

# Texas Commission on Environmental Quality

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## INTEROFFICE MEMORANDUM

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**Date:** January 11, 2010

**From:** Joseph T. Haney, Jr., M.S.   
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**Subject:** Health Effects Review of Ambient Air Monitoring Data Collected in TCEQ Region 12 during 2008

### Key Points

- The 2008 benzene averages being below the long-term, health-based comparison value at the Lynchburg Ferry and Galena Park sites represents a significant improvement in air quality in these areas.
- The reported 2008 average benzene concentration at the Lynchburg Ferry site indicates a continued decrease, and was below TCEQ's long-term, health-based comparison value for the first time since monitoring began at this site in 2003. Due to the significant and continued improvement in long-term benzene concentrations measured at Lynchburg Ferry, benzene is being removed from the Air Pollutant Watch List (APWL) area which contains this site (Site# [APWL1204](#)).
- The annual average benzene level reported for the Galena Park site in 2008 was also below TCEQ's long-term, health-based comparison value for the first time in several years. This site is contained within an APWL area for benzene (Site# [APWL1206](#)), and the Toxicology Division (TD) recommends a continued effort to control and/or reduce benzene emissions such that the long-term comparison value will continue to be met at this site.
- Although somewhat lower than the 2005-2007 averages, the 2008 benzene concentration at the Marathon-sponsored site in Texas City is above TCEQ's long-term, health-based comparison value. This site is within an APWL area for benzene (Site# [APWL1202](#)) and a reduction in benzene emissions in this area is recommended.
- The reported 2008 average 1,3-butadiene concentration at the Milby Park site indicates a continued downward trend and a significant reduction in reported annual concentrations over the last four years. The 2008 average meets the long-term goal in Emission Reduction Agreements (ERAs). In 2009, 1,3-butadiene was able to be removed from the APWL for this area (Site# [APWL1207](#)) due to significant improvements in long-term concentrations, which are below levels of health concern.
- Hourly levels of several volatile organic compounds (VOCs) monitored in the Lynchburg Ferry and Milby Park areas would result in the perception of odors if people were exposed. While direct, short-term health effects (e.g., eye irritation) would not be expected as a result of exposure to these concentrations, sufficiently strong and persistent odors have the potential to cause odor-related health effects (e.g., nausea, headaches). Due to the frequency and magnitude of exceedance of the styrene odor-based comparison value, reductions in styrene emissions have previously been recommended by the TD for these areas.

- There was a downward trend during 2008 in monitored styrene levels at Milby Park as a result of efforts by Goodyear in 2008 to address a potential source of elevated styrene emissions detected at the Milby Park monitor (e.g., voluntary ERA with the TCEQ, 25% reduction in permitted styrene emissions). The TD also recommends styrene emissions reductions for the Lynchburg Ferry site area.
- Acrolein has many sources and the sampling and analysis of it is difficult. While carbonyl analyses at the Deer Park site indicate concentrations below TCEQ’s health-based comparison values, the reported 2008 average acrolein levels based on co-located canister samples at this site, and some 24-hour levels, are above comparison values. However, TCEQ’s comparison values are conservative and are not threshold concentrations for health effects, and health effects would not be expected to occur based on a thorough evaluation of the reported results and scientific toxicological data.
- The reported 2008 average benzene concentration at the British Petroleum (BP)-sponsored site in Texas City indicates a continued decline, and was below TCEQ’s long-term, health-based comparison value for 2007 and 2008.

**Background**

The primary purpose of this memorandum is to convey the Toxicology Division’s (TD) evaluation of ambient air toxics sampling conducted at monitoring sites in Region 12-Houston during 2008. Additionally, summary information concerning various specific TCEQ actions (e.g., investigations) relevant to identifying and/or reducing emissions is provided for several of the areas/chemicals discussed. The TD reviewed summary results for VOCs from 24- and 1-hour canister samples, 1-hour automated gas-chromatography (autoGC) VOC samples, 24- and 1-hour carbonyl samples, 24-hour polycyclic aromatic hydrocarbon (PAH)/semivolatile organic compound (SVOC) samples, and 24-hour metals samples from filters designed to collect particulate matter with an aerodynamic diameter of 2.5 microns or less (PM<sub>2.5</sub>) and from filters collecting particulate matter with an aerodynamic diameter of 10 microns or less (PM<sub>10</sub>). Criteria pollutant (i.e., compounds having National Ambient Air Quality Standards) data were not evaluated in this memorandum. Appendix 1 contains a list of the target analytes that were evaluated for this review. Information regarding monitoring sites and target analytes is presented in Table 1 and summarized below:

- 24-hour canister VOC sampling at 16 sites
- 1-hour canister VOC sampling at 3 sites
- 1- and 24-hour carbonyl sampling at 3 sites
- 24-hour metals sampling at 3 sites
- 24-hour PAH/SVOC sampling at 1 site
- 1-hour autoGC VOC monitoring at...
  - 5 TCEQ sites
  - 7 Enhanced Industry-Sponsored Monitoring (EISM) sites
  - 1 TCEQ-Industry Agreed Order Monitoring site (AOM)
  - 1 USEPA/DOJ-Industry Agreement Monitoring site (EPA/DOJAM)

**Table 1. Air Toxics Sampling Site Information in TCEQ Region 12 for Year 2008**

County	EPA Site ID	City and Site Location	Network	Monitored Compounds
Brazoria	48-039-1003	<a href="#">Clute 426 Commerce St.</a>	TCEQ	VOC (24-hour canister)
Brazoria	48-039-0618	<a href="#">Danciger Along US Hwy 1459 in Brazoria County</a>	EISM	VOC (autoGC)
Brazoria	48-039-1016	<a href="#">Lake Jackson 109-B Brazoria Hwy 332-W</a>	EISM	VOC (autoGC)
Brazoria	48-039-0619	<a href="#">Mustang Bayou</a>	EISM	VOC (autoGC)

		<a href="#">Liverpool</a>		
Galveston	48-167-0005	<a href="#">Texas City, Ball Park 2516 ½ Texas Ave.</a>	TCEQ	VOC (24-hour canister)
Galveston	48-167-0056	<a href="#">Texas City, 34<sup>th</sup> St. 2212 North 34th St.</a>	EISM	VOC (autoGC)
Galveston	48-167-1034	<a href="#">Galveston, 99<sup>th</sup> St. 9511 Avenue V ½</a>	TCEQ	VOC (1- & 24-hour canister)
Harris	48-201-0036	<a href="#">Jacinto Port 1st St. and Elsbeth St.</a>	TCEQ	VOC (24-hour canister)
Harris	48-201-1039	<a href="#">Deer Park 4514 ½ Durant St.</a>	TCEQ	VOC (autoGC, 24-hour canister), Carbonyls, Metals, PAHs/SVOCs
Harris	48-201-0024	<a href="#">Houston, Aldine 4510 ½ Aldine Mail Rd.</a>	TCEQ	VOC (1- & 24-hour canister), Metals
Harris	48-201-1035	<a href="#">Houston, Clinton 9525 ½ Clinton Dr.</a>	TCEQ	VOC (autoGC), Carbonyls, Metals
Harris	48-201-0057	<a href="#">Galena Park 304 Stewart St.</a>	TCEQ	VOC (24-hour canister)
Harris	48-201-0026	<a href="#">Houston, Channelview 1405 Sheldon Rd.</a>	TCEQ	VOC (autoGC), Carbonyls
Harris	48-201-0061	<a href="#">La Porte, Shoreacres 3903 ½ Old Hwy 146</a>	TCEQ	VOC (24-hour canister)
Harris	48-201-0069	<a href="#">Houston, Milby Park 2201-a Central St.</a>	TCEQ	VOC (autoGC)
Harris	48-201-6000	<a href="#">Houston, Cesar Chavez 4829A Galveston Rd.</a>	TCEQ	VOC (autoGC)
Harris	48-201-1015	<a href="#">Baytown, Lynchburg Ferry 1001 B Lynchburg Rd.</a>	TCEQ/EISM	VOC (autoGC, 24-hour canister)
Harris	48-201-0617	<a href="#">Baytown, Wallisville Rd. 4727 Wallisville Rd.</a>	EISM	VOC (autoGC)
Harris	48-201-0307	<a href="#">Houston, Manchester/Central 9401 ½ Manchester Rd.</a>	TCEQ	VOC (24-hour canister)
Harris	48-201-0029	<a href="#">Tomball, NW Harris County 16822 Kitzman St.</a>	TCEQ	VOC (1- & 24-hour canister)
Harris	48-201-0055	<a href="#">Houston, Bayland Park 6400 Bissonnet St.</a>	TCEQ	VOC (24-hour canister)
Harris	48-201-0058	<a href="#">Baytown 7201 ½ Bayway Dr.</a>	TCEQ	VOC (24-hour canister)
Harris	48-201-0803	<a href="#">Haden Rd. (HRM-3) 1504 ½ Haden Dr.</a>	TCEQ/EISM	VOC (autoGC, 24-hour canister)
Harris	48-201-1049	<a href="#">Pasadena North 702 Light Company Rd.</a>	TCEQ	VOC (24-hour canister)
Galveston	N/A	BP North America Products, Inc.-Texas City 31 <sup>st</sup> St. (Between Texas Ave. and 5 <sup>th</sup> Ave.)	AOM	VOC (autoGC)
Galveston	N/A	Marathon Petroleum Company, LLC- Texas City 11 <sup>st</sup> St. S. at 6 <sup>th</sup> Ave. S.	EPA/DOJAM	VOC (autoGC)
Montgomery	48-339-0078	<a href="#">Conroe 9472A Hwy 1484</a>	TCEQ	VOC (24-hour canister)

All data collected at TCEQ monitors are analyzed by the TCEQ laboratory and should meet a 75% data completeness objective. At EISM monitors, data are collected by a third party contractor and should meet a 75% data completeness objective. The data collected at the AOM and EPA/DOJAM monitors are analyzed by a third party contractor and should meet an 85% data completeness objective. One-hour canister VOC, 1-hour autoGC VOC, and 1-hour carbonyl data were evaluated for potential acute health (e.g., irritation) and odor concerns, as were 24-hour sample results (VOCs, carbonyls, and metals). The annual averages from 1-hour autoGC and 24-hour samples (VOCs, carbonyls, and metals) were evaluated

for potential chronic health concerns. Measured chemical concentrations were compared to appropriate TCEQ health-, odor-, and vegetation-based comparison levels for ambient air. Information on ambient air comparison levels may be obtained via the internet (<http://www.tceq.state.tx.us/implementation/tox/AirToxics.html>) or by contacting the TD (512-239-1795).

## **Evaluation**

### 1-Hour Concentrations

The vast majority of the 1-hour canister VOC, autoGC VOC, and carbonyl concentrations were below their respective TCEQ short-term, health- and/or odor-based ambient air comparison levels. More specifically, over 99.997% of the approximately 3,730,000 1-hour VOC measurements from TCEQ and EISM autoGC monitors in Region 12 in 2008 were below their short-term comparison levels. Approximately 0.00005% of the hourly autoGC measurements collected in Region 12 in 2008 exceeded TCEQ short-term, health-based comparison levels. Approximately 0.002% exceeded odor-based comparison levels, and the majority of those occurred at two sites in close proximity to industrial sources and the Houston Ship Channel. One-hundred percent of the approximately 3,000 1-hour VOC concentrations from canister samples were below their respective short-term, health-based comparison levels, and only one chemical (p-diethylbenzene) in a single 1-hour VOC canister sample exceeded its odor-based comparison level. Additionally, except for a single exceedance of an odor-based comparison value (isovaleraldehyde), all of the approximately 740 1-hour carbonyl concentrations measured in Region 12 in 2008 were below short-term comparison values. Therefore, we would not expect short-term, adverse health effects or odors to be associated with the vast majority of hourly measurements reported for Region 12 in 2008.

