TCEQ Interoffice Memorandum

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Date:	July 27, 2011
Subject:	Health Effects Review of 2010 Ambient Air Network Monitoring Data in Region 12, Houston

Key Points

- Notably, annual averages for all chemicals and metals were below their respective longterm air monitoring comparison values (AMCVs) for the first time in many years of sampling.
- The 2010 benzene concentration at the Marathon-sponsored site in Texas City is below TCEQ's long-term AMCV for the first time since monitoring began in 2005. Due to historical AMCV exceedances, the Toxicology Division (TD) recommends continued efforts to maintain compliance with the long-term AMCV for benzene in this area.
- The 2010 benzene averages at the Lynchburg Ferry and Galena Park sites were below the long-term AMCV, which represents a significant and maintained air quality improvement in these areas.
 - The 2010 average benzene concentration at the Lynchburg Ferry site indicates a continued decrease and was below TCEQ's long-term AMCV for the third 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 was removed in 2010 from the Air Pollutant Watch List (APWL) area which contains this monitoring site (Site# <u>APWL1204</u>).
 - The annual average benzene level monitored at the Galena Park site in 2010 was also below the long-term AMCV for the third time in several years. As there are residences located appreciably closer to nearby industry than the monitor, the TD recommends a continued effort to control and/or reduce benzene emissions in the area and will continue to monitor benzene levels at this site to determine whether annual benzene averages remain appreciably below the long-term AMCV.
- The 2007-2010 annual average benzene concentrations at the British Petroleum (BP)sponsored site in Texas City continue to meet TCEQ's long-term AMCV. The TD recommends continued efforts so that the long-term AMCV will continue to be met at this site.

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- There were no odorous styrene concentrations monitored at the Milby Park site in 2010. The frequency of styrene odor-based AMCV exceedances at Milby Park has been reduced 100% from 2008 to 2010. However, the TD recommends continued vigilance to maintain this reduction.
- Hourly levels of a few volatile organic compounds (VOCs) monitored at the Lynchburg Ferry site would result in the perception of odors if people were exposed (e.g., styrene). 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).
- While there has been a 71% reduction in the number of odorous styrene concentrations at Lynchburg Ferry from 2005 to 2010, the TD recommends continued efforts to identify sources and reduce styrene emissions in the area due to the frequency of exceedance of the odor-based AMCV.

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 2010. 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 3-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_{2.5}) and from filters collecting particulate matter with an aerodynamic diameter of 10 microns or less (PM₁₀). Except for lead, data for criteria pollutants (i.e., compounds having National Ambient Air Quality Standards) were not evaluated for this memorandum. Appendix 1 contains a list of the target analytes evaluated for this review. Information regarding monitoring sites and target analyte data reviewed by the TD is presented in Table 1 and summarized below:

- 24-hour canister VOC sampling at 16 sites
- 1-hour canister VOC sampling at 3 sites
- 24-hour carbonyl sampling at 3 sites
- 3-hour carbonyl sampling at 1 site
- 24-hour metals sampling at 4 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
 - > 2 Attorney General-Temporary Injunction Monitoring sites (TIM)
 - 1 US Environmental Protection Agency (EPA)/DOJ-Industry Agreement Monitoring site (EPA/DOJAM)

County	EPA Site ID	Site Location	Network	Monitored Compounds
Brazoria	48-039-1003	<u>Clute</u> <u>426 Commerce St.</u>	TCEQ	VOC (24-hour canister)
Brazoria	48-039-0618	<u>Danciger</u> <u>Along US Hwy 1459 in</u> <u>Brazoria County</u>	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> Liverpool	EISM	VOC (autoGC)
Galveston	48-167-0005	<u>Texas City, Ball Park</u> 2516 ½ 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	Galveston, 99 th St. 9511 Avenue V ¹ / ₂	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/SVOCs
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 ½ Clinton Dr.	TCEQ	VOC (autoGC), Carbonyls, Metals
Harris	48-201-1034	Houston, East 1262 1/2 Mae Drive	TCEQ	Lead (TSP)
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)

 Table 1. Monitoring Sites Located in TCEQ Region 12

County	EPA Site ID	Site Location	Network	Monitored Compounds
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	48-201-0055	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 ½ Haden Dr.	TCEQ/EISM	VOC (autoGC, 24-hour canister)
Harris	48-201-1049	Pasadena North 702 Light Company Rd.	TCEQ	VOC (24-hour canister)
Galveston	N/A	BP North America Products, IncTexas City 31 st St. (Between Texas Ave. and 5 th Ave.)	TIM	Benzene (autoGC)
Galveston	N/A	BP North America Products, IncTexas City Logan St.	TIM	Benzene (autoGC)
Galveston	N/A	Marathon Petroleum Company, LLC-Texas City 11 st St. S. at 6 th Ave. S.	EPA/DOJAM	Benzene (autoGC)
Montgomery	48-339-0078	<u>Conroe</u> <u>9472A Hwy 1484</u>	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 also meet a 75% data completeness objective. The data collected at the EPA/DOJAM and TIM 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 3-hour

