

**Air Sampling at the
Texarkana Wood Treatment Facility
(TX 008056152)**

Final Report

Submitted to:

**Texas Environmental Health Institute
P.O. Box 13087
Austin, TX 78711-3087**

Submitted by:

**George P. Cobb, Todd A. Anderson, and Jaclyn Canas
TIEHH
PO Box 41163
Texas Tech University
Lubbock, TX 79409**

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Introduction

The Texarkana Wood Preserving (TWP) site is an inactive wood preserving plant located approximately 100 yards west of Days Creek just South of Texarkana, Texas (Figure 1). This area is fenced and is largely encompassed by a hedgerow of tall trees. A privately owned marshy area planted with small pines lies just outside the hedgerow to the east of the site. A private clear-cut area lies to the south of the site. Both of these areas have a high voltage electrical transmission line bisecting them. A railroad right of way lies along the WNW boundary of the site. It should also be noted that a plastics recycling operation lies 1000 yards to the NNW of the site. A plastic fabrication company is located 400 yards WSW of the site, just on the west edge of the railroad right of way.

The TWP utilized both creosote and pentachlorophenol in a steam/vacuum pressure treatment process from 1909-1984 (USEPA, 1993). The TWP is listed by the Environmental Protection Agency on the National Priorities List (TX 008056152). Several assessments of contamination related to activities at TWP have been conducted over the last several decades (USEPA, 1993). These assessments have focused primarily on groundwater, surface water, and soils. Polycyclic aromatic hydrocarbons (PAHs), pentachlorophenol, polychlorinated dibenzodioxins (PCDDs), and polychlorodibenzofurans (PCDFs) have been identified as contaminants of concern (COCs). However, given the volatile or semi-volatile nature of some of the COCs, air in and around TWP was of interest to be monitored to characterize inhalational exposure to persons working on site remediation and those living near the site. It is estimated that approximately 200 people live within one-third of a mile from TWP.

EPA has identified several COCs at the site that may be analyzed in air by broadly applicable standard testing protocols (USEPA, 1993). Volatile compounds of concern at the site include: 2-chlorophenol, benzene, ethylbenzene, *m*-xylene, *p*-xylene, *o*-xylene, 1,4-dichlorobenzene, 1,2,4-trichlorobenzene, and naphthalene. The PAHs mentioned as COCs for this site were: naphthalene, 2-methylnaphthalene, acenaphthene, dibenzofuran, benzo[a]anthracene, and benzo[a]pyrene. The standard list of tetrachloro- through octachloro- dibenzofurans and dibenzo-*p*-dioxins (USEPA, 1998; van den Berg et al. 2006) were also part of the COC list.

Methods

Sampling Design and Field Collection

Sampling included one upwind location and one downwind location that were off site as well as two locations on-site that were not along the primary wind vector (Figure 1). Weather data indicated southerly prevailing winds which were incorporated into our site selection (Figures 2-5). On the east side of the site, access was limited by two locked gates and a mile unmaintained, tree-lined road. On the north side of the site access was limited by a pair of rail lines, a 6 foot

high berm on the old road bed and approximately 0.4 miles of completely unmaintained road with sporadic arboreal growth in the road bed. Given the limited access to the site and the repeated public intrusion onto the site, we also considered the security of sampling equipment and personnel during site selection. Before sampling events were initiated, investigators contacted EPA, community officials, and land management authorities regarding our plans. We also visited the site with local officials.

Locations of sampling sites were identified well in advance of our first sampling trip (Figure 1). Site one was located upwind of the TWP at approximately 10-15 m SE of the entrance gate. Sites 2 and 4 were located, just inside the site border at the locations near the SW and NE corners of the TWP, respectively. Site 3 was located approximately 100 m from the home that is located at the east end of South 8th Street (where it arcs north along the rail road right-of-way). There are additional homes located on S 8th Street and S 6th Street. Air samples were taken quarterly over a one year period. EPA methods TO-9A, TO-13, and TO-15 were employed for PCDD/PCDF, PAH, and volatile compounds, respectively. Evacuated summa canisters (6 L) were provided by Columbia Analytical Services. Air samplers (4) were rented from Tisch Environmental, Inc (<http://www.tisch-env.com/tisch/index.asp>).

High volume and summa units were collocated at a given site. Each summa canister was placed approximately 3 m upwind of the sampling unit. Weather data were recorded with an automated weather station (Davis Vantage Pro 2). Due to the remote nature of the site and the inability to secure items in a sheltered location on site, the recording unit could not be left at the site to collect continuous data that would allow true max/min data and on-site wind roses. Data were recorded on data sheets several times during the day, normally when sampler or generator function was being checked.

PCDD/PCDF samples were collected during a 24 h period and PAH samples were collected for 16-24 hours. Each sampler was vented approximately 10 feet downwind. Power was supplied with propane generators to minimize the production of volatile or PAH compounds that might interfere with analyses. Generators were placed approximately 30 feet downwind of the high volume air samplers.

