HRVOC AOC FINAL REPORT

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EXECUTIVE SUMMARY

In early 2005 the Louisiana Department of Environmental Quality (LDEQ) issued Administrative Orders on Consent (AOC) to 15 facilities in the Baton Rouge Non-Attainment Area that emit highly reactive volatile organic compounds (HRVOC). The purpose of the AOC was to help identify emission sources of HRVOC that were contributing to ozone formation in the five parish area. The companies that received the AOC were: BASF, Chemtura, Dow, DSM, Enterprise, ExxonMobil Chemical, ExxonMobil Plastics, ExxonMobil Polyolefins, ExxonMobil Refinery, Placid, Plantation Pipeline, Occidental, Shell, Syngenta, and Williams Olefins.

The companies were ordered to install HRVOC (and other compounds) monitoring on or near their site boundaries. The monitors were to be put into operation by May 1, 2005, and continue for two years. In addition, six of the companies that are located in the North Baton Rouge area were ordered to perform audits of their HRVOC systems. The due date for the completion of the audits was May 1, 2005.

A total of 22 monitors were installed at the plants. All of the stations included a total hydrocarbon analyzer that sampled the air every three minutes and instrumentation to continuously monitor wind speed and direction. The total hydrocarbon analyzer was configured to provide a trigger whenever the sampled air contained hydrocarbons in excess of a pre-determined set point. When the trigger was initiated, a 20 minute sample was collected. Some of the plants installed gas chromatographs that immediately analyzed the collected sample and sent the information to plant personnel. Other plants sent the collected sample to a lab for analysis - a process that took a couple of weeks before the analysis was known. With each trigger event, plant personnel were required to respond by searching the plant for possible sources causing the trigger. All of the data and response findings were reported to LDEQ monthly.

The plants completed the audits by the due date. With a few minor exceptions, the auditors found that the plants were doing a proper job of identifying and monitoring sources where HRVOC could be emitted to the atmosphere.

The monitoring program resulted in a total of approximately 2,500 samples being analyzed by the plants. A portion of the samples contained significant amounts of HRVOC, especially ethylene and propylene. The majority of the samples contained mostly evaporative gas compounds, namely, butane, isopentane, propane, isobutane, pentane, and other hydrocarbons that are in gasoline. The source of most of the gasoline products was storage tanks that do not have vent collection. The next largest cause of strikes was emissions of various compounds that the plants are permitted to emit. Some strike samples showed compounds that were attributed by the plants to flares, and some strikes were caused by leaks, and maintenance and operating activities.

During the monitoring period, the number of strikes at the ten LDEQ-operated monitoring sites showed a significant decline of 25 percent. Strikes at the four urban Baton Rouge monitoring sites declined by 40 percent. Also, reports to LDEQ of unauthorized releases of HRVOC greater than 100 pounds in 24 hours showed a decrease of 60 percent, and the release quantities were much lower. This improved performance helped the Baton Rouge area to attain the old 1-hour ozone standard in 2006.

The monitoring program was terminated on December 31, 2006, because the affected facilities and LDEQ felt that no new data of any substantial value would be obtained by continuing the monitoring for an additional four months.

I. INTRODUCTION

On October 6, 2004, the Louisiana Department of Environmental Quality (LDEQ) issued Administrative Orders (AO) to 16 facilities in the Baton Rouge Ozone Nonattainment Area (BRNA). The AO required all of the facilities to implement a fenceline ambient air monitoring program by March 1, 2005. Additionally, six of the facilities were ordered to perform a comprehensive environmental audit of their Highly Reactive Volatile Organic Compounds (HRVOC) systems by the same date.

Upon request from all of the affected facilities except Plantation Pipe Line, LDEQ agreed to amend the AO and extend the deadlines for both the monitoring and the audit. The amended AO became an Administrative Order on Consent (AOC) and the deadline for beginning the monitoring program and completing the environmental audit was pushed back to May 1, 2005. The monitoring program was to continue for a two-year period. Plantation Pipe Line accepted the original AO requirements, but, after consultation with plant management, LDEQ revised their timeline to agree with that of the AOC facilities. The AO for the DSM Corporation facility in Addis was rescinded as a decision was made by DSM to shutdown the facility at the end of 2004 for economic reasons.

In December of 2006, after 20 months of monitoring, LDEQ was approached about the possibility of early termination of the monitoring program. The reasoning was that no new data of any substantial value would be obtained by continuing the monitoring for an additional four months. LDEQ concurred and letters were issued to each facility and the monitoring program was discontinued on December 31, 2006.