For the reported 1-hour concentrations that exceeded their respective short-term, health- and/or odor-based comparison levels, further evaluation was conducted to determine the potential for adverse health effects or odors. Benzene was the only chemical for which any of the reported 1-hour concentrations exceeded its respective short-term, health-based ambient air comparison level in 2008. These exceedances occurred only at the Lynchburg Ferry site monitor, where there were 2 hourly benzene concentrations above the short-term, ambient air comparison value of 180 ppb<sub>v</sub>, with a maximum concentration of 777 ppb<sub>v</sub>. In 2007, there were 4 such exceedances of the short-term, ambient air comparison value, with a maximum concentration of 913 ppb<sub>v</sub>. The maximum reported 2008 concentrations are significantly below benzene levels attributable to short-term, adverse health effects such as central nervous system depression and irritation. Therefore, exposure to these 1-hour concentrations would not be expected to cause short-term, adverse health effects. However, as these relatively high hourly levels contribute to long-term benzene concentrations at the Lynchburg Ferry site, which have historically been of some concern, the benzene emissions resulting in these elevated short-term levels should be reduced.

The reported 1-hour autoGC VOC concentrations that exceeded their respective odor-based comparison levels are shown below in Table 2. Four sites listed in Table 2 of the 2007 data review (Cesar Chavez, Clinton Dr., Deer Park, Lake Jackson) are no longer listed due to reductions in the measured isoprene concentrations at those four sites for 2008. In regard to odor comparison value exceedances based on Summa canister results, 1-hour canister results show a single 1-hour isovaleraldehyde concentration (0.11 ppb<sub>v</sub>) reported for the Clinton Dr. site that slightly exceeded its odor-based comparison value (0.1 ppb<sub>v</sub>). Additionally, due to the recent adoption of a very low odor-based comparison value for p-diethylbenzene (0.39 ppb<sub>v</sub>), a single 1-hour canister p-diethylbenzene concentration (0.45 ppb<sub>v</sub>) reported for the Galveston 99<sup>th</sup> St. site exceeded its odor-based value.

Site	Chemical	Number of 1-Hour Concentrations above Odor-Based Comparison Value	Maximum Measured Concentration (ppb <sub>v</sub> )	Odor-Based Comparison Value (ppb <sub>v</sub> )
Danciger	Isoprene	5	7.98	5
	n-Propylbenzene	1	7.29	3.8
Haden Rd.	Styrene	1	109.35	25
Lynchburg Ferry	Styrene	32 <sup>a</sup>	494.38	25
	Isoprene	6	11.63	5
Milby Park	Styrene	33 <sup>b</sup>	69.66	25
	Isoprene	1	5.70	5
Wallisville Rd.	Isoprene	1	5.23	5
	n-Propylbenzene	2	5.02	3.8

<sup>a</sup> The maximum 24-hour autoGC concentration (42.53 ppb<sub>v</sub>) exceeded the odor-based comparison value.

<sup>b</sup> The maximum 24-hour autoGC concentration (25.82 ppb<sub>v</sub>) slightly exceeded the odor-based comparison value.

The relatively high magnitude and/or frequency of the reported odor-based exceedances for styrene at the Lynchburg Ferry and Milby Park sites warrant further evaluation and discussion. Although the styrene concentrations reported at the Lynchburg Ferry and Milby Park sites would not be expected to cause direct acute health effects such as eye irritation, the perception of sufficiently strong and persistent unpleasant odors has the potential to cause odor-related health effects (e.g., nausea, headache).

#### *Lynchburg Ferry - Styrene*

At the Lynchburg Ferry site, there were 32 hourly styrene concentrations reported above the odor-based comparison value of 25 ppb<sub>v</sub>, with a maximum concentration of 494 ppb<sub>v</sub>. This represents an approximate 24% reduction in the number of odorous styrene concentrations when compared to 42 such concentrations reported in 2007 (maximum of 155 ppb<sub>v</sub>), and approximately a 38% reduction compared to 52 such concentrations reported in 2006 (maximum of 358 ppb<sub>v</sub>). When compared to the 92 odorous styrene concentrations reported for the Lynchburg Ferry site in 2005, which included a maximum concentration of 433 ppb<sub>v</sub>, the 32 occurrences in 2008 represent a reduction of approximately 65%. While there have been significant improvements in the frequency of styrene odor-based comparison value exceedances over this period, the maximum reported concentration for 2008 is somewhat higher than those reported for 2005-2007.

The direction of potential styrene sources near the Lynchburg Ferry site was evaluated by the TD through the use of hourly styrene autoGC data and wind directional data collected at the site. Based on both average styrene concentrations (Appendix 2a) and maximum concentrations (Appendix 2b) for 2008, styrene concentrations reported at the Lynchburg Ferry site were highest when winds were from the north/northeast, with lesser elevated styrene concentrations occurring when winds were from the west (and other directions). Maximum 2008 concentrations of approximately 195-338 ppb<sub>v</sub> occurred with winds from the north/northeast, with a maximum of approximately 102 ppb<sub>v</sub> occurring with winds from the west (Appendix 2b). Wind direction data were not available for the maximum hourly concentration of 494 ppb<sub>v</sub>. The source direction evaluation based on 2008 average styrene concentrations at this site (Appendix 2a) is similar to that contained in the TD evaluations of [2007 Region 12 data](#) and [2006 Region 12 data](#). Although the frequency of odorous styrene concentrations reported at the Lynchburg Ferry site

has decreased from 2005 to 2008, reductions in styrene emissions which contribute to odorous levels at the Lynchburg Ferry site continue to be recommended. Styrene is currently listed on the APWL for this area (Site# [APWL1204](#)) because of previously monitored odorous conditions, and the 2008 data support styrene remaining on the APWL for this area.

#### *Milby Park - Styrene*

At the Milby Park site, there were 33 odorous styrene concentrations reported in 2008. This number of exceedances above the odor-based comparison value is somewhat higher than the 28 such concentrations reported in 2007. The frequency of odorous styrene concentrations at the Milby Park site has been increasing over the past several years. The direction of potential styrene sources near the Milby Park site was evaluated by the TD through the use of hourly styrene autoGC data and wind directional data collected at the site. Similar to previous source direction analyses, based on average styrene concentrations (Appendix 3a) for 2008, styrene concentrations at the Milby Park site were highest when winds were from the east/southeast. Maximum 2008 concentrations of approximately 45-69 ppb<sub>v</sub> occurred with winds from the east/southeast (Appendix 3b), the general direction of a nearby industrial complex which includes Goodyear Tire & Rubber Company (Goodyear). In addition to source direction analyses, odorous levels of styrene (28 ppb<sub>v</sub>) were noted downwind of Goodyear in a TD evaluation of data collected during a December 13-19, 2007, TCEQ mobile monitoring trip. The City of Houston issued a Notice of Violation (NOV) related to odors to Goodyear during 2007, and another in 2008.

In previous reviews of annual Region 12 data, the TD has recommended reductions in styrene emissions which contribute to these odorous levels measured at the Milby Park site. Goodyear took steps during 2008 to address a potential source of the elevated styrene emissions detected at the Milby Park monitor. Specifically, Goodyear altered operational practices, amended their permit to include a 25% reduction in allowable styrene emissions, and signed a voluntary ERA with the TCEQ. As a result of these efforts during 2008, there has been a downward trend in the monitoring data for styrene at Milby Park. There was only 1 exceedance (25.5 ppb<sub>v</sub>) of the odor-based comparison value for styrene (25 ppb<sub>v</sub>) from July through December 2008 as compared to 19 exceedances over the same period in 2007. Styrene odor exceedance data for 2009 also show improvement compared to previous years. For example, from January through October 2009, there were only 2 exceedances of the odor-based comparison value compared to 19 exceedances during the same period in 2007, a reduction in exceedance frequency of approximately 90%. The TD will continue to monitor styrene concentrations at the Milby Park site to determine whether these improvements are maintained.

#### 24-Hour Concentrations

Six 24-hour Summa canister p-diethylbenzene concentrations in 2008 exceeded the recently adopted odor-based comparison value for this chemical (0.39 ppb<sub>v</sub>). The highest 24-hour concentrations of p-diethylbenzene measured at Manchester (0.96 ppb<sub>v</sub>) and Deer Park (0.57 ppb<sub>v</sub>) exceeded the odor-based value, as did the four highest 24-hour concentrations (2.21, 0.81, 0.63, and 0.49 ppb<sub>v</sub>) at the Pasadena North site. Additionally, the maximum 24-hour autoGC styrene concentration (25.8 ppb<sub>v</sub>) at the Milby Park site exceeded the odor-based comparison value (25 ppb<sub>v</sub>), as did the maximum 24-hour autoGC level (42.5 ppb<sub>v</sub>) at the Lynchburg Ferry site (other 24-hour styrene levels not available in summary data).

### *Deer Park- Acrolein*

Generally, the occurrence of acrolein in ambient air is widespread and primarily due to combustion. There are many sources of acrolein, including cars/trucks and other means of transportation (e.g., buses, railways, airports, construction equipment), fires, industry (e.g., industrial boilers and other emissions), and emissions from other combustion processes (e.g., smoke from wood/vegetation burning, lawn maintenance equipment). It can also form when other chemicals breakdown in the air (e.g., automobile exhaust VOCs). Prior to 2008, acrolein was a target analyte in carbonyl samples only. However, beginning in 2008, acrolein was also included as a target analyte in the every sixth-day 24-hour canister samples at the Deer Park site. Based on the carbonyl analyses at this site, the highest 24-hour concentration for 2008 was 0.16 ppb<sub>v</sub>, which is below the short-term, health-based comparison value (1 ppb<sub>v</sub>). However, five of the reported acrolein concentrations for 2008 based on co-located 24-hour canister samples at the Deer Park site (1.7, 1.6, 1.4, 1.2, 1.1 ppb<sub>v</sub>) are above the short-term, health-based comparison value and require further evaluation.

Acrolein results from the canister and carbonyl analyses are significantly different because of difficulties in the sample collection and analysis of acrolein, a highly reactive chemical. To the TD's understanding, both TCEQ and USEPA are evaluating which of the available methods may be most appropriate for accurate and precise measurements of acrolein in the future. Regardless of which analytical method utilized at Deer Park in 2008 may be more accurate for determination of the maximum 24-hour concentration, the TD would not expect short-term, adverse health effects to occur as a result of exposure to these concentrations based on data from available scientifically-conducted human and animal health effects studies (see below).

Since acrolein is reactive and highly water soluble, at sufficiently high exposure concentrations of sufficient duration, the most sensitive short-term effects are mild sensory irritation and point-of-entry respiratory effects. Well-conducted human studies demonstrate mild sensory (e.g., eye) and respiratory irritation at concentrations of approximately 300 ppb<sub>v</sub> and greater due to short-term exposure. Some short-term animal studies have also demonstrated respiratory effects at similar (approximately 300 ppb<sub>v</sub> and greater) concentrations. The maximum 24-hour acrolein concentrations reported for the Deer Park site in 2008 are well below these effects levels. Based on available human (as well as animal) toxicological data, the TD would not expect short-term, adverse health effects to occur as a result of exposure to these 24-hour concentrations. Additionally, these reported concentrations are below the short-term, health-based ambient air comparison value (4.8 ppb<sub>v</sub>) contained in the TD's Draft Development Support Document for Acrolein, as well as being less than the acute (< 14 day) inhalation minimal risk level (MRL of 3 ppb<sub>v</sub>) from the Agency for Toxic Substances and Disease Registry (ATSDR). Refer to the *Annual Average Concentrations* section below for a discussion of 2008 average acrolein concentrations at the Deer Park site.

### Annual Average Concentrations

Based on the approximately 5,300 24-hour metals measurements in Region 12 in 2008, all reported annual average concentrations of metals were below their respective long-term, health-based comparison levels. All annual average concentrations of carbonyls were also below their respective long-term, health-based comparison levels for ambient air based on the approximately 2,750 24-hour carbonyl measurements in 2008, as were the average concentrations for PAHs/SVOCs based on approximately 4,050 24-hour measurements. Except for benzene at the Marathon-sponsored 11<sup>th</sup> St. S. Texas City site and acrolein at the Deer Park site, based on the approximately 80,000 24-hour canister VOC measurements in Region 12, all average VOC concentrations for 2008 were below their respective long-

term, health-based comparison levels. Therefore, no long-term, adverse health effects would be expected due to exposure to those concentrations below their respective long-term, health-based comparison levels. Further examination was conducted for those chemicals with annual average concentrations above their respective long-term comparison levels to determine the potential for long-term, adverse health effects (see below). In addition, areas exhibiting reductions or increases of interest in reported annual benzene and 1,3-butadiene concentrations are discussed.

