Meteorological Conditions and Associated Temporal Trends in Total Non-Methane Hydrocarbon and Benzene Concentrations in the Corpus Christi Area

2008-2010 REPORT
The Neighborhood Air Toxics Modeling Project for Houston and Corpus Christi

Prepared for
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U.S. District Court, Southern District of Texas
Corpus Christi, Texas

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1. Introduction

A conceptual model was developed that describes the seasonality, day-of-week, and diurnal variability of concentrations of selected air toxics measured at ground monitoring stations located in the vicinity of the industrialized Corpus Christi Ship Channel. The conceptual model also describes meteorological conditions (e.g., seasonal temperatures, wind speeds, wind directions, frontal passages and other parameters) that are most likely to lead to higher concentrations of air toxics at these sites. The results of the conceptual model are important for the selection of historical periods that can be used to develop and test the air quality modeling tools developed for the Corpus Christi area. Additionally, the conceptual model identifies geographic areas that potentially contain emissions sources that impact air quality in the region. This report describes the methodology used for the development of the conceptual model and key findings.

1.1 The Corpus Christi Air Monitoring and Surveillance Camera Installation and Operation Project (CCQAP)

The development of the air toxics conceptual model for this study is primarily based on hourly measurements collected at the seven air quality monitoring stations maintained and operated by The University of Texas at Austin (UT) in support of the Corpus Christi Air Monitoring and Surveillance Camera Installation and Operation Project (CCAQP). A map of the Corpus Christi area showing the locations of the seven UT monitoring stations is provided in Figure 1-1. The monitoring stations were installed to measure pollutant concentrations throughout the industrialized Ship Channel area. The measurements collected at one or more monitoring stations include sulfur compounds (hydrogen sulfide and sulfur dioxide), total non-methane hydrocarbon compounds (TNMHC) and methane, and volatile organic compounds (VOC). In addition, meteorological observations of wind speed, wind direction, temperature, and relative humidity are collected at all UT monitoring stations. Figure 1-1 also provides the locations of the five Continuous Air Monitoring Stations (CAMS) maintained and operated by the Texas Commission on Environmental Quality (TCEQ). The CAMS network was previously established by TCEQ to fulfill urban air monitoring requirements as specified by EPA. Additional information on the CCAQP monitoring network can be found at the Corpus Christi Air Quality Project website (http://www.utexas.edu/research/ceer/ccaqp/).

Figure 1. Monitoring station locations.

1.2 Pollutants Analyzed for the Corpus Christi Air Toxics Conceptual Model

The conceptual model provided in this report relies heavily on an analysis of TNMHC concentrations to describe the spatial and temporal variability of air pollutant concentrations in the Ship Channel area. Emissions associated with industrial facilities in Corpus Christi comprise a large number of hydrocarbon compounds. The CCAQP measures TNMHC continuously at each of the seven monitoring to capture a broad range of hydrocarbon species. The measurement of high TNMHC concentrations is expected to be correlated with high concentrations of air toxic compounds that impact human health. The CCAQP network design provides the flexibility to trigger the collection of VOC canister samples during high TNMHC events. The canister samples are analyzed for a list of target compounds including air toxics of interest in the Corpus Christi area.

In addition to the TNMHC measurements, the Solar Estates and Oak Park monitoring stations are equipped with automated gas chromatographs (autoGCs) that continuously analyze for approximately 55 VOC compounds. The autoGC target compound list includes the air toxic pollutant benzene. The current conceptual model incorporates an initial analysis for benzene as a first step towards investigating air toxics that may impact human health in populated areas. Benzene was selected because of the importance to air quality in Corpus Christi associated with emissions from Ship Channel industrial facilities, notably the petroleum refining industry, and the recognized importance to human health risk and exposure assessments. Future versions of this conceptual model may include additional air toxics that have the potential to impact human health.

1.3 Previous Air Toxics Conceptual Models

Previous studies have identified seasonal patterns at selected sites or regions (e.g., Singh et al., 1992). The collection of sub-daily (e.g., 1-hour and 3-hour) samples to investigate diurnal patterns is limited, and is available on a national basis primarily in support of the photochemical assessment monitoring stations (PAMS) program (Demerjian, 2000; Main et al., 1998). Previous studies have investigated the diurnal variability of selected VOCs at selected sites or regions of the US (Singh et al., Spicer et al., 1996; Bortnick and Stetzer, 2002). Of particular interest to the conceptual model presented in this report, Reiss (2006) investigated the temporal and spatial variability of benzene and 1,3-butadiene using measurements collected during 1997 - 2004 in Houston, Texas. Although active monitoring stations during 1997 – 2004 were located throughout the Greater Houston Area, the majority of stations were located to the east of downtown Houston in the industrialized Ship Channel area. The network average benzene concentration averaged 0.93 ppbV with a factor of two variability between stations. For 1,3-butadiene, the network average was 0.57 ppbV with a factor of six variability. While individual sites were subject to large variability, the network average 1,3-butadiene concentrations showed little seasonality, while benzene was characterized by higher concentrations during winter. Investigation of the diurnal profiles indicated little weekend/weekday differences with the exception of the early morning rush hour period where weekday concentrations were slightly higher.

Recent national studies by Touma et al. (2006) and McCarthy et al. (2007) have analyzed data obtained from EPA's air quality system (AQS) to perform a comprehensive analysis of the diurnal and seasonal variability for air toxics compounds. AQS primarily archives concentration data ranging from 1-hour to 24-hours in duration collected at urban monitoring stations throughout the US. With regard to diurnal variability, both Touma et al. (2006) and McCarthy et al. (2007) identified air toxics with invariant, nighttime peak, morning peak, or daytime peak patterns. Compounds such as benzene and 1,3-butadiene were characterized by a meteorologically driven nighttime peak and a morning rush hour peak. Highly reactive hydrocarbon compounds, such as acetaldehyde and formaldehyde, were often characterized by a daytime peak, indicating production is likely driven by solar radiation and hydroxyl radical concentrations that reach maximum concentrations during midday.

Seasonal patterns were identified by the Touma et al. (2006) and McCarthy et al. (2007) studies as invariant, cool, or warm. Warm season species included acetaldehyde and formaldehyde, while concentrations of species such as benzene and 1,3-butadiene were typically greatest during the cool season. The cool season was characterized by the highest concentrations for a majority of the hydrocarbon air toxic compounds analyzed. In addition to meteorological conditions during the cool season more often favoring the accumulation of pollutants near the surface and lower removal rates by atmospheric oxidants, both studies suggested that some air toxics may be characterized by higher emissions during the winter months. Touma et al. (2006) and McCarthy et al. (2007) also noted that pollutants with the highest seasonal variability exhibited a factor-of-two difference (on average) in concentrations by season.

1.4 Future Development of the Corpus Christi Air Toxics Conceptual Model

This initial version of the air toxics conceptual model represents the first summary of its type utilizing the extensive data of the CCAQP and provides an important foundation for understanding air toxics concentrations in the region. It is expected that the conceptual model will be subject to continuing updates and enhancements. Future updates will likely address analyses for additional air toxic pollutants. It is also anticipated that on-going development of the air toxics emissions inventory and modeling tools will lead to specific investigation of important meteorological phenomena that impact air toxic concentrations not presented in the initial version of this report (e.g., impact of sea/bay breezes, urban heat island effects). In general, the air toxics conceptual model will be updated periodically to support project needs as they arise and to further test and verify the robustness of the existing results.

1.5 Report Layout

Section 2 presents a summary of the data and software tools used to develop the air toxics conceptual model for Corpus Christi. Summaries of the results for TNMHC and benzene are presented in Section 3 and Section 4, respectively. References are provided in Section 5. Appendix A and Appendix B provide the complete by-site analyses for TNMHC and benzene, respectively.

2. Data Sources

The hourly measurements collected during June 2005 – May 2008 at the seven CCAQP air quality monitoring stations provided the primary dataset used to develop the air toxics conceptual model for Corpus Christi. The Corpus Christi Trajectory Analysis Tool was used to analyze surface winds during air toxics events of interest. Regional transport was investigated using the National Oceanic and Atmospheric Administration (NOAA) back-trajectory models provided by the Earth System Research Laboratory (ESRL) and HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory). Surface weather maps, upper air charts, and infrared satellite images obtained from UNYSIS (http://weather.unisys.com) and/or NOAA were used to analyze the prevailing large-scale weather patterns. Measurements collected at National Weather Service (NWS) stations and CAMS in Texas were used to investigate local meteorological conditions. Each of these data sources is described in more detail below.

2.1 Corpus Christi Air Quality Project (CCAQP) Monitoring Data

UT operates seven air quality monitoring stations along the Corpus Christi Ship Channel in support of the CCAQP. Data collected at one or more monitoring stations include hydrogen sulfide (total reduced sulfur), sulfur dioxide, TNMHC, and meteorological (e.g., temperature, wind speed, wind direction, and relative humidity) measurements. In addition, hourly measurements of speciated volatile organic compounds (VOCs), including benzene, are collected continuously at the Oak Park and Solar Estates monitoring stations using autoGCs. Table 2-1 presents a summary of identification and geographic data for the CCAQP monitoring stations, including the suite of measurements used for the analyses presented in this report. (For a further description of these measurement data, the reader is referred to the CCAQP website at http://www.utexas.edu/research/ceer/ccaqp/index.html.)

Figure 2-1 provides a map showing the station locations along the Corpus Christi Ship Channel. Figure 2-1 also shows the locations of industrial facilities that are characterized by non-zero VOC emissions as contained in the 2005 Photochemical Modeling EI, which was obtained by Dr. David Sullivan of UT upon request to TCEQ. The property line boundaries for the industrial facilities are based on shape file data provided by Robert Opeila (TCEQ) to Dave Sullivan (UT) on October 6, 2008. The figure includes the locations of docks and terminals along the Ship Channel that may be used for ship loading and unloading operations.

Table 2-1. Descriptions and locations of CCAQP monitoring stations.

Monitor Name	CAMS #	AIRS ID	Address	Measurements
Port Grain	629	48-355-0036	2001B East Navigation Blvd.	Sulfur Compounds, Met, TNMHC
J. I. Hailey	630	48-355-0037	2702B East Navigation Blvd.	Sulfur Compounds, Met, TNMHC
West End Harbor	631	48-355-0038	3149B Suntide Rd.	Sulfur Compounds, Met, TNMHC
FHR Easement	632	48-355-0039	8401B Up River Rd.	Sulfur Compounds, Met, TNMHC
Solar Estates	633	48-355-0041	9122 Leopard St.	AutoGC, Sulfur Compounds, Met, TNMHC, Camera
Oak Park	634	48-355-0035	842 Erwin St.	AutoGC, Sulfur Compounds, Met, TNMHC
Dona Park	635	48-355-0034	5707 Up River Rd.	Sulfur Compounds, Met, TNMHC, Camera

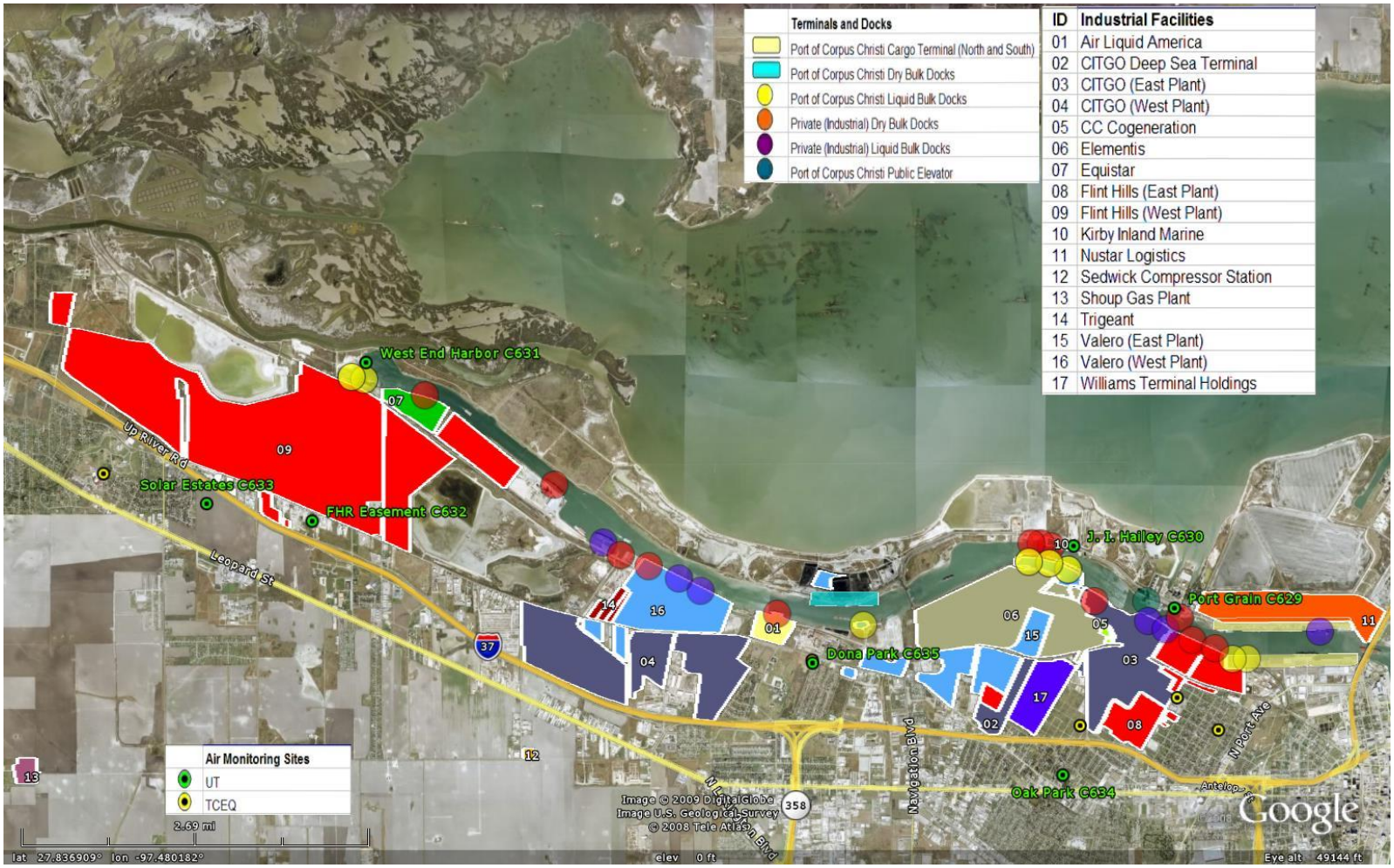

Figure 2-1. Locations of the seven CCAQP (UT) monitoring stations. The Ship Channel is located along the middle portion of map. Figure 2-1 includes the locations of industrial facilities that are characterized by non-zero VOC emissions in the 2005 TCEQ Photochemical Modeling EI. The figure also shows the locations of docks and terminals that may be used for ship loading/unloading operations.

2.1.1 TNMHC Measurements and Event-Triggered Canister Sampling

The conceptual model provided in this report relies heavily on an analysis of TNMHC concentrations to describe the spatial and temporal variability of air pollutant concentrations in the Ship Channel area. CCAQP uses the Thermo Electron Co (TECO) Model 55C Methane/Total non-methane analyzer to measure TNMHC concentrations because of its sensitivity at low concentration ranges and its fast 90-second cycle time. Refinery emissions are known to comprise a large number of hydrocarbon species (e.g., C2-C9 alkanes and alkenes, C6-C8 aromatics) and the TNMHC measurements provide a surrogate for a broad range of species.

The CCAQP network design provides the flexibility to trigger the collection of VOC canister samples during high TNMHC events. The TECO 55C was implemented to average 90-second observations to 5 minute averages for reporting purposes. However, the data-logger monitors the 90-second values, and if 10 consecutive values (900 seconds, or 15 minutes) are at or above 2000 ppbC, a 20-minute integrated canister sample is triggered. These event-triggered canister samples are analyzed by UT for a list of target compounds including air toxics of interest in the Corpus Christi area. These canister results have not been included in this report. This is partially because this initial conceptual model focuses on a statistical overview of all measurement data collected across the seven CCAQP monitoring stations throughout June 2005 – May 2008 as opposed to analyses of individual case studies. In addition, the collection of event-triggered samples has occurred relatively infrequently. It is anticipated that future versions of the conceptual model will incorporate the event-triggered canister results as appropriate.

2.1.2 Data Completeness

Table 2-2 presents the data completeness for hourly measurements collected during June 2005 – May 2008 at the seven CCAQP monitoring stations. The TNMHC measurement completeness ranges from 87.9% at Oak Park to 95.3% at FHR Easement. Benzene data completeness at the Solar Estates and Oak Park monitoring stations was 76.5% and 86.1%, respectively. Figures 2-2 and 2-3 present the monthly TNMHC and benzene data completeness, respectively, for each monitoring station during June 2005 - May 2008. The latter portion of 2005 is characterized by a relatively high number of TNMHC monthly capture values below 85% compared to other periods, including near-zero data capture for the October/November 2005 period at the Oak Park monitoring station. Figure 2-3 shows that the benzene data completeness at Solar Estates is less than 50% for August 2005, March 2006, April 2007, and September 2007. Table 2-2 indicates excellent overall data capture for meteorological parameters at all monitoring stations, with a minimum data completeness of 97.7% for relative humidity at West End Harbor.

Table 2-2. Percent data completeness during June 2005 - May 2008 (26304 possible hours) for hourly measurements collected at the seven CCAQP monitoring stations.

Station	TNMHC	Benzene	Temperature	Winds	Relative Humidity
Port Grain (C629)	92.8%	NA	99.0%	98.5%	99.3%
J. I. Hailey (C630)	93.8%	NA	98.1%	98.5%	98.5%
West End Harbor (C631)	93.9%	NA	98.9%	99.2%	97.7%
FHR Easement (C632)	95.3%	NA	98.6%	98.7%	98.8%
Solar Estates (C633)	93.9%	76.5%	98.8%	98.9%	99.1%
Oak Park (C634)	87.9%	86.1%	99.3%	99.1%	99.4%
Dona Park (C635)	91.6%	NA	99.2%	97.8%	98.6%
By-Site Average	**92.7%**	**81.3%**	**98.9%**	**98.7%**	**98.8%**

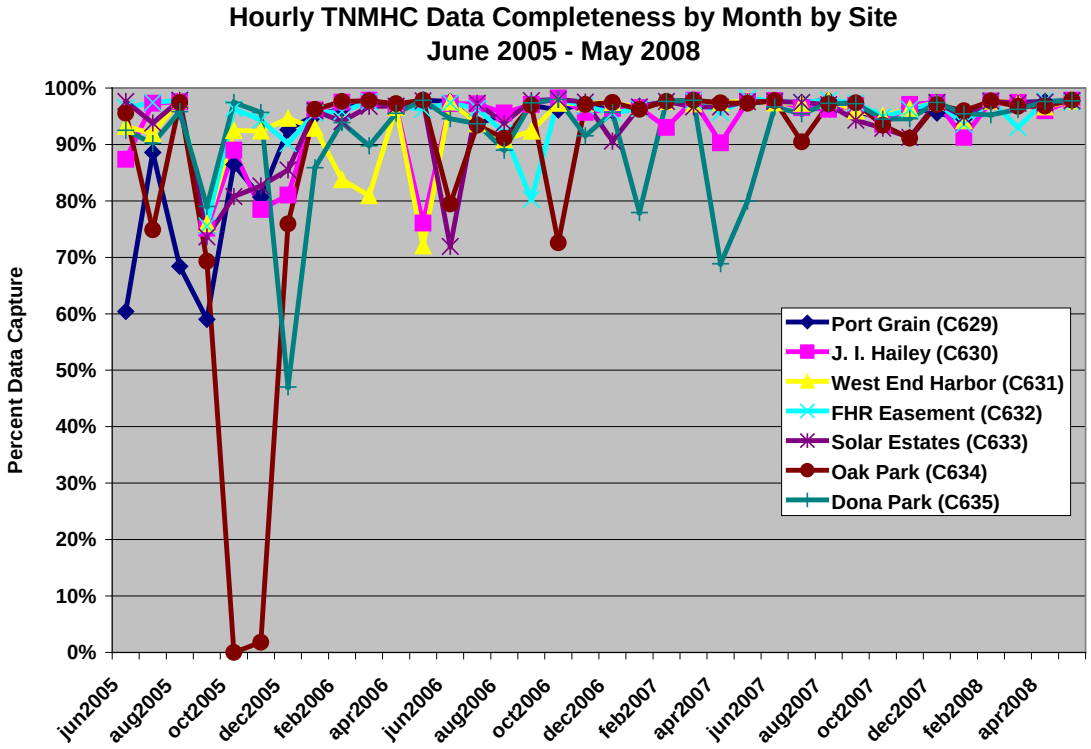

Figure 2-2. Monthly data completeness during June 2005 - May 2008 at the seven CCAQP stations for hourly TNMHC concentrations.