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carbonyl data were evaluated for potential acute health (e.g., irritation) and odor concerns, as were any 24-hour sample results (VOCs, carbonyls, and metals) that exceeded short-term air monitoring comparison values (AMCVs). 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 AMCVs. Information on AMCVs 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- and 3-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 AMCVs. More specifically, about 99.998% of the approximately 3,773,000 1-hour VOC measurements from TCEQ and EISM autoGC monitors in Region 12 in 2010 were below their short-term AMCVs. Approximately 0.0001% of the hourly autoGC measurements collected in Region 12 in 2010 exceeded TCEQ short-term, health-based AMCVs. Approximately 0.002% exceeded odor-based AMCVs, and just over 50% of those occurred at one site (Lynchburg Ferry) in very close proximity to industrial sources and the Houston Ship Channel. Additionally, except for eighteen exceedances of the odor-based AMCV for isovaleraldehyde at Clinton Dr., all of the approximately 4,000 3-hour carbonyl concentrations measured in Region 12 in 2010 were below their respective AMCVs. That is, approximately 99.6% of the 3-hour carbonyl levels were below their respective short-term, health- and odor-based AMCVs. Therefore, we would not expect short-term, adverse health effects or odors to be associated with the vast majority of 1- and 3-hour measurements monitored in Region 12 in 2010.

Further evaluation was conducted for the monitored concentrations that exceeded their respective short-term, health- and/or odor-based AMCVs to determine the potential for adverse health effects or odors. Benzene and isoprene were the only chemicals for which any of the monitored 1-hour concentrations exceeded their respective short-term, health-based AMCVs in 2010. These exceedances occurred only at the Lynchburg Ferry site monitor, where there was one hourly benzene concentration (246.5 parts-per-billion by volume or ppb_v) and three hourly isoprene concentrations (maximum of 27.5 ppb_v) above their short-term, health-based AMCVs of 180 and 20 ppb_v, respectively. This maximum monitored hourly benzene concentration is significantly below benzene levels attributable to short-term, adverse health effects such as central nervous system depression and irritation, with the same being true for isoprene. Therefore, exposure to these 1-hour concentrations would not be expected to cause short-term, adverse health effects. However, as relatively high benzene hourly levels contribute to long-term benzene concern, benzene emissions resulting in significantly elevated short-term levels should be prevented.

The monitored 1-hour autoGC VOC concentrations that exceeded their respective odor-based comparison levels are shown below in Table 2. Compared to the 2009 evaluation, the Deer Park, Lake Jackson, and Wallisville Rd. sites have been added due to a few isoprene odor-based AMCV exceedances. While the total number of odor-based AMCV autoGC exceedances in

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Region 12 in 2010 (75 exceedances) increased compared to 2009 (37 exceedances), the number was less than that in 2008 (82 exceedances) and 2007 (103 exceedances). In regard to 3-hour carbonyl sample results, eighteen 3-hour isovaleraldehyde concentrations $(0.11-0.66 \text{ ppb}_v)$ monitored at the Clinton Dr. site exceeded the odor-based AMCV (0.1 ppb_v), with twelve being less than two times the odor-based AMCV. Two-hundred twenty-one other 3-hour isovaleraldehyde measurements at Clinton Dr. were less than the odor-based AMCV.

Site	Chemical	Number of 1-Hour Concentrations above Odor-Based AMCV	Maximum Measured Concentration (ppb _v)	Odor-Based AMCV (ppb _v)
Danciger	Isoprene	11	9.5	5
Deer Park	Isoprene	1	5.4	5
Haden Rd.	Isoprene	14	10.5	5
Lake Jackson	Isoprene	3	11.4	5
	Styrene	27	265.0	25
Lynchburg Ferry	Isoprene	9	27.5	5
	m- + p-Xylene	2	110.7	41 ^a
Wallisville Rd.	Isoprene	1	10.8	5
Channelview	Isoprene	7	16.1	5

Table 2. Odor-Based AMCV Exceedances by 1-Hour AutoGC VOC Concentrations

^a The lowest of the odor thresholds for m- and p-xylenes.

The relatively high frequency of the monitored odor-based AMCV exceedances for styrene at the Lynchburg Ferry site in 2010 warrants further evaluation and discussion. Although the styrene concentrations monitored at the Lynchburg Ferry site 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). Although no odor-based AMCV exceedances occurred at the Milby Park site in 2010, this site is

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also discussed as it has been of historic interest due to frequent odor-based exceedances for styrene in previous years.

