

DATE: April 21, 2008

FILE REF:

TO: Air Toxics Files

FROM: Mark K. Allen – Air Toxic Chemist

SUBJECT: Benzene Monitoring in Waupaca - **FINAL REPORT**

Background

Waupaca is small city located in central Wisconsin (Waupaca County), with a population of approximately 5,800 people. The city is the location of two ThyssenKrupp Waupaca foundries – including the state's largest gray and ductile iron foundry (Plant 2/3). The foundry's number 1 plant is located at the north end of the city at 406 N Division St and plants 2/3 are located on the eastern side of the city, at 1955 Brunner Dr. The foundries reported total benzene emissions of 77,014 pounds per year (Plant 1 – 29,976 pounds/year & Plant 2/3 47,038 pounds/year) in 2006. The foundry is in the process of making permit revisions that may increase emissions and impact local air quality.

In order to verify modeling results and because of local citizen concerns about the foundry's emissions, the WDNR's Environmental Analysis and Outreach Section was requested to conduct air monitoring to assess the ambient concentration of hazardous air pollutants in the area around the foundries. Staff conducted an eight week air monitoring project in the city. Air monitoring was conducted at 10 sites using passive adsorbent sampling tubes. This memorandum will report on the details and results of the monitoring operation.

Project Monitoring Objectives

1. To measure ambient benzene concentrations at multiple locations.
2. To examine and assess site-to-site variations in measured benzene.
3. Where possible, to compare measured benzene concentrations to modeled concentrations.

Monitoring Method

Air sampling was conducted with passive adsorbent sampling tubes. The Wisconsin DNR has previously used these sampling devices in roadway studies and the basic procedures used in those roadway studies were also followed in the Waupaca Study. The sampling time was extended from a 7 day to a 14 day exposure. Benzene was the priority target compound and is the most significant risk driver in foundry emissions. Five additional compounds were measured and assessed as supporting compounds. The most significant supporting compound was toluene, other compounds were ethylbenzene, xylene, 2,2,4-trimethylpentane, and styrene.

Monitoring sites

Air was sampled at ten sites located throughout the city. All monitoring sites were Wisconsin Public Service (WPS) utility poles and the samplers were attached to mounts placed on the poles. The monitoring sites are listed in Table 1 by location. This table also indicates the primary purpose for choosing that site location. Location information for all sites was measured with a hand-held GPS units. The spatial information has been plotted and the site distribution in the city is shown in the photo in Figure 1.

Table 1: Air Monitoring Sites for Waupaca Benzene Study		
Site #	Site Description	Purpose
0	Parking lot of 450 Industrial Drive	East of Plant2/3
1	Directly north of foundry in vacant field between railroad and Highway K	Maximum Impact
2	North side of County Highway K, across from farm.	North of Plant 2/3, located in the modeled Red Zone:
3	Behind CAP Services playground	Sensitive Population
4	Parking lot of Town of Waupaca, Town Hall, on Highway E east of Constance Road.	Citizen Concerns
5	High point near edge of the modeled 1 Km influence. Shambeau Rd by Water Tower:	High Point Impact
6	North of Plant 1, on DeeLishus Drive	Plant 1
7	South East of Plant 1, @ Waupaca and Pine:	Plant 1
8	Outside of 1 Km zones of both plants, low traffic, On Shadowlake Road	Low Traffic Background Sensitive Population
9	Outside of 1KM zones, high traffic: on Demerest near Churchill:	High Traffic Background

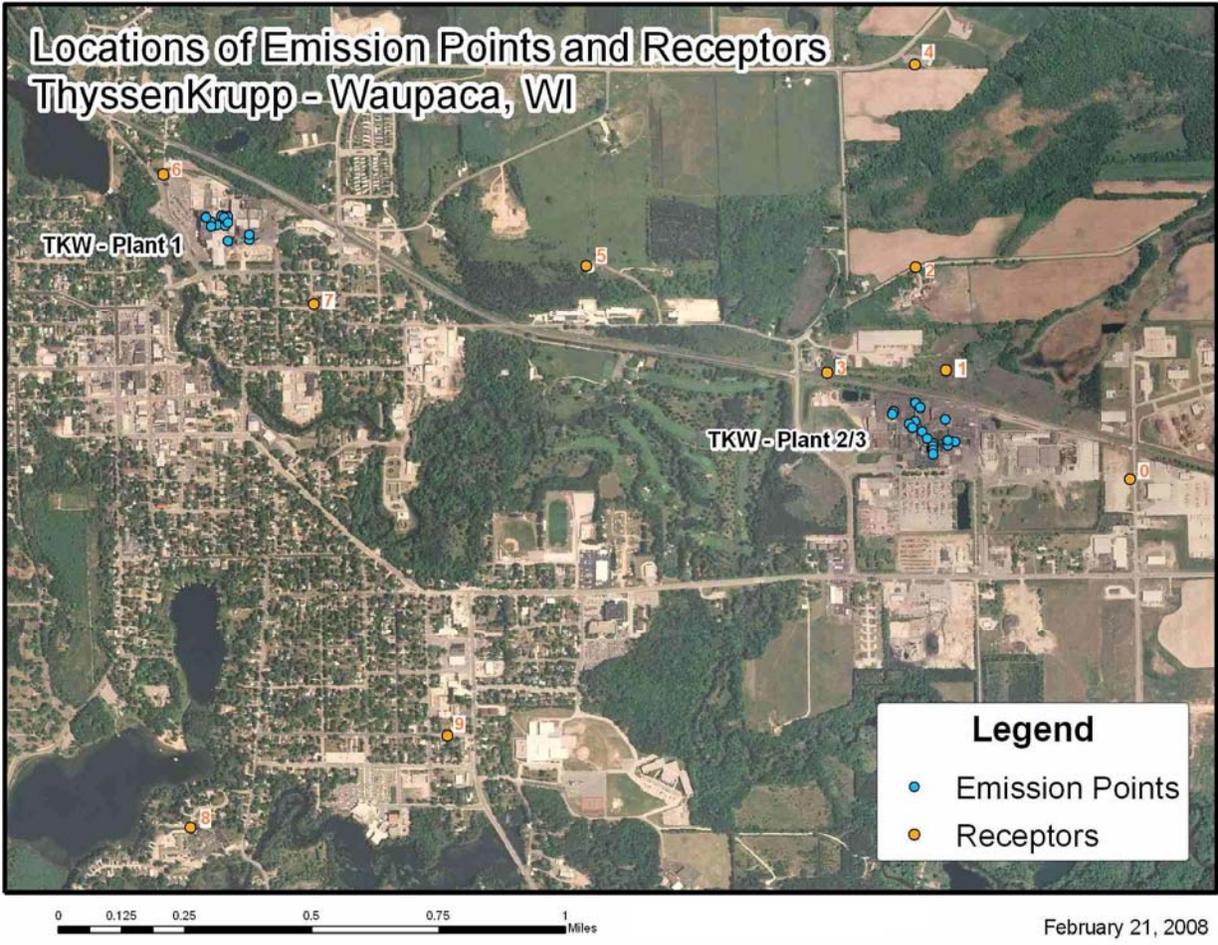


Figure 1: Aerial photo showing the foundry emission points (blue) and the 10 air monitoring sites (yellow with red numbers) used in the study.

Sampling Periods

Sampling was conducted over four separate two week time periods from December 19, 2007 to February 15, 2008. The last sampling period was extended to 16 days to avoid travel during a winter storm. The sampling periods are listed in Table 2 along with the estimated level of foundry activity. Plant activity reported in Table 2 is based on the foundry's report that no production work was done between the Christmas and New Year's holidays. Two metrics of plant activity, included in Table 2, are the quantity of iron poured and the tons of sand used.

Sample Set	Beginning Date	Ending Date	Plant Activity (summed for plants 1,2 &3)		
				Iron Poured (Tons)	Sand Used (Tons)
WB001	12/19/2007	01/02/2008	Low	12233	75588
WB002	01/02/2008	01/16/2008	Normal	25386	154644
WB003	01/16/2008	01/30/2008	Normal	36339	218462
WB004	01/30/2008	02/15/2008	Normal	39380	244589

Sampling period 4 (WB004) lasted 16 days rather than the usual 14 days. This occurred when a winter snow storm delayed the retrieval of the samples.