*Lynchburg Ferry - Benzene*

The reported 2008 annual average benzene concentration based on hourly samples collected at the autoGC at the Lynchburg Ferry site was 1.1 ppb<sub>v</sub>. The 75% data completeness objective was not met for the co-located, every sixth-day 24-hour canister sample site, which only collected 37 valid samples (average benzene concentration of 0.93 ppb<sub>v</sub>). Regardless, the annual average based on hourly autoGC samples (1.1 ppb<sub>v</sub>) more accurately represents the long-term average in 2008, and is below the long-term, health-based comparison value (1.4 ppb<sub>v</sub>) for the first time since monitoring began at the Lynchburg Ferry site in 2003 (see Figure 1). This represents a significant improvement in air quality and is likely the result of significant efforts in the area by TCEQ (e.g., focused agency resources, special investigations utilizing the latest technology, enhanced compliance and enforcement, source directionality evaluations), industry (e.g., ERAs), and others (e.g., Monument Area Air Quality Focus Group). For example, reductions in the annual benzene concentrations over the past few years may partially reflect the results of ERAs entered into in 2006 by TCEQ with several facilities (Oiltanking Houston, Vopak Terminals, Intercontinental Terminals) in the Lynchburg Ferry area to reduce VOC emissions, including benzene. The 2008 annual benzene average of 1.1 ppb<sub>v</sub> (autoGC) represents an approximate reduction of 27% when compared to the 2007 annual average, an approximate 54% reduction compared to the 2006 annual average, and an approximate 65% reduction compared to the 2005 annual average. This downward trend in annual benzene concentrations at the Lynchburg Ferry site is clearly evident (see Figure 1).

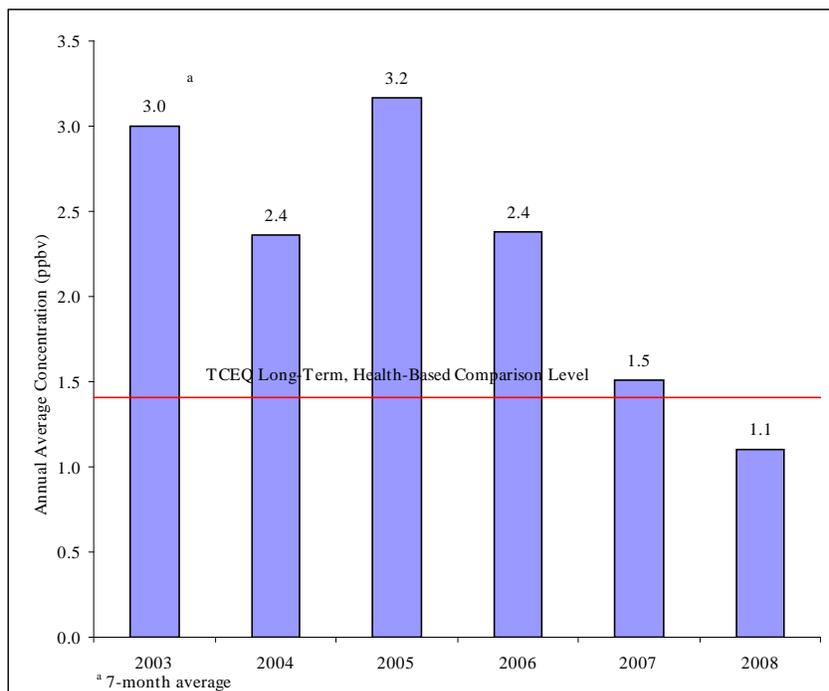


Figure 1. Annual Average Benzene Concentrations at the Lynchburg Ferry Site

Preliminary data for 2009 suggest that benzene concentrations in the Lynchburg Ferry area are similar to or slightly lower than those in 2008. The average of monthly autoGC means for benzene for January through October 2009 is 0.86 ppb<sub>v</sub>, compared to 1.1 ppb<sub>v</sub> over the same period in 2008. These lower averages may be attributable to TCEQ activities and other initiatives in the Lynchburg Ferry area.

TCEQ Region 12 staff report that activities in 2008 in the Lynchburg Ferry area included, but were not limited to the following:

- In response to benzene trigger level exceedances at the monitoring site (i.e., 5-minute concentrations  $\geq 50$  ppb<sub>v</sub>), Region 12 staff reviewed air concentration and meteorological data to identify potential sources, which often results in focused facility investigations, and the agency (Pollution Prevention) coordinated with the US Coast Guard to identify potential sources in the Houston Ship Channel (e.g., barges carrying benzene).
- More specifically, in response to benzene trigger level exceedances, Region 12 air investigators conducted enhanced investigations at Channel Shipyard and Southwest Shipyard, including use of the GasFindIR camera.
  - Region 12 conducted 2 special investigations at Channel Shipyard related to benzene triggers at the monitor, along with several area reconnaissance investigations.
  - Region 12 conducted 2 special investigations at Southwest Shipyard related to benzene triggers at the monitor, 3 reconnaissance investigations, and 1 Title V compliance investigation.
    - For Southwest Shipyard, a Findings Order (#2007-0794-AIR-E) became effective on 6/5/08.
  - Permit modifications have been implemented to reduce emissions at both Southwest Shipyard and Channel Shipyard.
- Region 12 conducted a stack test review, compliance investigation, and permit review at Kirby Inland Marine. An NOV was issued.
- A combination of reconnaissance investigations, compliance investigations, stack sampling reviews, and emission event investigations have been conducted at tank-for-hire facilities in the area (Halterman, Houston Fuel Oil Terminal). NOVs were issued to these 2 facilities.
- All reportable emissions events were investigated, resulting in the issuance of 20 Notices of Enforcement (NOEs) and 7 NOVs, including 2 NOVs related to benzene releases issued to Vopak Terminal-Deer Park located southwest of the Lynchburg Ferry site.
- Additionally, reconnaissance investigations with the GasFindIR camera are routinely performed every six weeks in the south Houston Ship Channel area along Battleground Road/Independence Highway.

In a collaborative attempt to reduce benzene emissions, several industrial facilities in the Lynchburg Ferry area previously formed the Monument Area Air Quality Focus Group (MAAQFG). The MAAQFG is comprised of: Rohm and Haas Texas Inc., Shell Chemicals Inc., Texas Molecular, Intercontinental Terminals, Channel Shipyard, Kirby Inland Marine, and Vopak Terminals-Deer Park. In December 2007, an automatic notification system was implemented that sends 5-minute high trigger values to the MAAQFG and TCEQ. An automatic alert is sent to TCEQ and MAAQFG members when hourly benzene concentrations reported at the Lynchburg Ferry monitor exceed an hourly benzene trigger concentration (referred to in the bullets above). These triggers signal MAAQFG members and TCEQ to initiate investigations. This enhanced project has created timely awareness of benzene emissions. TCEQ has continued to work in a collaborative effort with both the MAAQFG and the US Coast Guard to identify and mitigate potential sources of benzene emissions, both from barges in transit and stationary sources.

Efforts in this area have been successful, as evidenced by both the number of 5-minute trigger notifications and annual benzene concentrations decreasing over time.

As a result of successful efforts to reduce long-term benzene levels, benzene was proposed to be removed from the Lynchburg Ferry Air Pollutant Watch List area (Site# [APWL1204](#)) in September 2009. The annual benzene concentration decreased 65% from 2005 to 2008. The 2008 benzene concentration at the site is below the long-term, health-based comparison value (1.4 ppb<sub>v</sub>), and preliminary data for most of 2009 suggest that benzene concentrations in the Lynchburg Ferry area are similar to or slightly lower than those in 2008. The decreases in annual benzene levels in this APWL area are likely due to a continued and focused collaborative effort to reduce benzene emissions. Due to the significant and continued improvement in long-term benzene concentrations measured at the Lynchburg Ferry site, benzene is being removed from [APWL1204](#).

#### *Galena Park - Benzene*

The reported 2008 average benzene concentration based on every sixth-day 24-hour canister samples at the Galena Park site was 1.3 ppb<sub>v</sub>, and is below the long-term, health-based comparison value (1.4 ppb<sub>v</sub>) for the first time in several years (see Figure 2). This represents a significant improvement in air quality and is likely the result of significant efforts in the area by TCEQ (e.g., focused agency resources, special investigations utilizing the latest technology, enhanced compliance and enforcement), along with the cooperation of industry (e.g., ERAs). For example, this reduction in the annual benzene concentration may partially reflect the results of ERAs entered into in 2006 by TCEQ with several facilities identified during an earlier Find-and-Fix investigation (Kinder Morgan Terminals, Vopak Terminals, TEPPCO Pipeline) to reduce VOCs, including benzene. The 2008 average concentration is approximately 25% lower than the 2007 annual average of 1.7 ppb<sub>v</sub>, approximately 19% lower than the 2006 annual average of 1.6 ppb<sub>v</sub>, and approximately 35% lower than the 2005 annual average of 2.0 ppb<sub>v</sub>.

TCEQ efforts in the area have been significant, and the 2008 annual average appears to suggest a potential downward trend in annual benzene averages at the Galena Park site. In addition, available preliminary 24-hour canister data for January through October 2009 suggest continued improvement in benzene concentrations. The January through October 2009 average for benzene of 0.8 ppb<sub>v</sub> at the Galena Park site is approximately 33% lower than the average over the same period in 2008 (1.2 ppb<sub>v</sub>). However, whether the 2009 average for benzene at the Galena Park site will be lower than the 2008 average cannot be predicted. Although the 2008 benzene concentration at the Galena Park site was below the long-term, health-based comparison value, this area will remain on the APWL (Site# [APWL1206](#)) for benzene. The TD recommends a continued effort to control and/or reduce benzene emissions in the area such that the long-term, health-based comparison value will continue to be met at the Galena Park site, and will continue to monitor benzene concentrations at this site to determine whether current improvements are maintained.

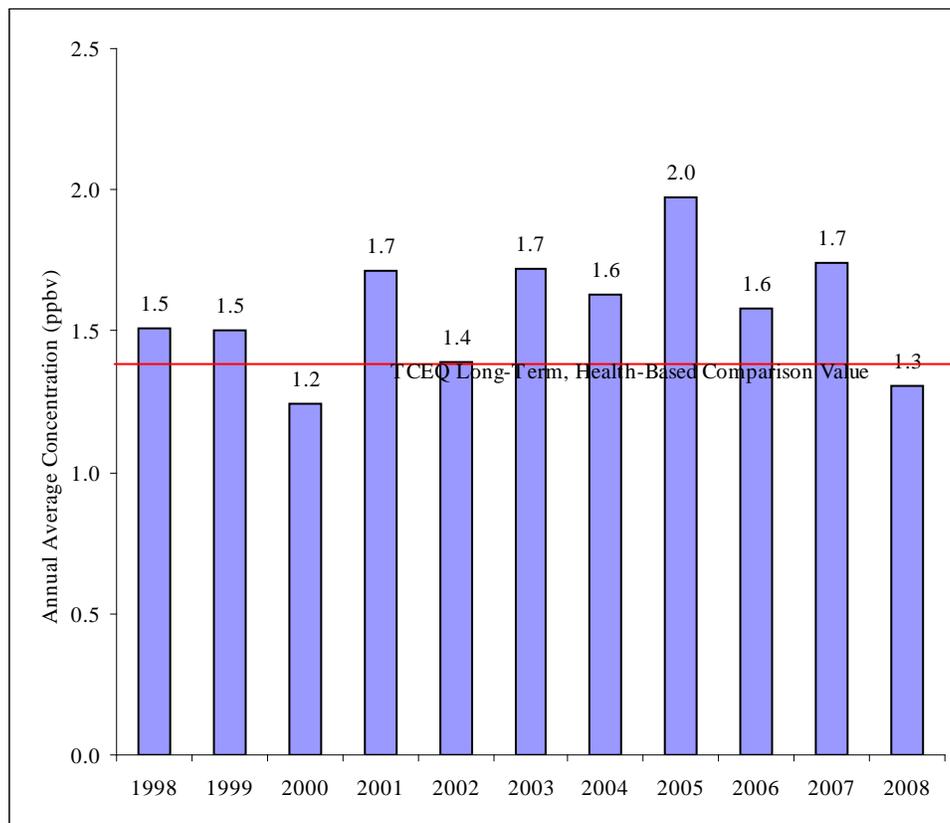


Figure 2. Annual Average Benzene Concentrations at the Galena Park Site

TCEQ activities in 2008 in the Galena Park area included, but were not limited to:

- Region 12 continued to conduct periodic focused investigations and reconnaissance investigations in the Galena Park Area.
- Region 12 conducted multiple GasFindIR investigations and stack test reviews at Kinder Morgan-Galena Park Terminals.
- Region 12 conducted GasFindIR investigations at Vopak-Galena Park Terminal and Texmark.
- All reportable emissions events were investigated, resulting in the issuance of 8 NOEs and 2 NOVs.

