Corpus Christi Air Monitoring and Surveillance Camera Installation and Operation Project

Quarterly Report for the Period

January 1, 2010 through March 31, 2010

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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May 26, 2010

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 March 31, 2010 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 27, and a summary of these analyses appear 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 COCP Project monitoring sites along with TCEQ sites and sites operated by Texas A&M at Kingsville (TAMUK) appears in Figure 1, below. Table 1, page 3, identifies the location and instrumentation found at each of the COCP Project sites. TCEQ and TAMUK sites provide some additional data used in analyses.





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	
Auto GC	automated gas chromatograph
TNMHC	total non-methane hydrocarbon analyzer (all except 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 27. Specifically, the appendix contains the following elements:

- Auto-GC Data Summary In examining the first quarter of 2010 hourly auto-GC data from Oak Park and Solar Estates, no measurements were found to have exceeded a short-term air monitoring comparison value (AMCV). Also, the quarterly averages of all species were below their respective long-term AMCVs. A summary appears in Appendix A, pages 11 through 14.
- **Benzene Trends at Auto-GC Sites** As has been discussed in recent reports, benzene concentrations have declined since the start of this project, and now may have leveled off. Results are in Appendix A, pages 14 and 15.
- **Benzene Concentrations Comparison** The data from other auto-GCs in Texas for the 1st Quarter of 2010 have been compiled and presented in tabular form to show how Corpus Christi data compare with other areas. Results are in Appendix A, page 16.

- **Canister Analysis** One species in one canister was found to have exceeded an AMCV (the odor effects screening level). A total of 16 canister samples were taken. Some results from analysis of the canisters from this quarter appear in Appendix A, pages 16 through 19.
- Huisache Benzene Data Analysis The Project was provided with the 15-minute time resolution benzene data collected by a private company (URS). These data have been shared as part of the ongoing health study being conducted by the federal Agency for Toxic Substances and Disease Registry (ATSDR). Some preliminary data analysis results are in Appendix A, pages 20 through 22.
- **Case Study of a Pollution Event** One pollution event that triggered a canister sample is discussed in Appendix A, pages 23 through 26.

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 development, quarterly and annual reports, meetings of the Project's Advisory Board and presentations to the local community organizations.

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 28 and 29.

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 28 and 29.

A. <u>Total Amount of COCP Funds and Other Funds Received Under the Project</u> The COCP funds received through March 31, 2010 totals \$7,516,776.49. This total includes interest earned through March 31, 2010. B. <u>Detailed List of the Actual Expenditures Paid from COCP Funds</u>

Expenditures of COCP funds during this quarter totaled \$248,618.79. The detailed breakdown of the actual expenditures is included in Appendix B, page 29. 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 \$12,910.45. 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 28 and 29.

D. <u>Balance as of March 31, 2010, in the COCP Account</u> The balance in the COCP account, including interest earned totals \$1,982,916.07.

E. <u>Expected Expenditures for the Funds Remaining in the COCP Account</u> The projected expenditures for the funds remaining totals \$1,982,916.07.

Quarterly Report Distribution List:

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APPENDIX A

Data Analysis for Corpus Christi Quarterly Report

January 1, 2010 through March 31, 2010

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Data Analysis for Corpus Christi Quarterly Report

This technical report describes recent results of monitoring and analysis of data under the Corpus Christi Air Quality Project for the period January 1 through March 31, 2010. The monitoring network is shown in Figure 1, page 2, and is described in Table 2 below. This report contains the following elements:

- A summary of Oak Park and Solar Estates auto-GC data for the 1st quarter
- A summary of Oak Park and Solar Estates benzene data for the 1st quarter
- Findings from canister analyses this quarter
- Analysis of data from an industry-sponsored benzene auto-GC monitor at Huisache.

TCEO	Description of Site		nt			
TCEQ CAMS#	L ocation		TNMHC (T) /			
	Location	Auto GC	Canister (C)	$H_2S \& SO_2$	Met Station	Camera
	Oak Park					
634	Recreation Center	Yes	Т		Yes	
	(UAK) Crain Elevator @					
620	Grain Elevator @		T P C	Vac	Vac	
029	Christi (CCG)		Iac	res	1 68	
	J. I. Hailey Site @					
630	Port of Corpus		T&C	Yes	Yes	
	Christi (JIH)					
	TCEQ Monitoring					
635	Site C199 @ Dona		T&C	Yes	Yes	Yes
	Park (DPK)					
	Port of Corpus					
631	Christi on West		T&C	Yes	Yes	
	End of CC Inner					
	Harbor (WEH)					
	Off Up River Road					
632	on Flint Hills		T&C	Yes	Yes	
	Resources					
622	Solar Estates Park	Vac	т	Vac	Vac	Vac
633	Road (SOE)	1 85	1	res	I es	res

	c •	• , •	• ,	1	1	•	• , ,•
Table 2. Schedule	of air	monitoring	sites,	locations a	and n	najor	instrumentation