Lynchburg Ferry – Styrene

At the Lynchburg Ferry site, there were 27 hourly styrene concentrations monitored above the odor-based AMCV of 25 ppb_v, with a maximum concentration of 265 ppb_v. This represents an approximate 35% increase in the number of odorous styrene concentrations when compared to 20 such concentrations monitored in 2009 (maximum of 102 ppb_v). However, it represents an approximate 16% decrease in the number of odorous styrene concentrations when compared to 32 such concentrations monitored in 2008 (maximum of 494 ppb_v), a 36% reduction compared to 42 such concentrations in 2007 (maximum of 155 ppb_v), a 48% reduction compared to 52 such concentrations in 2006 (maximum of 358 ppb_v), and a 71% reduction compared to the 92 odorous styrene concentrations monitored for the Lynchburg Ferry site in 2005 (maximum of 433 ppb_v). Thus, overall, there has been a significant improvement in the frequency of styrene odor-based AMCV exceedances over the 2005-2010 period (see Figure 1).



Figure 1. Exceedances of the Styrene Odor-Based AMCV at the Lynchburg Ferry Site

The TD recommends continued efforts to identify sources and reduce styrene emissions in the area. 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 2010, styrene concentrations monitored at the Lynchburg Ferry site were highest when winds were from the north/northeast, although winds from the southeast were also associated with elevated levels based on maximum concentrations (Appendix 2b). The source

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direction evaluation based on 2010 styrene concentrations at this site (Appendices 2a and b) is similar to that contained in previous TD evaluations (i.e., <u>2009 Region 12 data</u>, <u>2008 Region 12 data</u>, <u>2008 Region 12 data</u>, <u>2007 Region 12 data</u>, <u>2006 Region 12 data</u>) in that higher levels are associated with winds from the north/northeast. Additionally, it is similar to the source direction evaluation based on 2003-2010 average styrene concentrations (Appendix 2c) which shows that elevated levels are associated with winds from northerly directions.

The source direction evaluation is also consistent with the Air Pollutant Watch List (APWL) Boundary Work Group identifying the Channel Shipyard facility (located north/northeast of the Lynchburg Ferry monitor) as a major stationary contributor. Consequently, pursuant to a 2009 air permit amendment, efforts are being made at Channel Shipyard to reduce styrene emissions from previously uncontrolled styrene barge degassing operations which could cause elevated offsite impacts. More specifically, Channel Shipyard agreed to minimize the impact of styrene through the installation of a vapor destruction unit at the site's north dock, which is expected to be operational in the near future, and in 2011 Channel Shipyard began controlling all styrene emissions by performing all styrene barge degassing operations at its south dock, which currently has a control device. Channel Shipyard plans to continue this practice until the vapor destruction unit at the north dock is fully operational. Thus far, these efforts appear to be working since only two styrene odor-based AMCV exceedances (maximum of 38.4 ppb_v) have occurred January 1 through June 15, 2011, as compared to nine such exceedances (maximum of 265.0 ppb_y) over the same period in 2010, five such exceedances (maximum of 75.4 ppb_{y}) over the same period in 2009, eleven such exceedances (maximum of 195.3 ppb_v) over the same period in 2008, twelve such exceedances (maximum of 154.9 ppb_v) over the same period in 2007, fourteen such exceedances (maximum of 358.4 ppb_v) over the same period in 2006, and 40 such exceedances (maximum of 210.3 ppb_v) over the same period in 2005. That is, compared to 2005-2010 styrene data for January 1-June 15, the styrene odor-based AMCV exceedance frequency for 2011 has decreased 60-95%.

Although the frequency of odorous styrene concentrations monitored at the Lynchburg Ferry site has generally decreased from 2005 to 2010 and 2011 data may reveal even greater improvement, 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# <u>APWL1204</u>) because of previously monitored odorous conditions, and the 2010 data support styrene remaining on the APWL for this area.

Milby Park - Styrene

Milby Park styrene odor exceedance data for 2010 show obvious improvement compared to previous years (see Figure 2). There were no odorous styrene concentrations monitored at the Milby Park site in 2010 (maximum of 18.3 ppb_v) compared to two odor-based AMCV exceedances in 2009 (maximum of 28.7 ppb_v), 33 exceedances in 2008 (maximum of 69.7 ppb_v), 28 such instances in 2007 (maximum of 49.4 ppb_v), and 16 exceedances in 2006 (maximum of 53.8 ppb_v). Additionally, the maximum 1-hour concentration for 2010 (18.3 ppb_v) is well below those for 2006-2009 (28.7-69.7 ppb_v). Thus, there has been a significant improvement in both the frequency and magnitude of odorous styrene levels at the Milby Park monitor.

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Figure 2. Exceedances of the Styrene Odor-Based AMCV at the Milby Park Site

In previous reviews of annual Region 12 data, the TD has recommended reductions in styrene emissions which contribute to odorous levels measured at the Milby Park site. As mentioned in the evaluation of 2009 Region 12 data, Goodyear took steps during 2008 to address a potential source of the elevated styrene emissions detected at the Milby Park monitor. More specifically, Goodyear altered operational practices, amended their permit to include a 25% reduction in allowable styrene emissions, and signed a voluntary Emissions Reduction Agreement (ERA) with the TCEQ. As a result of these efforts, a decreasing trend in the monitored levels of styrene in Milby Park was evident beginning in 2008 (e.g., there was only 1 exceedence of the odorbased AMCV for styrene from July through December 2008 as compared to 19 exceedances over the same period in 2007). The improvement appears to be persisting as preliminary data indicate there were no exceedances of the styrene odor-based AMCV from January 1 through June 15, 2011. The TD will continue to monitor styrene concentrations at the Milby Park site to determine whether these improvements will be maintained.

