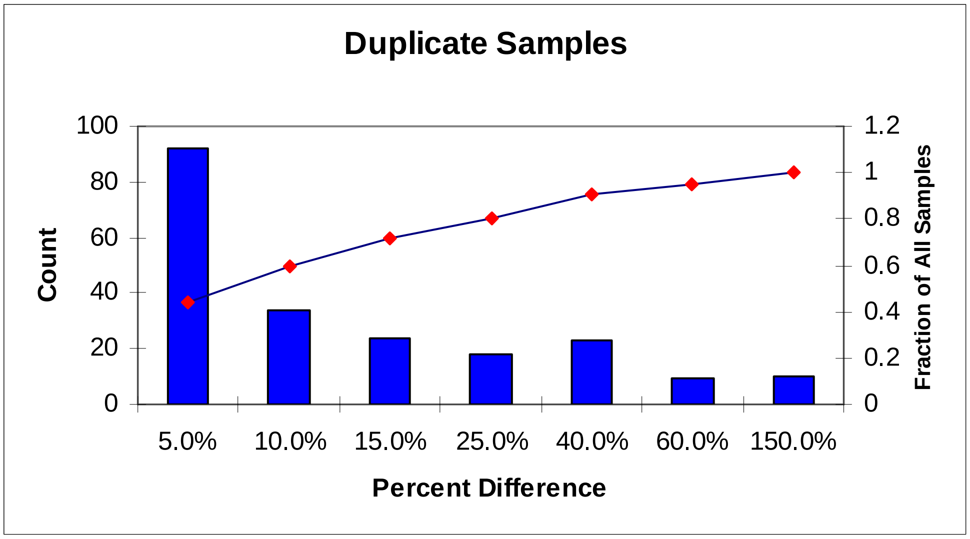


Figure 3-4: Histogram of the percent differences calculated for duplicate PAS samples. The line show the accumulating fraction of the data.

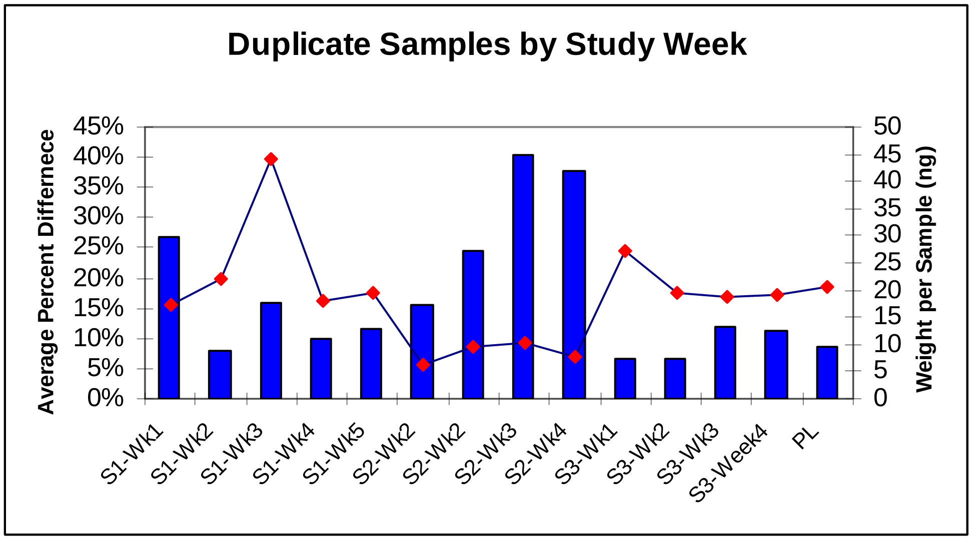


Figure 3-5: Average percent difference by study and week. PL samples are summarized samples at the PAMS site. The line show the average weight per tube on the sample.

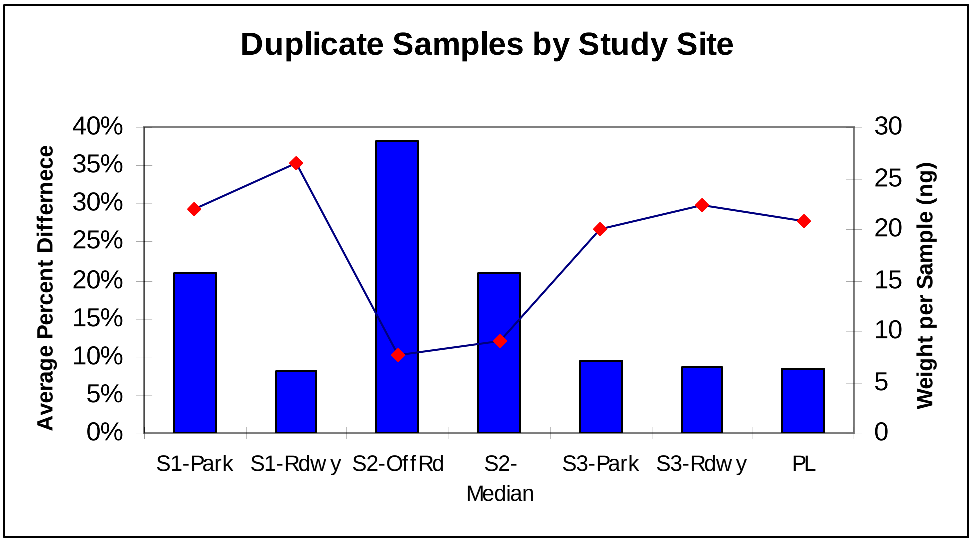


Figure 3-6: Average percent difference by study and study site. PL samples are summarized samples at the PAMS site. The line show the average weight per tube on the sample

Table 3-5: Summary of Duplicate Data Percent Difference by Compound

Compound	Average %Diff	Maximum % Diff
Benzene	10.90%	51.88%
Ethylbenzene	34.77%	138.78%
Toluene	8.30%	43.25%
m/p-Xylene	11.80%	81.10%
o-Xylene	15.14%	93.29%
224-TMP	9.92%	70.16%

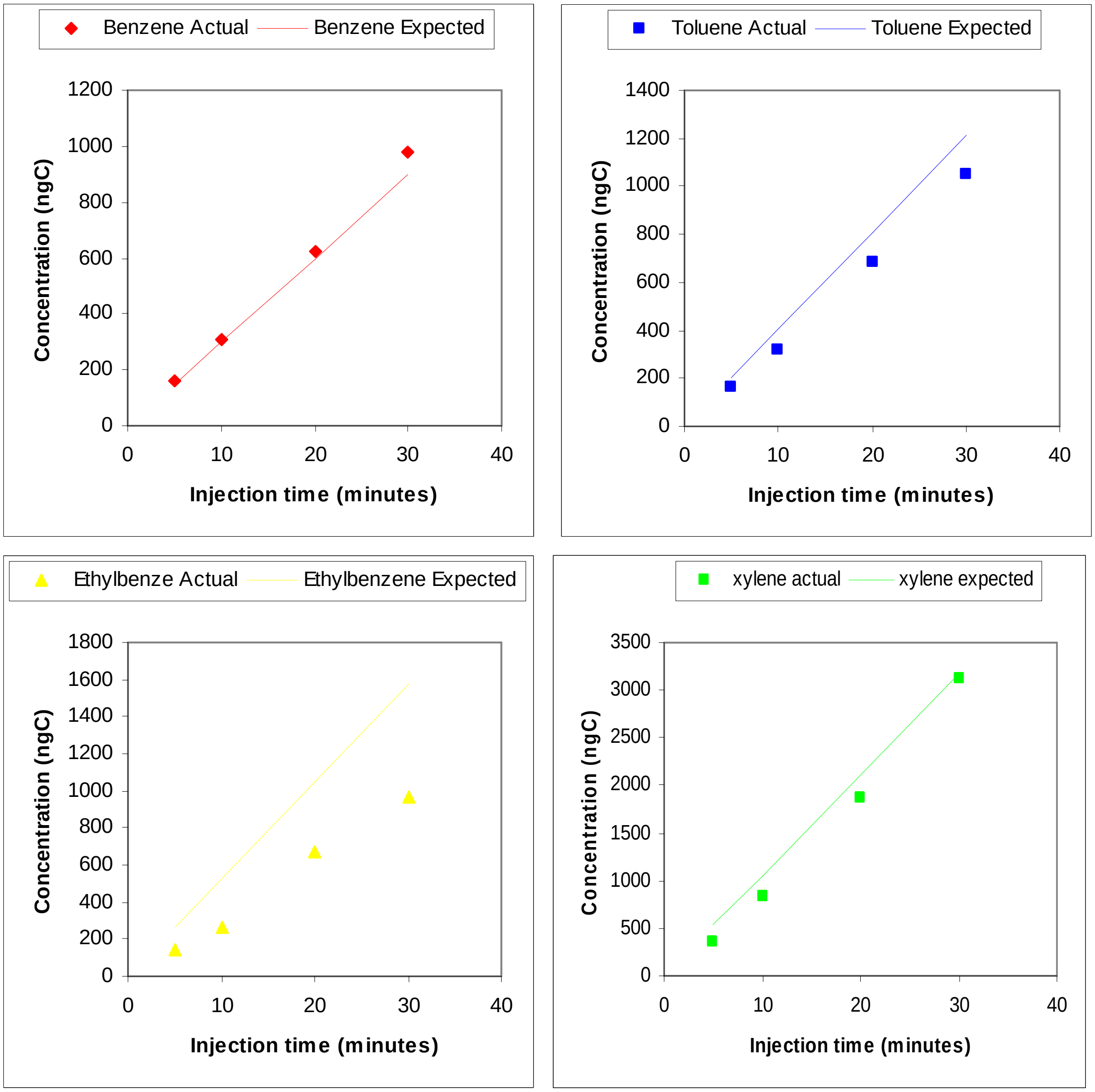
We completed the precision study by doing a paired statistical test by compound. This testing was done for all studies and is reported in Table 3-6. Calculated paired Student's t tests were evaluated using a 95% confidence level against t-critical for two tails For all compounds, all sites, and all studies, the calculated t values were less that t-critical. This indicates the duplicates can not be distinguished.

Table 3-6: Pair t values calculated for studies and sites.

		Calculated t Values for Duplicate Samples						
Study	Site	Benzene	Ethylbenzene	Toluene	m/p-Xylene	o-Xylene	224-TMP	**T-Critical**
1	Park	0.3463	0.6296	0.9672	-0.6069	1.4546	1.6411	2.7764
1	Rdwy	-1.4230	0.9322	-0.9709	-1.0649	-1.5631	-0.5348	2.7764
2	Off	-1.9982	0.3095	-2.5565	-0.0198	-1.0117	-1.5000	3.1824
2	Median	0.4544	-0.6676	-0.2272	0.3527	-0.4399	0.3253	3.1824
3	Park	0.7993	-0.3338	0.3858	1.1234	0.6170	1.0971	3.1824
3	Rdwy	-0.4545	0.0752	0.8343	-1.4849	-1.6840	0.5587	3.1824
Eval	PL	0.1518	0.3049	1.2093	-0.4290	-0.1844	0.9147	2.2622

3e. Linearity

In our normal standardization operation, standard gases are injected for a period of 40 minutes on to the adsorbent sampling tube. During analysis the sample is thermally desorbed from the adsorbent sampling tube trap, trapped on the ATD’s internal trap, then desorbed to the gas chromatograph, and analyzed. We tested for linearity using standards prepared by injecting standards onto the adsorbent sampling tubes for a fraction of the normal sampling time. In our study, we used time fractions of 0.125 (5 minutes), 0.25 (10 minutes), 0.50 (20 minutes), and 0.75 (30 minutes). A 6 L canister filled with a BETX standard was provided to us by the IEPA. Plots of the BETX compounds in units of ngC versus the minutes sampled are shown in Figures 3-7a,b,c,&d. Graphs show both the measured concentrations as points and the expected concentration line for the standard. While concentrations reported here are higher that typically seen in the ambient air, the graphs show linear responses for the analyses. As discussed earlier, the recovery of the compounds vary and the heavier compounds show a lower recovery with measured concentrations less than expected.



Figures 3-7a,b,c,&d.

3f. Method Comparison Studies

3f1. Passive Adsorbent Tube Sampling v. Auto GC (Parking Lot Comparison) The passive adsorbent sampling (PAS) tubes are deployed for a length of time (approximately a week), after analysis, we calculated the average concentration for each compound for the exposed time period. Two studies were done to test the (PAS) tubes against the existing active sampling (Auto GC) system used by the Wisconsin DNR. The first study was conducted during June, July, and August of 2006 and a second equivalent study was conducted during February and March of 2007. PAS tubes were deployed in the parking lot of the DNR Southeast Regional Headquarters (AQS # 550790026) for varying lengths of time. The PAS tube measurements were compared to the average compound concentrations determined using the established AutoGC sampling method. Hourly AutoGC measurements were averaged over the time period when the PAS tubes were exposed. Table 3-7 contains a summary of the measurement data used for this comparison. Comparison data is summarized in Table 3-8 and 3-9 and is also shown graphically in Figures 3-8 & 3-9.

Table 3-7: Summary of sample dates, exposure and replicates

Dates Exposed	Time Deployed	Time Retrieved	Hours Exposed	Number of Replicates	Average GC Hours
6/27/06 - 7/12/06	9:00	9:00	361	1	293
7/18/06 - 7/25/06	8:00	8:15	169	3	145
7/25/06 - 8/01/06	8:30	9:45	170	1	159
8/01/06 - 8/09/06	12:00	9:00	190	1	165
8/09/06 - 8/15/06	16:00	9:00	139	2	56
2/14/07 - 2/21/07	10:40	10:50	168	2	162
2/21/07 - 2/28/07	10:50	10:50	168	2	159
2/28/07 - 3/07/07	10:50	10:50	168	2	155

Table 3-8: 2006 Study results including Auto GC average concentration and average concentration for tube replicates.

Start	6/27/06		7/18/06		7/25/06		8/01/06		8/09/06	
End	7/12/06		7/25/06		8/01/06		8/09/06		8/15/06	
Parameter	AutoGC (ppbC)	PAS (ppbC)	AutoGC (ppbC)	PAS (ppbC)	AutoGC (ppbC)	PAS (ppbC)	AutoGC (ppbC)	PAS (ppbC)	AutoGC (ppbC)	PAS (ppbC)
Benzene	1.4192	1.264	1.2757	1.274	1.6116	1.496	1.7187	1.673	1.6149	1.4964
224-Tmp	2.1724	1.147	2.2073	1.298	2.8922	1.68	3.3111	2.362	3.3301	2.2095
Toluene	3.9131	2.881	3.9569	2.999	5.1351	3.625	5.4427	4.739	5.6759	4.0788
M/P-Xylene	1.8025	1.098	1.834	1.192	2.572	1.526	2.6722	2.039	2.8111	1.8262
O-Xylene	0.7918	0.493	0.8374	0.548	1.1419	0.647	1.1782	0.898	1.2477	0.7881
Ethyl-benzene	0.642	0.415	0.643	0.438	0.8464	0.546	0.8916	0.722	0.9421	0.6286

Table 3-9: 2007 Study results including Auto GC average concentration and average concentration for tube replicates.

Start	2/14/07		2/21/07		2/28/07	
End	2/21/07		2/28/07		3/07/07	
Parameter	Auto GC (ppbC)	PAS (ppbC)	Auto GC (ppbC)	PAS (ppbC)	Auto GC (ppbC)	PAS (ppbC)
Benzene	1.8781	1.6593	1.7822	1.3360	1.6660	1.3523
224-Trimethylpentane	1.7097	0.1352	1.6829	0.0973	1.2947	0.1122
Toluene	2.4733	1.7875	2.5039	1.4397	2.3673	1.7655
M/P-Xylene	1.2262	0.7282	1.2577	0.5256	0.9218	0.5935
O-Xylene	0.6439	0.3101	0.8334	0.2106	0.7166	0.2474
Ethylbenzene	0.5319	0.3221	0.7032	0.2396	0.7180	0.2533

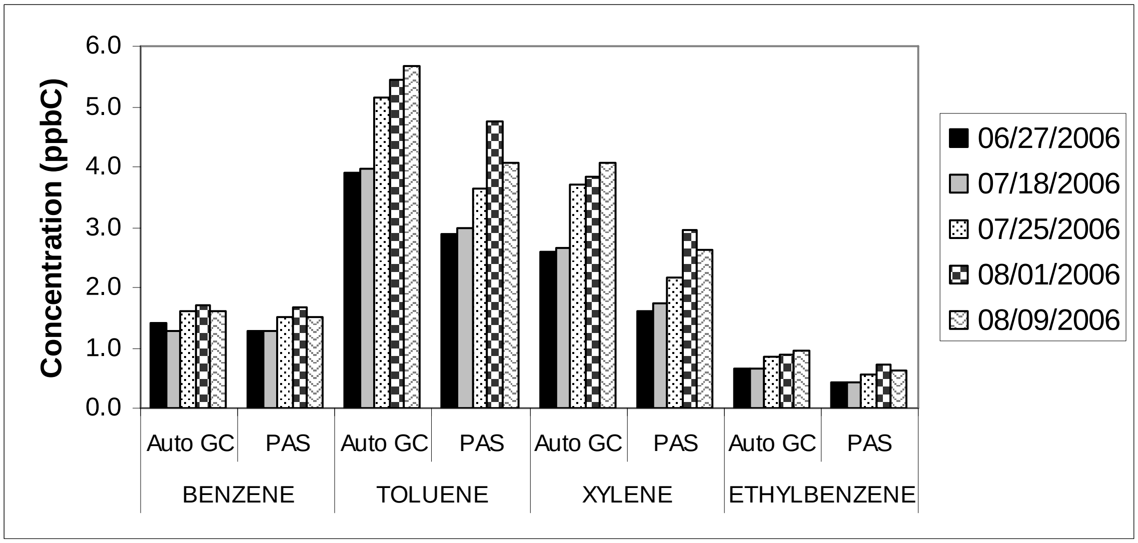


Figure 3-8: 2006 Comparisons of BETXs measured by AutoGC and captured on the PAS.

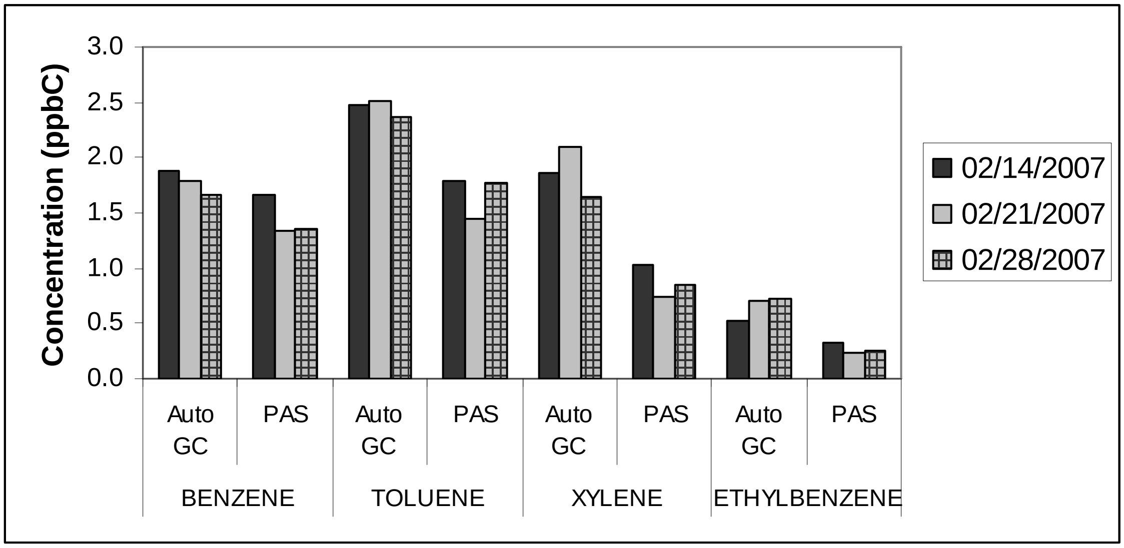


Figure 3-9: 2007 Comparisons of BETXs measured by AutoGC and captured on the PAS.

3f2. Passive Adsorbent Tube Sampling v.Canister Samples – During Field Study 1, PAS samples were collected at the Wisconsin DNR's air toxic monitoring site at Milwaukee Sixteenth Street Health Center (SSHC). Five sets of PAS were collected at the SSHC from 11/8/2006 until 12/13/2006. The measurements made with the PAS were then compared to the site's routine 24-hour canister samples. The canister samples are analyzed at the Wisconsin State Laboratory of Hygiene by chromatography with mass spectrometer detection. The comparison is shown in Figure 3-10. We have not attempted to statistically compare the data, but rather provide the data graphically to show that measurement by both methods are generally comparable.

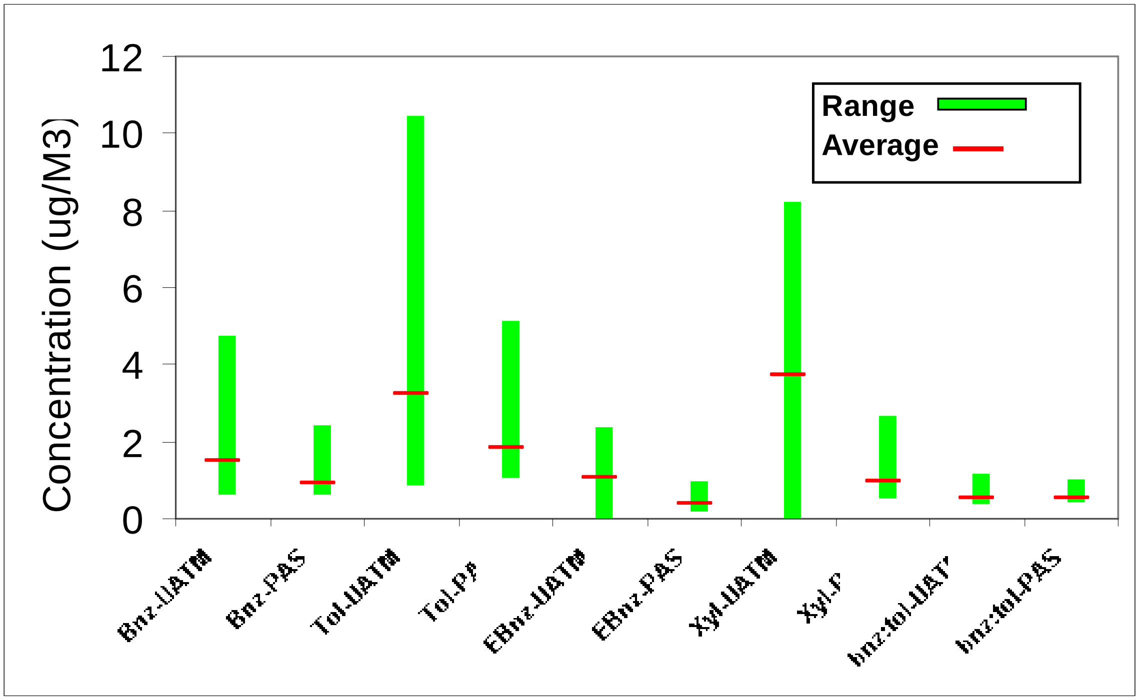


Figure 3-10: Comparison of the range and average values for samples collected at the Milwaukee SSHC site. Samples are collected with PAS and as canisters for UATM.

3.f3.<u>AutoGC analysis vs. Laboratory Analysis of passive canister samples</u> - Our first and third roadway studies included both passive sampling tubes and passive sampling canisters. The canisters were deployed at sites 990 at Kosciuszko Park and 995 on a north bound exit sign at Highway 94. The canisters provided a measurement of volatile organic compounds (VOCs) collected at each site for 1-hour of peak drive time. The canister pressure was increased using ultra zero ambient compressed air (see Table 3-10) and sealed for at least 24-hours before analyzing on the PAMS AutoGC at our Milwaukee Monitoring site. A total of thirteen canister pairs were deployed. Ten canister pairs were valid. Three of the ten valid pairs were then sent to the State Lab of Hygiene (SLOH) for an analysis of PAMS hydrocarbons.

We have assembled the results from both laboratories for selected compounds in Table 3-11. Our target compounds include, benzene, toluene, ethylbenzene, 224-trimethylpentane, and total xylenes (sum of m/p-xylene and o-xylene peaks). In addition to the individual results we have listed the percent differences of the field AutoGC from the laboratory gas chromatograph.

Table 3-10: Field data for canisters analyzed at the State Lab of Hygiene (SLOH) and at the WDNR southeast region headquarters.						
Field Code	**Site**	**Sample Date**	**Sample Time (CST)**	**Canister**	**Initial Pressure**	**Final Pressure**
RC07-009	Park	04/28/2007	7:00-8:00	WI-168	14.7	22
RC07-010	Highway	04/28/2007	7:00-8:00	WI-273	13.5	22.2
RC07-011	Park	05/01/2007	7:00-8:00	WI-239	14.1	22.2
RC07-012	Highway	05/01/2007	7:00-8:00	WI-274	14.9	22.7
RC07-025	Park	05/17/2007	7:00-8:00	WI-105	15	22.1
RC07-026	Highway	05/17/2007	7:00-8:00	WI-218	15	22.7

Table 3-11: Average and percent difference for each compound (Ethylbenzene N=3, all others N=6)				
Compound	**WSLH Average (ppbC)**	**Average Auto GC (ppbC)**	**Average % Diff**	**Max % Diff**
224-TRIMETHYLPENTANE	1.29	1.85	52.25%	154.63%
BENZENE	1.11	1.19	20.18%	88.21%
ETHYLBENZENE	2.62	1.88	18.34%	26.43%
TOLUENE	28.87	29.06	17.67%	69.63%
XYLENE	5.90	6.84	57.42%	109.40%

Table 3-12: Comparison Of Field Canister Samples Analyzed At The State Lab Of Hygiene (SLOH) And At The WDNR Southeast Region Headquarters.

Field Code	Compound	DNR value (ppbC)	SLOH value (ppbC)	Average	% diff
RC07-009	224 – TMP	1.14	0.73	0.94	56.16%
RC07-010	224 – TMP	2.4	2.3	2.35	4.35%
RC07-011	224 – TMP	0.66	0.94	0.8	-29.79%
RC07-012	224 – TMP	1.57	2.4	1.98	-34.58%
RC07-025	224 – TMP	4.77	0.61	2.69	681.97%
RC07-026	224 – TMP	0.54	0.76	0.65	-28.95%
RC07-009	Benzene	0.67	0.59	0.63	13.56%
RC07-010	Benzene	2.77	2.8	2.79	-1.07%
RC07-011	Benzene	0.57	0.58	0.57	-1.72%
RC07-012	Benzene	1.41	1.6	1.51	-11.88%
RC07-025	Benzene	0.93	0.36	0.64	158.33%
RC07-026	Benzene	0.76	0.73	0.75	4.11%
RC07-009	Ethylbenzene	0.53	<0.30	n/a	
RC07-010	Ethylbenzene	8.74	6.7	7.72	30.45%
RC07-011	Ethylbenzene	0.41	*D <0.46	n/a	
RC07-012	Ethylbenzene	0.61	0.48	0.55	27.08%
RC07-025	Ethylbenzene	0.27	<0.30	n/a	
RC07-026	Ethylbenzene	0.72	0.69	0.71	4.35%
RC07-009	Toluene	1.19	1.3	1.25	-8.46%
RC07-010	Toluene	160.57	160	160.28	0.36%
RC07-011	Toluene	1.05	1.3	1.17	-19.23%
RC07-012	Toluene	2.68	2.8	2.74	-4.29%
RC07-025	Toluene	2.28	1.1	1.69	107.27%
RC07-026	Toluene	6.59	6.7	6.65	-1.64%
RC07-009	Xylene	1.93	1	1.47	93.00%
RC07-010	Xylene	29.7	28.2	1.47	5.32%
RC07-011	Xylene	0.63	0.58	0.61	8.62%
RC07-012	Xylene	2.86	2.41	2.64	18.67%
RC07-025	Xylene	1.78	0.52	1.15	242.31%
RC07-026	Xylene	4.16	2.67	3.41	55.81%

3g. Experimental Determination of Diffusive Uptake Rate Constants

When using any passive sampler, the conversion of weight captured on the adsorbent to ambient concentration requires knowing the exposure time and the diffusive uptake rate constant (DRC). The diffusive uptake rate constant is an experimentally determined value that is compound and adsorbent specific. DRC values are typically determined using passive sampling devices in test chambers. All ambient data reported here was calculated using DRCs provided by Brown. Reviewing studies, Brown reported individual and average rate constants for benzene, toluene and xylenes. While we used Brown's DRC we also attempted to verify these values.

Our simple test chamber was constructed from a 12 inch segment of 1 inch stainless steel pipe. The chamber, shown in Figure 3-11, was capped on one end and the other end was connected to a tee fitting.

The tee fitting connected to a 1.8 L sample canister and to a valve used to seal the chamber. During tests a sampling tube with a diffusion cap is placed in the chamber, the chamber is evacuated, the evacuated sample canister is opened and a test gas is released into the chamber\canister assembly through the sealing valve. When the test chamber is filled with sample gas at a pressure equal to ambient pressure, the chamber is sealed. In our study, the passive sampling tube is exposed for a period of either 24 or 168 hours. At the conclusion of the exposure period, the sample canister is sealed and removed from the tee. The adsorbent tube is removed from the chamber, capped at both ends, sealed in a culture tube, and kept in the project freezer until analysis.

The weight of the compounds (benzene, toluene, and xylene) are measured on the tube and the concentrations determined in the sample canister. The experimental DRC is calculated from the adsorbent tube weight, compound concentration in the canister and the exposure time using the equation below. Calculated DRC are in units of ngC-ppmC^{-1}-minute^{-1} We report our calculated rate for two 24-hour test and two 168-hour tests in Table 3-13.

Calculation of Diffusive Uptake Rate Constant

DRC = (weight tube ngC)/ [(canister concentration/1000 ppbC/ppmC) * exposure time}

Our experimental values are much lower than those provided in the literature. Experimental values for a 24-hour exposure time appear more inconsistent than values from the two 168 hour studies. We do note that ambient concentrations calculated from Brown’s values and used in our study appear consistent with data from more established methods. We can not explain why our experiment failed to verify DRCs reported by Brown.   One possible explanation is that our test chamber was very simple and operates with static gas. Chambers described in the literature were more complex. Especially important may have been the gas circulating devices. It is possible compounds were initially taken into the adsorbent, but using a static chamber, an equilibrium formed in the area near the diffusion cap. When this equilibrium developed the gradient set up within the cap collapsed and uptake by the adsorbent stopped.

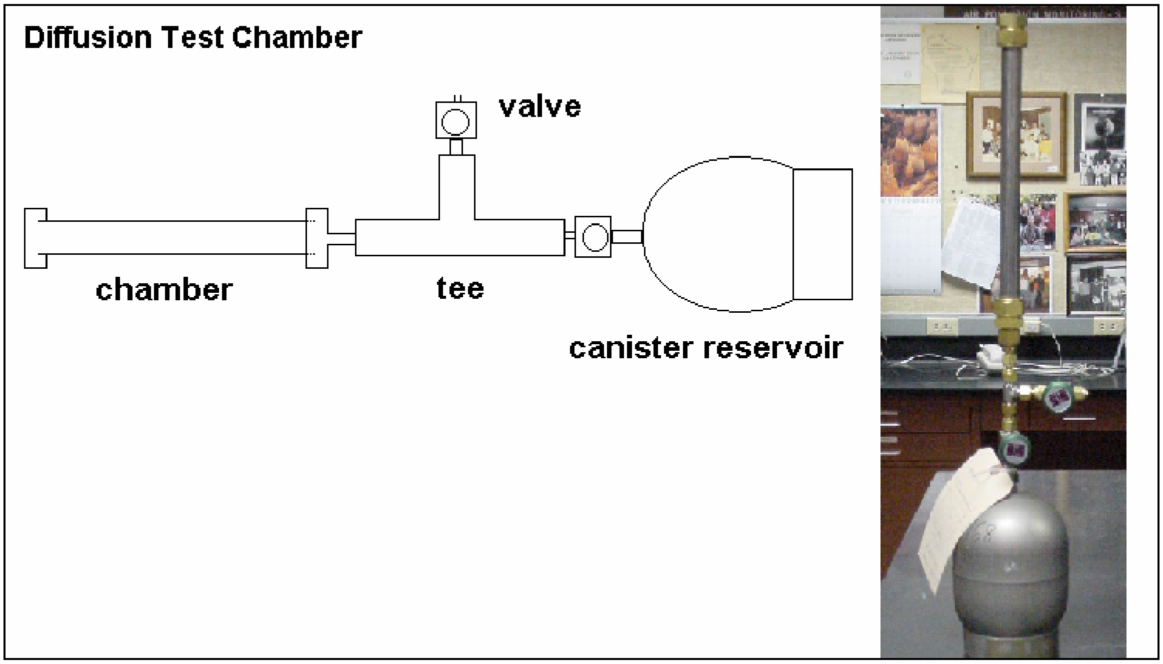


Figure 3-11: Diffusion Test Chamber built to test compound uptake and verify diffusive uptake rate constants used in the study.

Table 3-13: Experimental Diffusive Update Rates

	Study 1	Study 2	Study 3	Study 4	
Exposure Time (hours)	24	24	168	168	Reference Diffusive Rate Constant
Compound	Calculated DRC (ngC-ppmC^{-1}-minute^{-1})				
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

Section 4. Roadway Monitoring Field Studies

4a. Study Descriptions

Three field studies were conducted as part of this project. Two field studies were originally proposed in the project. An additional study (Study 2) was developed as a control study. This added study was requested by the projects steering work group to test findings in Study 1. Studies were set-up with a number of monitoring sites located along a line and placed in a close geographical area near a targeted roadway. Monitoring sites were set up at staggered distances from the road. All sites used in our studies were established locations, with most sites on city light poles. We also used local power poles and roadway sign poles as monitoring locations. Samplers were mounted on the poles during the studies. Studies were multi-week and samplers were typically deployed on Wednesday, then retrieved the following Wednesday. During the final week of Study 2 a snowstorm made sample retrieval dangerous and we collected these samples the following Friday, for a total sampling period of 9 days.

Study 1 was conducted as a transect of Interstate Highway 94 located to the south of Milwaukee's Menominee valley. The area was chosen because the topography places the highway at approximately the same elevation as the surrounding side streets. The area is also just inside the southern edge of the RAIMI domain used by Wisconsin modelers. This would allow monitoring data to be directly compared to modeled concentrations. A total of 10 sites were placed in a transect of the target roadway. In the study area the target roadway is oriented north-south. Sites were located in a park west of the roadway, then along a linear path perpendicular to the highway, ending with the eastern most site located on 1st Street. Site locations are shown in Figure 4-1. Note that all site maps list sites by only the last digit in the site number. Thus site 990 is designated 0 on the map. Figure 4-2a & 4-2b show two monitoring sites used during the study.

Figure 4-1: Map of Study 1 showing monitoring sites. Sites are arranged on a west to east transect across Highway 94.

Figure 4-2a & b: Photos show sampler used in Study 1. Left photo is a PAS and PCS collocated site located in Koscuiszko Park. The right photo is the PAS sampling site located next to the south bound lane of Highway 94.

Study 2 was planned after Study 1 data did not show the expected benzene gradient from the highway. We had hypothesized that traffic from adjacent roads emitted significant concentrations to contribute to a uniform concentration over all sampling sites. To test the hypothesis we moved outside the RAIMI domain to an isolated section of Interstate Highway 94 between Milwaukee and Madison. The test area was located to the west of Johnson Creek. In the test area the target highway is oriented east to west. To the north and south of the roadway are dead end roads used only by a small number of local residents. We felt the area would provide significant vehicular traffic on the target roadway with a minimal amount of adjacent traffic, and yet enough access and structures for the study. A total of 9 monitoring sites were used. Sites included a roadway median site, sites on the north and south shoulders of the highway, three sites to the north of the highway and three sites to the south of the highway. Site locations for Study 2 are shown in Figure 4-3.

Figure 4-3: Study 2 monitoring sites. Nine site are located on a south to north transect.

Study 3 was conducted as a second transect of Interstate Highway 94 in the same area as the first study. The project goal was to confirm and build on work in Study 1. Study 3 retained 6 sites used in Study 1, including the sites adjacent to the target roadway and the off roadway sites to the west. An additional 5 sites were added on a second perpendicular roadway located north of the original roadway. The goal was to confirm the original findings and to determine if measured concentrations would be similar on a second parallel transect. Study 3 was completed with only three additional sites because two sites on Burnham Street experienced significant vandalism. We would note to the reader, that in 15 weeks of deployment these were the only sites that experienced problems. Study 3 site locations are shown in Figure 4-4.

Figure 4-4: Study 3 monitoring sites. Site are located on transects on Grant Street and Burnham Street. The "X"ed sites were dropped due to vandalism

Table 4-1: Summary Data for Roadway Monitoring Field Studies

	Started	***Duration***	***Sites***	***Tube Sample***	***Canister Samples***
Study 1	11/08/06	5 weeks	10 plus 1 non-area site	55 ambient 10 duplicates 15 blanks	14 canisters (only 3 valid pairs)
Study 2	03/14/07	4 weeks	9	36 ambient 8 duplicates 12 blanks	0 canisters
Study 3	04/18/07	4 weeks	11 reduced to 9	36 ambient 8 duplicates 12 blanks	26 canisters (10 valid pairs)

4b. Study Results – Passive Adsorbent Samplers

4b1. Data Evaluation - Raw results provided by the analytical system for the passive adsorbent samples are in ngC per sample. These values are converted into ambient concentrations (ug/m^3) using the following equation:

((sample) – (blank)) / (CN) / (DRC) / (ET) * 1000 * (MW) / 24.46

Where: Sample = ngC per sample results
Blank = average ngC for associated blanks
CN = number of carbons in compound
DRC = diffusion uptake rate constant in ngC-ppmC^{-1}-minute^{-1}
ET = elapsed time in minutes
MW = compound molecular weight

Detailed analysis of results for benzene, toluene, ethylbenzene, total xylenes and 2,2,4-trimethylpentane were conducted. Resulting concentrations were the grouped for summary and statistical analysis. Duplicate results were averaged to provide a single value per site per sampling event. In addition, Toluene:Benzene ratios were calculated and examined following presentation of results.

Summary statistics were generated both on a per site basis and on a per week basis, and include average, maximum, minimum and standard deviation. Confidence intervals were calculated and applied to generate upper and lower confidence limits for graphical representation of the data.

Individual and summarized results are presented in both tables and graphs following. In addition, graphs showing the ambient concentrations as a function of distance to the roadway have been prepared and are included.

Student's T-tests were applied to both site and weekly groupings of the data to determine whether or not statistical differences exist between sites or weeks of the projects. All site combinations were generated for benzene results, and for the most distant site from the roadway. Tables summarizing the resulting T-factors generated by the statistical analysis are included following. Note that values presented in **boldface** are statistically relevant.

For other parameters, if no statistical differences were seen between the most distant site and the others, a T-test was generated comparing the highest and lowest concentration sites. If no statistical difference was seen in this test, comparisons were stopped and no table was prepared.

4b2. Results, Study 1

Study 1 was conducted in Milwaukee between November 6 and December 13, 2006. During this time, 5 weekly samples were collected at each of 10 sites. Two sites were duplicate sites. The sites were arranged generally along an east-west transect with Interstate 94 approximately in the middle of the array.

All site locations were determined multiple times using a hand-held GPS unit, and the resulting latitude and longitudes averaged to fix the location. Distances were calculated using the Haversine formula. Table 4-D1 provides a site list, including general location, distance in meters and direction from the middle of Interstate 94, and whether or not the site is a duplicate site. Figure 4-1 on page 35 of this report shows a map of the sites.

Table 4-D1: Study 1 Site List

Site	Location	Meters	Direction	Dupe?
990	Kosciuszko Park	590	West	Yes
991	2179 6th St (on Grant)	222	West	No
992	2200 5th Pl	130	West	No
993	5th and Grant, near I-94 Fence	55	West	No
994	I-94 SB	21	West	No
995	I-94 NB	21	East	Yes
996	2180 4th St	49	East	No
997	Lincoln Field	160	East	No
998	Parking Lot @ Horizon	288	East	No
999	2209 1st St	394	East	No

Table 4-7 summarizes results from each site, with averages, maxima, minima and relative standard deviations (RSD (%)) shown. Table 4-R1 on the following page summarizes results from each week of the study. Both tables are organized with sites listed from west to east. Sites 994 and 995 are closest to the roadway (both located between the main roadway and entrance/exit ramps on opposite sides of the highway).

Table 4-R1: Study 1 Summary of Results by Site (n = 5)

Parameter	**Site**	**990**	**991**	**992**	**993**	**994**	**995**	**996**	**997**	**998**	**999**
Benzene	**Average**	0.65	0.89	0.91	0.79	0.81	0.76	0.71	0.61	0.60	0.62
	maximum	1.13	1.79	1.57	1.44	1.32	1.25	1.10	0.95	1.10	1.09
	minimum	0.45	0.51	0.53	0.51	0.62	0.55	0.52	0.46	0.41	0.40
	RSD (%)	43.6%	57.3%	42.6%	47.6%	36.2%	38.1%	33.5%	33.2%	47.6%	45.0%
Toluene	**average**	1.16	1.88	1.90	1.55	1.47	1.40	1.33	1.06	1.11	1.20
	maximum	2.41	4.19	3.58	3.12	2.70	2.60	2.38	2.02	2.40	2.54
	minimum	0.71	0.87	1.16	1.02	1.00	0.95	0.93	0.74	0.66	0.64
	RSD (%)	61.1%	70.8%	50.5%	57.3%	47.4%	49.5%	46.2%	51.1%	66.2%	64.0%
Ethylbenzene	**average**	0.19	0.29	0.31	0.26	0.23	0.24	0.26	0.20	0.18	0.21
	maximum	0.35	0.65	0.60	0.52	0.46	0.43	0.59	0.37	0.41	0.53
	minimum	0.12	0.15	0.19	0.14	0.14	0.16	0.15	0.12	0.09	0.10
	RSD (%)	51.0%	69.9%	54.6%	57.6%	56.8%	45.3%	70.1%	51.9%	72.0%	86.8%
Total Xylenes	**average**	0.71	1.15	1.25	0.99	0.92	0.88	0.98	0.69	0.68	0.82
	maximum	1.49	2.57	2.33	2.03	1.73	1.62	2.13	1.33	1.54	1.90
	minimum	0.48	0.51	0.75	0.62	0.62	0.61	0.59	0.41	0.39	0.45
	RSD (%)	53.8%	62.5%	44.0%	51.4%	44.2%	42.2%	58.0%	47.8%	62.6%	65.6%
224-Trimethyl pentane	**average**	0.47	0.88	0.88	0.68	0.63	0.60	0.54	0.40	0.40	0.47
	maximum	0.99	2.10	1.56	1.33	1.16	1.08	0.96	0.77	0.89	0.96
	minimum	0.30	0.49	0.42	0.37	0.44	0.38	0.37	0.27	0.22	0.26
	RSD (%)	61.7%	77.5%	48.5%	54.2%	47.0%	45.6%	44.6%	53.2%	69.2%	61.0%

Note that average results do vary between the sites, with most maximum results observed at site 992, located approximately 130 meters west of the interstate. Model predictions place the maximum at the center of the interstate. Note also that the minimum benzene concentrations observed at all sites significantly exceed the modeled predictions of 0.04 – 0.27 ug/m^3 across the study locations.

Table 4-R2: Study 1 Summary of Results by Week (n = 10)

Parameter	site	8-Nov-06	15-Nov-06	22-Nov-06	29-Nov-06	6-Dec-06
Benzene	**average**	0.52	0.73	1.27	0.54	0.61
	maximum	0.70	0.89	1.79	0.80	0.77
	minimum	0.41	0.58	0.95	0.40	0.49
	RSD (%)	16.2%	13.6%	20.2%	22.6%	14.5%
Toluene	**average**	1.01	1.28	2.79	0.92	1.03
	maximum	1.61	1.63	4.19	1.50	1.62
	minimum	0.71	0.99	2.02	0.64	0.76
	RSD (%)	25.5%	17.3%	23.4%	29.1%	25.1%
Ethylbenzene	**average**	0.15	0.21	0.49	0.15	0.17
	maximum	0.23	0.27	0.65	0.21	0.29
	minimum	0.09	0.16	0.35	0.10	0.12
	RSD (%)	26.4%	15.9%	20.7%	24.0%	30.1%
Total Xylenes	**average**	0.61	0.82	1.87	0.59	0.65
	maximum	0.90	1.07	2.57	0.92	1.19
	minimum	0.39	0.60	1.33	0.44	0.41
	RSD (%)	25.3%	18.6%	21.3%	26.4%	33.8%
224-Trimethylpentane	**average**	0.36	0.51	1.18	0.44	0.48
	maximum	0.60	0.70	2.10	0.81	0.94
	minimum	0.22	0.35	0.77	0.24	0.28
	RSD (%)	30.5%	22.6%	33.4%	39.3%	39.1%

Note that the variability of the data (as measured by the RSD(%)) is greater within sites (Table 4-R1) than it is within weeks (Table 4-R2). This indicates that the individual results from each site are more closely related to the results obtained from the other sites during the same time period, than they are to the results obtained from the same site during the other weeks of the study period. In comparison, the RSD(%) of modeled values is about 58%, indicating that we observed less variability between the sites than expected.

Much of this variability appears to come from the third week of the study (22-Nov-06), where observed values of most parameters are more than twice that of the other weeks. Results for the remaining 4 weeks are summarized by site in Table 4-R3 on the following page. Note the significant decrease in RSD(%) when the third week is not included. Also note that the apparent differences between sites are more pronounced, with site 992 (130 meters west of the interstate) experiencing maximum concentrations of all parameters.