Legend

Auto GC	automated	gas	chromatograph
		~	U

TNMHC	total non-methane hydrocarbon analyzer (all except 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 However, because TNMHC is a concentrations in converted ppbV units. 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 it for some 47 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.
- 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 and12 chlorinated species. Canister samplers have operated at all seven UT/CEER sites, but currently only at five (CAMS 629, 630, 631, 632, and 635).
- Air Monitoring Comparison Values (AMCV) TCEQ is now using the AMCV terminology 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 May, 2010). 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.

• 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 or SO_2 , any measured concentration greater than the level of the state residential standards, which are 80 ppb for H_2S and 400 ppb for SO_2 , is considered "elevated." Note that the concentrations need not persist long enough to constitute an exceedance of the standard to be so regarded. 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 then 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).
- For benzene and other air toxics in canister samples or auto-GC measurements, any concentration above the AMCV is considered "elevated." Note that 20-minute 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 two auto-GC sites – Solar Estates C633 and Oak Park C634 – are presented. These two sites are located in residential areas generally downwind of industrial emissions under northerly winds. In examining aggregated data one observes similar patterns of hydrocarbons at the two sites, with concentrations averaging higher at Oak Park than at Solar Estates.

Tables 3 and 4, page 12, summarize data from the first quarter of 2010. These tables are available to TCEQ staff at <u>http://rhone.tceq.state.tx.us/cgi-bin/agc_summary.pl</u> (accessed April 2010). The tables show the average concentrations over the quarter, and the maximum one-hour and 24-hour average concentrations for 27 hydrocarbon species of interest for the period of interest. <u>Note that not all data have been validated and are thus subject to change.</u> All concentrations were greater than TCEQ's air monitoring comparison values (AMCV) during the first quarter of 2010.

In Tables 3 and 4, the "Num Samples" column includes all ambient samples, including those not yet validated. The "Mean" is calculated as a weighted average of daily averages and takes into account the number of samples flagged ambient for each day.

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

Tables 5 and Table 6, pages 13 and 14, show the means for the first quarter of each of the past five years, 2006 - 2010, for the 27 auto-GC hydrocarbon species of interest. The last column in each table is labeled as *Ratio 09-10 to 06-07*, which is the ratio of the average of the most recent two years to the first two years. So, for example, at Solar Estates the average benzene concentration for the 1st quarter of 2009 and 2010 is 0.27 ppbV, and the average benzene concentration for the 1st quarter of 2006 and 2007 was 0.385 ppbV. The most recent two-average is 70 percent of the first two-year average, a 30 percent reduction. A composite of all the percentages is in the last row of Table 5 and Table 6, which can be use to summarize the change over time:

- recent Solar Estate hydrocarbon concentrations are about 63 percent of earlier concentrations and
- recent Oak Park hydrocarbon concentrations are about 57 percent of earlier concentrations.