24-Hour Concentrations

Two 24-hour Summa canister p-diethylbenzene concentrations in 2010 exceeded the odor-based AMCV for this chemical (0.39 ppb_v), which is reported to have a sweet aromatic odor. The highest 24-hour concentration of p-diethylbenzene measured at the Pasadena North site (0.56 ppb_v) exceeded the odor-based value. The Pasadena North site is located in a heavily industrialized area. The highest 24-hour level monitored at the Manchester site (0.68 ppb_v), which is in a residential area, also exceeded the odor-based AMCV. While the p-diethylbenzene concentrations monitored at the Manchester site would not be expected to cause direct acute

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health effects, the perception of sufficiently strong and persistent unpleasant odors has the potential to cause odor-related health effects (e.g., nausea, headache).

Annual Average Concentrations

Notably, in 2010, all annual averages were below their respective long-term AMCVs for the first time in many years of sampling in Region 12:

- Based on the approximately 5,500 24-hour metals measurements, all monitored annual average concentrations of metals were below their respective long-term AMCVs or NAAQS (lead only);
- Based on the approximately 1,700 24-hour measurements, all annual average concentrations of carbonyls were also below their respective long-term AMCVs;
- Based on approximately 1,700 24-hour measurements, all annual average concentrations for PAHs/SVOCs were below long-term AMCVs; and
- Based on averages from approximately 82,500 24-hour canister measurements and approximately 3,773,000 hourly autoGC measurements (not counting over 19,000 measurements from three industry-sponsored autoGC sites (one EPA/DOJAM and two TIM)), all annual VOC concentrations were also less than their respective long-term AMCVs.

Thus, 100% of all annual averages were below their respective long-term, health-based AMCVs and no long-term, adverse health effects would be expected due to exposure to those concentrations. However, sites of ongoing agency and/or public interest for monitored annual benzene concentrations are discussed below.

Lynchburg Ferry - Benzene

The monitored 2010 annual average benzene concentration based on hourly samples collected at the autoGC at the Lynchburg Ferry site was 0.83 ppb_v. The annual average at the co-located, every sixth-day 24-hour canister sample site was 1.1 ppb_v. However, the annual average based on hourly autoGC samples (0.83 ppb_v) more accurately represents the long-term average in 2010 as it analyzed 7,245 hourly measurements in 2010 (83% of the year) compared to 57 valid canister samples covering only 1,368 hours (16%) of the year, providing over 5 times more temporal coverage. The annual average is below the long-term, health-based AMCV (1.4 ppb_v) for the third time since monitoring began at the Lynchburg Ferry site in 2003 (see Figure 3). The 2009 and 2008 annual averages of 0.89 and 1.1 ppb_v, respectively, were also below the long-term AMCV. This represents a significant improvement in air quality and is likely the result of significant efforts in the area by the TCEQ (e.g., focused agency resources, special investigations utilizing the latest technology, enhanced compliance and enforcement, source directionality evaluations), industry (e.g., ERAs, Monument Area Air Quality Focus Group), and others (e.g., US Coast Guard). The 2010 annual benzene average of 0.83 ppbv (autoGC) represents an approximate reduction of 7% when compared to the 2009 annual average, about a 25% reduction when compared to the 2008 annual average, an approximate reduction of 45% when compared to the 2007 annual average, an approximate 65% reduction compared to the 2006 annual average, and an approximate 74% reduction compared to the 2005 annual average. This downward trend in annual benzene concentrations at the Lynchburg Ferry site is clearly evident (see Figure 3).

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Figure 3. Annual Average Benzene Concentrations at the Lynchburg Ferry Site

Preliminary autoGC data for 2011 suggest that benzene concentrations in the Lynchburg Ferry area may be somewhat lower than those in 2010, although it is too early in the year to determine how the annual averages will ultimately compare. The preliminary 2011 January 1 through June 15 average of autoGC benzene measurements is 0.50 ppb_v compared to 0.84 ppb_v over the same period in 2010. Again, the significant decrease in annual averages over the past several years is likely attributable to TCEQ activities and other initiatives in the Lynchburg Ferry area.

TCEQ Region 12 staff report that activities in 2010 in the Lynchburg Ferry area included, but were not limited to, the following:

- Special investigations when relatively high levels of benzene were detected by area monitors. In response to benzene trigger level exceedances (1-hour levels $\geq 75 \text{ ppb}_v$) at the Lynchburg Ferry monitoring site, Region 12 staff reviewed air concentration and meteorological data to identify potential sources, which often resulted in focused facility investigations.
 - Region 12 air investigators conducted enhanced investigations at Channel Shipyard and Southwest Shipyard, which included the use of the GasFindIR camera.
 - Two Notices of Violation (NOV) were issued during two investigations at Channel Shipyard.