Table 4-R3: Study 1 Summary of Results by Site, without week 3 (n = 4)

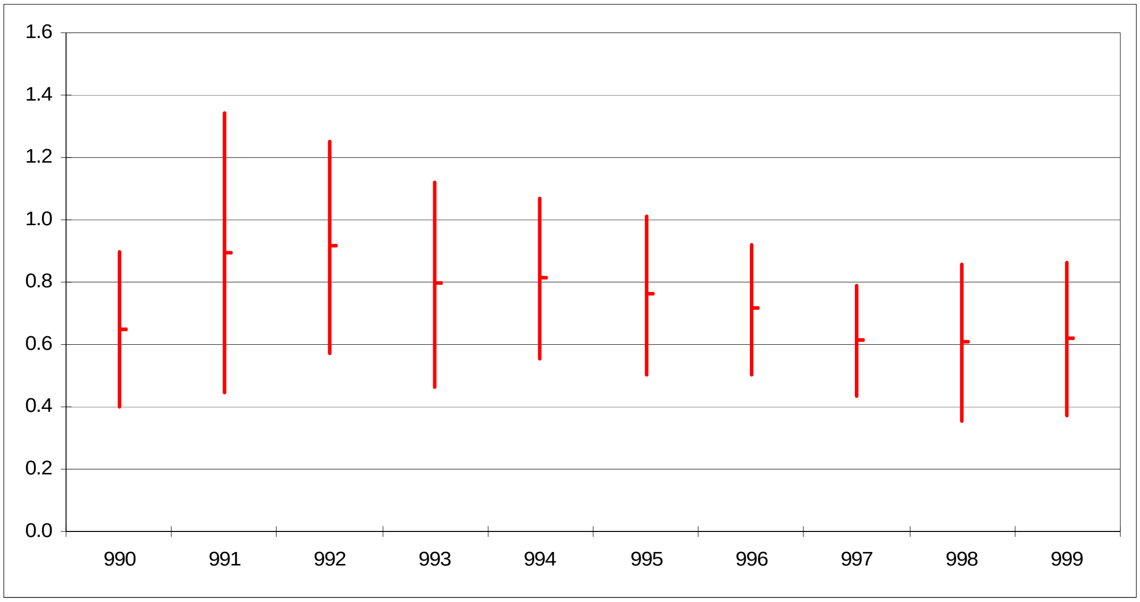
Parameter	site	990	991	992	993	994	995	996	997	998	999
Benzene	**average**	0.53	0.67	0.75	0.63	0.68	0.64	0.62	0.53	0.48	0.50
	maximum	0.66	0.80	0.89	0.79	0.80	0.77	0.77	0.64	0.58	0.62
	minimum	0.45	0.51	0.53	0.51	0.62	0.55	0.52	0.46	0.41	0.40
	RSD (%)	18.3%	18.4%	20.5%	18.4%	11.7%	16.2%	19.0%	15.7%	16.2%	18.6%
Toluene	**average**	0.85	1.30	1.48	1.16	1.17	1.09	1.06	0.83	0.79	0.87
	maximum	1.05	1.61	1.63	1.34	1.38	1.32	1.33	0.99	1.04	1.12
	minimum	0.71	0.87	1.16	1.02	1.00	0.95	0.93	0.74	0.66	0.64
	RSD (%)	17.0%	26.8%	14.9%	12.1%	13.6%	15.1%	16.9%	13.9%	21.5%	23.0%
Ethylbenzene	**average**	0.14	0.21	0.23	0.19	0.17	0.19	0.18	0.15	0.13	0.13
	maximum	0.16	0.27	0.29	0.22	0.23	0.22	0.23	0.20	0.17	0.19
	minimum	0.12	0.15	0.19	0.14	0.14	0.16	0.15	0.12	0.09	0.10
	RSD (%)	12.7%	28.3%	19.7%	18.7%	21.7%	12.1%	19.5%	22.3%	24.0%	32.1%
Total Xylenes	**average**	0.52	0.80	0.98	0.74	0.72	0.69	0.70	0.54	0.47	0.55
	maximum	0.63	1.07	1.19	0.86	0.85	0.83	0.86	0.75	0.60	0.73
	minimum	0.48	0.51	0.75	0.62	0.62	0.61	0.59	0.41	0.39	0.45
	RSD (%)	14.8%	30.4%	19.1%	13.5%	14.0%	14.6%	16.7%	27.8%	20.0%	23.0%
224- TMP	**average**	0.35	0.58	0.71	0.52	0.50	0.48	0.43	0.30	0.28	0.34
	maximum	0.41	0.70	0.94	0.61	0.56	0.55	0.49	0.35	0.38	0.43
	minimum	0.30	0.49	0.42	0.37	0.44	0.38	0.37	0.27	0.22	0.26
	RSD (%)	14.9%	15.9%	31.4%	19.5%	9.6%	15.4%	12.0%	11.8%	25.8%	23.4%

The following series of graphs present the data shown in the tables. Figures 4-RG1a to 4-RG1e illustrate results for each parameter grouped by site (as per Table 4-R1), showing the average and upper and lower confidence intervals. Note that while some sites seem higher than others (specifically sites 991 and 992), the confidence intervals overlap, indicating that little to no discernible difference is revealed.

Figures 4-RG2a to 4-RG2e illustrate the results on a weekly basis (as per Table 4-R2). Note that the third week of the study (11/22/2006) is significantly higher than the than the remaining four. This difference led to the decision to evaluate the results of the other four weeks together. Figures 4-RG3a to 4-RG3e illustrate the results grouped per site, without the third week of the study considered (as per Table 4-R3).

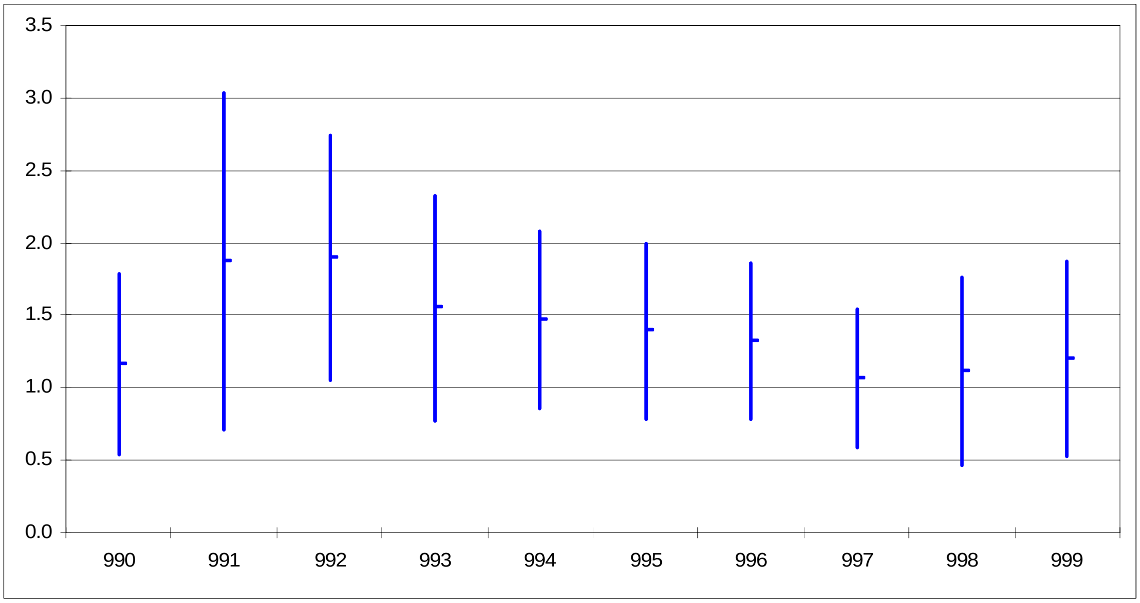
Finally, Figures 4-RG4a to 4-RG4e show individual results from each week of the study, plotted versus distance from the center of the interstate. Note that the scales of all weeks but the third are the same, while that of the third is two and a half time higher.

Figure 4-RG1a: Study 1 Benzene Results



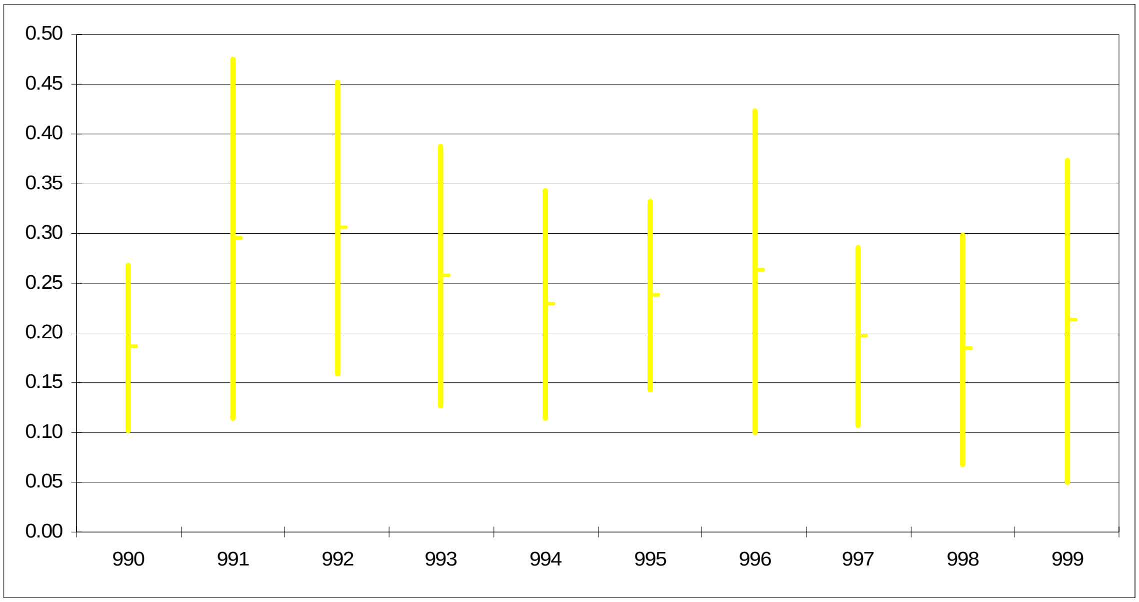
vertical axis = concentration in ug/m3
horizontal axis = site number

Figure 4-RG1b: Study 1 Toluene Results



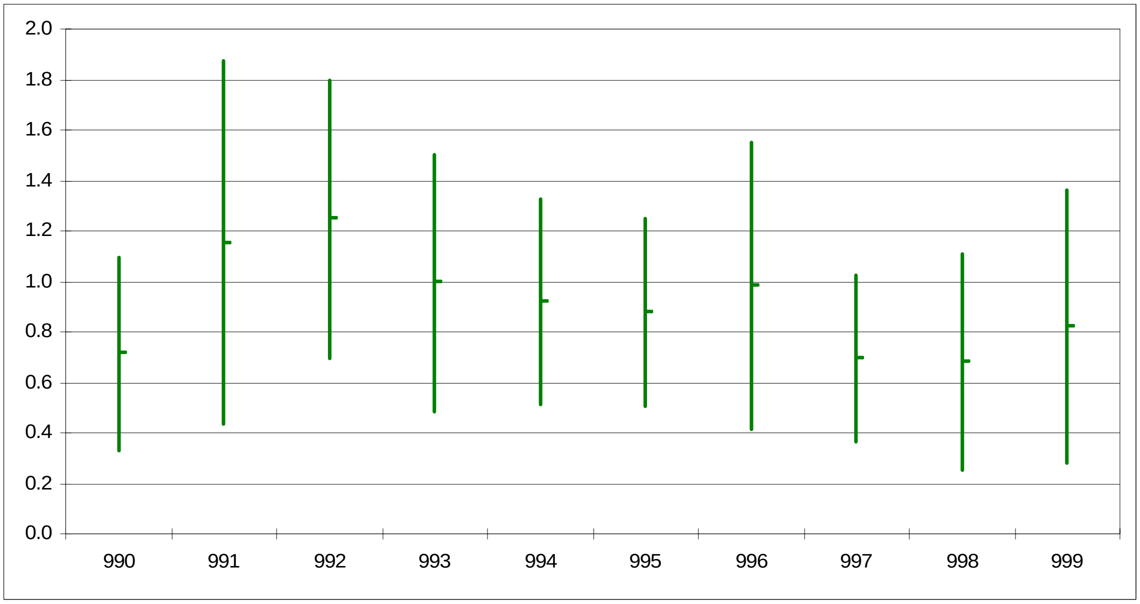
vertical axis = concentration in ug/m3
horizontal axis = site number

Figure 4-RG1c: Study 1 Ethylbenzene Results



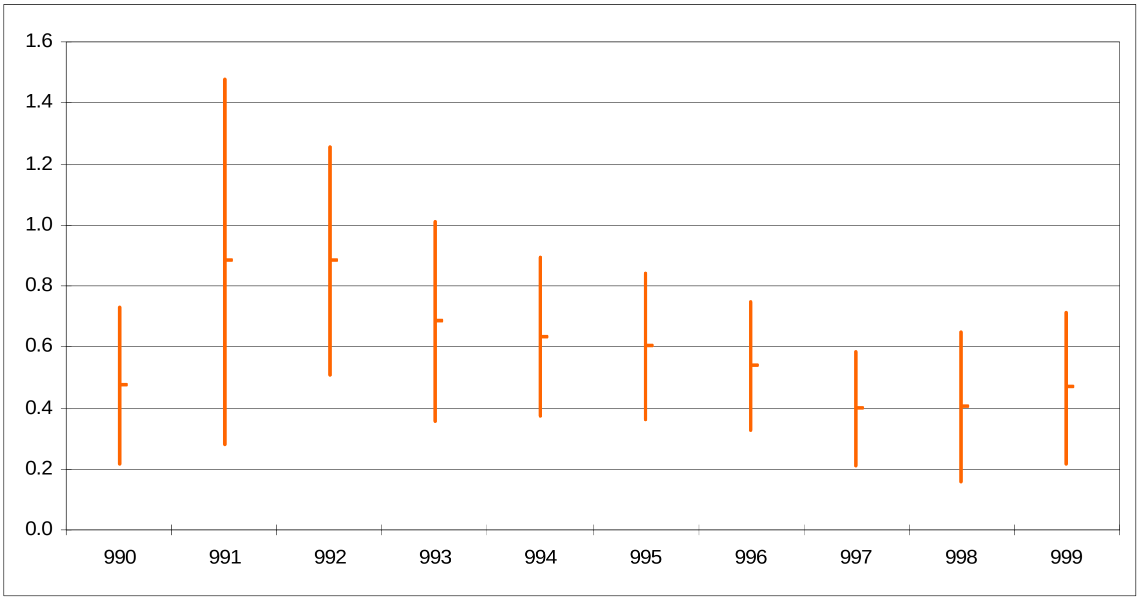
vertical axis = concentration in ug/m3
horizontal axis = site number

Figure 4-RG1d: Study 1 Total Xylene Results



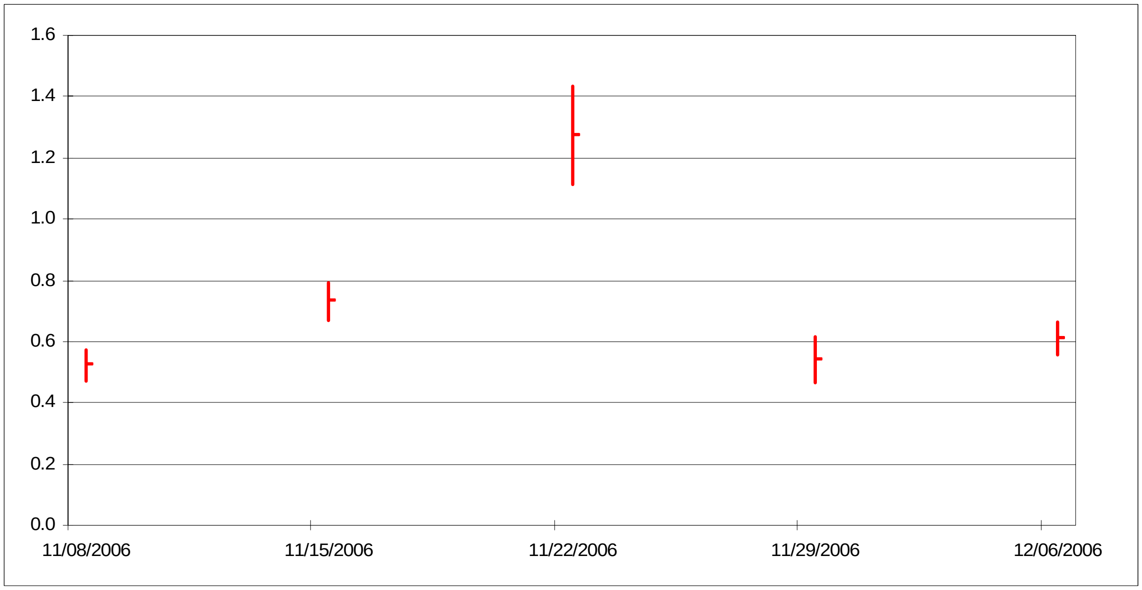
vertical axis = concentration in ug/m3
horizontal axis = site number

Figure 4-RG1e: Study 1 2,2,4-Trimethylpentane Results



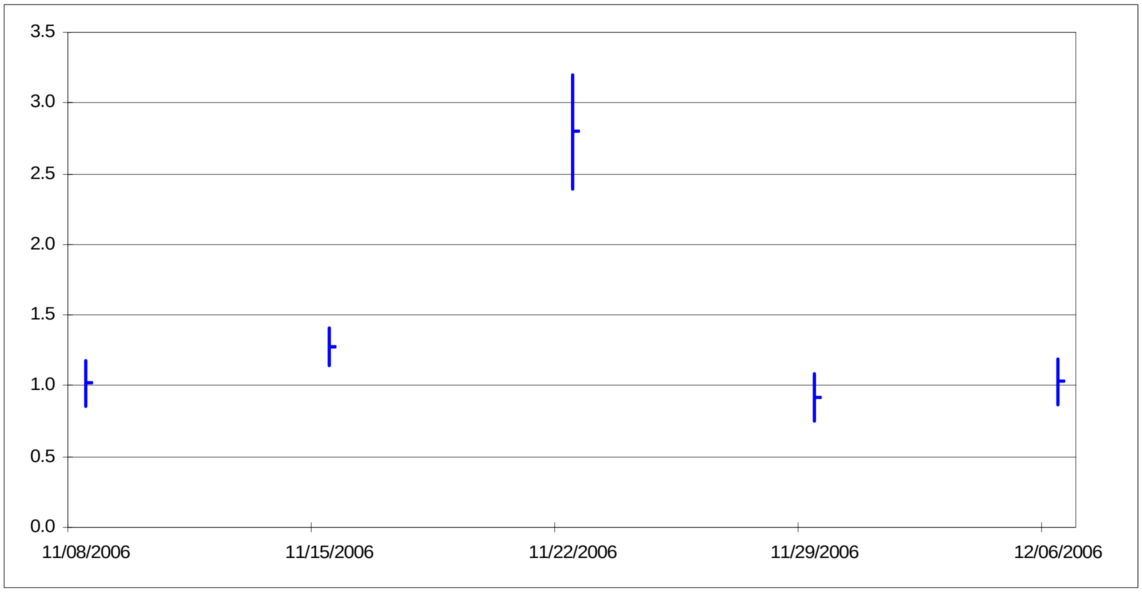
vertical axis = concentration in ug/m3
horizontal axis = site number

Figure 4-RG2a: Study 1 Benzene Results by Week



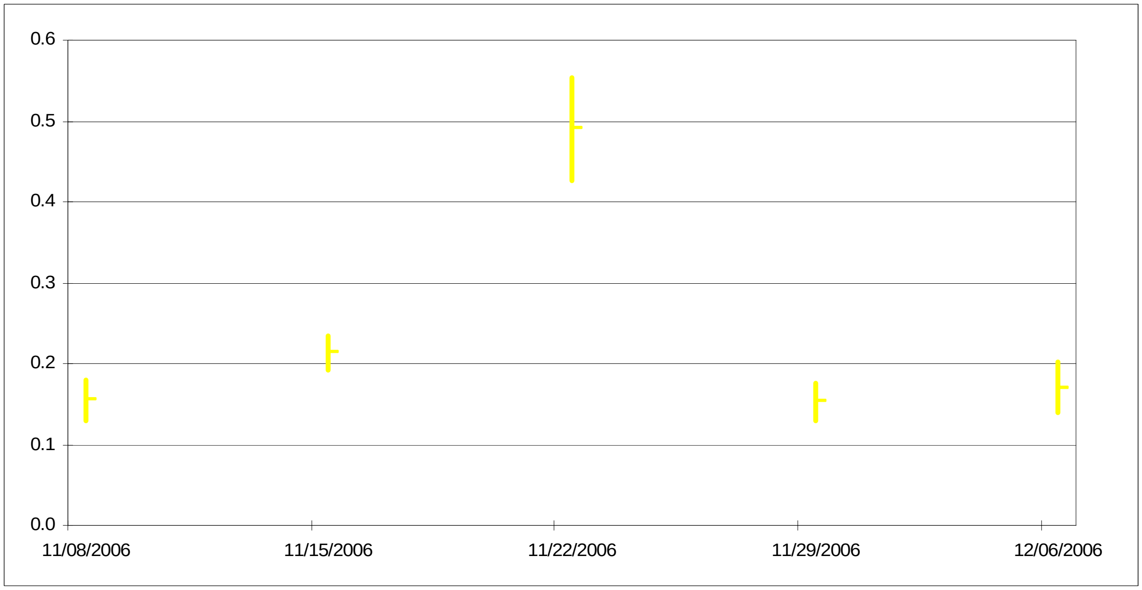
vertical axis = concentration in ug/m3
horizontal axis = start date

Figure 4-RG2b: Study 1 Toluene Results by Week



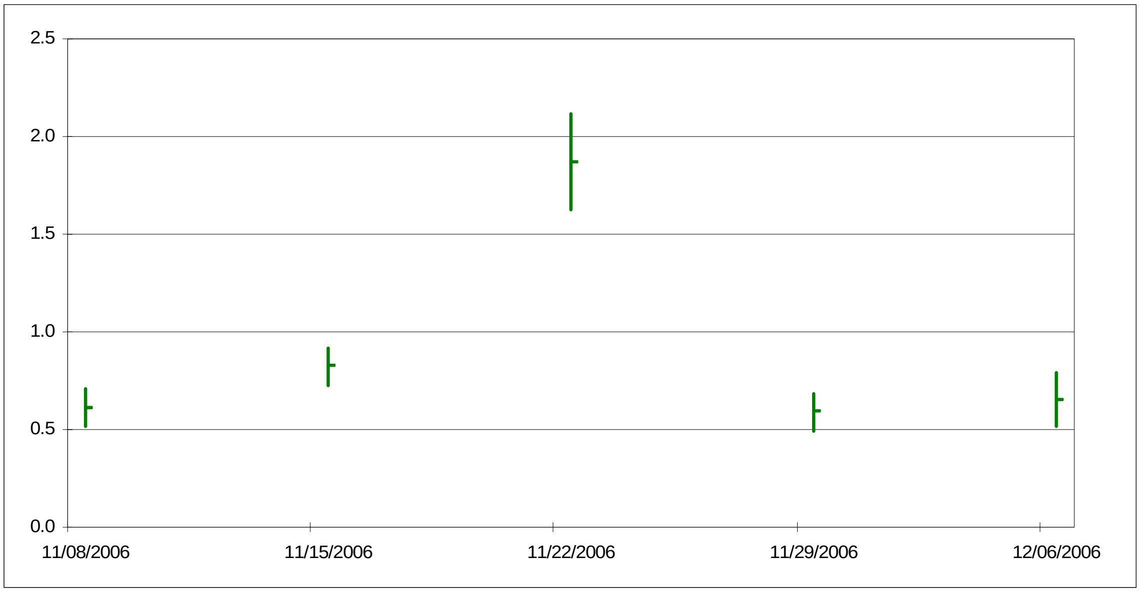
vertical axis = concentration in ug/m3
horizontal axis = start date

Figure 4-RG2c: Study 1 Ethylbenzene Results by Week



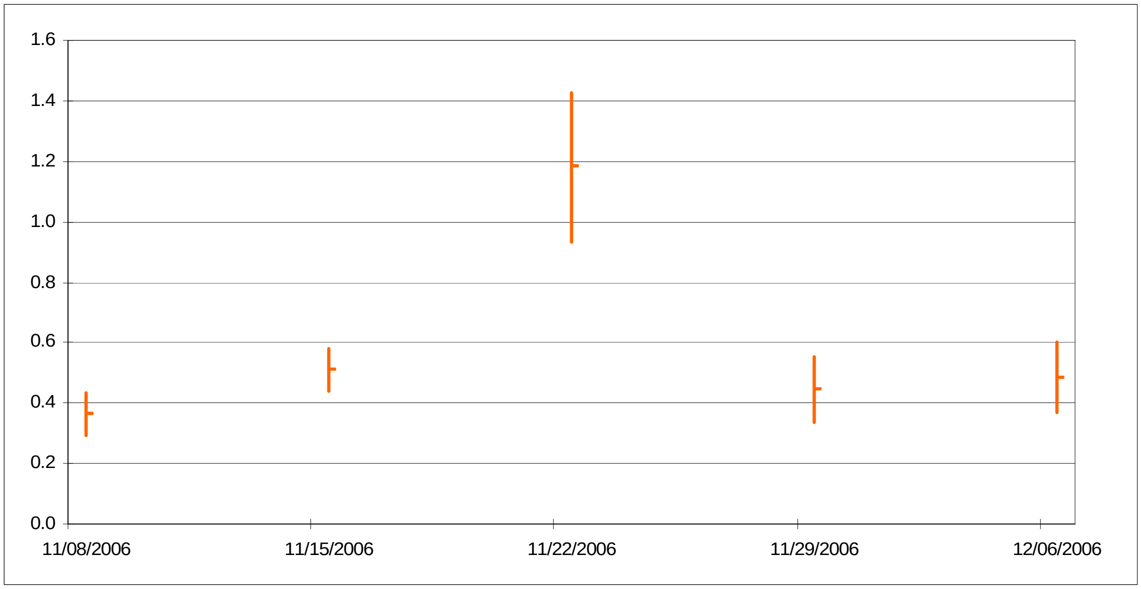
vertical axis = concentration in ug/m3
horizontal axis = start date

Figure 4-RG2d: Study 1 Total Xylene Results by Week



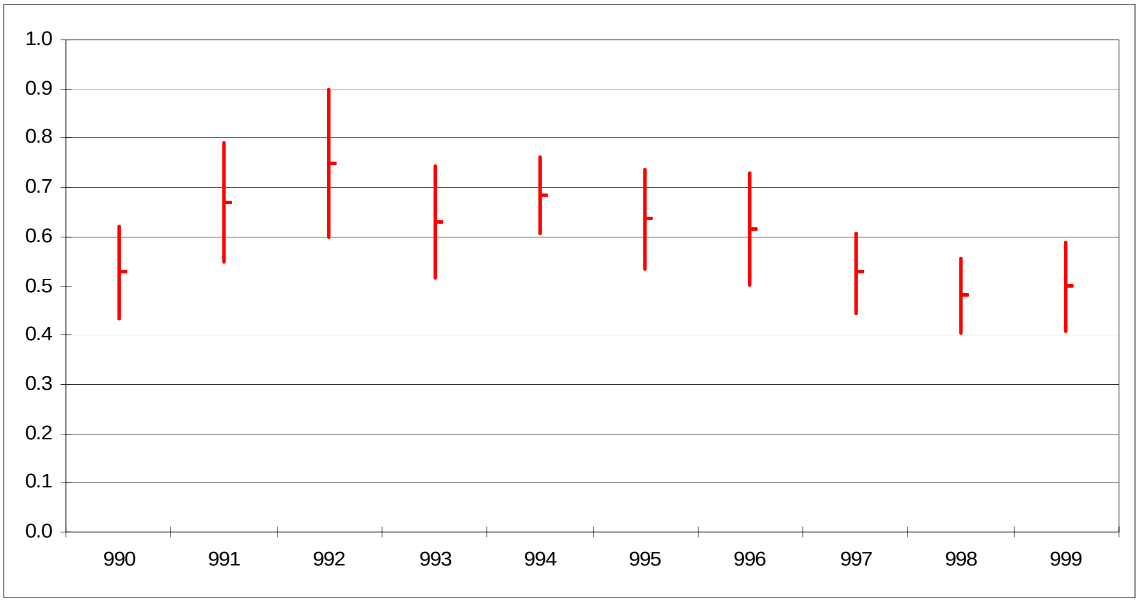
vertical axis = concentration in ug/m3
horizontal axis = start date

Figure 4-RG2e: Study 1 2,2,4-Trimethylpentane Results by Week



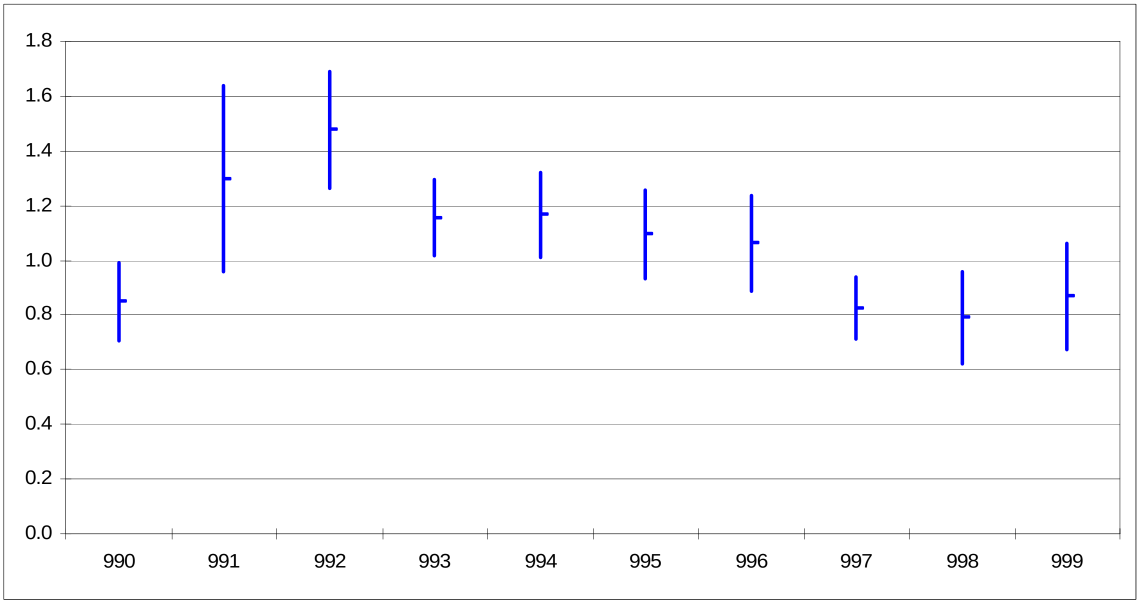
vertical axis = concentration in ug/m3
horizontal axis = start date

Figure 4-RG3a: Study 1 Benzene Results Without Third Week



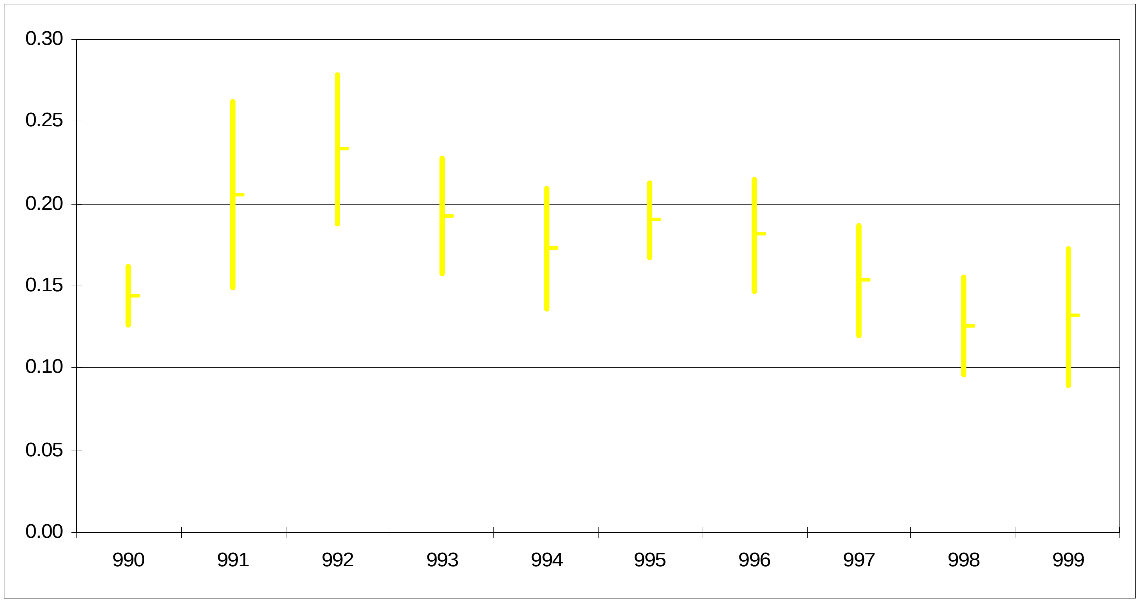
vertical axis = concentration in ug/m3
horizontal axis = site number

Figure 4-RG3b: Study 1 Toluene Results Without Third Week



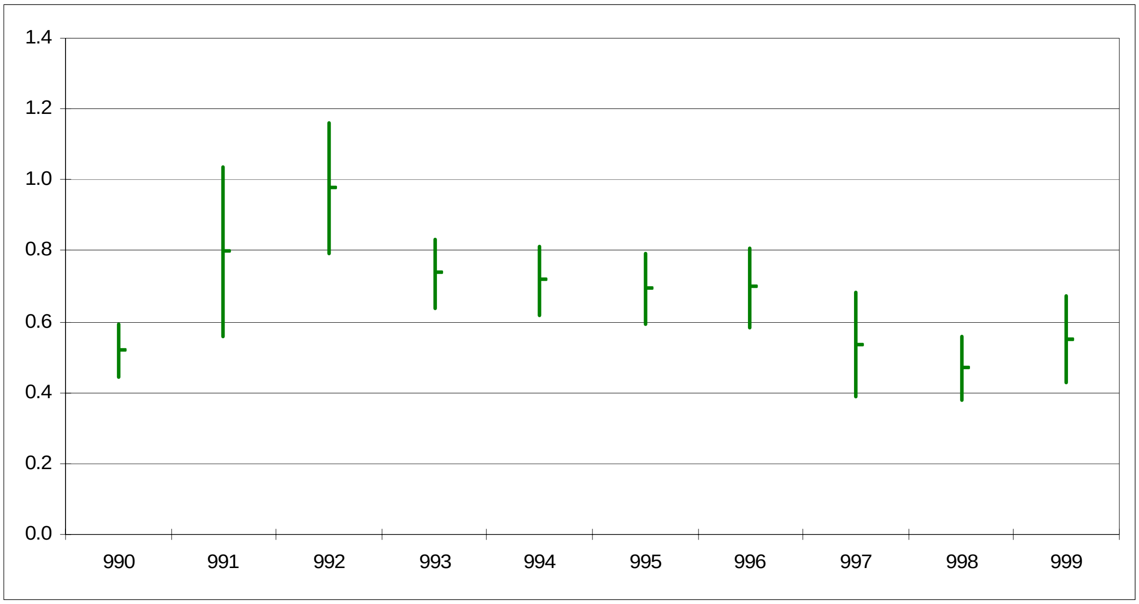
vertical axis = concentration in ug/m3
horizontal axis = site number

Figure 4-RG3c: Study 1 Ethylbenzene Results Without Third Week



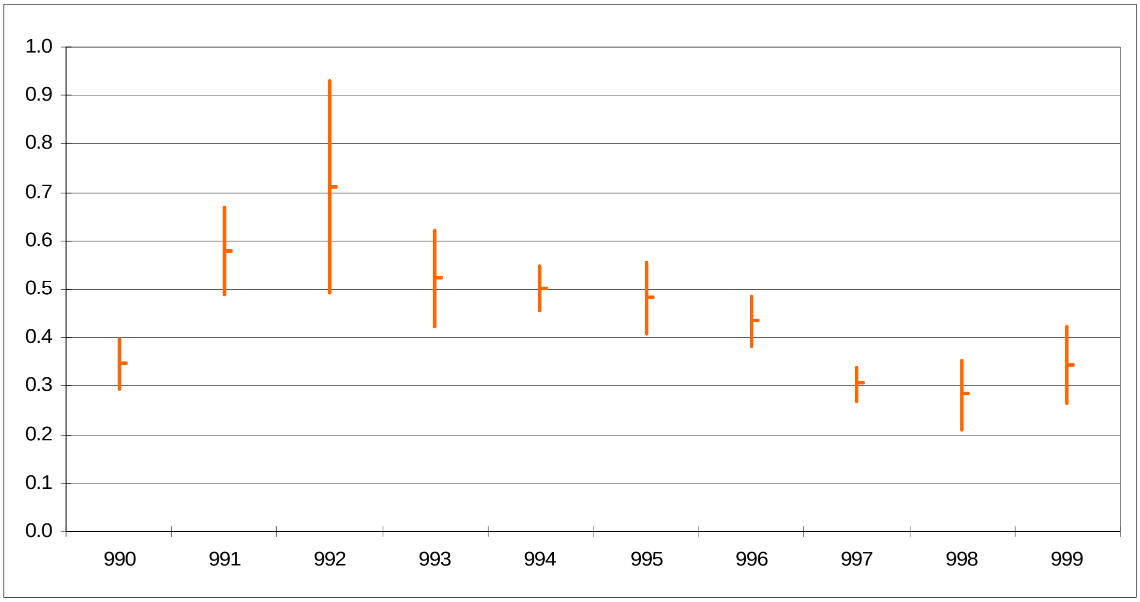
vertical axis = concentration in ug/m3
horizontal axis = site number

Figure 4-RG3d: Study 1 Total Xylene Results Without Third Week



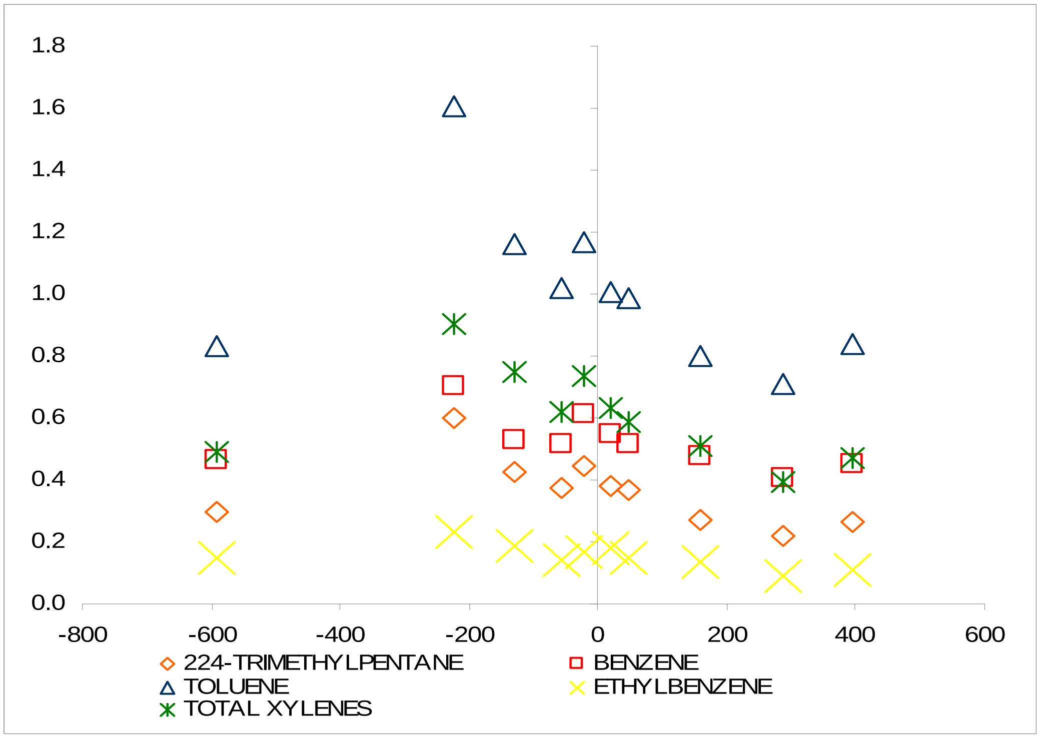
vertical axis = concentration in ug/m3
horizontal axis = site number

Figure 4-RG3e: Study 1 2,2,4-Trimethypentane Results Without Third Week



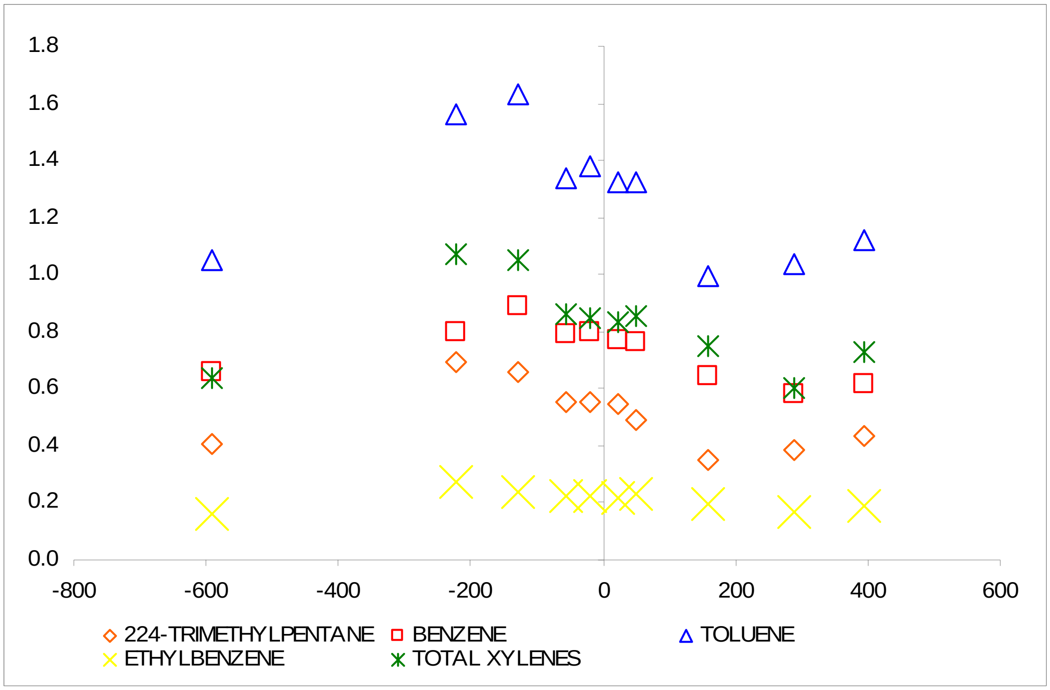
vertical axis = concentration in ug/m3
horizontal axis = site number

Figure 4-RG4a: Study 1 Results, 11/8 – 15/2006



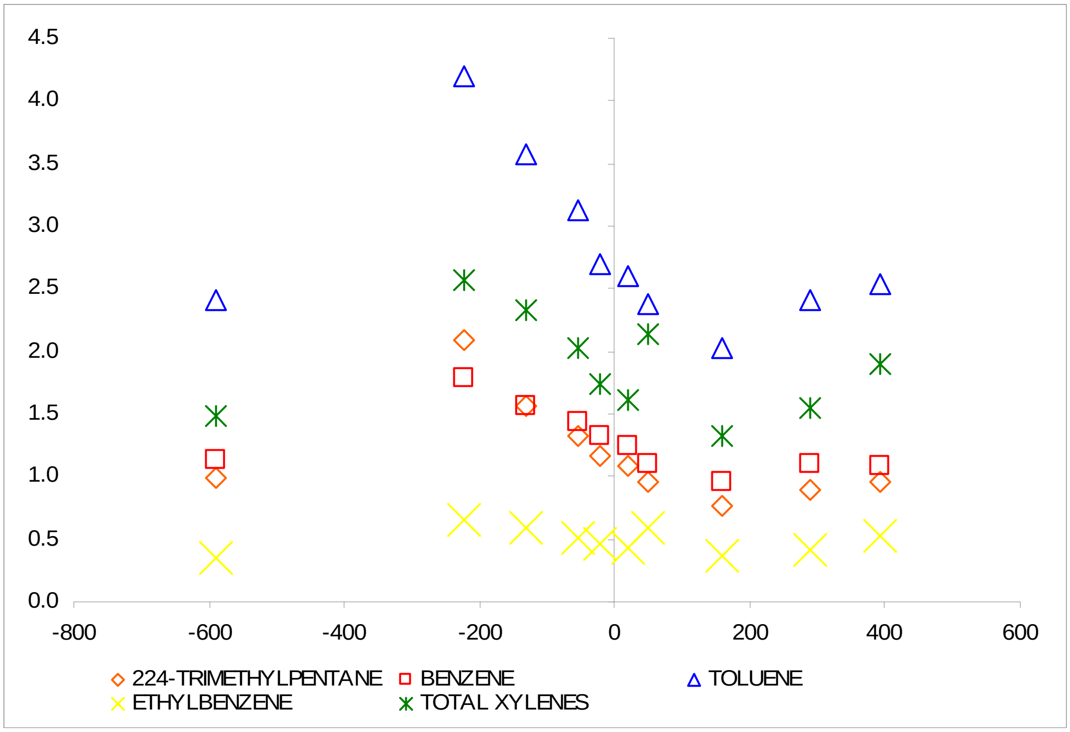
vertical axis = concentration in ug/m3
horizontal axis = distance to center of interstate, in meters

Figure 4-RG4b: Study 1 Results, 11/15 – 22/2006



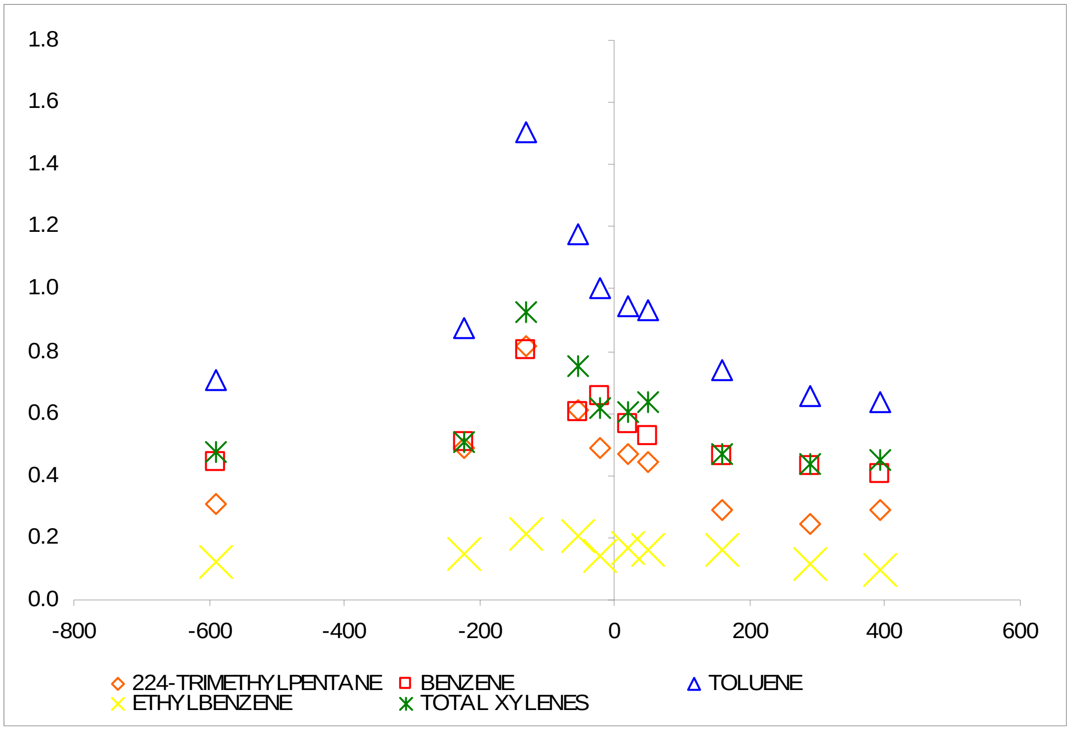
vertical axis = concentration in ug/m3
horizontal axis = distance to center of interstate, in meters

Figure 4-RG4c: Study 1 Results, 11/22 – 29/2006



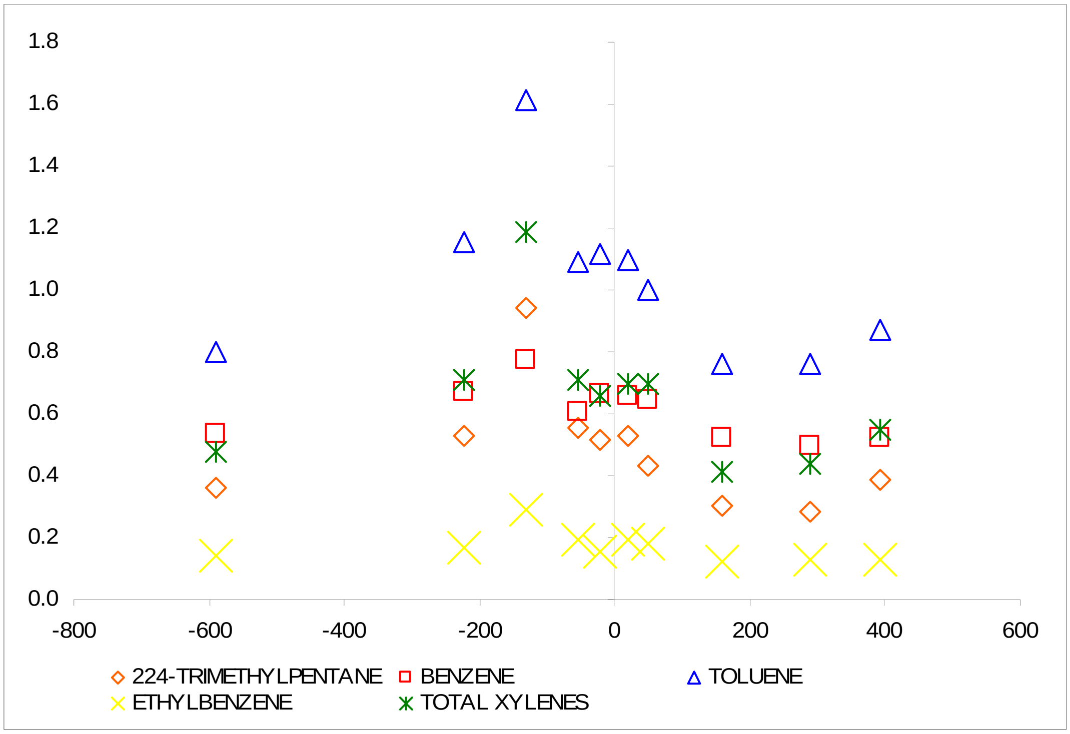
vertical axis = concentration in ug/m3
horizontal axis = distance to center of interstate, in meters

Figure 4-RG4d: Study 1 Results, 11/29 – 12/06/2006



vertical axis = concentration in ug/m3
horizontal axis = distance to center of interstate, in meters

Figure 4-RG4e: Study 1 Results, 12/06 – 13/2006



vertical axis = concentration in ug/m3
horizontal axis = distance to center of interstate, in meters

The apparent differences between sites are explored in the following tables, wherein the results of t-tests are shown. Statistical relevance is limited to determinations yielding 95% confidence of a two tail difference. With the exception of benzene, parameters showing no statistically significant differences are not tabulated below. Table 4-S1 below tabulates these values for benzene. No significant differences are apparent.