Results

Samples were analyzed by gas chromatography at the Wisconsin DNR's Milwaukee Air Laboratory. The gas chromatographic raw results are reported as weights and are in units of ngC per sample. The weight values are converted into ambient concentrations (ug/m3) using the following equation:

$$((\text{sample}) - (\text{blank})) / (\text{CN}) / (\text{DRC}) / (\text{ET}) * 1000 * (\text{MW}) / 24.46$$

Where:

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

Detailed analysis of results for benzene, toluene, ethylbenzene, total xylenes, 2,2,4-trimethylpentane, and styrene were conducted. Resulting concentrations were grouped for summary and statistical analysis. Analysis results are summarized in Table 3a -3 f. In the tables duplicate results are reported as a second result set for the site. The table also reflects the fact that two samplers – Sites 2 (County K) & 3 (playground) - were lost (perhaps as a result of the storm) during the 4th sampling period.

Table 3a: Benzene Analysis Results for Passive Sampling Tubes							
Site	Site#	Set 1 (ug/m3)	Set 2 (ug/m3)	Set 3 (ug/m3)	Set 4 (ug/m3)	Sites Average (ug/m3)	Sites RSD(%)
Industrial Drive	0	0.52	0.64	0.64	0.56	0.59	9.8%
Field by Foundry	1	0.54	0.58	0.71	0.54	0.59	13.2%
Field by Foundry	1	0.53	0.53	0.71	0.56	0.58	15.0%
County K by Farm	2	0.54	0.53	0.69	lost	0.59	14.9%
Playground	3	0.66	0.55	0.47	lost	0.56	16.9%
Town Hall	4	0.53	0.49	0.53	0.35	0.48	17.8%
Water Tower	5	0.54	0.53	0.55	0.48	0.53	6.1%
DeeLishus Drive	6	0.64	0.66	0.57	0.62	0.62	6.1%
Pine St	7	0.77	0.67	0.64	0.73	0.70	8.4%
Shadowlake Road	8	0.62	0.55	0.46	0.53	0.54	11.7%
Shadowlake Road	8	0.60	0.60	0.49	0.56	0.56	8.7%
Demerest near Churchill	9	0.87	0.76	0.66	0.69	0.75	12.7%
Sets Average		0.61	0.59	0.59	0.56		
Sets RSD (%)		17.9%	13.3%	15.3%	18.7%		

RSD is the relative standard deviation of the measurements and is expressed as a percentage. RSD is provided as a measure of the variability of the measurements in a set of data.

Table 3b: Toluene Analysis Results for Passive Sampling Tubes							
Site	Site#	Set 1 (ug/m3)	Set 2 (ug/m3)	Set 3 (ug/m3)	Set 4 (ug/m3)	Sites Average (ug/m3)	Sites RSD(%)
Industrial Drive	0	0.66	0.57	0.54	0.48	0.56	14.0%
Field by Foundry	1	0.64	0.63	0.61	0.50	0.59	10.8%
Field by Foundry	1	0.61	0.62	0.65	0.51	0.60	10.1%
County K by Farm	2	0.59	0.49	0.52	lost	0.53	9.3%
Playground	3	0.69	0.58	0.39	lost	0.55	27.8%
Town Hall	4	0.53	0.37	0.36	0.26	0.38	28.8%
Water Tower	5	0.54	0.40	0.38	0.31	0.41	23.4%
DeeLishus Drive	6	0.74	0.71	0.49	0.45	0.60	25.0%
Pine St	7	0.96	0.64	0.64	0.65	0.72	22.1%
Shadowlake Road	8	0.66	0.53	0.39	0.43	0.50	23.5%
Shadowlake Road	8	0.65	0.51	0.36	0.39	0.48	27.1%
Demerest near Churchill	9	1.14	0.95	0.65	0.72	0.86	26.1%
Sets Average		0.70	0.58	0.50	0.47		
Sets RSD (%)		25.5%	25.9%	23.6%	29.5%		

Table 3c: Ethylbenzene Analysis Results for Passive Sampling Tubes							
Site	Site#	Set 1 (ug/m3)	Set 2 (ug/m3)	Set 3 (ug/m3)	Set 4 (ug/m3)	Sites Average (ug/m3)	Sites RSD(%)
Industrial Drive	0	0.10	0.09	0.07	0.06	0.08	20.3%
Field by Foundry	1	0.11	0.08	0.09	0.07	0.09	20.7%
Field by Foundry	1	0.11	0.11	0.09	0.08	0.09	14.3%
County K by Farm	2	0.12	0.09	0.08	lost	0.10	21.4%
Playground	3	0.11	0.10	0.06	lost	0.09	25.9%
Town Hall	4	0.10	0.06	0.06	0.07	0.07	24.4%
Water Tower	5	0.09	0.07	0.07	0.04	0.07	26.7%
DeeLishus Drive	6	0.12	0.10	0.09	0.06	0.09	24.7%
Pine St	7	0.14	0.09	0.10	0.10	0.11	20.0%
Shadowlake Road	8	0.11	0.10	0.07	0.07	0.08	23.9%
Shadowlake Road	8	0.10	0.09	0.06	0.06	0.08	29.1%
Demerest near Churchill	9	0.19	0.17	0.10	0.09	0.14	36.2%
Sets Average		0.12	0.09	0.08	0.07		
Sets RSD (%)		23.2%	27.4%	19.3%	23.0%		

Table 3d: Xylenes Analysis Results for Passive Sampling Tubes							
Site	Site#	Set 1 (ug/m3)	Set 2 (ug/m3)	Set 3 (ug/m3)	Set 4 (ug/m3)	Sites Average (ug/m3)	Sites RSD(%)
Industrial Drive	0	0.34	0.34	0.25	0.22	0.29	21.2%
Field by Foundry	1	0.36	0.39	0.32	0.27	0.34	15.3%
Field by Foundry	1	0.35	0.39	0.37	0.27	0.35	15.7%
County K by Farm	2	0.36	0.29	0.32	lost	0.32	11.3%
Playground	3	0.41	0.35	0.22	lost	0.33	29.5%
Town Hall	4	0.31	0.20	0.19	0.14	0.21	32.8%
Water Tower	5	0.29	0.22	0.21	0.10	0.21	37.8%
DeeLishus Drive	6	0.48	0.45	0.30	0.21	0.36	35.2%
Pine St	7	0.67	0.40	0.36	0.34	0.44	34.5%
Shadowlake Road	8	0.38	0.34	0.21	0.20	0.28	33.4%
Shadowlake Road	8	0.38	0.29	0.18	0.16	0.25	41.6%
Demerest near Churchill	9	0.75	0.63	0.36	0.38	0.53	36.0%
Sets Average		0.42	0.36	0.27	0.23		
Sets RSD (%)		33.6%	31.6%	26.0%	38.1%		

Table 3e: 224-Trimethylbenzene Analysis Results for Passive Sampling Tubes							
Site	Site#	Set 1 (ug/m3)	Set 2 (ug/m3)	Set 3 (ug/m3)	Set 4 (ug/m3)	Sites Average (ug/m3)	Sites RSD(%)
Industrial Drive	0	0.16	0.12	0.16	0.13	0.15	15.1%
Field by Foundry	1	0.15	0.14	0.15	0.11	0.14	15.8%
Field by Foundry	1	0.14	0.12	0.15	0.13	0.13	7.2%
County K by Farm	2	0.16	0.12	0.15	lost	0.14	16.5%
Playground	3	0.16	0.15	0.13	lost	0.15	7.8%
Town Hall	4	0.13	0.14	0.12	0.08	0.12	22.9%
Water Tower	5	0.14	0.13	0.16	0.10	0.13	17.1%
DeeLishus Drive	6	0.19	0.20	0.18	0.14	0.18	16.0%
Pine St	7	0.27	0.23	0.18	0.23	0.23	15.6%
Shadowlake Road	8	0.16	0.18	0.17	0.13	0.16	14.3%
Shadowlake Road	8	0.18	0.16	0.14	0.11	0.15	21.4%
Demerest near Churchill	9	0.30	0.25	0.22	0.25	0.25	13.1%
Sets Average		0.18	0.16	0.16	0.14		
Sets RSD (%)		29.4%	27.7%	16.8%	39.5%		

