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

Quarterly Report for the Period

October 1, 2011 through December 31, 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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February 28, 2012

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 December 31, 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 33, 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

TOEO		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

Legena	
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)
	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 through 33. Specifically, the appendix contains the following elements:

- Auto-GC Data Summary In examining the validated <u>third</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 third quarter average concentrations were below each compound's long-term AMCVs. For <u>fourth</u> quarter data, the preliminary values were also below respective AMCVs. A summary of data appears in Appendix A, pages 12 through 21.
- **Benzene Summary** A review of the almost seven years of data is presented, with focus on the third and fourth quarter means from 2005 through 2011. Details appear in Appendix A, pages 22 through 26.

• Analysis of Sulfur Dioxide at Several Sites – In closing out 2011, the JIH CAMS 630 site continues to measure concentrations high enough and often enough to violate the SO₂ annual National Ambient Air Quality Standards (NAAQS). The Solar Estates CAMS 633 site did not measure any exceedances of the SO₂ NAAQS level during the fourth quarter, but continued to measure concentrations close to the NAAQS level. This subject is expanded upon in Appendix A, pages 26 through 33.

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 34 and 35.

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 34 and 35.

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

The COCP funds received through December 31, 2011 totals \$7,572,911.53. This total includes estimated_interest earned through December 31, 2011.

B. Detailed List of the Actual Expenditures Paid from COCP Funds

Expenditures of COCP funds during this quarter totaled \$237,682.82. The detailed breakdown of the actual expenditures is included in Appendix B, page 35. 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 estimated interest earned during this quarter totaled \$4,403.85. 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 34 and 35.

D. <u>Balance as of December 31, 2011, in the COCP Account</u> The balance in the COCP account, including estimated interest earned totals \$665,036.41.

E. <u>Expected Expenditures for the Funds Remaining in the COCP Account</u> The projected expenditures for the funds remaining totals \$665,036.41.

Quarterly Report Distribution List:

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APPENDIX A

Data Analysis for Corpus Christi Quarterly Report

October 1, 2011 through December 31, 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 October 1 through December 31, 2011 and a summary for calendar year 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 third and fourth 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 (SO₂) data from several sites.

TCEO		Monitoring Equipment					
CAMS#	Description of Site Location	Auto	TNMHC (T) /	$H_2S \&$	Met		
CANS#		GC	Canister (C)	SO_2	Station	Camera	
634	Oak Park Recreation Center	Vas	т		Vas		
034	(OAK)	105	1		105		
620	Grain Elevator @ Port of		T&C	Vas	Vas		
029	Corpus Christi (CCG)		Iac	105	105		
620	J. I. Hailey Site @ Port of		ፕዮር	Vac	Vac		
030	Corpus Christi (JIH)		Iac	105	105		
635	TCEQ Monitoring Site		T&C	Vas	Vas	Vac	
035	C199 @ Dona Park (DPK)		Iac	105	105	165	
	Port of Corpus Christi on						
631	West End of CC Inner		T&C	Yes	Yes		
	Harbor (WEH)						
	Off Up River Road on Flint						
632	Hills Resources Easement		T&C	Yes	Yes		
	(FHR)						
633	Solar Estates Park at end of	Vac	т	Vas	Vas	Vac	
033	Sunshine Road (SOE)	1.68	I	165	165	168	

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

Legend

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 January 2012). 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 Act¹. 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_{2.5}) 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.

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).

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

One species measured by this project and regulated by a NAAQS is sulfur dioxide (SO₂). Effective June 2, 2010, EPA modified the SO₂ 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 99th percentiles of the daily maximum one-hour averages. There is also a secondary SO₂ standard of 0.500 ppm (500 ppb) over three hours, not to be exceeded more than once in any one year. The reason that there has been little attention to the SO₂ 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 SO₂ was much more likely to be exceeded than the older NAAQS. With the addition of a new NAAQS for SO₂ 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_2S , any measured concentration greater than the level of the state residential standards, which is 80 ppb over 30 minutes, is considered "elevated." For SO₂, 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 SO₂ and H_2S 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 H₂S and SO₂, 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, lists the data completeness from the project auto-GCs during 2011 for the months for which data have been validated. During two different weeks in August 2011 there were some maintenance issues (thermal desorption failure August 12 - 18, and trap failure August 27 -September 3) at the Oak Park site. Despite low return that one month, data collection for the year meets all project requirements.