The sampling head of each high volume sampler was fitted with a PUF filter to sample dioxins/furans. For PAH analyses, a separate sample was collected using a glass fiber filter and XAD resin in the sampling head for both particulate and vapor phase PAHs. Sampling heads for dioxin/furan analysis were arranged similarly to those for PAHs, with the exception of PUF sorbent within a standard glass sleeve being used for dioxin/furan sampling (no glass fiber filter).

Sampling heads that contained both glass fiber filters and XAD resins were used to sample PAHs in particulate and vapor phases, respectively. Columbia Analytical Services provided PUF

filters spiked with a series of internal standards for dioxin/furan sampling. Columbia Analytical Services provided (flow calibrated) summa canisters for sampling volatiles.

During each sampling event, filters and cartridges were taken to and from the field at 4 °C in the dark. This is especially critical when dealing with PAHs that are susceptible to photolysis. We used field blanks and lab-spiked sampling media for all PAH analyses. As mentioned above Columbia Labs spiked PUF filters for PCDD and PCDF analyses before delivery to us. Field blanks consisted of entire sampling heads that were transported to the field and opened during the time that one of the sampling heads was installed and removed from a sampler. These sampling heads were treated as a sample in all other respects. With only four sampling locations in the study, it was impractical to collect field duplicates for this study.

Air samples for PAHs were taken using high volume samplers with PUF/XAD sorbent bed. A PUF sorbent was used to collect dioxins and furans. PAHs and dioxin/furans were collected for at least 24 hours at average sampling rates of 0.8-1.1 m³/min. The flow rate of each sampler was monitored periodically throughout the sampling interval with a calibration orifice (TE-5040, Tisch Environmental). For the collection of volatiles, evacuated summa canisters (6 L) were used. Canisters were metered to collect air over 24 hours. One blank summa canister was taken to and from the field.

From the cessation of sample collection to the time of analysis, all samples were chilled at approximately 4 °C on blue ice or dry ice. We shipped samples under appropriate chain of custody to the contract labs performing the respective analyses for dioxin/furan and volatiles. We transported samples for PAH determinations back to Lubbock, TX (the location of TraceAnalysis, Inc.).

Chemical Analyses

All analyses of air samples were sub-contracted to commercial laboratories. Columbia Analytical Services (Simi Valley, CA) were contracted to conduct volatiles analysis. TraceAnalysis, Inc (Lubbock, TX) were contracted for all PAH analyses. Determinations of dioxins and furans were contracted to Columbia Analytical Services, Houston, TX.

The preceding EPA evaluation of the site specified several of these analytes in these methods as contaminants of concern. Data usability was formally evaluated using standard review protocols.

Results

Field Data

Wind observations during sampling events verified that air moving from the site toward the downwind sampling site (Table 1). Monthly wind roses for each sampling month were obtained from Western Regional Climate Center (<http://www.wrcc.dri.edu/cgi-bin/rawMAIN.pl?ndTTEX>) to verify our field observations. The dominant wind direction and frequency were SE (16.1%), ESE (15.2%), and SSE (9.1%) during February (Figure 2), NNE (10.8%), SSE (10.5%), and NE (7.8%) during May (Figure 3). No wind direction exceeded 10% during August, and the most frequent wind directions were SSE (8.1%), and SE (7.4%) (Figure 4). The dominant wind directions during December (Figure 5) were WNW (9.1%), NE (8.7%), and W (7.5%). Using these data, site one was upwind during February, May and August 2009 sampling events, with site three being more directly downwind during those times. Conversely, site three is nearest to downwind during December 2009 sampling, with site 1 being more downwind for that sampling. Temperatures measured at the site ranged from 28 to 85 °F (Table 1) as would be expected for seasonal sampling. Rain preceded the first three sampling events by a few days. Rain coincided with initiation of the last sampling event and lasted for the first day of sampling.

Dioxins

PCDD and PCDF concentrations were determined at each site (Appendix A). These data were converted to TCDD Toxic Equivalents (TEQ) for reportage. TEQs in air ranged from 0.0867 pg/m³ at Site 4 during the December sampling event to 0.0005 pg/m³ at Site 2 during February sampling (Table 2 and Appendix B). The average TEQ of the 4 sampling events for sampling sites ranged from 0.0025 pg/m³ at Site 1 (control) to 0.0226 pg/m³ at Site 4. It appeared that Site 2 and 4 had higher TEQs than the other two sites during 2009. All sampling sites (no sample for Site 3) had elevated TEQs in December compared with other months (Figure 6). Data usability indicated that data were useful for evaluation of analyte concentrations with a note that the reported concentration appear to be biased low, even though falling within acceptable QA/QC guidelines.