Table 3f: Styrene Analysis Results for Passive Sampling Tubes							
Site	Site#	Set 1 (ug/m3)	Set 2 (ug/m3)	Set 3 (ug/m3)	Set 4 (ug/m3)	Sites Average (ug/m3)	Sites RSD(%)
Industrial Drive	0	0.04	0.10	0.01	0.01	0.04	96.7%
Field by Foundry	1	0.09	0.51	0.14	0.43	0.29	70.1%
Field by Foundry	1	0.10	0.58	0.30	0.42	0.35	57.3%
County K by Farm	2	0.04	0.12	0.07	lost	0.08	56.6%
Playground	3	0.18	0.31	0.02	lost	0.17	83.2%
Town Hall	4	0.02	0.01	0.01	0.02	0.01	36.1%
Water Tower	5	0.03	0.02	0.01	0.01	0.02	78.3%
DeeLishus Drive	6	0.04	0.01	0.00	0.01	0.02	97.4%
Pine St	7	0.03	0.01	0.00	0.01	0.01	95.2%
Shadowlake Road	8	0.02	0.03	0.01	0.01	0.02	67.7%
Shadowlake Road	8	0.02	0.01	0.01	0.01	0.01	65.7%
Demerest near Churchill	9	0.03	0.02	0.01	0.01	0.02	65.7%
Sets Average		0.05	0.15	0.05	0.09		
Sets RSD (%)		89.3%	141.7%	180.1%	187.6%		

Meteorological Results

The Wisconsin DNR did not directly collect any meteorological data for the project. Meteorological data for the study was obtained from the Waupaca Municipal Airport. Hourly measurements of temperature, wind speed and wind direction at the airport were obtained through the National Oceanic and Atmospheric Administration (NOAA) web site. The data is summarized in Table 4. A graphical display of the data as wind roses is provided in Appendix B to this report.

Table 4: Summarized Meteorological data collected at the Waupaca Municipal Airport during the study.				
Meteorological Parameter	Period 1	Period 2	Period 3*	Period 4
Temperature Average (°F)	23.3	25.8	8.5	15.5
Temperature Max (°F)	35.6	39.2	39.2	33.8
Temperature Min (°F)	5.0	-7.6	-14.8	-14.8
Vector Mean Wind Speed (mph)	4.1	2.7	6.2	3.7
Vector Mean Wind Direct (degrees) North = 0 and 360 degrees; South = 180	267	268	261	305
* Data was not available for 1/28/2008 and is not included in the summary.				

Discussion of Results

The measured concentration data shows that the benzene was very consistent across time (temporally) at a single location as well as across locations (spatially). The highest average of the measured benzene concentrations was 0.75 ug/m³ at site 9 (Demerest Street, high traffic background site). The lowest average of the measured benzene concentrations was 0.48 ug/m³ at site 4 (Waupaca Town Hall). The range of difference between average site benzene concentrations was 0.27 ug/m³. The average benzene concentration at the highest site is about 1.6 times higher than the average benzene concentration at the lowest site. Measurement variability when assessed across both the sites and the duration of the study was less than 20%, as measured by RSD (standard deviation/average).

When data is compared to the Wisconsin DNR's Milwaukee Roadway study, see Figure 2, the Waupaca benzene is less than the Milwaukee average at all but two sites. Waupaca sites 7 (Pine Street) and 9 (Demerest Street) have average measured concentrations that are greater than Milwaukee average, when the Milwaukee sites are analyzed as a composite. All Waupaca sites are less than the average value measured at the peak Milwaukee site, shown by the blue line in Figure 2. The values measured at sites 7 and 9 are similar in magnitude to the maximum Milwaukee sites. It should be noted that Waupaca Site 9, the study's high traffic site, recorded concentrations similar to the Milwaukee site (901). Both sites are located on roadways known to be part of major urban traffic routes, but neither site is directly on the high speed/high traffic volume highway system (e.g., interstate or state highways).

A more interesting picture of the data results when one examines the benzene to toluene ratio (hereafter abbreviated "benzene:toluene"). This parameter is useful, because the ratio found in exhaust gases is generally consistent. Thus, if a monitor is mainly impacted by mobile sources, the benzene:toluene should remain about the same throughout the study. If the benzene:toluene ratio changes between weeks or varies significantly between sites, it may reflect the influence of a nearby source, for example from the foundry operations. In this study, the benzene:toluene ratio shows variability and a shift in the benzene:toluene ratios occurs between the first data set and the remaining three data sets. A more extensive discussion of the general importance of the benzene:toluene ratio can be found in the Wisconsin DNR's Publication AM-384 2007, "Evaluation of Passive Sampling Techniques for Monitoring Roadway and Neighborhood Exposures to Benzene and Other Mobile Source VOCs Final Project Report".

The change in the benzene:toluene ratio seen in the study results from decreasing toluene concentrations observed while benzene concentrations remained steady. This suggests that the monitors were picking up decreased mobile source derived benzene and toluene, with an additional source of benzene maintaining benzene concentrations.

Benzene:toluene ratios in Waupaca are larger than those measured in Milwaukee in the first data set and the ratios increase in sets 2 through 4. The significance of the benzene:toluene data is seen when a statistical analysis is applied to the datasets. An explanation of the difference follows in the “Excess Benzene” discussion.

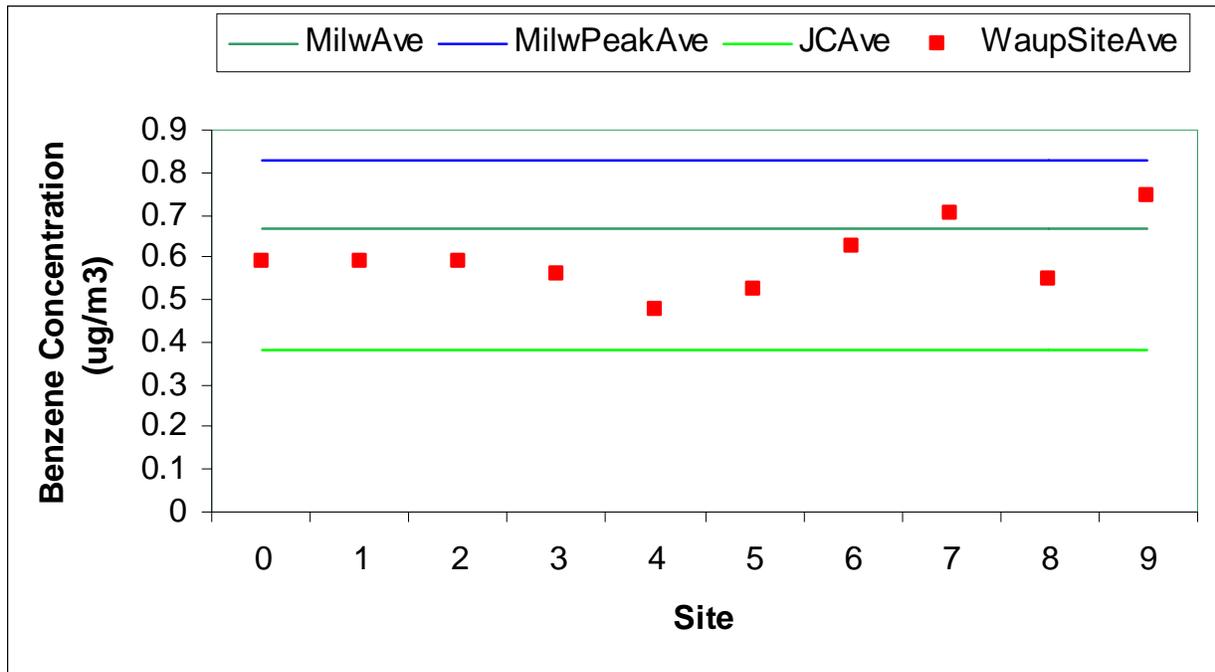


Figure 2: Comparison of the average benzene concentration measured by site compared to the average benzene concentration measured during the Wisconsin DNR’s roadway study. Average benzene measured at all Milwaukee study sites was 0.69 ug/m³ (dark green line), average benzene measured at the peak Milwaukee site was 0.83 ug/m³ (blue line), and the average measured benzene at all Johnson Creek (JC) study sites was 0.38 ug/m³ (light green line).