This Final Report is being written to summarize the events that led up to the AOC, the requirements of the AOC, the data that was collected, the significant findings and finally some conclusions from the program. Details of each facility's data and results can be found in the individual Final Reports included in Appendix D.

II. BACKGROUND

The issuance of the 1990 Clean Air Act resulted in the BRNA being designated in non-attainment of the 1-hour ozone standard and classified as a *serious* area because of the 164 parts per billion (ppb) design value in 1989. The attainment date was November 15, 1999. Emissions were reduced and design values declined, but, attainment was not reached by 1999. For failure to attain by the attainment date, the Environmental Protection Agency (EPA) re-classified the BRNA as a *severe* ozone area with a new attainment date of November 15, 2005. The reclassification to *severe* brought many new requirements such as reformulated gasoline, regulation of smaller businesses, increased offsets for new sources or modification of existing sources, and possible Clean Air Act Section 185 penalty fees if the area failed to attain the standard by 2005. Atmospheric modeling was performed to determine what needed to be done to bring the BRNA into attainment. The modeling determined that about a 30 percent decrease in oxides of nitrogen (NOx) would bring the design value to less than the 125 ppb, 1-hour ozone standard. A state regulation was promulgated that required facilities to add controls on boilers, heaters, furnaces, turbines and internal combustion engines by May 1, 2005 in order to obtain the necessary NOx reductions.

Observations in the years of 2002 to 2003 indicated that 1-hour ozone exceedances would not usually occur with only routine amounts of volatile organic compounds (VOC) and NOx in the atmosphere. However, under certain conditions, rapid ozone formation would occur and result in an exceedance. Monitoring results from many of these exceedances indicated a high rate and efficiency of ozone production that was limited to the immediate Baton Rouge area. These episodes corresponded very well to the kind of episodes that had been identified in the Houston/Galveston area. The Texas Air Quality Study 2000 concluded that the hydrocarbon reactivity during these episodes was often dominated by low molecular weight alkenes and aromatics. Air quality sampling in the Baton Rouge area showed substantial quantities of the same hydrocarbon precursors mentioned in the Texas study. The ozone formation experienced in the BRNA was thought to be the result of non-routine emissions of HRVOC.

Facilities handling HRVOC were asked to look at their operations and devise ways to reduce releases of HRVOC. An HRVOC workgroup of Industry, Environmental Groups and LDEQ was formed to further evaluate the specific causes of the BRNA ozone problem. The goals of the workgroup were to design and oversee studies and recommend solutions to help the area meet the November 2005 attainment date and avoid additional repercussions of continued non-compliance. The workgroup met bi-weekly over a six month period. In general, the workgroup concluded that not enough ozone precursor monitoring was in place and that the data that LDEQ was collecting was not being properly handled and analyzed. The specific recommendations were as follows:

- Upgrade the LDEQ monitoring network to include NOx and VOC monitoring at all BRNA stations
- Record all precursor monitoring data in both 5-minute and 1-hour increments
- Design and implement a database to store all monitoring and lab data together
- Contract a qualified company to perform a statistical analysis of the database

LDEQ accepted these recommendations and implemented them.

In June of 2004, the Environmental Protection Agency (EPA) began implementing the new 8-hour ozone standard, under which the BRNA was designated nonattainment and assigned a *marginal* classification with an attainment date of June 15, 2007. The new rule also provided for the revocation of the 1-hour ozone standard on June 15, 2005.

Monitoring during the 2004 ozone season utilizing the enhanced network showed that non-routine or episodic releases of HRVOC continued to be a problem - over 100 measurements of greater than 100 ppb HRVOC were observed by August. In addition to the unhealthy air, the ozone exceedances experienced during the 2004 ozone season made it impossible for the BRNA to achieve attainment of the 1-hour standard prior to the revocation of the standard in June 2005. Likewise, the lack of significant progress in reducing ozone was expected to make it exceedingly difficult for the BRNA to achieve attainment of the new 8-hour standard by the 2007 attainment date. This failure would likely result in reclassification to *moderate* and bring additional requirements for the area.

For these reasons LDEQ issued the AO in October 2004. As previously mentioned the AO was amended in December 2004 and became an AOC.

III. AOC REQUIREMENTS – Environmental Audit

The following six facilities were ordered to perform environmental audits.