Table 3. Solar Estates 1 st Quarter 2010 Auto-GC statistics						Table 4. Oak Park 1 st Quarter 2010 Auto-GC statistics				
Species, ppbV units	Num Samples	Mean	Peak 1hr	Peak 24-hr		Species, ppbV units	Num Samples	Mean	Peak 1hr	Peak 24-hr
Ethane	1,933	9.09	143.36	22.70		Ethane	1,888	9.38	150.20	25.21
Ethylene	1,933	0.52	15.02	2.27		Ethylene	1,888	0.90	52.72	4.93
Propane	1,933	5.64	89.10	16.25		Propane	1,887	6.16	159.17	21.57
Propylene	1,933	0.24	6.97	0.74		Propylene	1,888	0.43	38.44	3.39
Isobutane	1,933	1.74	23.48	5.60		Isobutane	1,888	2.11	70.11	6.07
n-Butane	1,933	2.78	32.50	7.87		n-Butane	1,888	3.55	57.07	8.29
t-2-Butene	1,933	0.07	2.43	0.29		t-2-Butene	1,888	0.10	1.01	0.34
1-Butene	1,933	0.06	2.23	0.29		1-Butene	1,888	0.08	3.52	0.40
c-2-Butene	1,933	0.05	1.91	0.23		c-2-Butene	1,888	0.06	0.86	0.27
Isopentane	1,933	1.33	18.82	3.88		Isopentane	1,888	2.14	34.62	7.25
n-Pentane	1,933	0.87	14.54	2.67		n-Pentane	1,888	1.41	16.90	6.16
1,3-Butadiene	1,933	0.04	9.77	0.61		1,3-Butadiene	1,888	0.04	0.74	0.12
t-2-Pentene	1,933	0.03	0.99	0.11		t-2-Pentene	1,888	0.07	2.27	0.35
1-Pentene	1,933	0.02	0.52	0.07		1-Pentene	1,888	0.03	0.70	0.16
c-2-Pentene	1,933	0.01	0.48	0.05		c-2-Pentene	1,888	0.02	0.91	0.15
n-Hexane	1,933	0.31	9.63	1.32		n-Hexane	1,888	0.50	8.86	2.11
Benzene	1,933	0.30	9.46	1.22		Benzene	1,888	0.49	7.02	1.60
Cyclohexane	1,933	0.18	3.97	0.51		Cyclohexane	1,888	0.22	3.60	0.70
Toluene	1,933	0.30	8.92	1.16		Toluene	1,888	0.70	62.62	3.91
Ethyl Benzene	1,933	0.03	1.44	0.15		Ethyl Benzene	1,888	0.03	0.88	0.10
m&p-Xylene	1,933	0.26	8.06	1.34		m&p-Xylene	1,888	0.13	2.55	0.42
o-Xylene	1,933	0.05	1.54	0.17		o-Xylene	1,888	0.04	1.00	0.12
Isopropyl Benz - Cumene	1,933	0.02	1.65	0.15		Isopropyl Benz - Cumene	1,888	0.03	1.17	0.29
1,3,5-Trimethylbenzene	1,933	0.02	1.31	0.10		1,3,5-Trimethylbenzene	1,888	0.01	0.48	0.05
1,2,4-Trimethylbenzene	1,933	0.04	5.79	0.44		1,2,4-Trimethylbenzene	1,888	0.03	1.46	0.12
n-Decane	1,933	0.05	3.69	0.25		n-Decane	1,888	0.02	0.62	0.09
1,2,3-Trimethylbenzene	1,933	0.01	0.66	0.05		1,2,3-Trimethylbenzene	1,888	0.01	0.39	0.04

		1				
Species, ppbV units	1Q06	1Q07	1Q08	1Q09	1Q10	Ratio 09-10 to 06-07
Ethane	9.86	10.56	7.61	8.07	9.09	84%
Ethylene	0.42	0.62	0.42	0.41	0.52	89%
Propane	6.23	6.40	4.43	4.79	5.63	83%
Propylene	0.35	0.30	0.17	0.21	0.24	69%
Isobutane	2.97	2.10	1.51	1.64	1.74	67%
n-Butane	3.58	3.69	2.61	2.63	2.77	74%
t-2-Butene	0.18	0.09	0.09	0.05	0.07	44%
1-Butene	0.06	0.07	0.04	0.04	0.06	77%
c-2-Butene	0.09	0.06	0.04	0.03	0.05	53%
Isopentane	2.08	1.76	1.33	1.32	1.33	69%
n-Pentane	1.18	1.13	0.82	0.83	0.87	74%
13-Butadiene	0.06	0.07	0.02	0.02	0.03	38%
t-2-Pentene	0.04	0.06	0.02	0.03	0.03	60%
1-Pentene	0.02	0.04	0.01	0.02	0.02	67%
c-2-Pentene	0.02	0.03	0.01	0.01	0.01	40%
n-Hexane	0.42	0.46	0.31	0.29	0.30	67%
Benzene	0.34	0.43	0.26	0.25	0.29	70%
Cyclohexane	0.27	0.31	0.18	0.17	0.17	59%
Toluene	0.36	0.52	0.29	0.32	0.29	69%
Ethyl Benzene	0.05	0.06	0.03	0.03	0.03	55%
m&p-Xylene	0.35	0.53	0.24	0.23	0.25	55%
o-Xylene	0.06	0.08	0.05	0.05	0.05	71%
Isopropyl Benz-Cumen	0.01	0.08	0.01	0.01	0.02	33%
135-Trimethylbenzene	0.02	0.04	0.02	0.01	0.02	50%
124-Trimethylbenzene	0.05	0.06	0.04	0.03	0.04	64%
n-Decane	0.03	0.06	0.03	0.02	0.05	78%
123-Trimethylbenzene	0.02	0.02	0.01	0.01	0.01	50%
Average percentage						63%