Statistical Analyses

To assist in the evaluation of the data and to better examine spatial and temporal variations, the monitoring data was analyzed using a paired T test and evaluated against the 2-tailed T critical value. Two types of analyses were conducted, first to look at site to site variations, and second to look at period to period variations. The data sets used for the analysis were the benzene data and the benzene:toluene ratios. Statistical analysis data is presented in the next four tables. In all tables, values exceeding critical T values are presented in bold. When a T value exceeds the critical T, the mean values being compared are statistically different.

A statistical analysis of the benzene concentration data first by site and then by period is shown in Tables 5a and 5b. With regard to spatial variation, Sites 0 through 2 are statistically the same as all the other

sites. Of the remaining sites, 7 and 9 show the greatest difference with site 4 & 5 and with sites 3,6 and 8.

With regard to temporal variation, when evaluated over the 4 sampling periods the benzene data is not statistically different.

Table 6b: : Period by Period Comparison of the Benzene to Toluene Ratios using the Paired T-Test; Data evaluated against a 2 Tailed T-Critical			
Period	2	3	4
1	4.0218	11.6108	8.3998
2		4.9892	3.5544
3			0.9591

Excess Benzene

The monitoring data presents a picture of Waupaca where the benzene concentrations remain constant over the eight week period while the toluene concentrations decrease. This results in increasing benzene:toluene ratios. The data suggests that there is an additional source of benzene maintaining the ambient concentrations. Two cases then develop during the monitoring project. During Case 1 benzene emissions are limited to background sources such as automobiles and residential activities, such as home heating. During Case 1 the foundry activity is low and emissions are at a minimum. Case 1 is limited to the first two week period. During Case 2 Waupaca air is subject to the Case 1 emissions, plus an additional source, thought at least in part, to be from the foundries. The benzene measured in both cases is identical. The monitoring conducted in this study did not measure any compounds that might reconcile the various sources of the benzene. What we can do is to examine the differences in benzene concentrations between the two cases.

This benzene concentration difference is assessed through the following calculation.

$$\text{Benzene Difference (ug/m}^3\text{)} = \text{Case 2 Benzene} - \text{Baselevel Benzene}$$

Where the Baselevel benzene concentration is determined by

$$\text{Baselevel Benzene} = \text{Case 2 Toluene} * \text{Case 1 Benzene to Toluene Ratio.}$$

The Benzene Difference shown in Table 7 suggests that on average an additional 0.13 ug/m³ was present in the ambient air. This additional benzene would be emitted by a source not operating during the first period. This additional source is assumed to be the foundry.

Site Number	Site Name	Average Excess (ug/m3)
0	Industrial Drive	0.20
1	Field by Foundry	0.12
1	Field by Foundry	0.09
2	County K by Farm	0.14
3	Playground	0.05
4	Town Hall	0.12
5	Water Tower	0.15
6	DeeLishus Drive	0.14
7	Pine St	0.17
8	Shadowlake Road	0.09
8	Shadowlake Road	0.16
9	Demerest near Churchill	0.12

Modeling and Monitoring

A USEPA dispersion model, AERMOD, was used to calculate concentrations at each monitor location. AERMOD is a state of the science dispersion model that is based on steady-state gaussian plume theory and is used across the U.S. to determine concentrations in the vicinity of industrial facilities. Source parameters input to AERMOD, such as stack height and exit gas velocity, were determined from previous modeling analyses for the TKW facilities. The data for Plant 2/3 was taken from the 2005 cumulative inhalation risk analysis as modified with 2005 reported emissions. The data for Plant 1 was taken from the 2003 operation permit analysis as modified with 2005 reported emissions. These parameters best represent the actual conditions at TKW during late 2007 and early 2008.

The dispersion model utilizes five years (1998-2002) of hourly meteorological data collected at the Clintonville, WI airport. For this study, several different concentrations were calculated, including the maximum monthly impact, the maximum December impact, the maximum daily impact during December, and the maximum two-week concentration covering the three data collection periods (Jan 2 - Feb 15).

Figure 3a and Figure 3b show a graphical comparison of average measured concentrations and the average modeled concentrations for the ten monitoring sites. The modeling results chosen for comparison were the maximum average concentration for two week periods in the time period when monitoring was conducted.

Figure 3a shows that the measured benzene concentrations are higher than the corresponding modeled concentrations at all sites. The large difference between the two sets of results occurs because the monitoring result will measure all benzene while the modeling results account only for the benzene from the foundry emissions (vehicle impacts and other possible emission sources of benzene were not included in the model).

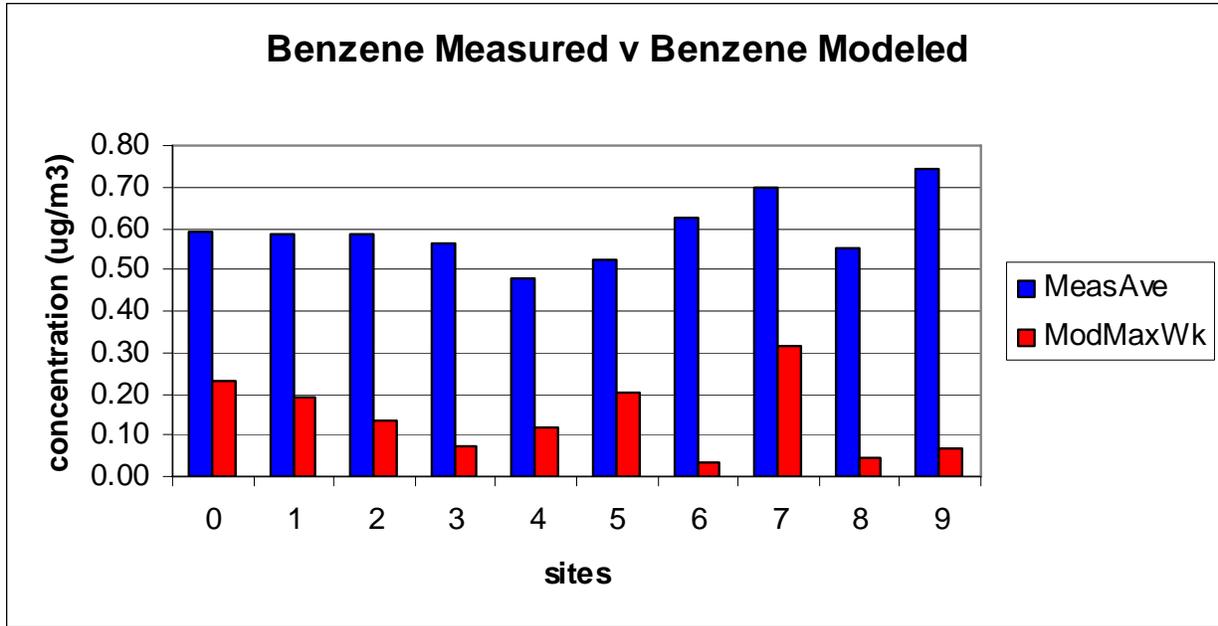


Figure 3a: Average benzene concentration measured from 12/19/07 to 2/15/08 compared to the modeled maximum concentration.

Figure 3b presents a comparison of the excess benzene, expressed as a difference, and the modeled benzene results. In this figure, we see that the results from the two methods while not identical are much more comparable. In this graph we see that at five sites, the measured concentrations exceed the modeled concentrations, and at five sites the modeled concentrations exceed the measured concentrations. Compared as a group, the two methods show a difference of 7.8%. The measured benzene concentrations support the result from the air dispersion computer model.