- Enterprise Products Operating L.P., AI# 40198 – Port Allen/West Baton Rouge Parish
- ExxonMobil Chemical Plant (BRCP), AI# 286 – Baton Rouge/East Baton Rouge Parish
- ExxonMobil Plastics Plant (BRPP), AI# 285 – Baton Rouge/East Baton Rouge Parish
- ExxonMobil Polyolefins Plant, AI# 3519 – Baton Rouge/East Baton Rouge Parish
- ExxonMobil Refinery, AI# 2638 – Baton Rouge/East Baton Rouge Parish
- Placid Refining Company, L.L.C., AI# 2366 – Port Allen/West Baton Rouge Parish

The environmental audit covered the following elements.

1. Audit (the Facility) to Document All Units That Handle HRVOC
2. Audit (units in Element 1) to Document All Potential Release Sources of HRVOC
3. Audit the LDAR (Leak Detection and Repair) Program for Those Components That Handle HRVOC
4. Conduct Testing of HRVOC Transport Activities (to confirm that emission estimates that are submitted to LDEQ are accurate)
5. Conduct Testing of Flares That Handle HRVOC (Since there isn't any technology available to measure the destruction efficiency of a flare, this element was to verify that the flare was meeting 40 CFR 60.18.)
6. Conduct Sampling of Cooling Tower Inlets with Potential HRVOC Emissions
7. Conduct Testing of Large Point Sources (to confirm that emission estimates that are submitted to LDEQ are accurate)

All plants submitted their Environmental Audit Report by the agreed upon date. These reports can be found in Appendix A.

IV. AOC REQUIREMENTS – Fenceline Monitoring

The AOC was issued to the following facilities in the BRNA that handle HRVOC

- BASF Corporation, AI# 2049 – Geismar/Ascension Parish
- Crompton Manufacturing Company, AI# 1433 – Geismar/Ascension Parish
- The Dow Chemical Company, AI# 1409 – Plaquemine/Iberville Parish
- DSM Copolymer, Inc., AI# 1395 – Baton Rouge/East Baton Rouge Parish
- Enterprise Products Operating L.P., AI# 40198 – Port Allen/West Baton Rouge Parish
- ExxonMobil Chemical Plant, AI# 286 – Baton Rouge/East Baton Rouge Parish
- ExxonMobil Plastics Plant, AI# 285 – Baton Rouge/East Baton Rouge Parish
- ExxonMobil Polyolefins Plant, AI# 3519 – Baton Rouge/East Baton Rouge Parish
- ExxonMobil Refinery, AI# 2638 – Baton Rouge/East Baton Rouge Parish

- Placid Refining Company, L.L.C., AI# 2366 – Port Allen/West Baton Rouge Parish
- Plantation Pipe Line Company, AI# 582 – Baton Rouge/East Baton Rouge Parish
- Shell Chemical LP, AI# 1136 – Geismar/Ascension Parish
- Syngenta Crop Protection, Inc., AI# 2367 – Geismar/Iberville Parish
- Vulcan Materials Company, AI# 3400 – Geismar/Ascension Parish
- Williams Olefins L.L.C., AI# 5565 – Geismar/Ascension Parish

The following name changes occurred after the AOC was issued.

- Crompton to Chemtura Corporation on December 31, 2005
- DSM to Lion Copolymer, LLC on November 10, 2005
- Vulcan to Occidental Chemical Corporation in April 2005

These 15 facilities were ordered to install fenceline monitoring as follows:

- A minimum of four air monitoring stations at or near the property boundary with a station positioned on each of the four main compass points
- At each station a continuous total non-methane organic carbon (TNMOC) analyzer capable of detecting VOC concentrations of 100 ppb or less for each 10-minute period
- With each TNMOC analyzer, a Summa canister sampler system capable of automatically collecting a 20-minute air sample when the analyzer exceeds a predetermined set point
- At one of the stations, a second Summa canister sampler system capable of collecting a 24-hour integrated sample once every six days for air toxics (This requirement was in the original AO, but, was removed from the AOC. The details of this requirement have been omitted from this report.)
- Supplement at least two of the stations with a 10-meter meteorological tower with sensors to continuously measure wind speed and direction as 10-minute averages

The predetermined set point for the main Summa canister sampler system was to be adjusted to insure at least an average of five samples per month. Each canister was to be analyzed by gas chromatography/flame ionization detection for all ozone precursors VOC on a list provided by LDEQ (see Appendix B). The analytical and quality assurance procedures were to be consistent with EPA analysis method 600-R-98/161. The minimum detection limits for the analysis as calculated by the method in 40 CFR Part 36(b) were to be no greater than 10 ppbCarbon for each of the VOC precursors on the list.