Table 4, on page 14, summarizes the <u>validated</u> average data values from the <u>third</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 January 2012). Table 5, on page 15, summarizes the as-yet-unvalidated average data values from the <u>fourth</u> quarter of 2011.

As noted in the preceding paragraph, Tables 4 and 5 show the averages (arithmetic mean of measured values) for 27 hydrocarbon species for the periods of interest, and Table 4 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 4 for the validated third quarter data and Table 5 for the as-yet-unvalidated fourth quarter data are shown graphically in Figures 2 and 3, respectively, on page 16. Figures 2 and 3 are plotted on the same y-axis scale, so they can be compared directly. Mean concentrations for all 27 species measured consistently above their respective method detection limits were higher in the fourth quarter 2011 than in the third quarter 2011. Similar mean concentration changes from third to fourth quarter have been observed in each year of monitoring for this project.

The rows for *benzene* are bold-faced in Tables 4 and 5 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.

Date	Oak Park	Solar Estates
Jan 2011	100	96
Feb 2011	84	77
Mar 2011	100	95
Apr 2011	100	80^{*}
May 2011	78	100
Jun 2011	69 [*]	93
Jul 2011	95	96
Aug 2011	56	95
Sep 2011	92	78
Oct 2011	99	83
Nov 2011	97	
Dec 2011		
Average	88	89

 Table 3. Percent data recovery by month, 2011, validated data only

* Months with planned preventive maintenance

Units ppbV	(Oak 3Q1	1	S	olar 3Q1	11	P	Palm 3Q11	
Species	Peak 1hr	Peak 24hr	Mean	Peak 1hr	Peak 24hr	Mean	Peak 1hr	Peak 24hr	Mean
Ethane	99.15	16.13	2.99	202.57	11.43	4.45	72.95	23.20	5.26
Ethylene	22.01	4.03	0.35	5.30	1.59	0.23	14.27	2.10	0.33
Propane	151.71	16.65	2.21	129.62	8.57	2.86	72.08	12.71	2.46
Propylene	16.46	2.57	0.26	21.46	1.40	0.20	6.85	0.98	0.15
Isobutane	60.51	6.11	0.75	52.12	3.69	1.08	28.12	5.48	1.00
n-Butane	82.48	8.00	0.92	46.67	4.04	1.27	50.04	13.16	1.45
t-2-Butene	0.48	0.15	0.06	0.41	0.19	0.05	1.22	0.30	0.04
1-Butene	0.53	0.11	0.02	0.47	0.11	0.01	0.76	0.22	0.06
c-2-Butene	0.78	0.10	0.02	0.51	0.06	0.02	1.05	0.30	0.03
Isopentane	34.27	4.79	0.73	23.02	2.15	0.76	31.96	10.03	1.01
n-Pentane	32.52	3.48	0.45	17.17	1.55	0.49	16.52	3.66	0.49
1,3-Butadiene	2.68	0.19	0.03	0.70	0.07	0.01	1.17	0.10	0.02
t-2-Pentene	0.43	0.09	0.03	0.44	0.07	0.01	1.88	0.64	0.05
1-Pentene	0.19	0.04	0.02	0.41	0.05	0.01	1.16	0.40	0.03
c-2-Pentene	0.31	0.04	0.01	0.36	0.04	0.00	1.01	0.34	0.03
n-Hexane	17.52	1.92	0.24	10.72	0.82	0.21	6.66	1.15	0.23
Benzene	8.05	1.55	0.18	2.37	0.65	0.11	15.07	1.65	0.18
Cyclohexane	6.12	0.64	0.08	4.57	0.40	0.11	8.73	1.16	0.09
Toluene	10.22	1.79	0.30	4.50	0.58	0.15	5.69	0.99	0.22
Ethyl Benzene	1.28	0.14	0.03	0.89	0.10	0.02	0.61	0.12	0.01
mp -Xylene	3.94	0.43	0.11	4.04	0.40	0.08	1.92	0.51	0.08
o-Xylene	1.16	0.14	0.03	0.94	0.10	0.02	0.56	0.18	0.02
Isopropyl Benzene	0.62	0.11	0.01	0.54	0.04	0.00	0.27	0.07	0.00
1,3,5-Trimethylbenzene	0.36	0.04	0.01	1.39	0.11	0.01	0.50	0.08	0.01
1,2,4-Trimethylbenzene	0.86	0.33	0.05	1.18	0.12	0.03	0.56	0.13	0.05
n-Decane	0.94	0.22	0.03	3.28	0.28	0.02	0.91	0.09	0.02
1,2,3-Trimethylbenzene	0.26	0.09	0.02	0.59	0.06	0.01	0.15	0.07	0.03

