# Corpus Christi Air Monitoring and Surveillance Camera Installation and Operation Project Case Number: 2:11-MC-00044

### **Quarterly Report for the Period**

# July 1, 2011 through September 30, 2011

Submitted to

The Honorable Janis Graham Jack US District Court for the Southern District of Texas Corpus Christi, Texas

Ms. Kathleen Aisling US Environmental Protection Agency, Region 6 Dallas, Texas

Ms. Susan Clewis Texas Commission on Environmental Quality, Region 14 Corpus Christi, Texas

#### Submitted by

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November 29, 2011

# I. Introduction

On October 1, 2003, the US District Court for the Southern District of Texas issued an order to the Clerk of the Court to distribute funds in the amount of \$6,700,000, plus interest accrued, to The University of Texas at Austin (UT Austin) to implement the court ordered condition of probation (COCP) project *Corpus Christi Air Monitoring and Surveillance Camera Installation and Operation* (Project). This quarterly report has been prepared pursuant to the requirements of the project and is being submitted to the US District Court, the US Environmental Protection Agency (EPA), and the Texas Commission on Environmental Quality (TCEQ).

# II. Project Progress Report

The focus of work during the quarter ending September 30, 2011 has been directed to the following activities.

# A. Operations and Maintenance Phase of the Project

A detailed description of the data analyses for this quarter appears in Appendix A, pages 6 through 28, and a summary of these analyses appears in this section.

The Project consists of a network of seven (7) air monitoring stations with air monitoring instruments and surveillance camera equipment. A map showing locations of the COCP Project monitoring sites along with TCEQ sites appears in Figure 1, below. Table 1, on page 3, identifies the location and instrumentation found at each of the COCP Project sites. TCEQ sites and some of the sites farther from the COCP area than the TCEQ sites, operated by Texas A&M at Kingsville (TAMUK) provide additional data used in these analyses.



Figure 1. Corpus Christi Monitoring Sites

TCEQ		Monitoring Equipment						
CAMS Nos.	Description of Site Location	Auto GC	TNMHC(T) & Canister(C)	H2S & SO2	Met Station	Camera		
634	Oak Park Recreation Center	Yes	Т		Yes			
629	Grain Elevator @ Port of Corpus Christi		T&C	Yes	Yes			
630	J. I. Hailey Site @ Port of Corpus Christi		T&C	Yes	Yes			
635	TCEQ Monitoring Site C199 @ Dona Park		T&C	Yes	Yes	Yes		
631	Port of Corpus Christi on West End of CC Inner Harbor		T&C	Yes	Yes			
632	Off Up River Road on Flint Hills Resources Easement		T&C	Yes	Yes			
633	Solar Estates Park at end of Sunshine Road	Yes	Т	Yes	Yes	Yes		

 Table 1. Schedule of Air Monitoring Sites, Locations and Major Instrumentation

# Legend

Legenu	
CAMS	continuous ambient monitoring station
Auto GC	automated gas chromatograph
TNMHC	total non-methane hydrocarbon analyzer (all except CAMS 634 & 633 also have
	canister hydrocarbon samplers)
$H_2S$	hydrogen sulfide analyzer
$SO_2$	sulfur dioxide analyzer
Met Station	meteorology station consisting of measurement instruments for wind speed, wind
	direction, ambient air temperature and relative humidity
Camera	surveillance camera

A discussion of data findings for the quarter appears in Appendix A, pages 6 though 28. Specifically, the appendix contains the following elements:

• Auto-GC Data Summary – In examining the validated <u>second</u> quarter of 2011 hourly auto-GC data from Oak Park, Solar Estates, and TCEQ's Palm sites no individual measurements were found to have exceeded a short-term air monitoring comparison value (AMCV). Also, the validated second quarter average concentrations were below each compound's long-term AMCVs. For <u>third</u> quarter data, the preliminary values were also below respective AMCVs. A summary of data appears in Appendix A, pages 12 through 15.

- **Benzene Summary** Average benzene concentrations have been relatively constant in recent years. The second and third quarter means from 2006 through 2011 are presented in Appendix A, pages 16 through 19.
- Analysis of Sulfur Dioxide at Several Sites This quarter the JIH CAMS 630 site continued to see concentrations of SO<sub>2</sub> close to the level of the SO<sub>2</sub> National Ambient Air Quality Standards (NAAQS), but no samples exceeding the NAAQS. However, the Solar Estates CAMS 633 site did measure two exceedances of the SO<sub>2</sub> NAAQS level. This subject is expanded upon in Appendix A, pages 19 through 24.
- **Case Study** A description of a pollution upset event from February 2011 that was detected by the relatively new TCEQ Palm auto-GC appears in Appendix A, pages 25 through 27.

#### B. Project Management and Planning

Project Management and Planning during this period has focused on the following four (4) major activities.

### 1. Air Monitoring Operations

Operations and maintenance of the seven monitoring sites reporting data via the TCEQ LEADS is on-going. The data can be accessed and reviewed at the project website (http://www.utexas.edu/research/ceer/ccaqp/).

#### 2. Communication and Reporting

The status of the Project has been communicated through the website, which is operational with portions under continual updating, quarterly and annual reports.

#### 3. Budget Monitoring

Budget monitoring during the period has focused on projects costs for Phase II – Sites Operation and Maintenance costs. Financial reports for the quarter are included in Appendix B, pages 29 and 30.

#### 4. Other Contributions

There were no other contributions made to the project during this quarter.

# **III. Financial Report**

As required, the following financial summary information is provided. Details supporting this financial summary are included in Appendix B, pages 29 and 30.

#### A. Total Amount of COCP Funds and Other Funds Received Under the Project

The COCP funds received through September 30, 2011 totals \$7,568,507.68. This total includes interest earned through September 30, 2011.

B. <u>Detailed List of the Actual Expenditures Paid from COCP Funds</u>

Expenditures of COCP funds during this quarter totaled \$91,942.72. The detailed breakdown of the actual expenditures is included in Appendix B, page 30. The activities for which these expenditures were used are detailed in Section II, on page 2 of this report

C. Total Interest Earned on COCP Funds during the Quarter

The interest earned during this quarter totaled \$5,506.42. A report providing detailed calculations of the interest earned on the COCP funds during each month of the quarter is included in Appendix B, pages 29 and 30.

D. <u>Balance as of September 30, 2011, in the COCP Account</u> The balance in the COCP account, including interest earned totals \$898,315.38.

E. <u>Expected Expenditures for the Funds Remaining in the COCP Account</u> The projected expenditures for the funds remaining totals \$898,315.38.

