Texas Commission on Environmental Quality

INTEROFFICE MEMORANDUM

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From:	Joseph T. Haney, Jr., M.S.		

Subject: Health Effects Review of Ambient Air Monitoring Data Collected in TCEQ Region 12 during 2007

Toxicology Section, Chief Engineer's Office

Key Points

- The reported 2007 average benzene concentration at the British Petroleum (BP)-sponsored site in Texas City indicates a continued decline, and is below TCEQ's long-term, health-based comparison value for the first time since monitoring began.
- While the reported annual average benzene concentration at the Lynchburg Ferry site continued to decrease in 2007, the average benzene level reported for the Galena Park site increased slightly. These sites are contained within Air Pollutant Watch List (APWL) areas for benzene, and reductions in benzene emissions in these areas continue to be recommended.
- TCEQ recently established a 24-hour canister volatile organic compound (VOC) sampling site (Pasadena North site, EPA Site ID 48-201-1049) on the south side of the Houston Ship Channel to help assess the potential for emissions from the south side of the channel to impact long-term benzene levels at the Galena Park site.
- The 2007 benzene concentration being below TCEQ's long-term, health-based comparison value and the further decrease in annual average benzene concentrations at the Texas City 34th St. site continue to support removal of Site# <u>APWL 1203</u> from the APWL in 2007.
- The 2007 benzene concentration at the Marathon-sponsored site in Texas City is above TCEQ's longterm, health-based comparison value. This site is within an APWL area for benzene, and a reduction in benzene emissions in this area is recommended.
- The reported 2007 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 three years. The 2007 average essentially meets the long-term goal in Emission Reduction Agreements (ERAs), and a re-evaluation of this APWL area is likely since a recent TCEQ toxicological assessment of the most up-to-date science and data for 1,3-butadiene (peer-reviewed by a panel of expert scientists) indicates that these reported annual averages are below levels of health concern.
- Hourly levels of several 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., headaches, nausea). Reductions in styrene emissions are recommended for these areas.

Background

The primary purpose of this memorandum is to convey the Toxicology Section's (TS) evaluation of ambient air toxics sampling conducted at monitoring sites in Region 12–Houston during 2007. Additionally, summary information concerning various TCEQ actions (e.g., investigations) is provided for several of the areas discussed in this evaluation. The TS 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) samples, and 24-hour metals samples from filters designed to collect particulate matter with an aerodynamic diameter of 2.5 microns or less (PM_{2.5}) and from filters collecting particulate matter with an aerodynamic diameter of 10 microns or less (PM₁₀). Criteria pollutant 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 18 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
- 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 2007.				
County	EPA Site ID	City and Site Location	Network	Monitored Compounds
Brazoria	48-039-1003	<u>Clute</u> 426 Commerce St.	TCEQ	VOC (24-hour canister)
Brazoria	48-039-0618	Danciger Along US Hwy 1459 in Brazoria County	EISM	VOC (autoGC)
Brazoria	48-039-1016	Lake Jackson 109-B Brazoria Hwy 332-W	EISM	VOC (autoGC)
Brazoria	48-039-0619	<u>Mustang Bayou</u> <u>Liverpool</u>	EISM	VOC (autoGC)
Galveston	48-167-0014	Galveston, Airport 8715 Cessna St.	TCEQ	VOC (24-hour canister)
Galveston	48-167-0053	Texas City, Nessler Pool 17th and 5th Ave.	TCEQ	VOC (24-hour canister)
Galveston	48-167-0005	<u>Texas City, Ball Park</u> 2516 ¹ / ₂ Texas Ave.	TCEQ	VOC (24-hour canister)
Galveston	48-167-0056	Texas City, 34 th St. 2212 North 34th St.	EISM	VOC (autoGC)
Galveston	48-167-1034	<u>Galveston, 99th St.</u> 9511 Avenue V ½	TCEQ	VOC (1- & 24-hour canister)
Harris	48-201-0036	Jacinto Port 1st St. and Elsbeth St.	TCEQ	VOC (24-hour canister)
Harris	48-201-1039	Deer Park 4514 ½ Durant St.	TCEQ	VOC (autoGC, 24-hour canister), Carbonyls, Metals, PAHs
Harris	48-201-0024	Houston, Aldine 4510 ½ Aldine Mail Rd.	TCEQ	VOC (1- & 24-hour canister), Metals