 Table 5. Solar Estates auto-GC 1st quarter means by year 2006 -2010

Species, ppbV units	1Q06	1Q07	1Q08	1Q09	1Q10	Ratio 09-10 to 06-07
Ethane	10.16	11.74	9.23	8.78	9.38	83%
Ethylene	1.12	1.10	0.89	0.75	0.90	74%
Propane	7.26	8.17	5.53	5.66	6.16	77%
Propylene	1.12	0.96	0.57	0.41	0.43	40%
Isobutane	3.33	3.18	2.47	2.00	2.11	63%
n-Butane	4.39	4.75	4.07	3.46	3.55	77%
t-2-Butene	0.21	0.24	0.20	0.07	0.10	38%
1-Butene	0.17	0.19	0.10	0.06	0.08	39%
c-2-Butene	0.16	0.15	0.13	0.04	0.06	32%
Isopentane	2.65	3.17	2.76	2.33	2.14	77%
n-Pentane	1.46	2.04	1.57	1.48	1.41	83%
13-Butadiene	0.05	0.09	0.06	0.02	0.04	43%
t-2-Pentene	0.10	0.14	0.09		0.07	58%
1-Pentene	0.05	0.07	0.05		0.03	50%
c-2-Pentene	0.05	0.06	0.04		0.02	36%
n-Hexane	0.71	0.74	0.44	0.51	0.50	70%
Benzene	0.81	1.04	0.46	0.43	0.48	49%
Cyclohexane	0.33	0.28	0.19	0.18	0.22	66%
Toluene	0.68	1.08	0.63	0.76	0.70	83%
Ethyl Benzene	0.07	0.08	0.06	0.05	0.03	53%
m&p-Xylene	0.26	0.25	0.16	0.18	0.13	61%
o-Xylene	0.10	0.08	0.06	0.06	0.04	56%
Isopropyl Benz-Cumen	0.03	0.05	0.03	0.02	0.03	63%
135-Trimethylbenzene	0.04	0.03	0.01	0.01	0.01	29%
124-Trimethylbenzene	0.08	0.08	0.05	0.04	0.03	44%
n-Decane	0.04	0.03	0.02	0.02	0.02	57%
123-Trimethylbenzene	0.02	0.03	0.01	0.01	0.01	40%
Average percentage						57%

Table 6. Oak Park auto-GC 1st quarter means by year 2006 -2010

2. Benzene Trends and Comparisons

Figure 2 on page 15 shows the trend for the first quarter mean concentrations for benzene in ppbV units at the Solar Estates and Oak Park auto-GCs operated by UT for 2006 – 2010, and at the URS's Huisache monitor for 2005 – 2009. (Details about the URS Huisache monitor appear on page 16.) As has been stated in past reports, the fourth and first quarters of the year have the highest benzene concentrations at these sites because of a higher frequency of northerly winds in Corpus Christi during winter months. As was stated earlier in this report, the TCEQ's long-term AMCV for benzene is 1.4 ppbV. Figure 2 shows that concentrations have declined since the first two years of UT monitoring, and were declining at least a year earlier at the Huisache site, but concentrations have remained relatively flat over the most recent three years. Figure 2. Mean benzene concentrations at two UT auto-GCs for the first quarter of each year 2006 – 2010, and the URS auto-GC for the first quarter of each year 2005 – 2009



To help put the concentrations at Solar Estates and Oak Park in a context, Table 7 on page 16 lists the mean and peak (1-hour and 24-hour average) benzene concentrations for the 1st quarter of 2010 for all auto-GCs operated for or by the TCEQ plus the two UT auto-GCs. The sites are listed in descending order on the mean.