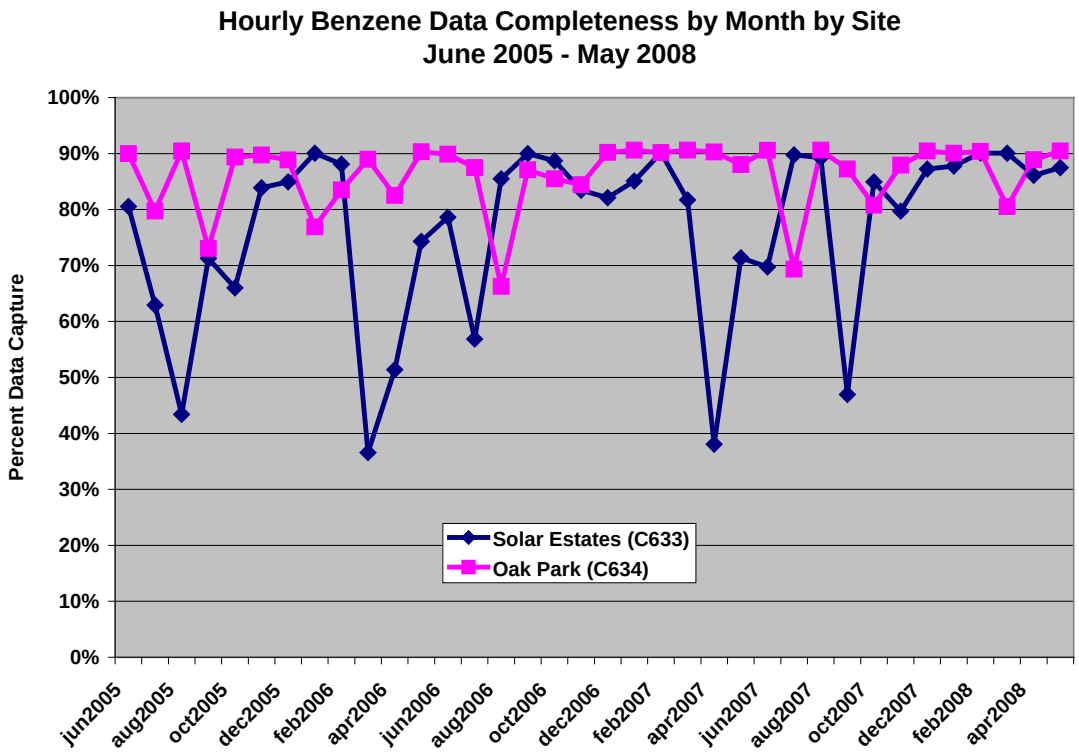

Figure 2-3. Monthly data completeness during June 2005 - May 2008 at the Solar Estates and Oak Park monitoring stations for hourly benzene concentrations.

2.2 Surface Back-Trajectories

To identify the local emissions sources at upwind industrial facilities that may impact measured pollutant concentrations at the seven CCAQP monitoring stations, a modified version of the Corpus Christi Trajectory Analysis Tool (http://www.utexas.edu/research/ceer/ccaqp/trajectory_tool.htm) was used to generate one-hour surface back-trajectories prior to high pollution events. The back-trajectories represent the hypothetical path of a near-surface air parcel assuming the parcel moves with the area-averaged winds as measured by the Corpus Christi Area network of surface monitoring stations. All available 5-minute observations of wind speed and wind direction measured at the monitoring stations within the Corpus Christi surface monitoring network are used for the trajectory calculation. Ideally, the trajectory would be based on continuous observations of wind speed and direction at all locations throughout the entire Corpus Christi area. In reality, observations of wind speed and wind direction are only available from a limited number of monitoring stations so that winds at locations away from the monitoring stations must be estimated using the available observations. An interpolation scheme is used to make these estimates.

The interpolation algorithm more heavily weights wind data from nearby monitoring stations. At the trajectory starting location, an inverse distance squared interpolation is used to estimate the average wind speed and wind direction at the requested start time. The average 5-minute wind speed and direction obtained from the inverse squared

interpolation is then used to advect (forward or backward in time) the hypothetical parcel over a 5-minute period. The hypothetical air parcel is assumed to move along a linear path at the average wind speed and direction of its starting location. A new average wind speed and direction is then interpolated at the new trajectory location using all available wind data for the next 5-minute period. The calculation procedure is repeated until the trajectory is complete for the requested duration.

2.3 National Weather Service Synoptic Analyses

The National Weather Service provides both surface weather maps and upper-air charts for the continental U.S. on a near real-time basis. These maps summarize data analyses that incorporate meteorological observations at airports and automated observing platforms, rawinsondes, radar scans, and present weather conditions from monitoring sites across the U.S. Contours of temperature, dewpoint temperature, pressure, wind direction, and wind speed were used to investigate the locations of large-scale synoptic features such as frontal troughs, high pressure ridges, and jet streaks. All upper level charts analyzed or discussed in this report were obtained from the Storm Prediction Center's Surface and Upper Air Maps website (http://www.spc.noaa.gov/obswx/maps). Surface weather maps were obtained from the UNISYS Weather website (http://weather.unisys.com). Twice-daily visible, infrared, and water vapor imagery obtained from the NOAA GOES satellite were also reviewed via the UNISYS website.

2.4 HYSPLIT Back-Trajectories

The Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model was used to investigate the large-scale weather patterns and source regions of air entering the Corpus Christi Area. HYSPLIT was developed by a joint effort between the National Oceanic and Atmospheric Administration (NOAA) and Australia's Bureau of Meteorology, and can be run interactively on the World Wide Web (http://www.arl.noaa.gov/ready/hysplit4.html). HYSPLIT uses meteorological model forecast data from the National Centers for Environmental Prediction (NCEP) archived by Air Resources Laboratory (ARL). All trajectories were calculated from the three-dimensional wind field provided by the Eta Data Assimilation System (EDAS) archived with a 40-km horizontal resolution.

2.5 Surface Wind Scatterplots

Surface wind scatterplots are used to illustrate the hourly resultant winds at an individual monitoring station. These scatterplots provide the east-west (or "U") and north-south (or "V") wind for individual hours. A hypothetical example of a wind component scatterplot is shown in Figure 2-4. Three plotted symbols (blue, yellow, and green) represent the resultant hourly wind direction and speed. The symbol color would be used to specify either nighttime or daytime hours. The x-axis provides the negative U vector component of the hourly resultant wind, while the y-axis provides the negative V vector component of the hourly resultant wind. The wind component scatterplot allows the viewer to identify the wind direction and wind speed based on the location of the symbol relative to the origin. An arrow drawn from the location of the symbol to the origin represents the wind direction. For example, the blue symbol in Figure 2-4 corresponds to an hourly resultant wind blowing from north to south. The wind speed is proportional to the length

of the arrow, and in this case is 10.0 m/s. Similarly, the yellow symbol represents an hourly resultant wind blowing from the southwest at 21.2 m/s while the green symbol represents an hourly resultant wind blowing from the east-southeast at 15.8 m/s.

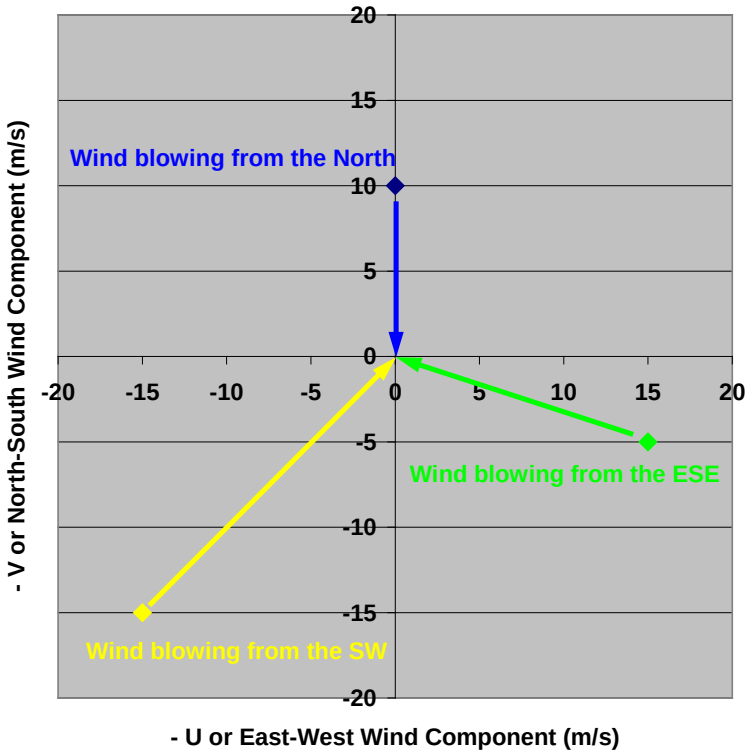

Figure 2-4. An example wind component scatterplot. Refer to the text for a discussion of data plotted on this chart.

3. Total Non-Methane Hydrocarbon (TNMHC) Analyses

This section presents the results of the conceptual model analyses for TNMHC. Due to the length of the analyses, the full results for each of the seven CCAQP monitoring stations are presented individually in Appendix A. Section 3.3 provides an integrated summary of the results across the CCAQP monitoring stations. The reader is referred to Section 3.4 for a one-page summary of the principal results.

3.1 Definition of High TNMHC Concentrations

For the purposes of the TNMHC conceptual model development, high TNMHC hours are defined as those hours characterized by a TNMHC concentration of 1000 ppbC or greater. The threshold value of 1000 ppbC was selected because the 1000 ppbC threshold level, which roughly corresponds to the 98th percentile concentration for all hourly CCAQP measurements collected during June 2005 - May 2008, provides a large enough dataset to allow robust statistics for the Corpus Christi area. The 1000 ppbC threshold level is lower than the 2000 ppbC threshold value currently used by the CCAQP Notification Alert Tool, which is a near real-time program that identifies possible pollution events for additional analysis in the Corpus Christi area. It is important to note that the 1000 ppbC threshold used for the purposes of this study is not based on a threshold for human health effects.

3.2 TNMHC Results by Monitoring Station

For each monitoring station, the conceptual model methodology included a consistent analysis method. The reader is encouraged to review Appendix A for a description of results addressing the following areas:

1.) Seasonal, Day of Week, and Diurnal Variability in TNMHC Concentrations

2.) Frequency and Duration of High TNMHC Events

3.) Local Meteorological Conditions during High TNMHC Events

4.) Large-Scale Weather Patterns during High TNMHC Events

5.) Upwind Emission Source Regions during High TNMHC Events

3.3 Integrated Summary of TNMHC Results

This section presents a summary and analysis of the TNMHC results provided for the individual monitoring stations in Appendix A of this report. All results are based on hourly TNMHC concentrations measured during June 2005 - May 2008 at the seven CCAQP monitoring stations.

3.3.1 Definition of High TNMHC Concentrations

The number of hours during June 2005 - May 2008 characterized by TNMHC concentrations of 1000 ppbC or greater is presented in Figure 3-1 for each of the seven CCAQP monitoring stations. Figure 3-1 presents the monitoring stations in west-to-east order along the Corpus Christi Ship Channel. At 2737 hours, FHR Easement is characterized by a substantially higher number of 1000 ppbC TNMHC hours compared to the other stations. For the remaining stations, the number of high TNMHC concentration hours varies from 40 hours at Solar Estates to 453 hours at J. I. Hailey.

NOTE: Routine operational activities in support of CCAQP include near real-time investigation of local emissions sources that may contribute to higher TNMHC events at the CCAQP monitoring stations. The atypically high number of 1000 ppbC TNMHC concentrations at the FHR Easement monitoring station may be associated with emissions from a small tank battery and rotary rig located several hundred feet to the south-southeast of FHR Easement.

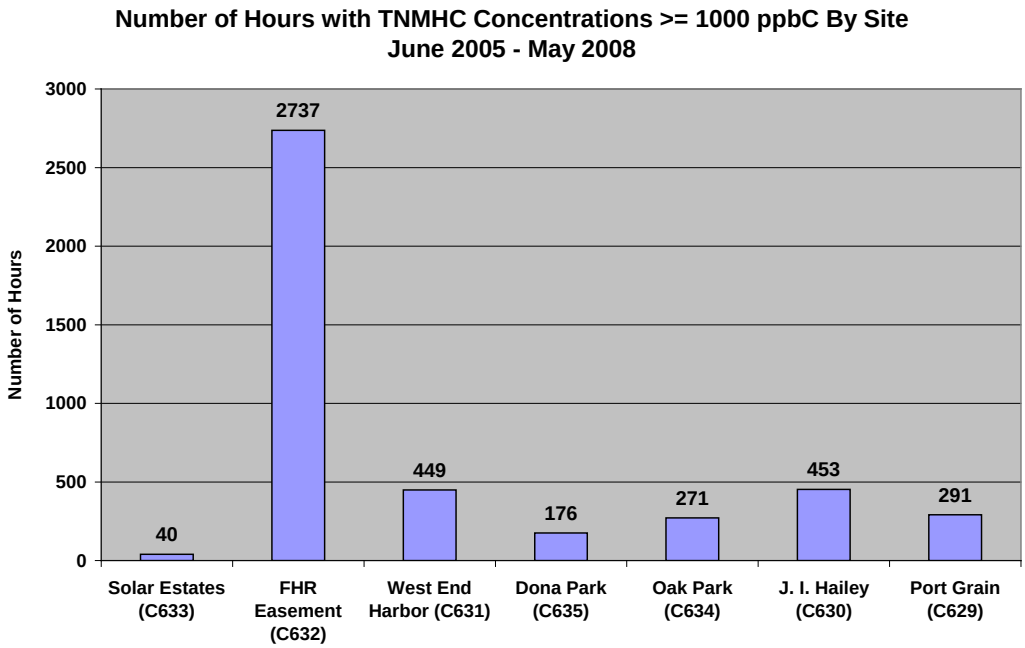

Figure 3-1. Number of hours during June 2005 - May 2008 characterized by TNMHC concentrations of 1000 ppbC or greater at each of the seven CCAQP monitoring stations.

3.3.2 Annual Number of High TNMHC Concentrations

Figure 3-2 shows the percentages at each site of the annual number of TNMHC concentrations of 1000 ppbC or greater that were recorded over three annual time periods. For each station, Figure 3-2 presents the percentage of the total number of 1000 ppbC TNMHC hours (shown in Figure 3-1) at each site grouped by consecutive 12-month summer through spring periods. For example, 48% of the 2737 hours above 1000 ppbC recorded at the FHR Easement occurred between summer 2005 and spring 2006. Conversely, only 22% of the 176 hours above 100 ppbC observed at Dona Park occurred during this period. West End Harbor is characterized by the largest relative change in frequency of higher TNMHC hours between Year 1 and Year 3, decreasing from 67% for Year 1 to 19% for Year 3. The FHR Easement, J. I. Hailey, and Port Grain monitoring stations are also characterized by decreases in the number of 1000 ppbC or greater TNMHC hours between Year 1 and Year 3. Solar Estates and Oak Park show little change Year 1 to Year 3, while Dona Park is the only station characterized by a substantial increase in the number hours between Year 1 and Year 3.

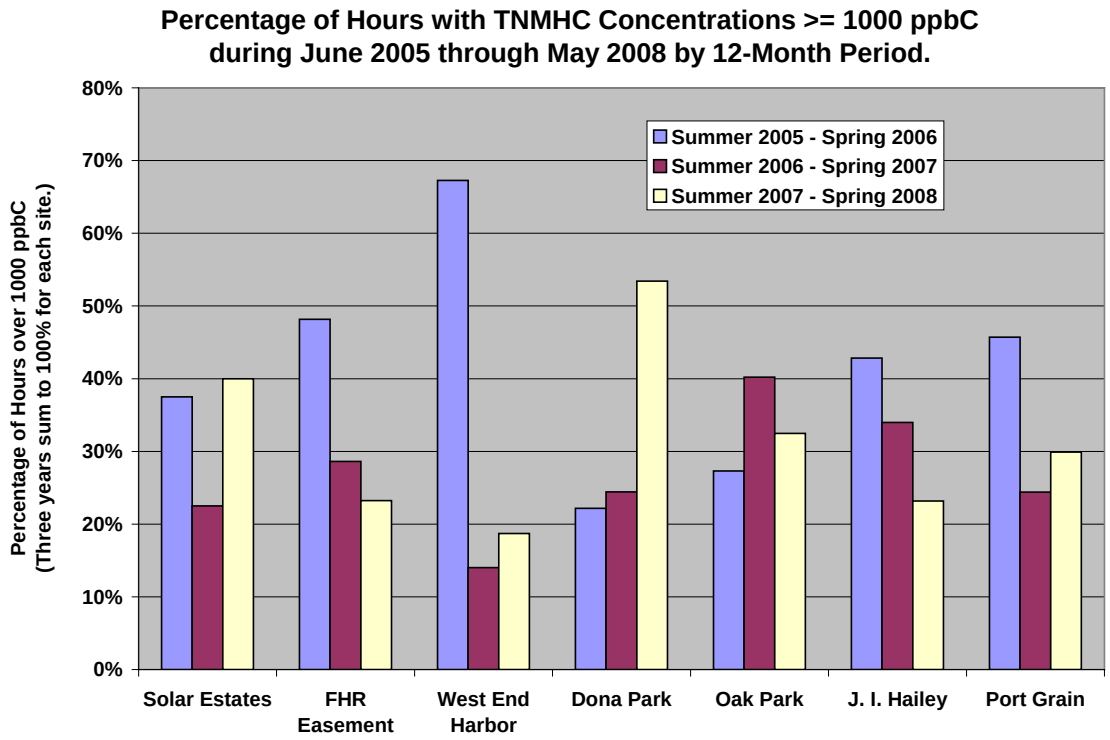

Figure 3-2. Percentage of 1000 ppbC TNMHC hours during June 2005 - May 2008 (shown in Figure 3-1) grouped by consecutive 12-month summer through spring periods.