Harris	48-201-1035	Houston, Clinton 9525 ¹ / ₂ Clinton Dr.	TCEQ	VOC (autoGC), Carbonyls, Metals
Harris	48-201-0057	Galena Park 304 Stewart St.	TCEQ	VOC (24-hour canister)
Harris	48-201-0026	Houston, Channelview 1405 Sheldon Rd.	TCEQ	VOC (autoGC), Carbonyls
Harris	48-201-0061	La Porte, Shoreacres 3903 ½ Old Hwy 146	TCEQ	VOC (24-hour canister)
Harris	48-201-0069	Houston, Milby Park 2201-a Central St.	TCEQ	VOC (autoGC)
Harris	48-201-6000	Houston, Cesar Chavez 4829A Galveston Rd.	TCEQ	VOC (autoGC)
Harris	48-201-1015	Baytown, Lynchburg Ferry 1001 B Lynchburg Rd.	TCEQ/EISM	VOC (autoGC, 24-hour canister)
Harris	48-201-0617	Baytown, Wallisville Rd. 4727 Wallisville Rd.	EISM	VOC (autoGC)
Harris	48-201-0307	Houston, Manchester/Central 9401 ¹ / ₂ Manchester Rd.	TCEQ	VOC (24-hour canister)
Harris	48-201-0029	Tomball, NW Harris County 16822 Kitzman St.	TCEQ	VOC (1- & 24-hour canister)
Harris	48-201-0030	Houston, Channelview North US Hwy 90 and Sheldon Rd.	TCEQ	VOC (24-hour canister)
Harris	48-201-0055	Houston, Bayland Park 6400 Bissonnet St.	TCEQ	VOC (24-hour canister)
Harris	48-201-0058	Baytown 7201 ½ Bayway Dr.	TCEQ	VOC (24-hour canister)
Harris	48-201-0803	Haden Rd. (HRM-3) 1504 ¹ / ₂ Haden Dr.	TCEQ/EISM	VOC (autoGC, 24-hour canister)
Galveston	N/A	BP North America Products, IncTexas City 31 st St. (Between Texas Ave. and 5 th Ave.)	AOM	VOC (autoGC)
Galveston	N/A	Marathon Petroleum Company, LLC- Texas City 11 st St. S. at 6 th Ave. S.	EPA/DOJAM	VOC (autoGC)
Montgomery	48-339-0078	<u>Conroe</u> 9472A Hwy 1484	TCEQ	VOC (24-hour canister)

All data collected at the 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 a 85% data completeness objective. One-hour canister VOC, autoGC VOC, and carbonyl data were evaluated for potential acute health (e.g., irritation) and odor concerns. 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 by contacting the TS (512-239-1795).

Evaluation

One-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 99.99% of the approximately 4,140,000 1-hour VOC measurements from TCEQ and EISM autoGC monitors in Region 12 in 2007 were below their short-term comparison levels.

Approximately 0.0001% of the hourly autoGC measurements collected in Region 12 in 2007 exceeded TCEQ short-term, health-based comparison levels. Approximately 0.0025% 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 8,100 1-hour VOC concentrations from canister samples were below their short-term, health- and odor-based comparison levels. Additionally, except for one exceedance of an odor-based comparison value, all of the approximately 1,200 1-hour carbonyl concentrations measured in Region 12 in 2007 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 2007.

For the reported 1-hour concentrations that exceeded their respective short-term, health- and/or odorbased 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. These exceedances occurred only at the Lynchburg Ferry site monitor, where there were 4 hourly benzene concentrations above the short-term ambient air comparison value of 180 ppb_v, with a maximum concentration of 912.74 ppb_v. These reported 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, these relatively high hourly levels contributed to the 2007 annual average exceeding the long-term, health-based comparison value at this site (see the *Annual Average Concentrations* section of this evaluation). Therefore, although there is a downward trend in annual benzene concentrations at the Lynchburg Ferry site, further benzene emission reductions are recommended to reduce both short- and long-term levels.

The reported 1-hour autoGC VOC concentrations that exceeded their respective odor-based comparison levels are shown below in Table 2. Additionally, a single 1-hour isovaleraldehyde concentration (0.481 ppb_v) reported for the Clinton Dr. site exceeded its odor-based comparison value (0.15 ppb_v).

Table 2. Odor-Based Comparison Value Exceedances by 1-Hour AutoGC VOC Concentrations					
Site	Chemical	Number of 1-Hour Concentrations above Odor-Based Comparison Value	Maximum Measured Concentration (ppb _v)	Odor-Based Comparison Value (ppb _v)	
Cesar Chavez	Isoprene	2	7.41	5	
Clinton Dr.	Isoprene	3	133.5	5	
Densigar	Isoprene	10	8.59	5	
Danciger	Styrene	2	32.16	25	
Deer Park	Isoprene	2	7.26	5	
Haden Rd.	Isoprene	5	13.6	5	
Lake Jackson	Isoprene	1	5.48	5	
	Styrene	42	154.94	25	
Lynchburg Ferry	Isoprene	4	7.32	5	
	Isopropylbenzene	2	120.83	100	
Milby Park	Styrene	28	49.38	25	
Wallisville Rd.	Isoprene	2	7.52	5	

The relatively high frequency and magnitude 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).