#### **Quarterly Report Distribution List:**

U.S. District Court Mr. Joseph Jasek, Assistant Deputy Chief USPO Mr. James Martinez, Supervising USPO
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# APPENDIX A

Data Analysis for Corpus Christi Quarterly Report

July 1, 2011 through September 30, 2011

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# Data Analysis for Corpus Christi Quarterly Report

This technical report describes results of monitoring and analysis of data under the Corpus Christi Air Monitoring and Surveillance Camera Installation and Operation Project, with primary focus on the period July 1 through September 30, 2011. The monitoring network is shown in Figure 1, on page 2, and is described in Table 2, below. This report contains the following elements:

- A summary of Oak Park, Solar Estates, and Palm (TCEQ) auto-GC data for the second and third quarters of 2011;
- Information on the trends for benzene concentrations at the two project auto-GCs in residential areas;
- A discussion of the sulfur dioxide (SO<sub>2</sub>) data from several sites;
- A description of a pollution upset event from earlier this year that was detected by the relatively new TCEQ Palm auto-GC.

<b>be 2.</b> Schedule of an monitoring sites, locations and major instrumentation							
TCEQ		Monitoring Equipment					
CAMS#	Description of Site Location	Auto	TNMHC (T) /	$H_2S \&$	Met		
CAND		GC	Canister (C)	$SO_2$	Station	Camera	
634	Oak Park Recreation Center ( <b>OAK</b> )	Yes	Т		Yes		
629	Grain Elevator @ Port of Corpus Christi ( <b>CCG</b> )		T&C	Yes	Yes		
630	J. I. Hailey Site @ Port of Corpus Christi ( <b>JIH</b> )		T&C	Yes	Yes		
635	TCEQ Monitoring Site C199 @ Dona Park ( <b>DPK</b> )		T&C	Yes	Yes	Yes	
631	Port of Corpus Christi on West End of CC Inner Harbor ( <b>WEH</b> )		T&C	Yes	Yes		
632	Off Up River Road on Flint Hills Resources Easement (FHR)		T&C	Yes	Yes		
633	Solar Estates Park at end of Sunshine Road ( <b>SOE</b> )	Yes	Т	Yes	Yes	Yes	

#### Table 2. Schedule of air monitoring sites, locations and major instrumentation

#### Legend

Legena	
Auto GC	automated gas chromatograph
TNMHC	total non-methane hydrocarbon analyzer (all except CAMS 633 & 634 also have
	canister hydrocarbon samplers)
$H_2S$	hydrogen sulfide analyzer
$SO_2$	sulfur dioxide analyzer
Met Station	meteorology station consisting of measurement instruments for wind speed, wind direction, ambient air temperature and relative humidity
Camera	surveillance camera

#### **Glossary of terms**

- **Pollutant concentrations** Concentrations of most gaseous pollutants are expressed in units denoting their "mixing ratio" in air; i.e., the ratio of the number molecules of the pollutant to the total number of molecules per unit volume of air. Because concentrations for all gases other than molecular oxygen, nitrogen, and argon are very low, the mixing ratios are usually scaled to express a concentration in terms of "parts per million" (ppm) or "parts per billion" (ppb). Sometimes the units are explicitly expressed as ppm-volume (ppmV) or ppb-volume (ppbV) where 1 ppmV indicates that one molecule in one million molecules of ambient air is the compound of interest and 1 ppbV indicates that one molecule in one billion molecules of ambient air is the compound of interest. In general, air pollution standards and health effects screening levels are expressed in ppmV or ppbV units. Because hydrocarbon species may have a chemical reactivity related to the number of carbon atoms in the molecule, mixing ratios for these species are often expressed in ppb-carbon (ppbV times the number of carbon atoms in the molecule), to reflect the ratio of carbon atoms in that species to the total number of molecules in the volume. This is relevant to our measurement of auto-GC species and TNMHC, which are reported in ppbC units. For the purpose of relating hydrocarbons to health effects, this report notes hydrocarbon concentrations in converted ppbV units. However, because TNMHC is a composite of all species with different numbers of carbons, it cannot be converted to ppbV. Pollutant concentration measurements are time-stamped based on the start time of the sample, in Central Standard Time (CST), with sample duration noted.
- Auto-GC The automated gas chromatograph collects a sample for 40 minutes, and then automatically analyzes the sample for a target list of 46 hydrocarbon species. These include benzene and 1,3-butadiene, which are air toxics, various species that have relatively low odor thresholds, and a range of gasoline and vehicle exhaust components. Auto-GCs operate at Solar Estates CAMS 633 and Oak Park CAMS 634. In June 2010 TCEQ began operating an auto-GC at Palm CAMS 83 at 1511 Palm Drive in the Hillcrest neighborhood.
- Total non-methane hydrocarbons (TNMHC) TNMHC represent a large fraction of the total volatile organic compounds released into the air by human and natural processes. TNMHC is an unspeciated total of all hydrocarbons, and individual species must be resolved by other means, such as with canisters or auto-GCs. However, the time resolution of the TNMHC instrument is much shorter than the auto-GC, and results are available much faster than with canisters. TNMHC analyzers operate at all seven UT/CEER sites.
- **Canister** Electro-polished stainless steel canisters are filled with air samples when an independent sensor detects that *elevated* (see below) levels of hydrocarbons (TNMHC) are present. Samples are taken for 20 minutes to try to capture the chemical make-up of the air. In most cases, the first time on any day that the monitored TNMHC concentration exceeds 2000 ppbC at a site for a continuous period of 15 minutes or more, the system will trigger and a sample will be collected. Samples are sent to UT Austin and are analyzed in a lab to resolve some 60 hydrocarbon and 12 chlorinated species.

Canister samplers operate at the five sites that do not take continuous hydrocarbon measurements with auto-GCs (CAMS 629, 630, 631, 632, and 635).

• Air Monitoring Comparison Values (AMCV) – The TCEQ uses AMCVs in assessing ambient data. Two valuable online documents ("fact sheet" and "AMCV document") that explain AMCVs are at

http://www.tceq.state.tx.us/implementation/tox/regmemo/AirMain.html#compare

(accessed July 2011). The following text is an excerpt from the TCEQ "fact sheet":

Effects Screening Levels are chemical-specific air concentrations set to protect human health and welfare. Short-term ESLs are based on data concerning acute health effects, the potential for odors to be a nuisance, and effects on vegetation, while long-term ESLs are based on data concerning chronic health and vegetation effects. Health-based ESLs are set below levels where health effects would occur whereas welfare-based ESLs (odor and vegetation) are set based on effect threshold concentrations. The ESLs are screening levels, not ambient air standards. Originally, the same long- and short-term ESLs were used for both air permitting and air monitoring.

There are significant differences between performing health effect reviews of air permits using ESLs, and the various forms of ambient air monitoring data. The Toxicology Division is using the term "air monitoring comparison values" (AMCVs) in evaluations of air monitoring data in order to make more meaningful comparisons. "AMCVs" is a collective term and refers to all odor-, vegetative-, and health-based values used in reviewing air monitoring data. Similar to ESLs, AMCVs are chemical-specific air concentrations set to protect human health and welfare. Different terminology is appropriate because air permitting and air monitoring programs are different.