3.3.3 Diurnal Variability of High TNMHC Concentrations

As presented in Appendix A of this report, the diurnal variability in the median and 75th percentile hourly THMHC concentration values for all monitoring stations reveals that the highest TNMHC concentrations typically occur during the nighttime and morning

periods. Figure 3-3 presents the frequency of occurrence of 1000 ppbC or greater TNMHC concentrations at each monitoring station grouped by 4-hour interval. The majority of monitoring stations are characterized by the highest frequency of occurrence during the 0400 CST through 0700 CST period. The by-site percentage of total 1000 ppbC TNMHC concentrations during this morning time period ranges from 19% at West End Harbor to 50% at Oak Park. Note that the J. I. Hailey and Port Grain monitoring stations, which are both located on the north side of the Ship Channel approximately one mile apart, are characterized by similar diurnal patterns. The FHR Easement and West End Harbor monitoring stations (and to a lesser extent Dona Park) are characterized by an elevated frequency of occurrence of higher TNMHC concentrations throughout the 2000 CST through 0700 CST period, with maximum values during the 0000 CST through 0300 CST period.

Highest concentrations during the nighttime hours have been reported for hydrocarbon compound concentrations in previous studies for locations throughout the US (Touma et al., 2006; Reiss, 2006; McCarthy et al., 2007). Lower nocturnal mixing heights result in a buildup of near-surface pollutants associated with emissions from ground-level sources. In addition, the nighttime period is more often associated with light to calm wind speeds, conditions that are unfavorable for efficient horizontal and/or vertical dispersion. During the daytime hours, typically higher wind speeds and greater mixing heights associated with additional mechanical turbulence provide enhanced dispersion and dilution of near-surface pollutants.

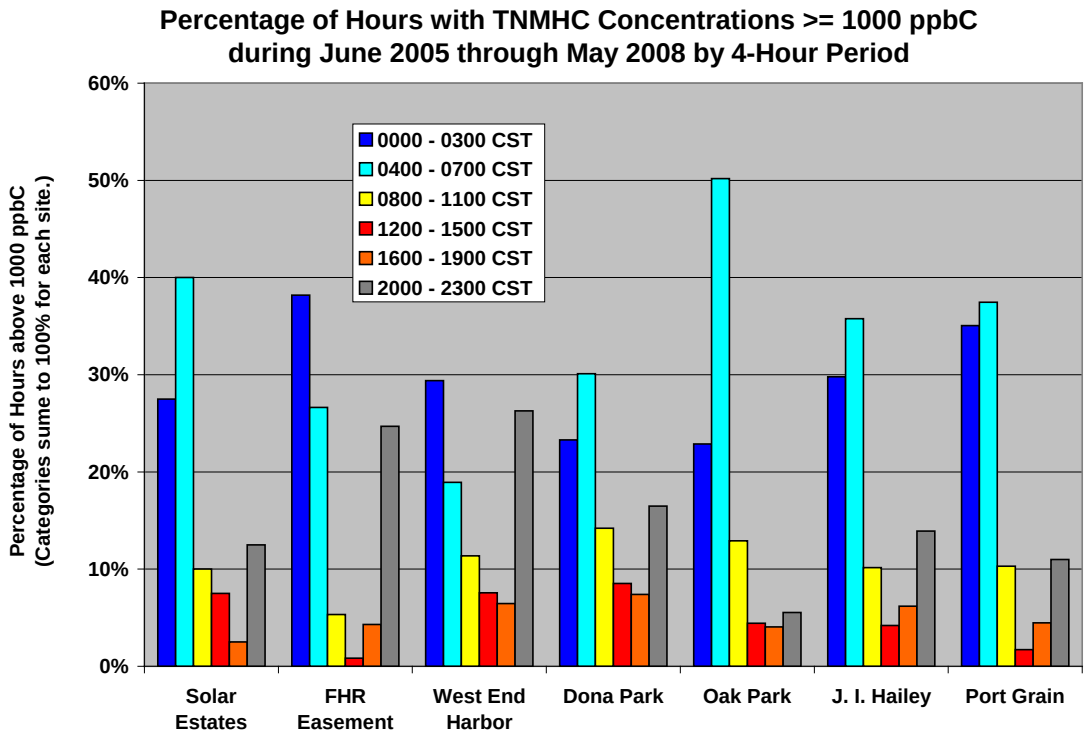

Figure 3-3. The percentage of the total number of 1000 ppbC TNMHC hours for June 2005 - May 2008 (shown in Figure 3-1) grouped by consecutive 4-hour periods.

3.3.4 Seasonal Variability of High TNMHC Concentrations

The seasonal frequencies of occurrence of TNMHC concentrations of 1000 ppbC or greater are shown in Figure 3-4 for each of the seven CCAQP monitoring stations. Most monitoring stations are characterized by relatively high frequencies of occurrence during the fall and winter seasons. The combined fall/winter percentage of total high TNMHC hours varies from 38% at West End Harbor to 87% at Dona Park. Spring is associated with a low frequency of occurrence of high TNMHC concentrations at all monitoring stations. The summer frequency of occurrence is only slightly greater compared to spring at the Solar Estates, Dona Park, and Oak Park stations. In contrast, relatively high frequencies of occurrence are noted for the remaining four monitoring stations during summer, with a frequency of occurrence at 43% and 51% at the FHR Easement and West End Harbor monitoring stations, respectively.

Figure 3-5 presents the average TNMHC concentrations by season at each of the seven CCAQP monitoring stations. The pattern of relative seasonal variability is similar to that shown in Figure 3-4. The maximum by-site seasonal concentrations range from 126 ppbC during winter at Solar Estates to 652 ppbC during summer at FHR Easement. The by-site ratios of maximum to minimum seasonal averages range from 1.5 for Dona Park to 3.2 for Oak Park.

Seasonal variability in high TNMHC concentrations is likely related to changes in local source emissions, pollutant removal rates, and atmospheric dispersion and dilution conditions (Touma et al., 2006; McCarthy et al., 2007). Mixing heights during the fall and winter months are likely lower, on average, compared to spring and summer. Cooler temperatures may be associated with lower removal rates for some TNMHC pollutants (e.g., caused by lower concentrations of atmospheric oxidants). In addition, as discussed in the following section of this report, the seasonal frequency of occurrence of wind direction will determine the impact of nearby emission sources at each monitoring station. The importance of sources located immediately to the south and southeast of the FHR Easement and West End Harbor monitoring stations likely explains the relatively high frequency of occurrence of summer events. Spring is associated with a low frequency of occurrence of high TNMHC concentrations at all monitoring stations. The frequency of occurrence of winds from source regions and relatively higher wind speeds may be contributing factors.

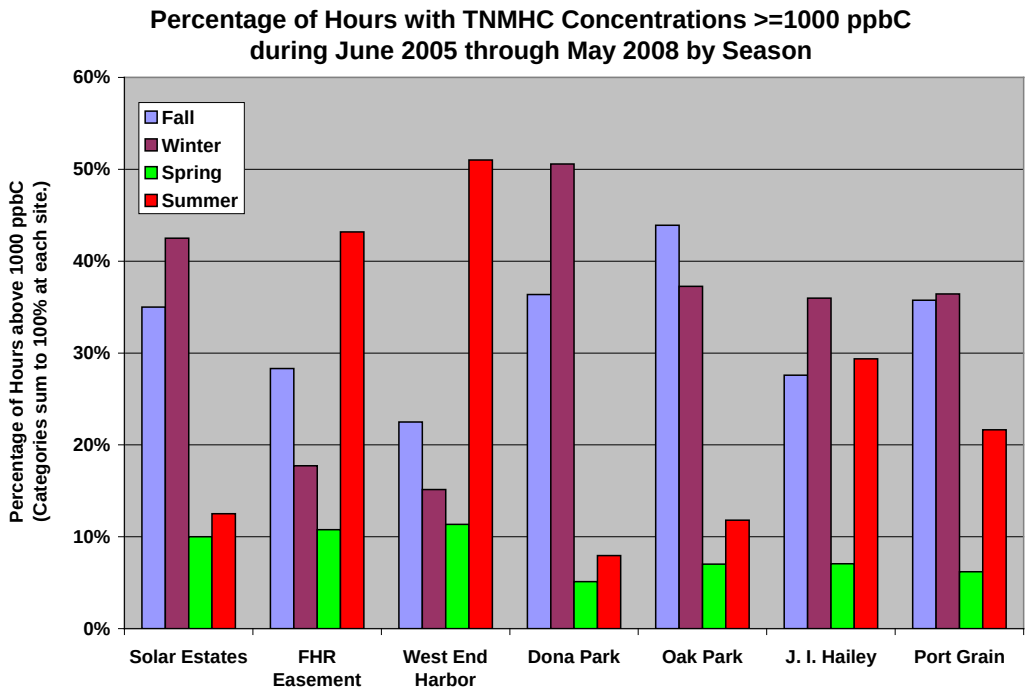

Figure 3-4. The percentage of 1000 ppbC TNMHC hours during June 2005 - May 2008 (shown in Figure 3-1) grouped by season.

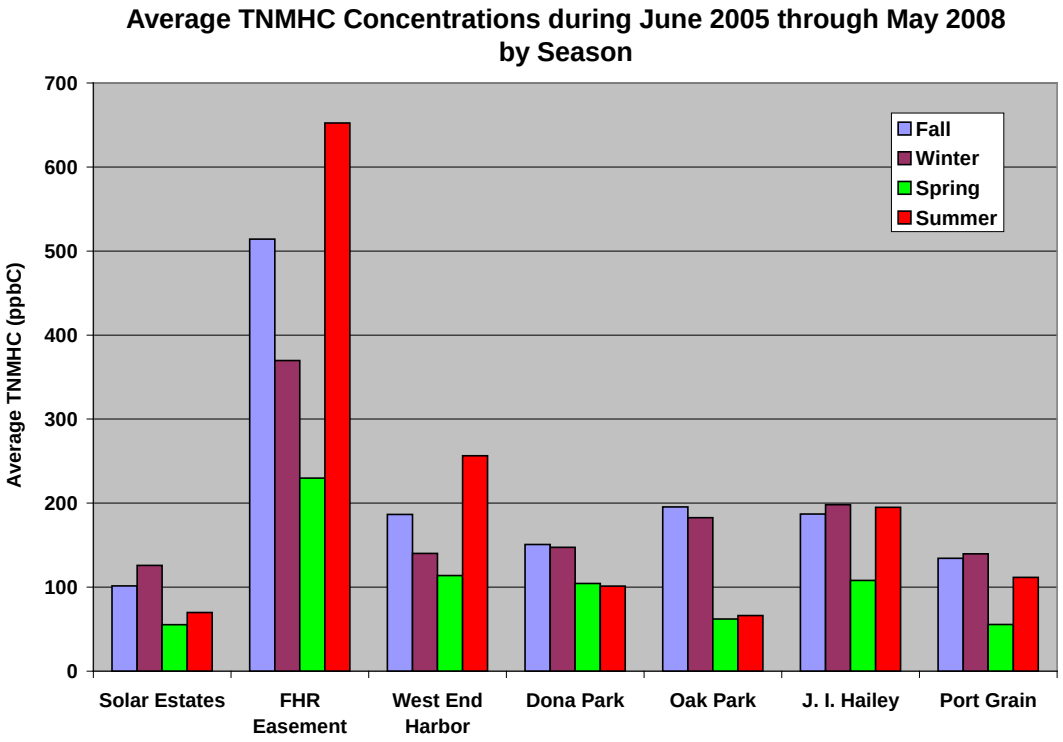

Figure 3-5. Average TNMHC concentrations by season using all available data collected during June 2005 - May 2008.

3.3.5 Surface Wind Direction and High TNMHC Concentrations

As presented in Appendix A of this report, the back-trajectory and wind direction analyses showed that most monitoring stations are characterized by strong wind directionality during high TNMHC events. This strong directionality suggests that one or more nearby emissions sources often dominate during high TNMHC events when defined by an hourly concentration threshold of 1000 ppbC or greater. Concentrations within a plume downwind of an emissions source would be expected to decrease with distance from the source, due, in part, to horizontal and vertical mixing between the plume and the surrounding atmosphere. The application of a relatively high threshold concentration likely selects for TNMHC events associated with emissions sources that are relatively nearby to each monitoring station.

Figure 3-6 presents the frequency of occurrence of high TNMHC concentrations by wind direction for each of the CCAQP monitoring stations. Note that the Solar Estates and especially Dona Park and Oak Park monitoring stations are most often characterized by winds with a northerly component during periods of high TNMHC concentrations. The strong seasonality of high TNMHC concentrations is likely strongly associated with the directionality shown in Figure 3-6. For example, note that high TNMHC events at the Solar Estates, Dona Park and Oak Park are most common during the fall/winter seasons, which are characterized by a relatively high frequency of occurrence of northerly winds in association with the periodic passage of cold fronts through South Texas. Port Grain and J. I. Hailey measure high TNMHC concentrations during a range of wind directions and high TNMHC concentrations occur with roughly equal frequencies during the fall, winter, and summer seasons at both stations. High TNMHC concentrations at the West End Harbor and FHR Easement monitoring stations overwhelmingly occur during periods of southeasterly or southerly resultant wind directions. Figure 3-4 demonstrates that high TNMHC events at these latter two monitoring stations occur most often during the summer months, which are predominantly characterized by southerly winds compared to the other seasons.

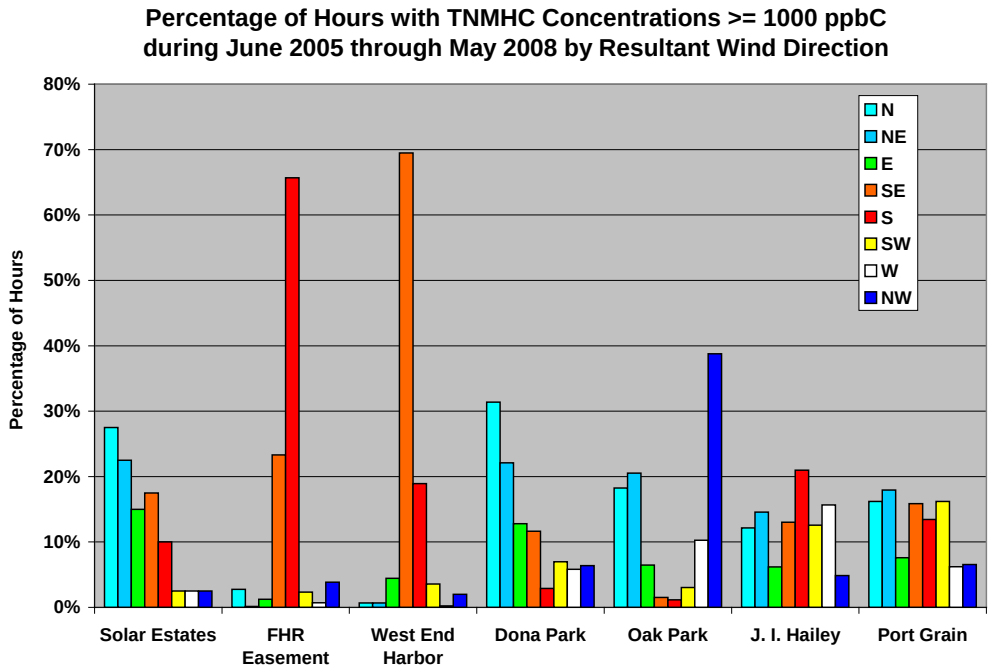

Figure 3-6. The percentage of 1000 ppbC TNMHC hours during June 2005 - May 2008 (shown in Figure 3-1) grouped by resultant wind direction.

3.3.6 High TNMHC Concentrations by Day of Week

Figure 3-7 presents the 75th percentile hourly TNMHC concentration values by day of week for each of the seven CCAQP monitoring stations. Although there is some tendency for Saturdays to be characterized by lowest concentrations (e.g., West End Harbor, J. I. Hailey, and Port Grain), substantial differences between weekdays and weekends are not observed. As presented in Appendix A of this report, the differences between weekdays and weekends were further investigated by calculating the median and 75th percentile concentrations values for weekdays/weekends by hour by season. Consistent and substantial differences between weekdays and weekends were limited to nighttime hours during winter at some monitoring stations. For example, Figure 3-8 for West End Harbor shows that the 0000 CST through 0900 CST period is characterized by relatively higher winter weekday concentrations compared to weekends. Figure 3-9 presents the results for Solar Estates, which shows relatively higher winter weekday concentrations compared to weekends throughout the nighttime and especially morning hours.

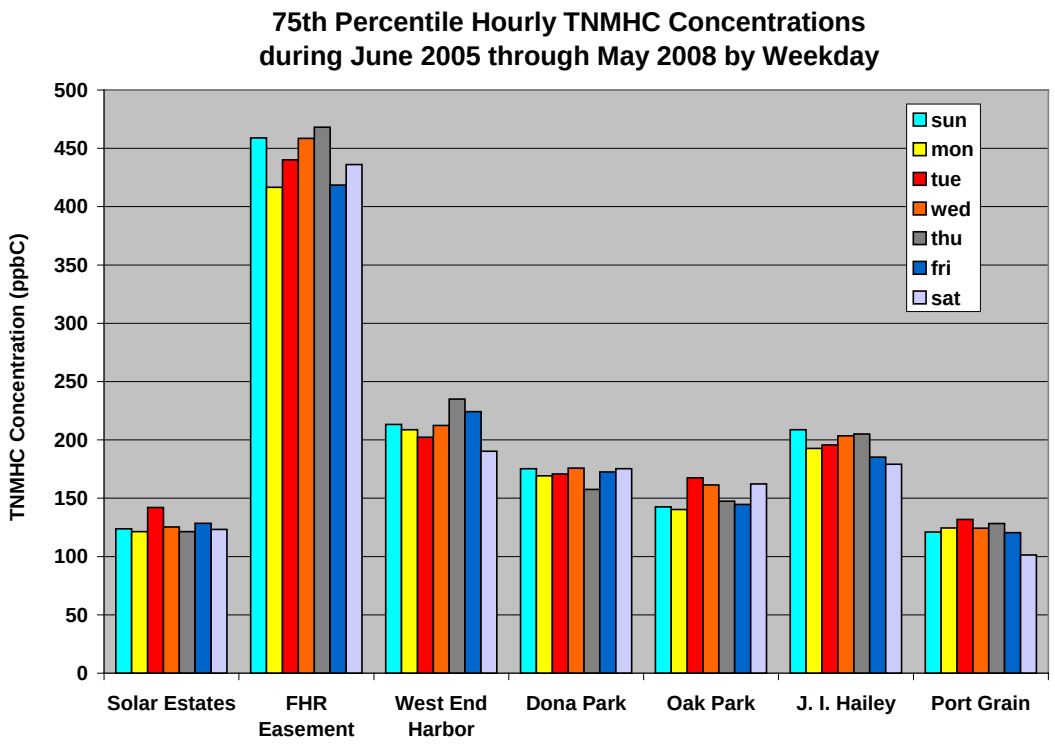

Figure 3-7. The 75th percentile TNMHC concentration values by day of week for June 2005 - May 2008.