At the Lynchburg Ferry site, there were 42 hourly styrene concentrations reported above the odor-based comparison value of 25 ppb_y, with a maximum concentration of 154.94 ppb_y. This represents an approximate 19% reduction in the number of odorous styrene concentrations when compared to 52 such concentrations reported in 2006, which included a higher maximum concentration of 358.35 ppb_v. When compared to the 92 odorous styrene concentrations reported for the Lynchburg Ferry site in 2005, which included a maximum concentration of 432.97 ppb_y, the 42 occurrences in 2007 represent a reduction of approximately 54%. The direction of potential styrene sources near the Lynchburg Ferry site was evaluated by the TS 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 2007, 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/northwest. Maximum 2007 concentrations of approximately 48-155 ppb, occurred with winds from the north/northeast, with maximums of approximately $47-65 \text{ ppb}_v$ occurring with winds from the west/northwest (Appendix 2b). The source direction evaluation based on 2007 average styrene concentrations at this site (Appendix 2a) is similar to that contained in the TS evaluation of 2006 Region 12 data. Although the frequency of odorous styrene concentrations reported at the Lynchburg Ferry site has decreased from 2005 to 2007, reductions in styrene emissions which contribute to odorous levels at the Lynchburg Ferry site are recommended. Styrene is currently listed on the APWL for this area (Site# APWL1204) because of the monitored odorous conditions, and the 2007 data should be considered when the status of this APWL listing is re-evaluated.

At the Milby Park site, there were 28 odorous styrene concentrations reported in 2007. This frequency is almost twice the number of odorous styrene concentrations (16) reported for the Milby Park site in 2006, and is seven times the number of such concentrations (4) reported for 2005. The direction of potential styrene sources near the Milby Park site was evaluated by the TS through the use of hourly styrene autoGC data and wind directional data collected at the site. Based on both average styrene concentrations (Appendix 3a) and maximum concentrations (Appendix 3b) for 2007, styrene concentrations at the Milby Park site were highest when winds were from the east/southeast. Maximum 2007 concentrations of approximately 35-49 ppb_y occurred with winds from the east/southeast (Appendix 3b). The source direction evaluation based on 2007 average styrene concentrations at this site (Appendix 3a) is similar to that contained in the TS evaluation of 2006 Region 12 data. In addition to the odorous styrene levels measured at the autoGC, on a December 13-19, 2007 TCEQ mobile monitoring trip, odorous levels of styrene were reported downwind of Goodyear Tire & Rubber Company, which is located just east/southeast of the Milby Park site. The City of Houston issued a Notice of Violation (NOV) related to odors to Goodyear Tire & Rubber Company during 2007, and another in 2008. The frequency of odorous styrene concentrations reported at the Milby Park site has increased from 2005 to 2007, and reductions in styrene emissions which contribute to these odorous levels are recommended. It is the TS's understanding that Goodyear Tire & Rubber Company has agreed to styrene reductions in their most recent permit action. The TS is currently evaluating whether styrene should be added to the APWL for this area (Site# APWL 1207).

Annual Average Concentrations

All reported annual average concentrations of detected metals were below their respective long-term, health-based comparison levels. Although arsenic was never detected at the Houston-Clinton Dr. site in 2007, the method detection limit for arsenic at this site was higher than the long-term, health-based comparison level. All annual average concentrations of carbonyls were below their respective long-term, health-based comparison levels for ambient air, as were a significant majority of the VOCs. Therefore, no long-term, adverse health effects would be expected due to exposure to those concentrations. 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 concentrations are discussed.

Lynchburg Ferry

The reported 2007 average benzene concentration at the Lynchburg Ferry site based on every sixth-day 24-hour canister samples was 1.43 ppb_v, while the annual average concentration based on hourly samples collected at the co-located autoGC was 1.51 ppb_v. While both are above the long-term, health-based comparison value of 1.4 ppb_v, the annual average based on hourly autoGC samples more accurately represents the long-term average in 2007. The direction of potential benzene sources near the Lynchburg Ferry site was evaluated by the TS using benzene autoGC data and wind directional data from the site. Based on both average benzene concentrations (Appendix 4a) and maximum concentrations (Appendix 4b) for 2007, benzene concentrations reported at the Lynchburg Ferry site were highest when winds were from the northwest, with lesser elevated concentrations occurring when winds were from the north/northeast. Additionally, average benzene concentrations (Appendix 4a) indicate that lesser elevated concentrations occurred when winds were from the southwest. Unlike the source direction evaluation for this site contained in the <u>TS evaluation of 2006 Region 12 data</u>, which indicated that the highest benzene levels were associated with winds from the north/northeast and southwest, the evaluation of 2007 data (Appendix 4a) indicates that the highest levels were associated with winds from the north/northeast.