- Rationale for Differences between ESLs and AMCVs A very specific difference between the permitting program and monitoring program is that permits are applied to one company or facility at a time, whereas monitors may collect data on emissions from several companies or facilities or other source types (e.g., motor vehicles). Thus, the protective ESL for permitting is set lower than the AMCV in anticipation that more than one permitted emission source may contribute to monitored concentrations.
- National Ambient Air Quality Standards (NAAQS) U.S. Environmental Protection Agency (EPA) has established a set of standards for several air pollutions described in the Federal Clean Air Act<sup>1</sup>. NAAQS are defined in terms of *levels* of concentrations and particular *forms*. For example, the NAAQS for particulate matter with size at or less than 2.5 microns (PM<sub>2.5</sub>) has a *level* of 15 micrograms per cubic meter averaged over 24-hours, and a *form* of the annual average based on four quarterly averages, averaged over three years. Individual concentrations measured above the level of the NAAQS are called *exceedances*. The number calculated from a monitoring site's data to compare to the level of the standard is called the site's *design value*, and the highest design value in the area for a year is the regional design value used to assess overall NAAQS compliance. A monitor or a region that does not comply with a NAAQS is said to be *noncompliant*. At some point after a monitor or region has been in noncompliance, the U.S. EPA may choose to label the region as *nonattainment*. A nonattainment designation triggers requirements under the Federal Clean Air Act for the development of a plan to bring the region back into compliance.

<sup>&</sup>lt;sup>1</sup> See <u>http://epa.gov/air/criteria.html</u> accessed October 2011

A more detailed description of NAAQS can be found on the TCEQ's Website at <u>http://www.tceq.texas.gov/airquality/monops/naaqs.html</u> (accessed October 2011).

One species measured by this project and regulated by a NAAQS is sulfur dioxide (SO<sub>2</sub>). Effective June 2, 2010, EPA modified the SO<sub>2</sub> NAAQS to include a level of 0.075 ppm, or 75 ppb averaged over one hour, with a form of the three-year average of the annual 99<sup>th</sup> percentiles of the daily maximum one-hour averages. The other two existing NAAQS for SO<sub>2</sub> are 0.03 ppm (30 ppb) averaged over one year and 0.14 ppm (140 ppb) averaged over 24 hours, not to be exceeded in any one year. There is also a secondary SO<sub>2</sub> standard of 0.500 ppm (500 ppb) over three hours, not to be exceeded in any one year. The reason that there has been little attention to the SO<sub>2</sub> NAAQS on this project until recently is that the State of Texas's standard of 0.400 ppm or 400 ppb over 30 minutes for SO<sub>2</sub> was much more likely to be exceeded than the older NAAQS. With the addition of a new NAAQS for SO<sub>2</sub> in June 2010, however, the situation has changed.

- Elevated Concentrations In the event that measured pollutant concentrations are above a set threshold they are referred to as "elevated concentrations." The values for these thresholds are summarized by pollutant below. As a precursor to reviewing the data, the reader should understand the term "*statistical significance*." In the event that a concentration is higher than one would typically measure over, say, the course of a week, then one might conclude that a specific transient assignable cause may have been the pollution source, because experience shows the probability of such a measurement occurring under normal operating conditions is small. Such an event may be labeled "statistically significant" at level 0.01, meaning the observed event is rare enough that it is not expected to happen more often than once in 100 trials. This does not necessarily imply the occurrence of a violation of a health-based standard. A discussion of "elevated concentrations" and "statistical significance" by pollutant type follows:
  - For H<sub>2</sub>S, any measured concentration greater than the level of the state residential standards, which is 80 ppb over 30 minutes, is considered "elevated." For SO<sub>2</sub>, any measured concentration greater than the level of the NAAQS, which is 75 ppb over one hour, is considered "elevated." Note that the concentrations of SO<sub>2</sub> and H<sub>2</sub>S need not persist long enough to constitute an exceedance of the standard to be regarded as elevated. In addition, any closely spaced values that are statistically significantly (at 0.01 level) greater than the long-run average concentration for a period of one hour or more will be considered "elevated" because of their unusual appearance, as opposed to possible health consequence. The rationale for doing so is that unusually high concentrations at a monitor may suggest the existence of unmonitored concentrations closer to the source area that are potentially above the state's standards.
  - For TNMHC, any measured concentration greater than the canister triggering threshold of 2000 ppbC is considered "elevated." Note that the concentrations need not persist long enough to trigger a canister (900 seconds) to be considered elevated.
  - For benzene and other air toxics in canister samples or auto-GC measurements, any concentration above the AMCV is considered "elevated." Note that 20minute canister samples and 40-minute auto-GC measurements are both compared with the short-term AMCV.

Some hydrocarbon species measured in canister samples or by the auto-GC generally appear in the air in very low concentrations close to the method detection level. Similar to the case above with H<sub>2</sub>S and SO<sub>2</sub>, any values that are statistically significantly (at 0.01 level) greater than the long-run average concentration at a given time or annual quarter will be considered "elevated" because of their unusual appearance, as opposed to possible health consequence. The rationale for doing so is that unusually high concentrations at a monitor may suggest an unusual emission event in the area upwind of the monitoring site.

#### 1. Auto-GC Data Summaries in Residential Areas

In this section the results of semi-continuous sampling for hydrocarbons at the three Corpus Christi auto-GC sites – UT's Solar Estates C633, UT's Oak Park C634, and TCEQ's Palm C83 – are presented. These three sites are located in residential areas. Solar Estates and Oak Park are generally downwind of industrial emissions under northerly winds. Palm, located near the TCEQ's Hillcrest and Williams Park sites in Figure 1, on page 2, is generally downwind under northerly and westerly winds. In examining aggregated data one observes similar patterns of hydrocarbons at all three sites.

Table 3, on page 13, summarizes the <u>validated</u> average data values from the <u>second</u> quarter of 2011. Data in this table are available to TCEQ staff at <u>http://rhone3.tceq.texas.gov/cgi-bin/agc\_summary.pl</u> (accessed October 2011). Table 4, on page 14, summarizes the as-yet-unvalidated average data values from the <u>third</u> quarter of 2011.

As noted in the preceding paragraph, Tables 3 and 4 show the averages (arithmetic mean of measured values) for 27 hydrocarbon species for the periods of interest, and Table 3 also shows the maximum one-hour values and the maximum 24-hour average concentrations for the quarter's validated data. All concentration values in the tables are in ppbV units. No concentrations or averages of concentrations from the 27 species were greater than TCEQ's air monitoring comparison values (AMCV). The average data columns in Table 3 for the validated second quarter data and Table 4 for the as-yet-unvalidated third quarter data are shown graphically in Figures 2 and 3, respectively, page 15.

The rows for *benzene* are bold-faced in Tables 3 and 4 owing to the concern that the concentrations for this species tend to be closer to the AMCV than are concentrations of other species. The benzene short-term AMCV is 180 ppbV and the benzene long-term AMCV is 1.4 ppbV.