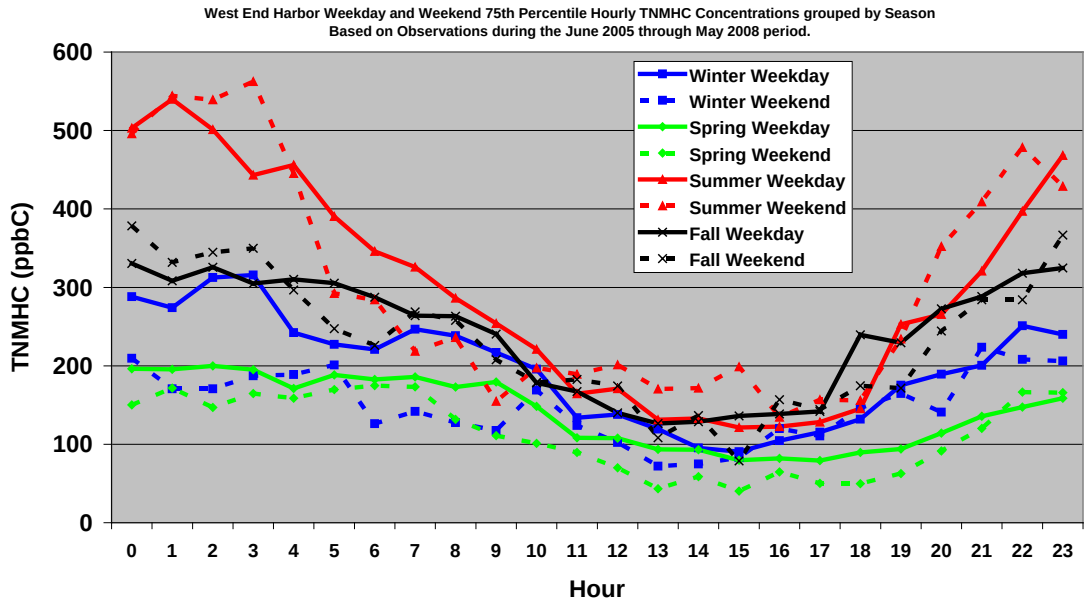

Figure 3-8. The 75th percentile hourly weekday and weekend TNMHC concentrations grouped by season at the West End Harbor monitoring station based on all valid data during June 2005 - May 2008.

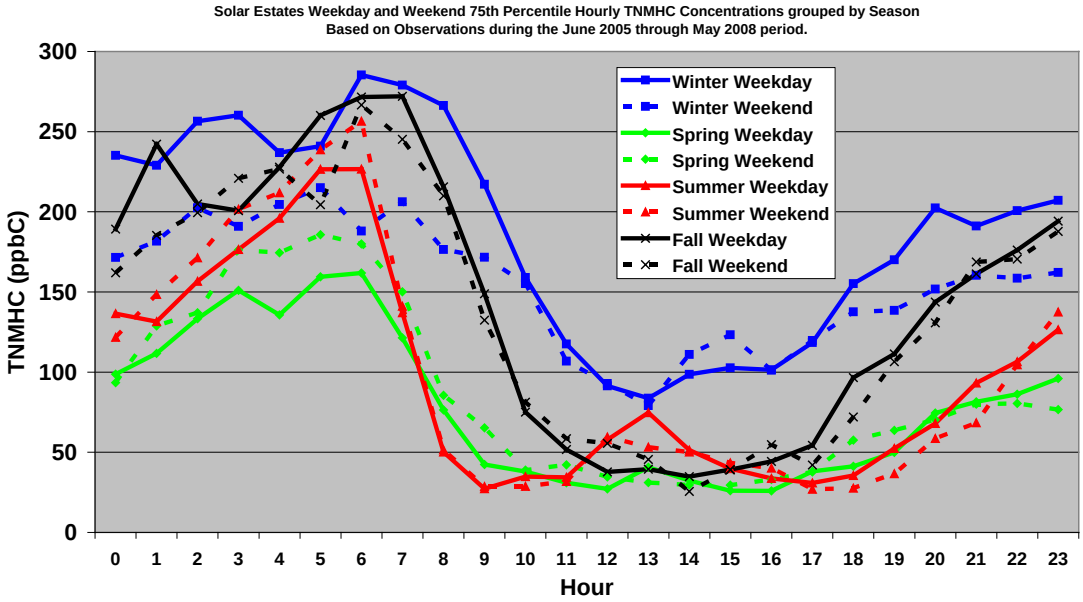

Figure 3-9. The 75th percentile hourly weekday and weekend TNMHC concentrations grouped by season at the Solar Estates monitoring station based on all valid data during June 2005 - May 2008.

To further analyze for any weekday/weekend differences, Table 3-1 presents both the winter median and 75th percentile TNMHC concentration values at each CCAQP monitoring station during the 0600 CST through 0800 CST period. The 0600 CST through 0800 CST period was chosen to correspond to the morning rush hour. Table 3-1 demonstrates that both the median and 75th percentile values are greater for weekdays compared to weekends at each of the seven monitoring stations. Figure 3-10 presents the percentage change between the weekend and weekday concentrations based on the concentration values shown in Table 3-3. Positive values in Figure 3-10 for both the median and 75th percentile metrics at all monitoring stations indicate that the weekday concentration values are relatively greater than the weekend concentrations. Figure 3-10 demonstrates that the three stations along the west end of the Ship Channel (Solar Estates, FHR Easement, and West End Harbor) are characterized by the largest weekend to weekday percentage differences mostly ranging between 30% and 45%. Oak Park and Dona Park are characterized by relatively small percentage differences, while J. I. Hailey and Port Grain show percentage differences generally between 20% and 25%.

Table 3-1. Median and 75th percentile hourly TNMHC concentration values during winter using data collected during 0600 CST through 0800 CST throughout June 2005 - May 2008.

Day of Week Parameters	Port Grain (C629)	J. I. Hailey (C630)	West End Harbor (C631)	FHR Easement (C632)	Solar Estates (C633)	Oak Park (C634)	Dona Park (C635)
Median							
Weekend	93	103	73	215	113	196	114
Weekday	111	130	103	276	147	198	127
Difference	18	27	30	61	34	2	13
Percentage Increase	19%	26%	42%	28%	30%	1%	11%
75th Percentile							
Weekend	178	235	139	329	190	361	194
Weekday	246	284	235	469	279	397	251
Difference	68	49	96	140	89	36	57
Percentage Increase	38%	21%	69%	43%	47%	10%	29%

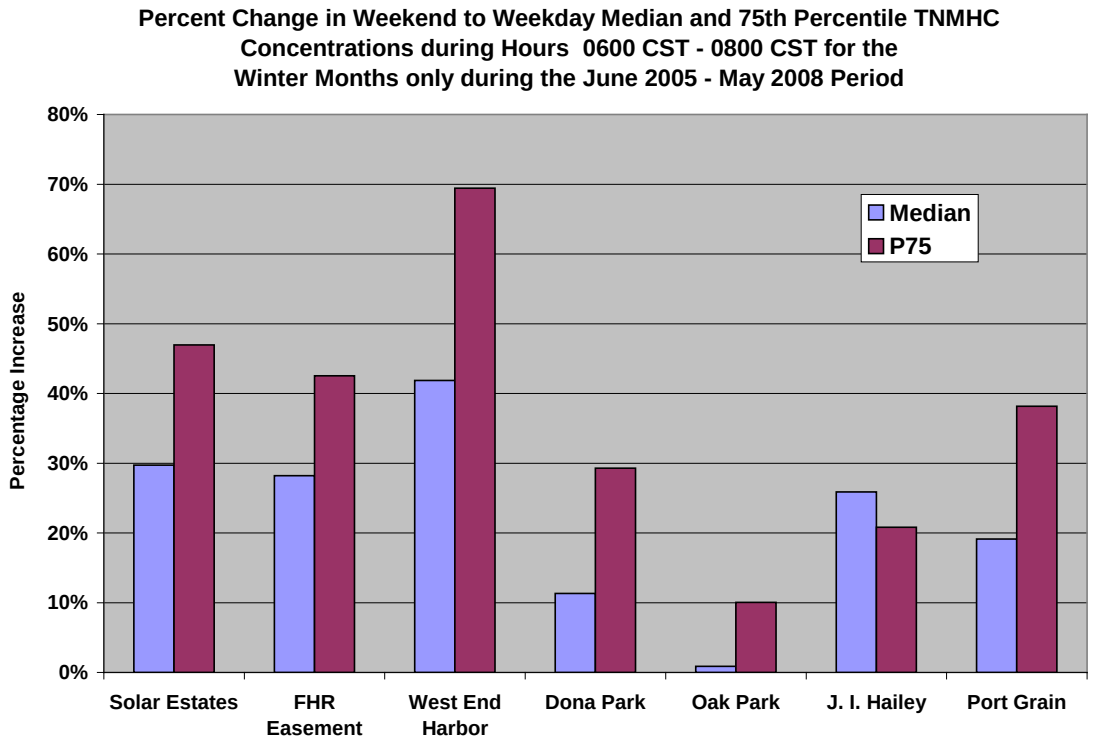

Figure 3-10. The percentage change between the hourly winter weekend and weekday median and 75th percentile concentrations for the 0600 CST through 0800 CST period during June 2005 through May 2008 (refer to Table 3-1 for raw values).

As previously mentioned, nighttime mixing heights during winter are often quite low, which may result in higher sensitivity in measured TNMHC concentrations to the impacts of local emissions sources. The spatial pattern of the differences between morning weekday and weekend concentration values shown in Table 3-1 and Figure 3-10 are not consistent with mobile sources as the principal cause. The diurnal profiles at some monitoring stations (refer to Figure 3-9 for Solar Estates) are characterized by a morning peak that may be associated with increased emissions from mobile sources. However, if mobile sources were an important contributor to TNMHC concentrations throughout the region, one might expect greater differences at the Oak Park monitoring station compared to those shown in Table 3-1 and Figure 3-9 since the Oak Park site is located relatively near a major roadway. The common occurrence of northerly winds during winter should often transport emissions from Interstate-37 mobile sources southward to Oak Park; however, substantial differences in weekend and weekday TNMHC concentrations do not occur. In addition, some monitoring stations are not characterized by a strong morning peak in TNMHC concentrations (e.g., refer to Figure 3-8 for West End Harbor), suggesting that emissions associated with the morning rush hour are not the dominant source. It is interesting that the largest percentage differences between weekday and weekend TNMHC concentration occurs at the West End Harbor monitoring station, which is also located farthest from the primary transportation corridors in the Corpus Christi area. In general, the primary contributing sources of weekend to weekday differences likely vary spatially throughout the Corpus Christi area, and may include differences in industrial activity such as ship loading/unloading along the Ship Channel in addition to impacts of mobile source emissions along local roadways and/or in support of industrial activity.

3.3.7 Duration of High TNMHC Events

Table 3-2 compares the duration of high TNMHC events (defined as one or more consecutive hours with concentrations >= 1000 ppbC) at each monitoring station. For all stations, the majority of events are one to two hours in duration. The percentage of events characterized by durations of 2 hours or less varies from 78.6% at FHR Easement to 93.8% at Port Grain. The percentage of events with durations greater than 4 hours ranges from 3% at Port Grain (5 of 177 events) to 13.4% at FHR Easement (149 of 1111 events). In general, the vast majority of TNMHC events (as defined by the 1000 ppbC threshold value) are of limited duration on an hourly time-scale.

Table 3-2. Duration of high TNMHC events (defined as one or more consecutive hours with concentrations >= 1000 ppbC) at the seven CCAQP monitoring stations.

Duration (Hours)	Port Grain (C629)	J. I. Hailey (C630)	West End Harbor (C631)	FHR Easement (C632)	Solar Estates (C633)	Oak Park (C634)	Dona Park (C635)
1	108	160	138	493	23	71	54
2	45	50	41	259	2	37	19
3	13	18	25	121	1	17	6
4	6	17	7	89	1	8	9
> 4	5	12	18	149	1	7	5
Total Events	**177**	**257**	**229**	**1111**	**28**	**140**	**93**
Duration as a Percentage of Total Events							
=< 2	**93.8%**	**88.7%**	**89.1%**	**78.6%**	**92.9%**	**89.3%**	**84.9%**
3 or 4	**10.7%**	**13.6%**	**14.0%**	**18.9%**	**7.1%**	**17.9%**	**16.1%**
> 4	**2.8%**	**4.7%**	**7.9%**	**13.4%**	**3.6%**	**5.0%**	**5.4%**

3.3.8 Local Emissions Source Regions

To identify local emissions sources at upwind industrial facilities that may impact TNMHC concentrations at the seven CCAQP monitoring stations, a modified version of the Corpus Christi Trajectory Analysis Tool was used to generate one-hour surface back-trajectories for all hours characterized by high TNMHC concentrations. The 1000 ppbC threshold concentration was used to define high TNMHC concentrations for most monitoring stations. The threshold concentration was lowered to 750 ppb at Solar Estates due to the limited number of hours characterized by concentrations of 1000 ppbC or greater. In contrast, FHR Easement is characterized by an atypically high number of 1000 ppbC TNMHC concentration hours (refer to Figure 3-1); therefore, the threshold level was raised to 3000 ppbC to capture only the highest concentrations All back-trajectories were initialized at the half-hour (i.e., midpoint) of the TNMHC one-hour averaging period.

Figure 3-11 through Figure 3-17 present the back-trajectories for each monitoring station over the Corpus Christi base map described in Section 2.1 of this report. The back-trajectories suggest that important emissions sources are generally located to the south and southeast of the West End Harbor and FHR Easement monitoring stations. The majority of back-trajectories for Solar Estates indicate source areas located to the northeast or southeast. The Dona Park back-trajectories indicate flow from the north clockwise through east-northeast, while Oak Park is characterized by a family of back-trajectories indicating potentially important source areas located to the northwest, north, and north-northeast. With the exception of easterly and/or east-southeasterly, the J. I. Hailey and Port Grain stations, located on the north bank of the Ship Channel, are characterized by back-trajectories that indicate a variety of upwind source regions. Both monitoring stations are embedded within the industrialized Corpus Christi area.

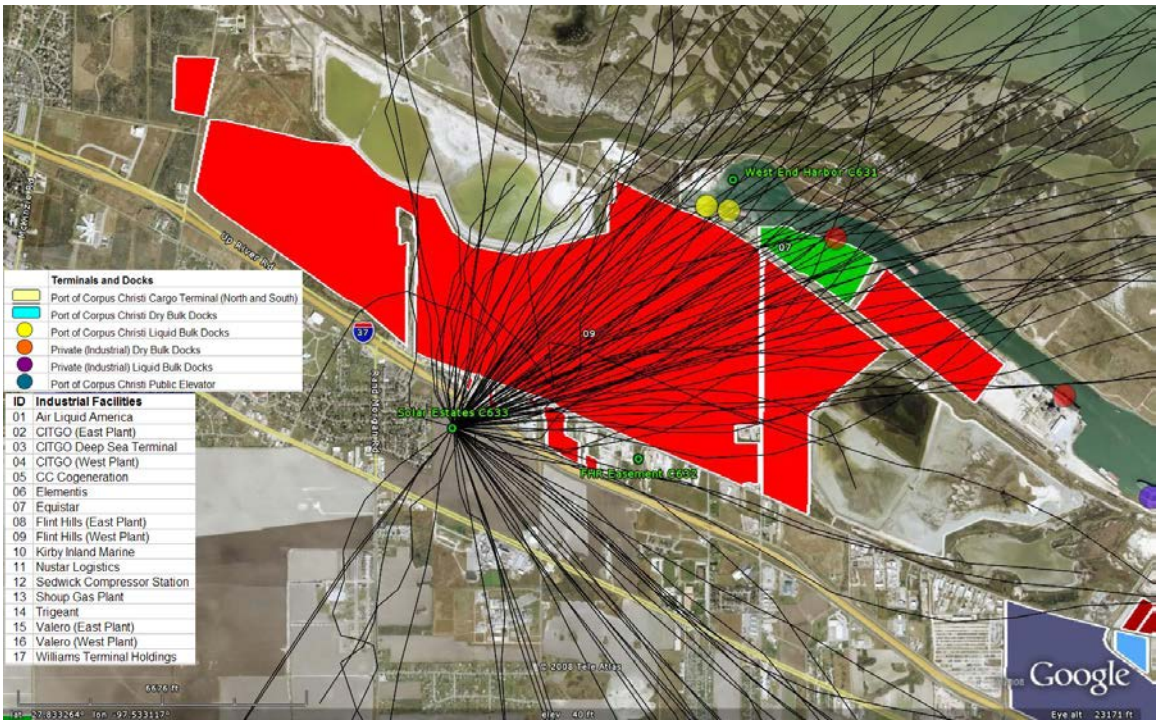

Figure 3-11. Surface back-trajectories as generated by the Corpus Christi Trajectory Analysis Tool for all hours characterized by a TNMHC concentration of 750 ppb or greater at the Solar Estates monitoring station during June 2005 - May 2008.

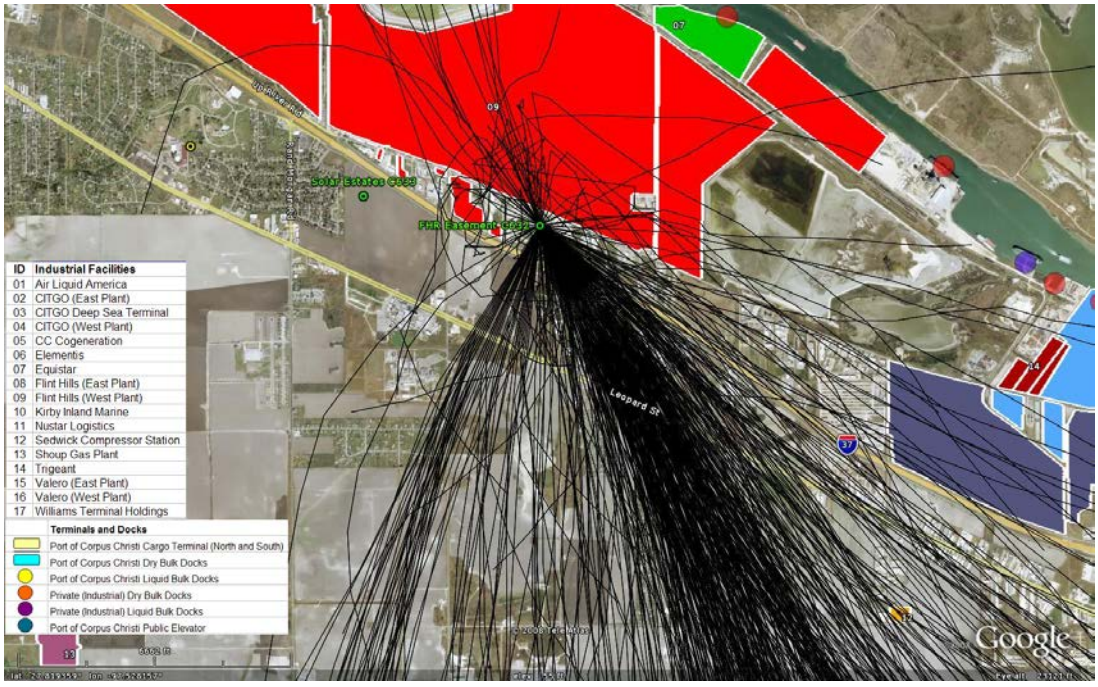

Figure 3-12. Surface back-trajectories as generated by the Corpus Christi Trajectory Analysis Tool for all hours characterized by a TNMHC concentration of 3000 ppb or greater at the FHR Easement monitoring station during June 2005 - May 2008.