 Table 4. Validated auto-GC statistics 3rd quarter 2011

Units ppbV	Oak 4Q11	Solar 4Q11	Palm 4Q11
Species	Mean	Mean	Mean
Ethane	9.69	9.57	14.15
Ethylene	0.65	0.40	0.67
Propane	7.07	7.25	9.14
Propylene	0.38	0.34	0.34
Isobutane	2.30	1.88	3.52
n-Butane	3.60	2.94	6.07
t-2-Butene	0.19	0.03	0.09
1-Butene	0.06	0.03	0.09
c-2-Butene	0.07	0.02	0.07
Isopentane	2.09	1.33	2.54
n-Pentane	1.42	0.91	1.53
1,3-Butadiene	0.03	0.04	0.03
t-2-Pentene	0.06	0.02	0.12
1-Pentene	0.03	0.02	0.08
c-2-Pentene	0.03	0.01	0.06
n-Hexane	0.62	0.36	0.54
Benzene	0.52	0.20	0.36
Cyclohexane	0.25	0.20	0.24
Toluene	0.58	0.25	0.42
Ethyl Benzene	0.05	0.03	0.03
mp -Xylene	0.17	0.18	0.17
o-Xylene	0.05	0.03	0.05
Isopropyl Benzene	0.04	0.01	0.02
1,3,5-Trimethylbenzene	0.02	0.02	0.02
1,2,4-Trimethylbenzene	0.05	0.03	0.07
n-Decane	0.03	0.03	0.03
1,2,3-Trimethylbenzene	0.01	0.06	0.02

 Table 5. Unvalidated auto-GC mean statistics 4th quarter 2011



Figure 2. Mean ppbV for 27 species at three auto-GCs, 3rd quarter 2011 (validated data)

Figure 3. Mean ppbV for 27 species at three auto-GCs, 4th quarter 2011 (unvalidated data)



Auto-GC monitoring began in March of 2005, so the first complete year of operation was 2006. The fourth quarter of 2011 closes out six years and ten months of full auto-GC monitoring and seven full years will be reached in March 2012. Time series of data from the Solar Estates auto-GCs for nine representative hydrocarbon species appear in Figure 4, on page 18, and a similar set of graphs of Oak Park appear in Figure 5, on page 19. The nine species are:

- ethane
- propane
- n-butane
- isobutane
- n-pentane
- isopentane
- benzene
- toluene
- isopropyl-benzene (cumene)

For each figure, four outlier points have been excluded to help highlight the seasonality shown by the ensemble of the data. In this set of eighteen graphs, the hourly data for each day have been averaged to create time plots of the daily (24-hour) averages. Units are parts per billion-volume. Tick marks on the x-axes correspond to January 1 each year. The seasonal pattern (higher in winter, lower in summer) is clear for each species. Such a seasonal pattern is typical in East Texas, and the pattern is generally ascribed to the facts that wind speeds are lower in winter allowing more frequent periods of stagnation, and atmospheric inversions last longer holding freshly emitted pollutants closer to the surface. An additional important factor for the Solar Estates and Oak Park CAMS sites is that the frequency of northerly winds increases in the winter, placing these sites downwind of the industrial area to the north more often. One species that does not follow the same "higher in winter, lower in summer" pattern is isoprene. This species, which is not among the 27 hydrocarbons discussed elsewhere in this report, is a chemical generally released into the air by vegetation and is referred to as a *biogenic* species. Its behavior is characterized as "higher in summer, lower in winter."