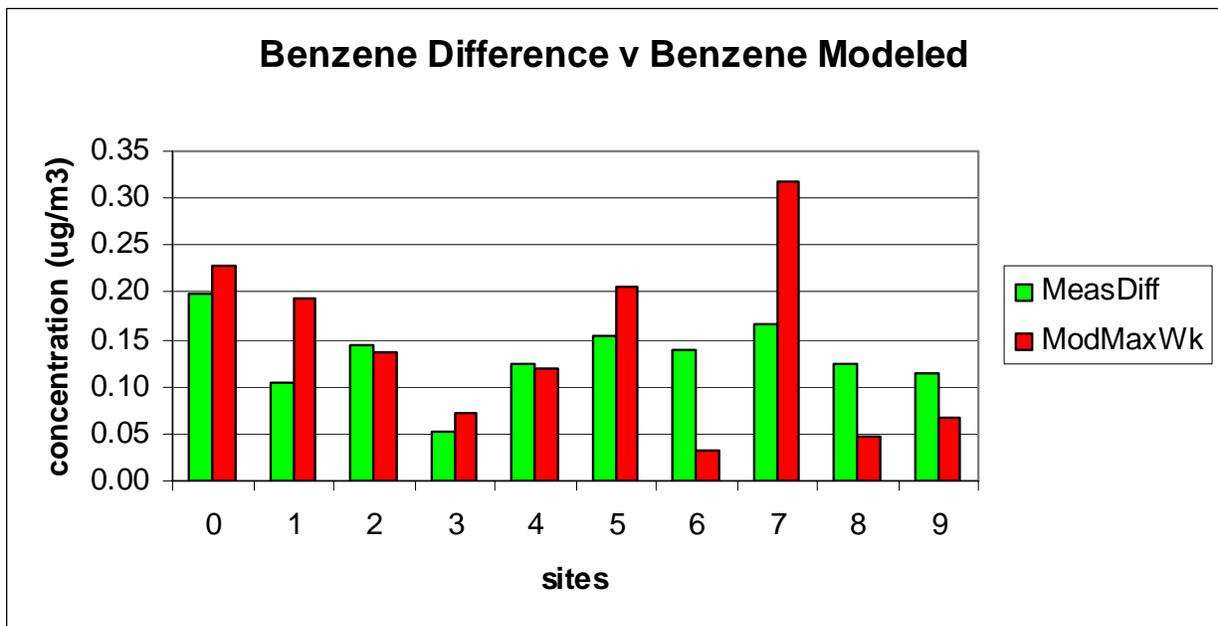


Figure 3b: Measured benzene difference between sampling period 1 and sampling period 2, 3 & 4 compared to the modeled maximum concentration for two week periods.

Alternate Analysis of Ambient Benzene Concentrations

This section of the report provides an alternative analysis of the foundry's contribution to local benzene concentrations. This alternate analysis uses the facility production data together with the measured benzene and toluene concentrations.

Production data, provided by the TKW foundry, shows plant activity during all four monitoring periods. The amount of the production varies significantly between periods 1, period 2, and periods 3&4. Production during periods 3&4 is very similar. The statistical analysis, provided earlier in this report, confirms differences in the benzene:toluene ratios during the sampling periods.

The correlation between the benzene:toluene ratios and the iron pour data suggests a strong relationship. Figure 4 shows plot of the benzene:toluene ratios and the iron pours.

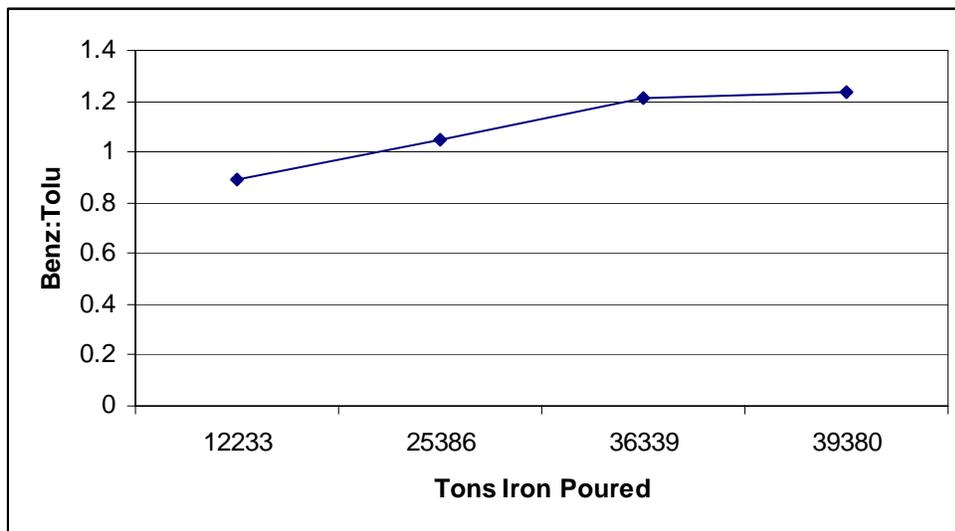


Figure 4: Plot of the benzene:toluene ratios plotted against the tons of iron poured. The benzene:toluene used in this graph is the average across all ten sites.

When the line is extrapolated back to the zero intercept, the calculation yields the baseline benzene:toluene ratio. This is assumed to be the benzene:toluene ratio when contributions from the foundries are excluded. Baseline benzene is that emitted by local area and mobile sources.

Table 8 reports the mathematical regression analysis of the data in Figure 4. In the analysis iron pours are compared to the benzene:toluene ratios calculated for each of the monitoring sites.

Table 8: Regression analysis data for measured Benzene to Toluene ratios compared to total iron poured				
Site #	Site	Correlation	Slope	Intercept
0	Industrial Drive	0.9298	1.44814E-05	0.6583
1	Field by Foundry	0.8945	1.02009E-05	0.7010
2	County K by Farm	0.9882	1.63511E-05	0.7067
3	Playground	0.8200	1.05054E-05	0.7814
4	Town Hall	0.8919	1.39981E-05	0.8879
5	Water Tower	0.9930	1.92703E-05	0.7815
6	DeeLishus Drive	0.9026	1.7512E-05	0.5905
7	Pine St	0.8430	9.72005E-06	0.7173
8	Shadowlake Road	0.9070	1.45729E-05	0.7441
9	Demerest near Churchill	0.9110	8.9691E-06	0.6318
	Average	0.9081	1.35581E-05	0.7206

Overall the regression analysis suggests good correlation between the measured benzene:toluene ratios and the foundry activity as measured by the tons of iron poured. The best correlations are seen at sites 2 (Highway K) and 5 (Water Tower). The variation of the correlation is low when assessed by a RSD of 6%. This analysis also provides baseline benzene:toluene ratios from the zero intercept values.

I next used the benzene:toluene intercept values in an analysis with the toluene data to calculate theoretical benzene concentrations from the foundries. The calculation for the benzene concentrations is shown by the equation below:

$$\text{Foundry Benzene (ug/m}^3\text{)} = \text{Benzene Concentration} - \text{Baselevel Benzene Concentration}$$

Where the Baselevel benzene Concentration is determined by:

$$\text{Baselevel Benzene} = \text{Toluene} * \text{Baselevel Benzene:toluene Ratio (intercept)}.$$

The foundry benzene concentrations were calculated and are displayed in Table 9.