Benzene sources located on the south side of the Houston Ship Channel also have the potential to impact the annual averages measured at the Galena Park site, especially those located in relative close proximity to the south/southeast of the Galena Park monitor (given predominant southeast winds). US Oil Recovery is one of the facilities on the south side of the Houston Ship Channel that was identified in a June 30, 2008, health effects review of mobile monitoring data (December 13-19, 2007) as potentially impacting benzene levels at the Galena Park site (Pasadena Refining and Houston Refining were also identified). Region 12 is conducting ongoing multimedia investigations at US Oil Recovery and has continued to find multiple issues. An NOE was issued in April 2008 for the failure to authorize air emissions and prevent the emissions of air contaminants. Another investigation conducted in 2008 resulted in an NOE issued to US Oil Recovery in February 2009 for several violations, including but not limited to: failure to obtain authorization to operate all processes (i.e., used oil recovery process, distillate process, wastewater

treatment process), which constitutes a violation of 30 TAC 116.110(a); failure to maintain complete and up-to-date records sufficient to demonstrate continuous compliance with the control requirement and/or exemption criteria for the boiler, storage tank, water separator, and wastewater streams, which constitutes various violations; failure to provide sufficient information to determine compliance or applicability for the Permit By Rule cited in a previous NOV; and failure to have the lid closed on the parts washer, which constitutes a violation of 30 TAC 115.412(1)(A) and (C). As a result of an emission event investigation, an NOE related to benzene releases was also issued in 2008 to Houston Refining. Similar to US Oil Recovery, Houston Refining is located on the south side of the Houston Ship Channel and has the potential to impact benzene levels at the Galena Park site.

TCEQ will continue to use information from various investigations, mobile and fixed-site monitoring (e.g., Pasadena North site located on the south side of the Houston Ship Channel), and the latest technology (GasFindIR) to aid in the identification of sources and reduction of benzene emissions impacting the Galena Park site area.

#### *Milby Park-1,3-Butadiene*

The Milby Park site area continues to be of interest to TCEQ and others. Annual average 1,3-butadiene levels continue to decline (see Figure 3). The reported 2008 average concentration of 0.9 ppb<sub>v</sub> at the Milby Park site is approximately: 13% lower than the reported 2007 average, 31% lower than the 2006 average, 41% less than the 2005 average, and 78% lower than the 2004 average concentration. The 2008 average 1,3-butadiene concentration is the lowest annual average measured at this site since monitoring began, and is well below the long-term, health-based comparison value (9.1 ppb<sub>v</sub>). Additionally, preliminary data for January through September 2009 indicate that 1,3-butadiene concentrations at Milby Park may be continuing to decline. The average of monthly autoGC means for January through September 2009 is 0.5 ppb<sub>v</sub>, approximately 45% lower than the average of 0.9 ppb<sub>v</sub> over the same period in 2008. The reductions in annual average concentrations of 1,3-butadiene can be attributed to corrective activities associated with the TCEQ voluntary ERAs entered into by Texas Petrochemical and Goodyear in 2004.

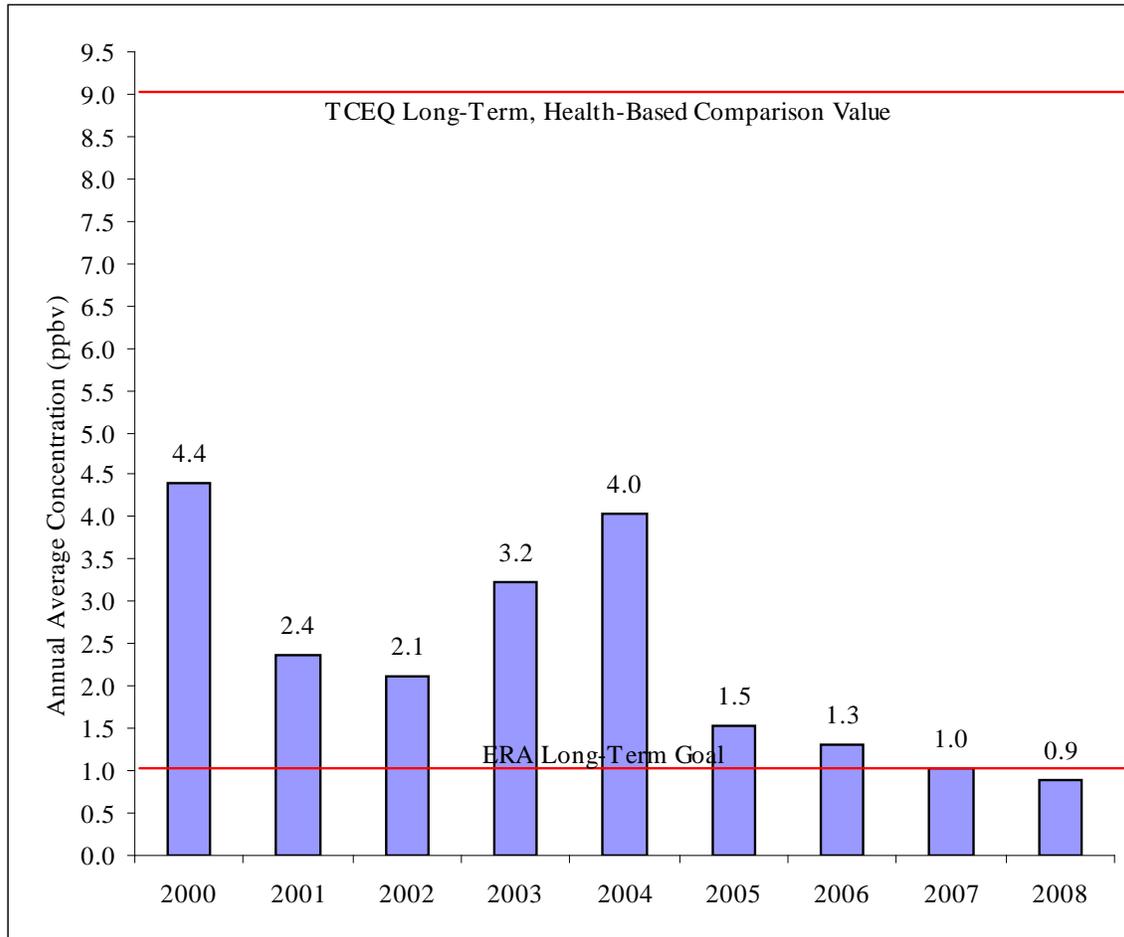


Figure 3. Annual Average 1,3-Butadiene Concentrations at the Milby Park Site

Recent annual averages for 1,3-butadiene indicate a continued downward trend at the Milby Park site and the 2008 annual average concentration is below the ERA long-term goal of 1 ppbv. This area (Site# [APWL1207](#)) was on the APWL for 10 years due to 1,3-butadiene levels which were historically considered to be elevated. However, in 2009, 1,3-butadiene was able to be removed from [APWL1207](#) due to significant improvements in long-term concentrations measured at the Milby Park site. Moreover, the results of a 2008 TD toxicological assessment of the most up-to-date science and data for 1,3-butadiene (see the [1,3-Butadiene Development Support Document](#)), which was peer-reviewed by a panel of expert scientists, indicate that these reported annual averages are below levels of health concern.

Despite the significant reduction in the annual average 1,3-butadiene concentration at the Milby Park site, TCEQ continues to conduct activities to help reduce emissions in the area. Region 12 activities in 2008 in the Milby Park area included, but were not limited to:

- Region 12 conducted an on-site comprehensive compliance investigation of facilities covered by one of Texas Petrochemicals’ two Title V permits, resulting in the issuance of an NOV.
- All reportable emissions events were investigated, resulting in the issuance of 7 NOEs and 4 NOVs to Texas Petrochemicals and 4 NOEs to Goodyear.

*Texas City Marathon-Sponsored 11<sup>th</sup> St. S. Site-Benzene*

Under a TCEQ agreed order (Agreed Order 2001-0575-AIR-E), Marathon Petroleum Company (Marathon) initially collected benzene data at this off-site monitor just north of Marathon from October 2004 to October 2005. Then, under a benzene emission investigation plan with TCEQ and EPA, Marathon collected data at the site from January 30, 2006, to January 31, 2007. Marathon again began collecting benzene data at the site on April 1, 2007, per an agreement with EPA and the US Department of Justice (DOJ). The site was moved 1 block north to the corner of 11<sup>th</sup> St. S. and 6th Ave. S. on November 5, 2007.

The 2008 average benzene concentration measured at the Marathon-sponsored site (1.8 ppb<sub>v</sub>) exceeds TCEQ's long-term, health-based screening value (1.4 ppb<sub>v</sub>), although it is somewhat lower than the 10- and 11-month averages for 2005-2007 (see Figure 4). Preliminary data for 2009 indicate that benzene concentrations at this site may be somewhat decreasing. For example, the January through June 2009 average is 1.8 ppb<sub>v</sub>, compared to averages of 2.1 ppb<sub>v</sub> and 2.5 ppb<sub>v</sub> over the same periods in 2008 and 2005, respectively, the only years for which data for this comparison are available.

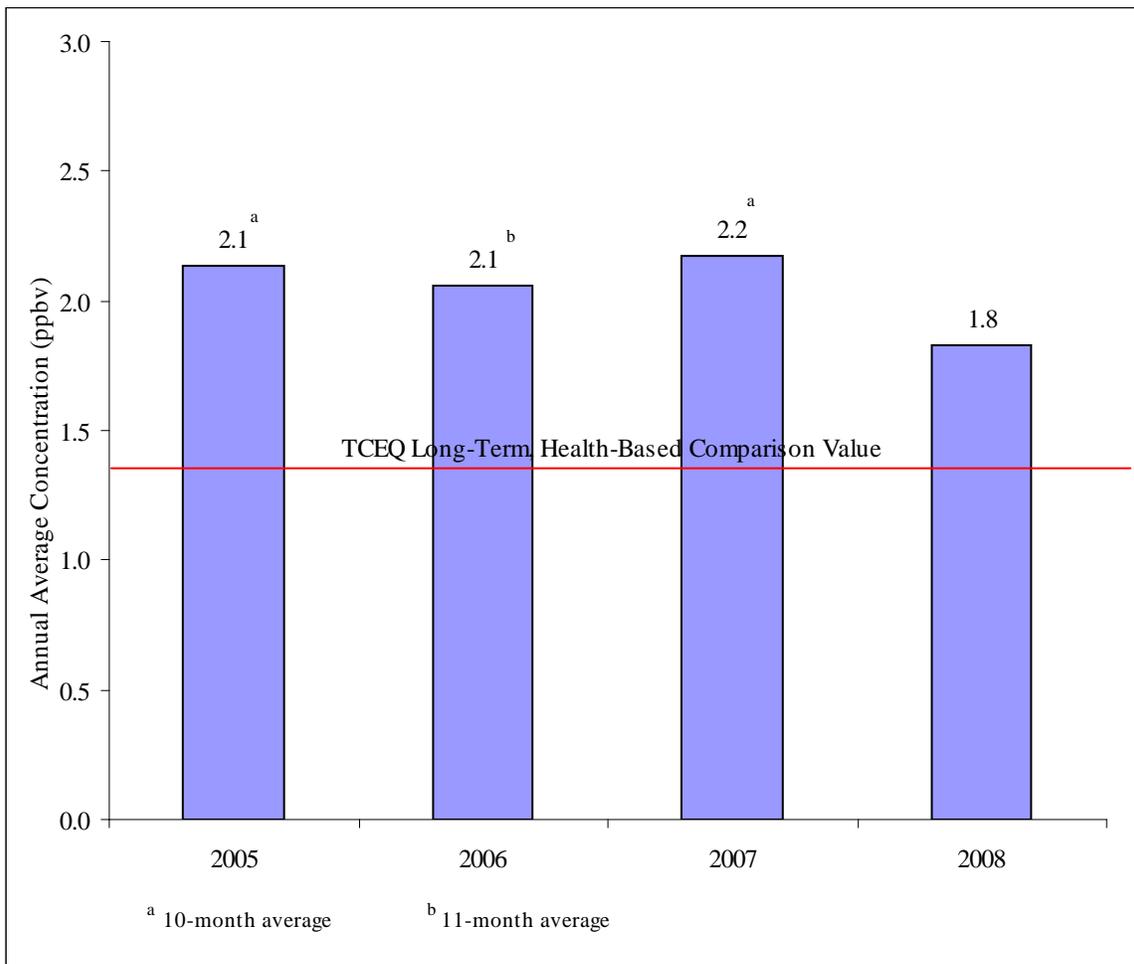


Figure 4. Annual Average Benzene Concentrations at the Marathon-Sponsored 11<sup>th</sup> St. S. Site

The area of Texas City located south of State Highway 1765, which contains this Marathon-sponsored site, is currently on the APWL (Site# [APWL1202](#)) for elevated long-term concentrations of benzene. Therefore, the identification of potential benzene sources which may be affecting long-term benzene levels at this site is important.