Site	County	Mean	Peak 1- Hr	Peak 24-Hr	Num > 1-Hr AMCV	Over Annual AMCV
Lynchburg Ferry	Harris	1.01	246.49	20.21	1	No
Channelview	Harris	0.5	7.54	1.51	0	No
Clinton	Harris	0.48	14.11	1.58	0	No
Chamizal	El Paso	0.48	7.23	1.57	0	No
Oak Park	Nueces	0.48	7.02	1.60	0	No
Lamar	Jefferson	0.39	14.35	1.39	0	No
Deer Park	Harris	0.38	56.12	3.27	0	No
Nederland HS	Jefferson	0.38	11.78	1.34	0	No
Haden Rd	Harris	0.36	10.43	1.31	0	No
Cesar Chavez	Harris	0.36	3.06	1.02	0	No
Mustang Bayou	Brazoria	0.35	13.49	2.39	0	No
Milby Park	Harris	0.32	5.51	1.32	0	No
Solar Estates	Nueces	0.29	8.30	0.91	0	No
Hinton	Dallas	0.26	2.83	0.79	0	No
Wallisville Rd	Harris	0.23	6.76	1.03	0	No
Texas City	Galveston	0.22	6.51	0.81	0	No
Fort Worth NW	Tarrant	0.21	1.98	0.55	0	No
Lake Jackson	Brazoria	0.17	1.12	0.36	0	No
Danciger	Brazoria	0.14	1.87	0.41	0	No

Table 7 Mean and peak concentrations of benzene at 19 active auto-GCs in Texas for 1st quarter 2010, ppbV units

3. Canister Analysis

Sixteen canister samples were taken in the fourth quarter of 2009. The rate at which canisters have been sampled has slowed down over the past three years. The lower rate of sampling is due to a lower frequency of occurrence of the threshold for triggering a sample (TNMHC > 2000 ppbC for 15 minutes). Table 8, page 17, shows the counts for the number of canister samples since April 2006 by quarter. The table shows that the fourth quarter of each year has had the most canister-triggering activity, and the second quarter has had the least. The last row is bold-faced because it is the most recently concluded quarter.

One short-term AMCV was exceeded during the last quarter.

Site	Date	Time CST	Species	ppbV	Odor ESL
CCG CAMS 629	2/16/2010	23:45	2-methylpentane	1,607	498

Quarter/year	Nulli of samples
2Q06	7
3Q06	4
4Q06	23
1Q07	10
2Q07	6
3Q07	9
4Q07	40
1Q08	3
2Q08	2
3Q08	6
4Q08	22
1Q09	15
2Q09	2
3Q09	4
4Q09	12
1Q10	16

 Table 8. Total number of canister samples at 5 sites by quarter

 Quarter/year
 Num of samples

A summary of the 16 canister samples appears in Table 9, on page 18. This table shows the site name, the approximate date/time start of the 20-minute sample, the approximate coincident TNMHC average concentrations from the TECO 55C instrument, and the summed mass of identified species ("SumPol"). Note that TNMHC and SumPol units are in ppbC. The graph in Figure 3, on page 19, shows the scatterplot of SumPol (y-axis) and approximate coincident TNMHC (x-axis). This "coincident" TNMHC value is only approximate, as the TNMHC data come from five-minute blocks of data, and canister samples can be initiated anytime within a five-minute block. Nevertheless, as has been shown in earlier reports, the agreement between estimated TNMHC and measured SumPol is highly statistically significant with a slope that is usually close to 1.0. The one pairing with the worst agreement this quarter was at Corpus Christi Grain on February 16, and the data show that TNMHC was changing very rapidly during this time period, thus introducing high uncertainty into the accuracy of the approximated coincident TNMHC. Note that with the Corpus Christi Grain CAMS 629 2/16/2010 record removed, the slope of the resulting regression is much closer to 1.0 (slope = 0.97).

The methane concentrations are also shown in Table 9 to suggest for which samples natural gas may have been a component. Baseline measured methane is generally from 1,700 - 2,200 ppbC. Twelve of the 16 samples appear to have significantly higher levels of methane, suggesting the presence of natural gas. This hypothesis is supported by the speciation results on the canisters. The 12 canisters with elevated coincident methane had ethane, propane, and other alkane species comprising the large majority of the sample mass. One sample, the West End Harbor CAMS 631 March 13 sample, appears to have had a mixture of natural gas and refinery emissions based on the canister speciation and back-trajectory. The graph in Figure 4, on page 19, shows the scatterplot of methane (y-axis) and coincident TNMHC (x-axis) during the 20-minute canister samples. Notice that in the linear fit to the data, when TNMHC equals zero, the methane value would be 1,986

ppbC, which is approximately the background concentration for this species. The linear relationship and the model formula (*methane* = 1.3*tnmhc + 1,986) may help identify the source of elevated TNMHC from natural gas operations. This relationship was established only with this quarter's data, but the analysis using this approach will be applied to the larger historical data set in later reports.