Figure 4. Solar Estates auto-GC, nine representative hydrocarbons, daily mean concentrations ppbV units, March 2005 – December 2011

Figure 5. Oak Park auto-GC, nine representative hydrocarbons, daily mean concentrations ppbV units, March 2005 – December 2011



As can be seen in the overall patterns of Figures 4 and 5, there is an overall downward trend apparent for some species. In Figures 6 and 7, on page 20 and 21, respectively, the annual average concentrations from 2005 through 2011 are shown for the 27 species listed and shown in earlier tables and graphs (see pages 14 -16). In Figures 6 and 7 it is clearer that for each species with mean concentrations greater than 0.1 ppbV, there is a general downward trend in annual means comparing the first three years (2005 - 2007) with the most recent four years (2008 - 2011). The first year, 2005, is missing the months of January and February. Based on the seasonality shown above, including these winter months would likely raise the mean concentration for 2005, further confirming the net downward trend.



Figure 6. Solar Estates auto-GC annual mean concentrations, ppbV units, 2005 - 2011



Figure 7. Oak Park auto-GC annual mean concentrations, ppbV units, 2005 - 2011

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. In recent years, concentration means have generally been relatively constant. Nevertheless, the 2011 annual benzene concentration means at the two project auto-GCs are the lowest annual means since the beginning of monitoring. Also, no individual one-hour benzene values have been measured above the AMCV since the beginning of monitoring. A time series for hourly benzene in ppbV units with two points annotated by date appears in Figure 8, 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 9, on page 23. The time series for Solar Estates appears in Figure 10, on page 23. Note the different y-axis scales for the two sites, as Oak Park does tend to measure higher concentrations than Solar Estates. Note that the data from the fourth quarter 2011 have not been validated yet.

As was discussed in the preceding section on page 17, the auto-GC data show strong seasonal patterns. This was shown in Figures 4 and 5, on pages, 18 and 19, respectively, for benzene and other species that had been combined into 24-hour averages. One can observe the same seasonal pattern of benzene concentrations at the sites using the actual measured one-hour data, which have a wide range of observed values compared to the 24-hour averages, with higher concentrations again tending more toward winter periods.

Figure 8. Oak Park hourly benzene 2005 – 2011, ppbV units, individual elevated values noted, no observations greater than the TCEQ's AMCV





Figure 9. Oak Park hourly benzene 2005 - 2011, ppbV units, two outliers removed

Figure 10. Solar Estates hourly benzene 2005 – 2011, ppbV units, no observations greater than the TCEQ's AMCV



Table 6, on page 24, shows a comparison of benzene concentration measured at auto-GCs in Texas for 2011. Twenty-four sites are operating around the state, and the data in the table are ordered in rows of decreasing concentrations. The first site listed in the table (Lynchburg Ferry, on the Houston Ship Channel) did not operate for the entire year. Oak Park is in the upper third among all sites, the TCEQ Palm site near the middle, and Solar Estates is in the lowest third. The TCEQ AMCV for long-term benzene is 1.4 ppbV