While above the long-term, health-based comparison value, the 2007 annual benzene average of 1.51 ppb_v (autoGC) represents an approximate reduction of 37% when compared to the 2006 annual average, and an approximate 52% reduction compared to the 2005 annual average (see Figure 1). The reduction in the annual benzene concentration for 2007 compared to 2006 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. Preliminary data for 2008 indicate that benzene concentrations in the Lynchburg Ferry area are continuing to decline. The average of monthly autoGC means for benzene for January through May 2008 is 0.95 ppb_v, compared to 1.95 ppb_v over the same period in 2007, a reduction of about 51%. These reductions may be attributable to TCEQ activities and other initiatives in the Lynchburg Ferry area.



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

TCEQ activities in 2007 in the Lynchburg Ferry area included, but were not limited to:

- In response to benzene trigger level exceedances at the monitoring site, Region 12 conducted enhanced investigations at Channel Shipyard and Southwest Shipyard, including use of the GasFindIR camera as well as conventional fugitive emission monitoring equipment to identify leaks from barges and on-shore facilities.
- Region 12 conducted 10 special investigations at Channel Shipyard related to benzene triggers at the monitor, 8 stack sampling investigations, 10 reconnaissance investigations, and 2 special focused investigations to identify leaks at the site. One Notice of Enforcement (NOE) and 1 NOV was issued.
- Region 12 conducted 3 special investigations at Southwest Shipyard related to benzene triggers at the monitor, 6 reconnaissance investigations, and 1 Title V compliance investigation. Two NOEs and an NOV were issued.
- As a result of these investigations and subsequent enforcement actions, corrective actions have been implemented:
 - For Southwest Shipyard, an Agreed Order with Denial (2005-0097-MLM-E) became effective on 4/13/2007, and a Findings Order (#2007-0794-AIR-E) became effective on 6/5/08;
 - For Channel Shipyard, a Final Judgment became effective on 6/12/07 (enforcement case #27388; District Court Docket #2005-54405) and Findings Order (#2007-0701-AIR-E) became effective on 11/9/07;
 - Permit modifications have been implemented to reduce emissions at both Southwest Shipyard and Channel Shipyard, and stack sampling activities have been conducted to determine compliance with permitting conditions.

- A combination of reconnaissance investigations, Title V 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, Oiltanking Houston). NOVs were issued to Halterman and Oiltanking Houston.
- Reconnaissance investigations were conducted at other potential sources in the area, including Flex Tank, K-Solv, Houston Marine, Barge Cleaning and Stolt Tank, and focused on-site investigations were conducted at K-Solv, Houston Marine, Barge Cleaning, and Stolt Tanks.
- An emission event investigation was conducted at K-Solv as a result of an explosion and fire related to tank truck loading operations, and an NOV was issued.

Regarding industry initiatives, several industrial facilities in the Lynchburg Ferry area previously formed the Monument Area Air Quality Focus Group (MAAQFC) in a collaborative attempt to reduce benzene emissions in this area. The MAAQFC 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. An automatic notification system alerts TCEQ and MAAQFC members to conduct investigations when hourly benzene concentrations reported at the Lynchburg Ferry monitor exceed an hourly benzene trigger concentration (referred to in the bullets above). TCEQ is working in a collaborative effort with both the MAAQFC and the United States Coast Guard to identify and mitigate potential sources of benzene emissions from barges in transit, as well as barge lightering activities in the Houston Ship Channel.

While the mean of monthly averages (January through May) at the Lynchburg Ferry autoGC site indicate that 2008 benzene levels are approximately ½ those over the same time period in 2007, whether the 2008 annual average will be above or below the long-term, health-based comparison level cannot be predicted. As reported annual averages for benzene have been of concern for potential long-term, adverse health effects, this area (APWL Site# <u>APWL1204</u>) will remain on the APWL and further benzene emission reductions are recommended.

Jacintoport

The Jacintoport neighborhood is in the Lynchburg Ferry area, located nearby to the northwest of the Lynchburg Ferry monitoring site. In 2006, an every-sixth-day 24-hour canister sampler site (EPA Site ID # 48-201-0036) was established in Jacintoport to further assess long-term benzene concentrations in the area. Unlike the 2007 benzene average at the Lynchburg Ferry site, the 2007 average at the Jacintoport site (1.09 ppb_v) is below the long-term, health-based comparison value. A 2006 NOE issued by TCEQ against K-Solv, which is located immediately southeast of the Jacintoport neighborhood, likely contributed to the 2007 benzene level at this monitor meeting the comparison value. Subsequent to the NOE, K-Solv entered into an ERA with TCEQ, which resulted in the installation of additional emission controls in 2006.