Table 4-S1: Study 1 T-Test Results for Benzene (df = 8, critical 2-tail = 2.306)

Site	991	992	993	994	995	996	997	998	999
990	-0.938	-1.230	-0.686	-0.900	-0.614	-0.385	0.236	0.244	0.171
991		-0.067	0.354	0.307	0.510	0.719	1.145	1.101	1.058
992			0.496	0.460	0.707	0.984	1.536	1.426	1.380
993				-0.092	0.157	0.405	0.947	0.889	0.835
994					0.287	0.593	1.257	1.131	1.075
995						0.283	0.935	0.850	0.788
996							0.718	0.645	0.575
997								0.046	-0.042
998									-0.077

While statistically significant results are not observed between the sites for any parameters, the graphs suggest that there may be differences. This is most apparent in graphs 4-RG4a to 4-RG4e, plotting the results from each week of the study against distance from the interstate, where the scale of the third week graph is almost three times that of the other weeks. It could be that differences are overwhelmed by the magnitude of variation introduced by the third week of sampling.

To test this hypothesis, results across all sites from each week were first subjected to t-tests to determine whether or not differences observed were statistically relevant. Results from these tests are shown in Table 4-S2 on the following page. These tests indicate that not only is week 3 (11/22/2006) different from each of the rest to a highly significant degree, but there are numerous additional statistically relevant differences between weeks. Note that most parameters show similar, but not identical, patterns of significant differences.

The implication of this is that each week's results, no matter what site they come from, have more in common with each other than they do with results of other samples collected at the same sites during different weeks. This fact suggests that these compounds diffuse much faster than accounted for by the model equations.

The data presented in Table 4-S2 indicates that week three (11/22/2006) is more different from the other weeks, than these weeks are different from each other. The figures 4-RG2a to 4-RG2e, summarizing each parameter's weekly results, show this difference clearly. Data from each site for all but the third week were subjected to t-tests to determine whether or not statistically relevant differences between sites can be observed. These results are presented in Tables 4-S3a through 4-S3e on the following pages. Note that patterns of significance vary considerably between the different parameters.

Table 4-S2: Study 1 Weekly t-Test Results (df = 18, critical 2-tail = 2.101)

Benzene

	11/15/2006	11/22/2006	11/29/2006	12/06/2006
11/08/2006	**-5.061**	**-8.766**	-0.405	**-2.263**
11/15/2006		**-6.215**	**3.810**	**2.880**
11/22/2006			**8.124**	**7.707**
11/29/2006				-1.437

Toluene

	11/15/2006	11/22/2006	11/29/2006	12/06/2006
11/08/2006	**-2.450**	**-8.018**	0.813	-0.119
11/15/2006		**-6.960**	**3.275**	**2.327**
11/22/2006			**8.409**	**7.960**
11/29/2006				-0.931

Ethylbenzene

	11/15/2006	11/22/2006	11/29/2006	12/06/2006
11/08/2006	**-3.498**	**-9.681**	0.112	-0.769
11/15/2006		**-8.170**	**3.843**	**2.202**
11/22/2006			**9.871**	**8.875**
11/29/2006				-0.897

Total Xylenes

	11/15/2006	11/22/2006	11/29/2006	12/06/2006
11/08/2006	**-3.112**	**-9.327**	0.299	-0.526
11/15/2006		**-7.749**	**3.399**	1.987
11/22/2006			**9.471**	**8.431**
11/29/2006				-0.766

224 Trimethylpentane

	11/15/2006	11/22/2006	11/29/2006	12/06/2006
11/08/2006	**-2.862**	**-6.299**	-1.229	-1.727
11/15/2006		**-5.167**	0.974	0.358
11/22/2006			**5.395**	**5.035**
11/29/2006				-0.484

Table 4-S3a: Study 1 (no week 3) t-Test Results for Benzene (df = 6, critical 2-tail = 2.447)

Site	991	992	993	994	995	996	997	998	999
990	-1.821	**-2.451**	-1.365	**-2.511**	-1.543	-1.163	0.015	0.781	0.424
991		-0.812	0.465	-0.204	0.415	0.638	1.932	**2.622**	2.216
992			1.238	0.750	1.224	1.389	**2.558**	**3.146**	**2.794**
993				-0.770	-0.077	0.180	1.457	2.167	1.768
994					0.740	0.976	**2.748**	**3.691**	**3.032**
995						0.267	1.661	2.437	1.980
996							1.243	1.944	1.561
997								0.835	0.441
998									-0.331

Table 4-S3b: Study 1 (no week 3) t-Test Results for Toluene (df = 6, critical 2-tail = 2.447)

Site	991	992	993	994	995	996	997	998	999
990	-2.389	**-4.789**	**-3.054**	**-2.973**	-2.227	-1.843	0.248	0.519	-0.146
991		-0.872	0.762	0.689	1.066	1.213	**2.582**	**2.624**	2.157
992			**2.477**	2.299	**2.799**	**2.939**	**5.268**	**4.955**	**4.130**
993				-0.108	0.577	0.831	**3.651**	**3.321**	2.381
994					0.645	0.885	**3.496**	**3.246**	2.367
995						0.263	**2.658**	**2.553**	1.754
996							2.209	2.188	1.453
997								0.341	-0.356
998									-0.579

Table 4-S3c: Study 1 (no week 3) t-Test Results for Ethylbenzene (df = 6, critical 2-tail = 2.447)

Site	991	992	993	994	995	996	997	998	999
990	-2.031	**-3.625**	-2.420	-1.403	**-3.162**	-1.877	-0.477	1.030	0.541
991		-0.746	0.383	0.942	0.492	0.725	1.561	2.445	2.070
992			1.397	2.033	1.676	1.808	**2.806**	**3.924**	**3.273**
993				0.751	0.108	0.459	1.595	**2.856**	2.210
994					-0.782	-0.309	0.790	1.972	1.478
995						0.439	1.808	**3.411**	**2.453**
996							1.141	2.391	1.808
997								1.202	0.798
998									-0.221

Table 4-S3d: Study 1 (no week 3) t-Test Results for Total Xylene (df = 6, critical 2-tail = 2.447)

Site	**991**	**992**	**993**	**994**	**995**	**996**	**997**	**998**	**999**
990	-2.180	**-4.519**	**-3.443**	**-3.089**	**-2.721**	**-2.517**	-0.180	0.863	-0.413
991		-1.165	0.468	0.627	0.794	0.763	1.843	**2.535**	1.805
992			2.269	**2.460**	**2.663**	**2.558**	**3.693**	**4.870**	**3.775**
993				0.295	0.605	0.539	2.246	**3.936**	2.309
994					0.310	0.264	2.006	**3.608**	2.041
995						-0.024	1.754	**3.268**	1.760
996							1.695	**3.052**	1.685
997								0.765	-0.158
998									-1.052

Table 4-S3e: Study 1 (no week 3) t-Test Results for 2,2,4-Trimethylpentane (df = 6, critical 2-tail = 2.447)

Site	**991**	**992**	**993**	**994**	**995**	**996**	**997**	**998**	**999**
990	**-4.424**	**-3.186**	**-3.099**	**-4.430**	**-3.022**	-2.388	1.329	1.416	0.058
991		-1.099	0.805	1.478	1.628	**2.759**	**5.566**	**5.049**	**3.861**
992			1.531	1.831	1.944	2.425	**3.596**	**3.645**	**3.100**
993				0.376	0.645	1.572	**4.041**	**3.831**	**2.770**
994					0.442	1.945	**6.577**	**5.020**	**3.392**
995						1.088	**4.317**	**3.838**	**2.546**
996							**4.081**	**3.362**	1.882
997								0.528	-0.884
998									-1.113

Summary of Observations

Several important observations can be made based on these results:

1) model predictions showing a sharp concentration gradient across study transect were not observed

2) maximum concentrations were observed at sites well removed from the interstate, also contradicting the model

3) observed concentrations of benzene were in all cases significantly higher than predicted

4) results from individual sites have more in common with results from other sites collected at the same time than they do with results obtained from the same site during different weeks

5) individual compounds show variable patterns of significant differences between the sites, implying either variable source inputs or atmospheric chemistry

4b3. Results, Study 2

Study 2 was conducted in rural Jefferson County between March 14 and April 13, 2007. During this time, 4 weekly samples were collected at each of 9 sites. Note that the final samples of the series were collected two days later than planned, due to an unexpected snow storm. Two sites were duplicate sites. The sites were arranged generally along a south to north transect with Interstate 94 approximately in the middle of the array.

All site locations were determined multiple times using a hand-held GPS unit, and the resulting latitude and longitudes averaged to fix the location. Distances were calculated using the Haversine formula. Table 4-D2 provides a site list, including general location, distance in meters and direction from the middle of Interstate 94, and whether or not the site is a duplicate site. Figure 4-2 on page 37 of this report shows a map of the sites.

Table 4-D2: Study 2 Site List

Site	Location	Meters	Direction	Dupe?
990	Siegmann Road @ Onahill Lane	547	South	Yes
991	Siegmann Road @ Olszewski Lane	219	South	No
992	Siegmann Road Closest to Hwy 94	72	South	No
993	I-94 East Bound Shoulder	21	South	No
994	I-94 Median Turnaround	6	South	Yes
995	I-94 West Bound Shoulder	21	North	No
996	South Lane at last house	70	North	No
997	South Lane 3rd pole from highway	171	North	No
998	South Lane Midway to Church Road	529	North	No

Table 4-R4 summarizes results from each site, with averages, maxima, minima and relative standard deviations (RSD (%)) shown. Table 4-R5 on the following page summarizes results from each week of the study. The tables are organized with sites arranged from south to north. Site 994 was located in the

median of the roadway, and thus should experience the highest concentrations according to the model theory.

Table 4-R4: Study 2 Summary of Results by Site (n = 4)

Parameter	site	990	991	992	993	994	995	996	997	998
Benzene	**average**	0.39	0.38	0.37	0.41	0.39	0.37	0.36	0.37	0.35
	maximum	0.43	0.45	0.47	0.48	0.44	0.42	0.42	0.48	0.41
	minimum	0.30	0.32	0.28	0.30	0.36	0.32	0.29	0.30	0.29
	RSD (%)	15.7%	14.4%	22.7%	20.1%	9.2%	14.8%	16.4%	22.0%	17.6%
Toluene	**average**	0.24	0.23	0.25	0.31	0.30	0.28	0.24	0.26	0.25
	maximum	0.36	0.36	0.33	0.38	0.41	0.38	0.32	0.39	0.31
	minimum	0.12	0.10	0.13	0.18	0.21	0.15	0.16	0.12	0.19
	RSD (%)	47.2%	46.4%	39.0%	29.6%	31.3%	40.7%	31.9%	48.1%	19.8%
Ethylbenzene	**average**	0.03	0.03	0.05	0.04	0.05	0.04	0.05	0.02	0.04
	maximum	0.06	0.04	0.13	0.09	0.07	0.05	0.09	0.03	0.09
	minimum	0.00	0.01	0.01	0.02	0.03	0.03	0.04	0.02	0.00
	RSD (%)	105.7%	59.4%	110.0%	79.7%	34.8%	22.6%	40.9%	13.7%	76.6%
Total Xylenes	**average**	0.08	0.10	0.11	0.17	0.14	0.10	0.10	0.10	0.13
	maximum	0.13	0.18	0.23	0.24	0.18	0.15	0.18	0.13	0.16
	minimum	0.04	0.04	0.05	0.11	0.08	0.07	0.04	0.07	0.06
	RSD (%)	53.3%	62.3%	78.1%	31.2%	32.5%	36.7%	57.6%	27.6%	38.1%
224-Trimethylpentane	**average**	0.07	0.06	0.16	0.09	0.08	0.08	0.05	0.05	0.09
	maximum	0.11	0.09	0.35	0.16	0.10	0.16	0.08	0.09	0.13
	minimum	0.04	0.04	0.05	0.06	0.06	0.02	0.01	0.01	0.06
	RSD (%)	47.1%	35.6%	88.1%	49.8%	18.2%	68.2%	59.3%	74.0%	36.4%

Note that the concentrations observed during this study are significantly lower than those obtained in the first study. In fact many of the values are below the estimated limits of quantitation and detection associated with this analysis, and therefore can not be considered entirely reliable. All benzene and toluene results do exceed these analytical limits and should be considered valid results. What is interesting to note is that the minimum benzene concentration observed during the study period (0.28 ug/m^3) exceeds the annual average predicted by the model for the Milwaukee study area (0.27 ug/m^3).

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Table 4-R5: Study 2 Summary of Results by Week (n = 9)

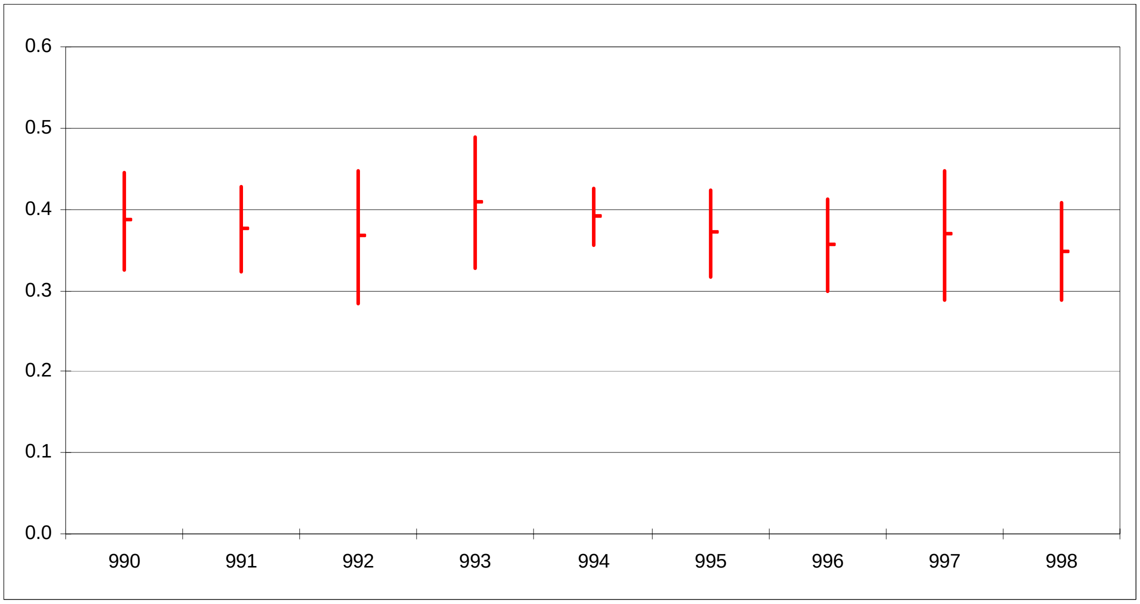
Parameter	site	14-Mar-07	21-Mar-07	28-Mar-07	04-Apr-07
Benzene	**average**	0.42	0.37	0.39	0.31
	maximum	0.48	0.44	0.47	0.37
	minimum	0.36	0.28	0.31	0.29
	RSD (%)	10.5%	15.7%	14.2%	7.7%
Toluene	**average**	0.21	0.34	0.34	0.16
	maximum	0.30	0.39	0.41	0.23
	minimum	0.18	0.27	0.26	0.10
	RSD (%)	16.8%	12.0%	14.5%	31.1%
Ethylbenzene	**average**	0.04	0.06	0.02	0.03
	maximum	0.06	0.13	0.09	0.09
	minimum	0.03	0.03	0.00	0.01
	RSD (%)	22.0%	52.0%	110.6%	76.5%
Total Xylenes	**average**	0.07	0.17	0.13	0.09
	maximum	0.15	0.24	0.18	0.16
	minimum	0.04	0.09	0.09	0.04
	RSD (%)	43.9%	29.2%	27.4%	50.3%
224-Trimethyl pentane	**average**	0.06	0.14	0.08	0.06
	maximum	0.09	0.35	0.17	0.11
	minimum	0.04	0.08	0.01	0.02
	RSD (%)	23.0%	59.7%	66.6%	47.9%

Note that the variability of the data (as measured by the RSD(%)) is again generally greater within sites (Table 4-R4) than it is within weeks (Table 4-R5). This indicates that the individual results from each site are more closely related to the results obtained from the other sites during the same time period, than they are to the results obtained from the same site during the other weeks of the study period. Note also that higher RSD(%) values are observed during this study than during the first study. This is a factor of lower absolute concentration values observed in the second study.

The following series of graphs present the data shown in the tables. Figures 4-RG5a to 4-RG5e illustrate results for each parameter grouped by site (as per Table 4-R4), showing the average and upper and lower confidence intervals. Note that, unlike the Milwaukee study, no discernible differences between sites are revealed.

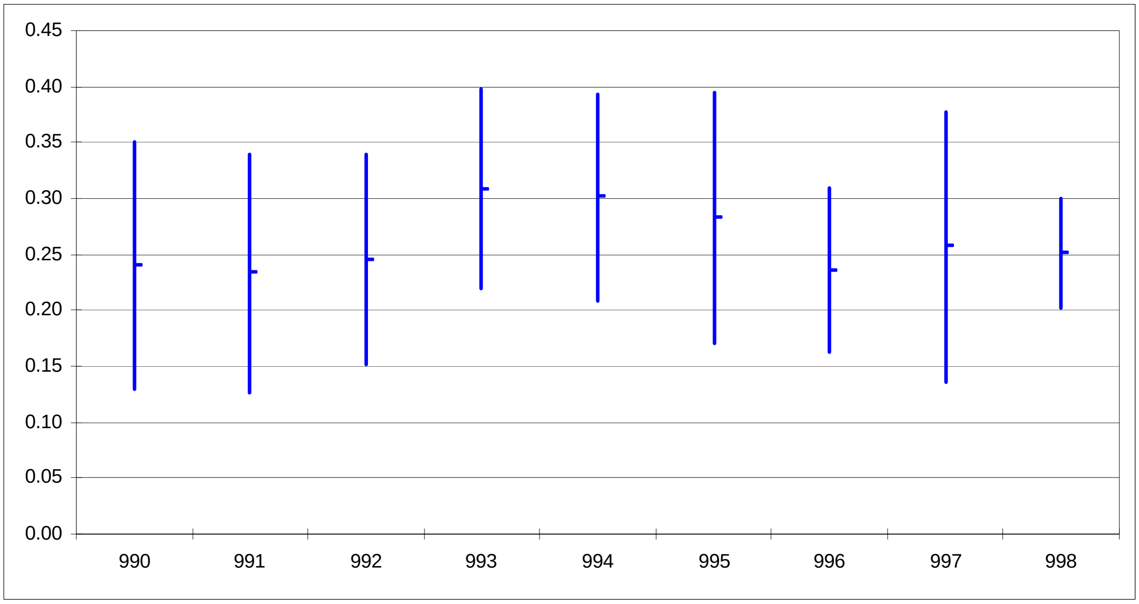
Figures 4-RG6a to 4-RG6e illustrate the results on a weekly basis (as per Table 4-R5). Figures 4-RG7a to 4-RG7d show individual results from each week of the study, plotted versus distance from the center of the interstate.

Figure 4-RG5a: Study 2 Benzene Results



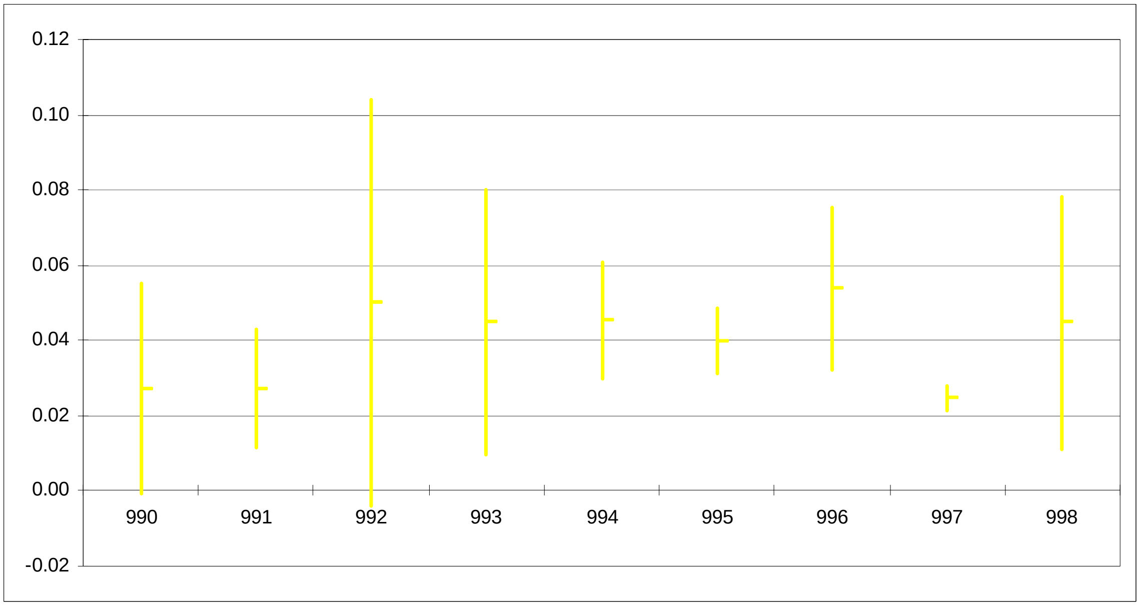
vertical axis = concentration in ug/m3
horizontal axis = site number

Figure 4-RG5b: Study 2 Toluene Results



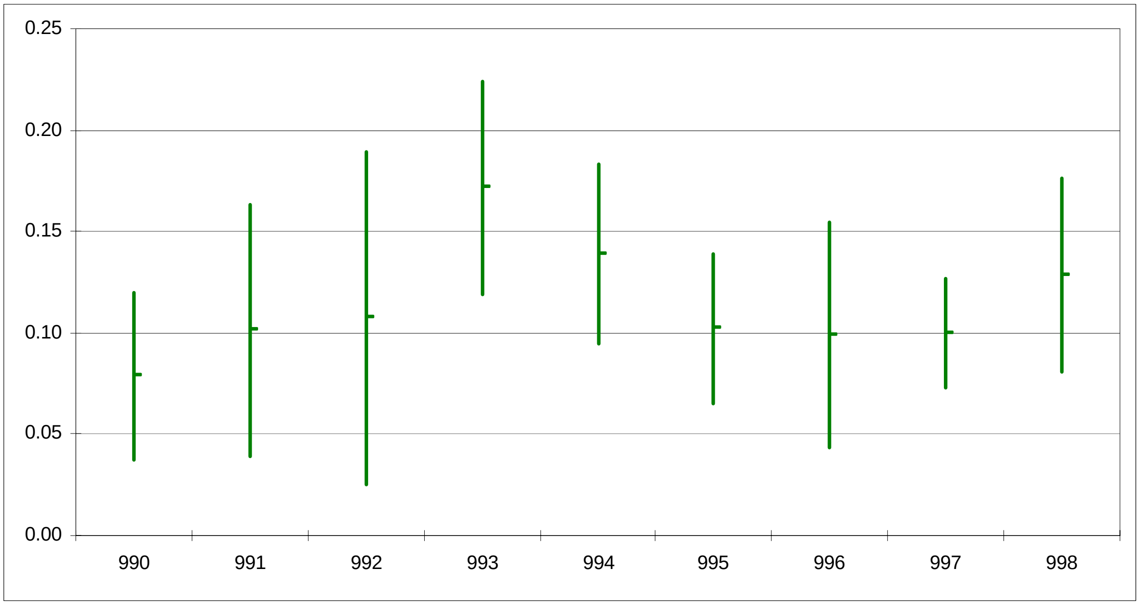
vertical axis = concentration in ug/m3
horizontal axis = site number

Figure 4-RG5c: Study 2 Ethylbenzene Results



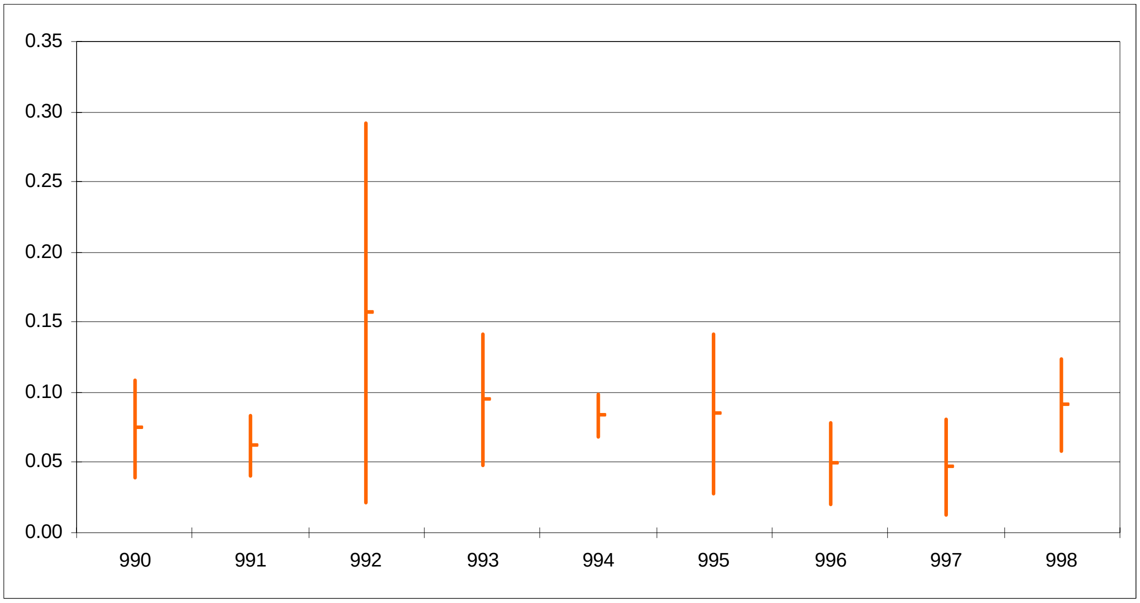
vertical axis = concentration in ug/m3
horizontal axis = site number

Figure 4-RG5d: Study 2 Total Xylene Results



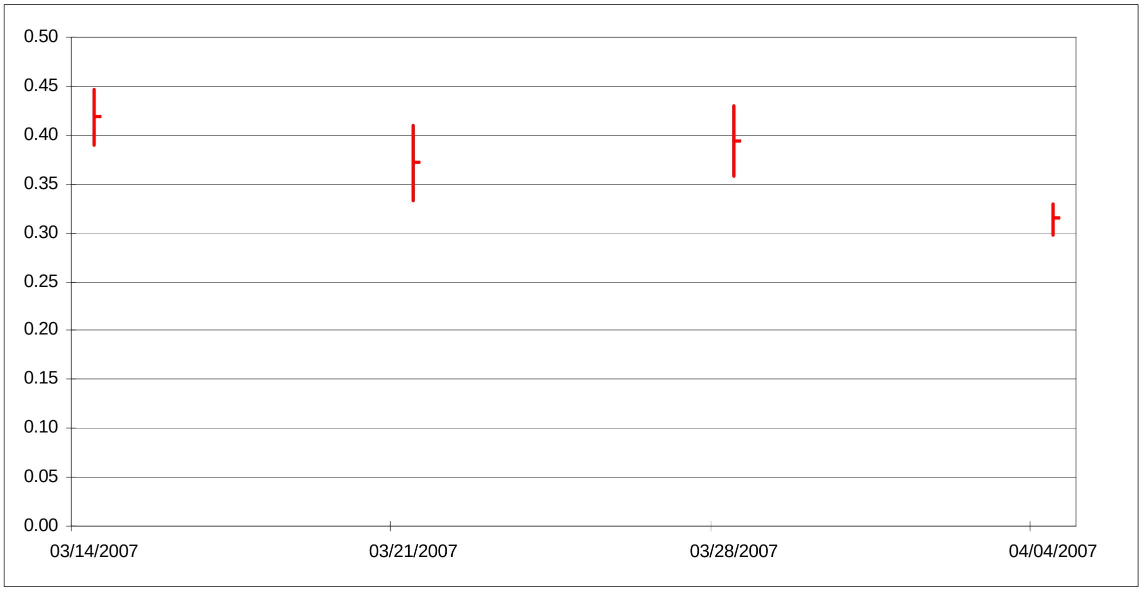
vertical axis = concentration in ug/m3
horizontal axis = site number

Figure 4-RG5e: Study 2 2,2,4-Trimethylpentane Results



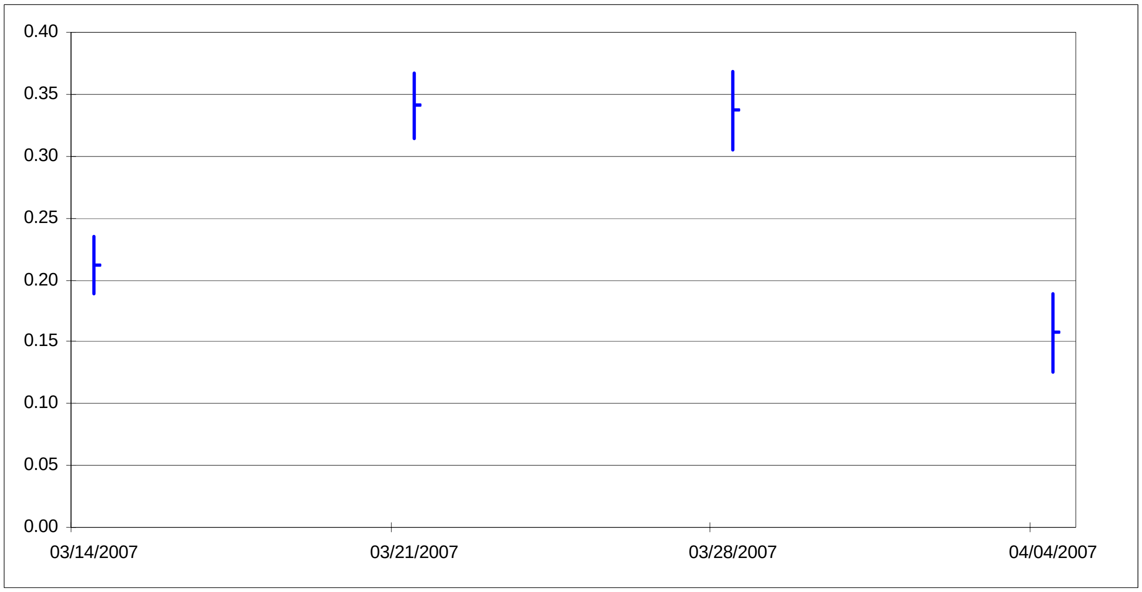
vertical axis = concentration in ug/m3
horizontal axis = site number

Figure 4-RG6a: Study 2 Benzene Results by Week



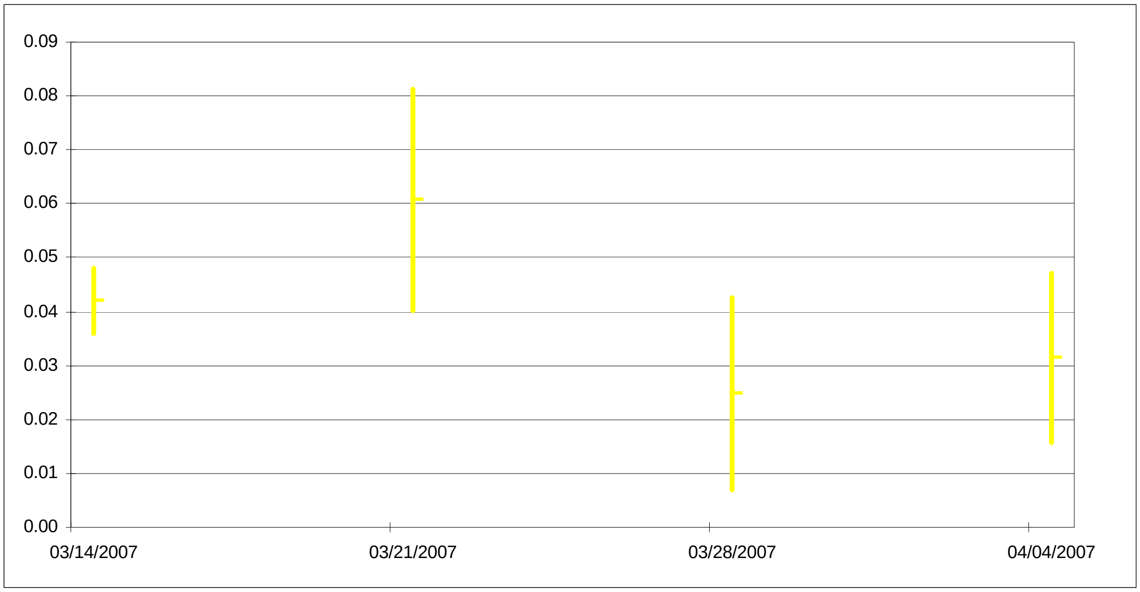
vertical axis = concentration in ug/m3
horizontal axis = start date

Figure 4-RG6b: Study 2 Toluene Results by Week



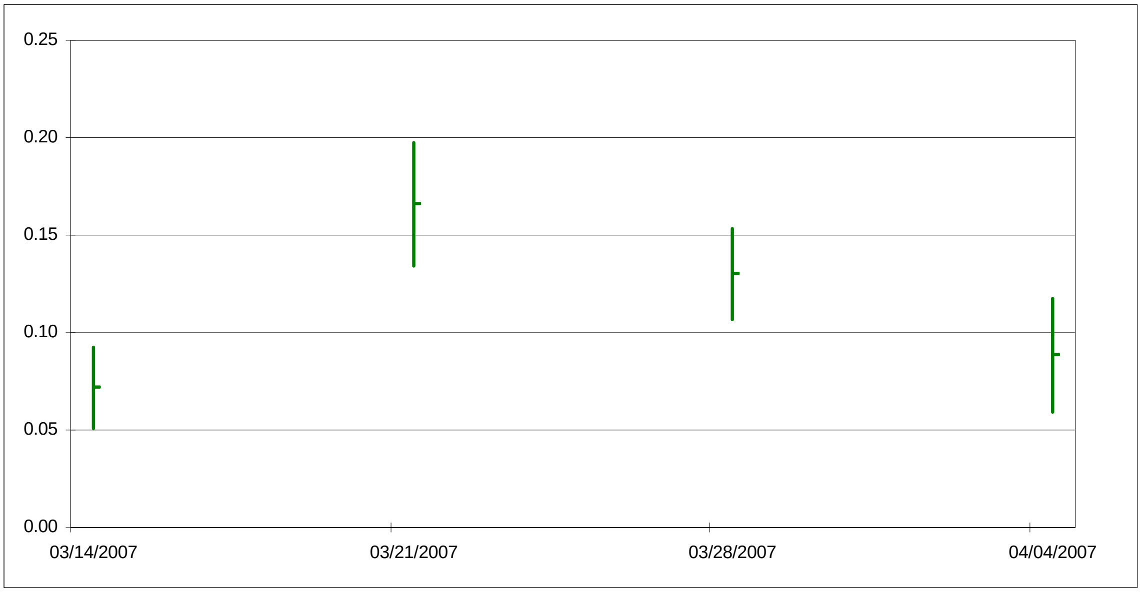
vertical axis = concentration in ug/m3
horizontal axis = start date

Figure 4-RG6c: Study 2 Ethylbenzene Results by Week



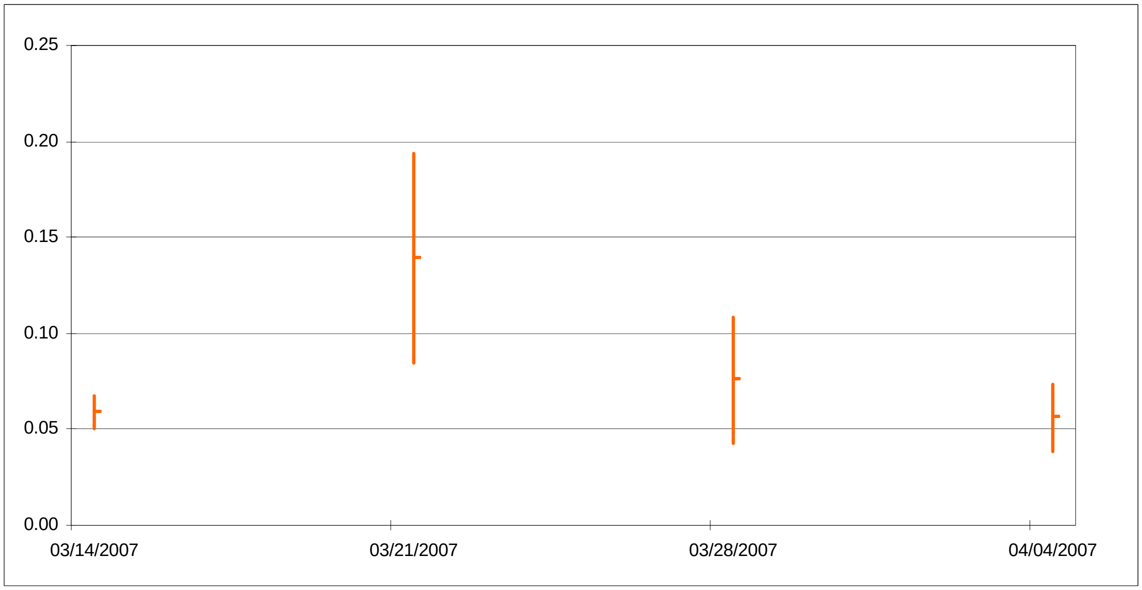
vertical axis = concentration in ug/m3
horizontal axis = start date

Figure 4-RG6d: Study 2 Total Xylene Results by Week



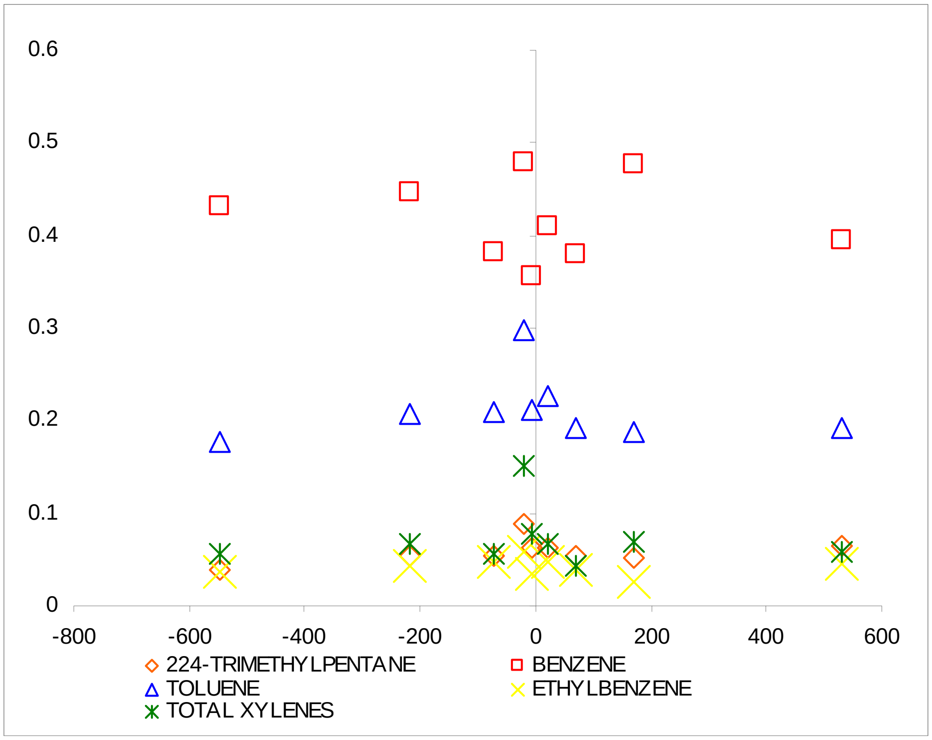
vertical axis = concentration in ug/m3
horizontal axis = start date

Figure 4-RG6e: Study 2 2,2,4-Trimethylpentane Results by Week



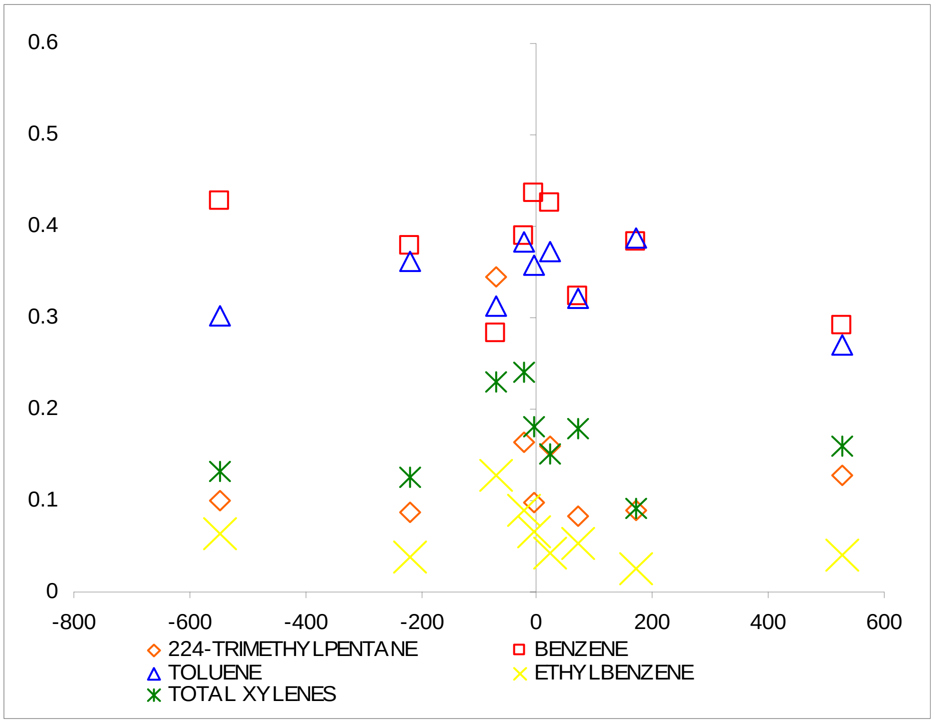
vertical axis = concentration in ug/m3
horizontal axis = start date

Figure 4-RG7a: Study 2 Results, 3/14- 21/2007



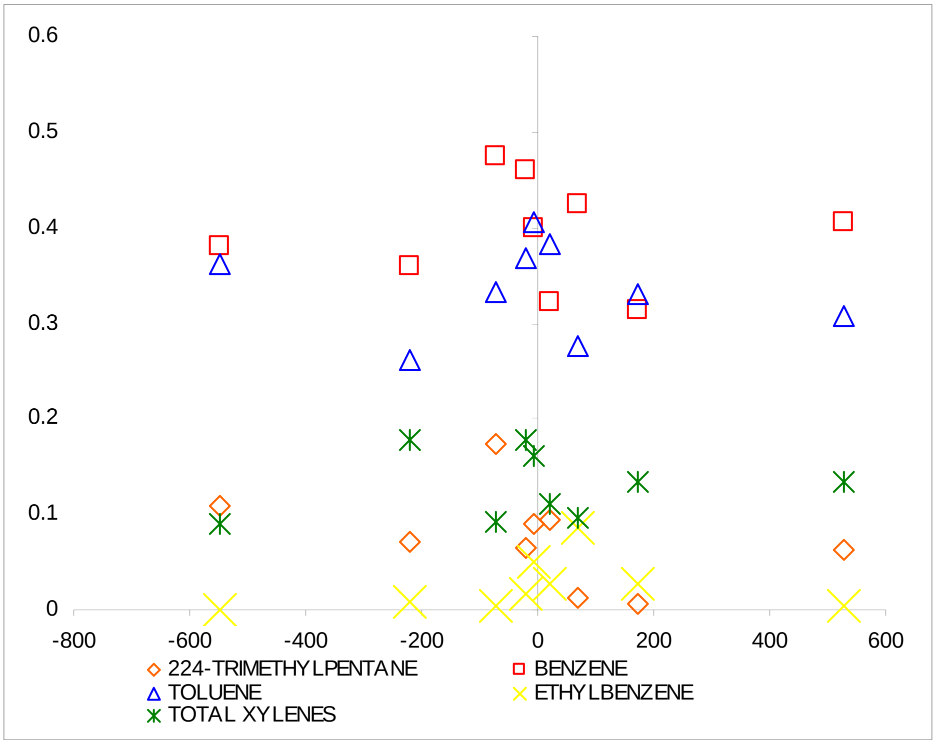
vertical axis = concentration in ug/m3
horizontal axis = distance to center of interstate, in meters

Figure 4-RG7b: Study 2 Results, 2/21 – 28/2007



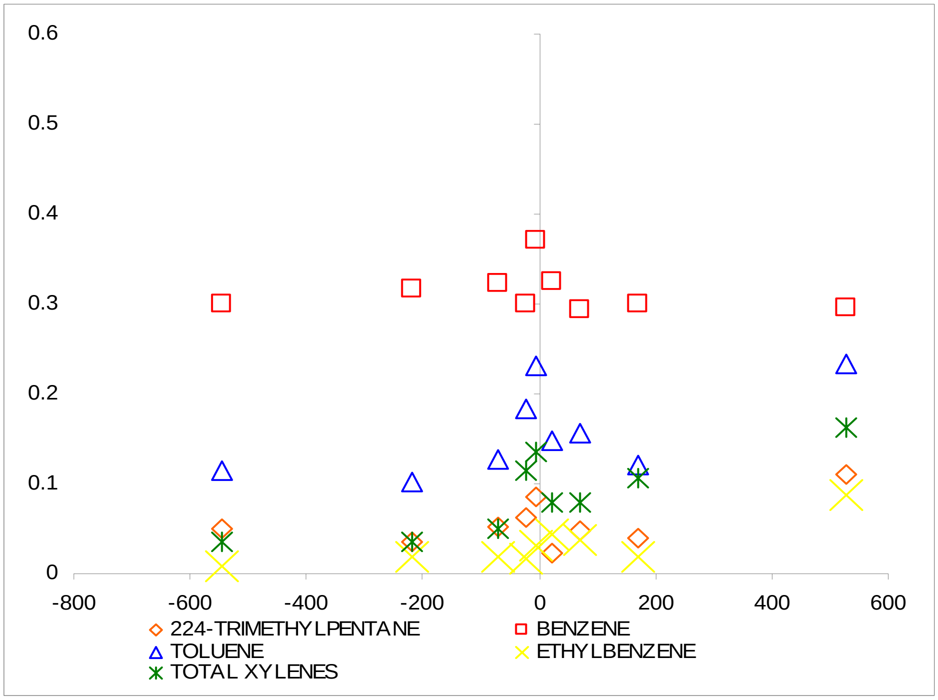
vertical axis = concentration in ug/m3
horizontal axis = distance to center of interstate, in meters

Figure 4-RG7c: Study 2 Results, 3/28 – 4/04/2007



vertical axis = concentration in ug/m3
horizontal axis = distance to center of interstate, in meters

Figure 4-RG7d: Study 2 Results, 4/04 – 13/2007



vertical axis = concentration in ug/m3
horizontal axis = distance to center of interstate, in meters

The apparent differences between sites are explored in the following tables, wherein the results of t-tests are shown. Statistical relevance is limited to determinations yielding 95% confidence of a two tail difference. With the exception of benzene, parameters showing no statistically significant differences are not tabulated below. Statistically relevant values are highlighted. Tables 4-S4a, 4-S4b and 4-S4c below tabulate these values for benzene, ethylbenzene and total xylenes. Note that the few statistically significant differences observed (shown in **bold**) have an absolute magnitude of less than 0.1 ug/m^3.