Site	Num Samples	Peak 1-Hr ppbV	Peak 24-Hr ppbV	Mean ppbV
Lynchburg	5,729	94.84	4.82	0.67
Channelview	7,309	10.08	1.47	0.40
Odessa Hays	7,548	5.65	1.04	0.32
Oak Park	6,929	16.73	2.00	0.31
Clinton	7,474	8.36	1.29	0.30
Chamizal	7,313	7.45	1.53	0.30
Nederland	7,704	26.26	1.90	0.29
Deer Park	7,292	37.08	3.21	0.28
Beaumont Downtown	7,484	9.04	1.05	0.28
HRM3	7,383	15.65	1.50	0.28
Cesar Chavez	7,492	7.21	1.38	0.27
Palm	7,541	28.16	4.70	0.26
Milby Park	7,575	5.85	1.35	0.22
Wallisville Rd	7,233	3.91	1.06	0.22
Fort Worth NW	7,540	2.13	0.57	0.18
Decatur Thompson	7,800	1.54	0.43	0.17
DISH	7,702	2.52	0.54	0.16
Texas City 34th St	7,671	16.00	0.94	0.16
Solar Estates	7,062	3.69	0.65	0.16
Hinton	7,483	1.63	0.61	0.15
Flower Mound Shiloh	7,806	8.63	0.60	0.13
Eagle Mtn Lake	7,593	4.09	0.35	0.10
Danciger	7,183	4.78	0.48	0.10
Lake Jackson	7,316	1.86	0.45	0.09

Table 6. 2011 benzene concentration summary at Texas auto-GCs, ppbV units

Table 7, on page 25, shows the validated third quarter summary statistics from the auto-GCs for benzene from 2005 – 2011. The validated third quarter means are graphed in Figure 11, on page 25. The means for TCEQ's Palm site are shown for 2010 and 2011. The third quarter means from 2008 through 2011 are statistically significantly lower than in the third quarters of the preceding three years, and this finding is similar to findings for other quarters in recent reports on this project. Following the third quarter summaries, the as-yet-unvalidated fourth quarter benzene averages are summarized in Table 8 and Figure 12, on page 26. The fourth quarter summaries include the TCEQ's Palm site for 2010 and 2011.

Oak	Year	Num. Obs.	Peak 1-hr	Peak 24-hr	Mean
	2005	1,792	26.538	3.704	0.302
	2006	1,771	51.150	7.780	0.520
	2007	1,818	26.371	2.085	0.421
	2008	1,732	5.880	1.303	0.226
	2009	1,896	9.502	2.217	0.281
	2010	1,655	38.847	2.673	0.271
	2011	1,541	8.055	1.555	0.180
Solar	Year	Num. Obs.	Peak 1-hr	Peak 24-hr	Mean
Solar	Year 2005	Num. Obs. 1,304	Peak 1-hr 4.188	Peak 24-hr 1.194	Mean 0.268
Solar	Year 2005 2006	Num. Obs. 1,304 1,707	Peak 1-hr 4.188 8.790	Peak 24-hr 1.194 1.109	Mean 0.268 0.322
Solar	Year 2005 2006 2007	Num. Obs. 1,304 1,707 1,670	Peak 1-hr 4.188 8.790 7.411	Peak 24-hr 1.194 1.109 1.069	Mean 0.268 0.322 0.248
Solar	Year 2005 2006 2007 2008	Num. Obs. 1,304 1,707 1,670 1,886	Peak 1-hr 4.188 8.790 7.411 1.773	Peak 24-hr 1.194 1.109 1.069 0.605	Mean 0.268 0.322 0.248 0.169
Solar	Year 2005 2006 2007 2008 2009	Num. Obs. 1,304 1,707 1,670 1,886 1,839	Peak 1-hr 4.188 8.790 7.411 1.773 2.083	Peak 24-hr 1.194 1.109 1.069 0.605 0.444	Mean 0.268 0.322 0.248 0.169 0.119
Solar	Year 2005 2006 2007 2008 2009 2010	Num. Obs. 1,304 1,707 1,670 1,886 1,839 1,620	Peak 1-hr 4.188 8.790 7.411 1.773 2.083 3.825	Peak 24-hr 1.194 1.109 1.069 0.605 0.444 0.589	Mean 0.268 0.322 0.248 0.169 0.119 0.155

 Table 7. Summary statistics for Benzene at Oak Park and Solar Estates, 3rd quarter 2005 –

 2011, ppbV units, (2011 validated)