As high hourly benzene levels can significantly impact the annual average at a site, the direction of potential benzene sources near the Marathon-sponsored site was evaluated using wind directional data associated with hourly benzene concentrations greater than 10 ppb<sub>v</sub> in 2008. Based on this analysis (see Figure 5), elevated concentrations above 10 ppb<sub>v</sub> were most frequently associated with winds from the southeast (106-173 degrees, with most between 133-173 degrees) and southwest (197-223 degrees). These directional results are similar to those discussed in the evaluation of [2007 Region 12 data](#), except that there were approximately 49% fewer benzene concentrations above 10 ppb<sub>v</sub> in 2008 at the Marathon-sponsored 11th St. S. site. The direction of potential benzene sources near this site was also evaluated by the TD through the use of all available 2008 air concentration data (not just concentrations greater than 10 ppb<sub>v</sub>) and wind directional data collected at the site (see Appendix 4). Similar to Figure 5, this source direction analysis shows that higher benzene levels occurred in 2008 when winds were from the southeast and southwest, where the nearby Marathon facility is located.

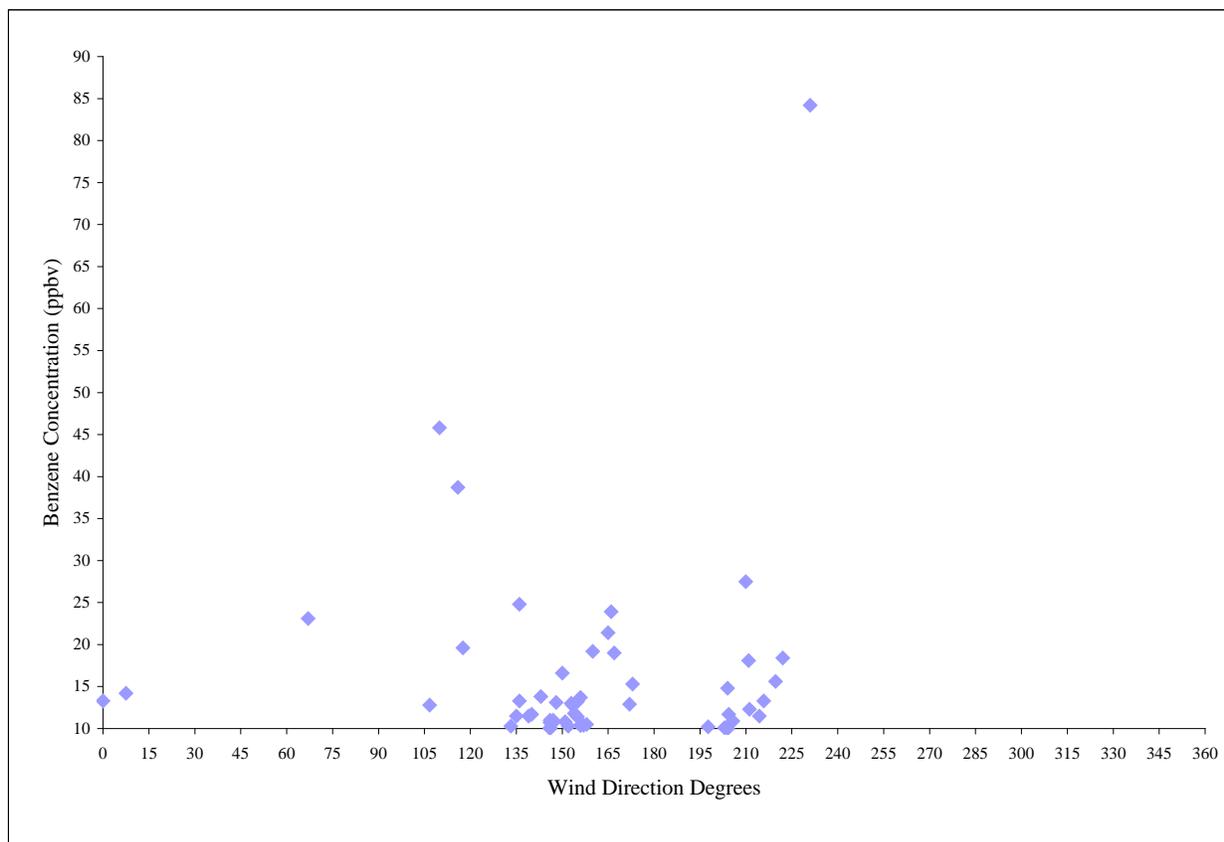


Figure 5. Hourly Benzene Concentrations > 10 ppb<sub>v</sub> vs. Wind Direction for 2008 at the Marathon-Sponsored 11<sup>th</sup> St. S. Site

In addition to the off-site 11<sup>th</sup> St. S. monitoring site, Marathon also provides on-site (generally upwind) air monitoring data. Although the public is not exposed to benzene on Marathon property, on-site hourly

data were also used to evaluate the direction of potential benzene sources both on- and off-site. Based on this analysis (see Figure 6), concentrations above 10 ppb<sub>v</sub> were most frequently associated with winds from the northwest (approximately 317-349 degrees), southwest (approximately 207-266 degrees), and east/northeast (approximately 54-103 degrees). Additionally, a few benzene concentrations above 10 ppb<sub>v</sub> were associated with north/northeast winds. These directional results are fairly similar to those discussed in the evaluation of [2007 Region 12 data](#), except that there were approximately 48% fewer benzene concentrations above 10 ppb<sub>v</sub> in 2008 at the Marathon on-site monitor. The direction of potential benzene sources near the on-site monitor was also evaluated through the use of all available 2008 air concentration data (not just concentrations greater than 10 ppb<sub>v</sub>) and wind directional data collected at this site (see Appendix 4). Similar to Figure 6, this source direction analysis shows that higher benzene levels at the on-site monitor occurred in 2008 when winds were from the east/northeast, southwest, and north/northwest, where various areas of the nearby Marathon facility are located.

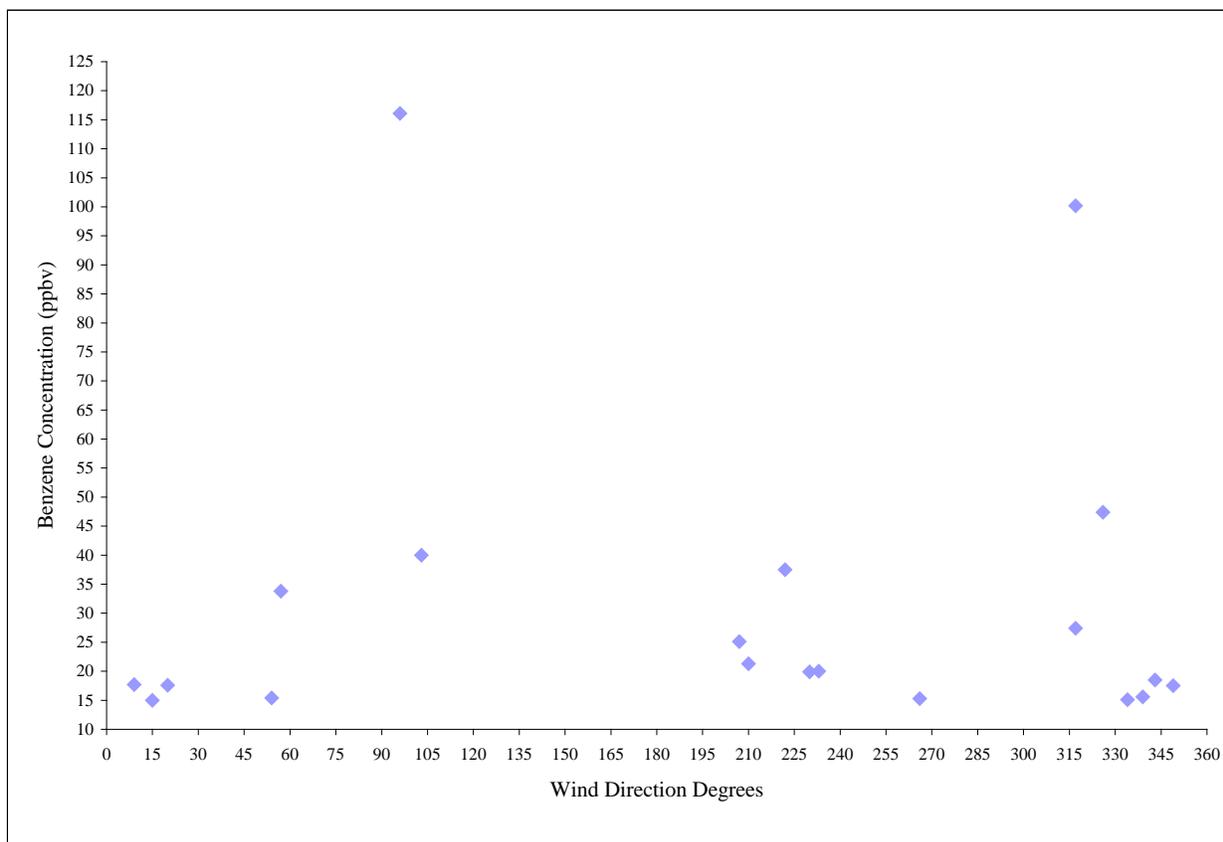


Figure 6. Hourly Benzene Concentrations > 10 ppb<sub>v</sub> vs. Wind Direction for 2008 at the Marathon-Sponsored On-Site Monitor

TCEQ activities in 2008 related to benzene in Texas City included, but were not limited to:

- Region 12 continued to conduct focused investigations and reconnaissance investigations in the Texas City Area to address on-going issues discovered through use of GasFindIR or visual inspections. On a periodic basis, regional investigators conduct surveillance of facilities in the Texas City area using the GasFindIR camera.