Units ppbV	Oak 1Q11				olar 1Q	11	Palm 1Q11			
	Peak	Peak		Peak	Peak		Peak	Peak		
Species	1hr	24hr	Mean	1hr	24hr	Mean	1hr	24hr	Mean	
Ethane	67.22	13.29	3.17	77.36	9.67	3.87	66.36	17.48	4.55	
Ethylene	23.45	1.75	0.35	5.97	0.72	0.21	51.75	3.88	0.38	
Propane	83.82	13.87	1.74	70.33	8.08	2.26	99.37	20.89	1.81	
Propylene	9.77	1.78	0.23	7.87	0.67	0.15	15.02	1.93	0.17	
Isobutane	26.27	3.89	0.56	27.8	2.78	0.82	210.91	23.8	0.94	
n-Butane	27.39	4.86	0.87	24.9	3.32	0.99	35.88	7.09	1.00	
t-2-Butene	0.57	0.11	0.03	0.48	0.06	0.01	1.2	0.28	0.03	
1-Butene	0.69	0.1	0.03	1.71	0.13	0.01	2.08	0.32	0.07	
c-2-Butene	0.5	0.1	0.02	0.45	0.04	0.01	0.8	0.25	0.02	
Isopentane	16.11	3.12	0.66	20.9	2.06	0.53	23.44	5.41	0.71	
n-Pentane	10.65	2.56	0.37	17.25	1.5	0.35	12.03	3.03	0.35	
1,3-Butadiene	0.23	0.05	0.02	0.22	0.04	0.02	0.23	0.04	0.02	
t-2-Pentene	0.56	0.06	0.02	0.64	0.05	0.01	1.48	0.24	0.04	
1-Pentene	0.37	0.03	0.01	0.14	0.04	0.01	0.9	0.15	0.02	
c-2-Pentene	0.31	0.03	0.01	0.21	0.02	<0.005	0.83	0.13	0.02	
n-Hexane	5.97	0.99	0.15	7.02	0.63	0.15	7.14	1.09	0.16	
Benzene	3.05	0.85	0.13	2.66	0.45	0.13	28.15	4.7	0.19	
Cyclohexane	3.24	0.61	0.06	2.91	0.28	0.08	6.54	0.62	0.06	
Toluene	3.71	1.09	0.17	1.9	0.48	0.14	3.49	0.98	0.18	
Ethyl Benzene	0.45	0.06	0.02	0.33	0.07	0.02	0.97	0.16	0.01	
mp -Xylene	1.7	0.19	0.06	4.83	0.56	0.09	4	0.64	0.08	
o-Xylene	0.65	0.07	0.02	0.69	0.1	0.02	1.27	0.21	0.02	
Isopropyl Benzene	0.59	0.12	0.01	0.62	0.06	<0.005	0.22	0.03	<0.005	
1,3,5-Trimethylbenzene	0.35	0.04	0.01	0.37	0.04	0.01	0.25	0.05	0.01	
1,2,4-Trimethylbenzene	0.78	0.1	0.02	0.48	0.11	0.03	0.29	0.26	0.04	
n-Decane	0.31	0.05	0.01	0.8	0.32	0.02	1.08	0.16	0.02	
1,2,3-Trimethylbenzene	0.27	0.03	0.01	0.38	0.17	0.01	0.3	0.06	0.02	

 Table 3. Validated auto-GC statistics 2<sup>nd</sup> quarter 2011

Units ppbV	Oak 3Q11	Solar 3Q11	Palm 3Q11
Species	Mean	Mean	Mean
Ethane	2.92	4.42	5.26
Ethylene	0.35	0.23	0.33
Propane	2.21	2.83	2.46
Propylene	0.26	0.19	0.15
Isobutane	0.75	1.07	1.00
n-Butane	0.92	1.25	1.45
t-2-Butene	0.06	0.04	0.04
1-Butene	0.02	0.02	0.06
c-2-Butene	0.02	0.02	0.03
Isopentane	0.73	0.75	1.01
n-Pentane	0.45	0.48	0.49
1,3-Butadiene	0.03	0.01	0.02
t-2-Pentene	0.03	0.01	0.05
1-Pentene	0.02	0.01	0.03
c-2-Pentene	0.01	< 0.005	0.03
n-Hexane	0.24	0.20	0.23
Benzene	0.18	0.10	0.18
Cyclohexane	0.08	0.11	0.09
Toluene	0.3	0.15	0.22
Ethyl Benzene	0.03	0.02	0.01
mp -Xylene	0.11	0.08	0.08
o-Xylene	0.03	0.02	0.02
Isopropyl Benzene	0.01	< 0.005	< 0.005
1,3,5-Trimethylbenzene	0.02	0.01	0.01
1,2,4-Trimethylbenzene	0.05	0.03	0.05
n-Decane	0.03	0.02	0.02
1,2,3-Trimethylbenzene	0.02	0.01	0.03

 Table 4. Unvalidated auto-GC mean statistics 3<sup>rd</sup> quarter 2011

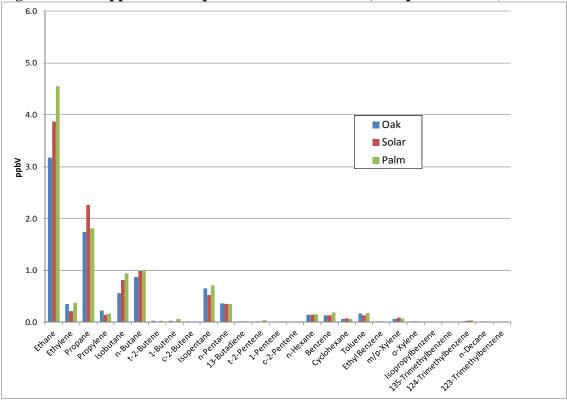
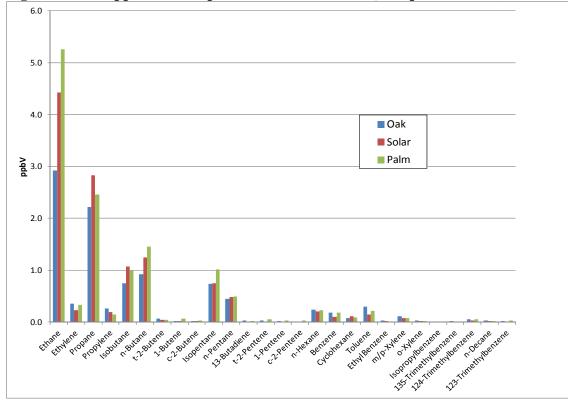


Figure 2. Mean ppbV for 27 species at three auto-GCs, 2<sup>nd</sup> quarter 2011 (validated data)

Figure 3. Mean ppbV for 27 species at three auto-GCs, 3<sup>rd</sup> quarter 2011 (unvalidated data)

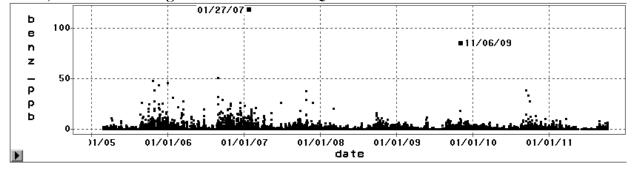


#### 2. Benzene Concentrations in Residential Areas

As has been discussed in past reports, benzene concentrations have been declining at the two auto-GCs operated at Oak Park CAMS 634 and Solar Estates CAMS 633 but in recent years concentration means have flattened out. No benzene values have been measured above the AMCV since monitoring began in 2005. A time series for benzene in ppbV units with two points annotated by date appears in Figure 4, below, for Oak Park. The two points are identified as statistical outliers, in that they are unusually high given the balance of the data. The same graph is reproduced without these two points in Figure 5, below. The time series for Solar Estates appears in Figure 6, on page 17. The two points identified in Figure 6 are the highest values observed at that site to date, but they are not statistical outliers. Note the different y-axis scales for the two sites, as Oak Park does tend to measure higher concentrations than Solar Estates. The 2010 – 2011 benzene data for the TCEQ's Palm site are shown for comparison purposes in Figure 7, on page 17. Note that the data from the third quarter 2011 have not been validated yet.