Polycyclic aromatic hydrocarbons (PAHs)

The highest total concentration of PAHs was 443.80 pg/m³ at Site 3 during the August sampling event, while the lowest was 16.49 pg/m³ at Site 4 during August sampling (Table 2 and Appendix C). The average concentrations of PAHs of the 4 sampling events for sampling sites ranged from 23.78 pg/m³ at Site 4 to 147.58 pg/m³ at Site 3. Site 3 appeared to have higher average PAH concentrations compared with other sampling sites, and this is due to the high PAH concentrations measured in the August sample (443.80 pg/m³). The highest concentration of PAHs (278.42 pg/m³) from Site 1 was observed during May, while Site 2 and 3 had elevated

concentrations (134.30 and 443.80 pg/m³, respectively) during August. All sampling sites had low concentrations of PAHs during February and December sampling (Figure 7). Data usability indicated that analyses were adequate for evaluating concentrations of PAHs in air with a few minor exceptions. Pyrene recovery was low for the December sampling at Site 3 and one blank sample had low recovery. Data for all other samples fall within acceptable QA/QC limits, but concentrations may be biased low.

Volatile organic chemicals (VOCs)

A total of 9 to 13 volatile compounds were detected in February, May, and August samples, whereas only 4 compounds were detected in December samples (Table 3 and Appendix D). Naphthalene was the only COC observed, and it occurred at one site during the February 2009 sampling event. Dichlorodifluoromethane and trichlorofluoromethane were measured in samples from all 4 sampling events, while ethanol, acrolein, acetone, and 2-butanone were measured in samples from 3 sampling events. The highest concentrations of dichlorodifluoromethane and trichlorofluoromethane were both measured at Site 4 during December sampling (3.0 and 1.6 µg/m³, respectively). Data usability evaluation noted the need for field duplicates to evaluate data precision. This extent of sampling was not proposed, but should be noted in evaluating these data.

Discussion

Time on site during sampling was normally 6 hours per day which covered at least three daily visits. It is possible that higher or lower temperatures occurred while investigators were on site. These values were not recorded. Similarly, wind speed and direction were monitored only when investigators were on site. Thus, excursions in wind speed or direction could have been missed. Weather service data shown in Figures 2-5 support our wind data.

With the exception of PAHs, air pollutant concentrations were low near the TWP site. The nearby rail line is the primary source of these compounds. This hypothesis is supported by the fact that PAH concentrations in air appeared higher at Site 3 than at each of the other sampling sites within this study, even though other pollutants did not follow this pattern. The highest observed total PAH concentration of 444 pg/m³ should be placed in context. This is important when considering the PAHs identified as COCs. COCs found in air near the site were naphthalene, 2-methylnaphthalene, acenaphthene, dibenzofuran. Naphthalene or phenanthrene was the most concentrated analytes in each sample from each site. Larger COCs, benzo[a]anthracene and benzo[a]pyrene, were not found in air samples. It is notable that no PAHs with 5 or more rings were found in air from or near the TWP site (Appendix C). Moreover the total concentration of PAHs with four rings never exceeded 22 pg/m³ (0.022 ng/m³).

ATSDR suggests that typical concentrations of PCDDs in urban air within the United States average 2.3 pg/m^3 (ATSDR, 1998). As with most studies of PCDD occurrence, OCDD and HpCDD congeners occur in highest concentration and 2,3,7,8-TCDD occurs in the least concentrations common congener (Smith et al. 1992). Underlying data from this estimate would be useful in predicting the TEQs from these areas for comparative purposes. Ambient air in the vicinity of a Superfund clean-up at Quail Run Trailer Park near St Louis, MO (USEPA, 1990) contained 1 pg/m^3 of 2,3,7,8-TCDD (Fairless et al. 1987). It should be noted that 2,3,7,8-TCDD rarely occurs in rural areas (Reed et al. 1990).

Few studies in the last decade have evaluated airborne PCDD or PCDF concentrations in air. The most common data involve emissions from incinerators. Literature searches for dioxins in air near waste sites yielded only 8 citations, while expanding the search to human exposure to dioxins in air produced 125 citations in the last decade. The information included in these citations was not helpful in placing the concentrations that we observed in the context of other emissions from hazardous waste sites. However evaluating the literature for emission factors did lead to some potentially useful data. TEQs ranged from 6.4 to 16.1 pg/m^3 near a municipal incinerator in Columbus, OH. The lower bound of this concentration range is 2 orders of magnitude higher than the highest concentration measured during the TWP investigation. This lowest concentration from Columbus was found approximately 1.2 miles from the incinerator (Lorber et al. 2000). At another site in Italy, the atmospheric range of TEQs near waste incinerators ranged from 337 - 10 fg/m^3 (0.337 to 0.01 pg/m^3). The lower bound was found approximately 1.2 miles from the incinerator (Lorber et al. 2000). The lower limit of this TEQ range, 0.01 pg/m^3 , exceeds TEQs observed for 10 of 15 samples collected on site or downwind of the TWP site. One study of global PCDD/PCDF emissions indicated that the average flux of dioxins from soil in temperate zones is $280 \text{ ng/m}^2/\text{yr}$ (Brzuzy and Hites 1996). The underlying data for that study also demonstrates that a range of 10 - $100 \text{ ng/m}^2/\text{yr}$ is most common in the south central US. This flux range translates to 28 - $280 \text{ pg/m}^2/\text{day}$. These data may be useful in predicting PCDD/PCDF concentrations in air from uncontaminated areas.