- All reportable emissions events were investigated, resulting in the issuance of 27 NOEs and 10 NOVs.
- Regarding benzene specifically, an NOV related to benzene releases was issued in 2008 to Sterling Chemicals, which is located east of the Marathon-Sponsored 11<sup>th</sup> St. S. site, and an NOV was also issued to Valero Refining, which is located south/southeast of the site.
- In addition to 1 NOV issued to Marathon for benzene releases following an emission event investigation, a focused benzene investigation was conducted at Marathon in May 2008. As a result, an NOE was issued on 9/8/08 that included several violations, including but not limited to:
  - violations associated with tank requirements (e.g., failure to repair external floating roof tank within 60 days of discovery of pinhole leaks in the roof deck, failure to maintain records of monitoring for carbon canister breakthrough during tank degassing (including degassing of benzene, gasoline, and crude oil tanks), failure to repair the tank floating roof primary seal within 45 days of determining the seal needed replacement, failure to maintain vacuum breakers in closed position);
  - open ended lines;
  - issues related to carbon canisters used as benzene control devices for wastewater treatment facilities.
- In addition to 5 NOEs and 3 NOVs issued to BP for benzene releases following emission event investigations, a focused benzene investigation was conducted by Region 12 in May-June 2008 at the BP Refinery (just west of Marathon). The investigation resulted in an NOE issued on 8/29/08 that included several violations, including but not limited to:
  - failure to meet the reporting requirements under 40 CFR 61 subpart FF (National Emission Standards for Benzene Waste Operations) by not reporting that API 1 and API 2 were on delay of repair;
  - failure to limit benzene content of the uncontrolled sources subject to Benzene Waste Organic NESHAP (BWON) requirements of 40 CFR 61 subpart FF to 2 Mg/yr in 2006;
  - failure to operate a temporary flare installed for the control of emissions from maintenance activities in 2006 according to the authorized limitations for benzene in Standard Permit 77811;
  - failure to comply with control device requirements for API 2;
  - failure to monitor more than 60 pumps at AU2 and/or ARU in February, May, and September 2007.
- An Office Permit Compliance Certification Review was conducted at BP in May 2008 and resulted in the issuance of an NOV on 9/2/08. Thirty nine violations were cited, including but not limited to:
  - failure to perform two quarterly visual inspections on exposed sewer lines that manage benzene-contaminated waste from April 1, 2007, through September 30, 2007;
  - failure to perform 11 quarterly visual inspections of manways and hatches on junction boxes in benzene-contaminated wastewater service on process units FCCU1, DDU, Alkylation 3, FCCU3, and UU3;
  - failure to perform five quarterly visual inspections of tanks in benzene contaminated wastewater service;
  - failure to operate the thermal oxidizer (EPN 293) with a temperature of 1400 degrees Fahrenheit or more on seven occasions occurring on six days from December 12, 2006, through March 7, 2007;
  - failure to perform quarterly visual inspections for the integrity of seals and gaskets on refinery oil/water separators;
  - failure to operate the W01 oil/water separator and PS3B south oil/water separator with closed hatches and vapor tight seals;

- failure to perform monthly bypass-valve inspections from October 2006 through March 30, 2007, for 15 carbon canisters on various individual drain systems across the refinery.

Additionally, at the request of the TD, the TCEQ Mobile Monitoring Team (MMT) conducted a May 31-June 7, 2008, ambient air monitoring trip in this APWL area in an attempt to identify benzene sources, including those which may be impacting benzene levels reported for the Marathon-sponsored site. Several measured short-term benzene concentrations (e.g., 270 ppb<sub>v</sub> in a 30-minute canister sample, 240 ppb<sub>v</sub> in an instantaneous canister) were detected above the short-term, health-based comparison value for ambient air (180 ppb<sub>v</sub>) downwind of a facility (Oiltanking Texas City LP) located south/southwest of Marathon. Short-term health effects would not be expected to occur as a result of exposure to these benzene concentrations as they are significantly below levels associated with short-term, adverse health effects such as central nervous system depression and irritation. However, these elevated short-term levels may contribute to long-term benzene concentrations at the Marathon-Sponsored 11<sup>th</sup> St. S. Site. Reductions in benzene emissions are recommended for this area, especially those impacting the Marathon-sponsored 11<sup>th</sup> St. S. site. This area (Site# [APWL1202](#)) will remain on the APWL until the TD has determined the benzene concentrations in the area are no longer of potential health concern.

#### *Texas City BP-Sponsored Site-Benzene*

Annual average benzene concentrations at the BP-sponsored site in Texas City have been declining since 2005 (see Figure 7). The reported 2008 average benzene concentration at the site (0.8 ppb<sub>v</sub>) is approximately 14% lower than the 2007 average, 53% lower than the 2006 average, and 70% lower than the 2005 average. While recent annual average benzene concentrations at the BP-sponsored site have shown a significant decrease and the 2007 and 2008 annual averages are below the long-term, health-based comparison value (1.4 ppb<sub>v</sub>), the benzene average concentration for January through September 2009 (1.7 ppb<sub>v</sub>) is higher than that over the same period for 2008 (0.8 ppb<sub>v</sub>) and 2007 (1.0 ppb<sub>v</sub>), although lower than that over the same period in 2006 (1.9 ppb<sub>v</sub>). Benzene concentrations may have been higher in 2009 (particularly January through May) due to a leaking, floating roof benzene storage tank discovered in May 2009. The tank was immediately emptied and taken out of service. BP reports that the benzene concentrations measured at the monitor are now back to normal. However, the higher concentrations measured in 2009 will cause the annual average to increase to a concentration greater than that in 2007, although how it will compare to previous years cannot be predicted.

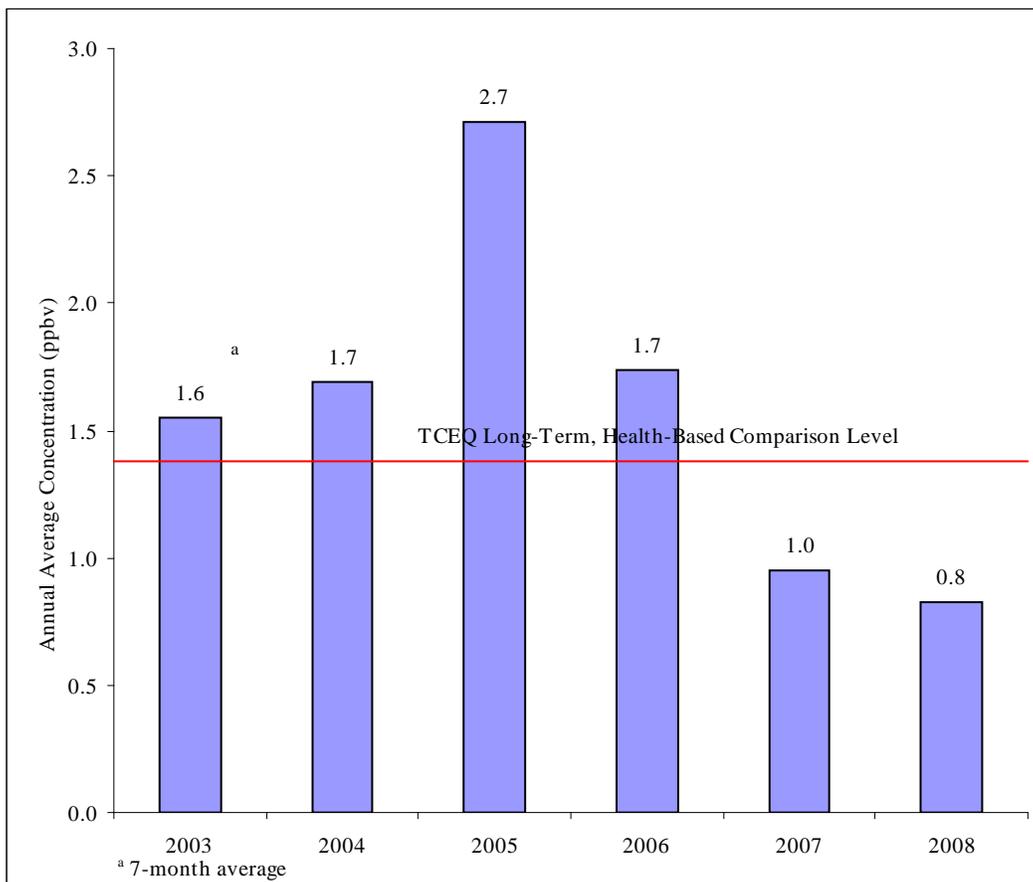


Figure 7. Annual Average Benzene Concentrations at the BP-Sponsored Site

Despite the 2005-2008 downward trend of benzene concentrations at the BP-sponsored site, the 2008 average at the nearby Marathon-sponsored site to the east is above the TCEQ long-term, health-based comparison level and over twice that reported in 2008 for the BP-sponsored site. As the area of Texas City which contains the BP-sponsored site is currently on the APWL (Site# [APWL1202](#)) for the elevated long-term concentrations of benzene reported in previous years, and high hourly benzene levels can significantly impact long-term averages, the direction of potential benzene sources near the BP-sponsored site was evaluated using wind directional data associated with hourly benzene concentrations greater than 10 ppb<sub>v</sub> in 2008 (see Figure 8). Based on this analysis, elevated concentrations above 10 ppb<sub>v</sub> were associated with winds from the south/southeast (primarily 167-195 degrees, but also 128-152 degrees), the direction of the BP facility.

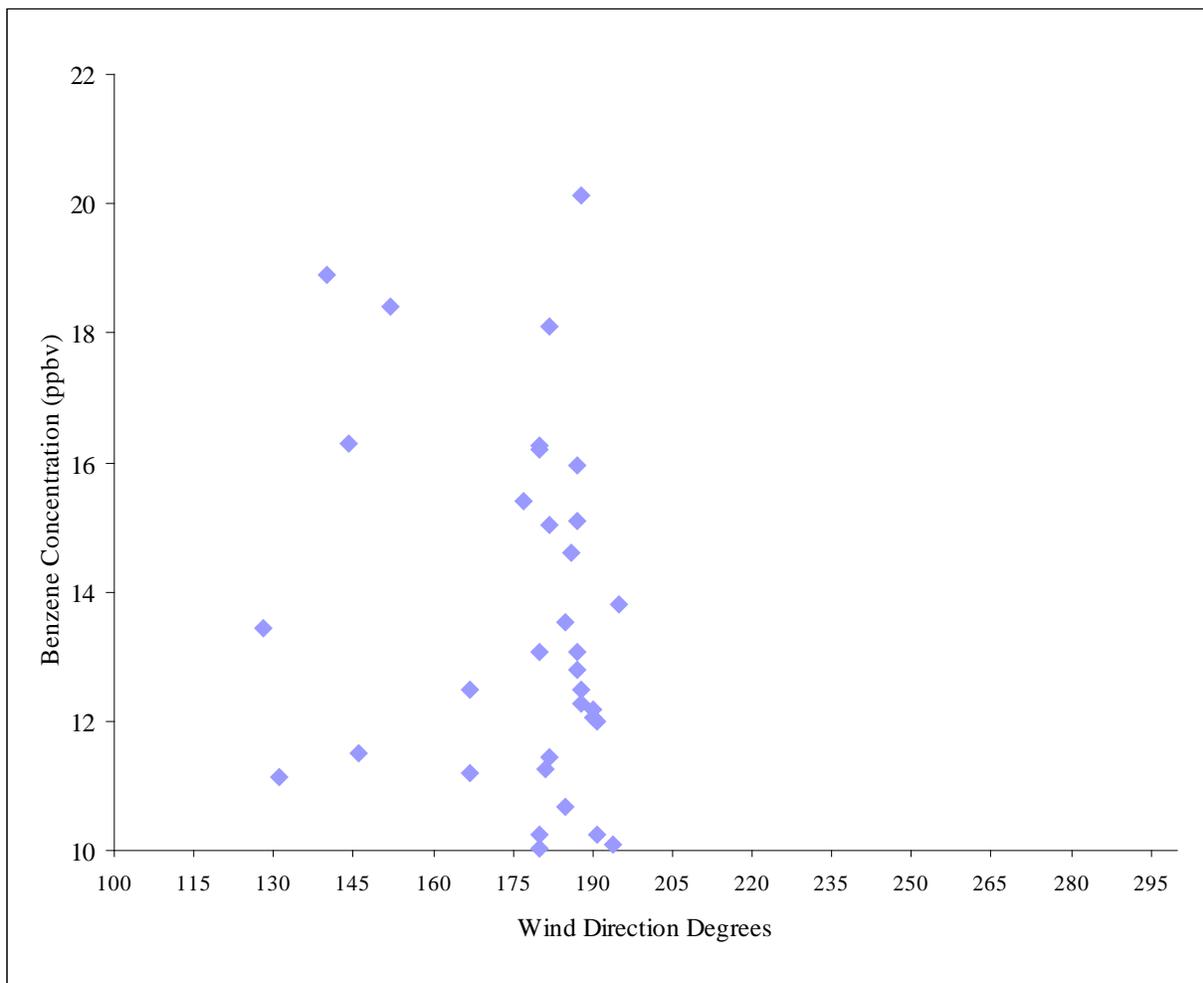


Figure 8. Hourly Benzene Concentrations > 10 ppbv vs. Wind Direction for 2008 at the BP-Sponsored Site

As previously mentioned, the TCEQ MMT conducted a May 31-June 7, 2008, ambient air monitoring trip in this APWL area and reported elevated short-term benzene levels (e.g., 270 ppbv in a 30-minute canister sample, 240 ppbv in an instantaneous canister) downwind of a facility (Oiltanking Texas City LP) located south/southeast of BP. While short-term, adverse health effects would not be expected to occur as a result of exposure to these levels, these elevated short-term levels may contribute to long-term benzene concentrations at nearby monitoring sites (e.g., Marathon-Sponsored 11<sup>th</sup> St. S. Site). Please see the *Texas City Marathon-Sponsored 11<sup>th</sup> St. S. Site-Benzene* section above for information regarding TCEQ activities in 2008 related to benzene in Texas City. This area (Site# [APWL1202](#)) will remain on the APWL until the TD has determined the benzene concentrations in the area are no longer of potential health concern.