Galena Park

The reported 2007 average benzene concentration based on every sixth-day 24-hour canister samples at the Galena Park site was 1.74 ppb_v , which exceeds TCEQ's long-term, health-based screening value (1.4 ppb_v). The 2007 average concentration is approximately 9% higher than the 2006 annual average of 1.58 ppb_v, but is less than the 2005 annual average of 1.97 ppb_v. Despite significant TCEQ efforts in the area, no downward trend in annual benzene averages at the Galena Park site is apparent (see Figure 2), although available 24-hour canister data suggests that the 2008 average may be lower (see the last paragraph of this section).



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

TCEQ activities in 2007 in the Galena Park area included, but were not limited to:

- A follow-up investigation to the Texas Air Quality Field Study II (TexAQS II) was conducted by Region 12 at Houston Refining, in addition to a benzene-focused investigation to evaluate compliance with state and federal regulations relating to the control of benzene emissions and to find specific emission points that may be contributing to monitored benzene levels at the Galena Park site. An NOE was issued.
- An investigation was conducted by Region 12 at the Galena Park Vopak Terminals focusing on the emissions generated by heated fuel oil storage tanks, process tanks, and stack emissions.
- A benzene-focused investigation was conducted by Region 12 at Pasadena Refining System Incorporated to evaluate compliance with state and federal regulations relating to the control of benzene emissions and to find specific emission points that may be contributing to monitored benzene levels at the site. An NOE was issued.
- A comprehensive compliance investigation and a reconnaissance investigation were conducted at Texmark Chemicals. Thirteen violations were cited in an NOE and an NOV was issued as a result of these investigations.
- During 2007, there were 4 NOVs and 26 NOEs issued to regulated entities in the Galena Park Area. Of those, 3 Excessive Emission Event (EEE) determinations were made at Houston Refining and 1 EEE determination was made at Valero Refining.
- Region 12 continues to conduct focused investigations and reconnaissance investigations in the Galena Park Area to address on-going issues discovered through use of GasFindIR or visual inspections.

In regard to previous and ongoing activities, in 2006 TCEQ negotiated ERAs with Kinder Morgan Terminals, Vopak Terminals, and TEPPCO Pipeline to reduce VOCs, including benzene. These facilities were identified during an earlier Find-and-Fix investigation. Reconnaissance investigations conducted by Region 12 investigators and mobile monitoring are ongoing efforts aimed at identifying and further

reducing benzene emissions in this area. For example, on a December 13-19, 2007 TCEO mobile monitoring trip, benzene concentrations that may contribute to elevated long-term benzene levels at the Galena Park site were reported nearby to the south/southeast, downwind of Texmark Chemicals, Kinder Morgan Terminals, and Vopak Terminals. 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). On the same December 2007 TCEO mobile monitoring trip, elevated benzene concentrations were reported on the south side of the Houston Ship Channel downwind of United States Oil Recovery, Pasadena Refining, and Houston Refining. These facilities were identified in a June 30, 2008 health effects review of the mobile monitoring data as potentially impacting benzene levels at the Galena Park site. TCEQ has recently established a new every-sixth-day 24-hour canister VOC sampling site (Pasadena North site, 702 Light Company Rd., EPA Site ID 48-201-1049), just south of United States Oil Recovery, to help assess the potential for benzene emissions from the south side of the Houston Ship Channel to impact long-term benzene levels at the Galena Park site. TCEO will continue to use information from various investigations, mobile and fixed-site monitoring (including the new Pasadena North site), and the latest technology (GasFindIR) to aid in the identification of sources and reduction of benzene emissions in the area.

Available 24-hour canister data for 2008 indicates that the January through May average for benzene at the Galena Park site is 1.04 ppb_v , which is approximately 26% less than the average of 1.41 ppb_v over the same period in 2007. However, whether the 2008 average for benzene at the Galena Park site will be lower than the 2007 average cannot be predicted. Despite TCEQ efforts to identify and reduce benzene emissions in the area, the reported levels are still of concern for potential long-term, adverse health effects. Therefore, this area will remain on the APWL (Site# <u>APWL1206</u>), and further benzene emission reductions are recommended.

Milby Park

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 2007 average concentration of 1.04 ppb_v at the Milby Park site is 20% less than the 2006 average of 1.30 ppb_v, and approximately 32% less than the 2005 average concentration of 1.52 ppb_v. It is the lowest annual average measured at this site since monitoring began. Source direction evaluations based on 2007 average and maximum 1,3-butadiene concentrations at this site are contained in Appendices 5a and 5b, respectively. The continued reduction in annual average concentrations of 1,3-butadiene can be attributed to continued corrective activities associated with the TCEQ voluntary ERAs entered into by Texas Petrochemical and Goodyear Tire & Rubber Company in 2004. In 2007, TCEQ has continued to monitor the ERAs made with Texas Petrochemical and Goodyear Tire & Rubber Company. Additionally, there were 5 NOVs and 13 NOEs issued to regulated entities in the Milby Park Area. Of those, 1 EEE determination was made at Texas Petrochemical.