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- Compliance investigations were also conducted at Southwest Shipyard. One NOV and one Notice of Enforcement (NOE) were issued.
- Combinations of reconnaissance investigations, compliance investigations, stack sampling reviews, and emission event investigations at Vopak Terminals and Intercontinental Terminals.
 - ▶ In 2010, one NOE and one NOV were issued to Vopak.
 - > In 2010, two NOEs and two NOVs were issued to Intercontinental Terminals.
 - A 2010 review of the Permit Compliance Certification (PCC) conducted for Vopak Terminals resulted in the issuance of violations that included:
 - Failure to seal open ended lines;
 - Failure to employ approved standards following tank roof landing;
 - Failure to maintain the pilot on the flare; and
 - Failure to maintain records of VOC emissions from tanks and from loading and unloading operations.
 - A 2010 review of the PCC conducted for Intercontinental Terminals resulted in the issuance of violations that included:
 - Failure to operate leak free operations during all land-based loading and unloading operations;
 - Failure to operate leak free operations during marine vessels for loading operations; and
 - Failure to conduct a ten year inspection of Tank 12-26.
- Cooperative efforts with Region 12, TCEQ Pollution Prevention (PP), and the US Coast Guard (USCG) to identify sources of monitored benzene spikes (5-minute concentrations ≥ 50 ppb_v) which could be related to barges in transit on the Houston Ship Channel. When short-term benzene spikes were monitored at the Lynchburg Ferry auto-GC from a wind direction associated with marine transit, an e-mail alert was sent to both TCEQ and USCG staff. The USCG utilized radar tracking information to identify the tug boat(s) in operation near the monitor at the time of the spike and PP staff then contacted the owner(s) to determine if any benzene-containing materials were being transported at the time. This effort raised awareness of the potential impact of emissions from barges and resulted in better adherence to emission reduction plans implemented by barge owners, tug and tow operators, and area industries.
- Reconnaissance investigations with the GasFindIR camera. These investigations were performed approximately every six weeks in the south Houston Ship Channel area along Battleground Road/Independence Highway.

As indicated in several previous annual reviews of Region 12 air data, several Lynchburg Ferry area industrial facilities previously formed the Monument Area Air Quality Focus Group (MAAQFG) in a collaborative attempt to reduce benzene emissions. An automatic alert is sent to the TCEQ and the MAAQFG when hourly benzene levels at the Lynchburg Ferry monitor exceed an hourly benzene trigger concentration ($\geq 75 \text{ ppb}_v$). These triggers initiate investigations by MAAQFG members and TCEQ and continue to create timely awareness of benzene emissions. The TCEQ continues to work collaboratively with both the MAAQFG and the USCG to identify and mitigate potential sources of benzene emissions from both barges in transit and stationary sources. Annual benzene concentrations and the number of 5-minute trigger

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notifications have decreased over time at the Lynchburg Ferry site, which indicate that efforts in this area have been successful.

As a result of successful collaborative efforts to significantly decrease ambient benzene concentrations, benzene was removed from the Lynchburg Ferry APWL area (Site# APWL1204) in 2010. However, the TD will continue to monitor benzene concentrations in the Lynchburg Ferry area to determine whether annual benzene concentrations remain below the long-term AMCV such that the long-term site average based on all available years of data combined eventually meets the long-term AMCV (1.4 ppb_y). Although the long-term site average is currently 1.75 ppb_v based on 7 complete years of data (2004-2010), it is important to note that the long-term AMCV for benzene is a lifetime (e.g., 70-year) average-concentration comparison value and in no way represents a distinct demarcation between where adverse long-term health effects would and would not be expected to occur, so comparison to a 7-year site average is conservative. Additionally, 120 ppb_v is the approximate continuous lifetime environmental exposure concentration corresponding to the lowest level of benzene exposure for which the EPA has indicated that they are fairly confident as being associated with increased cancer risk (40 ppm_v-years of occupational exposure). Thus, although somewhat above the long-term (i.e., lifetime) AMCV, exposure to the 7-year site average (1.75 ppb_v) for a lifetime would result in a cumulative exposure level that is about 69 times less than that identified by the EPA as being associated with elevated benzene cancer (e.g., AML) risk. Similar statements would apply to the evaluation of long-term site benzene averages at the Galena Park (13-year mean of 1.48 ppb_v) and Marathon 11th St. (6-year mean of 1.8 ppb_v) sites, which are discussed below.