Table 4-S4a: Study 2 T-Test Results for Benzene (df = 6, critical 2-tail = 2.447)

Site	991	992	993	994	995	996	997	998
990	0.235	0.381	-0.442	-0.160	0.365	0.705	0.332	0.880
991		0.203	-0.654	-0.468	0.140	0.506	0.149	0.695
992			-0.723	-0.558	-0.094	0.199	-0.048	0.356
993				0.377	0.760	1.038	0.682	1.183
994					0.627	1.030	0.506	1.227
995						0.368	0.038	0.560
996							-0.257	0.196
997								0.416

Table 4-S4b: Study 2 T-Test Results for Ethylbenzene (df = 6, critical 2-tail = 2.447)

Site	991	992	993	994	995	996	997	998
990	0.003	-0.739	-0.772	-1.104	-0.840	-1.481	0.176	-0.782
991		-0.801	-0.906	-1.609	-1.375	-1.965	0.303	-0.927
992			0.160	0.171	0.370	-0.129	0.924	0.170
993				-0.018	0.276	-0.433	1.128	0.010
994					0.600	-0.645	**2.561**	0.032
995						-1.190	**3.164**	-0.274
996							**2.628**	0.459
997								-1.164

Table 4-S4c: Study 2 T-Test Results for Total Xylene (df = 6, critical 2-tail = 2.447)

Site	991	992	993	994	995	996	997	998
990	-0.593	-0.611	**-2.729**	-1.958	-0.831	-0.568	-0.835	-1.536
991		-0.117	-1.701	-0.979	-0.024	0.056	0.044	-0.678
992			-1.290	-0.668	0.114	0.168	0.174	-0.430
993				0.922	2.127	1.861	2.389	1.195
994					1.263	1.110	1.491	0.329
995						0.096	0.104	-0.849
996							-0.027	-0.783
997								-1.018

All apparently statistically significant comparisons are between results which are less than the estimated limit of quantitation (LOQ). It is therefore likely that this study also contradicts the modeling prediction of an observable concentration gradient across the transect.

Results of t-tests between weeks are shown in Table 4-S5. These tests indicate that there are statistically relevant differences between the weeks. However, the magnitude of these differences is in most cases less than 0.1 ug/m^3. Only benzene and toluene are consistently greater than the estimated limit of quantitation. Note that there is no consistent pattern of significance between the different parameters.

Table 4-S5: Study 2 Weekly t-Test Results (df = 16, critical 2-tail = 2.120)

Benzene

	03/21/2007	03/28/2007	04/04/2007
03/14/2007	1.915	1.020	**6.190**
03/21/2007		-0.835	**2.712**
03/28/2007			**3.923**

Toluene

	03/21/2007	03/28/2007	04/04/2007
03/14/2007	**-7.155**	**-6.219**	**2.674**
03/21/2007		0.214	**8.608**
03/28/2007			**7.768**

Ethylbenzene

	03/21/2007	03/28/2007	04/04/2007
03/14/2007	-1.719	1.780	1.226
03/21/2007		**2.584**	**2.221**
03/28/2007			-0.547

Total Xylenes

	03/21/2007	03/28/2007	04/04/2007
03/14/2007	**-4.868**	**-3.670**	-0.918
03/21/2007		1.770	**3.517**
03/28/2007			**2.187**

224 Trimethylpentane

	03/21/2007	03/28/2007	04/04/2007
03/14/2007	**-2.860**	-0.966	0.278
03/21/2007		1.957	**2.853**
03/28/2007			1.029

Summary of Observations

Evaluation of data from Study 2 yields the following points of interest:

1) no concentration gradient across the study transect is observable,

2) minimum benzene concentrations exceed the predicted annual average for the Milwaukee roadway area, and

3) more variation is observed between weeks than between sites.

4b4. Results, Study 3

Study 3 was conducted in Milwaukee in the same general area as Study 1 between April 18 and May 16, 2007. During this time, 4 weekly samples were collected at each of 9 sites. Two sites were duplicate sites. The sites were arranged generally along a pair of west to east transects with Interstate 94 at the eastern end of the array. Two additional sites were included in the original study design, however vandalism prevented the collection of any samples from them.

All site locations were determined multiple times using a hand-held GPS unit, and the resulting latitude and longitudes averaged to fix the location. Distances were calculated using the Haversine formula. Table 4-D3 provides a site list, including general location, distance in meters and direction from the middle of Interstate 94, and whether or not the site is a duplicate site. Sites marked with an asterisk (*) denote those which were also a part of Study 1. Slight differences in distances are an result of GPS variability. Sites marked with a double asterisk (**) were discontinued due to repeated vandalism which prevented any samples from being successfully collected. Figure 4.4 on page 37 of this report shows a map of the sites.

Table 4-D3: Study 3 Site List

Site	Location	Meters	Direction	Dupe?
990*	Kosciuszko Park	588	West	Yes
991*	2179 6th St (on Grant)	222	West	No
992*	2200 5th Pl	126	West	No
993*	5th and Grant, near I-94 Fence	49	West	No
994*	I-94 SB	19	West	No
995*	I-94 NB	19	East	Yes
996	I-94 SB Betcher Exit	12	West	No
997	End Burnham on 5th Street	45	West	No
998	Corner Burnham and 5th Place	123	West	No
909**	Mid-block 6th & 7th Street	252	West	No
910**	SW Corner Burnham and 9th	542	West	No

Table 4-R6 summarizes results from each site, with averages, maxima, minima and relative standard deviations (RSD (%)) shown. Table 4-R7 on the following page summarizes results from each week of the study. Note all tables are arranged with sites listed from west to east, rather than in numerical order. Sites 994, 996 and 995 are all located along entrance and exit ramps of the interstate.

Table 4-R6: Study 3 Summary of Results by Site (n = 4)

Parameter	**site**	**990**	**991**	**992**	**998**	**993**	**997**	**994**	**996**	**995**
Benzene	**average**	0.48	0.79	0.69	0.74	0.67	0.59	0.62	0.69	0.58
	maximum	0.62	0.95	1.02	0.89	0.79	0.75	0.80	0.89	0.76
	minimum	0.39	0.69	0.54	0.66	0.51	0.45	0.47	0.61	0.47
	RSD (%)	20.4%	15.3%	32.0%	13.8%	18.3%	20.9%	22.1%	18.9%	22.8%
Toluene	**average**	0.96	1.67	1.48	1.44	1.27	1.19	1.22	1.25	1.05
	maximum	1.30	2.06	2.19	1.86	1.63	1.48	1.55	1.77	1.37
	minimum	0.75	1.46	1.21	1.25	1.11	1.04	1.05	1.05	0.89
	RSD (%)	24.2%	15.9%	31.5%	19.3%	18.5%	16.6%	18.3%	27.5%	20.4%
Ethylbenzene	**average**	0.14	0.26	0.24	0.20	0.17	0.23	0.20	0.18	0.15
	maximum	0.19	0.36	0.36	0.30	0.21	0.43	0.26	0.33	0.18
	minimum	0.08	0.18	0.16	0.15	0.12	0.12	0.13	0.10	0.14
	RSD (%)	32.6%	32.6%	37.4%	35.3%	27.5%	60.6%	26.6%	58.0%	10.3%
Total Xylenes	**average**	0.55	1.06	0.94	0.91	0.77	0.78	0.77	0.80	0.63
	maximum	0.80	1.45	1.50	1.23	1.07	1.13	1.08	1.39	0.87
	minimum	0.26	0.77	0.62	0.67	0.57	0.64	0.55	0.47	0.46
	RSD (%)	40.3%	27.7%	40.7%	25.8%	28.6%	30.0%	28.8%	51.0%	28.1%
224-Trimethyl pentane	**average**	0.50	0.98	0.84	0.82	0.72	0.68	0.67	0.74	0.57
	maximum	0.69	1.17	1.23	1.12	0.89	0.84	0.86	0.98	0.73
	minimum	0.41	0.80	0.69	0.67	0.62	0.58	0.56	0.63	0.48
	RSD (%)	25.9%	16.8%	31.2%	24.8%	16.7%	17.1%	20.6%	21.8%	19.0%

Note that in all cases, the two sites with the lowest concentrations are 990 (furthest from the roadway) and 995 (along the north bound interstate). Highest concentrations are observed at site 991 (220 meters west of the roadway, along Grant Street).

Table 4-R7: Study 3 Summary of Results by Week (n = 9)

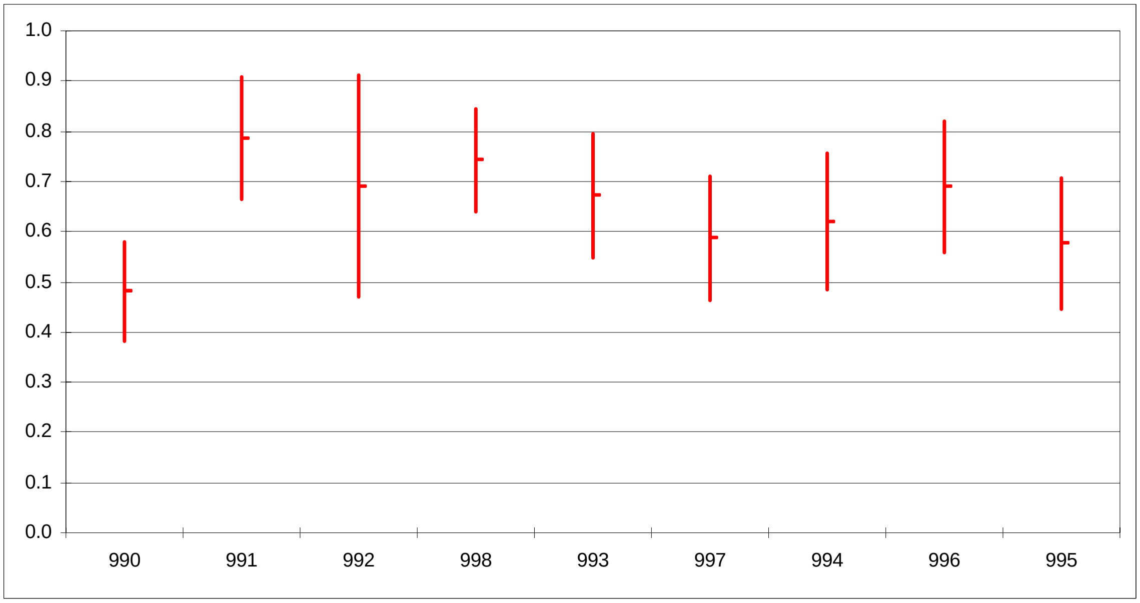
Parameter	date	18-Apr-07	25-Apr-07	02-May-07	09-May-07
Benzene	**average**	0.83	0.64	0.59	0.54
	maximum	1.02	0.74	0.82	0.69
	minimum	0.62	0.49	0.42	0.39
	RSD (%)	14.5%	12.3%	19.9%	19.2%
Toluene	**average**	1.69	1.15	1.15	1.13
	maximum	2.19	1.46	1.66	1.52
	minimum	1.30	0.75	0.89	0.88
	RSD (%)	18.1%	17.8%	20.1%	17.3%
Ethylbenzene	**average**	0.29	0.15	0.20	0.15
	maximum	0.43	0.20	0.30	0.20
	minimum	0.18	0.08	0.13	0.11
	RSD (%)	30.5%	27.0%	25.6%	20.1%
Total Xylenes	**average**	1.17	0.56	0.76	0.71
	maximum	1.50	0.77	1.10	0.92
	minimum	0.80	0.26	0.55	0.55
	RSD (%)	21.1%	26.5%	21.9%	17.9%
224-Trimethyl pentane	**average**	0.95	0.67	0.65	0.63
	maximum	1.23	0.80	1.05	0.89
	minimum	0.69	0.41	0.48	0.43
	RSD (%)	20.5%	17.9%	26.1%	20.7%

Note again that the variability of the data (as measured by the RSD(%)) is greater within sites (Table 4-R6) than it is within weeks (Table 4-R7). This indicates that the individual results from each site are more closely related to the results obtained from the other sites during the same time period, than they are to the results obtained from the same site during the other weeks of the study period. Again, weekly variability across the sites is less than predicted by the model.

The following series of graphs present the data shown in the tables. Figures4-RG8a to 4-RG8e illustrate results for each parameter grouped by site (as per Table 4-R6), showing the average and upper and lower confidence intervals. Note that apparent differences are similar to those obtained when evaluating the Study 1 with the third week excluded (Figures 4-RG3a to 4-RG3e).

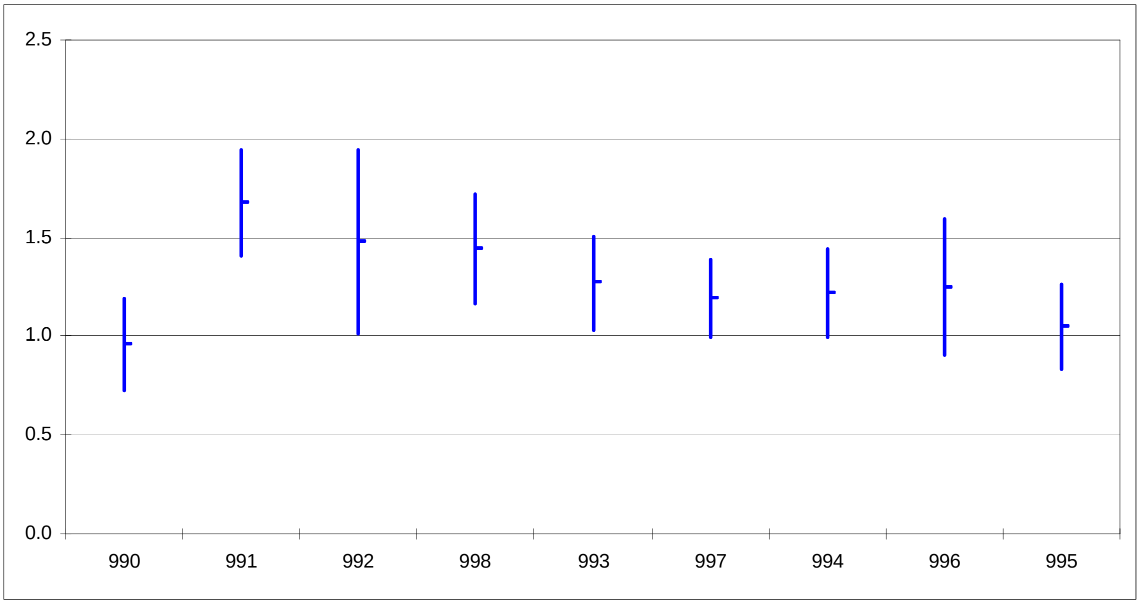
Figures 4-RG9a to 4-RG9e illustrate the results on a weekly basis (as per Table 4-R6). Figures 4-RG10a to 4-RG10d show individual results from each week of the study, plotted versus distance from the center of the interstate. Note how closely different sites at the same relative distance to the roadway follow each other in the latter graphs.

Figure 4-RG8a: Study 3 Benzene Results



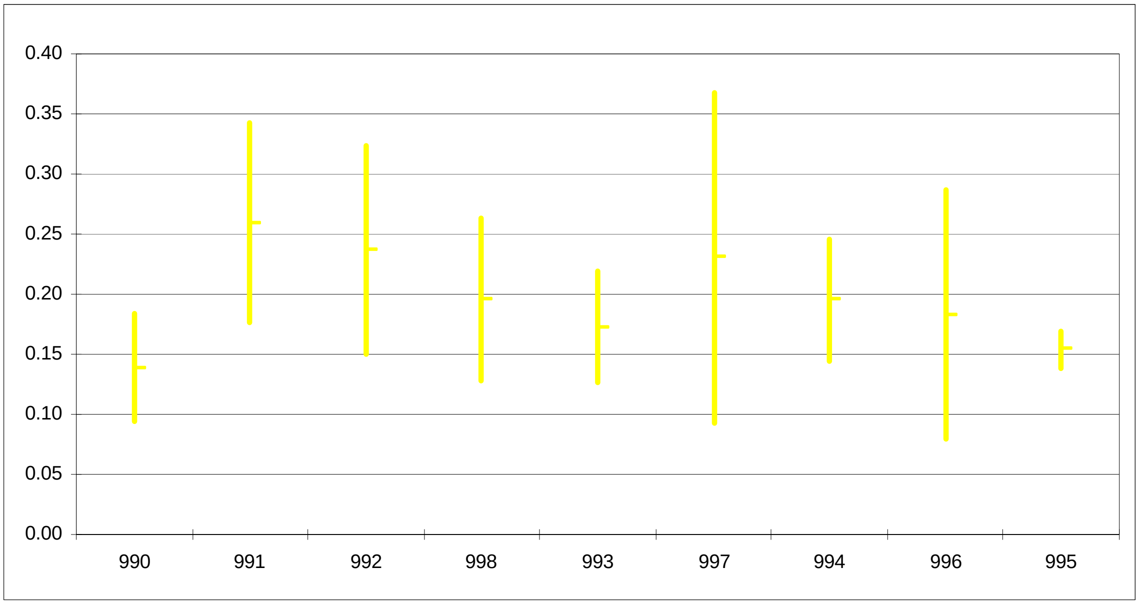
vertical axis = concentration in ug/m3
horizontal axis = site number

Figure 4-RG8b: Study 3 Toluene Results



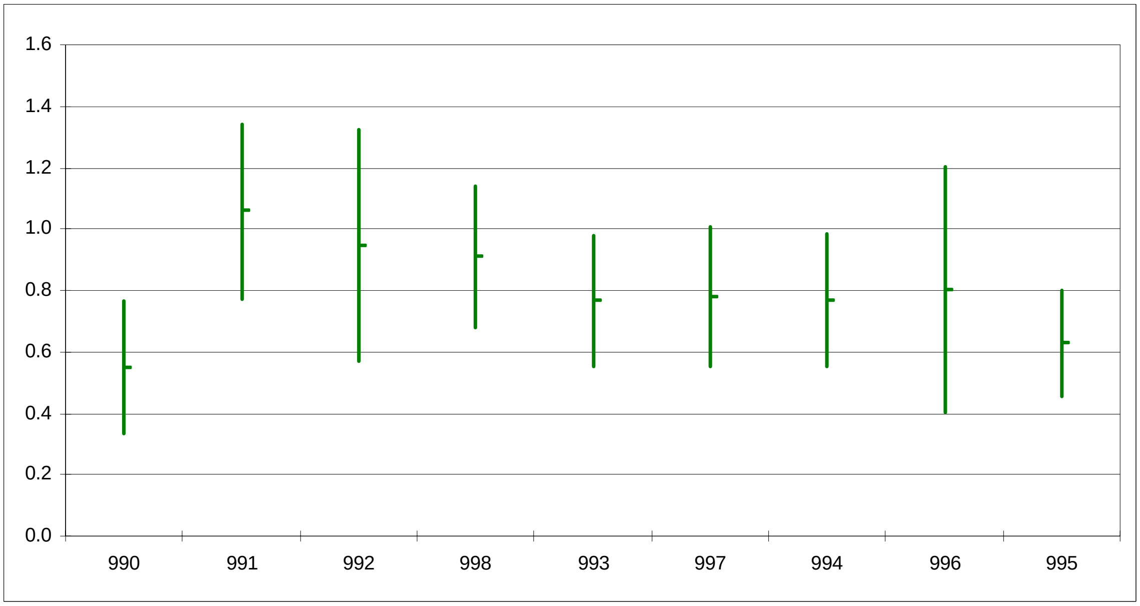
vertical axis = concentration in ug/m3
horizontal axis = site number

Figure 4-RG8c: Study 3 Ethylbenzene Results



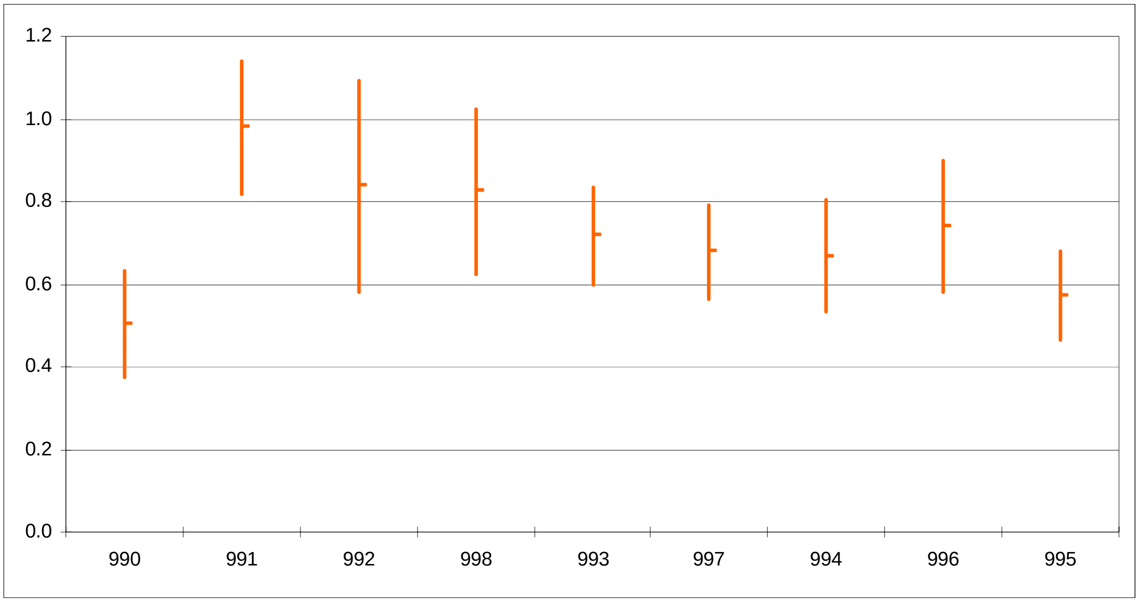
vertical axis = concentration in ug/m3
horizontal axis = site number

Figure 4-RG8d: Study 3 Total Xylene Results



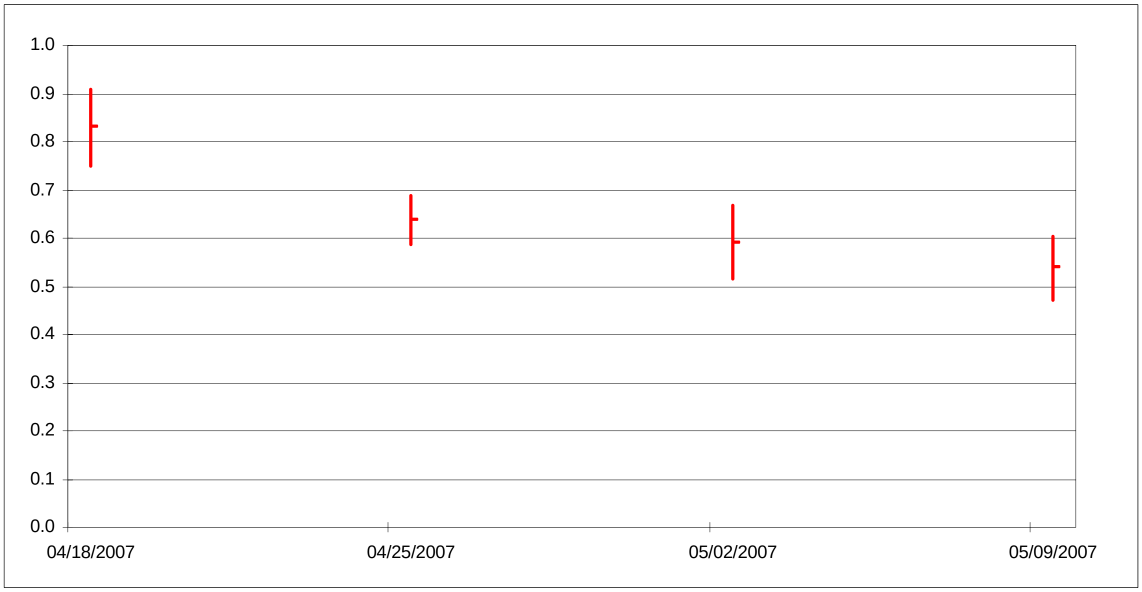
vertical axis = concentration in ug/m3
horizontal axis = site number

Figure 4-RG8e: Study 3 2,2,4-Trimethylpentane Results



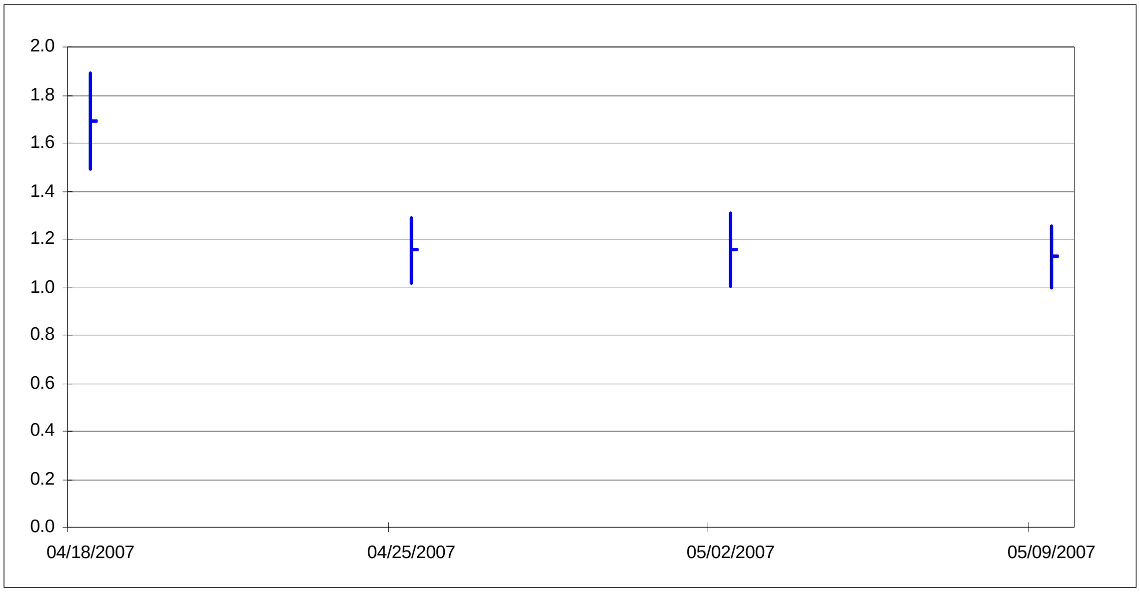
vertical axis = concentration in ug/m3
horizontal axis = site number

Figure 4-RG9a: Study 3 Benzene Results by Week



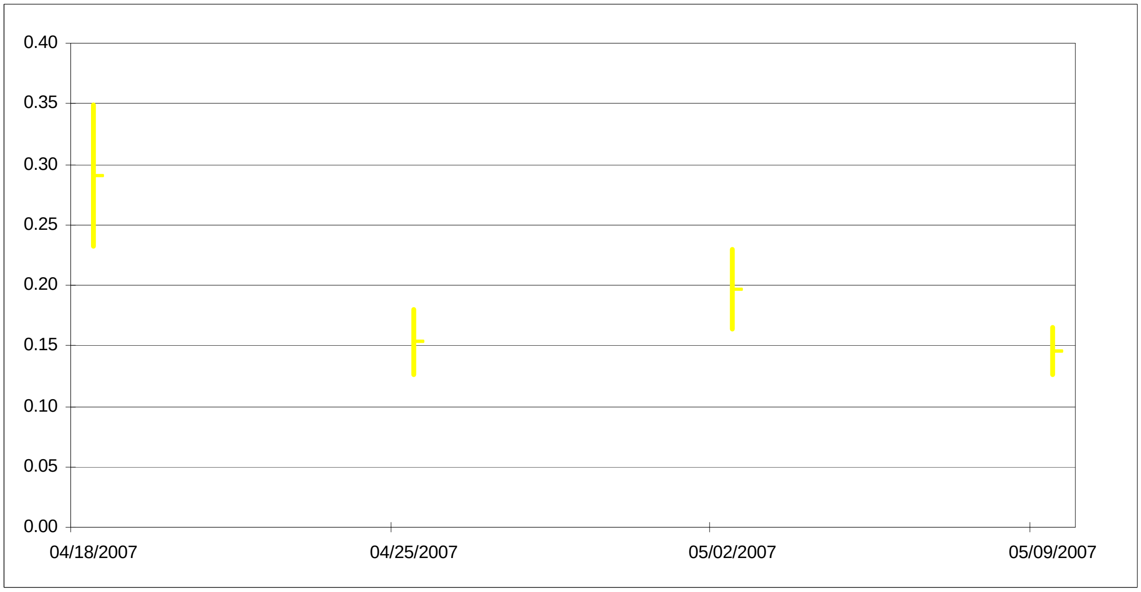
vertical axis = concentration in ug/m3
horizontal axis = start date

Figure 4-RG9b: Study 3 Toluene Results by Week



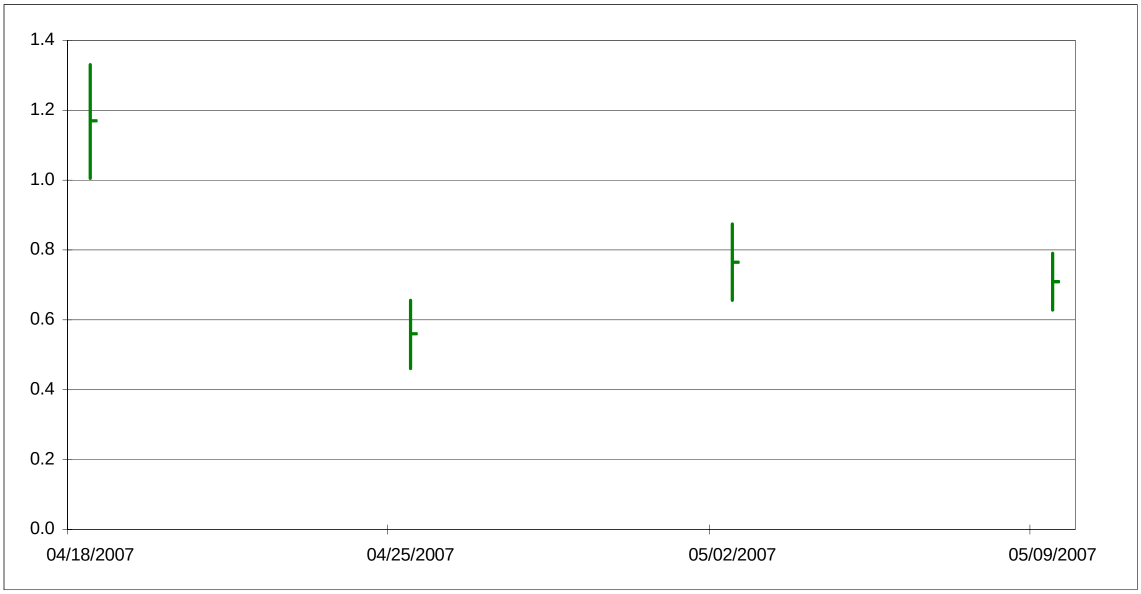
vertical axis = concentration in ug/m3
horizontal axis = start date

Figure 4-RG9c: Study 3 Ethylbenzene Results by Week



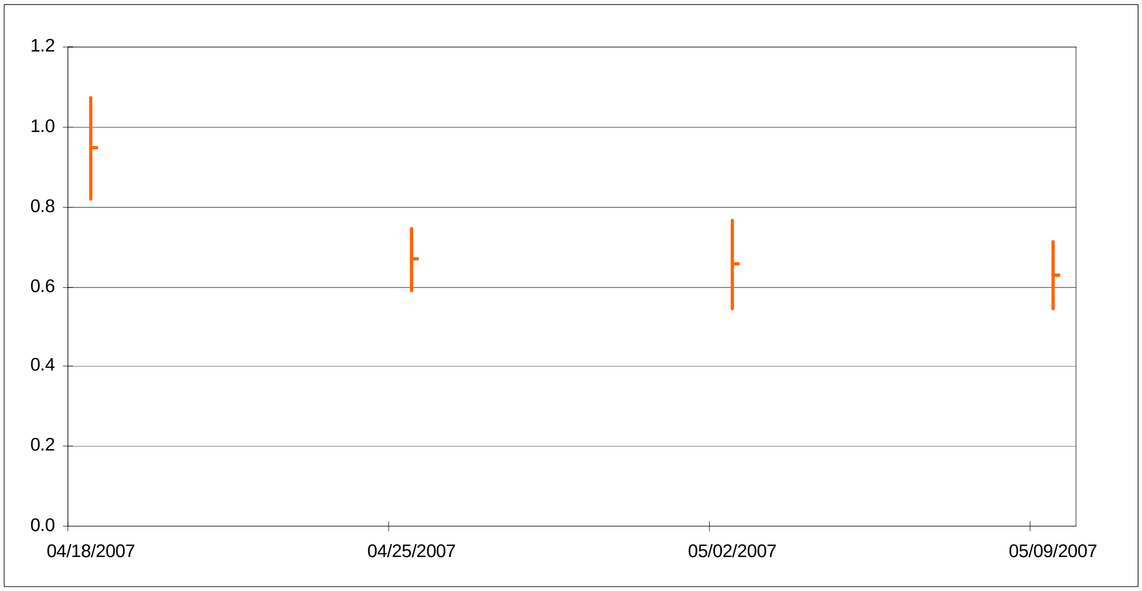
vertical axis = concentration in ug/m3
horizontal axis = start date

Figure 4-RG9d: Study 3 Total Xylene Results by Week



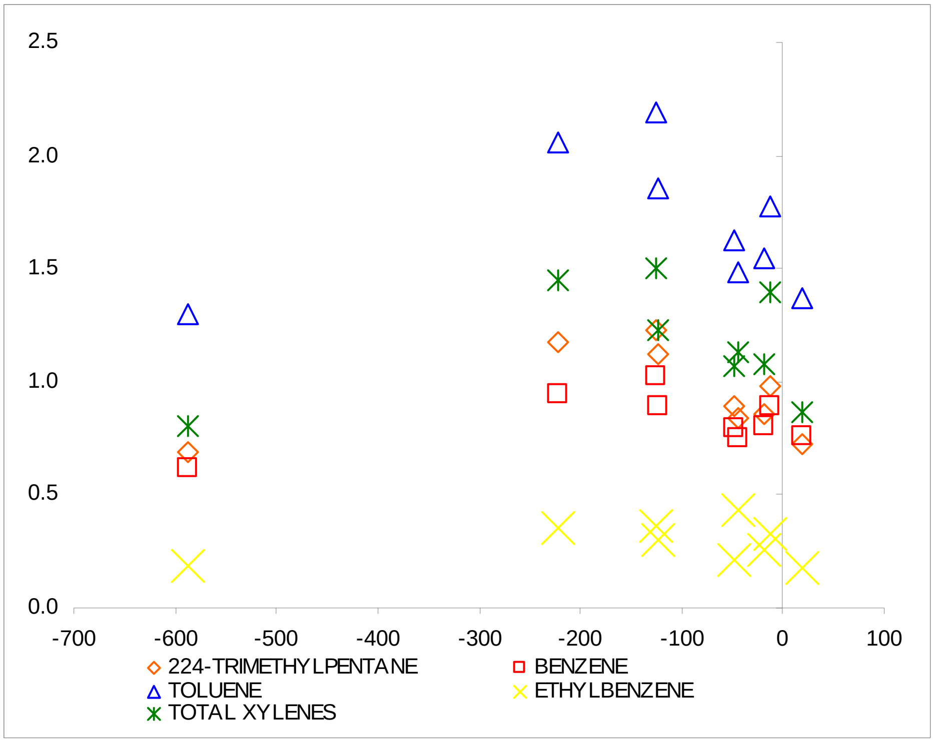
vertical axis = concentration in ug/m3
horizontal axis = start date

Figure 4-RG9e: Study 3 2,2,4-Trimethylpentane Results by Week



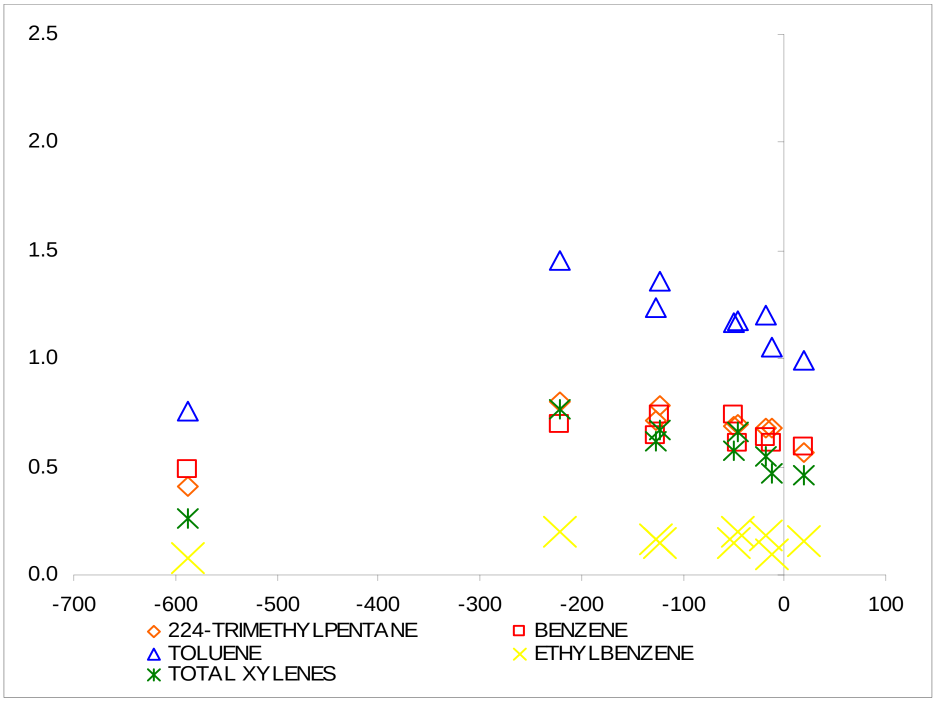
vertical axis = concentration in ug/m3
horizontal axis = start date

Figure 4-RG10a: Study 3 Results, 04/18- 25/2007



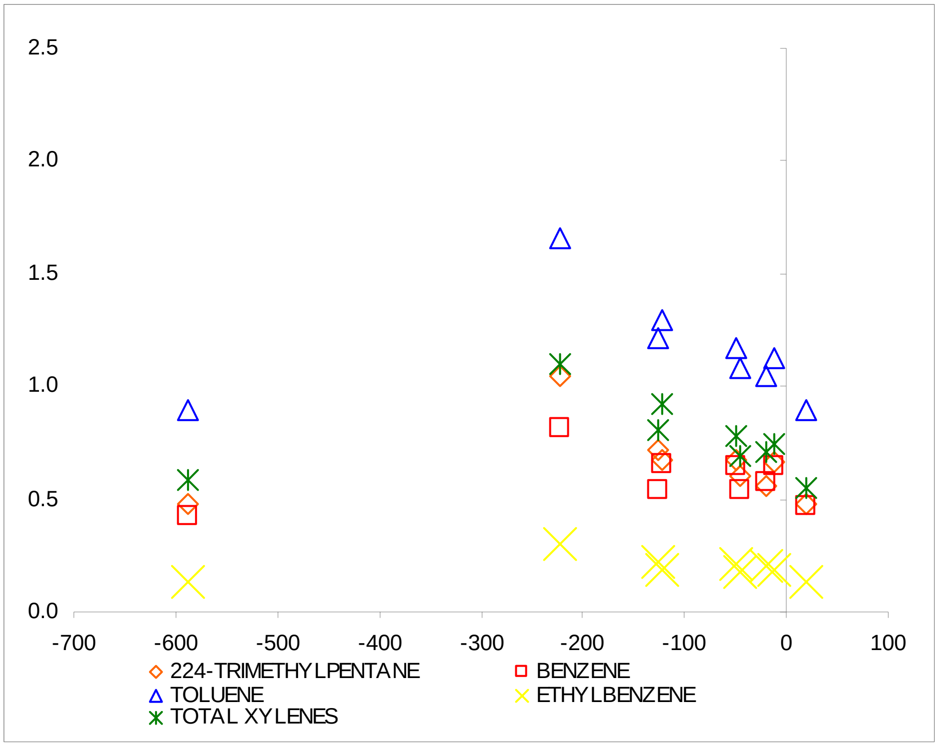
vertical axis = concentration in ug/m3
horizontal axis = distance to center of interstate, in meters

Figure 4-RG10b: Study 3 Results, 04/25 – 05/02/2007



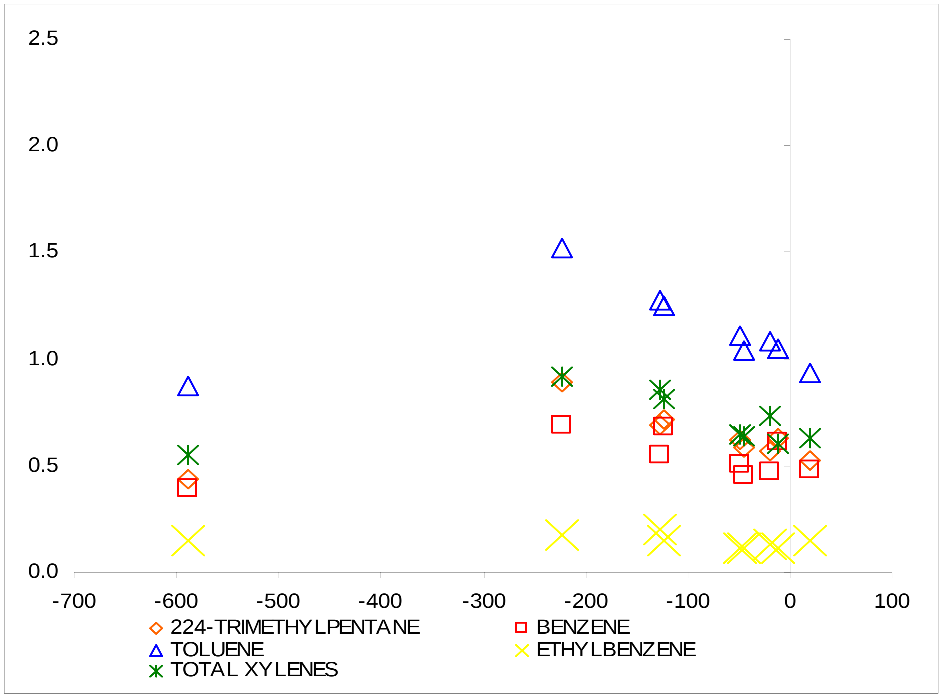
vertical axis = concentration in ug/m3
horizontal axis = distance to center of interstate, in meters

Figure 4-RG10c: Study 3 Results, 05/02 – 09/2007



vertical axis = concentration in ug/m3
horizontal axis = distance to center of interstate, in meters

Figure 4-RG10d: Study 3 Results, 05/09 – 16/2007



vertical axis = concentration in ug/m3
horizontal axis = distance to center of interstate, in meters

The apparent differences between sites are explored in the following tables, wherein the results of t-tests are shown. Statistical relevance is limited to determinations yielding 95% confidence of a two tail difference. Tables 4-S9a through 4-S9e below tabulate these values for all parameters. Note that statistically significant differences appear for all parameters.