Volatiles data from the study area are largely unremarkable. Naphthalene was the only COC identified at this site. Numerous COCs were absent from air samples: 2-chlorophenol, benzene, ethylbenzene, *m*-xylene, *p*-xylene, *o*-xylene, 1,4-dichlorobenzene, 1,2,4-trichlorobenzene, naphthalene. It is fairly obvious that volatile compound release was highest in the warmer months and that biological activity was at least partially responsible for volatile components (i.e., pinene and limonene) in the air.

References

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Tables and Figures

Table 1. Observed air temperature (°F) and wind conditions (mph) observed during sampling near the Texarkana Wood Preserving Site during 2009.

Sampling Event	Parameter	Mean	Max	Min	Direction Range
Feb	Temperature	68	75	62	
	Wind	2.5	12	0	SSW-ESE
May	Temperature	72	87	54	
	Wind	0.7	10	0	NW to NE, SSE to ESE
Aug	Temperature	76.7	85	65	
	Wind	4.5	9	0	N to SE
Dec	Temperature	37.2	50	28	
	Wind	1	5	0	W to NE

Table 2. Toxic Equivalents (TEQ) representing 2,3,7,8-TCDD equivalents (pg TCDD/m³) from each polychlorodibenzo-p-dioxin and polychlorodibenzofuran and total concentrations (pg/m³) of polycyclic aromatic hydrocarbons in air samples collected near the Texarkana Wood Preserving Site during 2009*.

	Sampling event	Site 1 Upwind	Site 2	Site 3 Downwind	Site 4
Total TEQs	February	0.0023	0.0005	0.0012	0.0008
	May	0.0015	0.0025	0.0018	0.0017
	August	0.0006	0.0082	0.0114	0.0012
	December	0.0058	0.0326	NA ^a	0.0867
	<i>Mean</i>	0.0025	0.0109	0.0048	0.0226
Total PAHs	February	24.93	33.99	49.16	26.21
	May	278.42	34.09	58.61	35.00
	August	34.64	134.30	443.80	16.49
	December	17.13	46.04	38.73	17.44
	<i>Mean</i>	88.78	62.10	147.58	23.78

*- Data for all analytes can be found in Appendices A, B, and C.

a- NA= not applicable. Sample was destroyed at the contract lab during chemical analysis.

Table 3. Volatile organic chemical (VOC) concentrations* ($\mu\text{g}/\text{m}^3$) in air samples collected at the Texarkana Wood Preserving Site during 2009**.

	Compound	Site 1	Site 2	Site 3	Site 4
Feb	Dichlorodifluoromethane (CFC 12)	2.1	ND^a	2.3	2.2
	<i>Ethanol</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>13</i>
	<i>Acrolein</i>	<i>0.91</i>	<i>1.8</i>	<i>1.2</i>	<i>ND</i>
	<i>Acetone</i>	<i>8.1</i>	<i>7.8</i>	<i>11</i>	<i>9.9</i>
	Trichlorofluoromethane	1.1	ND	1.1	1.1
	2-Propanol (Isopropyl Alcohol)	ND	ND	ND	2.4
	<i>2-Butanone (MEK)</i>	<i>1.3</i>	<i>1.6</i>	<i>1.5</i>	<i>1.9</i>
	Ethyl Acetate	2.1	ND	ND	3.6
	Toluene	ND	ND	ND	1.3
	Naphthalene	ND	ND	ND	1.1
	May	Dichlorodifluoromethane (CFC 12)	2.3	2.4	2.5
<i>Ethanol</i>		<i>12</i>	<i>10</i>	<i>24</i>	<i>ND</i>
<i>Acrolein</i>		<i>2.3</i>	<i>1.2</i>	<i>0.75</i>	<i>1.3</i>
<i>Acetone</i>		<i>31</i>	<i>13</i>	<i>8.4</i>	<i>10</i>
Trichlorofluoromethane		1.2	1.3	1.3	1.3
Vinyl Acetate		8.4	ND	ND	ND
<i>2-Butanone (MEK)</i>		<i>3.1</i>	<i>1.7</i>	<i>0.92</i>	<i>1.4</i>
n-Octane		1.0	0.77	ND	ND
d-Limonene		0.68	ND	ND	ND
Aug		Propene	1.5	ND	1.9
	Dichlorodifluoromethane (CFC 12)	2.4	2.3	2.2	2.2
	<i>Ethanol</i>	<i>ND</i>	<i>8.2</i>	<i>ND</i>	<i>12</i>
	<i>Acrolein</i>	<i>1.7</i>	<i>2.5</i>	<i>2.7</i>	<i>7.5</i>
	<i>Acetone</i>	<i>19</i>	<i>13</i>	<i>36</i>	<i>35</i>
	Trichlorofluoromethane	1.2	1.2	1.1	1.1
	2-Propanol (Isopropyl Alcohol)	ND	ND	1.7	3.0
	<i>2-Butanone (MEK)</i>	<i>2.8</i>	<i>2.3</i>	<i>7.0</i>	<i>9.2</i>
	4-Methyl-2-pentanone	ND	ND	ND	0.94
	Toluene	ND	0.83	0.80	0.88
	2-Hexanone	ND	ND	1.3	3.3
	alpha-Pinene	ND	1.5	ND	2.4
	d-Limonene	0.90	1.4	ND	9.9
	Dec	Propene	ND	5.9	ND
Dichlorodifluoromethane (CFC 12)		2.3	2.3	2.4	3.0
Trichlorofluoromethane		1.3	1.3	1.2	1.6
4-Methyl-2-pentanone		ND	0.87	ND	ND

*- Compounds in bold were measured in all 4 sampling events, while compounds in italics were measured in 3 sampling events.