#### *Deer Park- Acrolein*

Generally, the occurrence of acrolein in ambient air is widespread and primarily due to combustion. There are many sources of acrolein, including cars/trucks and other means of transportation (e.g., buses, railways, airports, construction equipment), fires, industry (e.g., industrial boilers and other emissions),

and emissions from other combustion processes (e.g., smoke from wood/vegetation burning, lawn maintenance equipment). It can also form when other chemicals breakdown in the air (e.g., automobile exhaust VOCs). While acrolein was a target analyte only in carbonyl samples prior to 2008, in 2008 it was added as a target analyte in the every sixth-day 24-hour canister samples at the Deer Park site. Based on the carbonyl analyses at this site, the 2008 average concentration was 0.036 ppb<sub>v</sub>, which is below the long-term, health-based comparison value (0.1 ppb<sub>v</sub>). However, the reported 2008 average acrolein concentrations based on co-located canister samples at the Deer Park site were 0.34 and 0.43 ppb<sub>v</sub>, which are above the long-term, health-based comparison value and require further evaluation.

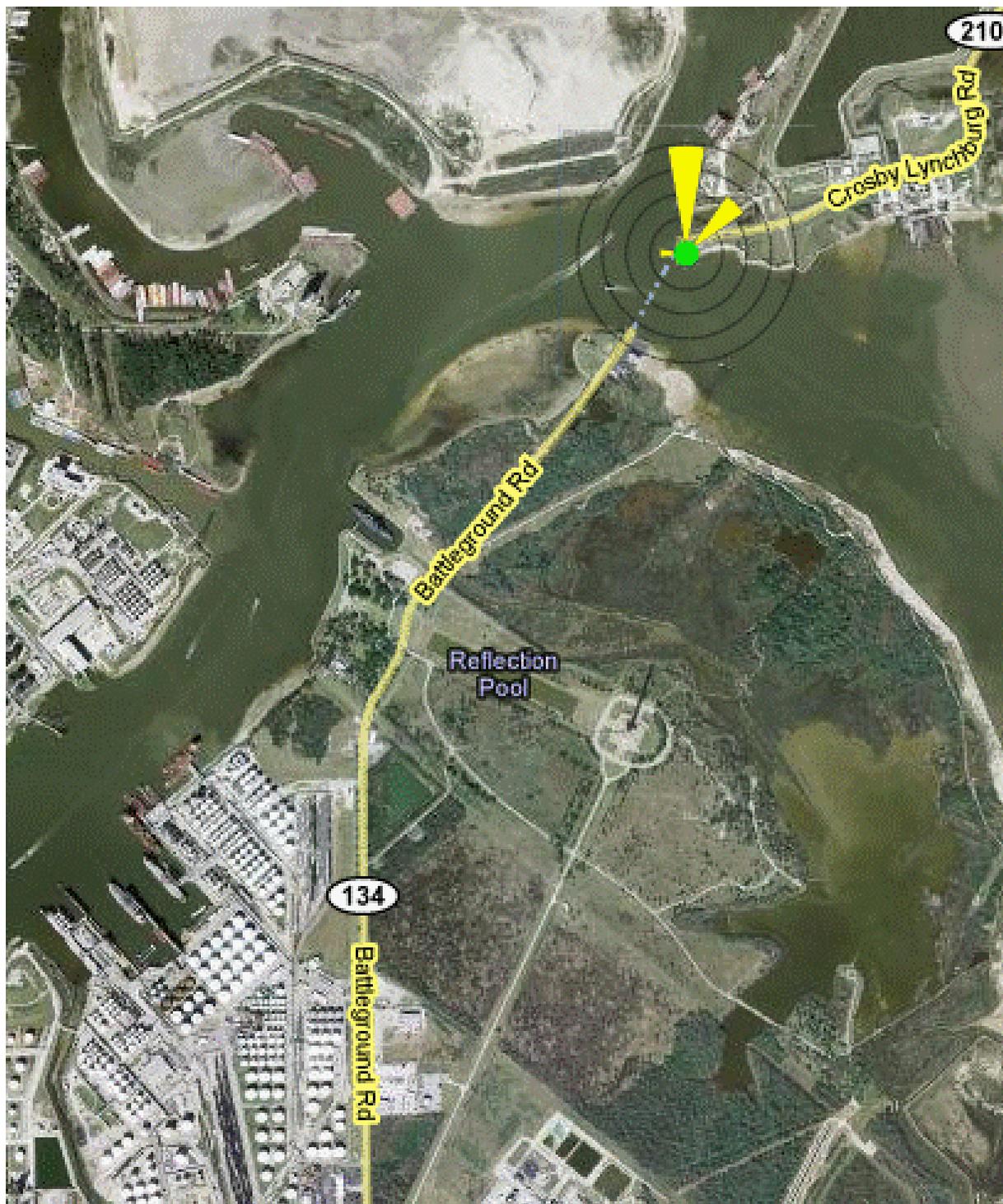
Acrolein results from the canister and carbonyl analyses are significantly different because acrolein is highly reactive and there are difficulties in the sample collection and analysis of acrolein. To the TD's understanding, both TCEQ and USEPA are evaluating which of the available methods may be most appropriate for accurate and precise measurements of acrolein in the future. Regardless of which analytical method utilized at Deer Park in 2008 may be more accurate for the calculation of an annual average, the TD would not expect long-term, adverse health effects to occur at the reported acrolein average concentrations based on data from available scientifically-conducted toxicological studies (see below).

Since acrolein is reactive and highly water soluble, at sufficiently high exposure concentrations of sufficient duration, the most sensitive long-term effects are point-of-entry respiratory effects. In laboratory animal (e.g., rats, dogs) exposure studies, no respiratory effects are observed in animals after long-term exposure to 200 ppb<sub>v</sub>, with respiratory effects observed at higher concentrations (e.g., 600 ppb<sub>v</sub> for mild/moderate respiratory epithelial hyperplasia in rats, 220 ppb<sub>v</sub> for respiratory histopathological inflammatory changes in dogs). Based on available toxicological data, no long-term, adverse health effects are expected to occur as a result of exposure to acrolein annual average concentrations of 0.036-0.43 ppb<sub>v</sub>.

If you have any questions regarding this memorandum, please contact me by phone at (512) 239-5691 or by email at [jhaney@tceq.state.tx.us](mailto:jhaney@tceq.state.tx.us). For questions regarding the APWL, you may visit the TCEQ website at [http://www.tceq.state.tx.us/implementation/tox/AirPollutantMain/APWL\\_index.html](http://www.tceq.state.tx.us/implementation/tox/AirPollutantMain/APWL_index.html).

Appendix 1. Monitored Air Toxics in TCEQ Region 12 for Year 2008			
Canister & AutoGC Target Analytes		Additional Canister Target Analytes	
1,2,3-Trimethylbenzene	Isoprene	1,1,1-Trichloroethane	Dichlorodifluoromethane
1,2,4-Trimethylbenzene	Isopropylbenzene	1,1,2,2-Tetrachloroethane	Ethyl Acetate *
1,3,5-Trimethylbenzene	Methylcyclohexane	1,1,2-Trichloroethane	Isobutyraldehyde *
1,3-Butadiene	Methylcyclopentane	1,1-Dichloroethane	m-Diethylbenzene
1-Butene	n-Butane	1,1-Dichloroethylene	m-Ethyltoluene
1-Pentene	n-Decane	1,2-Dibromoethane	Methyl butyl ketone (MBK) *
2,2-Dimethylbutane	n-Heptane	1,2-Dichloroethane	Methyl chloride
2,2,4-Trimethylpentane	n-Hexane	1,2-Dichloropropane	Methyl t-butyl ether *
2,3,4-Trimethylpentane	n-Nonane	1-Hexene + 2-Methyl-1-pentene	Methylene chloride
2,3-Dimethylpentane	n-Octane	2-Butanone *	Methyl isobutyl ketone *
2,4-Dimethylpentane	n-Pentane	2-Chloropentane	n-Propyl acetate *
2-Methyl-2-Butene	n-Propylbenzene	2-Methyl-3-hexanone *	n-Undecane
2-Methylheptane	o-Xylene	2-Methylpentane	o-Ethyltoluene
2-Methylhexane	Propane	2,3-Dimethylbutane	p-Diethylbenzene
3-Methylheptane	Propylene	3-Hexanone *	p-Ethyltoluene
3-Methylhexane	p-Xylene + m-Xylene	3-Methylpentane	t-2-Hexene
Acetylene	Styrene	3-Methyl-1-butene	Tetrachloroethylene
Benzene	t-2-Butene	3-Pentanone *	Trans-1-3-dichloropropylene
c-2-Butene	t-2-Pentene	4-Methyl-1-pentene	Trichloroethylene
c-2-Pentene	Toluene	Bromomethane	Trichlorofluoromethane
Cyclohexane		Butyl Acetate *	Vinyl Chloride
Cyclopentane		c-2-Hexene	
Ethane		Carbon Tetrachloride	
Ethylbenzene		Chlorobenzene	* Chemicals which were removed
Ethylene		Chloroform	from the canister target analyte list
Isobutane		Cis-1,3-dichloropropylene	in 2008 and do not meet the 75%
Isopentane		Cyclopentene	data completeness objective.
Carbonyls		Metals	
2,5-Dimethylbenzaldehyde	MEK/Methacrolein *	Aluminum (PM 10 and 2.5)	Copper (PM 10 and 2.5)
Acetaldehyde	o-Tolualdehyde	Antimony (PM 10 and 2.5)	Manganese (PM 10 and 2.5)
Acetone *	p-Tolualdehyde	Arsenic (PM 10 and 2.5)	Molybdenum (PM 10 and 2.5)
Acrolein	Propionaldehyde	Barium (PM 10 and 2.5)	Nickel (PM 10 and 2.5)
Benzaldehyde	Valeraldehyde	Cadmium (PM 10 and 2.5)	Selenium (PM 10 and 2.5)
Butyraldehyde		Chromium (PM 10 and 2.5)	Tin (PM 10 and 2.5)
Crotonaldehyde	* Acetone and MEK/Methacrolein	Cobalt (PM 10 and 2.5)	Zinc (PM 10 and 2.5)
Formaldehyde	did not meet the 75% data		
Heptaldehyde	completeness objective at the Clinton		
Hexanaldehyde	or Deer Park sites, and it was		
Isovaleraldehyde	not met for MEK/Methacrolein		
m-Tolualdehyde	at the Channelview site.		
PAHs/SVOCs			
1,1,1- Trichloro-2,2-Bis (P-Chlorophenyl) Ethane		Acenaphthylene	Endosulfan sulfate
1,1-Bis(4-Chlorophenyl)-2,2-Dichloroethane		Aldrin	Endrin
1,1-Dichloroethylidene Bis (4-Chlorobenzene)		Anthracene	Endrin Ketone
1,2,3,4,5,6- Hexachlorocyclohexane, Beta-		Benzo(a)anthracene	Fluoranthene
1,2,3,4,5,6- Hexachlorocyclohexane		Benzo(a)pyrene	Fluorene
1,2,3,4,5,6- Hexachlorocyclohexane, Delta.-		Benzo(b)fluoranthene	Heptachlor
2,3,4,6-Tetrachlorophenol		Benzo(g,h,i)perylene	Heptachlor Epoxide
2,4,5-Trichlorophenol		Benzo(k)fluoranthene	Indeno(1,2,3-cd)pyrene
2,4,6-Trichlorophenol		Chrysene	Lindane
2,4-Dichlorophenol		Dibenzo(a,h)anthracene	Methoxychlor
2,6-Dichlorophenol		Dieldrin	Naphthalene
4-Chloro-3-methylphenol		Endosulfan I	Phenanthrene
Acenaphthene		Endosulfan II	Pyrene