Table 9. Sixteen canister samples from 1Q10 compared to approximate coincident TECO 55C TNMHC, ppbC units. Italicized methane values show likely natural gas influence. Highest TNMHC concentrations are in **bold** font.

Site name	Date	Time CST	SumPol	TNMHC	Methane
CCG CAMS 629	1/2/2010	3:24	2,202	2,621	7,153
CCG CAMS 629	1/16/2010	19:34	1,437	1,593	4,288
CCG CAMS 629	1/21/2010	23:22	8,950	6,955	2,053
CCG CAMS 629	2/14/2010	7:02	2,184	2,133	4,744
CCG CAMS 629	2/16/2010	23:45	10,976	18,446	2,080
CCG CAMS 629	3/3/2010	8:07	7,185	9,181	2,229
DPK CAMS 635	1/6/2010	11:09	1,451	1,806	4,080
DPK CAMS 635	1/7/2010	7:33	2,349	2,648	5,002
DPK CAMS 635	1/13/2010	0:50	3,697	3,745	6,350
DPK CAMS 635	1/16/2010	17:42	2,470	3,042	6,307
DPK CAMS 635	2/14/2010	7:23	6,370	3,986	6,670
FHR CAMS 632	1/2/2010	23:57	466	370	2,435
JIH CAMS 630	1/16/2010	19:19	2,329	2,478	5,665
JIH CAMS 630	3/22/2010	6:16	1,504	1,559	2,954
WEH CAMS 631	3/13/2010	1:21	6,579	9,225	3,602
WEH CAMS 631	3/17/2010	3:33	1,356	1,023	2,090



Figure 3. SumPol vs TNMHC for 16 samples from 1Q10; see Table 9. above

Figure 4. Methane vs TNMHC for 11 of 12 samples with methane > 2,400 ppbC from 1Q10; see Table 9. above.



4. Huisache Benzene Data Analysis

The Project was provided with the 15-minute time resolution benzene data collected from 2005 – 2009 by a private company (URS) using a benzene-specific auto-GC at the TCEQ's CAMS 98 Huisache site. Figure 5, below, shows an aerial photo of the area around the site and the range and bearing to the Oak Park monitoring site. The Huisache benzene data have been shared with UT and the TCEQ as part of the ongoing Corpus Christi health study being conducted by the federal Agency for Toxic Substances and Disease Registry (ATSDR).

Figure 5. Aerial photo of URS Huisache site collocated with TCEQ CAMS 98, and the Oak Park CAMS 634 site.



Some preliminary analyses have been performed with the URS Huisache data. As a first step, the benzene data have been merged with coincident and collocated wind speed and direction data. The benzene concentrations were averaged by wind direction using kernel smoothing to achieve 1-degree directional resolution. Only data from 2006 - 2009 were used, to overlap the same period of monitoring by the Oak Park auto-GC. Benzene wind

directionality at Huisache peaks at 37 degrees with a mean of 6.7 ppbV, with a second peak at 288 degrees with a mean of 2.8 ppbV and a third peak at 333 degrees with a mean of 2.3 ppbV. Only winds with speed at or above 5 miles per hour used in this analysis. The results appear in the line plot in Figure 6, below.



Figure 6. Kernel smoothed mean benzene (ppbV units) at Huisache using data from 2006 – 2009

A similar approach was taken with the hourly Oak Park auto-GC data. Benzene wind directionality at Oak Park using 2006 - 2009 data peaks at 22 degrees with a mean of 3.2 ppbV, with a second peak at 335 degrees with a mean of 1.3 ppbV. Again, only winds with speed at or above 5 miles per hour used. The results appear in the line plot in Figure 7, page 22.



Figure 7. Kernel smoothed mean benzene (ppbV units) at Oak Park using data from 2006 – 2009.

One might hypothesize that the same emission sources may be contributing to the peaks at both sites. The map in Figure 8, page 23, shows the results of extending rays from each site in the direction of the two peaks at Oak Park and three peaks at Huisache. The northwest ray from Oak Park and the westernmost ray from Huisache intersect in the Magellan and Equistar tank farms adjacent to the Valero East refinery. More evidence that the same source affects both sites is that the concentrations at Huisache associated with this direction significantly declined from 2006 to 2007. It was over this same time period that concentrations from the northwest dropped at Oak Park.