Galena Park - Benzene

The monitored 2010 average benzene concentration based on every sixth-day 24-hour canister samples at the Galena Park site was 1.1 ppb_v, and is below the long-term, health-based AMCV (1.4 ppb_v) for the third time in several years (see Figure 4). The 2009 and 2008 annual averages of 0.82 and 1.3 ppb_v, respectively, were also below the long-term AMCV. The 2008-2010 averages represent a significant improvement in air quality that is likely the result of significant efforts in the area by the 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 previously entered into by the TCEQ with several facilities identified during an earlier Find-and-Fix investigation (Kinder Morgan Terminals, Vopak Terminals, TEPPCO Pipeline) to reduce VOCs, including benzene. While the 2010 average (1.1 ppb_v or 1.06 ppb_v unrounded) is approximately 29% higher than the 2009 average of 0.82 ppb_v, it is approximately 15% lower than the 2008 annual average of 1.3 ppb_v, 35% lower than the 2007 annual average of 1.7 ppb_v, 31% lower than the 2006 annual average of 1.6 ppb_v.

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Figure 4. Annual Average Benzene Concentrations at the Galena Park Site

TCEQ efforts in the Galena Park area have been significant, and the 2008-2010 annual benzene averages appear to suggest an overall downward trend. However, while the 2008-2010 annual average benzene concentrations at the Galena Park site were below the long-term AMCV, annual averages at the site have historically fluctuated above and below the AMCV (Figure 4). Thus, this area will remain on the APWL (Site# <u>APWL1206</u>). Since there are residences located appreciably closer to nearby industry than the monitor (i.e., there are homes between industry and the monitor), the TD recommends a continued effort to control and/or reduce benzene emissions in the area of the Galena Park site, and will continue to monitor benzene levels at this site to determine whether annual benzene concentrations remain appreciably below the long-term AMCV. If so, the long-term site average based on all available years of data combined (currently a 13-year mean of 1.48 ppb_v based on 1998-2010 data) will eventually meet the long-term (i.e., 70-year) AMCV (1.4 ppb_v).

TCEQ activities in 2010 in the Galena Park area included, but were not limited to, the following:

- Periodic focused investigations and GasFindIR reconnaissance investigations.
- Three NOVs were issued to Pasadena Refining Systems. In addition, a full on-site compliance investigation was conducted for the entire Pasadena Refining Systems site and resulted in 54 total violations.
 - There were 19 violations associated with an NOE and 35 violations associated with an NOV, including multiple violations related to emissions from flares.

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- Compliance investigations, emission event investigations, and a leak detection and repair (LDAR) investigation at Houston Refining resulted in the issuance of seven NOEs which included a total of 24 violations.
- Compliance investigations, emission event investigations, and a leak detection and repair (LDAR) investigation at Valero Houston Refinery resulted in the issuance of two NOEs, which included three violations.

The TCEQ has also continued to work cooperatively with industry in the area to help identify benzene sources of interest. For example, in August 2010, two fence line benzene-specific autoGCs became operational at the Kinder Morgan (KM) Galena Park Terminal. The monitors were installed under a cooperative agreement with KM in order to collect continuous, real-time benzene concentration data for a period of one year. Data from these monitors were shared with TCEQ and triggered alert messages when concentrations exceeded a set threshold. For each trigger, KM conducted an in-house investigation of the potential cause and provided a report to Region 12. Approximately 16 triggers were received between August 2010 and June 2011. An analysis of wind trajectories associated with the triggers was used to identify potential sources (e.g., KM loading/unloading operations) which may be impacting the Galena Park monitoring site. While this fence line monitoring project is scheduled to end in August 2011, data obtained during the course of the project will be evaluated to determine what, if any, subsequent actions need to be taken.

The TCEQ will continue to use information from various investigations, fixed-site monitoring, and the latest technology (GasFindIR) to aid in the identification of sources and reduction of benzene emissions impacting the Galena Park area.

Texas City Marathon-Sponsored 11th 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. Marathon then collected data at the site from January 30, 2006, to January 31, 2007, under a benzene emission investigation plan with the TCEQ and EPA. Marathon again began collecting benzene data at the site on April 1, 2007, per an agreement with the EPA and the US Department of Justice (DOJ). Then on November 5, 2007, the site was moved 1 block north to the corner of 11th St. S. and 6th Ave. S. Although the site was deactivated on December 31, 2010, a new agreement between Marathon and EPA was established for the 11th St. S. monitor with an effective date of July 1, 2011.

In 2010, for the first time since monitoring began, the annual average benzene concentration measured at the Marathon-sponsored site (0.92 ppb_v) met TCEQ's long-term AMCV (1.4 ppb_v) (see Figure 6). The 2010 average represents a 49-58% reduction compared to the 2005-2009 averages $(1.8-2.2 \text{ ppb}_v)$.