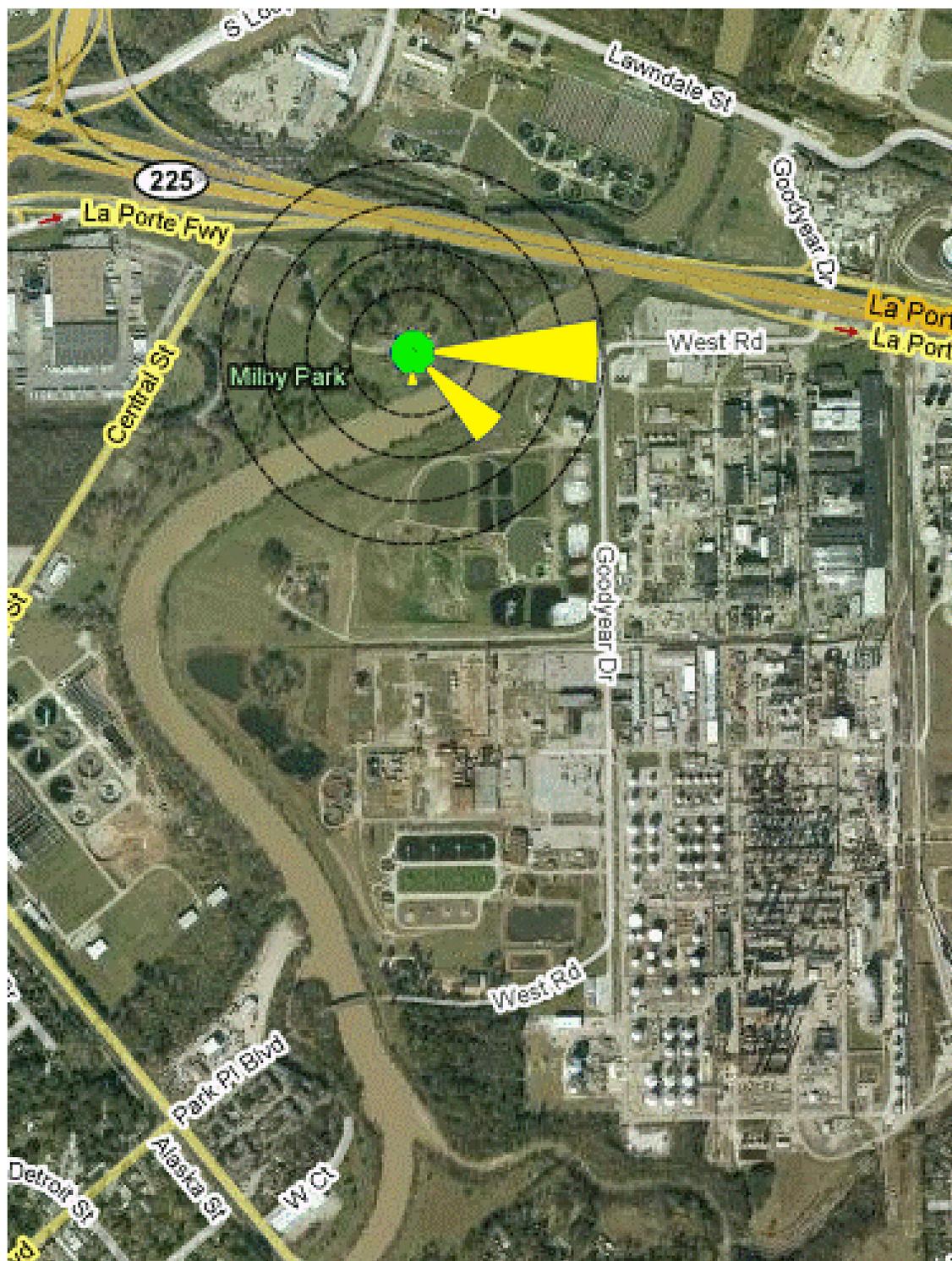
Appendix 2a. Source Direction Evaluation of Styrene Average Concentrations (2008) at the Lynchburg Ferry Site



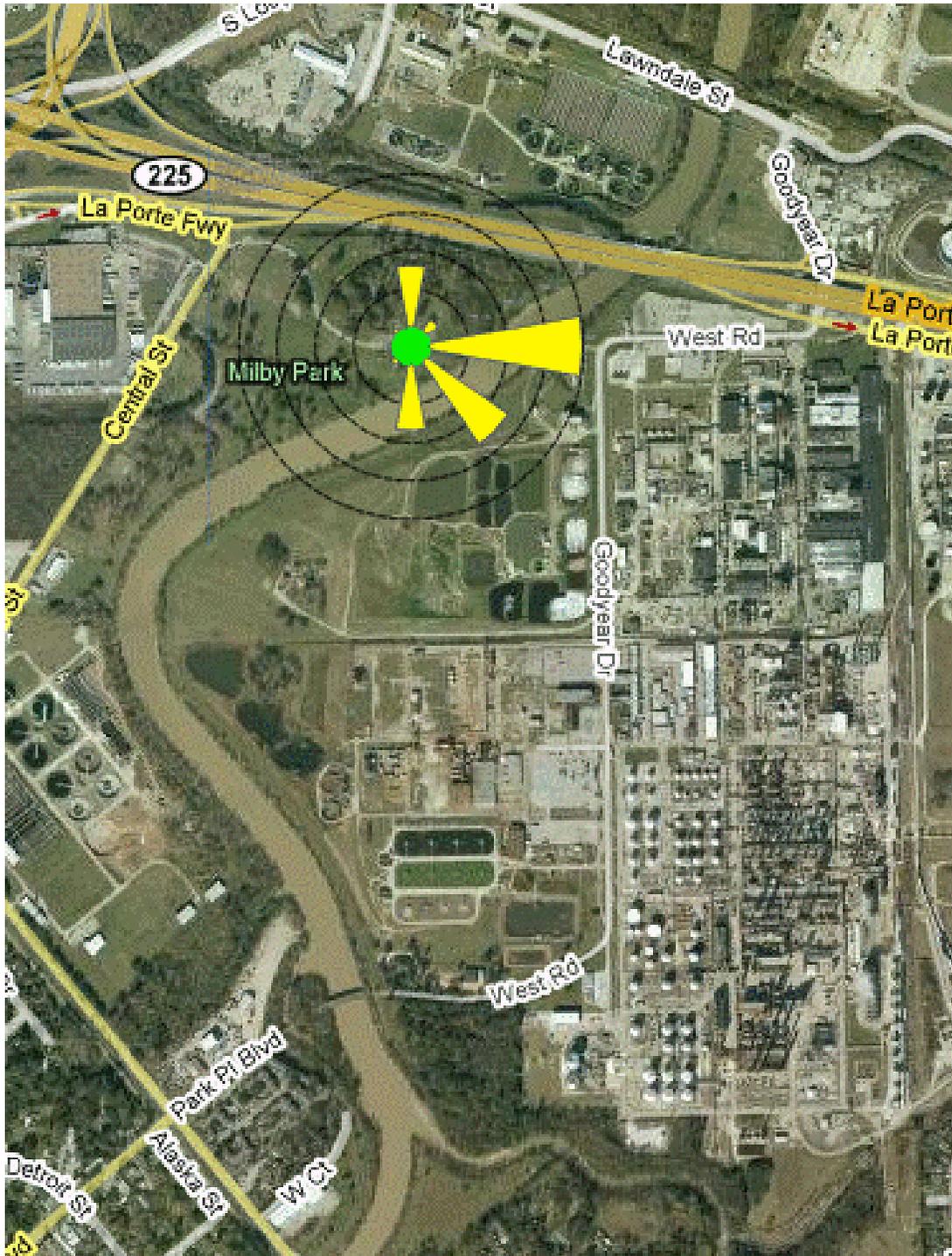
Appendix 2b. Source Direction Evaluation of Styrene Maximum Concentrations (2008) at the Lynchburg Ferry Site



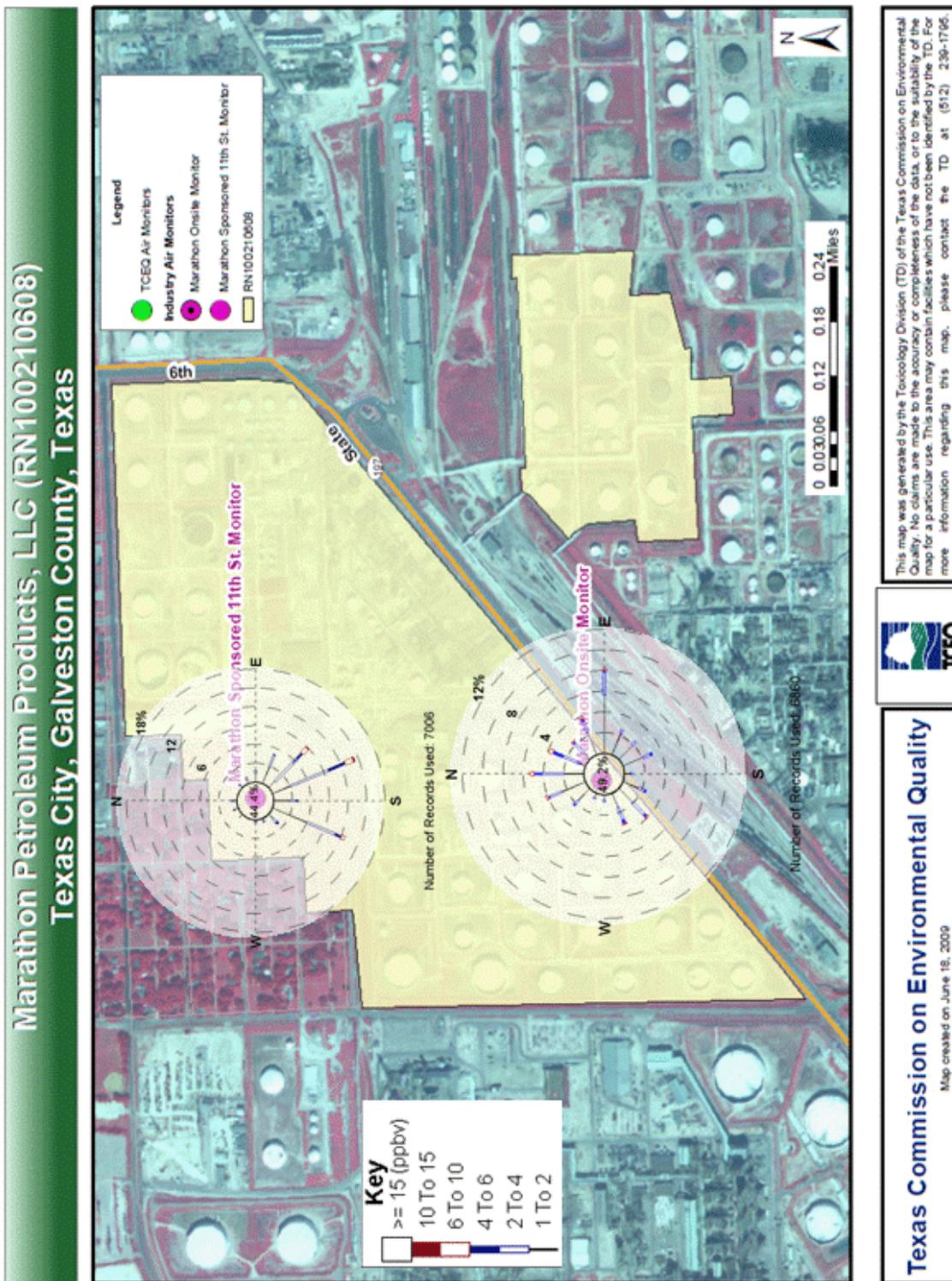
Appendix 3a. Source Direction Evaluation of Styrene Average Concentrations (2008) at the Milby Park Site



Appendix 3b. Source Direction Evaluation of Styrene Maximum Concentrations (2008) at the Milby Park Site



Appendix 4. Source Direction Evaluation of Benzene at the Marathon-Sponsored Off- and On-Site Monitors for 2008



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