**.- Data for all analytes can be found in Appendix D

a- ND= not detected



Figure 1. Air sampling locations used in 2009 to collect volatiles, polychlorinated dibenzo-p-dioxins, polychlorodibenzofurnans, and polycyclic aromatic hydrocarbons at the Texarkana Wood Preserving Site (TX 008056152).

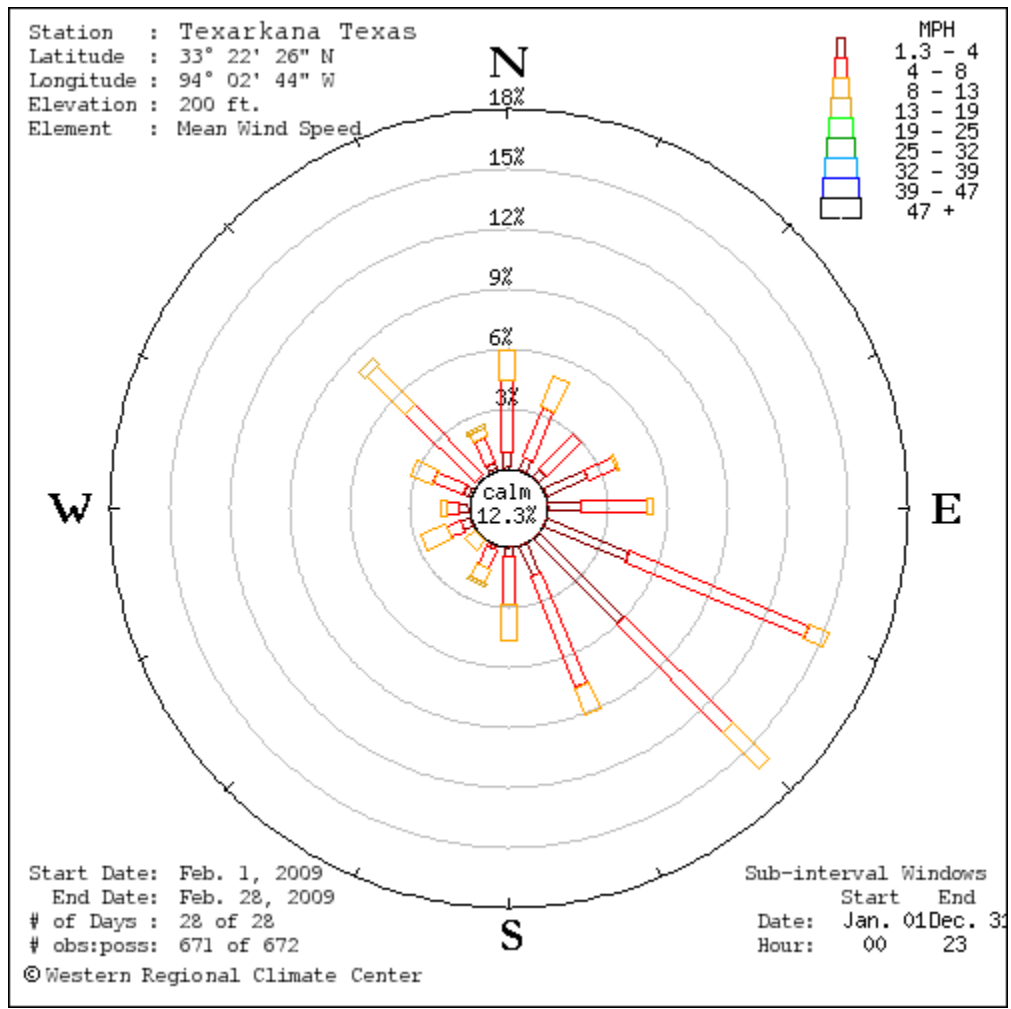


Figure 2. Wind rose in Texarkana, Texas during February 2009

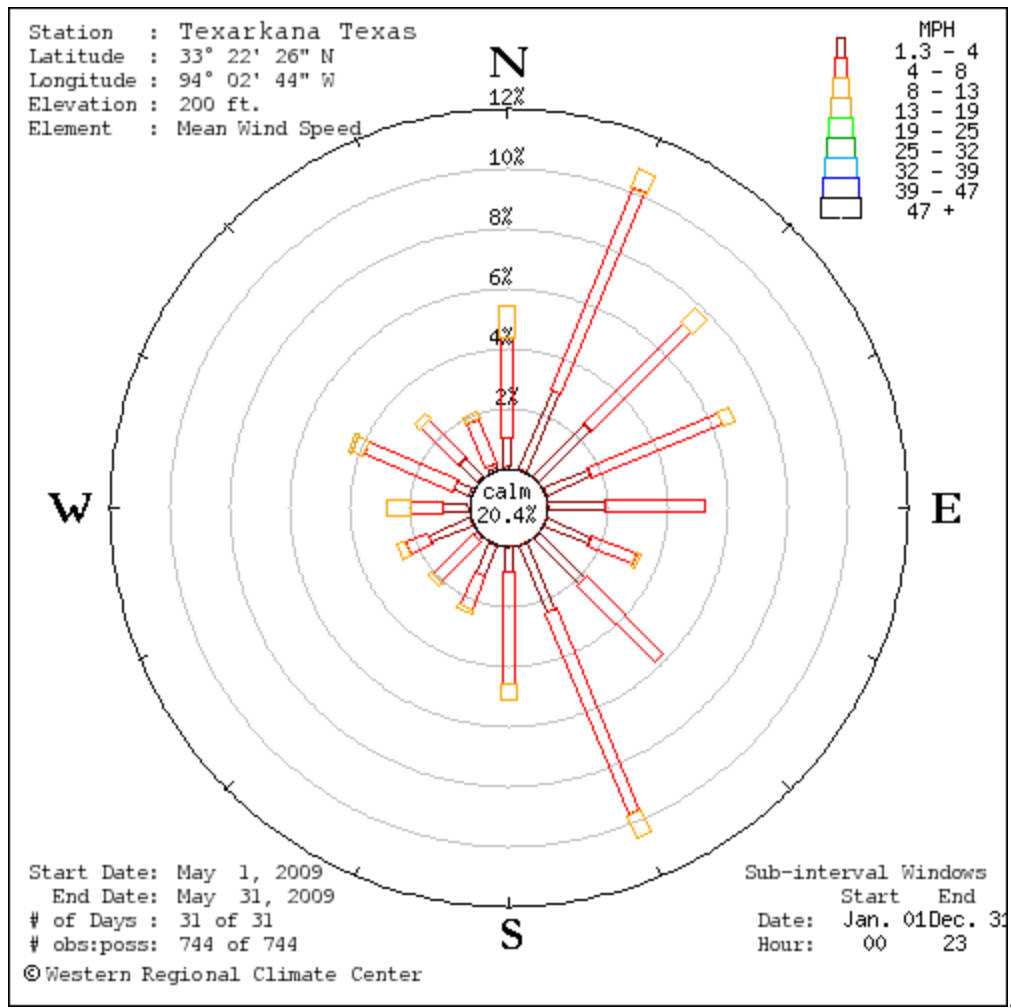


Figure 3. Wind rose in Texarkana, Texas during May 2009.