Each facility was ordered to develop procedures for responding to episodes when the canister system was triggered by TNMOC values at or above the set point and the wind direction indicated that the plant was upwind of the station. The procedures were to be used by plant personnel to help locate the likely source of the emission and were to include, as a minimum, a review of current unit operations, notation of special operations and activities, and a plant walk-through with a portable leak detector.

All data and response plan findings were to be reported to LDEQ on a monthly basis beginning June 15, 2005. An annual report was to be submitted at the end of each calendar year. The annual report for 2006 was replaced by the individual Final Reports included in the appendix.

After several negotiations with the individual affected facilities, LDEQ agreed to allow facilities to vary from the requirements spelled out in the AOC. Following is a summary of what was ultimately installed. Additional details can be found in the individual Final Reports.

- **Dow** – Two stations were installed upwind and downwind of the predominant wind direction at the plant. The stations were located a few miles away from the plant site in Addis and Plaquemine. Instead of the Summa canister sampler systems, gas chromatographs (GC) that were triggered by a high reading from the TNMOC analyzer were installed. NOx analyzers were installed at both sites.
- **Enterprise** - Two stations were installed upwind and downwind of the predominant wind direction at the plant. The stations were located at the plant boundaries. Instead of the Summa canister sampler systems, gas chromatographs that were triggered by a high reading from the TNMOC analyzer were installed.
- **ExxonMobil Chemical Plant and Refinery** – A total of five systems were installed for the two adjacent plants on the fencelines. In order to have units upwind and downwind of the plants year around, the units were moved three times per year. Instead of the Summa canister sampler systems, gas chromatographs that were triggered by a high reading from the TNMOC analyzer were installed.
- **ExxonMobil Polyolefins** - Two stations were installed upwind and downwind of the predominant wind direction at the plant. The stations were located at the plant boundaries. Instead of the Summa canister sampler systems, gas chromatographs that were triggered by a high reading from the TNMOC analyzer were installed.
- **ExxonMobil Plastics** – Two stations were installed on the fencelines. In order to have units upwind and downwind of the plants year around, the units were moved two times per year. Instead of the Summa canister sampler systems, gas chromatographs that were triggered by a high reading from the TNMOC analyzer were installed.
- **Geismar 6 (G6)** – BASF, Chemtura, Shell, Syngenta, Occidental and Williams committed to work together as one group called G6. Two new stations were installed a few miles away from the plant sites at Darrow and Hunt Correctional Institute. These stations were integrated with LDEQ's stations at Carville and Dutchtown thus putting stations in all directions from the six plant sites. All of the stations had a TNMOC analyzer, a Summa Canister sampler system and wind speed and direction indicators. G6 also installed NOx analyzers at the two new stations.
- **Lion** – Lion already had a continuously operating gas chromatograph unit in the main process area. The system drew samples from 14 locations on a sequential basis and analyzed the air for styrene, 1,3-Butadiene and acrylonitrile. One new station that conformed to the AOC requirements was installed on the Northwest fenceline.
- **Placid** – Three stations that conformed to the AOC requirements were installed on the Northwest, Northeast and South central fencelines.
- **Plantation** - Two stations that conformed to the AOC requirements were installed on the Northwest and Southwest fencelines.

The maps in Appendix C show the locations of the new monitoring stations.

V. ENVIRONMENTAL AUDIT SUMMARY

Following is a brief summary of the key points from the audits. The full reports are included in the appendix.

- The audits found components missing from the LDAR program in all plants except BRPP.
- One plant modified its flare blower in order to improve the ratio of air-assist to fuel flow in the flare and improve destruction efficiency. (Enterprise)
- Several recommendations were made by the audit team to improve the way that emissions are quantified. (ExxonMobil)
- Some plants were found to have open-ended lines without control. (BRCP, BRPP)
- The comparative monitoring audit in one plant identified a significant difference between the audit team leak rates and the plant's historical leak rates. (BRCP)
- All plants scored well in most phases of the audit.

VI. FENCELINE MONITORING – Significant Findings and Results

A. Following is a brief summary of the findings and results for each plant. Details can be found in the full reports in the appendix.