One can observe the seasonal pattern of benzene concentrations at the sites, with higher concentrations tending more toward winter periods. The second quarter of the year tends to have lower concentrations than the first and fourth quarters.

Figure 4. Oak Park hourly benzene 2005 – 2011, ppbV units, individual elevated values noted, no observations greater than the TCEQ's AMCV



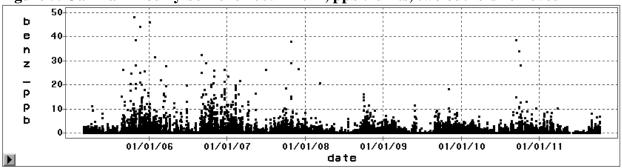


Figure 5. Oak Park hourly benzene 2005 – 2011, ppbV units, two outliers removed

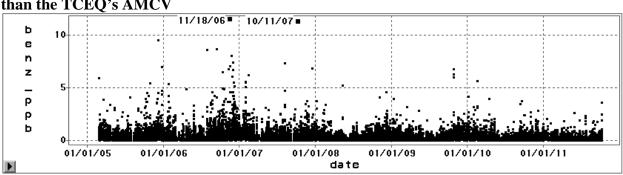


Figure 6. Solar Estates hourly benzene 2005 – 2011, ppbV units, no observations greater than the TCEQ's AMCV

Figure 7. TCEQ Palm hourly benzene 2010 – 2011, ppbV units, no observations greater than the TCEQ's AMCV

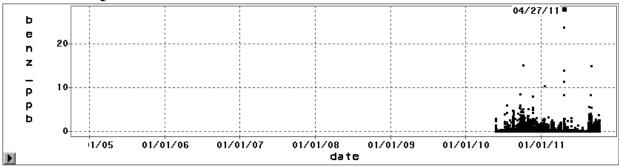


Table 5, on page 18, shows the second quarter summary statistics from the auto-GCs for benzene from 2005 – 2011. The second quarter average benzene concentrations at both sites show relatively little variability since 2008. The second quarter means are graphed in Figure 8, on page 18. The second quarter means from 2008 through 2011 are statistically significantly lower than in the second quarters of the preceding three years. Following the second quarter summaries, the third quarter benzene averages are summarized in Table 6 and Figure 9, on page 19, including the as-yet-unvalidated third quarter of 2011 means. The third quarter summaries include the TCEQ's Palm site, as the 2010 and 2011 third quarters both have complete data.

Oak	Year	Num. Obs.	Peak 1-hr	Peak 24-hr	Mean	
	2005	1935	11.388	1.276	0.203	
	2006	1913	19.986	3.273	0.307	
	2007	1956	16.570	3.737	0.316	
	2008	1948	3.721	0.790	0.137	
	2009	1953	11.681	1.399	0.173	
	2010	1935	4.428	1.348	0.137	
	2011	1585	3.053	0.846	0.129	
	-011				***=	
Solar	Year	Num. Obs.	Peak 1-hr	Peak 24-hr	Mean	
Solar		Num. Obs. 1619				
Solar	Year		Peak 1-hr	Peak 24-hr	Mean	
Solar	Year 2005	1619	Peak 1-hr 3.460	Peak 24-hr 0.728	Mean 0.254	
Solar	Year 2005 2006	1619 1489	Peak 1-hr 3.460 4.970	Peak 24-hr 0.728 0.840	Mean 0.254 0.182	
Solar	Year 2005 2006 2007	1619 1489 1307	Peak 1-hr 3.460 4.970 3.142	Peak 24-hr 0.728 0.840 0.915	Mean 0.254 0.182 0.228	
Solar	Year 2005 2006 2007 2008	1619 1489 1307 1781	Peak 1-hr 3.460 4.970 3.142 5.309	Peak 24-hr 0.728 0.840 0.915 0.633	Mean 0.254 0.182 0.228 0.130	

Table 5. Summary statistics for Benzene at Oak Park and Solar Estates, 2<sup>nd</sup> quarter 2005 – 2011, ppbV units

Figure 8. Mean concentrations of benzene during  $2^{nd}$  quarters by year at Oak Park (blue) and Solar Estates (red), 2005 - 2011, with lower values in 2008 - 2011 compared with 2005 - 2007

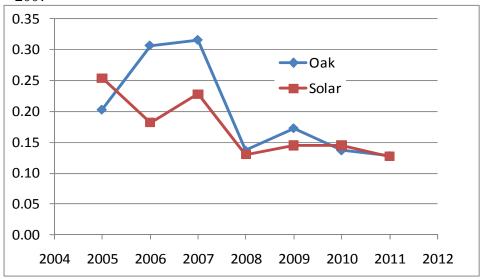
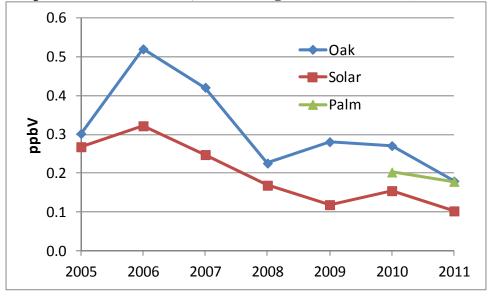


Table 6. Mean statistics for Benzene at Oak Park and Solar Estates, 3 <sup>rd</sup> quarter 2005	_
2011 Palm 2010 – 2011, ppbV units (2011 unvalidated)	

3 <sup>rd</sup> qtr/yr	Oak	Solar	Palm
2005	0.302	0.27	No GC
2006	0.520	0.32	No GC
2007	0.421	0.25	No GC
2008	0.226	0.17	No GC
2009	0.281	0.12	No GC
2010	0.271	0.16	0.203
2011	0.180	0.1	0.179

Figure 9. Unvalidated mean concentrations of benzene during 3<sup>rd</sup> quarters by year at Oak Park (blue) and Solar Estates (red), 2005 – 2011, with lower values in 2008 – 2011 compared with 2005 – 2007, and Palm (green) 2010 – 2011 (2011 unvalidated)



#### 3. Sulfur Dioxide Measurements at Corpus Christi Monitors

As has been discussed in recent reports, the JIH C630 site measures  $SO_2$  concentrations that do not comply with the EPA's  $SO_2$  NAAQS over the 2008 to 2010 period. One hour concentrations above 75 ppb are considered to be exceedances of the NAAQS. The maximum one hour value for each day at a site is logged, and at the end of the year the 99<sup>th</sup> percentile daily maximum is selected. This value is averaged with the same statistic from the previous two years, and the resulting three-year average is compared with 75 ppb to determine compliance. If a site collects a full year of data, then the 99<sup>th</sup> percentile value would be the 4<sup>th</sup> highest daily maximum for the year.