Table 4-S9a: Study 3 t-Test Results for Benzene (df = 6, critical 2-tail = 2.447)

Site	991	992	998	993	997	994	996	995
990	**-3.861**	-1.695	**-3.597**	-2.377	-1.319	-1.619	**-2.517**	-1.134
991		0.753	0.566	1.305	2.281	1.785	1.060	2.326
992			-0.411	0.140	0.801	0.524	-0.005	0.873
998				0.845	1.894	1.381	0.596	1.951
993					0.961	0.548	-0.204	1.050
997						-0.359	-1.138	0.121
994							-0.727	0.462
996								1.219

Table 4-S9b: Study 3 t-Test Results for Toluene (df = 6, critical 2-tail = 2.447)

Site	991	992	998	993	997	994	996	995
990	**-3.987**	-1.968	**-2.622**	-1.859	-1.525	-1.618	-1.385	-0.570
991		0.711	1.193	2.232	**2.839**	**2.547**	1.913	**3.594**
992			0.143	0.788	1.106	0.975	0.778	1.648
998				0.918	1.417	1.197	0.845	2.193
993					0.485	0.286	0.094	1.366
997						-0.189	-0.276	0.978
994							-0.130	1.103
996								0.974

Table 4-S9c: Study 3 t-Test Results for Ethylbenzene (df = 6, critical 2-tail = 2.447)

Site	991	992	998	993	997	994	996	995
990	**-2.516**	-1.970	-1.380	-1.027	-1.244	-1.638	-0.766	-0.626
991		0.365	1.163	1.794	0.358	1.294	1.126	**2.456**
992			0.730	1.282	0.082	0.812	0.780	1.844
998				0.558	-0.440	0.015	0.203	1.185
993					-0.782	-0.647	-0.181	0.747
997						0.469	0.538	1.086
994							0.206	1.526
996								0.544

Table 4-S9d: Study 3 t-Test Results for Total Xylene (df = 6, critical 2-tail = 2.447)

Site	991	992	998	993	997	994	996	995
990	**-2.772**	-1.789	-2.232	-1.398	-1.433	-1.401	-1.092	-0.557
991		0.461	0.792	1.589	1.483	1.575	1.009	**2.516**
992			0.164	0.809	0.739	0.799	0.507	1.503
998				0.885	0.780	0.870	0.447	1.915
993					-0.080	-0.010	-0.157	0.988
997						0.070	-0.100	1.037
994							-0.149	0.993
996								0.786

Table 4-S9e: Study 3 t-Test Results for 2,2,4-Trimethylpentane (df = 6, critical 2-tail = 2.447)

Site	991	992	998	993	997	994	996	995
990	**-4.538**	-2.292	**-2.654**	-2.411	-2.012	-1.736	-2.275	-0.815
991		0.920	1.180	**2.583**	**2.991**	**2.905**	2.086	**4.130**
992			0.077	0.843	1.114	1.150	0.641	1.876
998				0.914	1.245	1.274	0.658	2.182
993					0.456	0.534	-0.225	1.784
997						0.120	-0.610	1.338
994							-0.672	1.088
996								1.715

All of the results obtained during the third study are greater than the estimated LOQ, and can thus be considered generally reliable. The magnitude of the statistically significant differences tabulated above are all greater than 0.1 ug/m^3.

Weekly results across all sites were subjected to t-tests to determine whether or not differences observed were statistically relevant. Results from these tests are shown in Table 4-S10 on the following page.

Table 4-S10: Study 3 Weekly t-Test Results (df = 16, critical 2-tail = 2.120)

Benzene			
	04/25/2007	05/02/2007	05/09/2007
04/18/2007	**3.984**	**4.248**	**5.520**
04/25/2007		1.006	**2.333**
05/02/2007			1.025
Toluene			
	04/25/2007	05/02/2007	05/09/2007
04/18/2007	**4.361**	**4.188**	**4.659**
04/25/2007		0.005	0.295
05/02/2007			0.271
Ethylbenzene			
	04/25/2007	05/02/2007	05/09/2007
04/18/2007	**4.245**	**2.778**	**4.663**
04/25/2007		-2.031	0.403
05/02/2007			**2.619**
Total Xylenes			
	04/25/2007	05/02/2007	05/09/2007
04/18/2007	**6.344**	**4.062**	**4.968**
04/25/2007		**-2.747**	**-2.295**
05/02/2007			0.793
224 Trimethylpentane			
	04/25/2007	05/02/2007	05/09/2007
04/18/2007	**3.664**	**3.384**	**4.076**
04/25/2007		0.191	0.666
05/02/2007			0.363

Summary of Observations

Several important observations can be made based on these results:

1) while a concentration gradient across the study transect was observed, it was not of the magnitude or position as predicted

2) maximum concentrations were observed at sites well removed from the interstate, indicating that the contribution of side roads is underestimated in the model

3) observed concentrations of benzene were in all cases significantly higher than predicted

4) results from individual sites have more in common with results from other sites collected at the same time than they do with results obtained from the same site during different weeks

4c.Toluene:Benzene Ratio

The ratio of toluene to benzene has been explored as a means to evaluate distance from mobile emission sources (Gelencser, 1997). This parameter is useful, because the ratio found in exhaust gases is generally consistent, and because toluene and benzene decay at significantly different rates in the atmosphere. This provides a means to estimate the age of the air mass associated with the contaminants, with a high toluene to benzene ratio associated with fresh air masses and a close proximity to emission sources, and a low ratio associated with aged air masses and increased distance from sources.

There is a great deal of variability in the toluene to benzene ratios reported in the literature, but typically urban studies yield ratios in excess of 2 (toluene concentration exceeding benzene concentrations by more than a factor of 2), while some studies in less populated areas, or impacted by air masses moving through remote areas report ratios of less than 1.

The toluene:benzene ratios generated by the data in our studies tend to follow this pattern, with the urban sampling sites yielding ratios ranging from about 1.5 to about 2.3, and the rural results yielding ratios ranging from about 0.3 to 1.2. Tables 4-R8 through 4-R14 present summaries of the toluene benzene ratios for each study, grouped both by site and by week.

Table 4-R8: Summary of Toluene:Benzene Ratio Results by Site, Study 1 (n = 5)

Parameter	site	990	991	992	993	994	995	996	997	998	999
Toluene: Benzene Ratio	average	1.72	2.01	2.05	1.91	1.77	1.79	1.82	1.68	1.75	1.85
	maximum	2.13	2.34	2.28	2.16	2.04	2.08	2.17	2.12	2.18	2.32
	minimum	1.49	1.72	1.84	1.70	1.52	1.66	1.54	1.47	1.52	1.58
	RSD (%)	14.9%	14.9%	9.5%	9.4%	11.3%	9.8%	13.0%	15.4%	15.1%	15.6%

Table 4-R9: Summary of Toluene:Benzene Ratio Results by Week, Study 1 (n = 10)

Parameter	site	8-Nov-06	15-Nov-06	22-Nov-06	29-Nov-06	6-Dec-06
Toluene:Benzene Ratio	average	1.92	1.74	2.18	1.68	1.66
	maximum	2.29	1.95	2.34	1.94	2.09
	minimum	1.69	1.54	2.04	1.52	1.47
	RSD (%)	10.0%	6.8%	4.7%	8.6%	11.0%

Table 4-R10: Summary of Toluene:Benzene Ratio Results by Site, Study 1 without week 3 (n = 4)

Parameter	site	990	991	992	993	994	995	996	997	998	999
Toluene:Benzene Ratio	average	1.62	1.92	2.00	1.85	1.71	1.72	1.74	1.57	1.64	1.73
	maximum	1.80	2.29	2.19	1.98	1.90	1.84	1.92	1.69	1.78	1.85
	minimum	1.49	1.72	1.84	1.70	1.52	1.66	1.54	1.47	1.52	1.58
	RSD (%)	8.1%	14.0%	8.4%	7.0%	9.1%	4.8%	8.9%	5.8%	8.2%	7.5%

Table 4-R11: Study 2 Summary of Results by Site (n = 4)

Parameter	site	990	991	992	993	994	995	996	997	998
Toluene: Benzene Ratio	average	0.61	0.62	0.69	0.75	0.76	0.77	0.67	0.72	0.74
	maximum	0.95	0.96	1.10	0.98	1.01	1.19	0.99	1.05	0.92
	minimum	0.38	0.32	0.39	0.61	0.60	0.45	0.50	0.39	0.49
	RSD (%)	43.8%	45.6%	44.5%	23.2%	25.3%	43.5%	33.3%	51.2%	24.8%

Table 4-R12: Study 2 Summary of Results by Week (n = 9)

Parameter	site	14-Mar-07	21-Mar-07	28-Mar-07	04-Apr-07
Toluene: Benzene Ratio	**average**	0.51	0.93	0.87	0.50
	maximum	0.62	1.10	1.19	0.79
	minimum	0.39	0.71	0.65	0.32
	RSD (%)	15.4%	12.6%	21.5%	30.0%

Table 4-R13: Study 3 Summary of Results by Site (n = 4)

Parameter	site	990	991	992	998	993	997	994	996	995
Toluene: Benzene Ratio	**average**	2.00	2.13	2.15	1.93	1.91	2.05	1.99	1.79	1.83
	maximum	2.24	2.21	2.30	2.09	2.19	2.30	2.31	2.00	1.93
	minimum	1.54	2.03	1.93	1.83	1.58	1.93	1.83	1.71	1.69
	RSD (%)	15.7%	3.9%	7.5%	6.3%	14.2%	8.2%	10.8%	7.7%	6.1%

Table 4-R14: Study 3 Summary of Results by Week (n = 9)

Parameter	date	18-Apr-07	25-Apr-07	02-May-07	09-May-07
Toluene: Benzene Ratio	**average**	2.03	1.80	1.96	2.12
	maximum	2.18	2.10	2.24	2.31
	minimum	1.80	1.54	1.74	1.71
	RSD (%)	5.8%	10.2%	8.1%	10.7%

Apparent differences between the sites and the weeks were explored using Student's t-tests, the results of which are reported in Tables 4-S11 through 4-S16 following. Note that no table is presented for the intersite comparison for Study 2. This is because there were no statistically significant differences between sites. Statistically relevant differences observed are presented in **boldface**. Note that urban sites removed from the interstate, but located along side streets (991 and 992) tend to yield significantly higher toluene:benzene ratios, implying a greater source input than those sites located along the interstate highway. Note also that weekly differences from all three studies show statistically significant differences.

Table 4-S11: Study 1 T-Test Results for Tol:Benz Ratio (df = 8, critical 2-tail = 2.306)

Site	991	992	993	994	995	996	997	998	999
990	-1.642	**-2.333**	-1.392	-0.382	-0.548	-0.670	0.211	-0.201	-0.746
991		-0.292	0.603	1.450	1.373	1.082	1.827	1.431	0.861
992			1.185	2.241	2.212	1.687	**2.552**	2.054	1.326
993				1.156	1.055	0.680	1.624	1.127	0.433
994					-0.173	-0.353	0.613	0.150	-0.466
995						-0.215	0.789	0.302	-0.348
996							0.884	0.448	-0.146
997								-0.407	-0.940
998									-0.545

Table 4-S12: Study 1 Weekly t-Test Results (df = 18, critical 2-tail = 2.101)

	Toluene:Benzene Ratio			
	11/15/2006	**11/22/2006**	**11/29/2006**	**12/06/2006**
11/08/2006	**2.519**	**-3.870**	**3.180**	**3.039**
11/15/2006		**-9.024**	1.051	1.097
11/22/2006			**9.084**	**7.848**
11/29/2006				0.187

Table 4-S13: Study 1 (no week 3) t-Test Results for Toluene:Benzene Ratio (df = 6, critical 2-tail = 2.447)

Site	**991**	**992**	**993**	**994**	**995**	**996**	**997**	**998**	**999**
990	-2.060	**-3.569**	**-2.543**	-0.904	-1.385	-1.183	0.525	-0.311	-1.221
991		-0.459	0.489	1.388	1.429	1.212	**2.463**	1.854	1.311
992			1.371	**2.512**	**2.920**	2.279	**4.406**	**3.260**	**2.526**
993				1.403	1.659	1.135	**3.474**	2.195	1.333
994					-0.169	-0.253	1.479	0.610	-0.200
995						-0.148	2.419	0.987	-0.070
996							1.799	0.885	0.075
997								-0.874	-1.945
998									-0.891

Table 4-S14: Study 2 Weekly t-Test Results (df = 16, critical 2-tail = 2.120)

	Toluene:Benzene Ratio		
	03/21/2007	03/28/2007	04/04/2007
03/14/2007	**-8.996**	**-5.369**	0.122
03/21/2007		0.799	**6.746**
03/28/2007			**4.620**

Table 4-S15: Study 3 t-Test Results for Toluene:Benzene Ratio (df = 6, critical 2-tail = 2.447)

Site	**991**	**992**	**998**	**993**	**997**	**994**	**996**	**995**
990	-0.794	-0.866	0.387	0.440	-0.303	0.040	1.223	1.004
991		-0.266	**2.644**	1.557	0.804	1.183	**4.232**	**4.276**
992			2.156	1.550	0.851	1.192	**3.419**	**3.261**
998				0.176	-1.152	-0.464	1.576	1.239
993					-0.913	-0.483	0.781	0.520
997						0.452	2.437	2.202
994							1.581	1.316
996								-0.478

Table 4-S16: Study 3 Weekly t-Test Results (df = 16, critical 2-tail = 2.120)

Toluene:Benzene Ratio			
	04/25/2007	05/02/2007	05/09/2007
04/18/2007	**3.167**	1.081	-0.993
04/25/2007		-1.963	**-3.230**
05/02/2007			-1.686

Summary of Observations

Evaluation of the toluene to benzene ratios present in our dataset lead to several pertinent observations:

1) statistically significant differences exist between the different sites and weeks

2) maximum ratios, associated in the literature with the least aged air masses were observed at sites well removed from the interstate, indicating that the contribution of side roads is underestimated in the model

3) rural toluene to benzene ratios were reversed, with most benzene concentrations exceeding observed toluene concentrations

4d. Study Results – Passive Canister Samplers

As part of the work for Study 1 we collected paired canisters, with the first canister collected at our north bound Highway 94 exit site, hereafter roadway site and the second at our Kosciuszko Park site, hereafter the park site. Between 11/28 and 12/19 we collected 7 samples pairs. Only 3 of 7 pairs were considered valid. A sample pair is considered valid if both samples meet criteria for validity. The main criteria we used for validation was that the canister was filled to ambient pressure. Invalid canisters show a vacuum or partial vacuum indicating the canister did not sample. Valid canisters were processed and analyzed. Results were corrected for dilution. Results of the valid canisters are shown in Table 4-C1 and shown visually in Figure 4-C1 & 4-C2. Results show that benzene concentrations are lower at the park site, this is however an empirical judgment and we did not attempt any statistical testing.

Table 4-C1: Results for Passive Canister Samples collected in Field Study 1

Sample Date	Compound Name	Park Conc. (ug/m3)	Roadway Conc (ug/m3)
12/05/06	Benzene	1.139	1.29
12/11/06	Benzene	1.152	1.601
12/15/06	Benzene	0.808	0.831
12/05/06	Ethylbenzene	0.514	0.341
12/11/06	Ethylbenzene	0.483	1.093
12/15/06	Ethylbenzene	0.226	0.469
12/05/06	Toluene	1.826	3.103
12/11/06	Toluene	2.752	5.429
12/15/06	Toluene	1.29	1.754
12/05/06	Xylene	0.872	2.244
12/11/06	Xylene	3.697	3.385
12/15/06	Xylene	6.125	2.576
12/05/06	224-Tmp	1.199	1.568
12/11/06	224-Tmp	1.376	2.361
12/15/06	224-Tmp	1	0.708

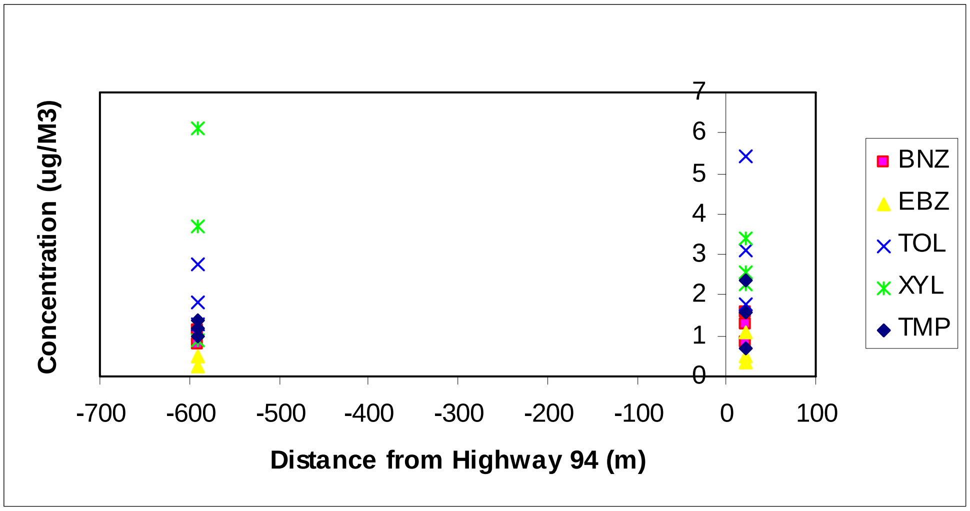


Figure 4-C1: Results of canister analysis for key roadway compounds. The x-axis represents west to east with the highway middle at 0. The park site is -590 meters and the roadway site 21 meters.

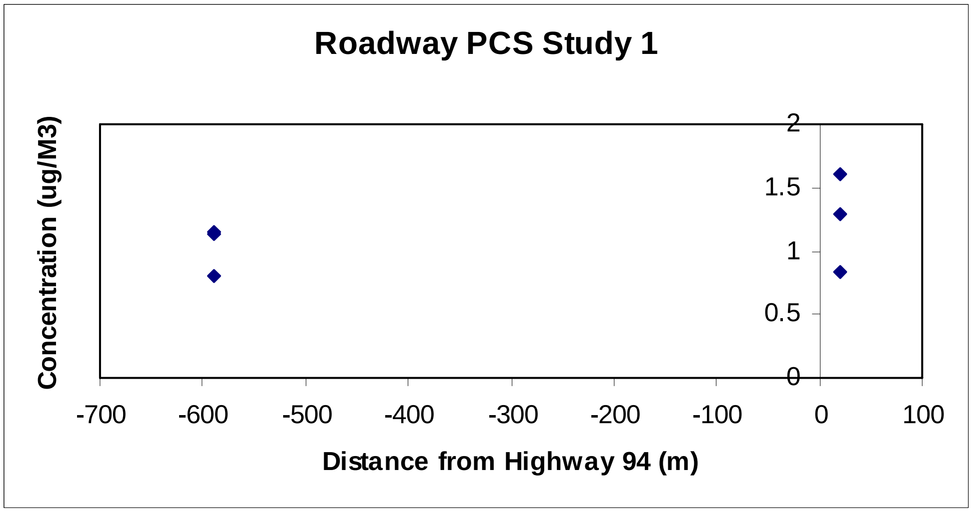


Figure 4-C2 Results of canister analysis for benzene at the park and roadway site. The x-axis represents west to east with the highway middle at 0. The park site is -590 meters and the roadway site 21 meters. Pair data suggests that concentrations are lower at the park site.

No canister testing was included as part of Study 2.

In Study 3 we repeated canister sampling conducted in Study1. We collected 13 canister pairs in total for this study. Ten sample pairs were judged valid. Canisters were analyzed for all 55 PAMS compounds. We report on benzene and 5 additional compounds used to support the benzene measurements.

Data for Study 3 is reported in Table 4-C2, including summary and statistical data. Data is also shown graphically in Figure 4-C3 & 4-C4. As in Study 1, the data suggests that benzene is lower at the park site.

The park mean benzene concentrations are lower and show less variability than the concentrations measured near the roadway. When the confidence intervals for the data are included (shown in Figure 4-C5), concentrations at the park site and the roadway site overlap, suggesting data is not statistically different. When data is analyzed as paired data and a “t” test applied, the data shows benzene concentrations at the park and at the roadway are statistically different.

An examination of the other BETXs also shows most are higher at the roadway site. However there is not a statistical difference in the site concentrations. Concentrations, particularly, toluene and xylene are both higher and more variable than expected based on the benzene. This suggests that there are other sources of these solvents. Meteorological data for Study 3 shows dominant winds are coming from the east. Located to the east of the study area is a marina and several boat repair facilities. These are minor sources that are not inventoried. While we can not predict or verify the compounds and emissions from these minor sources, we suspect they are included in the roadway canister samples.

Table 4-C2: Component Summary Report From Analysis Study 3 Passive Canister Sample

		BENZENE (ugm3)	TOLUENE (ugm3)	ETHYL-BENZENE (ugm3)	224 TMP (ugm3)	XYLENE (ugm3)
Park	Mean	0.70	2.38	0.49	1.20	0.88
	StDev	0.333	2.198	0.184	1.184	0.495
Roadway	Mean	1.08	20.11	1.54	1.47	2.88
	StDev	0.657	43.626	2.281	1.031	3.829
t- Statistic		**-1.91273**	-1.26984	-1.43327	-0.55882	-1.68037

* t-critical for all compound 1.833113

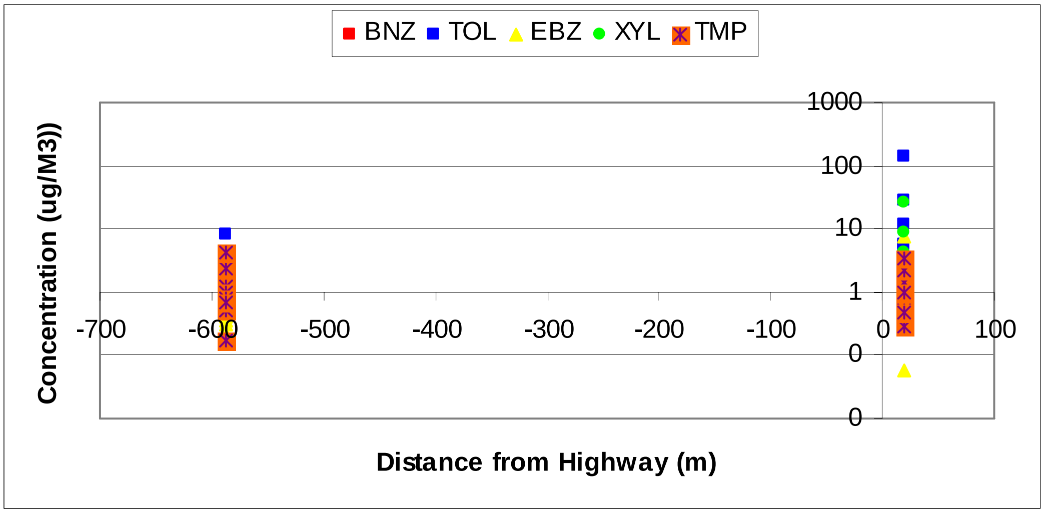


Figure 4-C3. Canister samples concentrations for Park and Roadway sites for all compounds (N=10). The x-axis represents west to east with the highway middle at 0. The park site is -590 meters and the roadway site 21 meters.

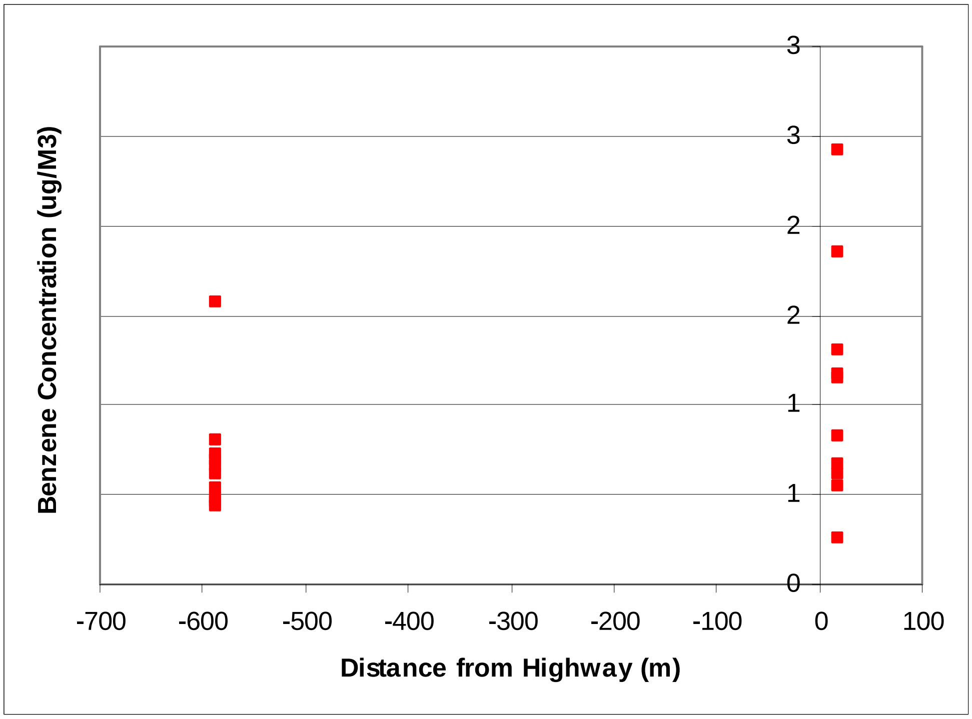


Figure 4-C4. Benzene concentration measured in canister samples collected at the Park and Roadway sites for Study 3 (N=10). The x-axis represents west to east with the highway middle at 0. The park site is -590 meters and the roadway site 21 meters.

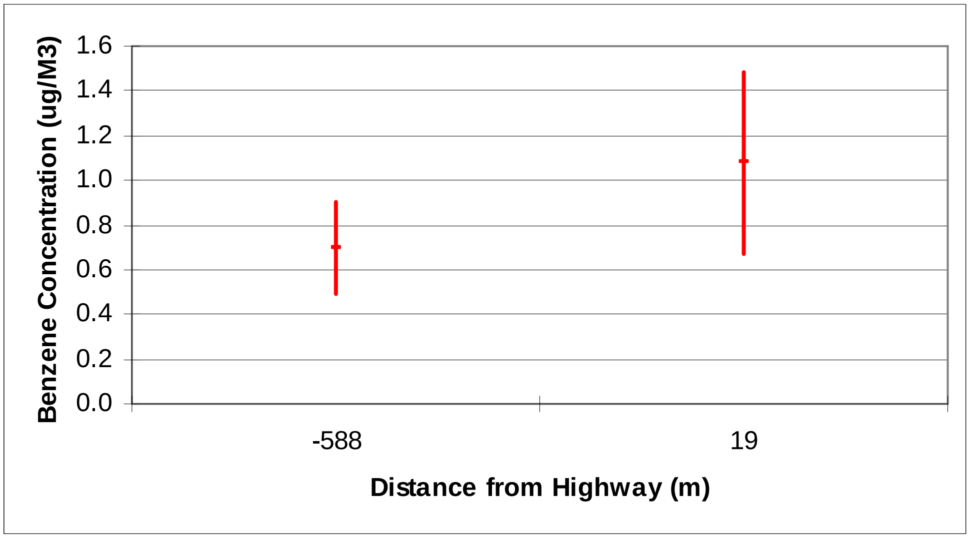


Figure 4-C5. Benzene concentration graphed as mean and the 95% confidence intervals for canister samples collected at the Park and Roadway sites for Study 3 (N=10). Overlap of the confidence intervals suggest site concentrations are not statistically different when evaluated as a set. The x-axis represents west to east with the highway middle at 0. The park site is -590 meters and the roadway site 21 meters.

4e. Comparison of passive techniques for the Field Study

Figures 4-E 1 & E2 show graphical comparisons of benzene concentrations measured by the two passive sampling techniques used in this study. As expected, the data shows that 1-hour peak concentrations are greater than weekly average concentration collected on passive adsorbent sampler. The graphs show that the benzene concentration data from the two methods are comparable in magnitude. This provides additional confidence that the two methods have accurately measured ambient benzene concentrations.

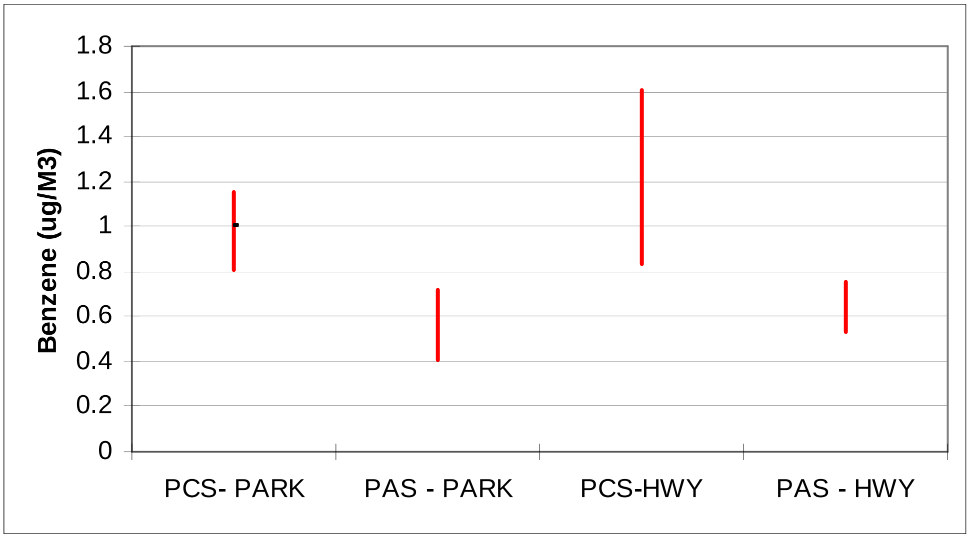


Figure 4-E1: Benzene concentration ranges for PCS and PAS collected in Study 1. Benzene is presented as the range of concentrations measured (n=3)

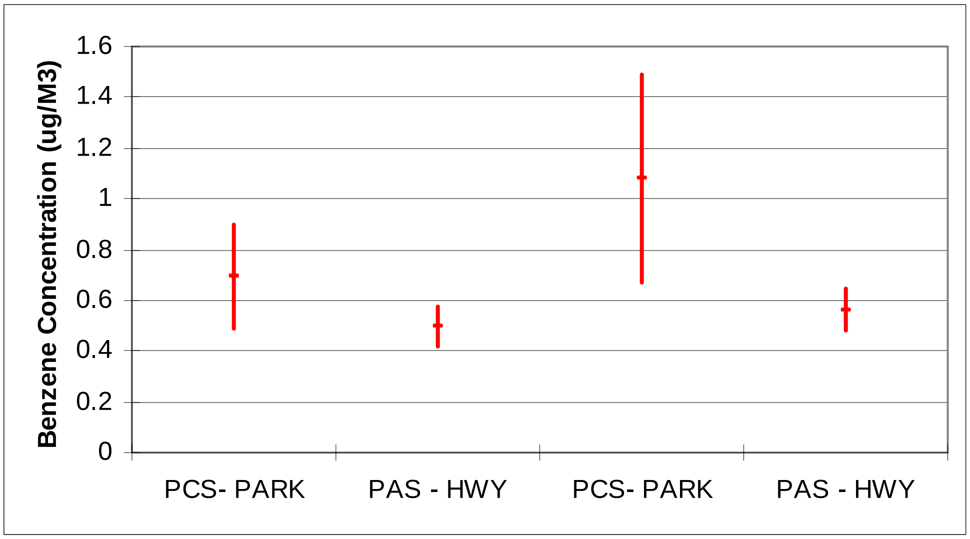


Figure 4-E2: Benzene concentration ranges for PCS and PAS collected in Study 3. Benzene is presented as the average concentration with the upper and lower 95% confidence intervals. (n=10)

4f. Roadway Benzene and Cancer Risk

Benzene is a known human carcinogen, is considered a non-threshold compound, and has no acceptable ambient concentration. Instead, benzene exposure is evaluated against the one-in-a-million cancer risk. This is an ambient concentration that when exposed to for a 70 year life time can be expected to cause one additional cancer in a population of one million individuals. For benzene we used a concentration of 0.128 ug/m3 as the one-in-a-million cancer risk benchmark.

Figure 4-f1 shows a graph of the model predicted concentrations at the 10 monitoring sites used in our Field Study 1. Included on the graph is the line for the one-in-a-million cancer risk concentration. The graph shows that the sites closest to the roadway have predicted concentrations greater than the benzene risk value. The graph also shows that concentrations drop quickly at sites away from the highway. Between distances of 100 to 150 meters the benzene concentration drops below the one-in-a-million cancer risk value.

Figures 4-f2a,b, and c show graphs of the average monitored concentration, along with 95% confidence intervals for the average values. The straight line on the graph represents the one-in-a-million cancer risk concentration. For all studies, we see that all study sites have average concentrations greater than the one-in-a-million cancer risk concentration. We also note that the one-in-a-million cancer risk concentration is less that the lower limit of the confidence interval, confirming there is an increase in cancer risk for individuals at distances greater than 500 meters from the highway.

Cancer risks are typically evaluated by long term exposures like those measured with the passive adsorbent samplers. In our studies, canister samples were collected for short term exposures during periods of increased highway traffic. These short term measurements were higher than the passive adsorbent samples. Canisters collected at the park site located approximately 600 meters from the highway showed an average benzene concentration of 1.06 ug/m3 (Study 1)and 0.71 ug/m3 (Study 3). These benzene concentrations are 8 times and 5.5 times the one-in-a-million cancer risk concentration, respectively.

Our study shows that modeling under predicts risk from benzene exposure throughout the entire monitoring area. Monitoring also shows that the risk is greater than one-in-a-million cancer risk for individuals at distances greater than 150 meters from the major highway. Modeling had predicted a decreased risk at distances greater than 150 meters.

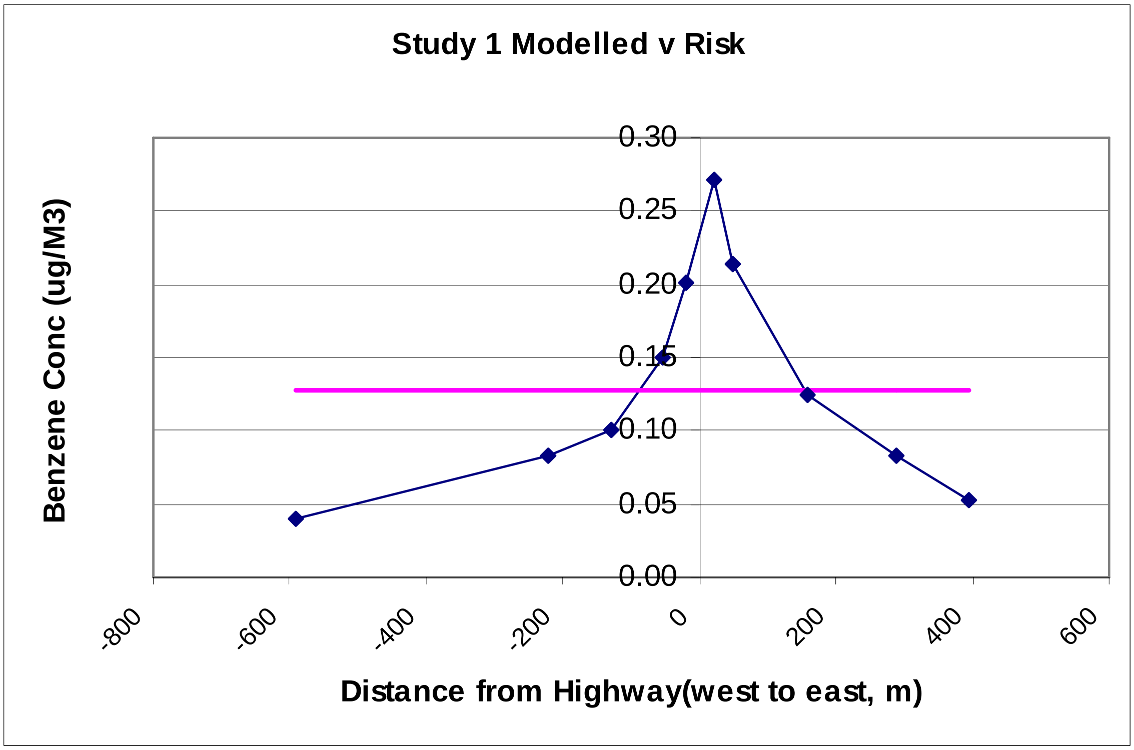


Figure 4-f1. Modeled benzene concentrations at site from west to east. Straight violet line is benzene cancer benchmark.

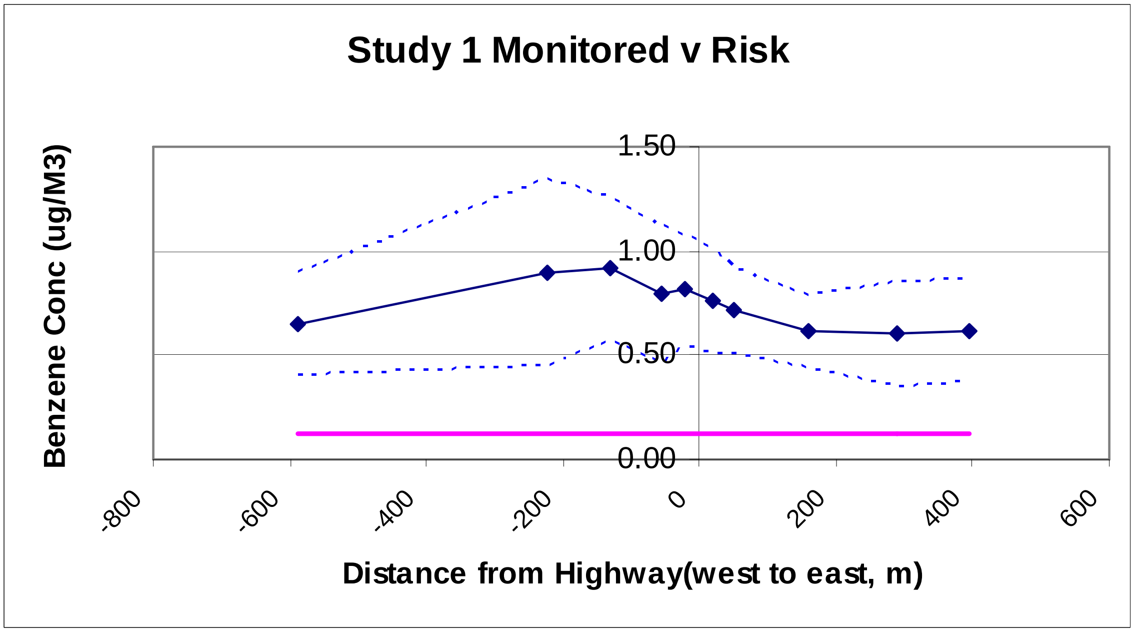


Figure 4-f2a. Average measured benzene concentrations at sites from west to east. Straight violet line near bottom is benzene cancer benchmark.

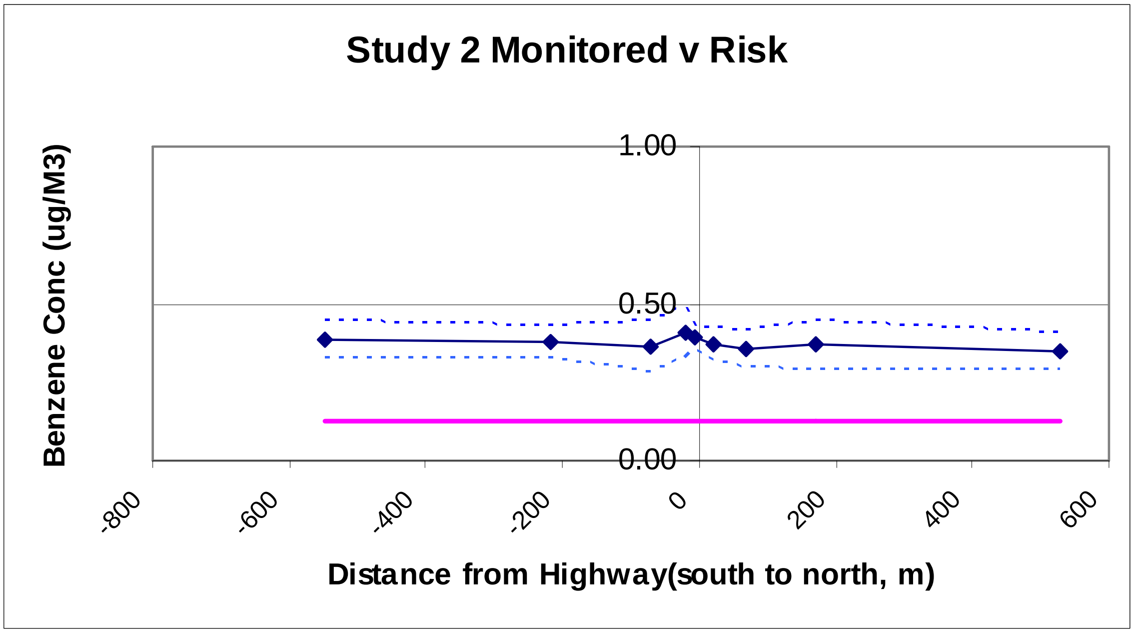


Figure 4-f2b. Average measured benzene concentrations at sites from south to north. Straight violet line near bottom is benzene cancer benchmark.