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

Preliminary data for 2008 indicates that 1,3-butadiene concentrations at Milby Park may be continuing to decline. The average of monthly autoGC means for January through May 2008 is 0.99 ppb_v, slightly lower than the average of 1.15 ppb_v over the same period in 2007. Although recent annual averages for 1,3-butadiene indicate a continued downward trend at the Milby Park site and the 2007 annual average concentration is essentially equal to the ERA long-term goal of 1 ppb_v, this area (APWL Site# <u>APWL</u> <u>1207</u>) is currently on the APWL. A re-evaluation of this APWL area is likely since a recent TS toxicological assessment of the most up-to-date science and data for 1,3-butadiene, which was peer-reviewed by a panel of expert scientists, indicates that these reported annual averages are below levels of health concern, as shown in Figure 3 (see the <u>1,3-Butadiene Development Support Document</u>).

Texas City Marathon-Sponsored 11th St. S. Site

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^{th} St. S. and 6th Ave. S. on November 5, 2007. As data collection at this site has been discontinuous, the benzene data do not cover any one full calendar year. For example, there are no 2007 data for the months of February and March at the Marathon-sponsored site. While the TS prefers that health evaluations of annual benzene averages be based a full calendar year of data, there are 10- or 11-month averages for 2005-2007. The 2007 average at the Marathon-sponsored site based on the 10 months of data available (approximately 2.17 ppb_v) exceeds TCEQ's long-term, health-based screening value (1.4 ppb_v). The 11-month 2006 average (approximately 2.06 ppb_v) and the 10-month 2005 average (approximately 2.28 ppb_v) were similar (see Figure 4). The area of Texas City located south of State Highway 1765, which contains the Marathon-sponsored site, is currently on the APWL (Site# <u>APWL1202</u>) for the elevated long-term concentrations of benzene.



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

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 by TCEQ staff using wind directional data associated with hourly benzene concentrations greater than 10 ppby from April-December 2007. Based on this analysis (see Figure 5), elevated concentrations above 10 ppb_v were most frequently associated with winds from the southeast (primarily 112-149 degrees) and southwest (primarily 199-225 degrees), with the highest six benzene concentrations occurring with winds from the southwest (208-219 degrees). More easterly winds (90-102 degrees) were associated with a few benzene levels greater than 10 ppby. The general wind directions most frequently associated with benzene concentrations greater than 10 ppb_v based on April-December 2007 data are depicted on a site aerial photograph in Appendix 6. The yellow-highlighted areas on the aerial in Appendix 6 are approximations of 112-149 degrees (southeast winds) and 199-225 degrees (southwest winds) from the Marathon-sponsored site. These areas are depicted to aid in the identification of benzene sources which may have contributed to the highest hourly benzene levels reported for 2007, but should not be interpreted to contain all potentially relevant benzene sources, and significant benzene sources impacting the monitor may be located at distances greater than those shown on the aerial. Additionally, unlike the pollution roses presented in this memorandum (Appendices 2-5), the lengths of the yellow areas shown in Appendix 6 do not correspond to the relative magnitude of the monitored levels from the directions depicted.



Figure 5. Hourly Benzene Concentrations $> 10 \text{ ppb}_v \text{ vs.}$ Wind Direction for April-December 2007 at the Marathon-Sponsored 11^{th} St. S. Site

Inclusion of data through March 2008 in the source direction evaluation results in the same conclusions regarding the wind directions associated with potential benzene sources (see Figure 6).



 $\label{eq:Figure 6.} Figure \ 6. \ Hourly \ Benzene \ Concentrations > 10 \ ppb_{\nu} \ vs. \ Wind \ Direction \ for \ April \ 2007-March \ 2008 \ at \ the \ Marathon-Sponsored \ 11^{th} \ St. \ S. \ Site$

In addition to the off-site 11th 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 by TCEQ staff to evaluate the direction of potential benzene sources both on- and offsite. Based on this analysis (see Figure 7), concentrations above 10 ppb_y were most frequently associated with winds from the east/northeast (approximately 59-104 degrees), southwest (approximately 208-253 degrees), and northwest (approximately 59-104 degrees). Additionally, benzene concentrations above 10 ppb_v were associated with other directions (i.e., north/northeast, west). The general wind directions most frequently associated with benzene concentrations greater than 10 ppby based on April-December 2007 data from the on-site monitor are depicted in green-highlight on the site aerial photograph in Appendix 6. The green-highlighted areas are provided to aid in the identification of benzene sources which may have contributed to the highest hourly benzene levels reported for the on-site monitor in 2007, and may have also contributed to the 2007 benzene levels reported for the off-site 11th St. S. monitor. However, these areas should not be interpreted to contain all potentially relevant benzene sources, and significant benzene sources impacting the on-site monitor may be located at distances greater than those shown on the aerial. The lengths of the green-highlighted areas shown in Appendix 6 do not correspond to the relative magnitude of the monitored levels from the directions depicted.