Site #	Site Name	Period 1 (ug/M3)	Period 2 (ug/M3)	Period 3 (ug/M3)	Period 4 (ug/M3)
0	Industrial Drive	0.084	0.264	0.283	0.249
1	Field by Foundry	0.095	0.139	0.282	0.188
1S	Field by Foundry	0.098	0.097	0.255	0.201
2	County K by Farm	0.127	0.186	0.320	----
3	Playground	0.121	0.095	0.170	----
4	Town Hall	0.064	0.162	0.208	0.120
5	Water Tower	0.119	0.212	0.256	0.238
6	DeeLishus Drive	0.205	0.240	0.282	0.357
7	Pine St	0.078	0.215	0.174	0.266
8	Shadowlake Road	0.097	0.132	0.150	0.193
8S	Shadowlake Road	0.147	0.237	0.240	0.286
9	Demerest near Churchill	0.150	0.164	0.249	0.235
	Average Foundry Benzene	0.115	0.179	0.239	0.233
	Iron Poured	12233	25386	36339	39380

Figure 5 compares the maximum measure foundry benzene to the modeled maximum two weeks concentrations. The data suggests that the model makes a reasonable estimate, although slightly low, of the foundry benzene impacts. The modeled benzene concentration exceeds the measure concentration at only site 7 (Pine Street). Sites 2, 6, 8 & 9 show the largest differences between measured and modeled benzene.

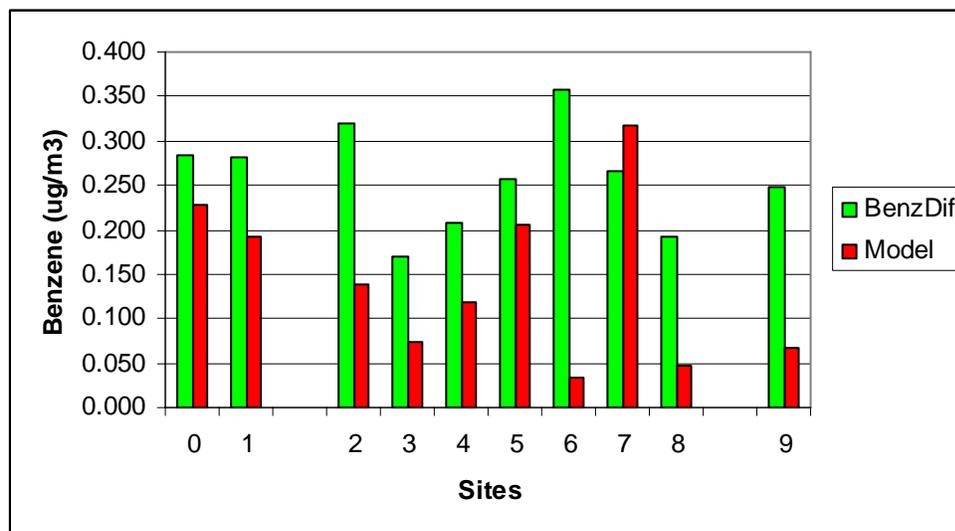


Figure 5: Maximum measured benzene difference compared to benzene predicted by computer modeling.

Canister Grab Samples

A second air sampling method was employed in Waupaca on a very limited basis. Grab samples were collected by monitoring staff on two days. Grab samples are collected by opening an evacuated passivated stainless steel canister. When opened, the canister fills quickly, less than one minute, with an air sample. The air sample is analyzed at the DNR's Milwaukee Air Laboratory. These samples

represent an instantaneous concentration (e.g., a “snapshot”). The samples were taken to measure air concentrations directly “down wind” of the foundry source. The air samples will also contain background concentrations upwind of the source plus the emissions from the source.

A summary of the canister data is presented in Table 10. The canister data shows that the instantaneous concentrations of benzene can be many times higher than the average benzene concentration measured by the primary study method (passive sampling tubes). The instantaneous samples represent peak values to which people may be exposed. When evaluating this data it is important to remember that these samples are taken downwind from a facility and represent peak concentrations over the sampling time for this grab sample. They do not reflect average exposures over a longer period.

Instantaneous measurements show the significantly more variability when compared to the longer passive measurements. This fact is shown by samples WC003 and WC004 which were collected 13 minutes and 100 meters apart and which showed that short term concentrations can vary by a factor of 6-7 (2.36 versus 15.76 ug/m3).

The canister data shows a shift in the benzene:toluene ratios. The 12/19 sample shows a benzene:toluene ratio of less than 1. The ratio is greater than 1 for all samples collected on 1/16. While this data set is limited, this strongly suggests additional benzene was being measured on 1/16. This information supports the changes in the benzene:toluene ratios seen in the adsorbent tubes samples collected during sampling periods 2, 3, & 4.

Sample ID	WC001	WC002	WC003	WC004
Date	12/19/2007	01/16/2008	01/16/2008	01/16/2008
Time	11:20	11:38	11:49	12:02
Site	2	4	2	Traillet Plot
Compound Name	Conc. ug/m3	Conc. ug/m3	Conc. ug/m3	Conc. ug/m3
Benzene	2.85	1.49	2.36	15.76
Toluene	6.66	0.84	0.54	7.30
Ethylbenzene	0.57	0.28	ND	0.73
Xylene	2.65	0.90	0.26	4.43
224-Trimethylpentane	0.65	0.62	0.66	1.14
Styrene	0.48	ND	ND	0.28

Conclusions:

The Wisconsin DNR conducted an eight week field study to examine benzene concentrations in Waupaca and the surrounding area. The project’s monitoring objectives were to examine the spatial and temporal distribution of benzene concentrations and to determine if any relationships exist between benzene concentrations and the proximity to the two foundry sites in the area. From the results of these studies we have concluded the following.

- Benzene was measured at all monitoring sites. The measured benzene showed low variability between the monitoring sites and between the time periods included in the study. The highest average benzene was measured at the high traffic background site on Demarest Road (Site 9). The lowest average measured benzene was measured at the Waupaca Town Hall (Site 4).

- The ratio of measured benzene to measured toluene showed much greater variability. This suggests that different factors affect the sites and that different factors affect the sampling periods. Because the benzene concentrations were consistent, the data shows that toluene concentration varied. Using the benzene:toluene ratios, a benzene difference was calculated to assess the extra benzene in the area when the foundry was in operation. This benzene difference averaged 0.132 ug/m³ extra benzene. The maximum benzene differences were measured at site 7 (0.166 ug/m³) and site 0 (0.199 ug/m³). These sites were downwind of the foundry during most of the study period.
- An alternative analysis combining the foundry production data with the monitoring data was used to calculate theoretical benzene concentration emitted by the foundries. The maximum concentration calculated was 0.239 ug/m³ during monitoring period 3.
- Measured benzene concentrations were much higher than the corresponding modeled benzene concentrations. This difference occurs because the model addresses only benzene from the foundry and does not account for any additional benzene sources in the area such as vehicles, household heating, or other unknown sources. The highest average benzene was measured at site 9 and suggests that mobile sources are a significant source of background benzene in the area. When the modeled concentrations are compared to the benzene difference (using a subtraction method made possible, when the foundry was not operating fully over the Christmas and New Year's holidays), the two methods show better agreement. While modeling and direct measurement results are different, each method supports the other as a reasonable assessment of benzene concentrations in the Waupaca area.

Appendix A: Waupaca Monitoring Project Data Quality Assessment

The primary data quality objective used in the Waupaca Monitoring Project Report was to provide a dataset of known quality for use in assessing the ambient benzene concentrations. The dataset would be constructed to be comparable to current fixed site PAMS monitoring.

To meet the objective, with special consideration for the critical benzene parameter, the monitoring results were evaluated against several standard measures of data quality. These measures of data quality include: completion, calibration accuracy, compound recovery, and precision.

The data evaluation for Benzene is based on the following information:

- Data completeness is greater than 95%,
- Calibration standards showed a 1.7% RSD between the pre and post evaluation studies,
- Multi-component standards were within control limits 11 of 12 runs,
- Recovery from the adsorbent tubes was 3.8% for a benzene standard and 4.2 % for benzene in a multi-component standard,
- Method precision for duplicate samples was 4.5%,
- Average blank values for benzene were 12.5% of the measured ambient samples.

A detailed evaluation of the data quality parameters is provided in the remaining part of this appendix.

Completeness: Evaluating completeness, we note that our original project plan called for the collection of samples at 10 sites for 3 to 4 sampling periods. In addition we planned to collect duplicate samples at 2 of the ten sites and to collect three study blanks with each samples set for a total of 15 samples per sample set. For the entire project we collected 58 of 60 planned samples. Sample media at site2 and site 3 were lost during period 4. There was no evidence that the samples were removed or vandalized and it is assumed the sampling tubes broke loose and were blown away. Several sampling tubes did drop from the holders during period 3 and 4 of the study. These tubes were considered suspect but passed an outlier evaluation and were therefore retained in the overall data set. Data completeness for the project is assessed as over 95%.