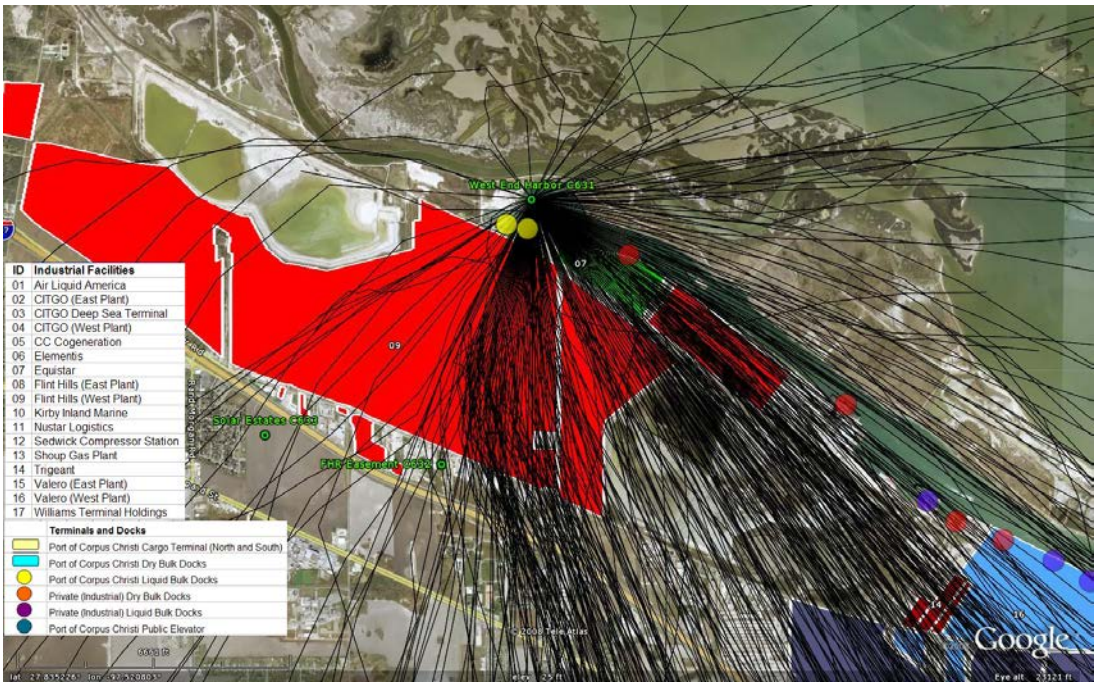

Figure 3-13. Surface back-trajectories as generated by the Corpus Christi Trajectory Analysis Tool for all hours characterized by a TNMHC concentration of 1000 ppb or greater at the West End Harbor monitoring station during June 2005 - May 2008.

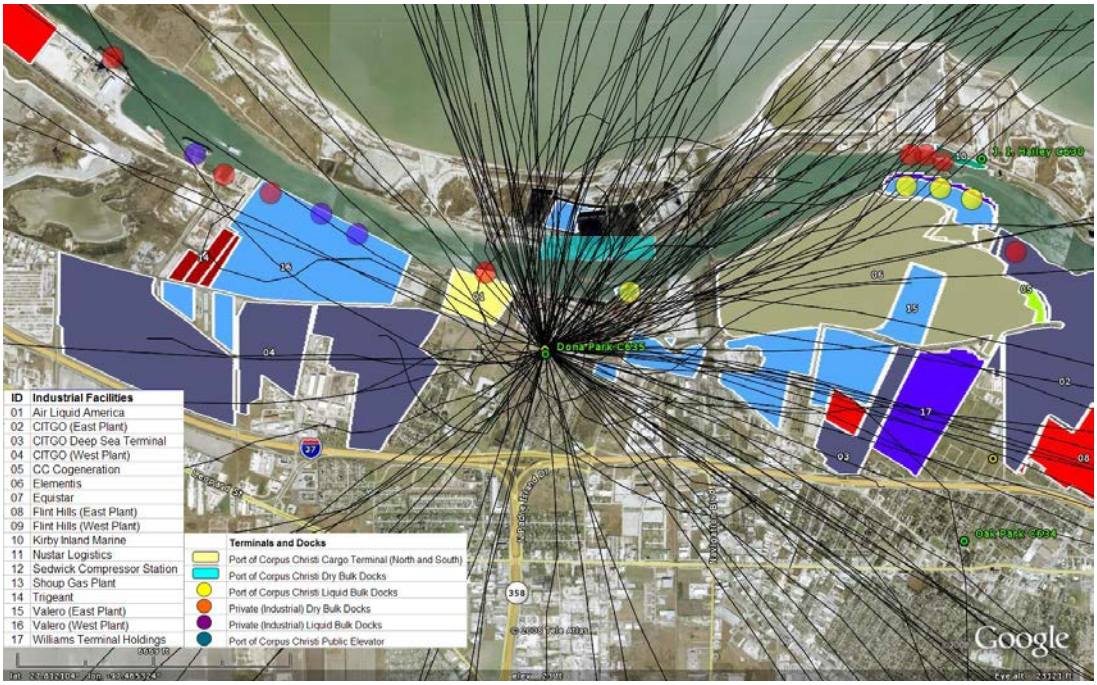

Figure 3-14. Surface back-trajectories as generated by the Corpus Christi Trajectory Analysis Tool for all hours characterized by a TNMHC concentration of 1000 ppb or greater at the Dona Park monitoring station during June 2005 - May 2008.

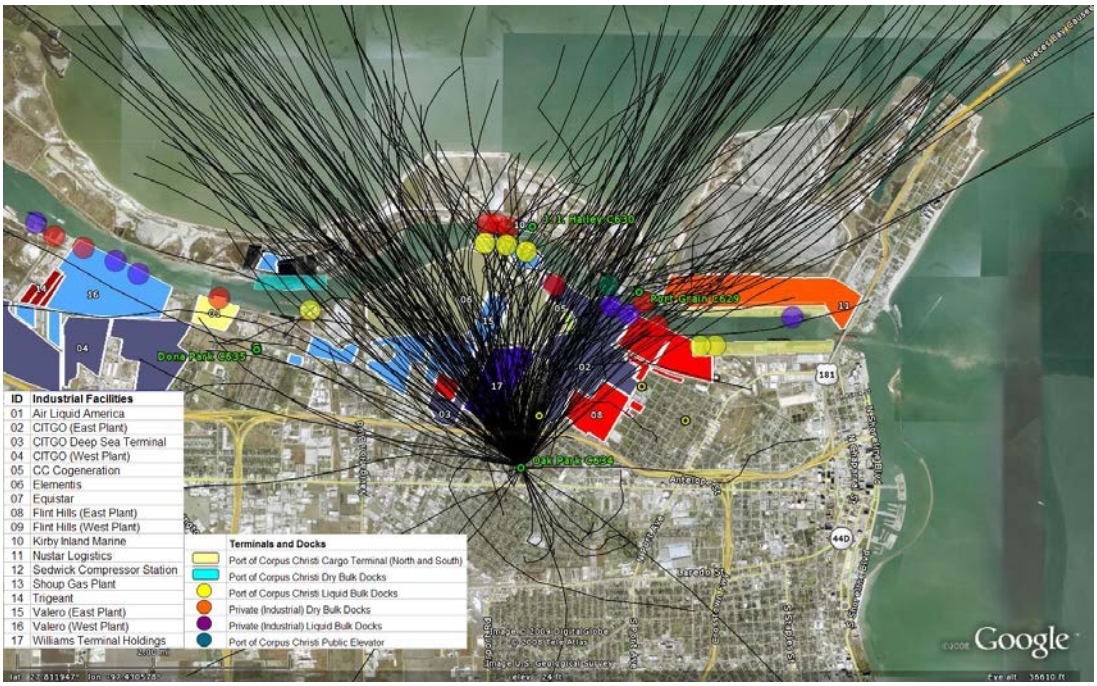

Figure 3-15. Surface back-trajectories as generated by the Corpus Christi Trajectory Analysis Tool for all hours characterized by a TNMHC concentration of 1000 ppb or greater at the Oak Park monitoring station during June 2005 - May 2008.

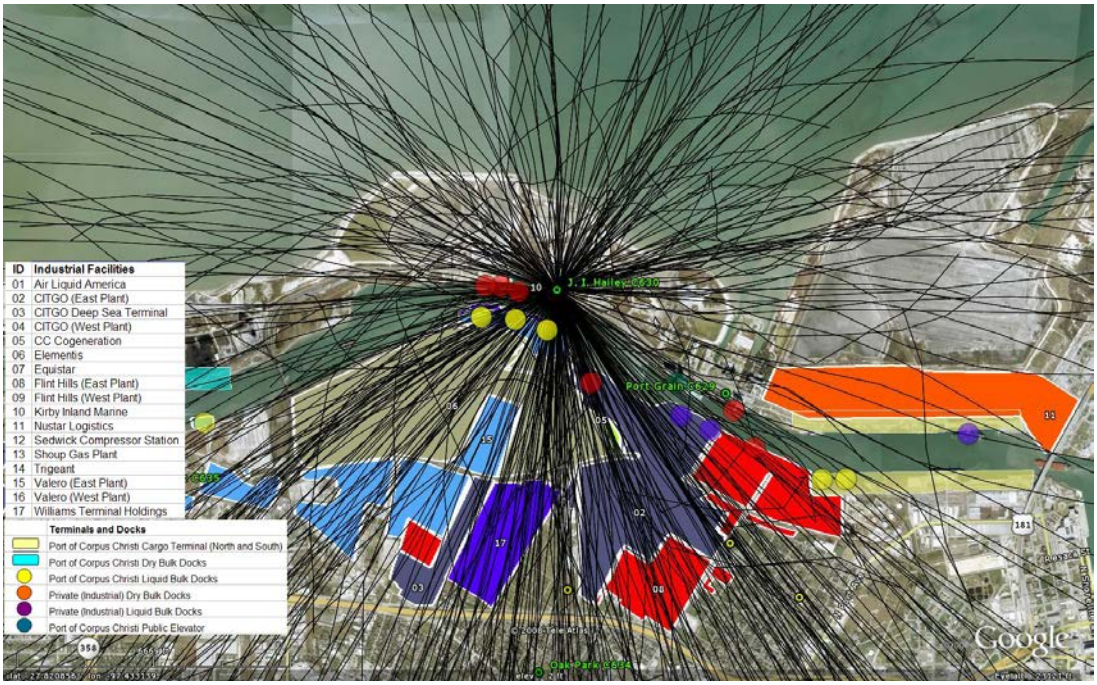

Figure 3-16. Surface back-trajectories as generated by the Corpus Christi Trajectory Analysis Tool for all hours characterized by a TNMHC concentration of 1000 ppb or greater at the J. I. Hailey monitoring station during June 2005 - May 2008.

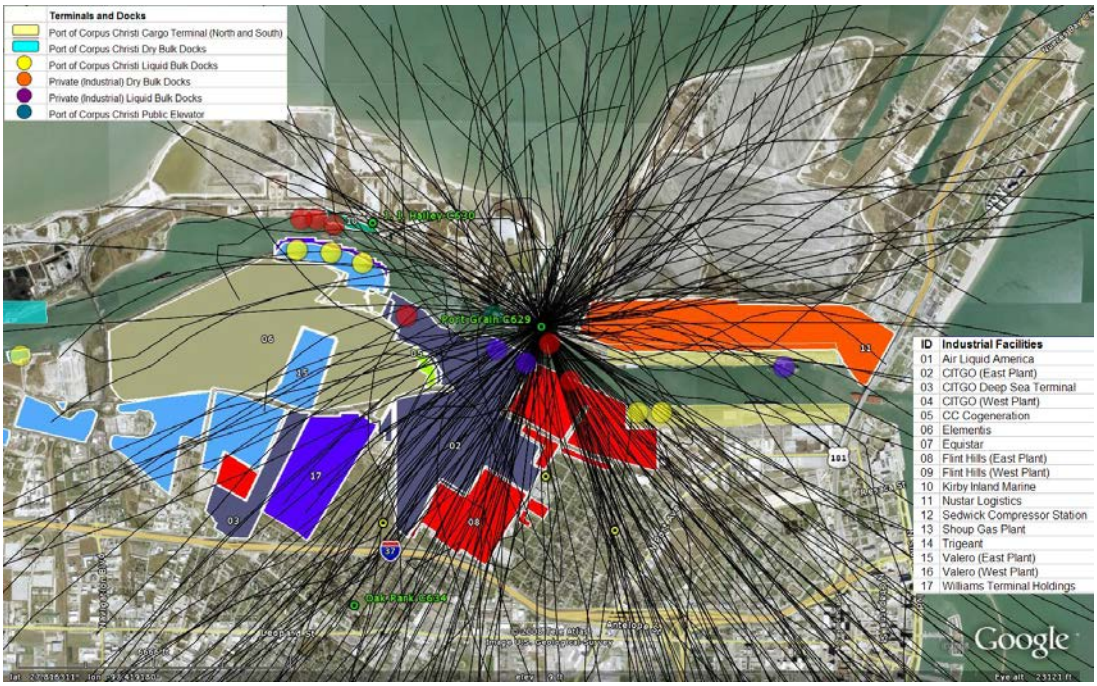

Figure 3-17. Surface back-trajectories as generated by the Corpus Christi Trajectory Analysis Tool for all hours characterized by a TNMHC concentration of 1000 ppb or greater at the Port Grain monitoring station during June 2005 - May 2008.

3.3.9 Spatial Scale of High TNMHC Events as Measured by the CCAQP Network

The back-trajectory and wind direction analyses presented in the previous sections of this report (in addition to the complete analyses provided in Appendix A) showed that most monitoring stations are characterized by strong wind directionality during high TNMHC hours. This strong directionality suggests that one or more nearby emissions sources often dominate during TNMHC events defined by an hourly concentration threshold of 1000 ppbC or greater. If emissions from nearby sources have a dominant influence on measured TNMHC concentrations at each monitoring station, we may expect that the spatial scale of high TNMHC concentrations as measured by the Corpus Christi network of monitoring stations is often limited.

During June 2005 - May 2008, TNMHC concentrations of 1000 ppbC or greater were measured at one or more of the seven monitoring stations during 3793 unique hours. Table 3-2 presents the number of hours characterized by one or more monitoring stations measuring TNMHC concentrations of 1000 ppbC or greater grouped by the number of monitors. The vast majority (87.0%) of high TNMHC events occurred at only one monitoring station. Events characterized by high TNMHC concentrations at three or more monitoring stations comprised only 2.4% (92 of 3793 hours) of all high TNMHC events.

Table 3-2. Number of hours with one or more monitoring stations characterized by TNMHC concentrations of 1000 ppbC or greater.

Number of Monitoring Stations with Hourly TNMHC >= 1000 ppbC	Number of Hours	Number of Hours (as Percentage of Total)
1	3299	87.0
2	402	10.6
3	65	1.7
4	20	0.5
5	3	0.1
6	4	0.1
7	0	0.0
Total	**3793**	**100.00**

To help account for overall meteorological conditions that may be favorable for high TNMHC concentrations, Table 3-3 presents analogous results to those shown in Table 3-2 using the daily maximum TNMHC concentrations at each monitoring station. Note that 788 unique days are characterized by one or more hourly TNMHC concentrations greater than or equal to 1000 ppbC at one or more monitoring stations. Days characterized by high TNMHC concentrations at three or more monitoring stations comprise 19.7 % (155 of 788 days) of all high TNMHC days. These latter events were most often characterized by winds with a northerly component at nearly calm to very light wind speeds less than 4 mph (as measured at the Dona Park monitoring station) during the early morning hours throughout the November through January period. These conditions are likely exceptionally conducive to high TNMHC concentrations across the Corpus Christi area compared to other months and times of day.

Table 3-3. Number of days with a maximum TNMHC concentration of 1000 ppbC or greater at one or more monitoring stations.

Number of Monitoring Stations with Daily Maximum TNMHC >= 1000 ppbC	Number of Days	Number of Days (as Percentage of Total)
1	384	48.7%
2	249	31.6%
3	93	11.8%
4	36	4.6%
5	18	2.3%
6	3	0.4%
7	5	0.6%
Total	**788**	**100.0%**

3.3.10 Lowest Daily Maximum TNMHC Concentrations as a Surrogate for Variability in Local Meteorological Conditions Conducive for High TNMHC

To investigate the change in seasonal baseline TNMHC concentrations, the hourly maximum concentrations were retrieved for each day during June 2005 - May 2008 at each of the seven CCAQP monitoring stations. The lowest daily maximum concentrations across the seven stations were extracted for additional processing. The lowest daily maximum concentration provides a surrogate for the relative favorability of overall meteorological conditions for high concentrations across the seven monitoring stations. Figure 3-18 presents the lowest daily maximum concentrations averaged over a 30-day averaging period. The annual variation of the baseline TNMHC concentrations is characterized by maximum values during the fall and winter seasons and lowest concentrations during spring. Maximum values of 400 ppbC were common during winter 2006, compared to maximum values of 250 ppbC and 325 ppbC during winter 2007 and winter 2008, respectively. Lowest spring concentrations generally range from 50 ppbC to 100 ppbC. The annual variability in baseline monthly concentrations is likely due, in part, to (1) changes in seasonal patterns that impact the frequency of occurrence of local meteorological conditions favorable to the accumulation of ground-level pollutants such as TNMHC, and (2) changes in the seasonal frequency of occurrence of northerly winds that are generally required for high TNMHC concentrations at 3 of the 7 monitoring stations (i.e., Solar Estates, Oak Park, and Dona Park). The TNMHC emission rates from important industrial sources in the Corpus Christi area may be characterized by seasonal variability as well.