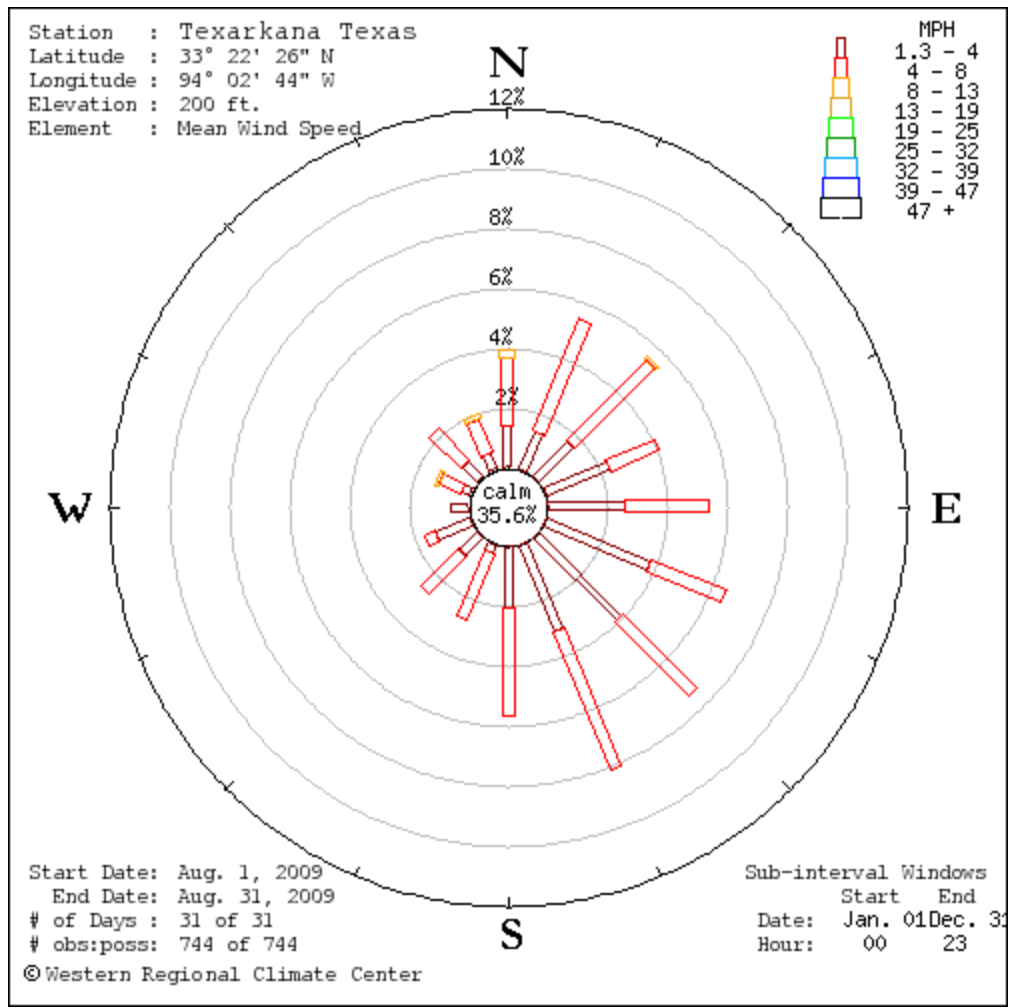


Figure 4. Wind rose in Texarkana, Texas during August 2009.

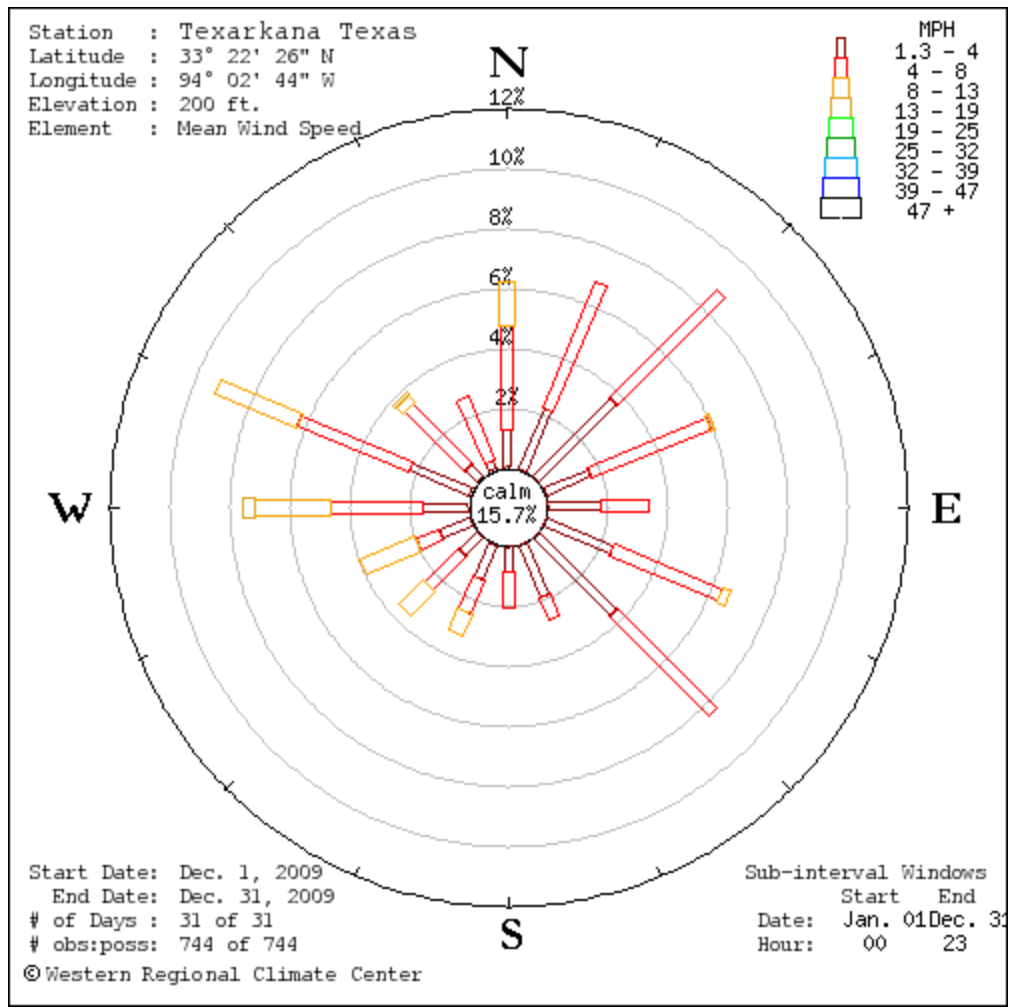


Figure 5. Wind rose in Texarkana, Texas during December 2009.