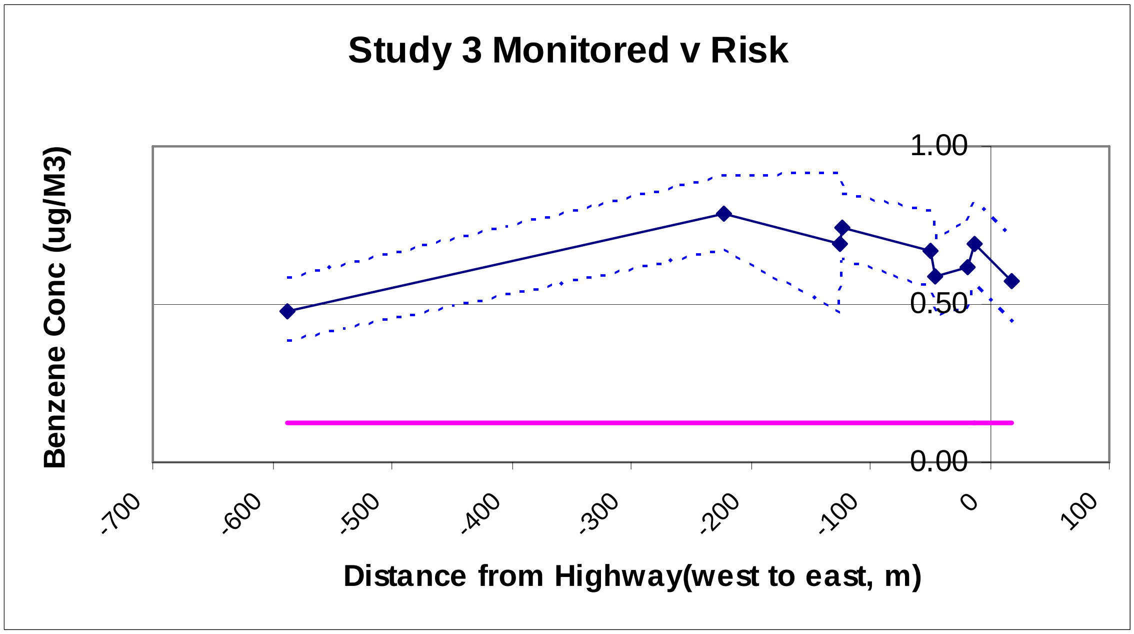


Figure 4-f2c. Average measured benzene concentrations at sites from west to east. Straight violet line near bottom is benzene cancer benchmark.

4g. Study Traffic Counts

The Wisconsin DOT estimated daily average traffic for Interstate Highway 94 in Milwaukee near Lincoln Street (Study 1& 3) is 99,800 vehicles/day. The actual average daily traffic at this location during Study 1 was 87,525 vehicles/day. The most common peak travel hour for Study 1 was 16:00 (55.56%). The actual average daily traffic during Study 3 was 100,659 vehicles/day, with the most common peak travel hour at 16:00 (52.94%).

The Wisconsin DOT estimated daily average traffic for Highway 94 west of Johnson Creek is 35,600 vehicles/day. Actual average daily traffic for Highway 94 west of Johnson Creek during Study 2 was 36,663 vehicles/day. The most common peak travel hour was 16:00 (76.47%).

Study 3 included passive canister samples at sites 990 and 995. The canisters had a timer set to collect for 1-hour, beginning collection at 7:00. The traffic counts indicate the most common peak travel hours were 16:00 (52.94%), 15:00 (23.53%), 12:00 (11.76%), 17:00 (5.88%) and 7:00 (5.88%). The 12:00 and 15:00 peak travel hours occurred on weekends, while the 16:00, 17:00 and 7:00 peak travel hours occurred on weekdays. Graph 4-T1 shows peak travel hour traffic counts (averaged for each day of the week) as compared to the 7:00 traffic counts (averaged for each day of the week). The weekday peak traffic counts are similar to the 7:00 canister collection time traffic count (see Graph 4-T1). The weekend peak traffic counts, however, are very different from the 7:00 canister collection time traffic count (see Graph 4-T1).

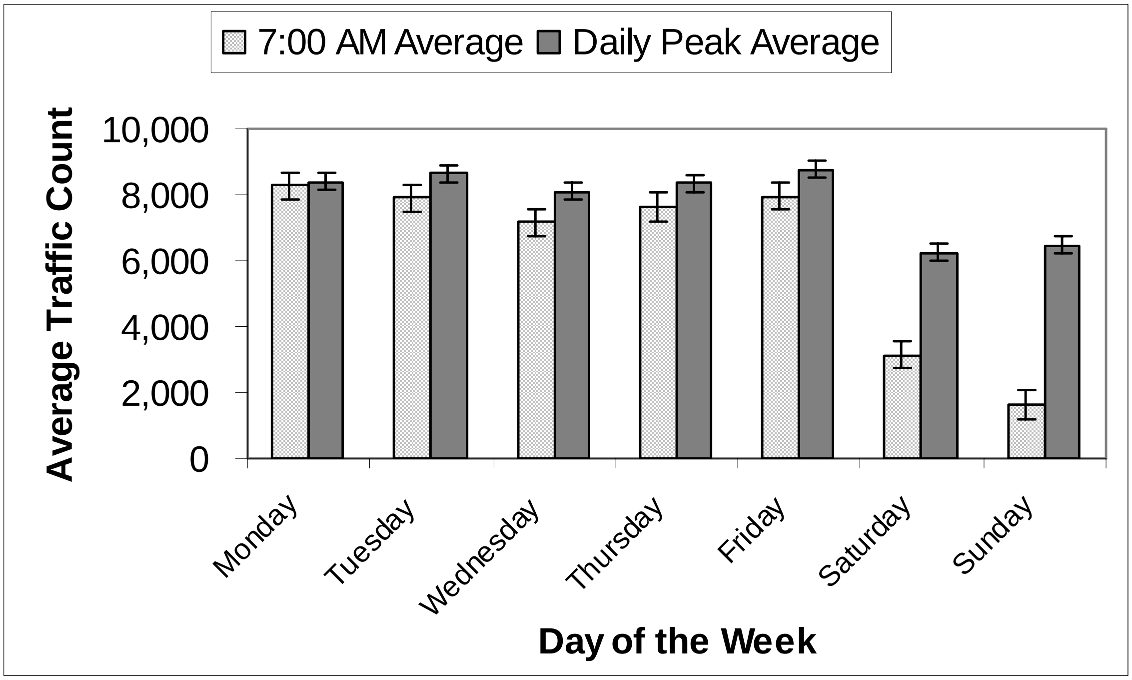


Figure 4-T1: Study 3, hourly roadway counts showing 7:00 am traffic count on weekday and weekends (averaged for all weeks) compared to daily peak traffic count, including percent difference for each day.

Table 4-T1: Traffic count hourly averages for Study 1, including traffic count per hour, minimum hour count and maximum hour count for each week.

Study 1	Week 1	Week 2	Week 3	Week 4
Average	4186	3696	3379	4051
Start Time	11/10/06 2:00	11/21/06 2:00	11/27/06 2:00	12/4/06 2:00
End Time	11/8/06 16:00	11/21/06 16:00	11/27/06 7:00	12/4/06 16:00
Min	600	256	431	499
Max	7429	7653	7021	7570

Study one was run 11/08/06 through 12/13/06 traffic counts available only through 12/4/06.

Table 4-T2: Traffic count hourly averages for Study 2, including traffic count per hour, minimum hour count and maximum hour count for each week.

Study 2	Week 1	Week 2	Week 3	Week 4
Average	1545	1534	1842	1606
Start Time	3/18/07 4:00	3/26/07 2:00	4/4/07 2:00	4/8/07 2:00
End Time	3/16/07 17:00	3/23/07 16:00	3/30/07 16:00	4/8/07 17:00
Min	136	159	195	104
Max	3877	3938	4168	5207

Table 4-T3: Traffic count hourly averages for Study 3, including traffic count per hour, minimum hour count and maximum hour count for each week.

Study 3	Week 1	Week 2	Week 3	Week 4
Average	4099	4327	3603	4078
Start Time	4/19/07 4:00	5/1/07 9:00	5/5/07 9:00	5/13/07 4:00
End Time	4/20/07 16:00	4/30/07 16:00	5/7/07 7:00	5/11/07 16:00
Min	127	338	0	551
Max	8,254	8,680	8,085	9,041

The hour 5/5/07 9:00 showed zero traffic count (we suspect this is in error).

4h. Study Meteorology Data

We looked at two primary meteorology parameters for this study. The first was temperature and the second wind direction. To a lesser extent we looked at wind speed, as it effected the overall mean wind direction. Meteorological data came from two sources; the first was the Wisconsin DNR's monitoring station at the Milwaukee Sixteenth Street Health Center. This monitoring site is located approximately 2 Km to the northwest of the area used in Studies 1 and 3. For Study 2 we used National Weather Service (NWS) data collected at the Sullivan Station located approximately 48 Km southeast from the study area.

Data reviewed and summarized for Study 1 and 3 started at 09:00 for the deployment date to 08:00 of the pick-up date. This provided 168 hourly measurements. For Study 2 we summarized data for 15:00 for the deployment date to 09:00 of the pick-up date. Data from the NWS was provided as 3 measurements per hour, but some hourly data was missing and the average number of data points used was 400. A summary of the average, maximum and minimum temperatures is provided in Table 4-M1. The table provides data for each week of each study. A summary of the vector mean wind speed (VMWS), vector mean wind direct (VMWD) and the fraction of wind octal is provided in Table 4-M2. For more detailed study of the winds, wind roses for each study week are provided in Appendix D of this report.

Analysis of the temperature data shows that the three studies cover the wide range of temperatures Wisconsin experiences. The initial study occurred in late fall with temperatures dropping through the study. This first study covers the widest overall range of temperature (33.8 degrees Celsius) and saw the lowest temperature in the study (-14 degrees Celsius). The second study, conducted in early spring, saw the widest average temperature range of 13.2 degrees Celsius. Study 2 started and ended with average temperatures below zero, but experienced warmer temperatures in the middle weeks. The final study followed directly on Study 2, but temperatures were now becoming more stable on average. In Study 3, average, maximum, and minimum temperatures were very consistent. The range of average temperatures in Study 3 was less than 5 degrees Celsius. These consistent temperatures may have contributed to the very consistent pollutant concentrations seen in Study 3.

Winds varied throughout the three studies. Three wind patterns were seen in during Study 1. During the first two weeks, winds came from the north. During week 3, southerly winds dominated. The final two weeks experienced westerly winds. Week 1 of the second study was the only period where calm winds dominated the wind regime. In Study 2, winds varied coming from both the west and east (including northeastern winds). As we saw with temperatures, the winds were very consistent over Study 3 with primarily easterly winds. The dominant winds throughout the study were from 45 to 135 compass degrees.

Table 4-M1: Roadway Study - Temperature Summary Report in Celsius					
Study 1 (Data from WDNR's Milwaukee SSHC Site)					
Study Week	1	2	3	4	5
Start Date	11/08/06	11/15/06	11/22/06	11/29/06	12/05/06
Average	6.4	3.8	9.7	-4.6	-1.1
Max	19.8	11.3	16.1	15.2	8.9
Min	0.6	-1.6	2.3	-13.7	-14
Study 2 (Data from NWS's Sullivan site)					
Study Week	1	2	3	4	(week 4 ran to 4/13)
Start Date	03/14/07	03/21/07	03/29/07	04/04/07	
Average	-0.7	12.7	7.8	-0.5	
Max	13	26	14	9	
Min	-9	2	0	-7	
Study 3 (Data from WDNR's Milwaukee SSHC Site)					
Study Week	1	2	3	4	
Start Date	04/18/07	04/25/07	05/02/07	05/09/07	
Average	13.1	11.6	13.6	16.1	
Max	29.4	29.9	26.2	33.6	
Min	4.5	4.8	7.1	6.8	

Roadway Study Meteorology Summary

Study	Week	VMWS (mph)	VMWD (deg.)	Fraction of Winds by Octants								
				Calm	45	90	135	180	225	270	315	360
1	1	2.0	355.0	0.01	0.19	0.08	0.00	0.13	0.15	0.06	0.09	0.30
1	2	3.3	347.0	0.00	0.19	0.04	0.00	0.09	0.15	0.03	0.24	0.27
1	3	2.5	167.6	0.00	0.09	0.14	0.13	0.26	0.28	0.05	0.03	0.02
1	4	4.8	276.7	0.01	0.05	0.00	0.00	0.01	0.21	0.31	0.18	0.23
1	5	6.1	235.4	0.00	0.00	0.00	0.02	0.17	0.39	0.17	0.18	0.07
2	1	1.2	43.9	0.23	0.13	0.12	0.10	0.05	0.08	0.02	0.09	0.18
2	2	2.8	185.8	0.17	0.02	0.13	0.13	0.13	0.24	0.09	0.08	0.02
2	3	3.8	118.7	0.04	0.02	0.35	0.25	0.07	0.04	0.17	0.07	0.00
2	4	5.9	158.7	0.04	0.05	0.21	0.07	0.04	0.01	0.07	0.29	0.23
3	1	1.6	105.7	0.00	0.31	0.16	0.10	0.17	0.17	0.04	0.04	0.02
3	2	3.1	6.5	0.01	0.35	0.17	0.04	0.01	0.16	0.07	0.11	0.08
3	3	4.9	81.9	0.00	0.15	0.38	0.25	0.10	0.03	0.07	0.02	0.00
3	4	2.0	11.4	0.00	0.31	0.17	0.08	0.07	0.15	0.11	0.02	0.08

Study 1 data collected at the WDNR's Milwaukee SSHC Site.
Study 2 data collected at the NWS Sullivan Station
Study 3 data collected at the WDNR's Milwaukee SSHC Site

Table 4-M2: Summary of wind speed and wind direction for the three Field Studies.

Section 5. Discussion Results and Success of the Project

5a. Review of Project Goals

In reviewing the work on this project we looked at goals set forth in the projects Quality Assurance Project Plan. Our assessment of the project compared to the three main goals follows.

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

We successfully developed methods for sampling and for sample analysis. This included techniques for passive canister sampling for short-term sampling and passive adsorbent tubes for longer timed measurements.

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

We tested the passive sampling systems using standard test methods as well as comparisons to existing methods. Adsorbent tubes were tested directly against the automated field gas chromatograph as well as against the laboratory's T015 GCMS analysis.

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

The passive samplers were used in three field studies to test assumptions predicted by modeling benzene concentrations near urban area roadways.

5b. Evaluation of Passive Methods

In our project QAPP we set forth a simple data quality objective.

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

We have been able to meet this objective, especially for our critical parameter benzene. We have successfully met the goal for other supporting parameters, but not for all the target compounds in Table 3-4. The QAPP listed the following criteria for measures of data quality: completion, accuracy, precision, and comparability. Our assessment of the methods follows.

- Evaluating completeness, we note that our original plan for the project called for 2 field studies. We eventually carried out 3 studies. We were able to collect and analyze all samples for Studies 1 and 2. Our third study was planned for 11 sites, but we collected samples at only 9 sites. The loss of 2 sites was due to vandalism. We believe that data from the 9 sites have met our study goals. We would also note that during Study 2 noise problems in the GC detector did compromise some data. Completion of canister data was less successful. In Study 1 we collected 7 canister pairs but only 3 were determined to be valid. By Study 3 we were much more successful, collecting 10 of 13 planned sample canister pairs.

- Based on comparisons with both automated GC and canister sampling, we conclude that the passive adsorbent sampling method generates data comparable to established methods, but note that the data is biased low to the established methods.

- From our study of the PAS blank samples, we conclude that background weights of target compounds are not significant enough to invalidate the method but must be addressed in processing the data. We have corrected all ambient result for blanks taken with the samples. We used the average weight of the prep, trip, and field blank results to correct the ambient data. We also conclude that the background is a result of residuals on the cleaned adsorbent tube and we saw no evidence of contamination in either the field or the trip blanks.

- We conclude that on average the precision of the passive adsorbent samplers is good. We noted that the average percent difference between duplicate benzene samples was 10.9% and the average for toluene was 8.3%.

- Finally we tried to verify the Diffusive Rate Constants for the passive adsorbent samplers but were unable to successfully do this. We therefore conclude that we would need to use literature DRC to calculate all ambient concentrations. We observed good comparisons with established methods when we did use the literature DRCs. We took our DRC from Brown (1999).

5c. Conclusions from Roadway Field Studies

We conducted three field studies to examine the relationship between benzene concentrations and distances from heavily trafficked roadways. In our studies, the heavily trafficked highways were sections of Wisconsin's Interstate Highways. Two studies were located across an urban highway and one control study across a rural highway. From these studies we have concluded the following.

- Measured benzene concentrations at all sampling sites for Study 1 were higher than the concentrations that had been predicted by computer models. The concentrations were confirmed for six of the 10 sites in Study 3. We conclude that the model missed some unknown sources or that the model underestimated the vehicular emissions. We recommend first that the modeler integrate the emission models with the stationary source models to determine if, when taken together, these models better predict the ambient benzene.

- In all three studies the measured ambient benzene concentrations were more uniform across the transects than suggested by the model. This was confirmed by multiple samples collected over periods of 5 weeks, 4 weeks and 4 weeks. We conclude that benzene is diffusing out to a uniform concentration more quickly than predicted by the computer model.

- We observed that average benzene concentrations in a study showed much greater variability between individual weeks of the study than between individual sites used in the studies. This shows results from individual sites have more in common with results from other sites collected at the same time than they do with results obtained from the same site during different weeks. This supports the second conclusion that concentrations are more uniform across a transect of a roadway than predicted.

- We observed that in the urban study peak benzene concentrations were observed not on the interstate highway, but rather on the parallel city roadway to the west of the highway. The observed peak along Milwaukee's Sixth Street was noted in both Study 1 and Study 3, but was only statistically significant in Study 3. We conclude that urban traffic routes may have significant mobile source emission even though these routes have less traffic volume. We hypothesize that this may be because traffic is moving through an area more slowly and in a stop-start fashion. Traffic on the interstate highway were moving quickly through the area with no stopping.

- We observed that the Toluene to Benzene ratio differed between study locations and between sites with the studies. The Toluene to Benzene ration at the rural control site was inverted from that seen in the urban site. During Study 2 we observed benzene concentrations consistently greater that the toluene concentrations. We are unable to explain this observation. During Studies 1 and 3, conducted along the Milwaukee urban interstate, toluene concentrations were always greater than the benzene concentrations. We did observe statistically different ratios of benzene to toluene between the highway sites and the peak benzene sites to the west of the highway. We can not explain this difference but hypothesize that it may be related to how the vehicles are operating in each area, as noted in the above our fourth observation.

- Finally we observed that benzene concentrations at all study sites were higher than the one-in-a-million risk concentration of 0.128 ug/m3. Computer models predict that at distances of 100 to 150 meters from the roadway the benzene concentration drops below the one-in-a-million risk concentration benchmark. We conclude that risk above the one-in-a-million risk concentration benchmark are present at distances up to 600 meters from the heavily trafficked highway.

5d. Benefits of the Project:

The project has provided an evaluation of two passive techniques that facilitate multi-site roadway monitoring. Our project focused on developing monitoring methods to measure benzene concentrations near roadways and adjoining neighborhoods. The project measured other volatile mobile sources emissions to support the benzene measurements. New monitoring methods tested included passive adsorbent sampling for long term (7 day) concentrations and passive canister sampling for measuring short term peak (1 hour) concentrations. In evaluating the new methods we used as reference the measurements made at Wisconsin's existing fixed monitoring stations. Our project goal successfully developed in-house capabilities to use these new methods and to collect data that will support risk assessment modeling, providing data for ground truthing emission models and risk models. We expect that future uses of the techniques will evaluate shifting emission patterns that may result from the extensive highway reconstruction, vehicle and fuel changes.

6. References:

Allen, M.K., D. Grande, and T. Foley, (1996) "Monitoring Reformulated Gasoline in Milwaukee, Wisconsin", *Proceedings of the 1996 International Symposium on Measurements of Toxic and Related Air Pollutants*, VIP-64, AWMA:Pittsburgh, pp. 319-325,.

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Appendices

A. Roadway Study Proposal
B. Quality Assurance Project Plan
C. Passive Canister Evaluation
D. Wind Roses

Appendix A: Roadway Study Proposal

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

Application Category: Method Evaluation and Comparison

Organization: Wisconsin Department of Natural Resources

Contact Information:

Contact Person:	Mark K. Allen
Phone:	608-266-8049
Fax:	608-267-0560
E-mail:	mark.allen@dnr.state.wi.us

Funding Request: **$79,211**

Project period: April 15, 2006 to June 30, 2007

Project Description:

Passive sampling technologies can be useful for extending our knowledge of personal exposures to volatile air pollutants. Current technologies for sampling volatile organic compounds (VOCs) include actively sampled (pressurized) canisters and field deployed gas chromatographic systems. The current technologies have high costs associated with both sampling and analysis. The current technologies also often require a large foot print in the location that is being monitored. Passive monitoring techniques can be used at a smaller cost per sample and often require only a minimal footprint.

The Wisconsin DNR will develop in-house analytical methods to analyze air samples captured in passively sampled canisters and air pollutants trapped on passively sampled adsorbent tubes. The passively samples canister can provide short-term (less than 24 hours) measurements of VOCs. Passively sampled canister require no external power. This results in a relatively simple deployment to the field. Passively sampled adsorbent tubes capture VOCs through the diffusion process. The adsorbent tubes are less expensive than canisters and are easier to prepare for sampling. A number of adsorbent tubes can be deployed to an area of interest to provide *saturation* sampling. The adsorbent sampling tube provides a longer averaging time. While the longer time is less useful for studying atmospheric chemistry and physics, it does provide a time scale more relevant to existing risk assessment modeling.

Goals for the monitoring project will be the following:

1. Develop easily deployed sampling units for both passive canisters and adsorbent tubes.
2. Develop in-house analytical methods for passively sampled canisters and adsorbent tubes using existing analytical systems.
3. Test the passive sampling systems to establish comparability to existing active sampling systems used by the Wisconsin DNR.
4. Deploy the passive systems in a field study and use this information to optimize designs to support risk assessment modeling.

Background Information on Roadway Exposure:

Benzene is ubiquitous aromatic hydrocarbon formed in many combustion processes. Benzene is a known human carcinogen and is consider one of the most significant risk drivers in the urban environment.

Mobile source emissions make up the major source of benzene in the urban environment (Fruin et.al., 2001). Models show that the exposure from roadways is related to the distance from the roadway (Funk and Lurmann, 2001). Monitoring studies suggest that for mobile source pollutants, like benzene, the outdoor and indoor air concentration are similar and indicate ambient air is the most important exposure driver (Paynes-Struges et. al., 2004).

A review of Wisconsin's air emission inventory for the year 2000 shows a total of 37 facilities in Milwaukee reporting a total of more than 16850 pounds of benzene emissions. The majority of these emissions (over 14750 pounds) are accounted for by 14 primary metal industries (foundries and metal casting). Petroleum products terminals, motor manufacturing, pipelines, power generation and wastewater treatment account for the majority of the remaining reported emissions (over 2090 pounds).

Roadway emissions are important because Milwaukee is location of a major urban interstate roadway, Highway 94. Construction of Highway 94's Marquette interchange began in 2005 and will be continue until 2008. This construction may have significant impact on mobile source roadway emissions in the city.

Therefore questions remain about benzene in the urban environment that warrants further study. How accurate are current stationary source and mobile source inventories in predicting ambient benzene concentrations? Are major roadways significant sources of benzene? How quickly is benzene dispersed from the roadways to the adjoining environment? What are benzene exposures in neighborhood environment?

The Wisconsin DNR's development of passive sampling techniques will provide a tool to better understand the sources, transport, and diffusion of benzene from roadways. While benzene will be the primary focus of the project, related hydrocarbons will be monitored to assist in assessing the sources and impact of the benzene.

Soundness of Proposed Methodology

The development and testing of passive monitors for monitoring concentration of benzene and other aromatic hydrocarbons was been reported by Brown, et. al. (1981). In a later paper Brown et. al.(1999) discussed the use of these passive sampler for mobile source related pollutants, including benzene, toluene, and xylenes. The technique will use commercially available diffusion tubes designed for analysis by a Perkin-Elmer gas chromatographic system, like that used at Wisconsin's Milwaukee PAMS site. This gas chromatographic system is operated during the peak ozone months, June through August. We will enlarge the scope of work by conducting analyses of the passive samples before June and after August. The current analysis parameters will provide a solid base for the passive sample analysis, development time for the method should be minimal.

Wisconsin DNR's current methodologies and methods have been proven in the Photochemical Assessment Monitoring Station (PAMS) and Urban Air Toxic Monitoring (UATM) projects. These current methodologies will provide the benchmarks for comparisons of the passive technologies. Currently pressurized whole air samples in passivated canisters are analyzed at the Wisconsin State Laboratory of Hygiene. The Wisconsin State Laboratory of Hygiene has analyzed PAMS and UATM monitoring samples for the Wisconsin DNR since 1994. Hourly benzene values are collected at the Type 2 PAMS site using a Perkin-Elmer Ozone Precursor analyzer (AutoGC). This unit has been in operation at the Wisconsin site in Wisconsin since 1999. Other monitoring parameters collected at fixed-long term sites include ozone, carbon monoxide, wind speed and wind direction. The Wisconsin DNR has established operating procedures for these parameters including Standard Operating Procedures (SOPs) and Quality Assurance Project Plans (QAPPs).

The Wisconsin DNR has an established record for carrying out environmental studies similar to that proposed. In 1995 WDNR staff conducted a short intensive study of reformulated gasoline components

(Allen, Grande and Foley, 1996). This monitoring project included monitoring near roadways as well as exposure studies during vehicle refueling.

Benefits of the Project:
The project will provide an evaluation of two new techniques that can be used for roadway monitoring. The passive methods will be useful for evaluating emissions on the roadways and the diffusion of the benzene into adjoining areas. The monitoring technique should provide data for ground truthing emission models and risk models. The technique will also be useful in evaluating shifting emission patterns that may result from the extensive highway reconstruction planned for the Marquette interchange.

Statement of Work Tasks:
<u>Task 1:</u> Develop the guidance documents for staff to initiate and complete the monitoring project

Objectives: Develop analysis SOPs, field monitoring plans, and quality assurance projects plans for sampling and analysis.

Methods: The Quality Assurance Project Plan (QAPP) will be developed to ensure that monitoring is consistent with existing state, regional and national quality assurance goals. The Project Monitoring Plan plans will include detailed information on monitoring sites, sampling schedules, staff work assignments, and data management. Existing DNR databases will be assessed for the ability to store and manage project data. If necessary, a plan will be developed to handle data that does not conform to the existing database standards.

Outputs: Guidance documents for project staff to use in conducting the monitoring study

Outcomes: The guidance documents will provide staff with knowledge of what work is expected in the project, how the work should be carried out, and how to proceed if and when problems develop.

Completion time: by June 1, 2006.

<u>Task 2:</u> Procure and assemble passive monitoring system for canister and adsorbent tubes.

Objectives: To purchase or procure through other means (loans, rental, ect.) additional equipment or supplies required for the project.

Methods: Capital equipment and supplies will be procured using standard State of Wisconsin procedures for obtaining resources. Wisconsin DNR staff will assemble and install all necessary monitoring equipment.

Outputs: Sampling equipment for the study

Outcomes: The procurement and assembly of the sampling systems will provide the necessary tools for monitoring staff to conduct the study.

Completion time: June 30, 2006

<u>Task 3:</u> Develop analytical methods for the analysis of passive samples.

Objectives: To develop analytical methods and procedures for the analysis of benzene and other mobile source VOCs captured in passive samples. To demonstrate that high confidence in the analytical measurements made in this project.

Methods: The development and optimization of an analytical method on the Perkin Elmer gas chromatographic system will use standard gas chromatographic techniques. Standard quality control elements including blanks, replicate analyses and spiked recoveries will be used to demonstrate the quality of the measurement.

Outputs: Analytical parameters for the gas chromatographic analysis of samples collected in the field study.

Outcomes: The analytical method and procedures will be critical to the analysis of field study samples

Completion time: June 30, 2006

Task 4: Validate the passive sampling methods.

Method: Passive samplers will be collocated with currently used active sampling systems. Samples from both systems will be analyzed according to established protocols. Data from both systems will be evaluated to establish the comparability of the passive and active sampling systems.

Outputs: Additional sampling data.

Outcomes: The data generated from this task will establish the comparability of the study data to existing data that has been collected in the Milwaukee urban area.

Completion Time: September 15, 2006.

Task 5: Conduct a preliminary field roadway monitoring study

Objectives: Conduct a spring preliminary sampling study for benzene and MS-VOCs along a roadway in the Milwaukee Urban area.

Methods: Air samples will be collected using the passive techniques developed. This study will use a single linear transect of the roadway centering on the median and extending outward away from the roadway.

Outputs: An initial and limited dataset for roadway VOCs.

Outcomes: The initial dataset will validate the field study designs.

Completion time: The preliminary field monitoring study will be completed before October 15, 2006.

Task 6: Roadway Monitoring Study

Objectives: Use information from the preliminary roadway study and summertime validation. Deploy a field study to demonstrate roadway exposure to benzene and show how that exposure changes as you move from the roadway to residential neighborhoods adjoining the roadway. This study is expected to use a more complex array of samplers.

Method: The field study will use the passive sampling techniques. Sampling will take place along a major roadway. Saturation sampling in an adjoining neighborhood will be used to track changes in concentration as a function of distance from the roadway. Passive canister samples will be used for short term concentrations.

Outputs: Additional field data to complete the study dataset

Outcomes: This task will complete the field study part of the project.

Completion Time: Roadway study will be completed by April 1, 2007.

Collaboration:

The Wisconsin DNR will work with the Wisconsin Department of Health and Family Services in planning and conducting the roadway field studies. The Wisconsin DHFS will be directly involved in determining exposure from field measurements. The Wisconsin DHFS may extend roadway studies into the indoor air of residences near targeted roadways.

A letter of support from the Wisconsin Department of Health and Family Services is attached as Attachment A to this proposal

Project Budget:

a. Personnel	$35,765
b. Fringe Benefits	$10,964
c. Contractual Costs	$4,832
d. Travel	$2,632
e. Equipment	0
f. Supplies	$17,200
g. Other	$0
h. Total Direct Costs	$71,393
i. Total Indirect Costs: must include documentation of accepted indirect rate	$7,818
j**. Total Cost**	**$79,211**

<u>Additional Resources:</u> The above budget reflects the funds needed to complete this project. The project will make use of existing equipment and monitoring sites. Included are canister samples and a gas chromatographic analysis system. Existing monitoring sites in Milwaukee will be used for the field validation of the passive sampling systems.

Quality Assurance for the Project:

The primary goal for this project is to develop reliable passive sampling technique for the investigation of benzene exposure from mobile sources. Quality assurance goals for the project will be to construct reliable database of measurements made with the passive sampling methods. The database will provide information to show the passive methods provide good data, to establish comparability with the current sampling methods, and to show how the passive monitors can be used for roadway field studies. Important quality assurance tasks for this project include the following:

- Develop necessary quality assurance plans for the project. Quality assurance plans should identify the methods to be used and quality control procedures for evaluating data quality from the testing.
- Develop and document analytical methods for sampling using established protocols to optimize the analyses.
- Develop a data management plans to store and review project data.
- Use established statistical tests to compare results from existing VOC methodologies with the new passive methods.

Reporting

The Wisconsin DNR will provide quarterly technical reports detailing the project activities during the previous 90 days. The report will also address any significant findings that will affect activities in the next calendar quarter.

A final report on the project will be submitted to the designated EPA Project Officer by June 30, 2007. The final report will describe the work completed in the study, summarize the data in the study, report on the quality of the data, and provide a preliminary analysis of the data. The preliminary data analysis will address the concentration gradients of benzene and other vehicle related pollutants originating at the roadways.

The Wisconsin DNR will work with EPA's Air Quality System staff to include ambient monitoring data in the AQS database. It may be necessary for AQS to develop specific method codes for the passive sampler that will be used in the study.

References:

Allen, M.K., D. Grande, and T. Foley, (1996) "Monitoring Reformulated Gasoline in Milwaukee, Wisconsin", *Proceedings of the 1996 International Symposium on Measurements of Toxic and Related Air Pollutants*, VIP-64, AWMA:Pittsburgh, pp. 319-325,.

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Funk T.H. and F. W.Lurmann (2001) "Using GIS to investigate children's exposure to air pollution". Presentation at the *Twenty-First ESRI International User Conference, San Diego, CA, June 9-13* (STI-2107).

Paynes-Struges, D.C., Burke, T.A., Breysse, P., Diener-West, M., and Buckley, T.J., (2004) "Personal Exposure Meets Risk Assessment: A Comparison of Measured and Modeled Exposures and Risks in an Urban Community", Environmental Health Perspectives, 112(5), 589-598.

Attachment A: Letter of Support from Wisconsin Department of Health and Family Services

Lloyd Eagan, Director
Bureau of Air Management - AM/4
Wisconsin Department of Natural Resources
101 S. Webster Street
Madison, WI 53707

Subject: Letter of Support for EPA Air Toxics Monitoring Grant Proposal

Dear Ms. Eagan:

I am sending this letter to express the Wisconsin Department of Health and Family Services (DHFS) strong support for your EPA grant proposal "Evaluation of Passive Sampling Techniques for Monitoring Roadway and Neighborhood Exposures to Benzene and Other Mobile Source VOCs." This project marks another important step in our efforts to utilized air quality monitoring data in our environmental and public health tracking activities.

DHFS believes this work will allow us to better characterize exposures to benzene and other transportation source pollutants in nearby residential areas. The findings of this project will allow transportation officials to more directly consider public health and residential air quality impacts within long-term transportation planning. We expect that the use of this monitoring methodology will also have broad application for other public health related air quality issues.

In addition to our expressed support for this project, DHFS intends to add a complementary component by concurrently monitoring residential indoor air within the monitoring areas of this proposal. DHFS has already allocated capacity for sample analysis at the Wisconsin State Laboratory of Hygiene for this purpose. The DHFS component will provide additional insight into proportional contributions from roadways and other sources (e.g. attached garages) to overall human exposure in these areas.

Please include this letter with your grant application materials submitted to the EPA. If you, EPA officials, or other grant reviewers have questions about this letter of support or our related monitoring plans, please contact either myself at (608) 266-1253, or Chuck Warzecha at (608) 267-3732. Thank you for your continued work to protect the health of Wisconsin citizens through improved air quality.

Sincerely,

Dr. Henry Anderson, M.D.
Chief Medical Officer for Environmental and Occupational Health
Wisconsin Department of Health and Family Services

Attachment B: Biographical Information of Key Project Monitoring Personnel

MARK KENNETH ALLEN – Project Manager

EDUCATION:

Master of Science in Analytical Clinical Chemistry
University of Wisconsin, Madison, Wisconsin
awarded 1986

Bachelor of Science in Medical Technology
University of Wisconsin, Madison, Wisconsin
awarded 1978

WORK EXPERIENCE:

Wisconsin Department of Natural Resources
Bureau of Air Management, Monitoring Section
February 13, 1990 to present
November 24, 1985 to August 18, 1989

Served as leader worker for ozone precursor monitoring projects conducted in southeastern Wisconsin. These projects include: *Nonmethane Organic Compound Monitoring in Milwaukee (1987 to 1990); Lake Michigan Ozone Study (1990 and 1991 field monitoring programs); and Enhanced Ozone Monitoring in Southeastern Wisconsin (1992 to present).*

Served as leader worker for air toxics monitoring projects conducted throughout Wisconsin. Some of these projects have included: *Urban Air Toxic Monitoring (1991 to present); Statewide testing of landfill gas emissions (1986 and 1992); Statewide monitoring of prescribed burning (1992); and Statewide monitoring of mercury in deposition (1993 to present).*

Wisconsin Occupational Health Laboratory
University of Wisconsin
Center for Health Sciences
August 21, 1989 to February 12, 1990

Operated and maintained the laboratory's Hewlet Packard 5995 gas chromatograph/mass spectrometer. Prepare quality control samples that are analyzed by the chemists as part of the laboratory's quality control program. Performed gas chromatographic analysis of air samples captured on charcoal adsorbent tubes.

Clinical Toxicology Laboratory
University of Wisconsin Clinical Science Center
August 14, 1978 to November 22, 1985

Performed chemical analyses of biological samples for therapeutic and emergency drug monitoring. Operated and maintained laboratory instruments, including gas and liquid chromatographs; a UV-VIS spectrophotometer; and a mass spectrometer. Investigated, developed and implemented new methods for drug analysis.

PUBLICATIONS:
Allen,M.K., Sponseller,B.,and Rodger,B., “Monitoring Mercury Deposition Using Passive Samplers”, *Presented at the 1998 International Symposium on Measurements of Toxic and Related Air Pollutants*, RTP,NC (September 1998).

Allen,M.K.and Sponseller,B.,“ Monitoring Mercury Deposition In Wisconsin 1996-1997”, *Presented at the 1998 International Symposium on Measurements of Toxic and Related Air Pollutants*, RTP,NC (September 1998).

Allen, M.K., Miller, E., and Leair, J., “Development of an Intelliegent Canister/Cartridge Sampler for the Collection of Ozone Precursors or Air Toxics”, *Proceedings of the 1996 International Symposium on Measurements of Toxic and Related Air Pollutants*, VIP-64, AWMA:Pittsburgh, pp 227-233, (1996).

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DAVID E. GRANDE – Field Study Technical Leader

EDUCATION

University of Wisconsin-Madison
Graduate Studies in the Institute of Environmental Studies, 1998 - 2000
Graduate Studies in Biochemistry, 1983 - 1984

University of Nebraska at Lincoln
Bachelor of Science in Chemistry, 1983

WORK EXPERIENCE

Wisconsin Dept. of Natural Resources, Bureau of Air Management, Air Monitoring Section
Air Toxic Monitoring Chemist
November 1994 to Present

Wisconsin Urban Air Toxics Monitoring Program (ongoing) Establishing and operating a network for the determination of a variety of toxic air pollutants in Wisconsin's urban atmospheres, including PCBs and pesticides, VOCs and carbonyl compounds.

Photochemical Assessment Monitoring (PAMS) (ongoing) Participation in the PAMS monitoring program includes quality control testing of the air samplers and data analysis.

Ambient Mercury Monitoring (ongoing) Investigating ambient mercury concentrations using Tekran analyzers in a variety of locations around Wisconsin, both near major emitting facilities including a major mercury recycler and a chlor-alkali plant, and in urban environments.

Biogenic Hydrogen Sulfide Generation, 2002 and 2003 Investigating emissions generated at a bottom draw water impoundment. Emissions observed during lake stratification.

Air Impacts of Livestock Operations (ongoing) Investigations into ammonia and hydrogen sulfide emissions and ambient concentrations associated with different livestock operations.

Fox River Remediation Air Monitoring, 1999, Design and implementation of a multi-site study for the investigation of PCB concentrations associated with dredging and landfilling of contaminated sediments from the Fox River.

Ammonia from a Wastewater Solids Composting Facility, 1998, a year and a half long study observing ammonia concentrations downwind of a biosolid production facility, during which the facility incorporated several process and facility design changes to mitigate emissions.

Hazardous Air Pollutant Emissions from Wood-Fired Boilers, 1996, Investigation of HAP emissions from a wood and coal fired boiler; correlations between operating parameters, CO and specific HAP emissions determined.

Reformulated Gasoline Air Monitoring Study, 1995, ambient roadside study related to the impact of reformulated gasoline on the air environment conducted after the introduction of RFG in the Milwaukee area.

Resource Management Associated, Short term consultant
March 1996

Participated in air monitoring efforts in Mariupol, Ukraine, intended to provide technical support and training for the operations of and monitoring strategies incorporating gas chromatography for the evaluation of ambient hydrocarbon concentrations.

Clean Air Engineering, Inc. Chemist and Manager of Analytical Services
June 1985 – November 1988

Clean Air Engineering (now CAE) is an air pollution source testing firm with a wide range of expertise. Duties included:

Extensive Gas Chromatographic (GC) determinations of VOC in workplace air and emission streams; GC operations, maintenance and operator training. Innovative source VOC test design and implementation, from test plans, through sampling and analysis, to reporting of results. Developed method to determine capture efficiency of VOC sources. Method effectively removed assumptions based on coating VOC content, and was both accurate (±2% relative known standards) and precise (±3% between duplicate determinations) Laboratory operations, including expansion of services to include hazardous waste analysis.

Publications:

Green Bay Urban Air Toxics Monitoring, A Summary Report for the Period July 1991 – June 1995, Wisconsin DNR Publication Number PUBL-AM-218-97, 1997.   Author

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Wisconsin Urban Air Toxics Monitoring, An Interim Report for the Period July 1997 – June 2000, Wisconsin DNR Publication Number PUBL-AM-311-00, 2000. Author

Ammonia Monitoring Project at West Central Wisconsin Biosolids, Ellsworth, Wisconsin (October 1997 – June 1999), Wisconsin DNR Publication Number PUBL-AM-304-00. Author

Fox River Remediation Air Monitoring Report, Ambient PCBs During SMU 56/57 Demonstration Project, August – November, 1999, Wisconsin DNR Publication Number PUBL-AM-310-00, 2000. Author

Reformulated Gasoline Air Monitoring Study, Wisconsin DNR Publication Number AM-175-95, 1995. Co-author

Monitoring Reformulated Gasoline in Milwaukee, Wisconsin, Proceedings of the 1996 International Symposium on Measurements of Toxic and Related Air Pollutants, VIP-64, AWMA:Pittsburgh, pp. 319-325, (1996). Co-author

Correlating Benzene, Total Hydrocarbon and Carbon Monoxide Emissions from Wood-Fired Boilers, Proceedings of the 1997 AWMA Annual Meeting, 97-TA34.05, 1997 Co-author

Spatial Distribution of Airborne PCBs in Milwaukee, Wisconsin DNR Publication Number AM-342 2004. Author.

Appendix B:
Quality Assurance Project Plan

For

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

Table of Contents

PROJECT APPROVAL

1. Project Manager

__________________________________ __________
Signature Date

2. Monitoring Quality Assurance Officer

__________________________________ __________
Signature Date

3. Monitoring Section Chief

__________________________________ __________
Signature Date

4. Environmental Science Section Chief

__________________________________ __________
Signature Date

5. Director Bureau of Air Management

__________________________________ __________
Signature Date

Acronyms and Abbreviations

AD	Absolute Difference
AQS	Air Quality System
ATMP	Air Toxics Monitoring Program
ATD	Automatic thermal desorption system
AUTOGC	Perkin Elmer Ozone Precursor Analysis System
CFR	Code of Federal Regulations
COC	chain of custody
DAS	data acquisition system
DP1	capillary gas chromatography column coated with 100% dimethylsiloxane
DQA	data quality assessment
DQOs	data quality objectives
FSTL	Field Study Technical Leader
GC	gas chromatography
GIS	geographical information systems
GLP	good laboratory practice
HRGC	high resolution (capillary) gas chromatography
LIMS	Laboratory Information Management System
MPA	monitoring planning area
MQOs	measurement quality objectives
MSA	metropolitan statistical area
NIST	National Institute of Standards and Technology
PAS	Passive adsorbent sampler
PC	personal computer
PCS	Passive canister sampler
PD	percent difference
PLOT	porous layer open tubular chromatography column
PM	Project Manager
QA/QC	quality assurance/quality control
QA	quality assurance
QAO	quality assurance officer
QAPP	quality assurance project plan
QMP	quality management plan
SER	Southeast Region
SOP	standard operating procedure
WDNR	Wisconsin Department of Natural Resources

B. PROJECT MANAGEMENT

This monitoring project will passively collect air samples near selected roadway and in neighborhoods adjacent to the targeted roadways. The projects' goals are to evaluate the passive sampling techniques and to use the techniques to evaluate benzene concentration gradients near the roadways. The project will be conducted by the Environmental Sciences Section of the Bureau of Air Management, Wisconsin DNR. The Air Monitoring Section of the Bureau of Air Management will supply critical support for the study. Elements of the project managements are detailed in this section.

A.1 Roles and Responsibilities

Project Manager – Mark Allen will serve as overall project manager for the project.
Field Study Technical Leader – David Grande will oversee the field studies and sample collection.
Field Operations - Southeast District Field Monitoring Staff will be assigned responsibility for the collection of samples and general project operations. This will include the collection of quality control samples.
Data Validation – Data validation will be the responsibility of the ESS staff.
Data analysis – Jeff Myers will take lead responsibility in end-use data analysis. Jeff will evaluate the study data in relation to project goals to evaluate benzene concentration gradients.

A.2. Distribution List

A read only electronic copy of this document will be available to all WDNR staff through the department's intranet service. Electronic copies of the document will be specifically provided to the individuals listed below. Hardcopies of the document will be placed in the project handbook. The Project Manager and the Field Study Operations Leader will have copies of the project handbook. Additional copies of the project handbook will be placed at the WDNR-SER's air monitoring laboratory.

Electronic Copies of Quality Assurance Project Plan Distribution List
Motria Caudill – Region 5, USEPA
Eileen Pierce - AM/7
Jon Heinrich - AM/7
Edward Miller - SER
Mark Allen - AM/7
David Grande - AM/7
Steve Schuenemann - AM/7

A.3. Problem Definition/Background

A.3.1 Problem Statement and Background

Benzene is ubiquitous aromatic hydrocarbon formed in many combustion processes. Benzene is a known human carcinogen and is consider one of the most significant risk drivers in the urban environment. Mobile source emissions make up the major source of benzene in the urban environment (Fruin et.al., 2001). Models show that the exposure from roadways is related to the distance from the roadway (Funk and Lurmann, 2001). Monitoring studies suggest that for mobile source pollutants, like benzene, the outdoor and indoor air concentration are similar and indicate ambient air is the most important exposure driver (Paynes-Struges et. al., 2004).

A review of Wisconsin's air emission inventory for the year 2000 shows a total of 37 facilities in Milwaukee reporting a total of more than 16850 pounds of benzene emissions. The majority of these emissions (over 14750 pounds) are accounted for by 14 primary metal industries (foundries and metal casting). Petroleum products terminals, motor manufacturing, pipelines, power generation and wastewater treatment account for the majority of the remaining reported emissions (over 2090 pounds).

Roadway emissions are important because Milwaukee is location of a major urban interstate roadway, Highway 94. Construction of Highway 94's Marquette interchange began in 2005 and will be continue until 2008. This construction may have significant impact on mobile source roadway emissions in the city.

Therefore questions remain about benzene in the urban environment that warrants further study. How accurate are current stationary source and mobile source inventories in predicting ambient benzene concentrations? Are major roadways significant sources of benzene? How quickly is benzene dispersed from the roadways to the adjoining environment? What are benzene exposures in neighborhood environment?

The Wisconsin DNR's development of passive sampling techniques will provide a tool to better understand the sources, transport, and diffusion of benzene from roadways. While benzene will be the primary focus of the project, related hydrocarbons will be monitored to assist in assessing the sources and impact of the benzene.

A.3.2. List of Target Pollutants

The pollutant target list for the study will be hydrocarbons analyzed on the DP-1 column of the Perkin Elmer Ozone Precursor Analyzer. The compounds are listed below in Table A1.