Calibration Accuracy: Calibration accuracy is evaluated based on a consistent calibration standard and on recovery of compounds from a second multi-component standard. The first evaluation parameter is based on the area response of the calibration standard. The calibration standard is sampled from a canister and is analyzed on both columns of the gas chromatographic system. A total of ten calibration runs were made beginning with pre-study checks on 12/01/2007 and continuing through to post study check on 2/19/2008. The benzene calibration standard had an average area count of 204194 with RSD of 1.7%. The propane calibration standard showed a declining response beginning at 71041 and ending at 60812. The propane averaged 67493 with an RSD of 6.8%.

The multi-component standard is sampled from a canister and is analyzed on both columns of the gas chromatographic system. Analysis results are reported in ppbC and the data is evaluated as the compounds target value +/- 20%. Table A1a summarizes the evaluation the results of 12 analyses conducted during the course of the project. A smaller number of multi-component standard runs were conducted using the single column analysis mode. This is show in Table A1b. The most obvious fact from this analysis is that the styrene recovered from the standard is much less than is expected and I believe that styrene, a reactive compound, was lost from the standard cylinder. The target concentration for styrene is therefore higher than the actual amount added to the test canister.

Table A1a: Multicomponent Standard Analysis run as a two column analysis.				
Compound	N	Values Within CL	average	Target
Benzene	12	11	27	32
Toluene	12	9	35	42
Ethylbenzene	12	11	22	26
o-Xylene	12	12	23	25
m/p-Xylene	12	11	34	41
2,2,4-Trimethylpentane	12	12	29	33
Styrene	12	0	13	30

Table A1b: Multicomponent Standard Analysis run on only the DP-1 analytical column				
Compound	N	Values Within CL	average	Target
Benzene	4	4	28	26
Toluene	4	3	37	34
Ethylbenzene	4	4	22	21
o-Xylene	4	4	23	20
m/p-Xylene	4	2	34	33
2,2,4-Trimethylpentane	4	4	30	26
Styrene	4	0	13	24

Compound Recovery: Recovery is the ability to remove a compound from the adsorbent trap. This is assessed by spiking the standard on an adsorbent tube and analyzing the tube. The recovery is the measured compound weight divided by the expected compound weight. The recovery of the benzene standard and a multi-component standard is reported in Tables A2a and A2b. While benzene recovery is good there is declining recovery of other study compounds. The other compounds, especially toluene, are measured to support and better understand the benzene measurements. Supporting compounds are not evaluated for their direct impact but rather for the relative concentration as related to benzene.

Table A2: Compound Recovery from Adsorbent Traps				
Table A2a. Single component calibration standard				
Compound	N	Average	Target	% Recovery
Benzene	5	149.0	143.6	103.8%
Table A2a. Multi-component recovery standard				
Benzene	9	63.91	61.34	104.2%
Toluene	9	70.22	94.97	73.9%
Ethylbenzene	9	32.55	67.74	48.1%
o-Xylene	9	34.06	65.13	52.3%
m/p-Xylene	9	45.12	106.81	42.2%
2,2,4-Trimethylpentane	9	59.25	92.50	64.1%
Styrene (Actual)	9	21.53	33.99	63.3%

Method precision: Analysis of the compounds on the adsorbent tubes is destructive and allows only single analysis. Precision is evaluated using duplicate samples and combines both sampling and analytical precision. For the Waupaca study duplicate samples were collected at site 2 and site 8. Duplicate samples are assigned equal weight in the precision determination and this is evaluated by the absolute difference of the sample concentration divided by the average concentration of the duplicate samples. A summary of the precision data is provided in Table A3.

Compound Name	Conc. Max (ug/M3)	Conc. Min (ug/M3)	%Diff Max	%Diff Min	% Diff Mean
Benzene	63.26	45.66	7.9%	0.7%	4.5%
Toluene	54.13	31.29	7.7%	1.0%	4.3%
Ethylbenzene	8.53	4.69	31.1%	0.4%	10.2%
M/P-Xylene	20.74	10.07	15.9%	1.3%	8.3%
O-Xylene	11.17	3.99	33.8%	4.4%	15.0%
224-Trimethylpentane	15.84	9.08	19.1%	4.4%	12.5%
Styrene	47.17	0.54	86.8%	1.9%	35.0%

Study Blanks: The last parameter evaluated is the concentrations measured in blank samples. The field study relied on three types of blanks. The blanks were used to assess field study samples and the goal is to have ambient sample easily distinguishable from the blank samples. In calculating concentrations for all ambient samples the compound weights on the tube were first blank corrected for the average blank value specific to the sample set. A description of the blanks follows.

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.

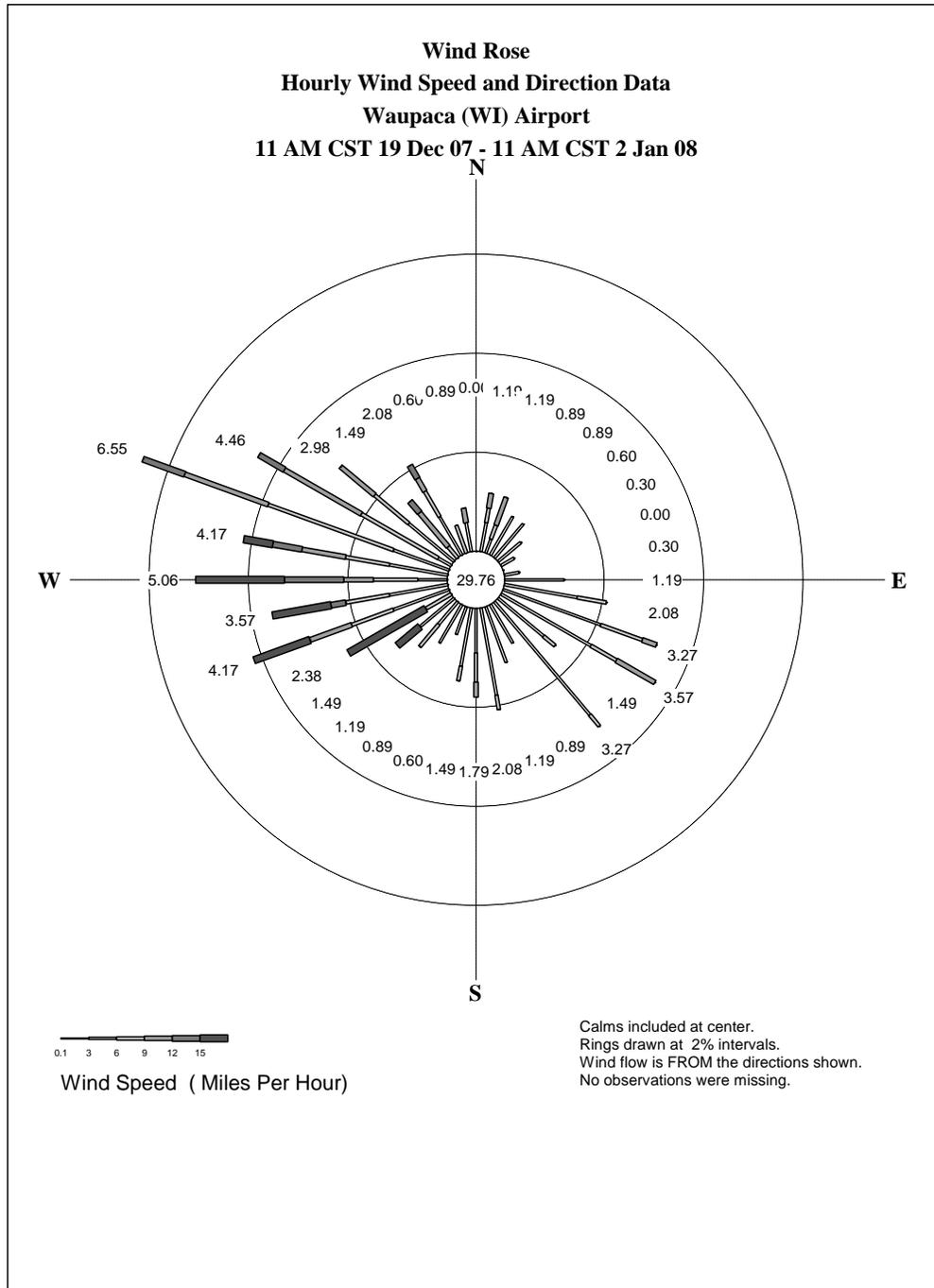
Field Blanks – Field blanks travel to the field site with the samples for deployment and retrieval. The field blank is uncapped and fitted with a diffusion cap for a period of approximately five minutes, usually during one of the sampling tube deployments. While the sampling tubes are exposed, the field 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 the four sampling periods. 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 A4.