- **Dow** – Seven strikes occurred during the monitoring period with the trigger set at the minimum value of 1.0 ppm. Only one of the strikes occurred when Dow was upwind. Typical TNMOC values were around 0.5 ppm. Due to the lack of strikes and in order to gather background data, the GCs were manually triggered on six-day cycles beginning in September 2005. The analyses usually showed low levels of ethane, propane and sometimes ethylene. The lack of trigger activity brings into question whether or not the stations were located too far from the plant site to be effective for monitoring plant emissions. Dow reported two unauthorized discharges (RQ) that were greater than 100 pounds of ethylene in 2006,
- **Enterprise** – Approximately 160 strikes occurred with the set points at 3 ppm. The vast majority of the strikes had an evaporative gasoline profile and were with the wind coming from offsite in the Southerly direction. For the few strikes that originated in the plant, the source was not found except for a leak on an exchanger in July 2006. Instrumentation problems occurred off and on throughout the course of the monitoring period with the GC and TNMOC analyzers and with the wind sensors.

  In June 2004 propylene strikes occurred at the Capitol and LSU monitors with the wind coming from the direction of Enterprise. Upon investigation it was determined that Enterprise was flaring propylene at the time. As a result Enterprise performed an engineering analysis of the flare system that showed that excess air was being used on the flare to minimize smoking. As part of the AOC, Enterprise modified the system such that the air flow to the flare was adjusted in relation to the gas flow at three set points of low, medium and high gas flow. Since the modification, only one significant propylene strike at the Capitol site occurred in the 2-year period of 2005-06 with the wind coming from the direction of Enterprise. In 2004 alone there were four such propylene strikes at the Capitol monitor. Enterprise does continue to flare on a regular basis. Alternatives to

flaring such as reducing the amounts going to the flare and/or recycling to the process should continue to be explored.

- **ExxonMobil Chemical Plant and Refinery** – Approximately 500 actionable strikes occurred with set points at the five monitors ranging from 3.5 to 9 ppm. About 30 percent of these were later determined to be from offsite sources. Several tools were developed to help the response team to locate the likely source. These tools included back-track trajectories, scatter-plots, infra-red camera technology and categorizations of 15 typical refinery streams. The response team was very successful in locating the likely, or contributing, source about 50 percent of the time. This was a remarkable success rate considering that the site is spread over 2200 acres. Sources located included storage tank-top components, heat exchanger leaks into steam and water systems, permitted operations such as sampling/tank clearing/maintenance, component and piping leaks, and loading/unloading activities. The Chemical Plant and Refinery reported a total of eight unauthorized discharges (RQ) of HRVOC greater than 100 pounds in 2006 – one for a mixture of toluene and xylenes, four for propylene, one for toluene, and two for ethylene.

  As already stated, about 30 percent of the strikes were caused by offsite sources. Many of these strikes were a higher concentration than the typical highs from the facilities. The Department of Public Works refueling yard at the Southwestern corner of the refinery was believed to be a contributor to some of these strikes.
- **ExxonMobil Plastics** – There were approximately 170 strikes with the set points at 2.41 and 4.61 ppm. No process leaks occurred during the monitoring period. Approximately 50 percent of the triggers were caused by offsite evaporative gasoline emissions coming from the Southeasterly direction. The actionable strikes were attributed to permitted emissions from the product finishing sections and the flare. The plant utilizes a purge gas recycle system to recover and re-use process vapors. Ethylene emissions from emergency releases from the reactors are being reduced through reliability improvements of reactor instrumentation systems. The frequency of these episodes has been significantly reduced - nine in 2006 versus a high of 55 in 1997. The plant reported eight unauthorized discharges (RQ) of ethylene greater than one hundred pounds in 2006.
- **ExxonMobil Polyolefins** – There were a total of 59 strikes with the set points at 2.48 and 3.52 ppm. No process leaks that contributed to the strikes were reported for the monitoring period. Most of the strikes were low-level and attributed to permitted emissions, usually the flare, or nothing was found. A few were caused by offsite emissions. In 2005 the plant voluntarily installed a regenerative thermal oxidizer to destruct inert vent emissions, resulting in a 30 percent site-wide emissions reduction.
- **G6** – There were approximately 130 actionable strikes at the four monitors with the set points at 1.0 to 1.25 ppm. About 70 percent of the strikes were at the Carville monitor. Many of these strikes were caused by refueling operations at the military base on which the station is located. The Carville station was re-located in May 2006 to reduce this local influence, however, nuisance strikes related to agricultural activities near the new site continued to plague the Carville site. Some of the strikes when the plants were upwind occurred while flaring or other emissions from the plants were taking place, but, nothing conclusive was ever found during the individual plant responses. This raises the question as to whether or not the monitors were located too far from the plants to be effective for monitoring plant emissions. The G6 plants reported five unauthorized discharges (RQ) of

HRVOC greater than 100 pounds in 2006 – Occidental: ethylene, Chemtura: toluene, Syngenta: toluene, Williams: one for ethylene and one for propylene.