Only one exceedance day occurred at JIH C630 in the second quarter of 2011 and none occurred in the third quarter of 2011 at the site. However, Solar Estates C633 measured two exceedance days and one near miss during the third quarter of 2011. The recent history of SO<sub>2</sub> monitoring at

Solar Estates is that elevated concentrations that would have been exceedances under the current NAAOS had been measured in 2005 and 2006, after which none were measured until August 17, 2011. A time series of the hourly  $SO_2$  data at Solar Estates from the start of monitoring appears in Figure 10, below. A second graph covering the most recent three years (January 2009 – October 2011) using the 5-minute time scale data appears in Figure 11, below. Data measured on a shorter time scale have greater maximum concentrations than data measured on longer time scales, which is evident in comparing Figures 10 and 11. Figure 11 helps to identify when the change in behavior of the data began, which is late-May 2011.

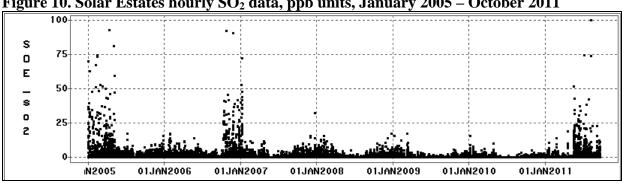
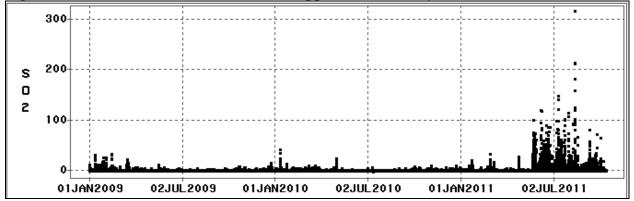


Figure 10. Solar Estates hourly SO<sub>2</sub> data, ppb units, January 2005 – October 2011





The monitor closest to Solar Estates is the Flint Hills Resources CAMS 632 (FHR C632) site. Figure 12, on page 21, shows the 5-minute time scale data for FHR C632 from January 2009 -October 2011. The range of concentrations at FHR C632 is much smaller than at Solar Estates. FHR C632 is located near a refinery, and is affected more frequently by nearby SO<sub>2</sub> emissions presumed to be associated with oil refining. A close examination of Figure 12 reveals that in summer months of 2009 and 2010, the SO<sub>2</sub> concentrations at FHR C632 were lower than in the recent summer months of 2011. This is made more evident in Figure 13, on page 21, which shows only the FHR SO<sub>2</sub> data from June through August in 2009, 2010, and 2011.

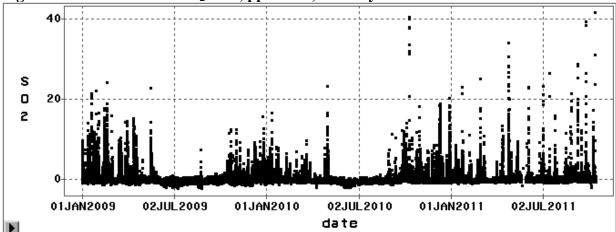
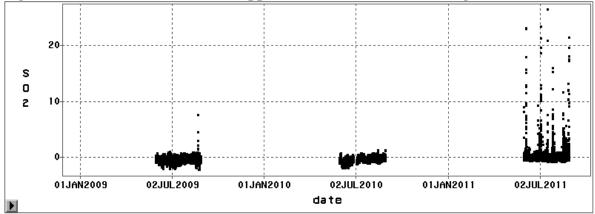


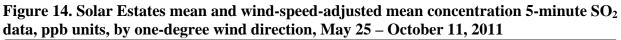
Figure 12. FHR 5-minute SO<sub>2</sub> data, ppb units, January 2009 – October 2011

Figure 13. FHR 5-minute SO<sub>2</sub> data, ppb units, months of June – August, 2009 – 2011



By merging the wind direction and wind speed measurements with  $SO_2$  data for the two sites, estimates as to the source may be derived. Figure 14, on page 22, shows the mean concentration of SO<sub>2</sub> as a function of wind direction using two approaches. The line graph labeled "SO2 Mean" is the simple average value associated with each angle degree wind direction using the 5-minute time scale data from May 25, 2011 through October 11, 2011. The line graph labeled "so2 ws Mean" is the "wind speed adjusted" average value associated with each degree wind direction. Wind speed adjustment tries to take into account that, in general, higher speed winds produce lower concentrations and lower speed winds produce higher concentrations, all else held equal. So by multiplying concentrations by the coincident wind speed and dividing the product by the average wind speed one can reduce the effects of varying wind speed on concentrations resulting from a constant emission. The results for the two approaches are consistent that an emission source lies at an approximate south-southeast bearing (160 degrees around from north) away from Solar Estates. A similar analysis is shown in Figure 15, on page 22, for FHR C632, where west-southwest winds are associated with the highest mean concentrations. The key direction for FHR is spread over a wider range of angles than for Solar Estates. An issue here is that winds from the west are less frequent than other directions, and westerly winds in Corpus Christi are more likely to be light and variable than winds from other directions. So whereas the analysis for Solar Estates can be conducted on mean concentrations by one-degree resolution angle of direction, the analysis at FHR is conducted with five-degree wind bins. The intersection of rays from Solar Estates at 160 degrees and from FHR at 240

degrees occurs at an industrial facility on Leopard Street. The TCEQ emissions inventory does not have a record for  $SO_2$  emissions near this location.



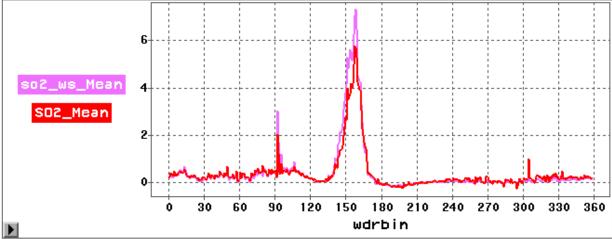
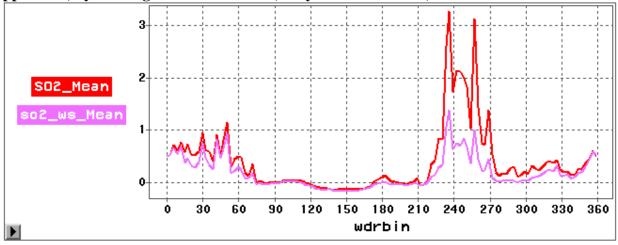


Figure 15. FHR mean and wind-speed-adjusted mean concentration 5-minute SO<sub>2</sub> data, ppb units, by five-degree wind direction, May 25 – October 11, 2011



A different question to ask about concentrations related to wind direction is "how often are concentrations measured above some threshold for each wind direction?" After all, a high average concentration could be the result of a small number of isolated individual samples that are statistical outliers. A method sometimes used to address this is referred to as probability density function (PDF) analysis. For PDF analysis, one selects a threshold concentration and then counts how many times for a given wind direction that threshold is exceeded, and then one divides this count by the count of wind observations in that same direction. The result is the fraction of times the threshold was exceeded by wind direction. In applying this method using 10-degree wind direction bins for both sites, one sees results similar to the mean-by-wind direction results. The overall mean concentrations since May 25, 2011 – October 11, 2011 at the two sites are 0.05 ppb at FHR and 1.11 ppb at Solar Estates. Various thresholds were tested for each site. Figures 16 and 17, on page 23, show the results of using thresholds of 2.0 ppb at

Solar Estates and 1.5 ppb at FHR. In both cases, the results show the threshold surpassed around 20 percent of the time in the peak mean concentration directions.