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Figure 6. Annual Average Benzene Concentrations at the Marathon-Sponsored 11th St. S. Site

TCEQ activities in 2010 related to benzene in Texas City included, but were not limited to, the following:

- Focused investigations and reconnaissance investigations in the Texas City area to address on-going issues discovered through use of GasFindIR or through visual observations. Fence-line reconnaissance investigations during normal business hours and at night.
- At the BP Texas City Refinery in 2010:
 - > There were 21 NOEs and five NOVs issued.
 - A full site inspection was conducted at the BP Texas City refinery from May 26 through June 14, 2010. A total of 49 violations were identified with 17 violations associated with an NOE, and 32 violations associated with an NOV. The violations cited included:
 - Failure to inspect and/or repair tank seals;
 - Exceeding NO_X, CO, SO₂ and ammonia emission limits;
 - Failure to operate NO_X, CO, SO₂ and HRVOC analyzers;
 - Failure to seal open ended lines;
 - Failure to monitor pumps, connectors and valves; and
 - Failure to conduct stack testing.
 - The BP Texas City Refinery was also issued an NOE along with an Excessive Emission Event determination for Incident 138052 which began on April 6, 2010

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and ended May 16, 2010. The event resulted in the release of over 500,000 lbs of emissions including over 17,000 lbs of benzene.

- Additionally, one NOV was issued to BP Chemical in 2010 as a result of a 2009 compliance investigation.
- During 2010, a full compliance investigation conducted at Marathon resulted in the issuance of an NOV and an NOE. As a result, 22 violations were cited and included:
 - Failure to maintain flare pilot lights;
 - ➢ Failure to maintain with a cap or plug open end lines;
 - Failure to maintain a minimum of 300 BTU/scf on P-1; and
 - Failure to maintain a temperature of at least 1400 degrees F within the wastewater thermal oxidizer.
- Other compliance investigations in 2010 resulted in the issuance of six NOVs and two NOEs in 2010.

The area of Texas City located south of State Highway 1765, which contains this Marathonsponsored site, is currently on the APWL (Site# <u>APWL1202</u>) for elevated long-term concentrations of benzene. Although the 2010 benzene average at the 11th St. S. site was below the long-term AMCV, this area will remain on the APWL until the TD has determined that reduced benzene concentrations in the area are maintained. Future agency activities should continue to help ensure continued compliance with the long-term AMCV.

Texas City BP-Sponsored Site-Benzene

The BP-sponsored 31st St. site monitor (and a BP on-site monitor) was previously operated under a BP agreement with the TCEQ. However, in 2009, BP entered into a Temporary Injunction with the Attorney General's Office (No. D-1-GV-09-000921) which required BP to operate the two existing monitors and an additional monitor (the Logan St. monitor) which began operating in April 2010. The BP-sponsored 31st St. site monitor is discussed here because of continued interest due to historical long-term AMCV exceedances for benzene.

Annual average benzene concentrations at the BP-sponsored 31st St. site in Texas City have declined significantly from 2005 to 2010 (see Figure 7). The monitored 2010 average benzene concentration at the site (0.42 ppb_v) is well below the long-term AMCV (1.4 ppb_v) . It is approximately 70% lower than the 2009 average, 48% lower than the 2008 average, 58% lower than the 2007 average, 75% lower than the 2006 average, and 84% lower than the 2005 average. Additionally, the long-term site average (7-year mean of 1.4 ppb_v based on 2004-2010 complete years of data) does not exceed the long-term (i.e., 70-year) AMCV.

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

The area of Texas City which contains the BP-sponsored 31st St. site is currently on the same APWL as the Marathon-sponsored site (Site# <u>APWL1202</u>) for elevated long-term concentrations of benzene monitored in previous years. The TD recommends continued efforts so that the long-term AMCV will continue to be met at the BP-sponsored 31st St. site. Please see the *Texas City Marathon-Sponsored 11th St. S. Site-Benzene* section above for information regarding TCEQ activities in 2010 related to benzene in Texas City. This area (Site# <u>APWL1202</u>) will remain on the APWL until the TD has determined that reduced benzene concentrations in the area are maintained.

If you have any questions regarding this memorandum, please contact me by phone at (512) 239-5691 or by email at <u>Joseph.Haney@tceq.texas.gov</u>. For questions regarding the APWL, you may visit the TCEQ website at

http://www.tceq.state.tx.us/implementation/tox/AirPollutantMain/APWL_index.html.