Figure 11. Mean concentrations of benzene during 3^{rd} quarters by year at Oak Park (blue) and Solar Estates (red), 2005 - 2011, with lower values in 2008 - 2011 compared with 2005 - 2007



4 th qtr/yr	Oak	Solar	Palm
2005	1.300	0.409	No GC
2006	1.144	0.577	No GC
2007	0.680	0.373	No GC
2008	0.633	0.306	No GC
2009	0.808	0.284	No GC
2010	0.502	0.232	0.454
2011	0.519	0.197	0.359

Table 8. Mean statistics for Benzene at Oak Park and Solar Estates, 4th quarter 2005 – 2011 Palm 2010 – 2011, ppbV units (2011 unvalidated)

Figure 12. Unvalidated mean concentrations of benzene during 4th 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. In updating the data through 2011, the site again shows noncompliance for the 2009 – 2011 three year period. One hour concentrations above 75 ppb are considered to be individual exceedances of the level of the NAAQS. The maximum one hour value for each day at a site is logged, and at the end of the year the 99th 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 99th percentile value would be the 4th highest daily maximum for the year. The resulting statistic is called the *design value* for a monitoring site. Table 9, on page 27, contains the design values for Corpus Christi monitors (TCEQ and UT) for recent threeyear periods. The JIH CAMS 630 site shows noncompliance in each three-year period to date. The site with the second highest design value over the entire seven year monitoring period is the Solar Estates CAMS 633 site with 51 ppb over the 2005-2007 period. Solar Estates also had the second highest design value (30 ppb) among nine sites for the most recent three year period. Details about the emissions sources upwind of the JIH CAMS 630 site and the Solar Estates CAMS 633 site appear below.

Table 9. SO ₂ NAAQS design values for Corpus Christi area sites, ppb units, values gr	eater
than 75 ppb represent noncompliance	

Years	C21	C4	C629	C630	C631	C632	C633	C635	C98
2005-2007	8	24	34	119	38	21	51	34	36
2006-2008	8	21	31	131	33	19	31	31	32
2007-2009	9	18	30	89	32	17	21	23	28
2008-2010	9	17	26	103	21	13	11	22	33
2009-2011	9	12	19	80	15	13	30	20	27

Recent quarterly reports have discussed the hypothesis that ship operations near the docks located south of the JIH site are responsible for the exceedances measured at JIH. Some work at the TCEQ looking at on-land emission reports provided by industry and logs of ships operations at the docks during an elevated SO2 episode from September 25 - 27, 2011 show that although ships are the likely main emissions source affecting JIH, on some occasions on-land emissions also affect the site. Figure 13, on page 28, shows a graph of each measured one hour concentration at or above 75 ppb at JIH since the start of monitoring plotted against the coincident wind direction resultant. All exceedances fall into one of two categories: within a narrow wind direction between 160 and 190 degrees or within a more dispersed southwesterly direction. Points in these two categories are plotted with different symbols in Figure 13.



Figure 13. JIH C630 hourly SO_2 measurements exceeding 75 ppb by wind direction, 2005 - 2011

Using the mean peak direction at JIH at 177 degrees and the secondary direction at 230 degrees, and combining this direction information along similar directionality assessments at the Port Grain CAMS 629 and TCEQ Huisache CAMS 98 sites, a set of rays can be placed on a map to look for any common upwind key areas among the sites. Figure 14, on page 29, is an aerial map of the ship channel and refinery area around JIH, with rays drawn in the key directions associated with highest SO₂ concentrations for three CAMS sites. On-land emission sources from the TCEQ emissions inventory are plotted as red dots for the largest emission sources, and white dots for smaller sources. The directionality at Grain CAMS 629 is relatively weak owing to the relative rare appearance of strong southwest winds. Nevertheless, data interpretation for the Grain site provides additional evidence of the impact of ship emissions.