 $\label{eq:Figure 7. Hourly Benzene Concentrations > 10 \ ppb_v \ vs. \ Wind \ Direction \ for \ April \ 2007-March \ 2008 \ at \ the Marathon-Sponsored \ On-Site \ Monitor$

TCEQ activities in 2007 in this area included, but were not limited to:

- Benzene focused investigations were conducted by Region 12 at Marathon and BP Texas City. NOEs are under development.
- Region 12 conducted follow-up investigations to TexAQS II at Marathon, BP Texas City, and Valero Texas City.

- During 2007 there were 16 NOVs and 33 NOEs issued to regulated entities in the Texas City Area. Of those, 3 EEE determinations were made at the Valero Texas City Refinery and 4 EEE determinations were made at BP Texas City.
- Region 12 continues 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.

At the request of the TS, the TCEQ Mobile Monitoring Team (MMT) recently conducted ambient air monitoring in this APWL area in an attempt to identify benzene sources, including those which may be impacting the benzene levels reported for the Marathon-sponsored site. The MMT report for the May 31-June 7, 2008 mobile monitoring trip is currently being prepared and may contain useful information for prioritizing TCEQ inspections of facilities in this area. Reductions in benzene emissions are recommended for this area, especially those impacting the Marathon-sponsored site. This area (APWL Site# <u>APWL1202</u>) will remain on the APWL until the TS has determined the benzene concentrations in the area are no longer of potential health concern.

Texas City BP-Sponsored Site

The reported 2007 average benzene concentration at the BP-sponsored site (0.95 ppb_v) in Texas City is approximately 45% less than the 2006 average (1.74 ppb_v), and approximately 65% less than the 2005 average (2.71 ppb_v). Recent annual average benzene concentrations at the BP-sponsored site have shown a significant decrease, and the 2007 annual average concentration is below the long-term, health-based comparison value (see Figure 8).



Figure 8. Annual Average Benzene Concentrations at the BP-Sponsored Site

The area of Texas City which contains the BP-sponsored site is currently on the APWL for the elevated long-term concentrations of benzene reported in previous years. Despite the continued downward trend of benzene concentrations at the BP-sponsored site, the 10-month 2007 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 for the BP-sponsored site. In addition to the off-site 31th St. monitoring site, BP provides on-

site (generally upwind) air monitoring data which may be useful in identifying the general direction of sources that may be impacting area monitors. Although the public is not exposed to benzene on BP property, on-site 15-minute data were used by TCEQ staff to evaluate the direction of potential benzene sources both on- and off-site. From an overall perspective for 2007, elevated benzene concentrations measured at the on-site BP location occurred during periods of northwesterly winds (direction of BP facility) and southwesterly winds. As previously mentioned, the MMT report for the May 31-June 7, 2008 mobile monitoring trip is currently being prepared and may contain useful information for prioritizing TCEQ inspections of facilities in this area. This area (APWL Site# <u>APWL1202</u>) will remain on the APWL until the TS has determined the benzene concentrations in the area are no longer of potential health concern.

Texas City-34th St. Site

A notable development in 2007 was removal of the area located north of Farm-to-Market Road 1764 (Site# <u>APWL1203</u>) from the APWL due to significant reductions in annual average benzene concentrations from 2004 to 2006 at the Texas City 34^{th} St. site. The reported 2007 average of 0.25 ppb_v at the Texas City 34^{th} St. site indicates a continued significant reduction in annual benzene concentrations. It is approximately 39% less than the 2006 annual average of 0.41 ppb_v, approximately 68% less than the 2005 annual average of 0.78 ppb_v, and approximately 85% less than the 2004 annual average of 1.63 ppb_v (see Figure 9). The 2005-2007 benzene concentrations being below the long-term, health-based comparison value and the further decrease in annual average benzene concentrations at the Texas City 34^{th} St. site continue to support removal of Site# 1203 from the APWL in 2007.