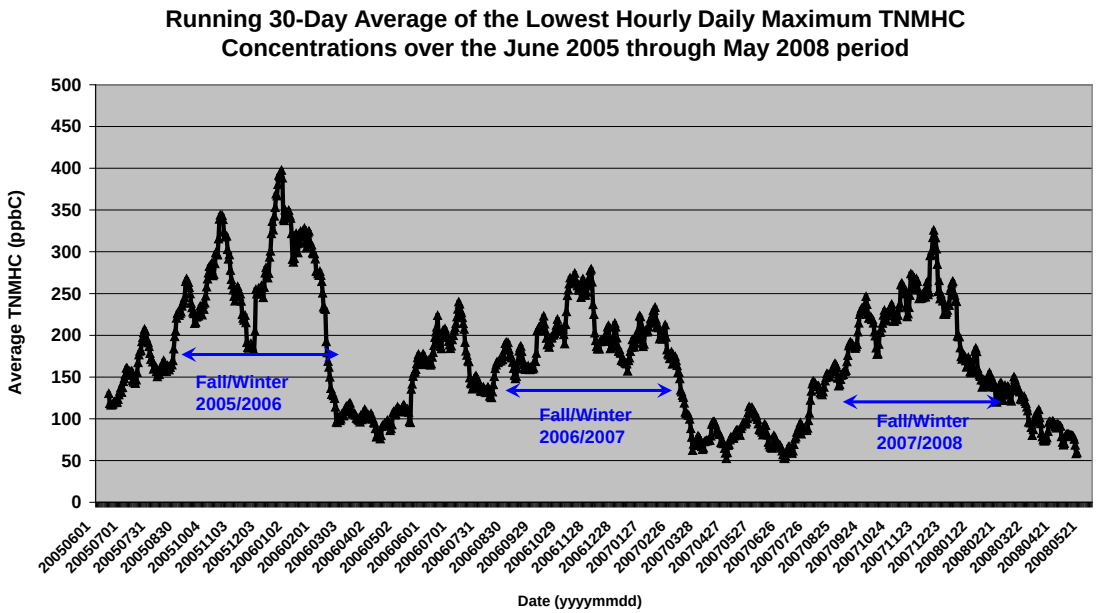

Figure 3-18. Lowest daily maximum hourly TNMHC concentrations measured at the seven CCAQP monitoring stations averaged over a running 30-day period during June 2005 through May 2008.

3.3.11 Local and Large-Scale Weather Patterns during High TNMHC Events

The synoptic-scale weather patterns during the highest TNMHC days have been reviewed for each monitoring station in Appendix A of this report. In general, the surface weather maps often show a high pressure ridge that extends southward, southwestward, or westward into Texas. These surface high pressure systems are typically characterized by weak horizontal pressure gradients over the Corpus Christi area and are associated with light wind speeds and (likely) stable atmospheric conditions. Days characterized by high TNMHC concentrations commonly showed calm to light northwesterly or northeasterly morning winds, followed by light to moderate late morning/afternoon easterly winds becoming east-southeasterly to southeasterly during the late afternoon hours. The clockwise rotation of the coastal wind direction has often been observed along the upper Texas coast, and is likely associated with the diurnal and inertial components of the land and sea breeze circulations (Nielsen-Gammon et al., 2005a, 2005b; UT, 2008) that become most apparent during periods of large-scale weather patterns characterized by weak horizontal pressure gradients. High TNMHC events often occurred during periods of northerly winds that were associated with cold fronts that had moved through South Texas. This scenario was most frequent during high TNMHC events at the Oak Park, Dona Park, and Solar Estates monitoring stations. Wind speeds during these northerly wind events were nearly calm to very light (< 5 mph). Temperatures ranged between 50 F and 80 F, with relative humidity values most often greater than 70%, though lower relative humidity values were not uncommon during events associated with drier air transported into South Texas behind cold fronts.

At the Port Grain and J. I. Hailey monitoring stations, hours with high TNMHC concentrations often occurred either following the passage of cold fronts during periods of northerly winds, or, more commonly, during periods of southwesterly or southerly winds ahead of approaching or stationary fronts located over northern or central Texas. This latter scenario was typically characterized by surface winds with a southeasterly component in the Corpus Christi area. Wind speeds generally ranged between 5 mph and 10 mph. Since high TNMHC events occurred throughout the year over a wide variety of wind directions, temperatures during high TNMHC events ranged between 50 F and 90 F. Southerly winds dominated during high TNMHC events at the FHR Easement and West End Harbor monitoring stations associated with onshore flow from the Gulf of Mexico during summer. Temperatures were most often warm ranging between 70 F and 90 F with relative humidity values greater than 70%. During seasons other than summer, hours with high TNMHC concentrations often occurred during southerly flow ahead of approaching or stationary fronts located over northern or central Texas. A few high TNMHC events occurred under the influence of north-northwesterly winds associated with the passage of a cold front through the Corpus Christi area.

3.4 TNMHC Summary

Average TNMHC concentrations at the seven CCAQP monitoring stations during June 2005 - May 2008 varied from 88 ppbC at Solar Estates to 441 ppbC at FHR Easement. The number of hours characterized by TNMHC concentrations of 1000 ppbC or greater ranged from 40 hours at Solar Estates to 2737 hours at FHR Easement. Higher TNMHC concentrations most often occurred during the nighttime hours, with a maximum frequency of occurrence during the 0000 CST through 0700 CST period. Day-of-week analyses revealed that most seasons were not characterized by weekday/weekend differences. Consistent and substantial differences were limited to nighttime hours during winter at some monitoring stations.

The seasonal analyses demonstrated that higher TNMHC concentrations commonly occurred during fall/winter, but were relatively rare during the spring. The maximum by-site average seasonal concentrations ranged from 126 ppbC during winter at Solar Estates to 652 ppbC during summer at FHR Easement. The seasonal variability of high TNMHC concentrations is likely related, in part, to the seasonal frequency of occurrence of wind direction. Most monitoring stations are characterized by strong wind directionality during higher TNMHC events, suggesting the importance of site-specific emissions sources. Sources located to the south and southeast may be a factor in the high frequency of occurrence of summer events at the FHR Easement and West End Harbor monitoring stations. Higher TNMHC events at the Solar Estates, Dona Park and Oak Park monitoring stations most often occur during hours characterized by winds with a northerly component, which are most common during fall/winter. Higher TNMHC concentrations at the Port Grain and J. I. Hailey monitoring stations occur with roughly equal frequencies during fall, winter, and summer, and are associated with a wide range of wind directions.

A crucial component of the TNMHC analyses at each of the seven CCAQP monitoring stations was the generation of back-trajectories for TNMHC hours with concentrations of 1000 ppbC or greater. The results identify potentially important geographic emissions source regions. There are multiple sources of uncertainty associated with the generation of individual back-trajectories (e.g., refer to the Corpus Christi Trajectory Analysis Tool website http://www.utexas.edu/research/ceer/ccaqp/trajectory_tool.htm); however, the patterns that emerge when analyzing a relatively large number of back-trajectories should provide a good indication of the most frequent upwind areas. The reader is referred directly to Figures 3-11 through 3-17 for geographic maps showing the results of the back-trajectory analyses for each monitoring station.

The synoptic-scale weather patterns on the highest TNMHC days often show a high pressure ridge that extended southward, southwestward, or westward into Texas. Days characterized by three or more monitoring stations with maximum TNMHC concentrations greater than 1000 ppbC most often occurred during conditions of calm to light northerly surface winds during the early morning hours throughout the November through January period. At the Port Grain and J. I. Hailey monitoring stations, high TNMHC concentrations often occurred either following the passage of cold fronts during periods of northerly winds, or, more commonly, during periods of southwesterly or southerly winds ahead of approaching or stationary fronts located over northern or central Texas. Onshore southerly flow from the Gulf of Mexico dominated during high TNMHC events at the FHR Easement and West End Harbor monitoring stations.

The variability of the lowest daily maximum (baseline) TNMHC concentrations suggests that the maximum baseline TNMHC concentrations occurred during fall/winter with minimum values during spring. The 30-day average concentrations ranged from 50-100 ppbC during spring to 250-300 ppbC during winter.

4. Benzene Analyses

This section presents the results of the conceptual model analyses for benzene. Due to the length of the analyses, the full results for hourly benzene concentrations (collected via autoGC) at the Solar Estates and Oak Park monitoring stations are presented individually in Appendix B. In addition, Appendix B includes a summary of 24-hour canister data collected by the Community Air Toxics Monitoring Network (CATMN) in Corpus Christi.

4.1 Definition of High Benzene (Hourly) Concentrations

For the purposes of the benzene conceptual model development, high benzene hours are defined as those hours characterized by a benzene concentration of 30 ppbC or greater at the Solar Estates or Oak Park monitoring stations. The threshold value of 30 ppbC was selected because: 1) 30 ppbC is the minimum concentration that generally captures pollution events of interest based on routine CCAQP analyses; and, 2) the 30 ppbC threshold level, which corresponds to the 99th percentile concentration for all hourly CCAQP measurements collected during June 2005 - May 2008, provides a sufficient dataset to allow robust statistics for the Corpus Christi area.

The threshold concentration of 30 ppbC is well below the short-term concentration values determined by TCEQ to impact human health. TCEQ evaluates both measured and predicted (e.g., using dispersion and/or photochemical modeling) concentrations for selected air toxic compounds, including benzene, based on comparison to Effects Screening Levels (ESLs) and Reference Values (ReVs). ReVs are typically used to evaluate measured concentrations for their potential to cause health and welfare effects on sensitive human populations. ESLs are typically used in the air permitting process as comparison levels to help ensure that authorized emissions of air contaminants do not cause or contribute to air pollution. If the predicted (i.e., modeled) maximum air concentrations are below the acute (e.g., short-term or one-hour) and chronic (e.g., long-term or annual) ESLs, adverse impacts on human health and welfare are not expected. TCEQ generally sets the ESL values to 30% of the ReVs. For benzene, the health-based REVs are currently set to 1080 ppbC and 516 ppbC for acute and chronic exposure, respectively. The corresponding acute and chronic ESLs for benzene are 324 ppbC and 8.4 ppbC, respectively. Note that the benzene concentration threshold value of 30 ppbC used in support of conceptual model development is 9.3% of the acute ESL value of 324 ppbC. For further information on the development of the ReVs and ESLs for benzene, the reader is referred to the TCEQ Toxicology Section's report "Benzene, Development Support Document, Final, October 15, 2007" (Haney, 2007).

4.2 Historical 24-Hour Canister Results for Benzene

Previous analyses in support of the CCAQP have investigated the relationship between wind direction and 24-hour benzene measurements collected by the Community Air Toxics Monitoring Network (CATMN). In support of CATMN, TCEQ has collected samples at multiple monitoring stations within various Texas metropolitan areas since 1992. The samples are collected in evacuated stainless steel canisters over an integrated

24-hour period from midnight to midnight. Typically, samples are collected on an every 6th day schedule.

Table 4-1 presents the site identification and geographic information for CATMN monitoring in the Corpus Christi area during the 1993 through 2008 period. Figure 4-1 shows a map of the locations of these monitoring stations. (Note that Figure 4-1 also shows the locations of the two autoGC CCAQP monitoring stations Solar Estates and Oak Park.) The CATMN samples were collected at most locations on an every 6th day schedule with the exception of the November through April period during the years 1998 through 2005, which were characterized by every day sampling at the Huisache monitoring station. Following collection, CATMN samples are analyzed by TCEQ for target compounds in accordance with appropriate USEPA methods using gas chromatography and mass spectrometry detection.

Table 4-1. Description, period of operation, and number of samples at Corpus Christi CATMN Stations.

Monitor Name	CAMS #	AIRS ID	Operational Period	Number of Samples
Navigation*	121	483550020	01/01/1993 - 09/29/2002	508
Hillcrest	170	483550029	11/01/1998 - 05/30/2008	693
Poth*	164	483550030	12/05/1996 - 10/02/1998	84
Huisache	98	483550032	10/26/1997 - 05/30/2008	1512
Dona Park	635	483550034	10/05/2002 - 05/30/2008	317

*Note that Navigation and Poth were not active during the 2005 through present period.

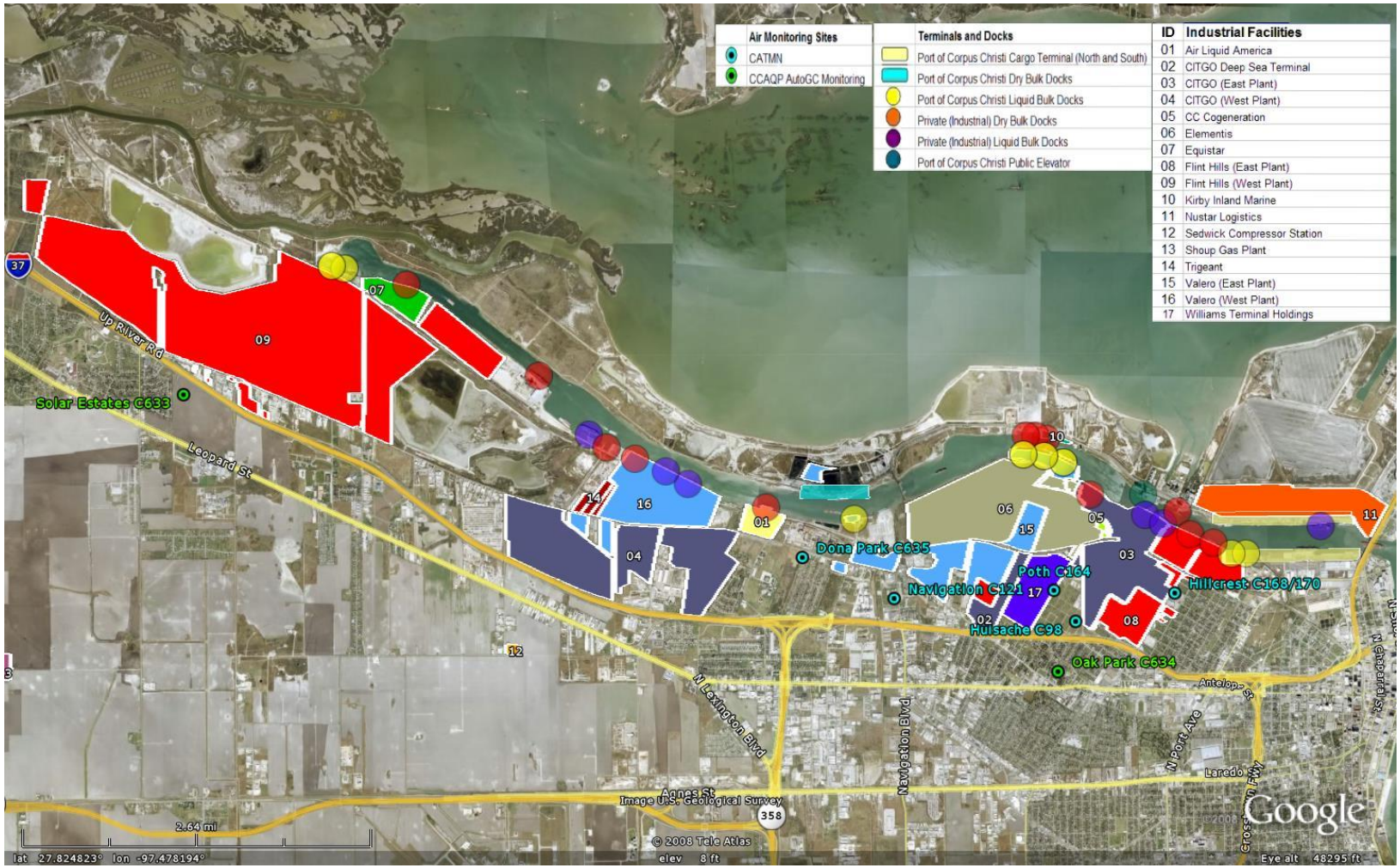

Figure 4-1. Locations of the five CATMN monitoring stations (blue) and two autoGC CCAQP stations (green).

4.3 Benzene Results by Monitoring Station

For the Solar Estates and Oak Park monitoring stations, the conceptual model methodology included a consistent analysis method. The reader is encouraged to review Appendix B for a complete description of results addressing the following areas:

1.) Seasonal, Day of Week, and Diurnal Variability in Benzene Concentrations

2.) Frequency and Duration of High Benzene Events

3.) Local Meteorological Conditions during High Benzene Events

4.) Large-Scale Weather Patterns during High Benzene Events

5.) Upwind Emission Source Regions during High Benzene Events

In addition, Appendix B includes an analysis of the relationship between wind direction and 24-hour benzene measurements collected by Corpus Christi CATMN stations.

4.4 Integrated Summary of Benzene Results

This section presents a summary and analysis of the benzene results provided for the individual monitoring stations in Appendix B of this report. These results are based on hourly benzene concentrations measured at Solar Estates and Oak Park during June 2005 through May 2008 and available CATMN 24-hour canister sampling for the 1993 through 2008 period.

4.4.1 Average Benzene Concentrations

Figure 4-2 presents the average benzene concentrations at the Oak Park and Solar Estates monitoring stations based all available hourly benzene measurements during June 2005 - May 2008. In addition, Figure 4-2 provides the average benzene concentrations at the CATMN stations during June 2005 – May 2008 using all available 24-hour sampling data. (Refer to Table 4-1 for a summary of the CATMN sampling periods. Figure 4-1 provides a map showing all monitoring locations.) The stations in Figure 4-2 are presented in west-to-east order of location along the Corpus Christi Ship Channel. The average benzene concentrations vary widely between the monitoring stations, ranging from 1.93 ppbC at Solar Estates to 8.92 ppbC at Huisache. The average concentration at Oak Park, which is located only 0.4 miles to the south-southwest of Huisache, is substantially lower at 3.75 ppbC. Both the Oak Park and Huisache monitoring stations measure highest concentrations during periods characterized by northeasterly winds, which suggests a local emissions source immediately to the northeast of Huisache. Figure 4-3 presents the by-site maximum 2005 through 2007 average benzene concentrations for selected Texas metropolitan areas. Houston and Corpus Christi are characterized by the highest concentrations in Texas.

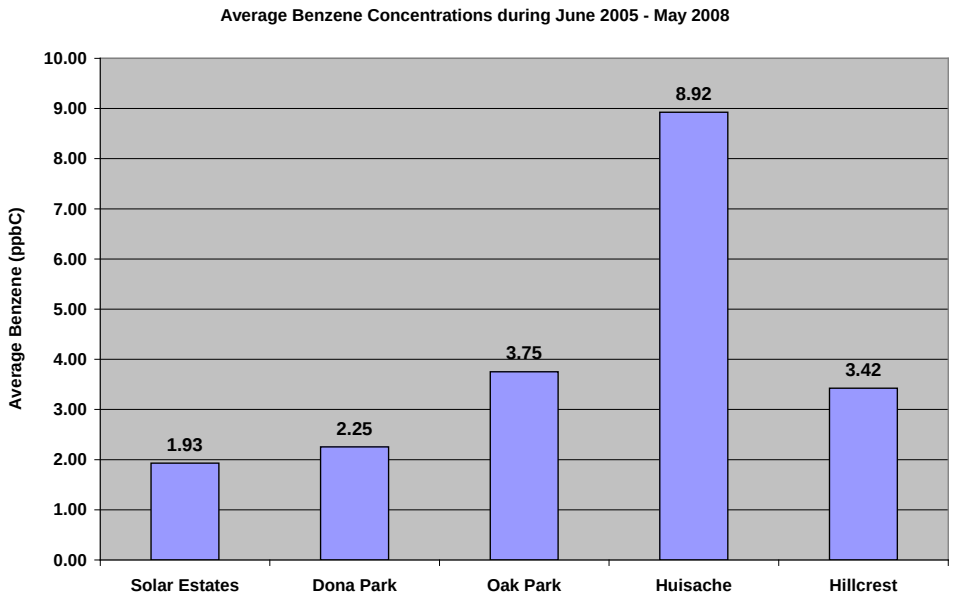

Figure 4-2. Average benzene concentrations during June 2005 – May 2008 for (1) CCAQP Oak Park and Solar Estates monitoring stations using all available hourly measurements, and (2) Corpus Christi CATMN stations using all available 24-hour sampling measurements.