Figure 14. Rays drawn in key directions associated with highest SO₂ concentrations at three CAMS sites: JIH, CC Grain, and TCEQ Huisache CAMS 98



The recent history of SO_2 monitoring at Solar Estates is that elevated concentrations that would have been exceedances under the current NAAQS had been measured in 2005 and 2006, after which none were measured until July 14, 2011. A time series of the hourly SO_2 data at Solar Estates from the start of monitoring appears in Figure 15, on page 30. As is clear in this figure, there have been three distinct periods of elevated SO_2 being measured at Solar Estates. Using the five-minute time resolution data and a close examination of the SO_2 and wind directions, a fine time resolution estimate for the onset and turn-off of SO_2 at the Solar site can be made. The precision of the estimate is based on the frequency of southeast winds around the start//end points.

- Period 1: Beginning before mid-Dec. 2004 (start of monitoring program) // Ending May 11, 2005, 2 pm CST
- Period 2: Beginning between Oct. 5, 2006, 9 pm CST and Oct. 6, 2006, 6:45 pm CST // Ending between Jan. 12, 2007, 4 pm CST and Jan. 13, 2007, 2 am CST

• Period 3: Beginning May 25, 2011, 11:50 am CST

Using 25 ppb as a threshold for "elevated concentrations" (upper 0.1 percentile value in 2011 using data from all Corpus Christi SO₂ monitors) the following facts emerge

1. From January 1, 2005 – May 11, 2005, there were 50 elevated hourly observations, 90 percent of observations between 146 and 164 degrees resultant wind direction.

2. October 5, 2006 – January 12, 2007, there were 39 hourly observations, 90 percent of observations between 145 and 161 degrees. Other observations greater than 25 ppb were from the northeast.

3. May 25, 2011 – December 31, there were 33 observations, 100 percent between 153 and 165 degrees resultant wind direction.

Elevated observations persist into early 2012.



Figure 15. Solar Estates hourly SO₂ data, ppb units, January 2005 – December 2011

To further characterize the SO₂ at Solar Estates, three forms of analysis are presented below. Figure 16, on page 31, shows the mean concentration of SO₂ as a function of wind direction using data since May 25, 2011 through December 31, 2011. Because the southeast winds are the most frequent winds in the area, and this is also the peak upwind concentration direction, a high resolution directionality analysis using 3-degree wind bins is possible. The result is a very sharp peak in the mean, suggesting the emission source lies in a narrow upwind angular sector close to 159 degrees (bin from 157.5 to 160.5 degrees) bearing from the CAMS site. This 159 degree peak is not symmetric, and between 150 and 165 degrees concentrations average 2 ppb or higher. It should also be noted that wind direction accuracy is generally specified to be ± 5 degrees, 95 percent confidence level. In compiling an ensemble of data over several months, comparisons among other monitors and persistent measurement of similar concentrations in a particular direction suggest that random error in direction measurements at Solar Estates is actually less than ± 5 degrees, 95 percent confidence level.

Hourly values with the resultant wind between 150 and 165 degrees from May 25, 2011 through December 31, 2011 represent 1,016 observations out of 5,304 total hours, which is 19 percent of all hours over the this period. Using these hours, the mean concentration by day of the week was calculated, and it was clear that concentrations on Mondays through Fridays were much higher than on weekends. The next step was to calculate the average concentration by hour of the day just for weekdays, to prevent dilution from the low-concentration weekends. Figure 17, on page

31, show these results. Elevated concentrations appear to be more prominent Monday – Friday, 4 a.m. – 6 p.m. CST. Lastly, using only hours between 4 a.m. – 6 p.m. CST, the mean concentration by day of week was calculated again and these results are graphed in Figure 18, on page 32. As noted above, concentrations are significantly lower on Sundays (x-axis value "1") and a little higher on Saturdays than on Sundays (x-axis value "7"), but even Saturday is significantly lower than other days of the week.

Figure 16. Mean Solar Estates SO₂ concentration by wind direction May 25 – Dec. 31, 2011, 3-degree wind bins



Figure 17. Mean SO₂ concentration by hour CST at Solar Estates under southeast winds on weekdays, mean, May 25 – Dec. 31, 2011







Having these characterizations in terms of average concentrations by wind direction, by time of day, and by day of week, UT is actively planning on a mobile monitoring field experiment tentatively scheduled for some weekdays in mid-February 2012.