The northeast ray from Oak Park actually passes over Huisache, and may be associated with the slightly more easterly northeast ray from that site. If so, the source may be relatively close to Huisache, because the rays diverge beyond that location. Further study is needed to assess the wind direction accuracy at Huisache. The collocated TCEQ and URS wind instruments do appear to match closely, but the wind directions and speeds at the site may be affected by the proximity of the large above-ground storage tanks to the northeast. Note that the mean concentration at Huisache is more than twice the mean concentration at Oak Park, suggesting the emission source is closer to Huisache, which is obvious from Figure 8.

Figure 8. Two Oak Park benzene peak rays in red, and three Huisache benzene peak rays in blue.



5. Case Study of a Pollution Event February 16, 2010

At the Port Grain (CCG) CAMS 629 site on February 16, at 11:30 p.m. CST, TNMHC concentrations swiftly rose from background levels of 200 ppbC to over 11,000 ppbC and then 26,000 ppbC ten minutes later. The graphs in Figures 9 and 10 on page 25 show the 5-minute time series of data for TNMHC, methane, SO₂, H₂S, wind speed and wind direction at the site. The highest TNMHC concentrations were associated with a narrow upwind direction around 200 degrees. The sudden rise in H₂S as the winds shifted to 220 – 230 degrees does not seem to have been related to this event. The surface back-trajectory from the start of the canister collection is shown in two versions in Figures 11 and 12 on page 26. Figure 10 is taken directly from the Corpus Christi on-line trajectory tool, while Figure 12, with greater detail about land use, was made by exporting the 5-minute time resolution trajectory points generated by the trajectory tool and then filling in intermediary points with interpolation to go to 1-minute time resolution. Points in Figure 12 are denoted by the number of minutes back in time from 11:45 p.m. CST.

There was a reported upset at the CITGO Corpus Christi Refinery East Plant on 1802 Nueces Bay Blvd. on February 16 between 6:25 and 6:35 p.m. CST. The cause reported on the TCEQ's Emission Event Reporting Database¹ was as follows:

While blending to Tank 1016, product was seen spilling out of the overflow slots. Investigation revealed that the tank reference height in OHMS was lower than what was noted in the tank's strapping table. This resulted in a gauge reading that was lower than the actual product level.

The reported action taken was as follows:

Transfer to the tank was immediately stopped and Tank 1016 was lined up to Tank 1032 to bring down the inventory in Tank 1016. Foam was applied to the spilled material on the ground and spill was cleaned up. An investigation team was formed to identify root cause of event and provide corrective actions. Investigation is still ongoing at this time; upon completion of the investigation, updated information will be provided to the Agency. Hexanes include C6s less Benzene; Heptanes includes C7+ (less Toluene and Xylene).

Figure 12, the more detailed back-trajectory map, also shows the location of Tank 1016 taken from the TCEQ's 2005 modeling emissions inventory. This tank lies nearly directly along the idealized centerline of the modeled surface back-trajectory. As noted above, the report says the upset involved hydrocarbons with 6 to 7 carbons. The species and concentrations in the canister sampled at 11:45 p.m. CST are shown in Figure 13, page 27 . The canister's mass is mostly in C4 – C7 hydrocarbon species. Although the emission event report explicitly excludes benzene, the canister sample did contain this species.

Earlier in the evening, at 7:35 p.m. CST, the JIH CAMS 630 site measured 3,600 ppbC TNMHC with a slight coincident bump-up in SO_2 as the winds shifted from 140 through 160 to 180 degrees. The elevated TNMHC rose to a peak and dropped over the 15 minutes that the wind passed through 160 degrees. The back-trajectory from JIH at 7:35 p.m. CST passed very close to Tank 1016. No canister was triggered at JIH, however.

¹ See <u>http://www11.tceq.state.tx.us/oce/eer/index.cfm?fuseaction=main.getDetails&target=135901</u> accessed April 2010



Figure 9. Time series of TNMHC, methane, and wind direction, late Feb. 16 to early Feb. 17, CST.

Figure 10. Time series of TNMHC, SO₂, H₂S, and wind speed, late Feb. 16 to early Feb. 17, CST.