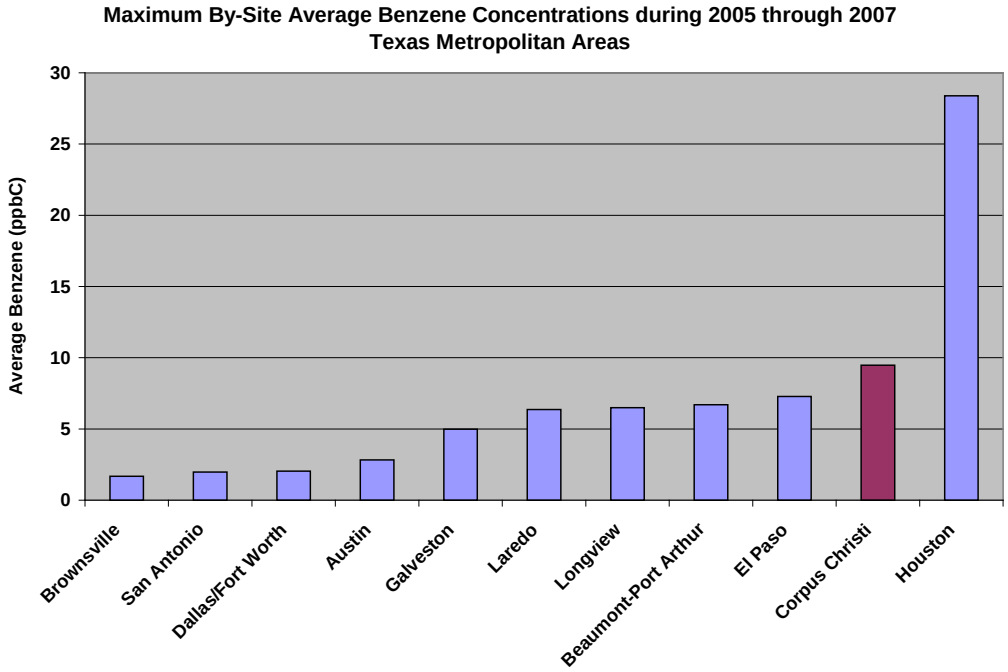

Figure 4-3. Comparison of the by-site maximum average benzene concentrations during 2005 through 2007 for selected Texas metropolitan areas.

4.4.2 Annual Benzene Concentration Trends

The CATMN observations provide a sufficient dataset to investigate trends in benzene concentrations over the past ten years. Figure 4-4 presents the average benzene concentrations at the Huisache, Hillcrest, and Dona Park monitoring stations over consecutive summer through spring periods. These stations were selected because (1) the stations are operational through the current period (i.e., through year 2008) and (2) observations are available for five or more consecutive years during the past decade. As shown in Figure 4-4, the average benzene concentrations for the most recent period range from 1.98 ppbC at Dona Park to 6.71 ppbC at Huisache. The Hillcrest concentrations reveal no discernable trend. For the Huisache monitoring station, the most recent period is characterized by the lowest concentration; however, data from future years will be necessary to determine if this identifies a trend towards lower concentrations rather than year-to-year variability. The Dona Park monitoring station, which measures the lowest concentrations among the three monitoring stations, is characterized by a tendency towards lower concentrations.

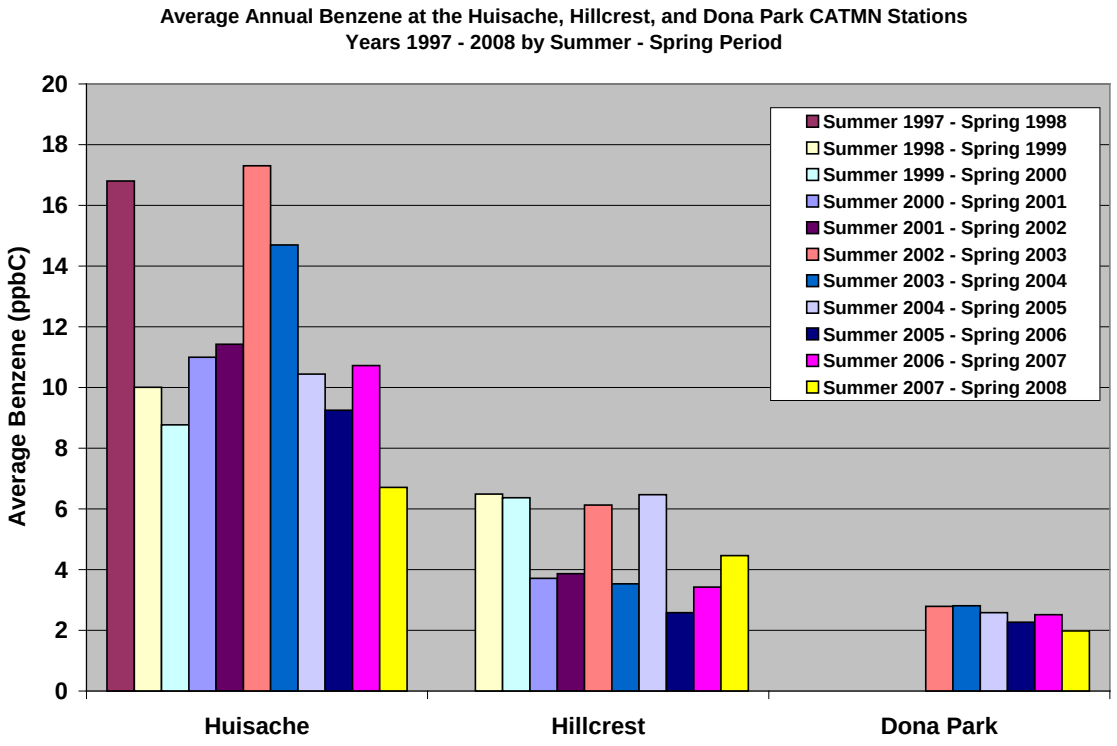

Figure 4-4. Comparison of average benzene concentrations over consecutive summer through spring periods at the Huisache, Hillcrest, and Dona Park CATMN monitoring stations.

4.4.3 Seasonal Variability of High Benzene Concentrations

Figure 4-5 presents the average benzene concentrations by season. All stations are characterized by maximum concentration values during fall/winter. To investigate the year-to-year variability in relatively high hourly benzene concentrations, Figure 4-6 presents the number of hours during June 2005 - May 2008 characterized by concentrations of 30 ppbC or greater at the Solar Estates and Oak Park monitoring stations. Consistent with the results shown in Figure 4-5 for all benzene monitoring stations, hourly concentrations of 30 ppbC or greater are most frequent during fall/winter and least frequent during the summer. In addition, note that summer 2007 - spring 2008 is characterized by a substantially lower frequency of occurrence of benzene concentrations of 30 ppbC or greater at both Solar Estates and Oak Park compared to the previous two years.

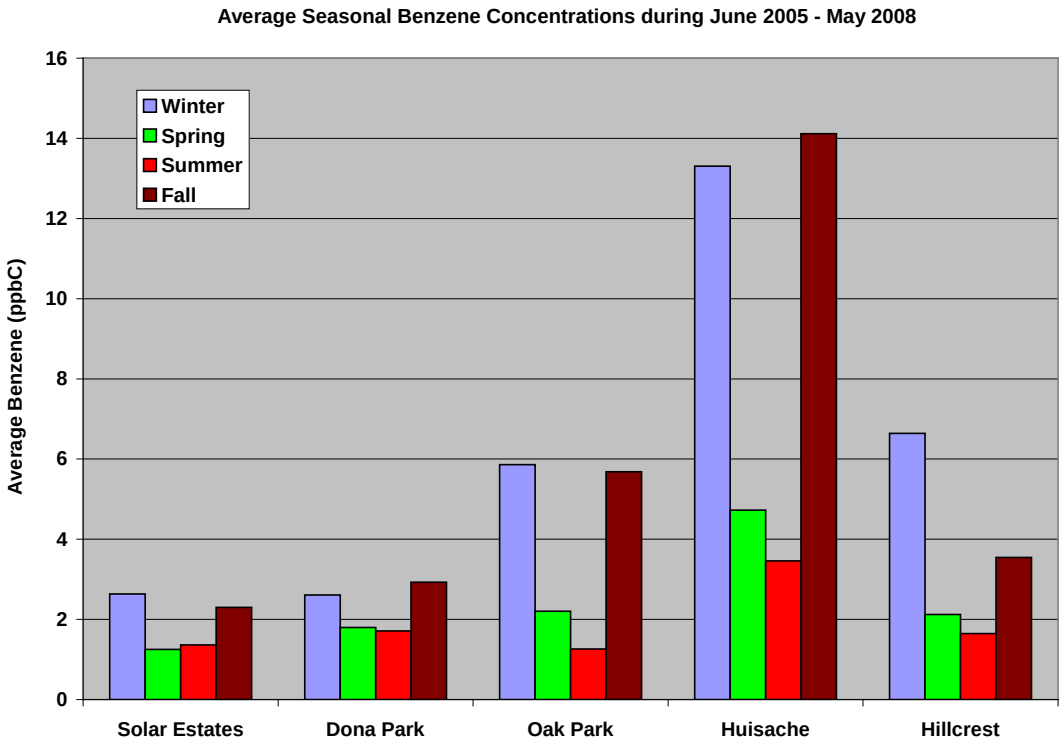

Figure 4-5. Average benzene concentrations by season using all available measurement data as presented in Figure 4-2.

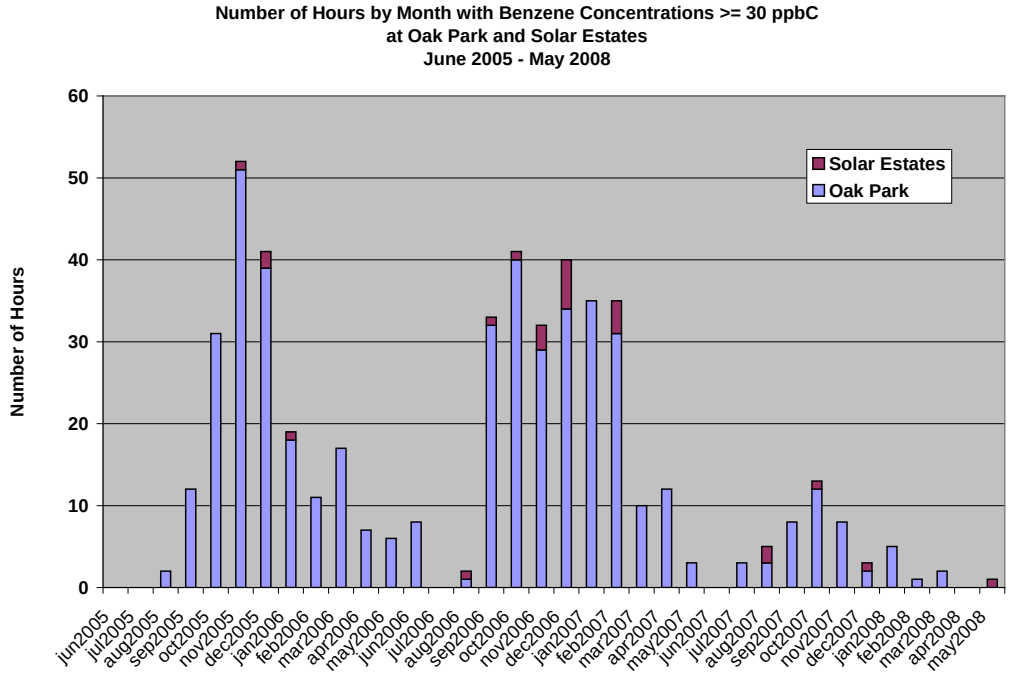

Figure 4-6. Monthly number of hours during June 2005 - May 2008 characterized by benzene concentrations of 30 ppbC or greater at the Solar Estates and Oak Park monitoring stations.

4.4.4 Diurnal Variability of High Benzene Concentrations

As presented in Appendix B this report, the diurnal variability in the median and 75th percentile hourly benzene concentration values reveals that the highest benzene concentrations typically occur during the nighttime and morning periods. Figure 4-7 presents the frequency of occurrence of 30 ppbC benzene concentrations by hour of day. The highest frequency of occurrence at both stations occurs during the morning time period, with maximum values during the 0400 CST through 0800 CST period at Oak Park and during the 0500 CST through 0900 CST period at Solar Estates.

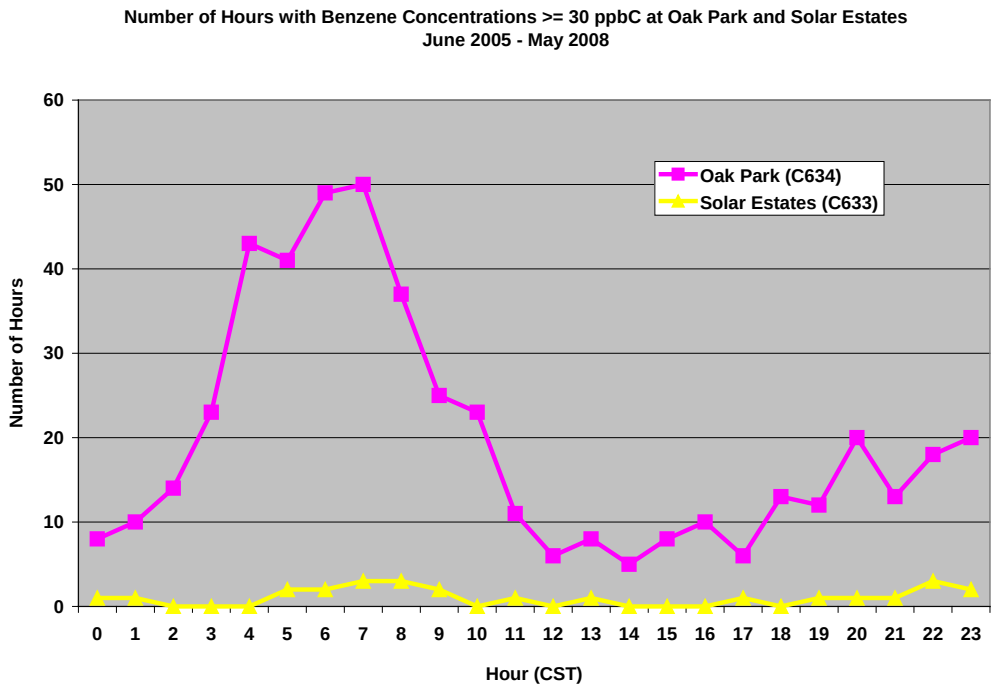

Figure 4-7. Number of hours during June 2005 - May 2008 characterized by benzene concentrations of 30 ppbC or greater at the Solar Estates and Oak Park monitoring stations by hour of day.

4.4.5 Day-of-Week Variability of Benzene Concentrations

Figure 4-8 presents the 75th percentile hourly benzene concentration values by day of week for the Solar Estates and Oak Park monitoring stations. At Solar Estates, the 75th percentile values range from 2.1 ppbC on Sunday to 2.5 ppbC on Tuesday. At Oak Park, the 75th percentile values range from 2.5 ppbC on Sunday to 3.4 ppbC on Saturday. Sunday is characterized by the lowest concentrations values at both monitoring stations. To further investigate differences between weekdays and weekends, the 75th percentile weekday and weekend hourly TNMHC concentration values were calculated by hour by season. Figure 4-9 and Figure 4-10 present the results for the Solar Estates and Oak Park monitoring stations, respectively. The diurnal profiles for both stations show a morning peak in concentrations during the 0600 CST through 0800 CST period that may be associated with emissions from mobile vehicles during the rush hour period. At Solar Estates, the 75th percentile benzene values are characterized by relatively higher concentrations on weekdays compared to weekends throughout the day during fall/winter, with maximum difference during the nighttime and morning hours. In contrast, note that Oak Park is not characterized by consistent and substantial differences between weekday and weekend fall/winter concentrations. Interestingly, although the absolute concentrations during spring are relatively low, spring is generally characterized by higher concentrations on weekends compared to weekdays at both monitoring stations.

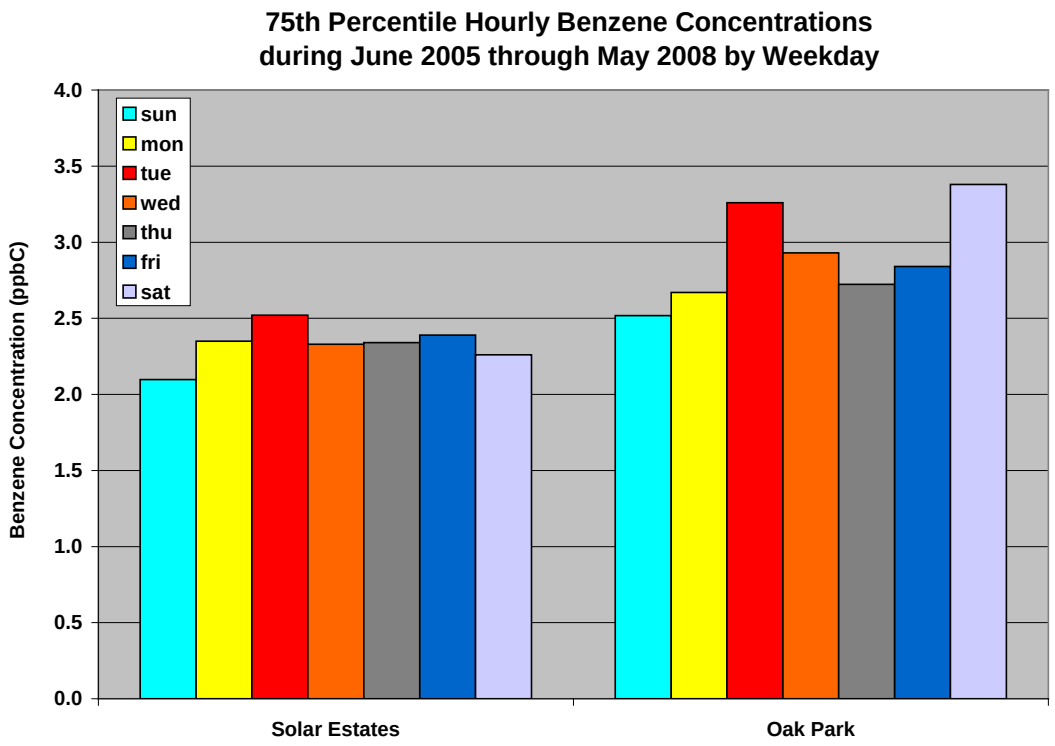

Figure 4-8. The 75th percentile hourly benzene concentration values by day of week for June 2005 - May 2008.