Figure 9. Annual Average Benzene Concentrations at the Texas City-34th St. Site

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

Appendix 1. Monitored Air Toxics in TCEQ Region 12 for Year 2007			
Canister & AutoGC Target Analytes Additional Canister Target Analytes			
1,2,3-Trimethylbenzene	n-Hexane	1,1,1-Trichloroethane	Methylisobutylketone
1,2,4-Trimethylbenzene	n-Nonane	1,1,2,2-tetrachloroethane	n-Propyl Acetate
1,3,5-Trimethylbenzene	n-Octane	1,1,2-Trichloroethane	o-Ethyltoluene
1,3-Butadiene	n-Pentane	1,1-Dichloroethane	p-Diethylbenzene
1-Butene	n-Propylbenzene	1,1-Dichloroethylene	p-Ethyltoluene
1-Pentene	n-Undecane	1,2-Dibromoethane	t-2-Hexene
2,2-Dimethylbutane	o-Xylene	1,2-Dichloroethane	Tetrachloroethylene
2,2,4-Trimethylpentane	Propane	1,2-Dichloropropane	Trans-1-3-Dichloropropylene
2,3,4-Trimethylpentane	Propylene	1-Hexene + 2-methyl-1-pentene	Trichloroethylene
2,3-Dimethylpentane	p-Xylene + m-Xylene	2-Butanone	Trichlorofluoromethane
2,4-Dimethylpentane	Styrene	2-Chloropentane	Vinyl Chloride
2-Methyl-2-Butene	t-2-Butene	2-Methyl-3-hexanone	
2-Methylheptane	t-2-Pentene	2,3-Dimethylbutane	
2-Methylhexane	Toluene	3-Hexanone	
2-Methylpentane		3-Methylpentane	
3-Methylheptane		3-Methyl-1-Butene	
3-Methylhexane		3-Pentanone	
Acetylene		4-Methyl-1-Pentene	
Benzene		Bromomethane	
c-2-Butene		Butyl Acetate	
c-2-Pentene		c-2-Hexene	
Cyclohexane		Carbon Tetrachloride	
Cyclopentane		Chlorobenzene	
Ethane		Chloroform	
Ethyl Benzene		Cis-1,3-dichloropropylene	
Ethylene		Cyclopentene	
Isobutane		Dichlorodifluoromethane	
Isopentane		Ethyl Acetate	
Isoprene		Isobutyraldehyde	
Isopropylbenzene		m-Diethylbenzene	
Methylcyclohexane		m-Ethyltoluene	
Methylcyclopentane		Methyl butyl ketone (MBK)	
n-Butane		Methyl chloride	
n-Decane		Methyl t-Butyl ether	
n-Heptane		Methylene chloride	
Ca	rbonyls	Metals	
2,5-Dimethylbenzaldehyde	p-Tolualdehyde	Aluminum (PM 2.5)	Aluminum (PM 10)
Acetaldehyde	Propionaldehyde	Antimony (PM 2.5)	Antimony (PM 10)
Acetone	Valeraldehyde	Arsenic (PM 2.5)	Arsenic (PM 10)
Acrolein	·	Barium (PM 2.5)	Barium (PM 10)
Benzaldehyde		Cadmium (PM 2.5)	Cadmium (PM 10)
Butylaldehyde		Chromium (PM 2.5)	Chromium (PM 10)
Crotonaldehyde		Cobalt (PM 2.5)	Cobalt (PM 10)
Formaldehyde		Copper (PM 2.5)	Copper (PM 10)
Heptaldehyde		Manganese (PM 2.5)	Manganese (PM 10)
Hexanaldehyde		Molybdenum (PM 2.5)	Molybdenum (PM 10)
Isovaleraldehvde		Nickel (PM 2.5)	Nickel (PM 10)
m-Tolualdehyde		Selenium (PM 2.5)	Selenium (PM 10)
MEK/Methacrolein		Tin (PM 2.5)	Tin (PM 10)
o-Tolualdehyde		Zinc (PM 2.5)	Zinc (PM 10)
		((*******)

Appendix 2a. Source Direction Evaluation of Styrene Average Concentrations (2007) at the Lynchburg Ferry Site



Appendix 2b. Source Direction Evaluation of Styrene Maximum Concentrations (2007) at the Lynchburg Ferry Site



> Appendix 3a. Source Direction Evaluation of Styrene Average Concentrations (2007) at the Milby Park Site



> Appendix 3b. Source Direction Evaluation of Styrene Maximum Concentrations (2007) at the Milby Park Site



> Appendix 4a. Source Direction Evaluation of Benzene Average Concentrations (2007) at the Lynchburg Ferry Site



Appendix 4b. Source Direction Evaluation of Benzene Maximum Concentrations (2007) at the Lynchburg Ferry Site



> Appendix 5a. Source Direction Evaluation of 1,3-Butadiene Average Concentrations (2007) at the Milby Park Site



> Appendix 5b. Source Direction Evaluation of 1,3-Butadiene Maximum Concentrations (2007) at the Milby Park Site



Appendix 6. Source Direction Evaluation of Benzene Concentrations > 10 ppb_v (April-December 2007) at the Marathon-Sponsored Off- and On-Site Monitors