Figure 11. Surface back-trajectory from CCG C629 February 16, 2010, 23:45 CST

Figure 12. Surface back-trajectory from CCG C629 2/16/10, 23:45 plus location of 2/16/10 reported upset_____





Figure 13. Canister composition, CCG C629 February 16, 2010, 23:45 CST

Conclusions from the First Quarter 2010 Data

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

- First quarter benzene concentrations at the auto-GCs show an overall significant downward trend since 2007, with a flattening out over the past three years. All auto-GC species of interest show a decline from the first two years of monitoring.
- New terminology in use by TCEQ Toxicology Division is leading to a change in how the relationship of measured concentrations to key reference levels is communicated. Henceforward, references to effects screening levels (ESLs) and reference values (ReVs) will be replaced with references to air monitoring comparison values (AMCVs).
- Periodic air pollution events continue to be measured on a routine basis, but values of hydrocarbons above the air monitoring comparison values levels are rarely observed. No measurements exceeded AMCVs this quarter in the auto-GC data or canister data.
- New data provided from the industry-sponsored Huisache site allows new analysis for trends and for directionality. Coupled with directional analysis from Oak Park, a relatively small area of above-ground storage tanks may constitute one of the key source areas for benzene emissions.
- A close look at the relationship between methane and TNMHC may help quickly identify when natural gas emissions have been the source of elevated concentrations.

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 01/01/10 - 03/31/10

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

 Total Grant Amount:
 \$6,761,716.02

 Total Interest Earned:
 \$755,058.47

 Total Funds Received:
 \$7,616,776.49

B. Summary of Expenditures Paid by COCP Funds

	[Year 3	Year 4	Year 5	Yezr 6	Year 7	Yrs 1-7	Prior Activity	Current Activity	Encumbrances	Remaining Balance
	1	Budget	Budget	Budget	Budget	Budget	Adjusted Budget		01/01/10 - 03/31/10		3/31/2010
Salaries-Prof	12	\$216,128.63	\$160,652.00	288,279.40	299,633.00	318,499.00	\$1,281,192.03	(\$971,384.24)	(\$86,234.35)	(\$18,555.78)	\$205,036.68
Salaries-CEER	15	\$19,606.37	\$15,636.00	33,123,00	30,948.00	29,880.00	\$129,193.37	(\$103,510.88)	(\$8,800.91)	(\$13,912.65)	\$2,968.95
Fringe	14	\$47,984.00	\$38,783.00	58,333.00	72,728.00	78,643.00	\$305,100.00	(\$214,783.37)	(\$20,317.24)	(\$7,173.29)	\$62,848.10
Communication	42					900.00	\$900.00	(\$\$80.00)	(\$225.00)	\$0.00	\$495.00
Other/C-Analysis	47/68	\$50,474,00	\$73,500.00	(8.656.40)	73,500.00	4,219.00	\$122,849.60	(\$49,928.00)	(\$21,315.00)	\$0.00	\$51,706.60
Supplies	50	\$86,844.00	\$33,500.00	68,676.00	122,682.00	65,386.00	\$447,763.73	(\$343,663.32)	(\$16,291,29)	(\$8,715.29)	\$79,193.63
	51		\$20,300.00	8,000.00		7,070.00	\$30,792.27	(\$16,911.78)	(\$28.00)	(\$361.28)	\$13,491.21
Subcontract	62-64	\$1,965,693.00	\$314,022.00	296,734.00	346,289.00	341,523.00	\$3,264,261.00	(\$2,906,110.71)	(\$81,244.16)	\$0.00	\$296,906,13
Travel	75	\$2,300.00	\$2,000.00	7,719.00	9,000.00	6,712.00	\$30,191.00	(\$20,838.73)	(\$1,734.30)	\$0.00	\$7,619.97
Equipment	80	\$0.00	\$0.00	0.00			\$0.00	\$0.00	\$0.00	\$0.03	\$0.00
Indirect Costs	90	\$359,855.00	\$98,759.00	112,531.00	143,217.00	127,490.00	\$841,852.00	(\$658,072.62)	(\$32,428.54)	\$0.09	\$151,350.84
TOTALS		\$2,758,885.00	757,152.00	852,739.00	1,097,997.00	978,322.00	\$6,454,195.00	(\$5,285,241.63)	(\$248,618.79)	(\$45,719.29)	\$871,615.29

C. Interest Earned by COCP Funds as of 03/31/10

Prior Interest Earned:	\$742,148.02
Interest Earned This Quarter:	\$12,910.45
Total Interest Earned to Date:	\$755,058.47

D. Balance of COCP Funds as of 03/31/10

Total Grant Amount:	\$5,761,718.02
Total Interest Earned:	\$755,058,47
Current Q. Expenses	(\$248,618.79)
Total Expenditures:	(\$5,285,241.63)
Remaining Balance:	\$1,982,916.07

i certify that the numbers are accurate and reflect acutal expanditures for the quarter Jones STA S