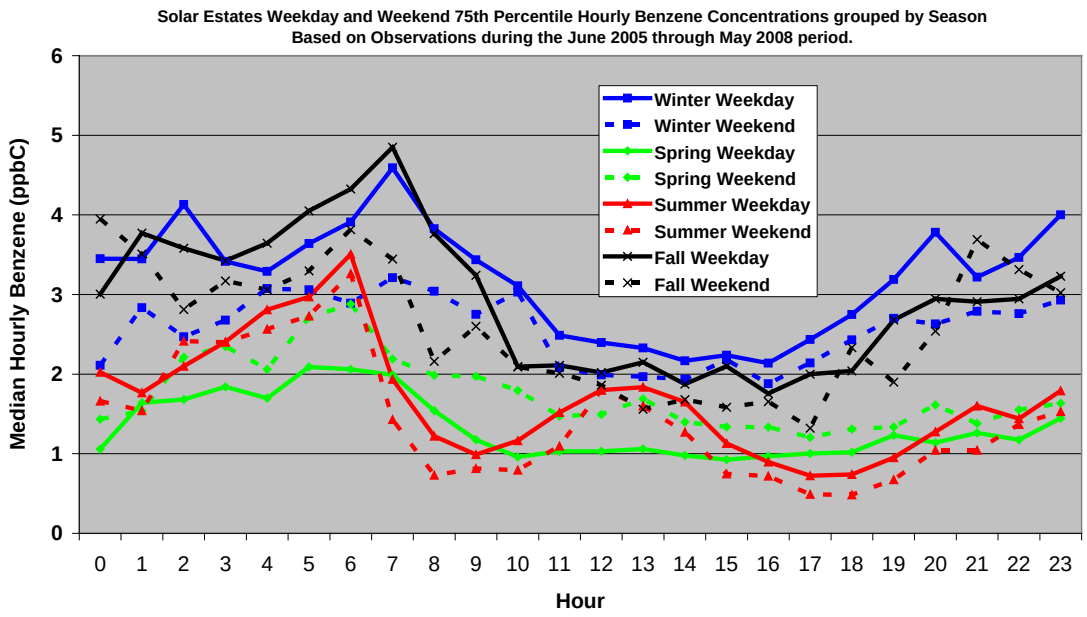

Figure 4-9. The 75th percentile hourly weekday and weekend benzene concentrations grouped by season at the Solar Estates monitoring station based on all valid data during June 2005 - May 2008.

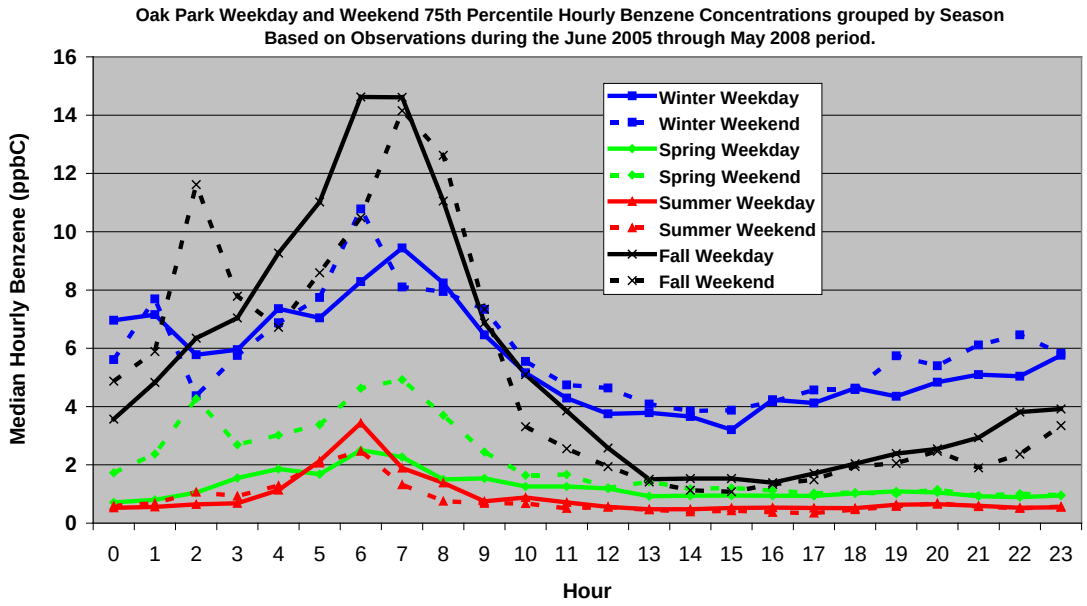

Figure 4-10. The 75th percentile hourly weekday and weekend benzene concentrations grouped by season at the Oak Park monitoring station based on all valid data during June 2005 - May 2008.

4.4.6 Wind Direction and High Hourly Benzene Concentrations at Solar Estates and Oak Park

The frequency of occurrence of benzene concentrations of 30 ppbC or greater grouped by wind direction is presented in Figure 4-11 for the Oak Park and Solar Estates monitoring stations. Both stations show a peak in the number of higher benzene concentrations during hours characterized by winds with a northerly component. At Oak Park, 54% of high benzene hours occur during north-northeasterly winds. Virtually all remaining hours with benzene concentrations of 30 ppbC or greater at Oak Park are characterized by winds with a northerly component. At Solar Estates, 60% of high benzene hours are characterized by north-northeasterly or northeasterly winds. A majority of the remaining hours are characterized by winds with an easterly component.

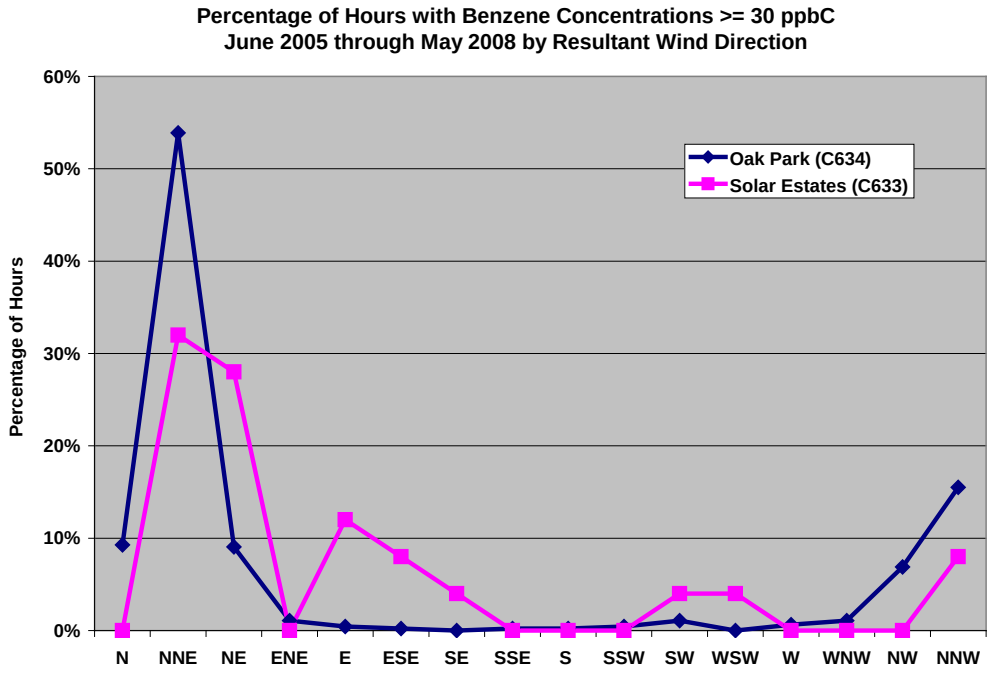

Figure 4-11. The percentage of the total number of 30 ppbC benzene hours for June 2005 - May 2008 grouped by resultant wind direction.

4.4.7 Local Emission Source Regions using AutoGC Data

To identify the local emissions sources at upwind industrial facilities that may impact benzene concentrations, a modified version of the Corpus Christi Trajectory Analysis Tool was used to generate one-hour surface back-trajectories for all hours characterized by benzene concentrations of 30 ppbC or greater at either the Solar Estates or Oak Park monitoring stations. All back-trajectories were initialized at the half-hour (i.e., midpoint) of the one-hour averaging period.

Figure 4-12 and Figure 4-13 present the back-trajectories for Solar Estates and Oak Park, respectively. The back-trajectories suggest that important emissions sources are generally located to the northeast of Solar Estates and to the north-northwest through (especially) north-northeast of Oak Park.

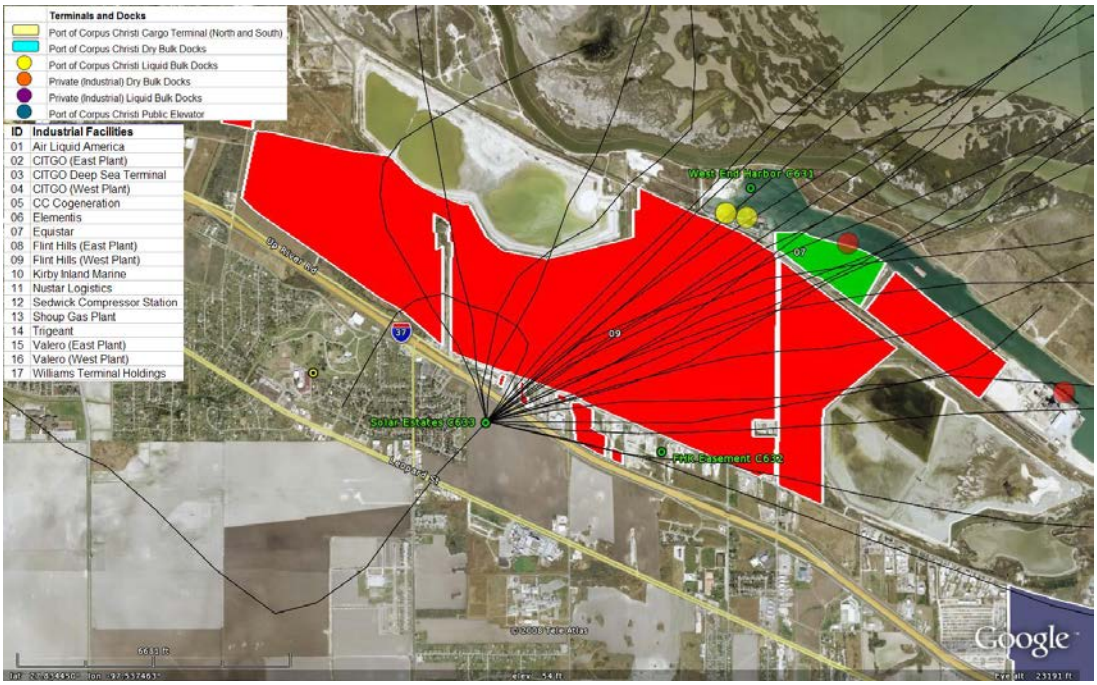

Figure 4-12. Surface back-trajectories as generated by the Corpus Christi Trajectory Analysis Tool for all hours characterized by a benzene concentration of 30 ppb or greater at the Solar Estates monitoring station during June 2005 - May 2008.

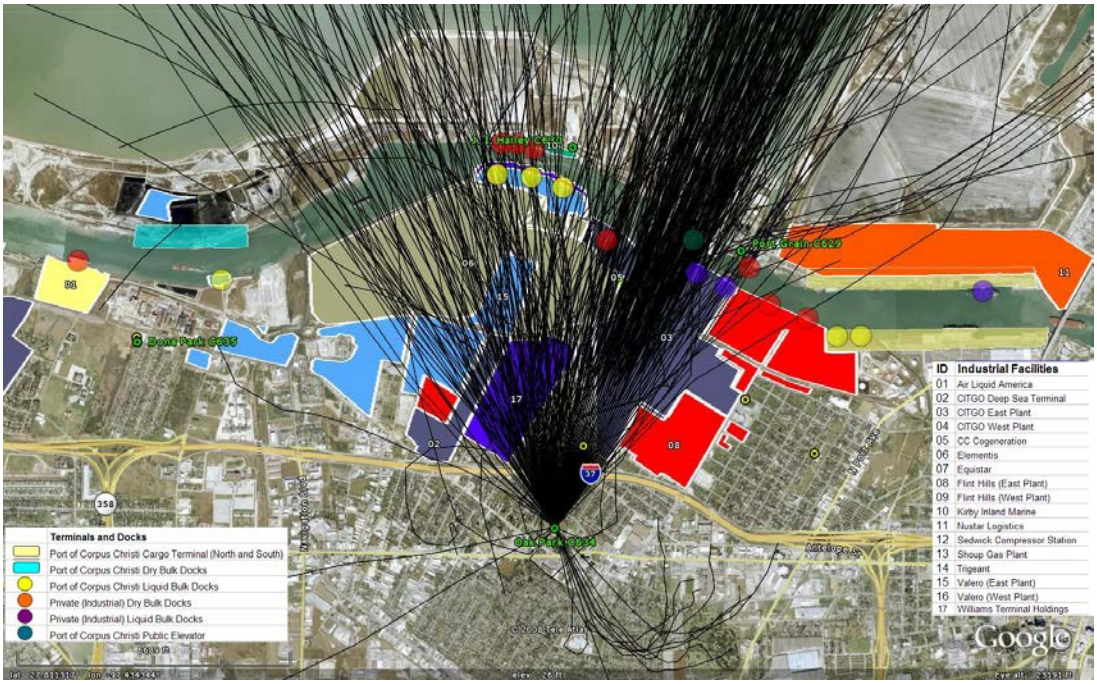

Figure 4-13. Surface back-trajectories as generated by the Corpus Christi Trajectory Analysis Tool for all hours characterized by a benzene concentration of 30 ppb or greater at the Oak Park monitoring station during June 2005 - May 2008.

4.4.8 Local Emission Source Regions using CATMN and AutoGC Data

As presented in Appendix B of this report, in order to investigate the locations of possible sources of benzene emissions impacting the CATMN monitoring stations, hourly wind data at the monitoring stations shown in Table 4-1 were retrieved for all CATMN sampling days. A resultant daily wind direction, representative of the average winds across the Corpus Christi area, was calculated using the available CATMN hourly wind data. The 24-hour benzene concentrations at each monitoring location were merged with the daily resultant wind directions, and mean benzene concentrations were calculated as a function of wind direction. To help account for the impacts of varying wind direction over a given 24-hour period, a smoothing factor was used that incorporates a bell-shaped weighting factor applied over a 20 degree wind direction range centered on the daily resultant wind direction.

The results of the benzene-wind direction analysis for the CATMN stations are presented more fully in Appendix B of this report. The reader is cautioned that the results for each monitoring station are based on all available sampling data, which, as shown in Table 4-1, are characterized by differences in the number of samples and the periods of collection. In addition, the results should be interpreted with caution since wind direction often varies substantially during a 24-hour period.

Figure 4-14 presents the results of the CATMN directional analysis, with lines from each monitoring station representing upwind directions associated with relative maximum values in the average benzene concentrations. In addition, directional lines were added for the Oak Park monitoring station based on the hourly results presented in the previous section of this report. Based on the pattern of the directionals, two potentially important source regions are identified to the northeast of the Navigation and Huisache monitoring stations.

Figure 4-14. Directional lines at each of the CATMN stations representing the wind directions characterized by relative maximum values in the average benzene concentrations (refer to Appendix B for a summary of the CATMN by-site wind direction analysis). Directional lines have been added for the CCAQP Oak Park monitoring station based on the wind direction results presented in Figure 4-11.

4.5 Benzene Summary

Using all available data collected at the CCAQP and CATMN monitoring stations during the 1993 through 2008 period, average benzene concentrations in Corpus Christi ranged from 1.93 ppbC at Solar Estates to 8.92 ppbC at Huisache. The annual average concentrations at the Huisache and Hillcrest CATMN stations show no clear historical trends. The Dona Park CATMN station, which measured relatively lower concentrations compared to Huisache and Hillcrest, is characterized by a tendency towards lower concentrations over the 2002 through 2008 period. The maximum by-site seasonal average concentrations varied from 2.63 ppbC at Solar Estates to 14.11 ppbC at Huisache. All monitoring stations are characterized by highest concentrations during fall/winter.

At the two CCAQP autoGC monitoring stations, the number of hours characterized by benzene concentrations of 30 ppbC or greater is 25 hours at Solar Estates and 473 hours at Oak Park. The diurnal variability of hourly benzene concentrations reveals that high concentrations are most frequently measured during the 0400 CST through 0900 CST period, which encompasses the morning rush hour. At both stations, the day-of-week analysis demonstrates a weak pattern of lowest concentrations on Sunday. During winter at Solar Estates, the morning is characterized by consistent and substantial differences between the hourly weekday and weekend concentrations. In contrast, the hourly diurnal

profiles do not reveal weekday/weekend differences at Oak Park. Interestingly, although the absolute spring concentrations are low compared to winter, both Oak Park and Solar Estates are characterized by higher concentrations on weekends compared to weekdays during spring.

The wind direction and back-trajectory analyses identify consistent upwind geographic sources regions during high benzene events at Oak Park and Solar Estates. Oak Park is dominated by flow from either the north-northwest or (especially) north-northeast. At Solar Estates, winds are generally from the northeast or east. The reader is referred directly to Figures 4-12 through 4-13 for geographic maps showing the results of the back-trajectory analyses for each monitoring station. Incorporating these results with wind direction analyses performed using the 24-hour CATMN data suggests potentially important source regions located to the northeast of the Navigation and Huisache CATMN stations.

5.0 References

Bortnick, S.M., Stetzer, S.L., 2002. *Sources of variability in ambient air toxics monitoring data*. Atmospheric Environment 36, 1783–1791.

Demerjian, K.L., 2000. *A review of national monitoring networks in North America*. Atmospheric Environment 34, 1861-1884.

Haney, J.T., Jr., 2007. *Development Support Document, Final, October 15, 2007, Benzene, CAS Registry Number: 71-43-2.* Toxicology Section, Texas Commission on Environmental Quality (TCEQ).

McCarthy, M.C., Hafner, H.R., Chinkin, L.R., Charrier, J.G., 2007. *Temporal variability of selected air toxics in the United States.* Atmospheric Environment 41, 7180-7194.

Nielsen-Gammon, J., Tobin, J., McNeel, A., Li, G., 2005a. *A conceptual model for eight-hour ozone exceedances in Houston, Texas Part I: Background ozone levels in eastern Texas*. 52 pp., technical report, Houston Adv. Res. Cent., Houston, Tex.

Nielsen-Gammon, J., Tobin, J., McNeel, A., 2005b. *A conceptual model for eight-hour ozone exceedances in Houston, Texas Part II: Eight hour ozone exceedances in the Houston-Galveston metropolitan area*. 79 pp., technical report, Houston Adv. Res. Cent., Houston, Tex.

Reiss, R., 2006. *Temporal trends and weekend-weekday differences for benzene and 1,3-butadiene in Houston, Texas.* Atmospheric Environment 40, 4711-4724.

Singh, H.B., Salas, L., Viezee, W., Sitton, B., Ferek, R., 1992. *Measurement of volatile organic-chemicals at selected sites in California.* Atmospheric Environment Part A—General Topics 26 (16), 2929-2946.

Spicer, C.W., Buxton, B.E., Holdren, M.W., Smith, D.L., Kelly, T.J., Rust, S.W., Pate, A.D., Sverdrup, G.M., Chuang, J.C., 1006. *Variability of hazardous air pollutants in an urban area.* Atmospheric Environment 30 (20), 3443-3456.

Touma, J.S., Cox, W.M., Tikvart, J.A., 2006. *Spatial and Temporal Variability of Ambient Air Toxics Data.* Journal of the Air and Waste Management Association 56, 1716-1725.

UT, 2008. *Conceptual Model of the Large-Scale Weather Features, Local Meteorological Conditions, and Long-Range Transport Patterns on High Ozone Days for the Victoria Area.* The University of Texas at Austin. Prepared for the Texas Commission of Environmental Quality and City of Victoria, July 2008.