160, 0.2 9 0 E 0.1 ρ d f 110 0.0 30 180 210 300 Û 60 90 120 150 240 270 330 360 wdr\_10

Figure 16. Solar Estates, fraction of times SO<sub>2</sub> exceeds 2 ppb when wind blows in a given 10-degree wind direction bin, May 25 – October 11, 2011

Figure 17. FHR, fraction of times SO<sub>2</sub> exceeds 1.5 ppb when wind blows in a given 10degree wind direction bin, May 25 – October 11, 2011

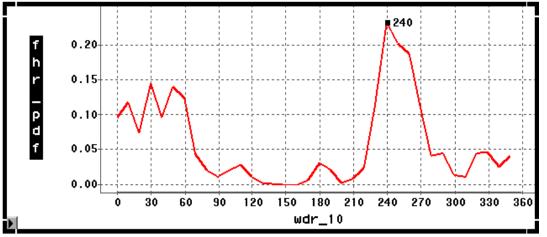
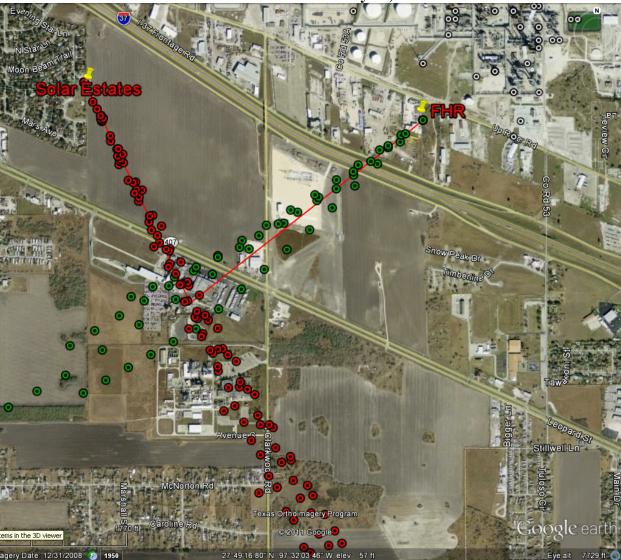


Figure 18, on page 24, shows a map made from surface back trajectories from Solar Estates and FHR associated with select elevated SO<sub>2</sub> measurements. Eight surface back-trajectories from Solar Estates using the time of the peak five-minute value within hours with mean SO<sub>2</sub> greater than 37.5 ppb (one-half the level of the NAAQS) and three from FHR with statistically-significantly elevated concentrations based on its lower range of concentrations taken under "good" wind conditions. As was mentioned earlier, when FHR measures SO<sub>2</sub> from the southwest, winds are generally light and variable and thus less amenable for back trajectory analysis. Thus, cases were selected with winds showing little variation over 20 minutes. The white and black dots in Figure 18 show points corresponding to SO<sub>2</sub> emission sources from the TCEQ's 2009 emission inventory provided in October 2011 by the TCEQ Chief Engineer's Office. Based on the 2009 emission inventory, there are no reported SO<sub>2</sub> industrial sources on Leopard St. in this area.

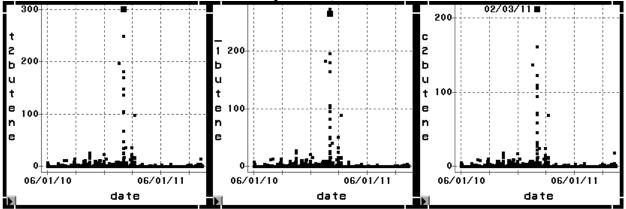
Figure 18. Surface back-trajectories from Solar Estates and FHR corresponding to periods with elevated SO2 and consistent wind flow since May 25, 2011



#### 4. Episode Case Study: Upset Detected at TCEQ Palm Auto-GC

In comparing auto-GC measurements among monitoring sites, some unusual measurements at the Palm site during the first quarter of 2011 stood out. The very cold weather during the first week in February 2011 led to UT CEER temporarily suspending monitoring at its sites; however, TCEQ sites continued operating. The Palm auto-GC data on February 3, 2011 at 7 and 8 CST include higher than expected c-2-butene, t-2-butene, 1-butene concentrations. This is apparent in Figure 19, below, which shows the time series graphs for hourly concentrations of these three species at Palm since June 2010. In addition to the measurements on the morning of February 3, elevated butene isomer concentrations were also measured at Palm on January 18 at 17 CST under northerly winds, and over several hours on February 1 and February 2, also under northerly winds. None of the recorded values were above an AMCV, and elevated concentrations on January 18, February 1 and 2 do not appear to be relatable to an upset report. However, a reported event at CITGO East on February 3 at 7:40 CST (150252) is listed in the TCEO's upset database. One of the two reported volatile organic compound sources in the upset report was upwind of the monitor, that being the Cumene Flare EPN 446. The listing of compounds in the upset report included "butene." A listing of the emissions reported in that upset event appears in Table 7, on page 26.

Figure 19. TCEQ Palm auto-GC time series of three butene isomers (ppbC units, which relate to total mass and not AMCV comparisons)

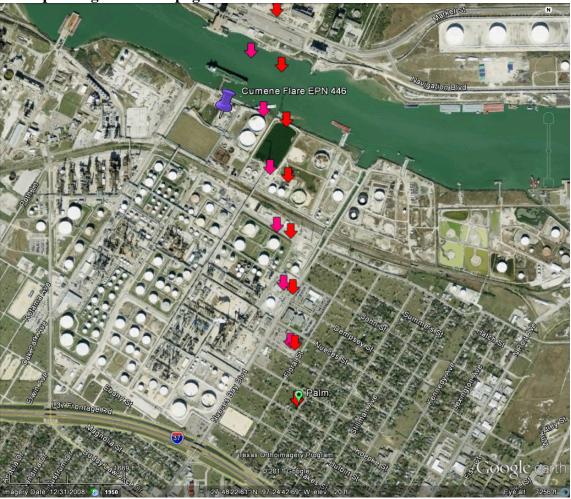


As was noted above, because of the cold weather most of the monitoring sites were shut down on February 3, 2011. As a result, the on-line UT CEER surface trajectory tool will not produce output for this date. However, surface back-trajectories using only the data from the Palm site were constructed for 7 and 8 a.m. CST, February 3. These are shown in Figure 20, on page 27, along with the location of the Palm site and the presumed emission source.