TABLE A1: DP-1 Column Target List

Critical	Priority	Base
BENZENE	N-HEXANE 224-TRIMETHYLPENTANE TOLUENE M/P-XYLENE O-XYLENE 123-TRIMETHYLBENZENE	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

Target compounds are organized in to three categories. Benzene is the critical target compound for this study. Sampling and analysis variables, in the study, should be optimized to provide benzene concentrations with the highest data confidence. Priority target compounds will be important in supporting the benzene measurements and in establishing the sources of the measured benzene. Providing good quality assurance information of these compounds is important. Base compounds are target compounds that will also be measured by the analyses. Providing good quality assurance information on these compounds is desired but not required.

A.3.3 Target Locations for Study

Monitoring will be conducted along roadways in the Milwaukee urban interstate corridor. Targeted roadways will be within the Wisconsin DNR's Regional Air Impact Modeling Initiative (RAIMI) domain. Initial modeling will transect the roadway placing monitor at the roadway and at predetermined distances from the roadway. Follow-up monitoring may use the same transect design or more complex monitor placement schemes.

A.4. Project/Task Description

A.4.1 Description of Work to Perform

The Wisconsin DNR will develop in-house analytical methods to analyze air samples captured in passively sampled canisters and air pollutants trapped on passively sampled adsorbent tubes. The passively samples canister can provide short-term (less than 24 hours) measurements of volatile organic compounds (VOCs). Passively sampled canisters require no external power. This results in a relatively simple deployment to the field. Passively sampled adsorbent tubes capture VOCs through the diffusion process. The adsorbent tubes are less expensive than canisters and are easier to prepare for sampling. A number of adsorbent tubes can be deployed to an area of interest to provide *saturation* sampling. The adsorbent sampling tube provides a longer averaging time. While the longer time is less useful for studying atmospheric chemistry and physics, it does provide a time scale more relevant to existing risk assessment modeling.

A.4.2. Project Goals

Develop knowledge for the use and analysis of two easily deployed passive air sampling units. The methods include both passive canisters and passive adsorbent tubes. Sub goals for the project are listed below.

- Develop in-house analytical methods for passively sampled canisters and adsorbent tubes using existing analytical systems.
- Test the passive sampling systems to establish comparability to existing active sampling systems used by the Wisconsin DNR.
- Deploy the passive systems in a field study and use this information to optimize designs to support risk assessment modeling.

A.4.3. Field Activities

- Develop easily deployed sampling units for both passive canisters and adsorbent tubes. The passive canister must have a timer to begin sample collection at an assigned time. The passive adsorbent sampler must have a protective housing.
- Test the passive sampling systems to establish comparability to existing active sampling systems used by the WDNR
- Deploy the passive systems in a field study and use this information to optimize designs to support risk assessment modeling. Samplers will be deployed in an initial study. Data from the spring study will be assessed and evaluated to optimize a larger fall field study.

A.4.4. Laboratory Activities

- Optimize the current parameters and the performance of the PAMS AutocGC system.
- Using the model parameters provide by IEPA develop analytical methods for both the passively sampled canisters and adsorbent tubes on the AutoGC system.
- Analysis field samples collected in the study on the AutoGC system.
- Review and validate analysis data

A.5. Project Assessment Techniques

The Project Manager and FSTL will monitor and assess work on the project. Formal assessments will be made in quarterly reports to the Air Program managers. Quarterly reports will be issued listing the project activity during the previous 90 days. The report will also address any significant findings that will affect activities in the next calendar quarter.

A.6. Schedule of Activities

The project will have five major areas of activities that include

- Pre-study preparations until June 2006
- A method summertime method evaluation study June through August 2006

- A fall roadway study completed by October 2006
- A follow-up roadway study completed before May 2006
- Post study evaluation and reporting completed by June 2007

A.7. Project Records

Important project record will include field notebook, sampling records, analysis chromatograms and chromatographic reports, laboratory notebooks, project database, quarterly reports, quality assurance reports and a final project reports. Records handling is addressed below:

Field sampling notebook will be used by operation staff to record significant information about the project field study. The notebook will be keep at the SER air laboratory will field study equipment and supplies.

Field sampling records will be hardcopy records completed by operation staff. Data from the records will be entered into the project database. Hardcopies will be retained with the project files.

Analysis chromatograms and chromatographic reports will be maintained electronically on the AutoGC systems control and data computer. Data will be in formats compatible with Perkin Elmer's TotalChrom software. Results data will be transferred to the project's ACCESS database.

Laboratory notebooks will be used by staff to record significant information about the analysis procedure and the AutoGC. The notebook is keep with the AutoGC. The notebook for this project is also used for the PAMS project. This project will not have a separate laboratory notebook.

The project database will be in ACCESS format. The database will be located on a DNR network accessible fileservice. Data from the project database can be exported to other software program for additional analysis and review.

Quarterly reports will be prepared using WORD software. Copies of the reports will go to EPA staff and WDNR's Monitoring Section and ES section chiefs. An electronic copy of the reports will be kept on a WDNR DNR network accessible fileservice. A hardcopy of the report will be added to the project files.

Quality assurance reports will be prepared using EXCEL and WORD software. Copies of the reports will go to EPA staff and WDNR's Quality Assurance Officer, the Monitoring section chief and the ES section chief. An electronic copy of the reports will be kept on a WDNR DNR network accessible fileservice.

The final project reports will be prepared using EXCEL and WORD software. Copies of the reports will go to EPA staff, the WDNR's Quality Assurance Officer, the Monitoring section chief, the ES section chief, all WDNR staff participating in the project. An electronic copy of the final reports will be placed on the WDNR's internet WEB page and will be generally accessible to all interested parties.

A.8.0. Quality Objectives and Criteria for Measurement Data

A.8.1. Data Quality Objectives

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

A.8.2. Measurement Quality Objectives

The quality of the dataset will be assessed using standard measurement parameters for completion, accuracy, precision, and compatibility. The parameters will be defined as follows;

Completion – is the percentage of planned samples that are collected, analyzed and reported. Completion will be assessed as the number of samples collected / number of samples planned * 100%

Accuracy – is measured as the deviation of the measured value from a true value. Accuracy is assessed as the percent difference from the expected (spiked) value. The percent difference is calculated as (measured concentration – expected concentration)/(expected concentration) * 100%.

Precision – is the repeatability of a measurement. Precision will be assessed as the using standard deviation when triplicate measurements are collected. For duplicate measurement precision will be assessed as a percent difference from the primary sample. Here the percent difference is calculated as (measured duplicate concentration – measured primary concentration)/(measured primary concentration) * 100%.

Comparability - is a measure of the bias between this study's data and data collected from established and reported methods. The Wisconsin PAMS program will be the reference program for this project. Bias will be assessed visually using a scatter plot of concentration measured by each method. Numerically bias will be assessed by the slope and intercept calculated from concentrations of the test and reference method.

A.9. Special Training Requirements/Certification

The Field Study Technical Leader (FSTL) will provide in-service training to operations staff. The FST Leader will develop a list of criteria for operation staff to assess the readiness of operations staff to conduct monitoring operations. Training will include safety training for staff working close to roadways. The FST Leader will follow up on and resolve any problems operation staff encounter in conducting the study.

The Field Study Technical Leader will train field staff operators. The FSTL will on the basis of the training, certify that operations staff are prepared to conduct sampling.

A.10. Documentation and Records

All hardcopy documentation and hardcopy field records will be stored in the designated project file.

Electronic copies of data and documentation will be stored on a DNR network accessible fileservice. The data will be stored in a subdirectory of the AMPAMS fileservice. Electronic data that does not required immediate access will be compacted (ZIPPED). Compact disk copies will be made of all ZIPPED files. The CDs will be stored in the project file.

B. MEASUREMENT/ DATA ACQUISITION

B11. Sampling Design

B11.1. Scheduled Project Activities, Including Measurement Activities

The project will center on three monitoring activities.

- The first activity will be to validate the passive sampling methods during the summertime PAMS monitoring season. During this activity PAS and PCS will be collocated with currently used active sampling systems. Samples from both systems will be analyzed according to established protocols. Data from both systems will be evaluated to establish the comparability of the passive and active sampling systems. The goal is to complete this work by August 31, 2006.

- In the fall of 2006 we will conduct a preliminary field roadway monitoring study. The preliminary study will collect benzene and associated hydrocarbons along a linear transect centered on a Milwaukee Urban Interstate Roadway. PASs will be deployed at intervals along the roadway transect. PCSs will be used for short term measurements at the roadway centerline. The goal is for the preliminary field monitoring study will be completed before October 30, 2006.

- The third and final activity is to conduct a second follow-up roadway monitoring study. The final study will be planned using information from the preliminary roadway study and summertime validation. Project staff will deploy a field study to demonstrate roadway exposure to benzene and show how that exposure changes as you move from the roadway to residential neighborhoods adjoining the roadway. This second study is expected to use a more complex array of PAS. Sampling will again take place along a major roadway. Saturation sampling in an adjoining neighborhood will be used to track changes in concentration as a function of distance from the roadway. PSC will again be used for short term concentrations. The goal is to complete the second roadway study by May 1, 2007.

B.11.2. Rationale for the Design

The development and testing of passive monitors for monitoring concentration of benzene and other aromatic hydrocarbons was been reported by Brown, et. al. (1981). In a later paper Brown et. al.(1999) discussed the use of these passive sampler for mobile source related pollutants, including benzene, toluene, and xylenes. The technique will use commercially available diffusion tubes designed for analysis by a Perkin-Elmer gas chromatographic system, like that used at Wisconsin’s Milwaukee PAMS site. This gas chromatographic system is operated during the peak ozone months, June through August. We will enlarge the scope of work by conducting analyses of the passive samples before June and after August. The current analysis parameters will provide a solid base for the passive sample analysis, development time for the method should be minimal.

Wisconsin DNR’s current methodologies and methods have been proven in the Photochemical Assessment Monitoring Station (PAMS) and Urban Air Toxic Monitoring (UATM) projects. These current methodologies will provide the benchmarks for comparisons of the passive technologies. Currently pressurized whole air samples in passivated canisters are analyzed at the Wisconsin State Laboratory of Hygiene. The Wisconsin State Laboratory of Hygiene has analyzed PAMS and UATM monitoring samples for the Wisconsin DNR since 1994. Hourly benzene values are collected at the Type 2 PAMS site using a Perkin-Elmer Ozone Precursor analyzer (AutoGC). This unit has been in operation at the Wisconsin site in Wisconsin since 1999. Other monitoring parameters collected at fixed-long term sites include ozone, carbon monoxide, wind speed and wind direction. The Wisconsin DNR has established operating procedures for these parameters including Standard Operating Procedures (SOPs) and Quality Assurance Project Plans (QAPPs).

The Wisconsin DNR has an established record for carrying out environmental studies similar to that proposed. In 1995 WDNR staff conducted a short intensive study of reformulated gasoline components (Allen, Grande and Foley, 1996). This monitoring project included monitoring near roadways as well as exposure studies during vehicle refueling.

B11.3. Procedure for Locating and Selecting Environmental Samples

The method validation study will be conducted at the Milwaukee PAMS monitoring site (AQS 55-079-0026). Additional sample may be collected at other PAMS and Urban Air Toxics monitoring sites.

The location for the roadway study will selected based a several criteria including the following; safe access for WDNR staff, a high traffic count, pervious RAMI modeling along the roadway, and a nearby population that might be affected by the vehicular traffic.

RAMI Modeling Domain
West Boundary – 35th Street
North Boundary – Wisconsin Ave
South Boundary – Lincoln Ave
East Boundary – Lake Michigan

B11.4 Monitoring Site Selection

Specific criteria for selecting a target roadway area for the study will be as follows.

1. Roadway should be within the Milwaukee RAMI modeling study. The domain for this modeling study is bound by Michigan Avenue on the North, 35th Street on the west, Lincoln Street on the South and Lake Michigan on the East.
2. The target roadway should be on the same elevation as the surrounding area. The goal of the study is to look at horizontal distribution of benzene concentrations. Vertical distributions should be minimized.
3. The target roadway should have a minimum number of heavily traveled side roads. We would like to isolate the target roadway as much as possible.
4. The presence of a local residential population near the roadway that will provide our DHFS partners to target in a possible home exposure study.

B.12. Sampling Methods Requirements

B12.1. Purpose/Background

Passive sampling uses monitoring techniques that allow air sampling without a need for large external support. Passive canister samplers (PSC) do not require a pump to fill the canister. Instead the canister vacuum draws the air into the canister until the inside pressure equals the outside pressure. A mechanical regular insure a uniform sampling rate over the filling period. Regulars are available for a variety of standard fill time (60, 180, and 1440 minutes). In the absence of a regulator the canister fills in minutes for a peak grab sample.

Prior to sampling the canisters are prepared by cleaning and evacuation. Cleaning the canister involve several cycles of purging with zero air followed by evacuation. The canister is heated during the cleaning process by a heat belt. A final hard evacuation to less than 5 mmHg completes the cleaning and preparation process. In the field the canister is tagged with a field unique field number. The most critical information is used to properly identify the sample.

Passive adsorbent samplers (PAS) collect pollutants through a gradient process. Pollutants in the air migrate into the adsorbent material. PAS are sometimes called diffusion samplers. The pollutant sample is collected at a rate controlled by physical processes of the sample moving into the adsorbent bed. This differs from active sampling where an air sample is drawn across the adsorbent bed.

PAS are prepared for sampling by a “Blanking” process. The blanking process is identical to the initial stage of the analysis process. The sample tube is heated and purged with a inert carrier gas. The adsorbent tube is tagged with a unique field ID. Again the most critical information is used to properly identify the sample.

B.13. Sample Custody

The QAPP will address sample Chain-of-Custody only as required for routine surveillance or information-gathering samples. While requirements are less strict than used for enforcement or litigation samples, proper Chain-of-Custody procedures must be followed to insure a complete and accurate dataset.

Field record tracking records and forms (see Appendix X) which identify sampling personnel, sampling techniques and field conditions are required and will act as a Chain-of-Custody Record. The site operator is responsible for maintaining sample custody until the State Laboratory of Hygiene or other analytical agency accepts the sample, or until the sample is picked up by the shipping service.

Custodial responsibilities for VOC and carbonyl samples will be shared by the Bureau of Air Management personnel and the analysis laboratory personnel. The Monitoring Section Data Unit will track the sample field records from initial shipment of the sample collection devices to final disposition. The completed final record will become part of the permanent record stored at the Bureau.

All field samples require these field record tracking forms. All samples will be assigned a unique number for identification purposes. Samples will be labeled in the manner listed in Table 3.

Table B2. Sample labeling protocol.

Sample Type	**Place label**
Adsorbent tubes (PAS)	-taped label on transport tube
Canisters (PCS)	-label on tag attached to canister
After sampling, all field samples will be placed in a small plastic cooler. The cooler will be transported to the SER Headquarter. At the headquarter sample will be stored in a designated refrigerator until analyzed. Canister samples do not require refrigeration.	

B.14. Analytical Methods Requirements

B.14.1. Purpose/ Background

The primary analytical method for this study will be gas chromatography. Air samples collected in passive canister or on passive adsorbent tubes will be analyzed by thermal desorption followed by gas chromatography with flame ionization detection. Canister samples will be analyzed on both a DP-1 column and an Al2O3 column. Adsorbent tubes will be analyzed only on the DP-1 column. When operating on two analytical column the system can detect and quantify 55 target hydrocarbons. The study will focus on 34 target compounds with benzene designated as critical and 6 other compounds designated high priority compounds.

B.14.2 Preparation of Samples

At the laboratory, the non-pressurized canisters from the passive sampler are pressurized with zero air. This operation consisted of connecting the canister to a cylinder of dry ultra zero air through a manifold with a pressure gauge and a control valve. The initial pressure of the canister is measured, the zero gas was allowed to flow into the cylinder, and a final canister pressure is measured. The concentration of the sample is proportional to the canister pressure and the dilution factor for the sample is then $P_{final}/P_{initial}$. Once diluted and pressurized the canister are allowed to equilibrate at least 24-hour before any analysis is performed. The canister is attached to the Perkin Elmer gas chromatographic system used for the analysis of PAMS hydrocarbons. Analysis results from the diluted canisters must be corrected using the dilution factor.

Adsorbent tubes are capped and kept at 4 degrees C until analysis. Samples are placed in the sampler carousel and the analysis system activated. The carousel will move individual tubes into the analysis pathway. The adsorbent tubes are heated and desorbed onto the system's internal trap. The internal trap is then heated with compounds desorbed and transferred to the analytical columns.

B.14.3 Analysis Methods

The analysis gas chromatographic system is a commercial Perkin Elmer system capable of automated sample processing, analysis, and data acquisition. The primary components are a sample introduction system, sample conditioning system (for moisture removal), sample concentration system (for sample enrichment), cryofocusing trap (as an option for improving peak shape and resolution), gas chromatograph with FID(s), and a data acquisition and processing system. The system uses two analytical columns to provide separation of hydrocarbons over a C6 to C12 range. The system is computer controlled using Perkin Elmer's TotalChrom software.

B.14.4. Internal QC and Corrective Action for Measurement System

Compound are identified based on the retention time (RT) automatically assigned by the analysis system. The retention time is minute fraction for a compound peak to elute after injection on the columns. A normal chromatographic analysis will yield a retention time table listing the RT and peak area for all compounds detected. RT values will remain constant for a compounds on a correctly functioning analytical column. The data acquisition will assign a identity to peak based on RT and a concentration based on peak area.

Chromatogram will be reviewed to determine if any shifts have occurred in the RT values for the analysis. If a shift has occurred the analysis program will be adjusted to correctly identify the peak. The peak area will be calibrated by a two component gas containing know quantities of propane (AL2O3 column) and benzene (DP-1 column). A 55 component gas is periodically analyzed as a control. If components in the 55 compounds control gas are not within an assigned concentration range the system must be recalibrated.

B.14.5. Sample Contamination Prevention, Preservation and Holding

Canisters are evacuated to less than 5 mm Hg prior to sampling and are sealed with a bellow type valve. In the field, a timer will open the sampling train allowing the air sample to enter the canister. At the end of the sampling period, the timer will close the sampling train. During sample retrieval the canister valve is manually closed. The canister valve should remain closed to protect the sample until processing (dilution/pressurization) and analysis.

Adsorbent tubes should be capped in the field and placed in a Teflon capped culture tube. Tube samples should be held in the laboratory refrigerator until analysis. To minimize possible contamination tubes should only be handled with gloved hands.

B.15. Instrument/Equipment Testing, Inspection, and Maintenance Requirements

The passive sampling system will require minimal maintenance. Prior to being deployed the canister sample will be visually inspected for any problem. The operator should verify the sampling timer is correctly set.

Passive sampling tubes will be blanked and store in the refrigerator prior to sampling. A the sampling site the tube should be visually inspected prior to deployment.

The analysis system will undergo an annual inspection and maintenance. This will include replace any consumable parts according the schedule in Appendix 1. All set points for temperature and gas flow will be checked. Test analysis of a gas chromatograph blank, a system blank, a zero gas blank, a calibration standard and a multi-component standard will be analyzed and reviewed according to the criteria listed below.

B.16. Instrument Calibration and Frequency

B.16.1 Instrumentation Requiring Calibration

The gas chromatographic analysis system must be calibrated to correctly identify target compounds and to quantify the concentrations of compounds in the samples. Calibration for identification will use a 55 compounds standard. The standard will be analyzed a minimum of 4 times a day on three days. A Retention Time table will be developed for the data processing program. Unknown compounds will be identified when their retention time falls with a window center on the RT from the RT table. Standard RT windows previously develop by WDNR staff will be used.

Compounds concentrations are proportional to the peak area. A quantitative two component standard will be used for quantification. The gas chromatographic systems flame ionization detector will respond in proportion to the number of carbons in a hydrocarbon compound. The calibration standard contains propane and benzene in a nominal concentration of 10 ppb. The calibration standard for the project in carbon is then propane 30 ppbC (part per billion Carbon) and benzene 60 ppbC. The quantitative standard will be analyzed a minimum of 4 times a day on three days. Peak areas from all runs will be analyzed and a peak response factor will be calculated from the average peak area divided by the concentration in ppbC. Unknown peaks will be quantified by dividing the unknown's peak area by the RF. The analysis system is typically calibrated at the start of the project and at the end of the project. The calibration standard is periodically analyzed to verify that calibration has been maintained.

B.16.2. Calibration Standard Materials and Apparatus

Commercially prepared standard gases will be used. The supplier is required to provide a certificate of analysis with the measured gas concentrations and an estimate of the measurement error.

B.17. Inspection/Acceptance for Supplies and Consumables

Critical supplies will include commercially prepared adsorbent tubes and standard gases.

- Adsorbent tubes will be visually inspected upon arrival. All new tubes will be blanked. At least 10% of al new tubes will be analyzed after blanking to insure no residual target compounds are present on the tubes.

- Standard gases will be analyzed and compared with older outgoing standards. Based on a calibration using older (and established) standards the new standards should be within expected error of the certified concentration. In addition, analysis standard are split with the WDNR's in-house laboratory at the Wisconsin State Laboratory of Hygiene. On an annual basis.

B.18. Data Acquisition Requirements

B.18.1 Acquisition of Measurement Data

Two level of data acquisition will be used on this project.

- The first is manual data acquisition of field data. Once acquired and logged field data will be keyed into the project database. Fieldsheets will be retained for a period of one year following the project. The electronic database will be retained for at least a period of 5 years.

- The second level of acquisition is automated data acquisition by the GC data system. The original data files (.RAW). will be generated by the system. The GC system will automatically process the data files to identify and quantify the target compounds detected in the samples. Data processing will generate a result file (.RST) and a text report file (.TX1). Copies of the three files will be achieved for a minimum period of 5 years.

B.19. Data Management

B.19.1 Background and Overview

Field sheet and results data will be managed in a project database created using ACCESS software. Within the database will be two tables contain the field and analysis results data. Additional tables created in the database will support the two main tables. Supporting tables will contain definitions for coding used in the main database tables. Table B3 contains field definitions for the main database.

Table B3. Project Database Tables

Fielddata				
Field 1	Sample ID	Text	8	RB06-001
Field 2	Site Code	Text	6	MW001
Field 3	Date Deployed	Date		4/1/2006
Field 4	Sample Date	Date/Time		4/2/2006 07:00
Field 5	Duration	Number		180
Field 6	Date Retrieved	Date		4/2/2006
Field 7	Sample Type	Text	2	Q2
Field 8	Canister/Tube Number	Text	6	WI166
Field 9	Valid	Text	1	Y
Field 10	Comments	Text	50	
Results				
Field 1	Sample ID	Text	8	RB06-001
Field 2	Parameter Code	Number		45201
Field 3	Method Code	Number		126
Field 4	Concentration	Number		3.21
Field 5	Units	Text	4	ppbC
Field 6	Data Flag	Number		0
Field 7	Comments	Text	50	

B19.2 Data Recording

Field data will be recorded manually on field sampling forms (fieldsheets). Data on the manual forms will later be keyed into the database. Results data will be collected by the gas chromatographic system. Raw GC data will be processed by the TotalChrom software to identify and quantify the detected target compounds. The text report file from each run will be processed by VOCDat software to initially screen data and to format to import to the project database.

19.3 Data Validation

Data will be validated at three levels for the project.

- Level 0 validation of the data focuses on the completeness and accuracy of the database information. Are all required data fields filled. Is the information in the field correct. Do all field samples have match results. Do all results have matching field data.

- Level 1 validations address the quality of the data collected. The primary effort here is to correctly flag the data and add necessary comments. Validation should focus on the identification and quantification of the data.

    - Level 2 validation address the quality of the data relative to the project data quality objectives. Validation will focus on accuracy when compared to an outside laboratory, sampling precision, and comparability to established methods.

B.19.4 Data Transformation

Two important data transformations will be made in this project.

- The first will be the correction of the instrument canister data for dilutions that occur as the canister is taken from ambient to a pressurized state. Canister must be pressurized for the gas chromatographic analysis. The instrument canister data is converted to the ambient concentration when multiplied by a dilution factor of Pressure Final/ Pressure Initial.

  C (ambient) = C (instrument) *(Pressure Final / Pressure Initial)

- The second data transformation will be the conversion of weight per sample for the adsorbent tube to an ambient concentration. The conversion is based on Equation 19.2

  C (ambient) = weight per sample / (theoretical diffusive uptake rate * exposed time)

B.19.5. Data Summary and Characterization
Data will typically be summarized and statistically characterized using EXCEL spread sheet software. Spreadsheet software will provide basic summary information including data counts, data averages, date ranges (including minimums and maximums) and data variability (as standard deviations). Spread sheet software also allows basic data plotting to visually inspect the data.

B.19.6. Data Storage and Retrieval
Data will be stored on the DNR's internal network at a central located file that can be accessed by all project staff. Upon completion of the project the database, and all electronic files related to the project will be achieved to compact disks. A hardcopy of the final report and all project data will be keep in the monitoring sections files for a minimum of five years.

C. ASSESSMENT/OVERSIGHT

C.20. Assessments and Response Actions
Assessment of the field sampling project and the sample analysis will be made by staff directly assigned to these tasks. Any problems and corrective action will be relayed to the Project Manager or the FSTL. E-mail messages will be the preferred method to alert the project manger of problems.

The project manager will check on progress each week.

C.21. Reports to Management

Quarterly reports on the project will be made to the designated EPA staff, the WDNR Monitoring Section Chief, the WDNR Environmental Sciences Section Chief, the SER Monitoring Supervisor, and project staff.

A final report will also be made to EPA staff, the WDNR Monitoring Section , the WDNR Environmental Sciences Section Chief, WDNR Environmental Sciences Section Chief the SER Monitoring Supervisor, and project staff..

C.22. Data Review

Data will be periodically reviewed and validated. If data review indicates a problem corrective action will be taken to insure data validity.

Upon completion of the field studies and the complete analysis of all collected samples the project database will undergo a final review. The data base will provide a measure of each target compound for each sample collected. As part of the final review each data record will be given a final data flag to indicate the quality of the data against the goals set in this QAPP.

Data will be summarized and that summary will include the completeness of the field studies, the results for quality control tests and the comparability of study methods to established methods.

The final data base will be forwarded to data end users for their evaluation and use in charactering roadway benzene concentrations.

D. VALIDATION AND USABILITY

D.23. Validation, Verification and Analysis Methods

The overall goal is to create a complete set of monitoring data of know data quality for the end data users. To accomplish this the project staff will collect field samples, analyze those samples, and report the analysis data. Data will be validated against goals set forth in section 19.3. The data end users will examine and evaluate the near roadway benzene concentration gradients using the data supplied by the study.

D.24. Reconciliation with Data Quality Objectives

The DQO for this project is to create a complete dataset of know quality for use in evaluating roadway emission and validating risk assessment modeling for roadways. After the data set is assembled it can be evaluated against the goals in the DQO. This evaluation will focus on meeting several criteria including the following:

- Have the passive methods successfully provided data to create a complete data set for spring and fall roadway monitoring studies?
- Is the data in the data of good quality when evaluated for accuracy and precision as defined in this QAPP?
- Is the dataset comparable to data collected at the fixed PAMS site? If a bias is shown between the active and passive methods exist can that bias be reliably quantified?
- Can the dataset show the expected concentration fall off between sites close to the target roadway and sites located a greater horizontal distances from the roadway.

Appendix C: Experimental Test Of A Passive Canister Sampling System

State of Wisconsin

CORRESPONDENCE/MEMORANDUM

DATE: February 1, 2002 FILE REF:

TO: Air Monitoring Files

FROM: Mark K. Allen – AM/7 MKA

SUBJECT: AN EXPERIMENTAL TEST OF A PASSIVE CANISTER SAMPLING SYSTEM

Terminology

Throughout this report I will be using some basic terms to describe various sampling systems and canister samples. To assist the reader, I have listed these terms here along with my definitions.

Active Sampling – air sampling using an electrically powered pump to move air into the canister. This technique usually ends with the canister pressure greater than the ambient air pressure.

Passive sampling – air sampling that does not use a pump to move air. In this report passive sampling is conducted by allowing the vacuum inside the canister to draw in the air sample. When passive sampling the final pressure in the canister can not exceed the ambient air pressure.

Pressurized canister – sampling canister filled with an air sample or standard to a pressure of 2 to 2.5 times the ambient pressure.

Non-pressurized canister – sampling canister filled with an air sample or standard to a pressure equal to or slightly less than the ambient pressure.

Evacuated canister – at the start of sampling all canisters are evacuated to a pressure of not more than 5 mm Hg absolute. These canisters are considered clean, empty and ready to collect a sample.

Background

The passivated stainless steel canister is a reliable tool for the collection of whole air samples at monitoring stations and in field studies. The whole air sample collected in the canister can be transported to the laboratory for complex chemical analyses, usually a gas chromatographic analysis. The WDNR has used the canisters since the 1987 to collect samples that have been analyzed for photochemically reactive hydrocarbons and for volatile air toxics. Analysis of whole air samples in the canister can provide reliable subpart-per-billion quantification of selected pollutants. Use of canisters has been limited because the active sampling systems currently used have required a 120-volt AC power source. The 120-volt AC power is required to drive sampling pumps need to actively pump air into the canister to a pressure of 15 to 25 psig (30 to 40 psia).

Non-electrical passive sampling systems are available to collect samples using the vacuum to draw air into the canister. These passive sampling systems can be configured to sample for less than 1 hour to 1 week. One draw back of all passive system is that at the end of sampling the operator has a non-pressurized canister (final pressure is <0 psig). Current analytical systems require a pressurized canister to allow for draw off of analytical samples. In addition our current understanding of the physics at the canister surface suggest that analytical results from a non-pressurized canister may not equal a pressurized canister. This occurs because some high molecular weight volatile compounds appear to adhere to the canister surface at lower canister pressures.

One possible approach to using a passive sampling system is to collect non-pressurized canisters in the field. At the laboratory, zero air is added to the canister to dilute the sample and increase the canister pressure. After an equilibration time the canister sample is analyzed in the same manner as a pressurized canister. The analytical results must of course then be corrected for the dilution.

I conducted a field experiment to test the passive sampling system. I also tested the dilution and analysis system to show that results from the passive system are similar to those collected using an active sampling system. This paper will report on the results of this experiment and will show that the passive sampling system can be used for collecting field samples.

Sampling systems

Two sampling systems were used to collect collocated samples for this test. These sampling systems are diagrammed in figures 1a and 1b.

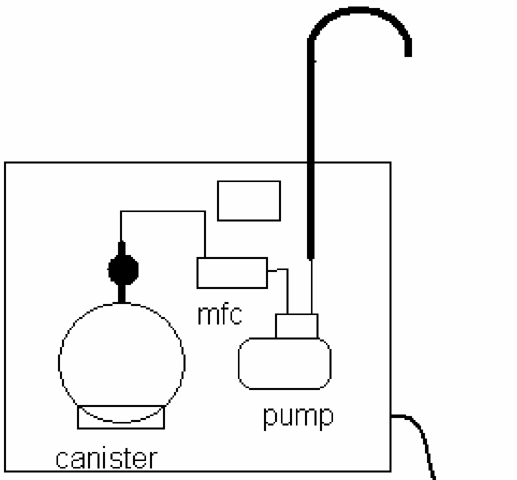


Figure 1a: Active Sampling System

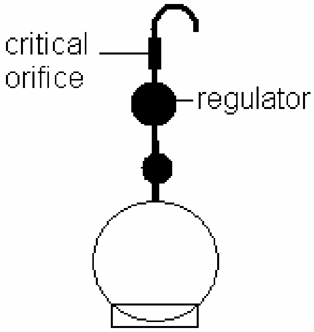


Figure 1b: Passive Sampling System

The first system is an active sampling system designed and built by DNR staff. Housed in a weather- proof case, the system consists of a pump, an electrical mass flow controller, a power supply and a digital display showing the flow rate. The system requires 120 volts AC power that must be supplied from an electrical outlet, a generator, or an inverter with battery. To operate the system, an evacuated canister is connected to the system the pump is turned on and the canister valve opened. The sampling flow rate is set by the operator to collect a pressurized canister in a designated time period. For this test 3-hour samples were collected at a flow rate of 80 cc/min. The estimated end pressure was 21 psig.

The passive sampling system was purchased from the ENTECH Corporation. The system consists of a mechanical pressure regulator and a critical orifice. All canisters are evacuated to less than 5 mm Hg prior to sampling. The vacuum in the canister will draw in the air sample. The regulator maintains the necessary pressure drop for the critical orifice to function. The critical orifice restricts the sampling flow to collect a uniform sample over a designated period. To operate the system an evacuated canister is attached to the sampler. The system is placed in the desired sampling location and the canister valve is opened. At the conclusion of the sampling period the canister valve is closed and the sampler removed from the canister. The system I purchased from ENTECH was configured to collect a 3-hour sample when attached to a six-liter canister. This system includes an attached pressure gauge that shows the canister filling. During the 3-hour sampling period the pressure gauge when from –27 psig to 0 psig.

Test Method

A total of five pairs of collocated 3-hour samples were collected for the study. Samples were collected at three monitoring sites used by the WDNR. All sites had a source of electrical power for the active sampler. The passive sampler was placed on top of the active sampling canister. Both samplers were manually started at the same time and the samplers stopped at the same time.

After sampling the non-pressurized canister from the passive sampler was pressurized with zero air. This operation consisted of connecting the canister to a cylinder of dry ultra zero air through a manifold with a pressure gauge and a control valve. The initial pressure of the canister was measured, the zero gas was allowed to flow into the cylinder, and a final canister pressure was measured. The concentration of the sample is proportional to the canister pressure and the dilution factor for the sample is then $P_{final}/P_{initial}$.
Once diluted and pressurized the canister was allowed to equilibrate at least 24-hour before any analysis was performed.

All samples were analyzed on a Perkin Elmer gas chromatographic system used for the analysis of PAMS hydrocarbons. Canisters were analyzed in pairs over a three-day period. Following the analysis all data was processed and placed in a ACCESS database. The results from the diluted canisters were corrected using the dilution factors. Finally data from the paired samples was compared for individual canister pairs and for all canister pairs together.

Results

Total Hydrocarbons were measured as total nonmethane organic compounds (TNMOC) in each canister. The concentrations ranged from 32 ppbC to 177 ppbC. The percent difference in the sample was calculated as (passive concentration – active concentration)/active concentration. The percent differences ranged from 2.5% to 40.6% and averaged 22%. For all pairs the passive canister had a higher concentration.

A total of 270 species (54 species times 5 samples) were compared in this study. A subset of 193 pairs had measurable concentration in both the active and passive canister. The comparison statistic used was the absolute percent difference and was calculated as (absolute value (passive concentration – active concentration))/active concentration. The absolute percent differences for compounds measure > 1ppbC ranged from 0.0% (2-methylheptane) to 50.8% (n-hexane) and averaged 10.8%. For all measurable pairs the absolute percent difference was 21.6%.

Data is summarized in Table 1 and in Figures 2a & 2b.

Discussion and Recommendations

In evaluating the passive sampling system for use I wanted to determine if the non-pressured canister could provide measurement comparable to the active system which the WDNR currently uses. To do this I focused on the three criteria listed below.

- Compounds collected in the non-pressurized must yield analytical results similar to the concentration measured from the pressurized canister.
- Compounds lost through dilution must be minimal
- There should be not significant interferences added to the sample by the dilution process.

The analysis data shows that the criteria were met. Differences did show up between the non-pressurized canister and the pressurized canisters but these appear to be random differences. The differences also showed a pattern seen with active canisters in which the differences between two canister samples was related to concentration with acceptable differences for concentrations less than 1ppbC ranging from 70% to 100%. There appear to be some loss of compounds between the pressurized and non-pressurized as shown by the compounds detected in the pressurized canister but not in the non pressurized canister. In all cases the lost compounds were at concentration of <1 ppbC. Finally there were a minimal number of interfering compounds that appeared in the non-pressurized canister. Two compounds were noted the first eluting just after 1,2,4-trimethylbenzene and the second eluting just prior to 2,3-dimethylbutane. These compounds will not interfere with the PAMS analysis. I am not yet certain that they will not interfere with the air toxics analysis. I will continue to review data to determine if any problems occur.

Based on the experiment conducted here the Air Monitoring Program should make use of the passive sampling system to collect non-pressurized canisters. Actively sampled pressurized canisters should remain the primary method of sample collection for permanent sites and special studies. The passive canister system can be quickly deployed for investigations. In addition the passive system can, with a minimum amount of training be given to Air Program Staff. Concerned citizens may also be given the sampler to collect samples for investigation.

Table 1: Summary Data for Active/Passive Canister Pairs

Sample Pair	1	2	4*	5	6
Total Nonmethane Organic Compounds (TNMOC)					
Average Conc.(ppbC)	41.23	70.22	32.3	105.25	177.12
% Difference between canister	40.6%	25.0%	26.6%	16.2%	2.5%
Target Species					
Total Number	54	54	54	54	54
Non Detects in Active Sample	8	4	24	3	2
Non Detect in Passive Sample	12	9	9	6	0

Measurable Pairs	34	41	21	45	52
Average Absolute % Difference	30.7%	25.2%	25.6%	20.3%	12.4%
Min % Difference	4.6%	1.7%	2.9%	0.3%	0.0%
Max % Difference	39.6%	72%	8.2%	26.1%	40.4%
Species showing max % Difference	n-propane	Acetylene	n-butane	Methyl-cyclohexane	m-ethyl toluene

* The passively samples canister for Pair #3 was invalidated due to an operator error. Canister Pair #6 was added to the test to replace the pair.

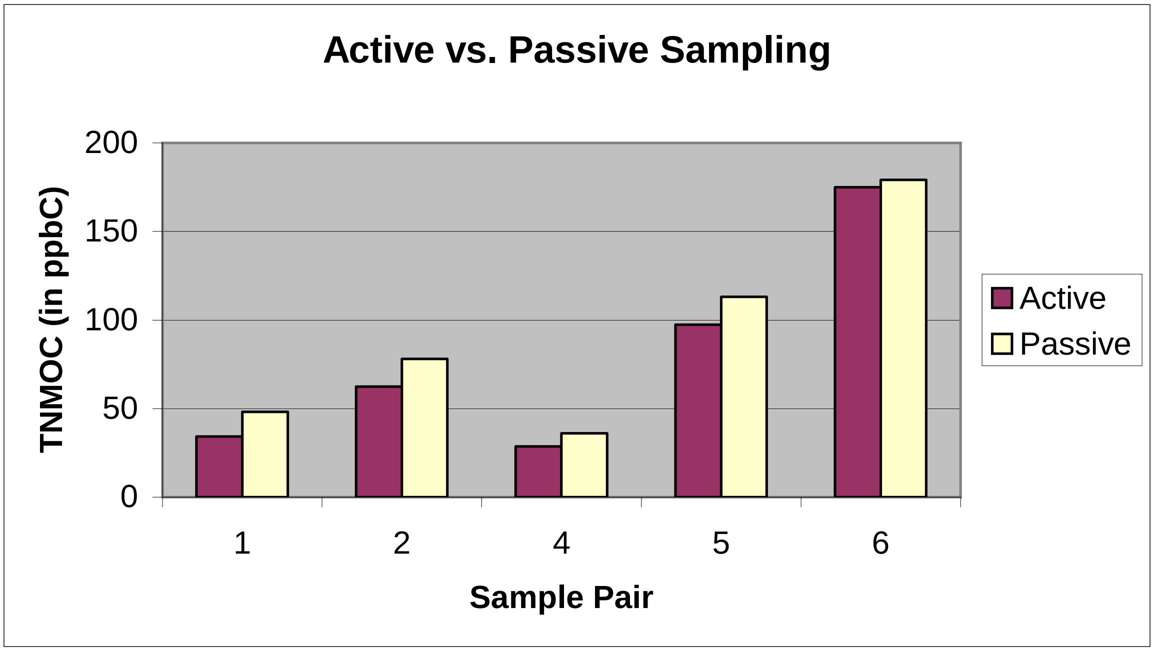


Figure 2a: Bar graph showing the total nonmethane organic compounds concentrations in the

collocated canisters.

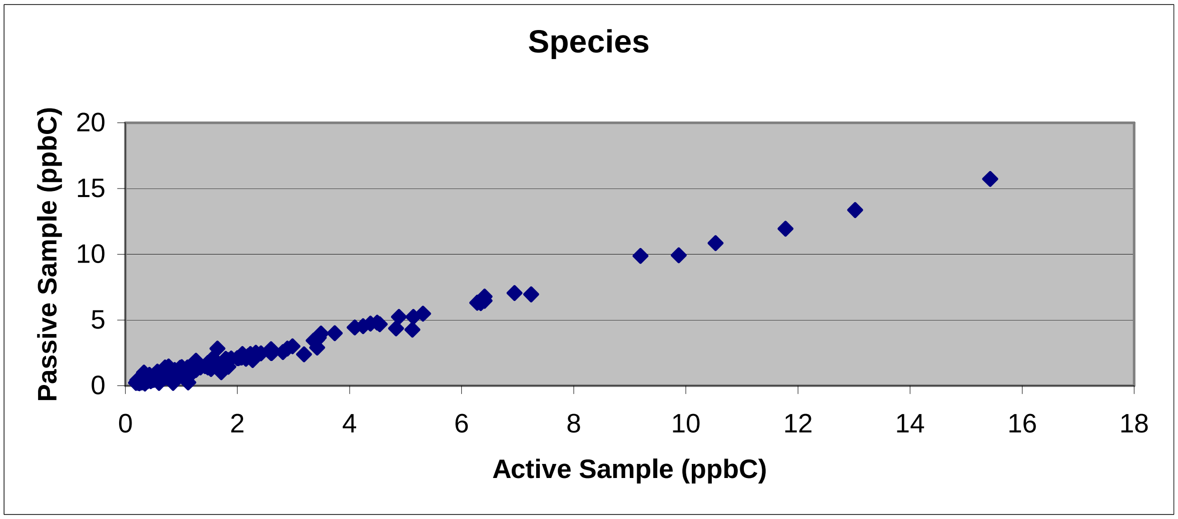
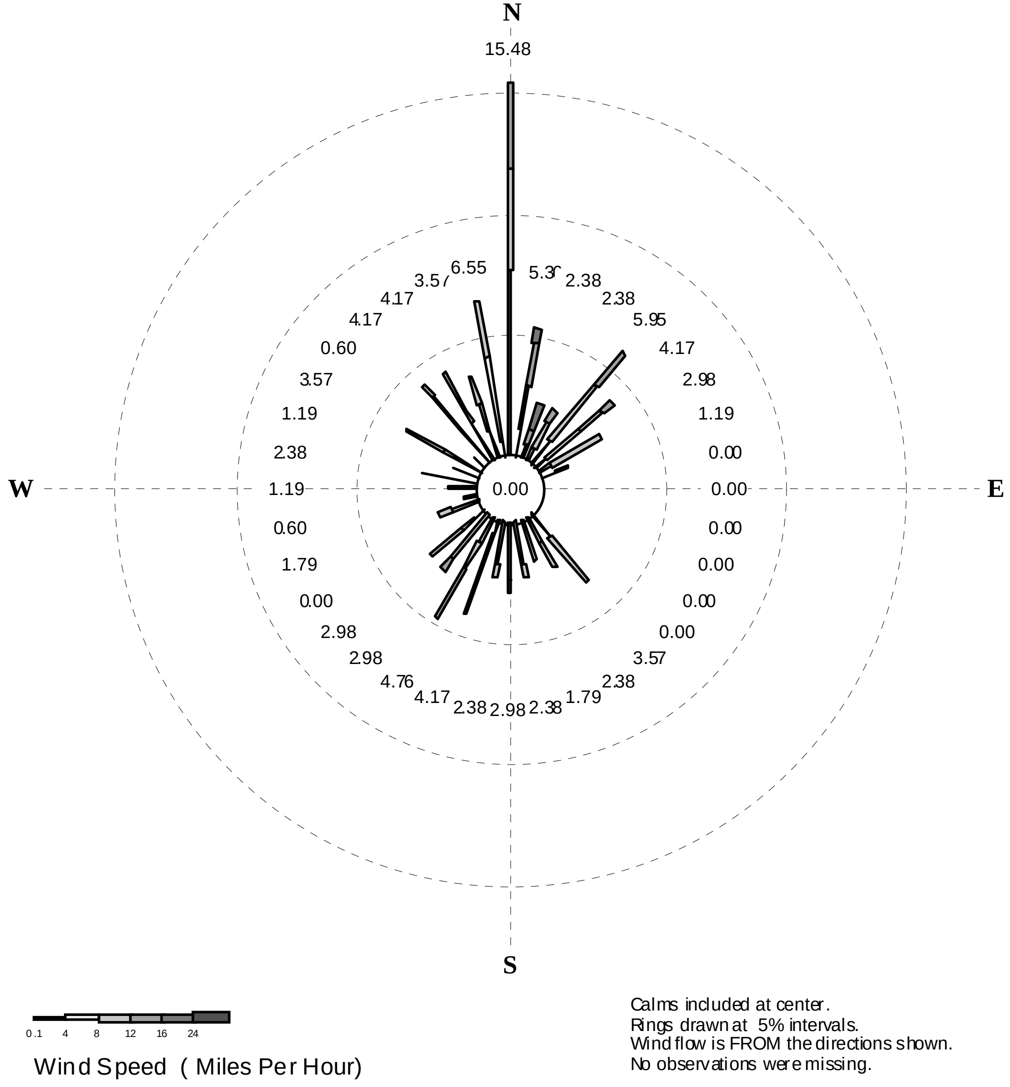


Figure 2b: Scatter plot of species concentrations for all collocated canisters.
A regression analysis yielded and r2 = 0.988 (n=193).