Appendix 1. Monitored Air Toxics in Region 12 in 2010

1,1,2,2-Tetrachloroethane	Bromomethane	Methylcyclohexane
1,1,2-Trichloroethane	c-1,3-Dichloropropylene	Methylcyclopentane
1,1-Dichloroethane	c-2-Butene	m-Ethyltoluene
1,1-Dichloroethylene	c-2-Hexene	n-Butane
1,2,3-Trimethylbenzene	c-2-Pentene	n-Decane
1,2,4-Trimethylbenzene	Carbon Tetrachloride	n-Heptane
1,2-Dichloropropane	Chlorobenzene	n-Hexane
1,3,5-Trimethylbenzene	Chloroform	n-Nonane
1,3-Butadiene	Chloromethane (Methyl	n-Octane
1-Butene	Chloride)	n-Pentane
1-Hexene + 2-Methyl-1-Pentene	Cyclohexane	n-Propylbenzene
1-Pentene	Cyclopentane	n-Undecane
2,2,4-Trimethylpentane	Cyclopentene	o-Ethyltoluene
2,2-Dimethylbutane	Dichlorodifluoromethane	o-Xylene
(Neohexane)	Dichloromethane (Methylene	p-Diethylbenzene
2,3,4-Trimethylpentane	Chloride)	p-Ethyltoluene
2,3-Dimethylbutane	Ethane	Propane
2,3-Dimethylpentane	Ethyl Benzene	Propylene
2,4-Dimethylpentane	Ethylene	Styrene
2-Chloropentane	Ethylene Dibromide (1,2-	t-1,3-Dichloropropylene
2-Methyl-2-Butene	Dibromoethane)	t-2-Butene
2-Methylheptane	Ethylene Dichloride (1,2-	t-2-Hexene
2-Methylhexane	Dichloroethane)	t-2-Pentene
2-Methylpentane (Isohexane)	Isobutane	Tetrachloroethylene
3-Methyl-1-Butene	Isopentane (2-Methylbutane)	Toluene
3-Methylheptane	Isoprene	Trichloroethylene
3-Methylhexane	Isopropylbenzene (Cumene)	Trichlorofluoromethane
3-Methylpentane	m & p-Xylene	Vinyl Chloride
4-Methyl-1-Pentene	m-Diethylbenzene	
Acetylene	Methyl Chloroform (1,1,1-	
Benzene	Trichloroethane)	

List 1. Target VOC Analytes in Canister Samples

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List 2. Target Carbonyl Analytes

2,5-Dimethylbenzaldehyde	Formaldehyde	o-Tolualdehyde
Acetaldehyde	Heptaldehyde	Propanal - Propionaldehyde
Acetone	Hexanaldehyde	p-Tolualdehyde
Acrolein	Isovaleraldehyde	Valeraldehyde
Benzaldehyde	Methyl Ethyl Ketone	
Butyraldehyde	(MEK)/Methacrolein	
Crotonaldehyde - 2-Butenal	m-Tolualdehyde	

List 3. Target Metal Analytes

Aluminum (PM _{2.5} , PM ₁₀)	Chromium VI (TSP)*	Nickel ($PM_{2.5}$, PM_{10})
Antimony (PM _{2.5} , PM ₁₀)	Cobalt (PM _{2.5} , PM ₁₀)	Selenium (PM _{2.5} , PM ₁₀)
Arsenic (PM _{2.5} , PM ₁₀)	Copper ($PM_{2.5}$, PM_{10})	Tin (PM _{2.5} , PM ₁₀)
Barium ($PM_{2.5}$, PM_{10})	Lead (PM _{2.5} , PM ₁₀ , TSP)	Zinc (PM _{2.5} , PM ₁₀)
Cadmium (PM _{2.5} , PM ₁₀)	Manganese (PM _{2.5} , PM ₁₀)	
Chromium (PM _{2.5} , PM ₁₀)	Molybdenum (PM _{2.5} , PM ₁₀)	

*Only monitored at the Deer Park monitoring site; TSP = total suspended particulate.

List 4. Target PAH Analytes

Acenaphthene Acenaphthylene Anthracene Benzo(a)anthracene Benzo(a)pyrene Benzo(b)fluoranthene Benzo(g,h,i)perylene Benzo(k)fluoranthene Chrysene Dibenzo(a,h)anthracene Fluoranthene Fluorene Indeno(1,2,3-cd)pyrene Naphthalene Phenanthrene Pyrene Linda Vasse, Division Director, Region 12, et al. July 27, 2011 Page 21 of 25

1-Butene
1-Pentene
1,2,3-Trimethylbenzene
1,2,4-Trimethylbenzene
1,3-Butadiene
1,3,5-Trimethylbenzene
2-Methyl-2-Butene*
2-Methylheptane
2-Methylhexane
2,2-Dimethylbutane
2,2,4-Trimethylpentane
2,3-Dimethylpentane
2,3,4-Trimethylpentane
2,4-Dimethylpentane
3-Methylheptane
3-Methylhexane
Acetylene
-

Benzene c-2-Butene c-2-Pentene Cyclohexane Cyclopentane Ethane Ethyl Benzene Ethylene Isobutane Isopentane Isoprene Isopropyl Benzene -Cumene Methylcyclohexane Methylcyclopentane n-Butane n-Decane

n-Heptane n-Hexane n-Nonane n-Octane n-Pentane n-Propylbenzene n-Undecane* o-Xylene p-Xylene + m-Xylene Propane Propylene Styrene t-2-Butene t-2-Pentene Toluene

*Only monitored at the Danciger, Lake Jackson, Texas City 34th St., Wallisville Rd., Haden Rd., and Lynchburg Ferry monitoring site. Linda Vasse, Division Director, Region 12, et al. July 27, 2011 Page 22 of 25

Appendix 2a. Source Direction Evaluation of Styrene Average Concentrations (2010) at the Lynchburg Ferry Site



Appendix 2b. Source Direction Evaluation of Styrene Maximum Concentrations (2010) at the Lynchburg Ferry Site



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Appendix 2c. Source Direction Evaluation of Styrene Average Concentrations (2003-2010) at the Lynchburg Ferry Site



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cc:

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