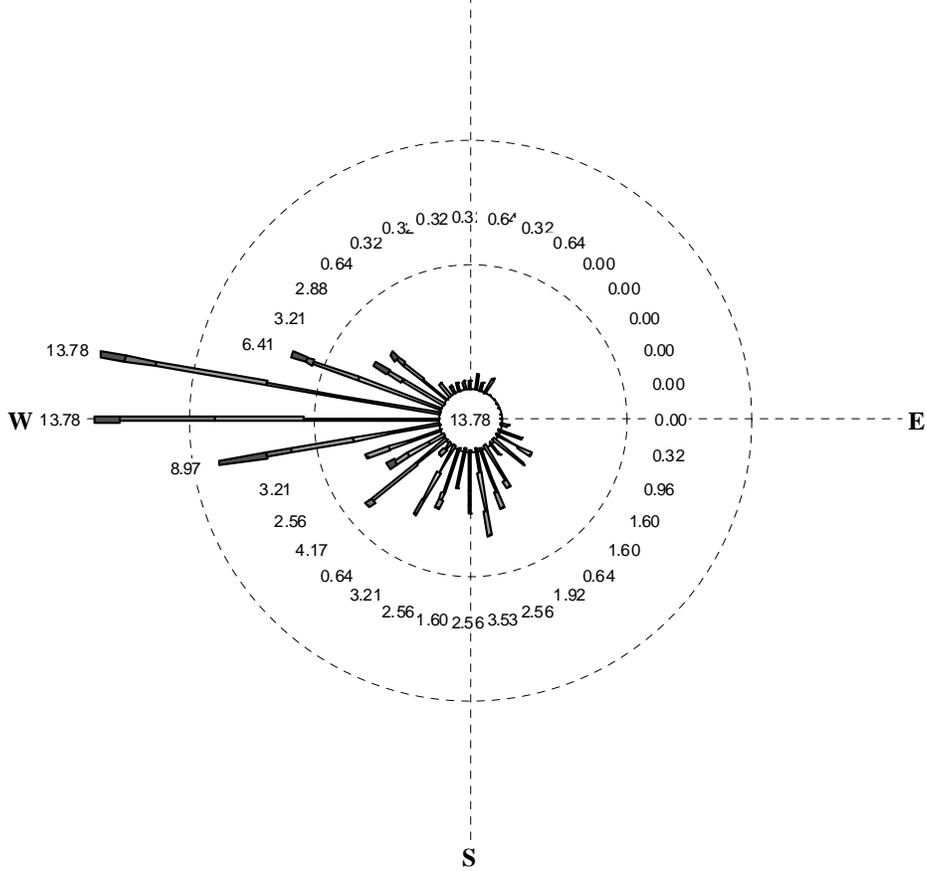
Table A4: Summary of Operational Blanks used in Waupaca Study

Table A4: Summary of Operational Blanks used in Waupaca Study				
A4a. Field Blanks	N	Detects	Average	Max
224-Trimethylpentane	4	4	3.07	4.27
Benzene	4	4	5.00	7.09
Ethylbenzene	4	2	0.23	0.65
Xylene	4	1	0.08	0.47
Styrene	4	1	0.03	0.12
Toluene	4	4	1.84	2.25
A4b. Prep Blanks	N	Detects	Average	Max
224-Trimethylpentane	4	4	2.67	2.85
Benzene	4	4	4.16	7.26
Ethylbenzene	4	0	0.00	0.00
Xylene	4	0	0.00	0.00
Styrene	4	0	0.00	0.00
Toluene	4	4	1.61	2.23
A4c. Trip Blanks	N	Detects	Average	Max
224-Trimethylpentane	4	4	3.00	3.26
Benzene	4	4	4.82	6.31
Ethylbenzene	4	1	0.06	0.23
Xylene	4	0	0.10	0.78
Styrene	4	0	0.00	0.00
Toluene	4	4	1.54	2.85

Appendix B: Wind Rose Graphics for Four Monitoring Periods



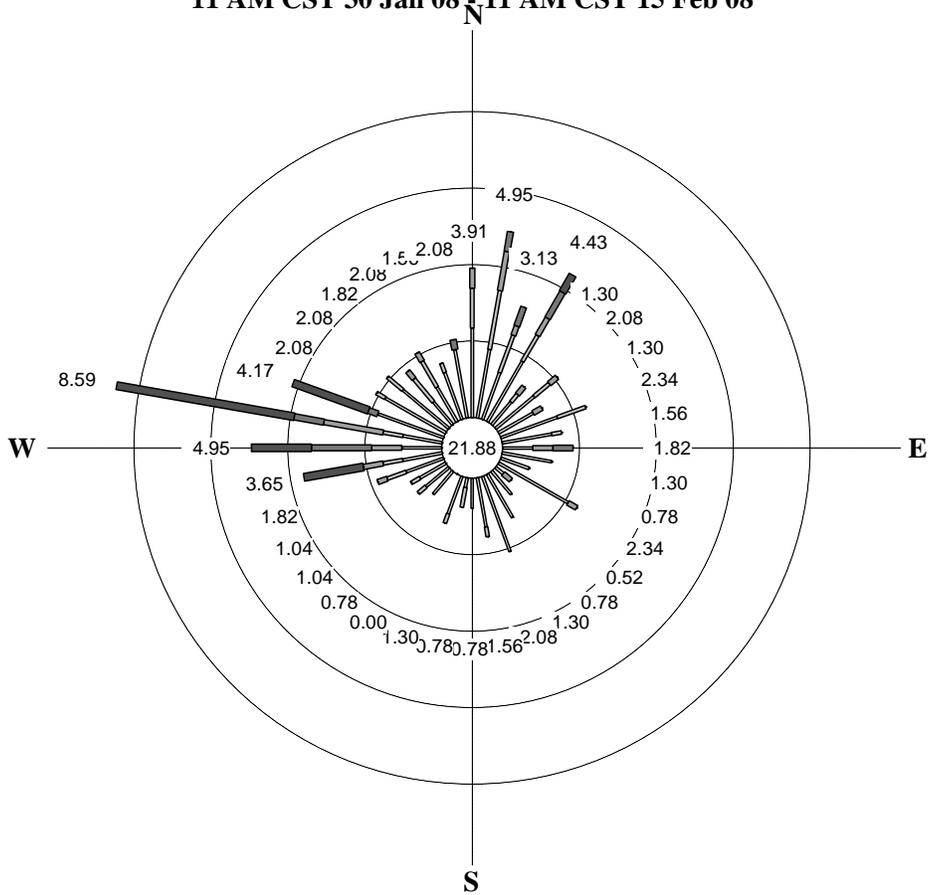
Wind Rose
Hourly Wind Data
Waupaca (WI) Airport
11 AM CST 16 Jan - 11 AM CST 30 Jan 08
(not including the missing 24 hrs of wind data for 28 Jan 08)



0.1 3 6 9 12 15
 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.

Wind Rose
Hourly Wind Data
Waupaca (WI) Airport
11 AM CST 30 Jan 08 - 11 AM CST 15 Feb 08



Wind Speed (Miles Per Hour)

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