Conclusions from the Fourth Quarter 2011 Data

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

- Third and fourth 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, but no auto-GC hydrocarbon values were observed above the TCEQ AMCV levels this quarter or during 2011 for the 27 species tracked for this project.
- No exceedances of the EPA SO₂ NAAQS level were measured this quarter. However, the JIH CAMS 630 site finished 2011 with an SO₂ design value that is greater than the 75 ppb level of the NAAQS.
- An examination of SO₂ data at the Solar Estates and the FHR C632 site continues to suggest that an industrial facility on Leopard St may be producing unreported SO₂ emissions. Detailed characterization of the behavior of SO₂ concentrations at Solar Estates will help plan a mobile monitoring field study planned for February 2012.

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 10/01/2011 - 12/31/2011

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

 Total Grant Amount:
 \$6,761,718.02

 Total Interest Earned:
 \$811,193.51

 Total Funds Received:
 \$7,572,911.53

B. Summary of Expenditures Paid by COCP Funds

	[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		10/01/11 - 12/31/11		12/31/2011
Salaries-Prof	12	\$216,128.63	\$160,652.00	\$286,279.40	\$299,633.00	\$318,499.00	\$1,218,732.94	(\$1,183,826.02)	(\$21,254.86)		\$13,652.06
Salaries-CEER	15	\$19,606.37	\$15,636.00	\$33,123.00	\$30,948.00	\$29,880.00	\$162,071.37	(\$161,965.38)	(\$106.00)		-\$0.01
Fringe	14	\$47,984.00	\$38,783.00	\$58,333.00	\$72,728.00	\$76,643.00	\$285,059.91	(\$276,150.36)	(\$15,873.53)	(\$7,373.77)	-\$14,337.75
Communication	42	\$0,00	\$0.00	\$0.00	\$0.00	\$0.00	\$1,845.00	(\$1,485.00)	(\$90.00)		\$270,00
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	(\$505,803.14)	(\$3,037.67)		\$3,337.38
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	(\$3,430,742.12)	(\$96,201.10)		\$11,637.69
Program Income	66*	\$0.00	\$0.00	\$0,00	\$0.00	\$0.00	\$0.00	(\$126,995.29)	(\$80,524.75)	(\$18,866.26)	-\$226,386.30
Travel	75	\$2,300.00	\$2,000.00	\$7,719.00	\$9,000.00	\$6,712.00	\$30,191.00	(\$29,976.25)	(\$127.48)		\$87.27
Equipment	80	\$0.00	\$0.00	\$0.00	\$0.00	\$0.00	\$0.00	50.00	\$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	(\$822,153,74)	(\$20,467.43)		\$39,342.53
TOTALS		\$2,758,885.00	\$757,152.00	\$862,739.00	\$1,097,997.00	\$1,284,945.02	\$5,761,718.02	(\$6,670,192.30)	(\$237,682.82)	(\$26,240.03)	(\$172,397.13)

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

Salaries-Prof	66	\$49,298.65
Salaries-CEER	66	\$6,359.13
Fringe	66	\$0.00
Communication	66	\$0.00
 Other/C-Analysis	66	\$0.00
Supplies	66	\$24,656.90
Quality Assurance	66	\$0.00
Subcontract	66	\$0.00
Program Income	66	\$0.00
Travel	66	\$210,07
Equipment	66	\$0,00
TOTAL		\$80,524.75

C. Interest Earned by COCP Funds as of 12/31/11

Prior Interest Earned:	\$806,789.66
Interest Earned This Quarter:	\$4,403.85
Total Interest Earned to Date:	\$811,193.51

D. Balance of COCP Funds as of 12/31/11

Total Grant Amount:	\$6,761,718.02
Total Interest Earned:	\$811,193.51
Current Q. Expenses	(\$237,682.82)
Total Expenditures:	(\$6,670,192.30)
Remaining Balance:	\$665,036.41

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