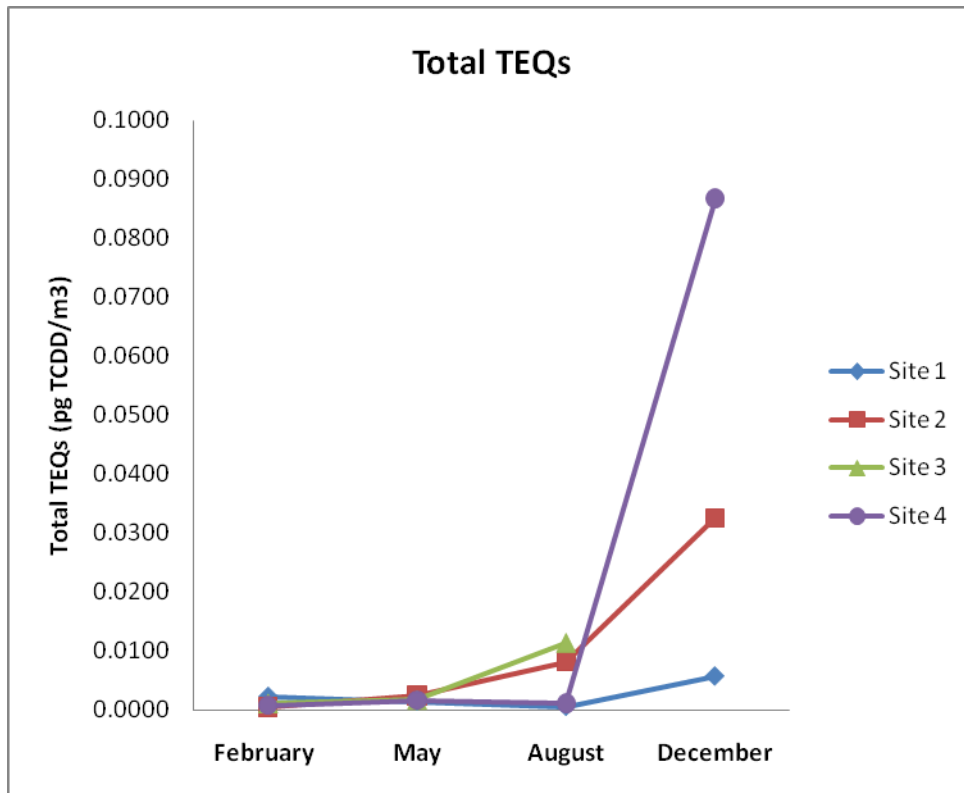


Figure 6. Toxic Equivalents (TEQ) representing 2,3,7,8-TCDD equivalents (pg TCDD/m³) from each polychloro dibenzo-p-dioxin and polychloro dibenzofuran in air samples collected near the Texarkana Wood Preserving Site during 2009. Site one is the nearest to upwind during Feb, May and August sampling. Site three is nearest to downwind during December sampling.

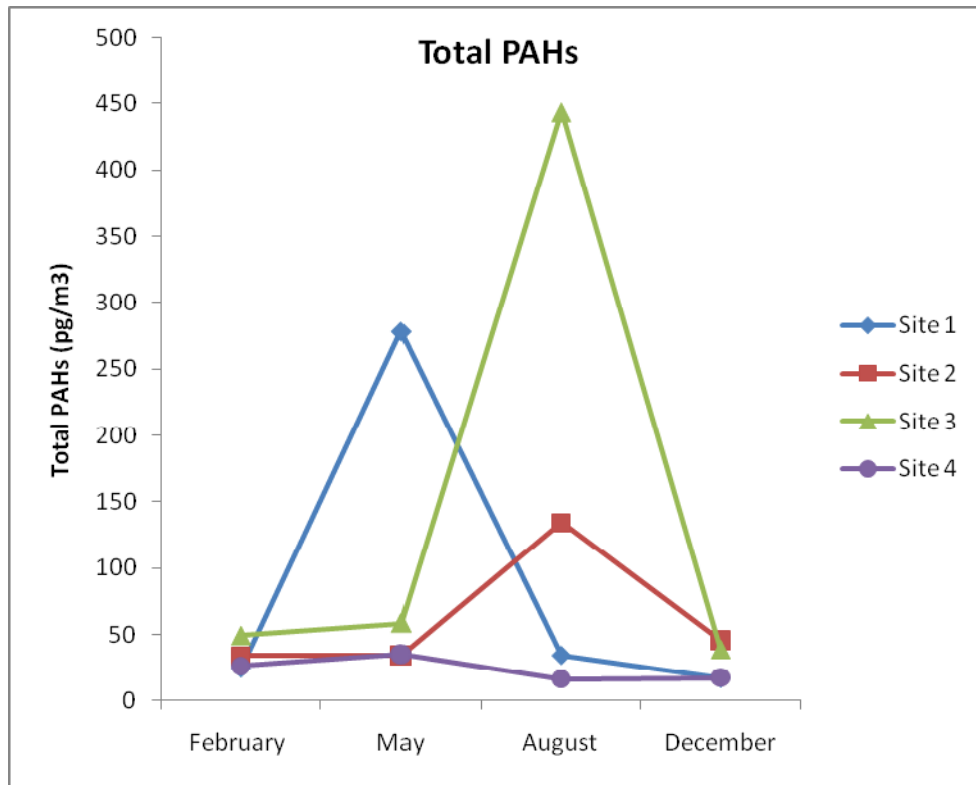


Figure 7. Total concentrations (pg/m^3) of polycyclic aromatic hydrocarbons in air samples collected near the Texarkana Wood Preserving Site during 2009. Site one is the nearest to upwind during Feb, May and August sampling. Site three is nearest to downwind during December sampling.