Source 2: Cumene Flare, EPN number 446							
Contaminant	Authorization Lir		Amount Released				
Benzene	6722A/8653A	0.0	0.55 lbs (est.)				
Butane, N-	6722A/8653A	0.0	7.78 lbs (est.)				
Butene	6722A/8653A	0.0	0.93 lbs (est.)				
Carbon Monoxide	6722A/8653A	0.0	32.55 lbs (est.)				
Ethylene (gaseous)	6722A/8653A	0.0	0.7 lbs (est.)				
Hydrogen Sulfide	6722A/8653A	0.0	9.23 lbs (est.)				
Isobutane	6722A/8653A	0.0	10.53 lbs (est.)				
Nitric oxide	6722A/8653A	0.0	4.56 lbs (est.)				
Pentane	6722A/8653A	0.0	9.58 lbs (est.)				
Propane	6722A/8653A	0.0	27.08 lbs (est.)				
Propylene (Propene)	6722A/8653A	0.0	0.73 lbs (est.)				
Sulfur dioxide	6722A/8653A	0.0	851.85 lbs (est.)				

Table 7. Emission upset report on February 3, 2011 at emission source shown in Figure 20,page 27

Figure 20. Surface back trajectories, one minute time steps, from 7 (magenta) and 8 (red) CST on February 3, 2011 from Palm auto-GC site, passing near emission upset location corresponding to Table 7 page 26.



#### **Conclusions from the Third Quarter 2011 Data**

In this quarter's report, several findings have been made:

- Second and third quarter benzene concentrations at the auto-GCs remain well below the TCEQ's AMCVs.
- Periodic air pollution events continue to be measured on a routine basis, no values above the TCEQ AMCV levels were observed this quarter. Two exceedances of the EPA SO<sub>2</sub> NAAQS level was measured this quarter at the Solar Estates CAMS 633 site.
- An examination of SO<sub>2</sub> data at the Solar Estates and the FHR C632 site suggests that an industrial facility on Leopard St may be producing unregulated SO<sub>2</sub> emissions.
- A review of data from earlier in 2011 showed some values of butene species higher than expected at the one-year old TCEQ Palm auto-GC, and two elevated measurements on February 3, 2011 were relatable to a reported emission upset.

Further analyses will be provided upon request.

# APPENDIX B

Financial Report of Expenditures Financial Report of Interest Earned

#### Corpus Christi Air Monitoring and Surveillance Camera Installation and Operation Project

#### Accounting Report for the Quarter 07/01/2011 - 09/30/2011

A. Total Amount of COCP Funds and Other Funds Received Under This Proposal

Total Grant Amount:	\$6,761,718.02
Total Interest Earned:	\$806,789.66
<b>Total Funds Received:</b>	\$7,568,507.68

B. Summary of Expenditures Paid by COCP Funds

	ſ	Year 3	Year 4	Year 5	Year 6	Year 7	Yrs 1-7	Prior Activity	Current Activity	Encumbrances	Remaining Balance
		Budget	Budget	Budget	Budget	Budget	Adjusted Budget		07/01/11 - 09/30/11		9/30/2011
Salaries-Prof	12	\$216,128.63	\$160,652.00	\$286,279.40	\$299,633.00	\$318,499.00	\$1,218,732.94	(\$1,170,885.17)	(\$12,940.85)	(\$15,352.58)	\$19,554.34
Salaries-CEER	15	\$19,606.37	\$15,636.00	\$33,123.00	\$30,948.00	\$29,880.00	\$162,071.37	(\$148,109.67)	(\$13,855.71)		\$105.99
Fringe	14	\$47,984.00	\$38,783.00	\$58,333.00	\$72,728.00	\$76,643.00	\$285,059.91	(\$268,296.87)	(\$7,853.49)	(\$3,019.50)	\$5,890.05
Communication	42	\$0,00	\$0.00	\$0.00	\$0.00	\$0.00	\$1,845.00	(\$1,350.00)	(\$135.00)		\$360.00
Other/C-Analysis	47/68	\$60,474.00	\$73,500.00	-\$8,656.40	\$73,500.00	\$14,219.00	\$114,455.00	(\$114,455.00)	\$0.00		\$0.00
Supplies	50	\$86,844.00	\$33,500.00	\$68,676.00	\$122,682.00	\$72,797.32	\$512,178.19	(\$510,479.37)	\$4,676.23	(\$331.00)	\$6,044.05
Quality Assurance	51	\$0.00	\$20,300.00	\$8,000.00	\$0.00	\$7,070.00	\$16,640.00	(\$16,640.00)	\$0.00		\$0.00
Subcontract	62-65	\$1,965,693.00	\$314,022.00	\$296,734.00	\$346,289.00	\$591,523.00	\$3,538,580.91	(\$3,369,310.09)	(\$61,432.03)		\$107,838.79
Program Income	66*	\$0,00	\$0,00	\$0.00	\$0.00	\$0.00	\$0.00	(\$140,617.19)	\$13,621.90	(\$9,458.11)	-\$136,451.40
Travel	75	\$2,300.00	\$2,000.00	\$7,719.00	\$9,000.00	\$6,712.00	\$30,191.00	(\$29,721.77)	(\$254,48)		\$214.75
Equipment	80	\$0.00	\$0.00	\$0,00	\$0.00	\$0.00	\$0.00	S0.00	\$0.00		\$0.00
Indirect Costs	90	\$359,855,00	\$98,759.00	\$112,531.00	\$143,217.00	\$167,601.70	\$881,963.70	(\$808,384,45)	(\$13,769.29)		\$59,809.96
TOTALS		\$2,758,885.00	\$757,152.00	\$862,739.00	\$1,097,997.00	\$1,284,945.02	\$6,761,718.02	(\$6,578,249.58)	(\$91,942.72)	(\$28,159.19)	\$63,366.53

B.1. Summary of Program Income (66) Expenditures

Salaries-Prof	66	(\$15,393.70)
Salaries-CEER	66	\$0.00
Fringe	66	\$0.00
Communication	66	\$0.00
Other/C-Analysis	66	\$0.00
Supplies	66	(\$23,274.23)
Quality Assurance	66	\$0.00
Subcontract	66	\$11,471.83
Program Income	66	\$0.00
Travel	66	\$0.00
Equipment	66 _	\$40,818.00
TOTAL		\$13,621.90

C. Interest Earned by COCP Funds as of 09/30/11

Prior Interest Earned:	\$801,283.24
Interest Earned This Quarter:	\$5,506,42
Total Interest Earned to Date:	\$806,789.66

D. Balance of COCP Funds as of 09/30/11

Total Grant Amount:	\$8,761,718.02
Total Interest Earned:	\$806,789.66
Current Q. Expenses	(\$91,942.72)
Total Expenditures:	(\$6,578,249.58)
Remaining Balance:	\$898,315.38

I certify that the numbers are socurate and reflect acouts expenditures for the quarter Mither A Martinick Accounting Certification