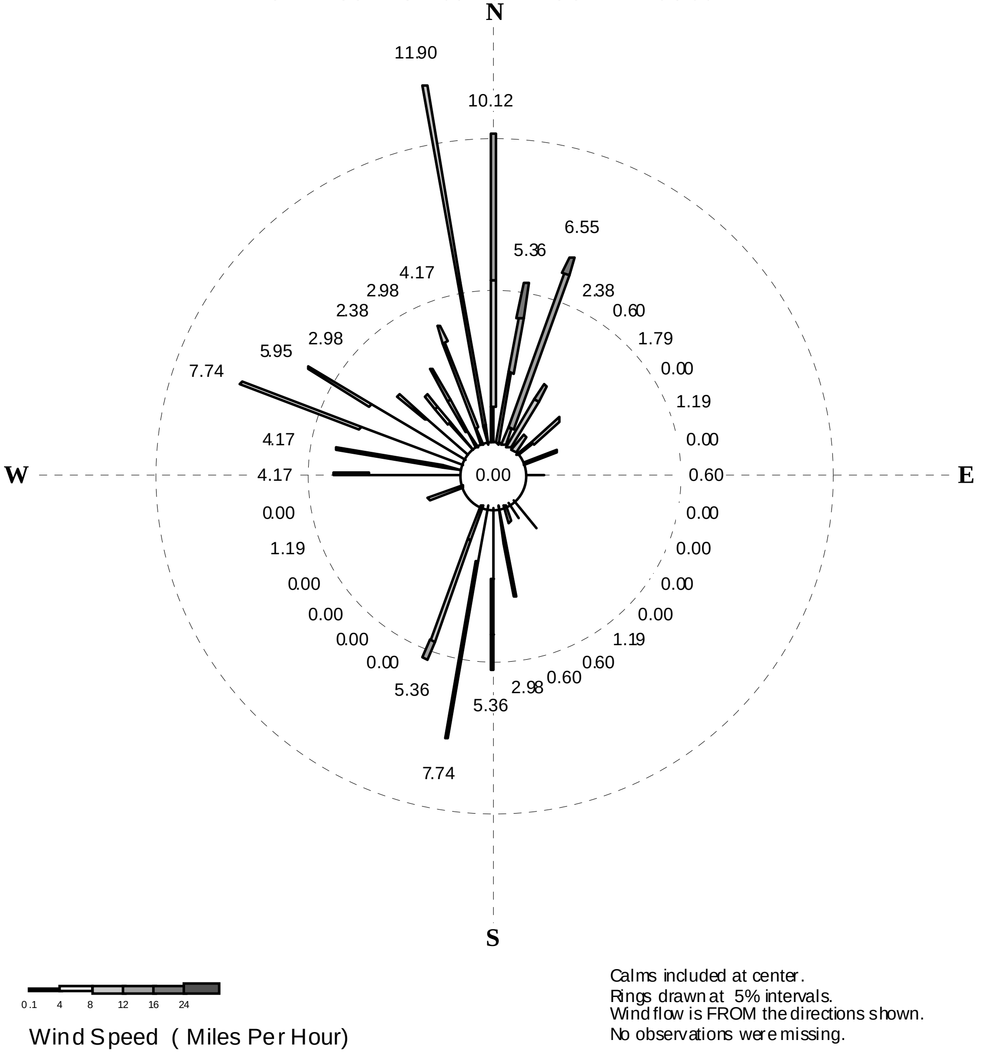
Appendix D: Wind Roses for Field Studies

Site-Week Wind Rose
of Hourly Wind Speed/Direction Data
Milwaukee 16th St. Health Ctr (550790010)
9AM CST 8 Nov - 8AM CST 15 Nov 06



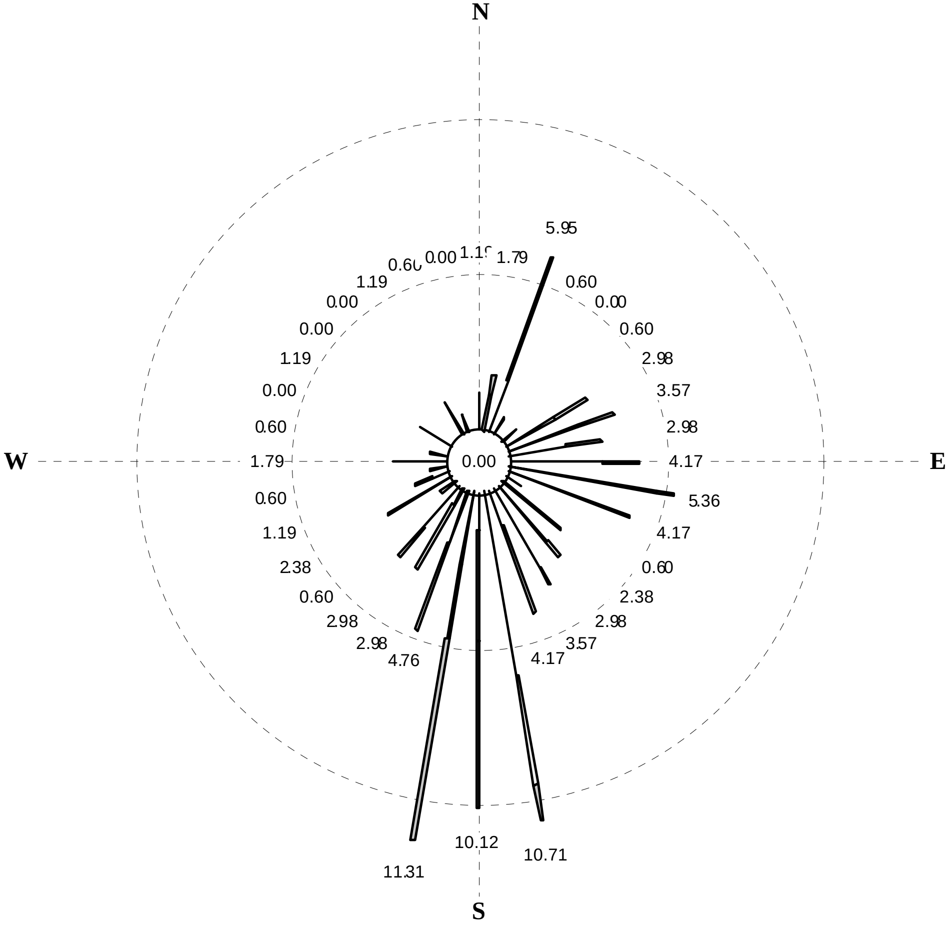
Calms included at center.
Rings drawn at 5% intervals.
Wind flow is FROM the directions shown.
No observations were missing.

Site-Week Wind Rose
of Hourly Wind Speed/Direction Data
Milwaukee 16th St. Health Ctr (55079001 0)
9AM CST 15 Nov - 8AM CST 22 Nov 06



Calms included at center.
Rings drawn at 5% intervals.
Wind flow is FROM the directions shown.
No observations were missing.

Site-Week Wind Rose
of Hourly Wind Speed/Direction Data
Milwaukee 16th St. Health Ctr (550790010)
9AM CST 22 Nov - 8AM CST 29 Nov 06

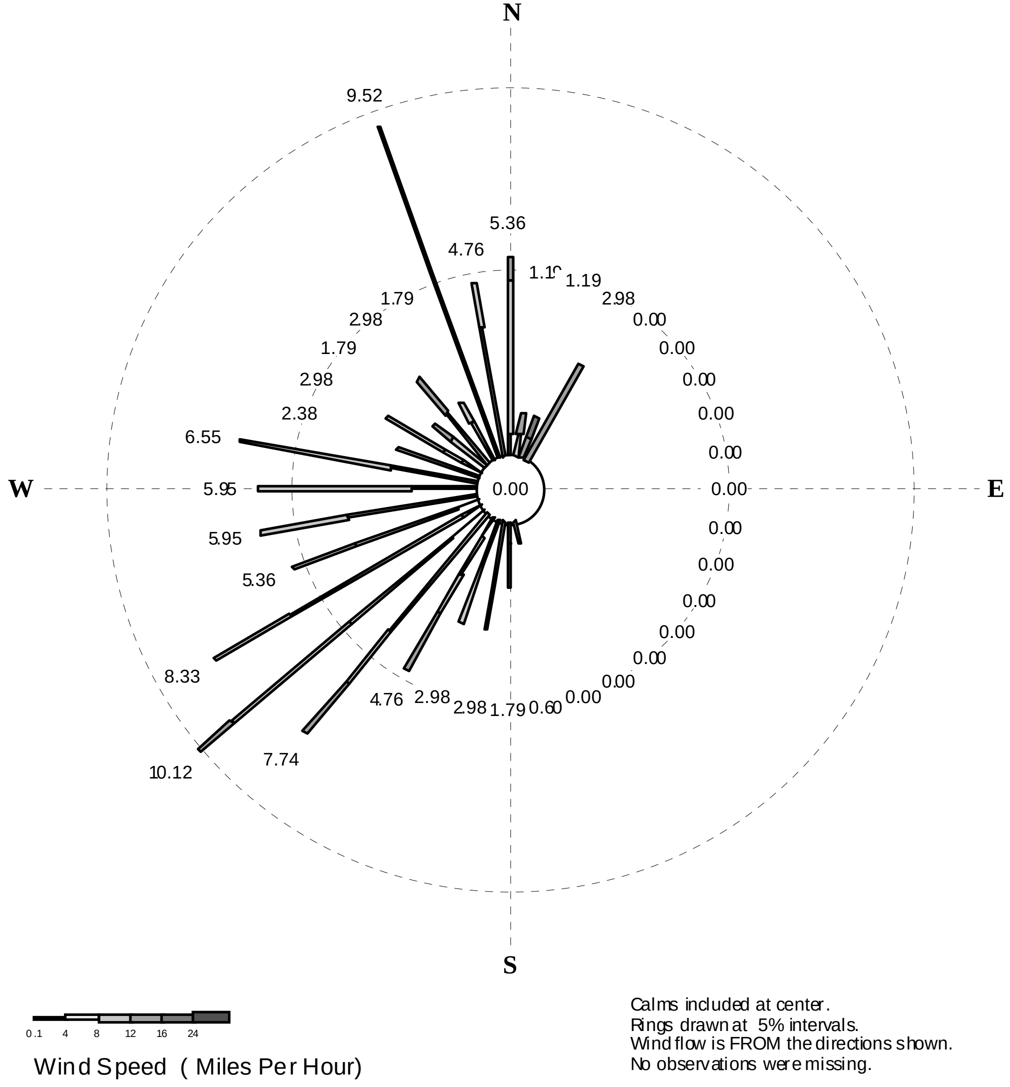


0.1 4 8 12 16 24

Wind Speed (Miles Per Hour)

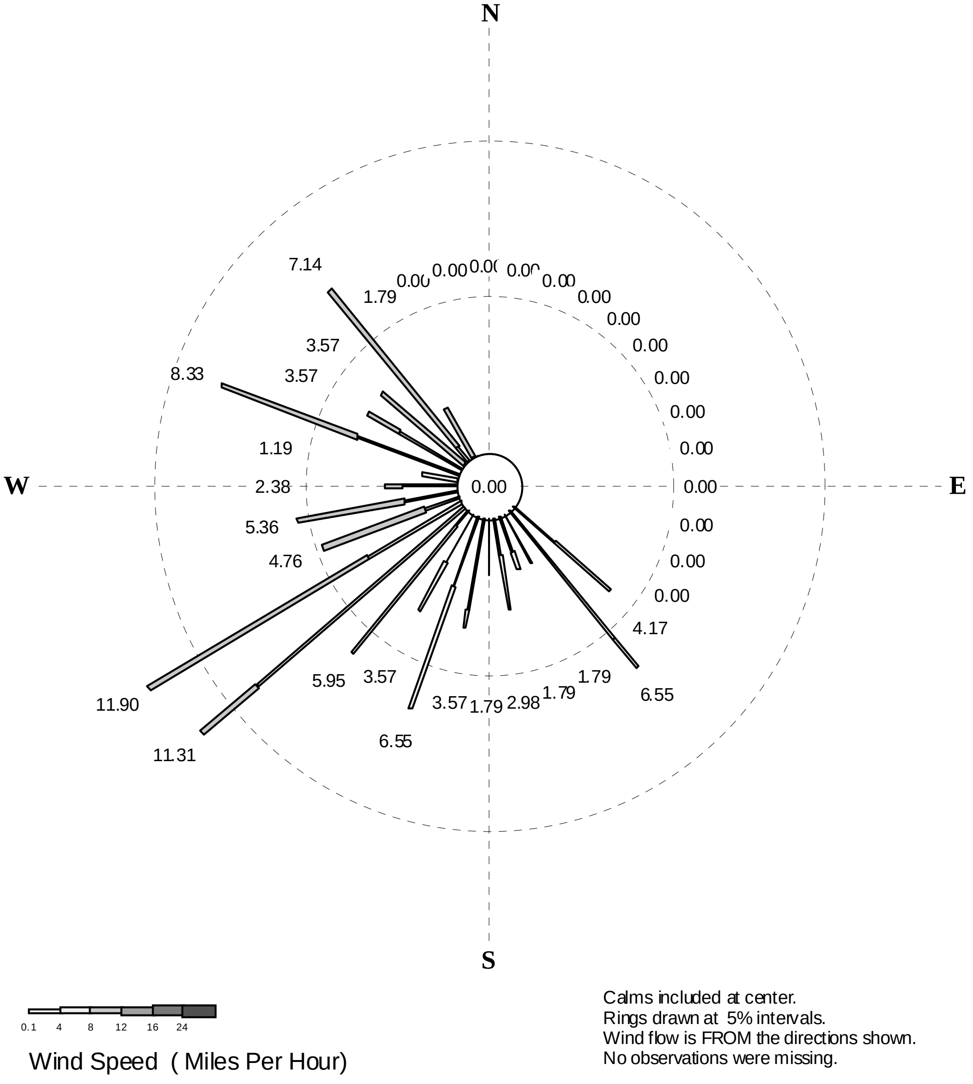
Calms included at center.
Rings drawn at 5% intervals.
Wind flow is FROM the directions shown.
No observations were missing.

Site-Week Wind Rose
of Hourly Wind Speed/Direction Data
Milwaukee 16th St. Health Ctr (55079001 0)
9 AM CST 29 Nov - 8AM CST 6 Dec 06



Calms included at center.
Rings drawn at 5% intervals.
Wind flow is FROM the directions shown.
No observations were missing.

Site-Week Wind Rose
of Hourly wind Speed / Direction Data
Milwaukee 16th St. Health Center (550790010)
9 AM CST 6 Dec - 8 AM CST 13 Dec 06



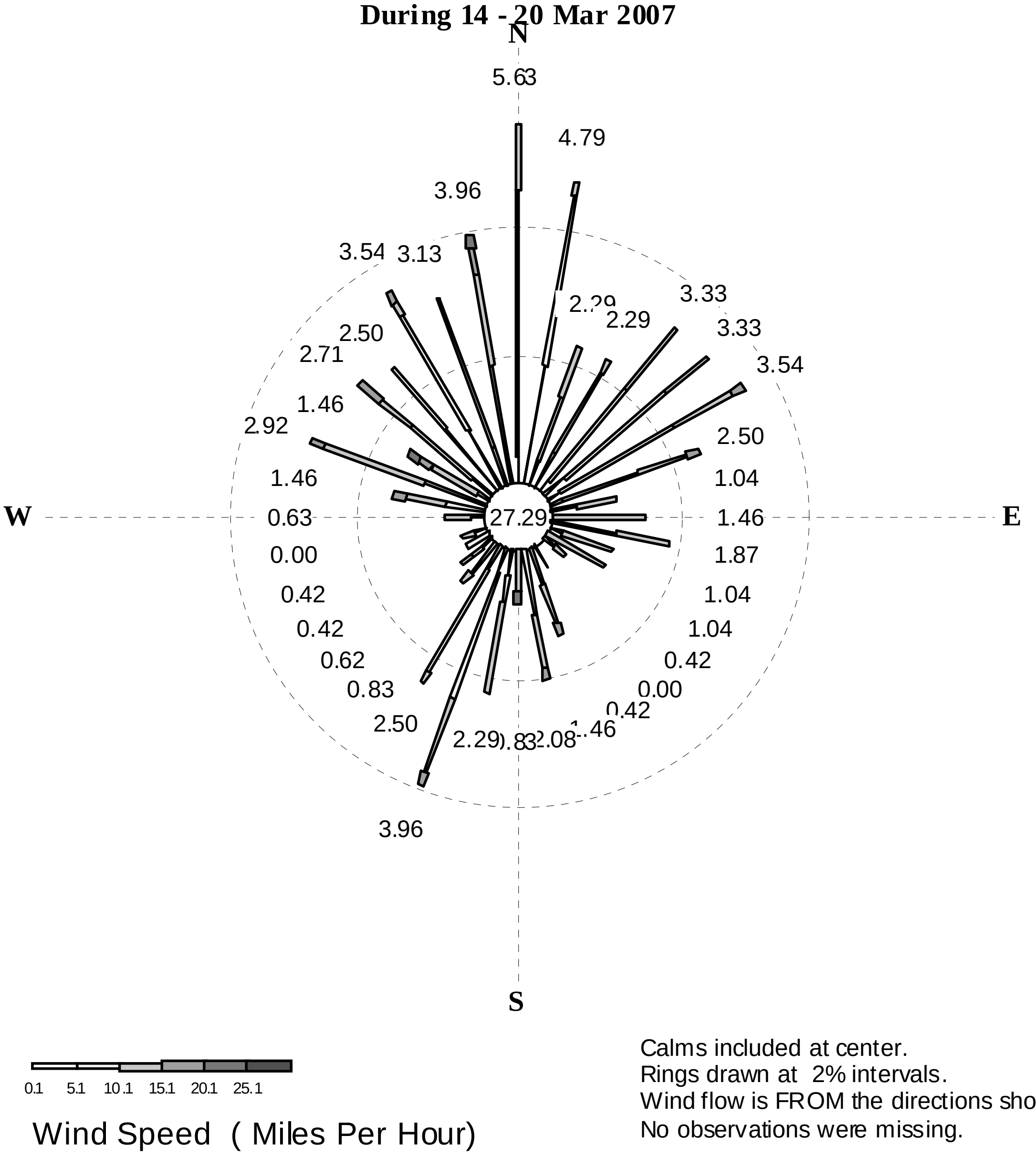
Calms included at center.
Rings drawn at 5% intervals.
Wind flow is FROM the directions shown.
No observations were missing.

Wind Rose

National Weather Service - Sullivan, Wis

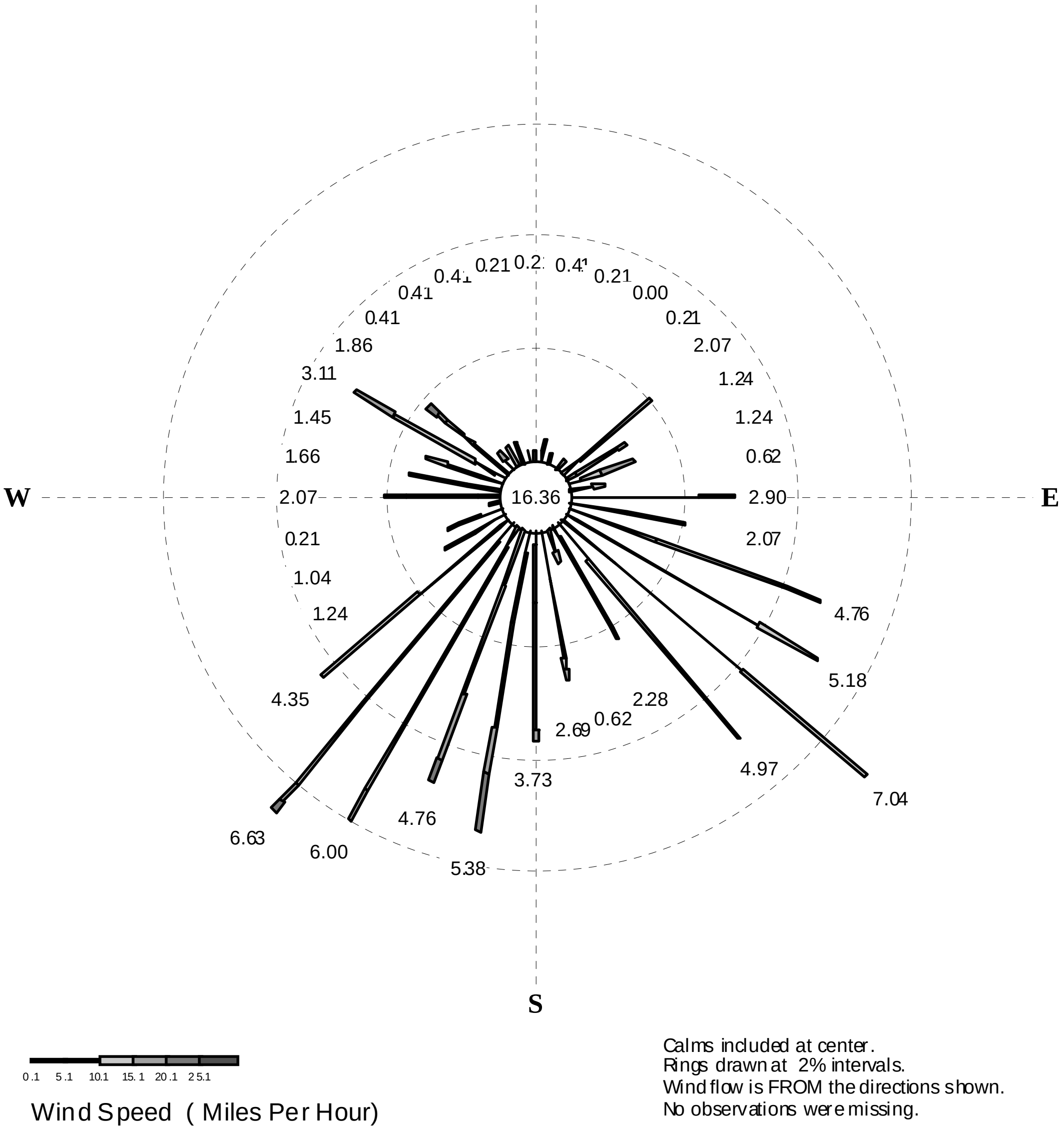
480 Hourly Wind Data Hours (including calms)

During 14 - 20 Mar 2007



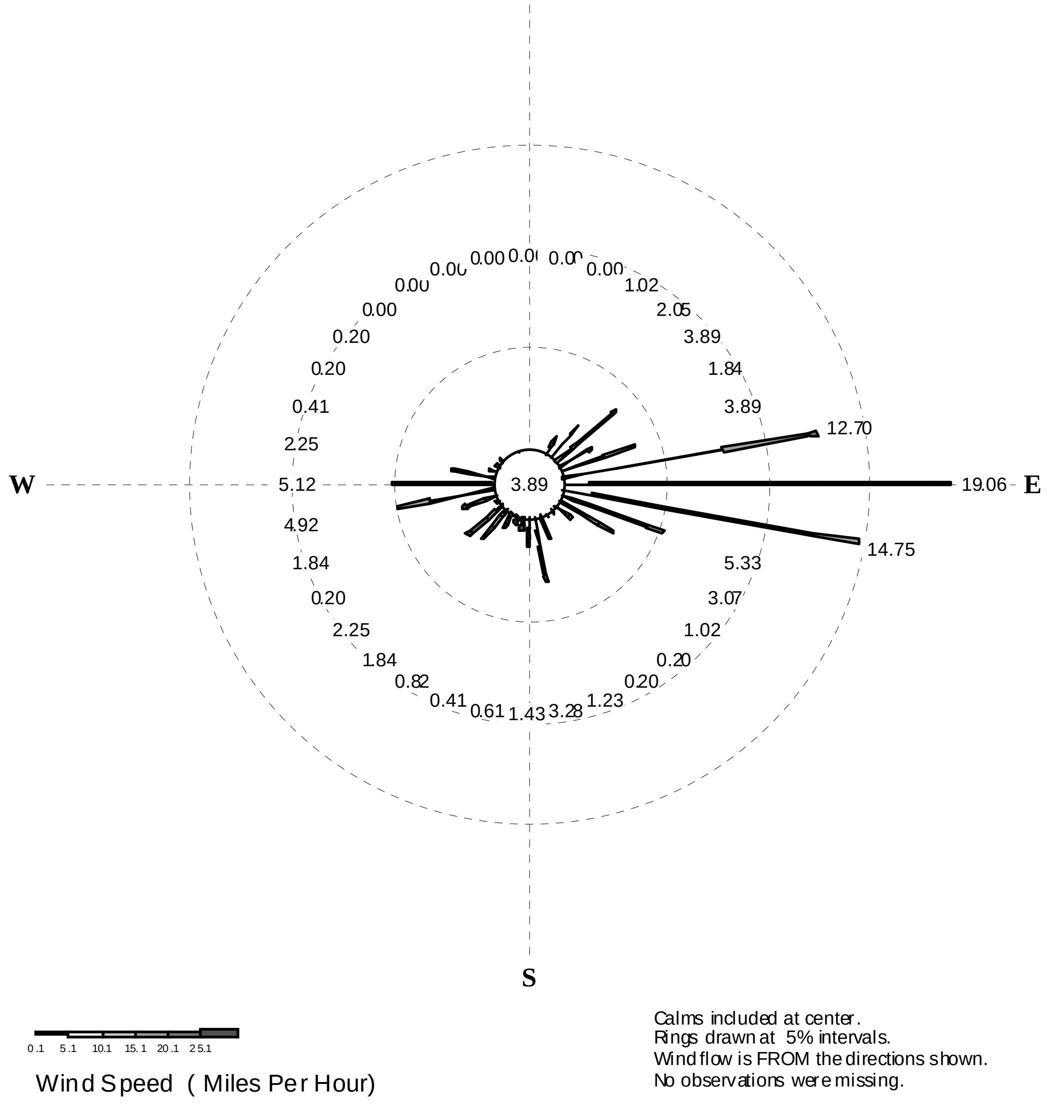
Calms included at center.
Rings drawn at 2% intervals.
Wind flow is FROM the directions shown.
No observations were missing.

Wind Rose
National Weather Service - Sullivan, Wis
483 Wind Data Hours (including calms)
During 21 - 28 Mar 07



Calms included at center.
Rings drawn at 2% intervals.
Wind flow is FROM the directions shown.
No observations were missing.

Wind Rose
National Weather Service - Sullivan, Wis
488 Wind Data Hours (including Calms)
During 28 Mar - 3 Apr 07



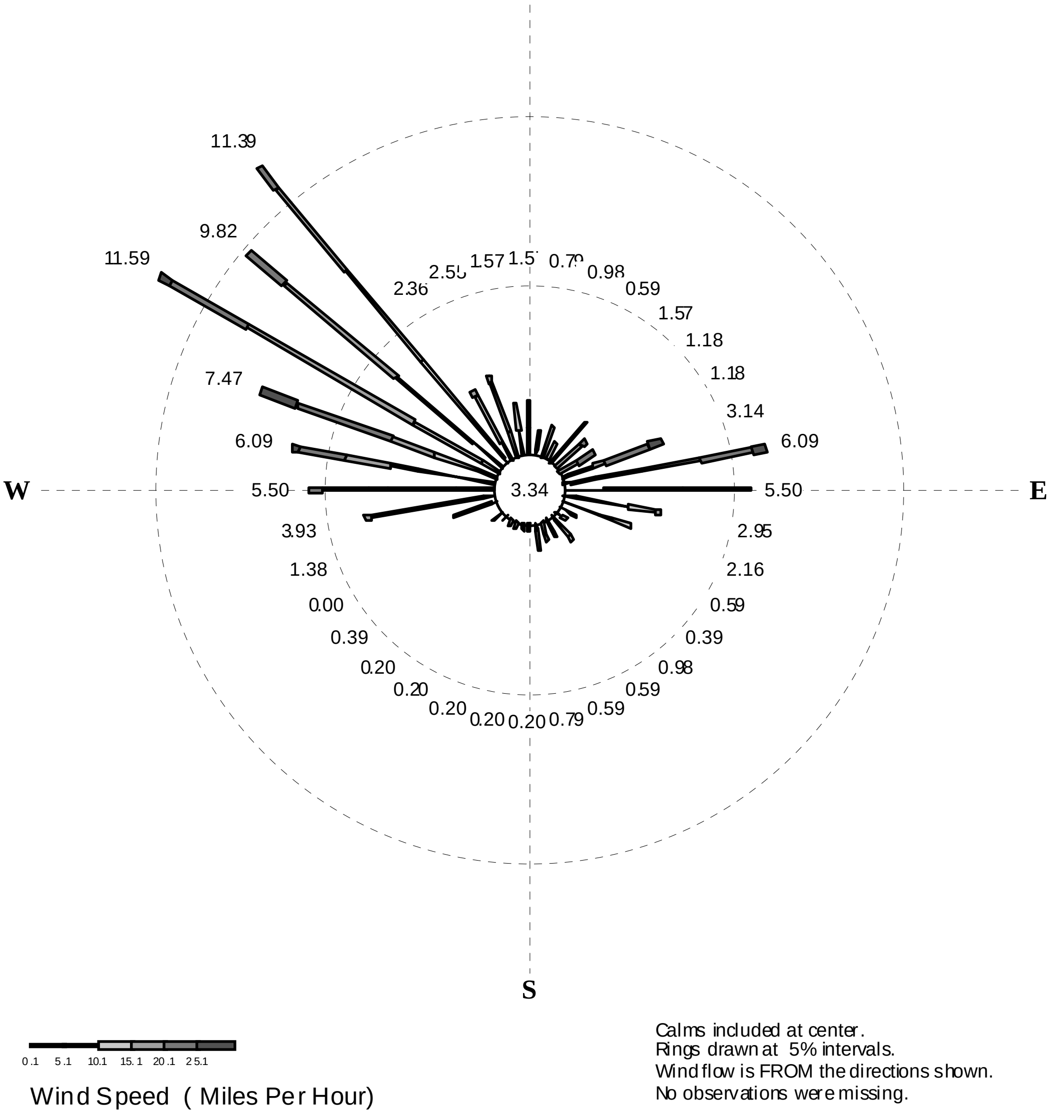
Calms included at center.
Rings drawn at 5% intervals.
Wind flow is FROM the directions shown.
No observations were missing.

Wind Rose

National Weather Service - Sullivan, Wis

509 Wind Data Hours (including calms)

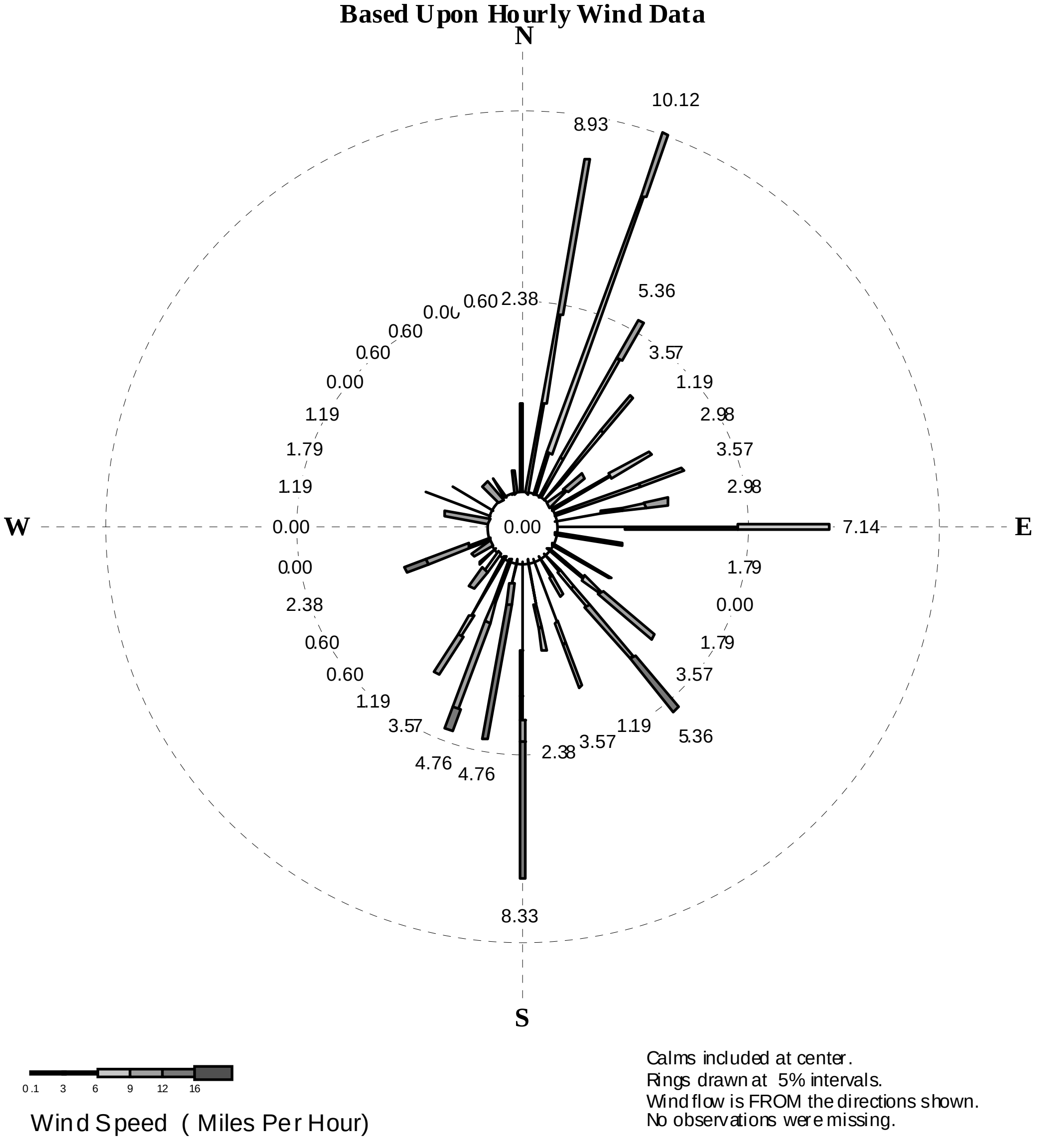
During 4 - 13 April 2007



Calms included at center.
Rings drawn at 5% intervals.
Wind flow is FROM the directions shown.
No observations were missing.

Weekly Wind Rose

Milwaukee 16th St. Community Health Center
10 AM CST 18 April to 9 AM CST 25 April 07
Based Upon Hourly Wind Data

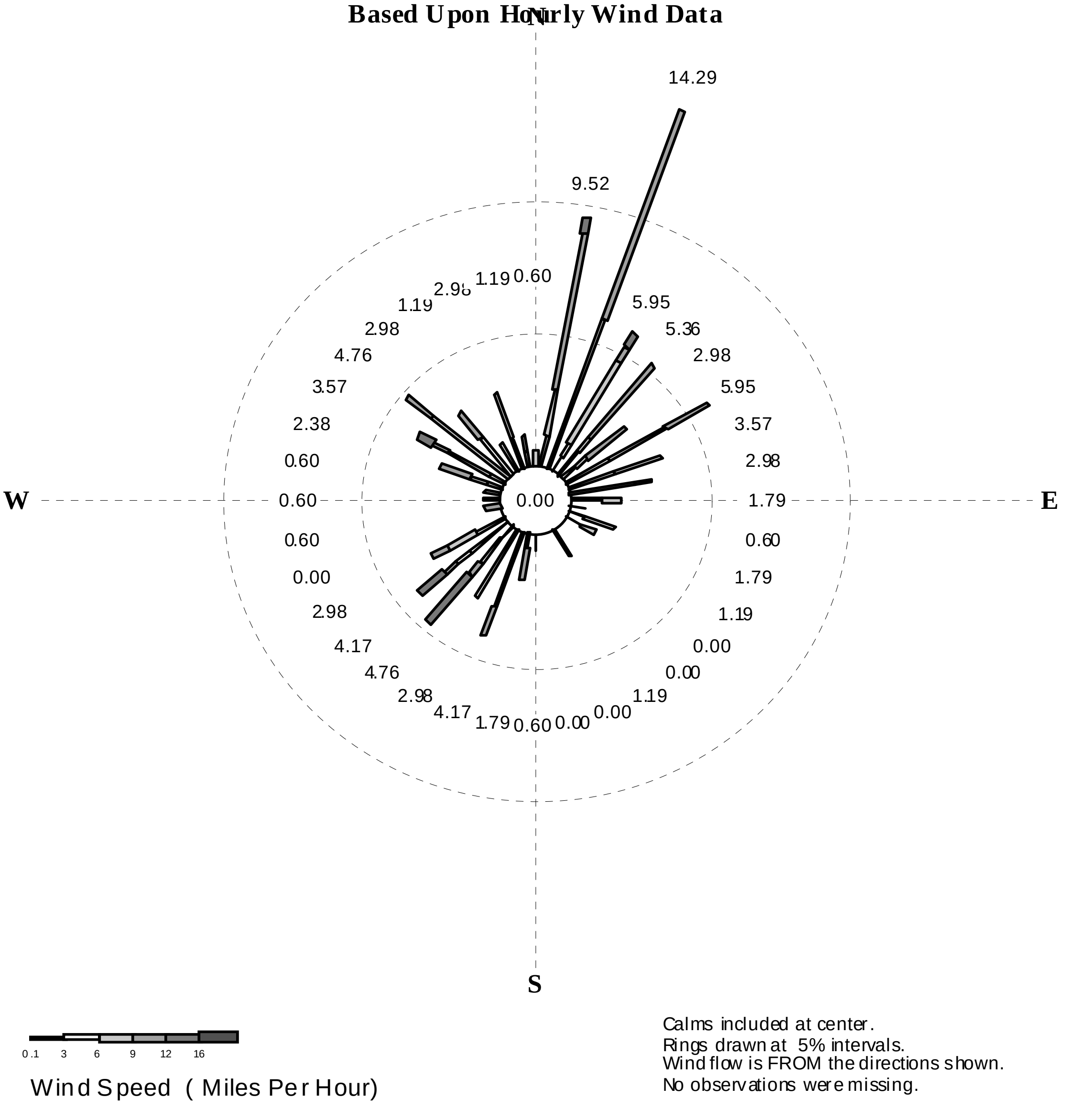


Wind Speed (Miles Per Hour)

Calms included at center.
Rings drawn at 5% intervals.
Wind flow is FROM the directions shown.
No observations were missing.

Weekly Wind Rose

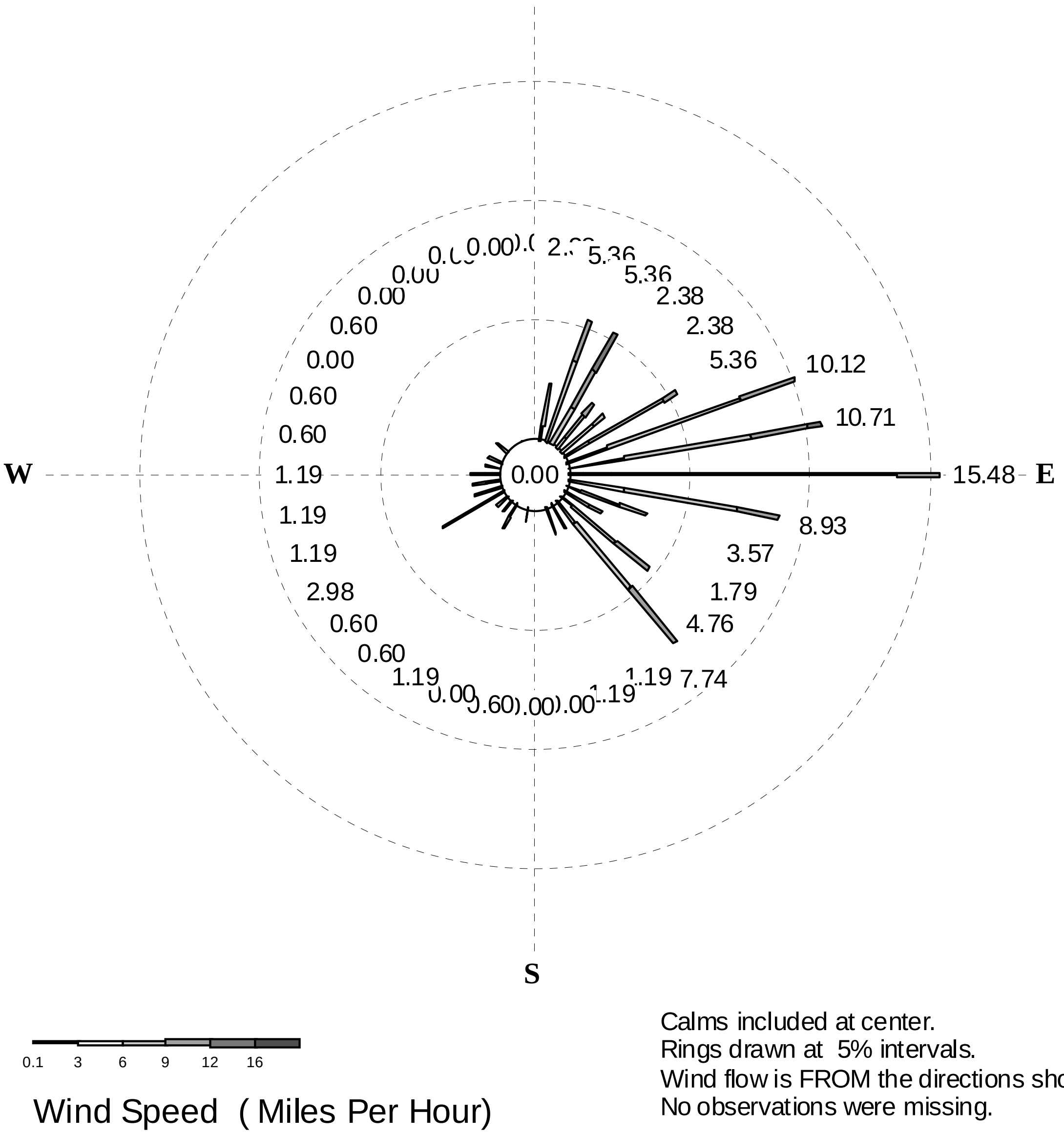
Milwaukee 16th St. Community Health Center
10 AM CST 25 April to 9 AM CST 2 May 07
Based Upon Hourly Wind Data



Calms included at center.
Rings drawn at 5% intervals.
Wind flow is FROM the directions shown.
No observations were missing.

Weekly Wind Rose

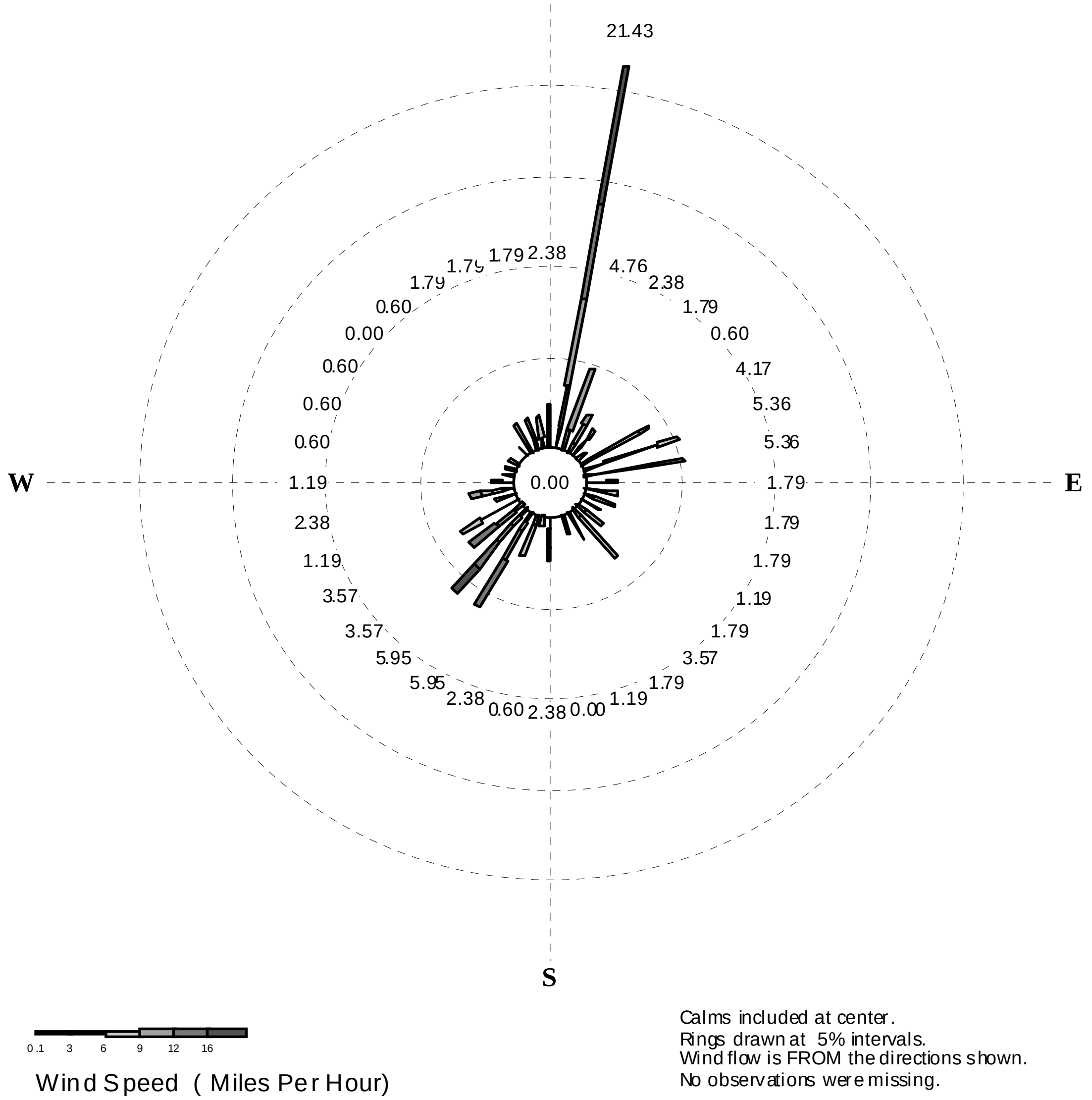
Milwaukee 16th St Community Health Center
10 AM CST 2 May to 9 AM CST 9 May 2007
Based upon Hourly Wind Data



Calms included at center.
Rings drawn at 5% intervals.
Wind flow is FROM the directions shown.
No observations were missing.

Weekly Wind Rose

Milwaukee 16th St. Community Health Center
10 AM CST 9 May to 9 AM CST 16 May 07
Based Upon Hourly Wind Data



Calms included at center.
Rings drawn at 5% intervals.
Wind flow is FROM the directions shown.
No observations were missing.

State of Wisconsin
Department of Natural Resources