Through the course of the program, some of the G6 facilities identified ways to reduce emissions. Chemtura discovered and repaired several minor leaks on railcars. They also found and repaired a leak on a compressor using the HAWK camera. Occidental installed a containment project to eliminate ethylene emissions related to one of their processes. Syngenta replaced leaking relief devices on two toluene storage tanks.

- **Lion** – There were over 700 strikes with the set points at 5 (GC) and 10 (TNMOC) ppm. This total includes numerous strikes from offsite. In August 2006 the GC system was modified to eliminate some of the local sample points. About 20 percent of the strikes that were investigated were attributed to operations and maintenance activities such as purging or draining equipment and flushing lines. About 25 of the strikes were attributed to process leaks or process upsets. The leaks were immediately repaired when possible otherwise a work order was written for the repair. For the remaining actionable strikes, the source was not found. The GC was configured to show only 1,3-Butadiene and styrene from the Ozone Precursor VOC List. The canister analyses showed mostly chemicals that are not handled in the plant except for some that showed 1,3-Butadiene and styrene. The plant changed ownership in 2005 and there were some interruptions in the monitoring program due to the transition.
- **Placid** – There were over 800 strikes with the set points at 13, 15 and 17 ppm. About half of the strikes were attributed to emissions from general tank operations and loading-unloading operations which, in many instances, were taking place just a short distance from the monitors. For most of the remaining strikes, no emission source was found by the response team or the report did not describe the response actions that were taken. From the fenceline data, Placid has discerned a potential relationship between product movements through certain tanks and VOC strikes at the monitors. Consequently, as part of a proposed refinery expansion, Placid is proposing to install vent collection and treatment on 13 tanks.
- **Plantation** – Approximately 250 strikes occurred with the set points at 5.5 and 6 ppm. The tanks are either floating roof, both internal and external, or normal atmospheric tanks – none have vent collection. Most monitored emissions are the result of routine operations of filling, storing and emptying the gasoline products that are handled by the facility. The South monitor was impacted by a gasoline source to the Southeast – possibly Metro Airport. Plantation has reduced emissions from about 1,800 tons per year to less than 700 tons per year by modifying operational practices.

B. The fenceline monitoring program had a positive impact on LDEQ monitors and on the unauthorized releases (RQs) that are reported to the agency. The following table shows the number of strikes and the number that contained significant amounts of HRVOC.

Strikes at LDEQ Monitors

	Total Strikes			HRVOC >100 PPB Strikes		
	2004	2005	2006	2004	2005	2006
Baker	31	27	33	26	18	15
B Plaquemine	3	5	1	0	0	1
Capitol	86	66	64	11	16	6
Carville	23	57	60	0	8	8
Dutchtown	1	3	6	0	1	5
F Settlement	0	0	2	0	0	0
G Tete	0	0	0	0	0	0
LSU	28	22	4	1	0	0
P Allen	80	64	73	18	15	18
Pride	0	0	1	0	0	0
Southern	113	32	36	21	4	7
Total	365	276	280	77	62	60

The table shows that during the fenceline monitoring program years of 2005 and 2006, there was a decrease in total strikes of about 25 percent and a similar decrease in strikes with significant amounts of HRVOC. Southern and LSU were the two sites that showed the greatest improvement. The other two urban area monitors, Port Allen and Capitol, also showed good improvement. Baker and the rural sites at Bayou Plaquemine, Dutchtown, French Settlement, Grosse Tete and Pride were relatively unchanged. The increase at Carville was addressed earlier in this section. Not shown in the table is another significant improvement. The number of 1,3-Butadiene strikes decreased from eight in 2004 to just one in 2005 and 2006. This improvement allowed the state to meet the 1,3-butadiene toxic standard for the first time.

The next table shows the unauthorized releases reported to LDEQ from facilities in the BRNA.

Chapter 39 HRVOC Reportable Quantities: >100 lbs

	Number	Total Amount (lbs)	>1000 (lbs)	>10,000 (lbs)	Largest (lbs)
2003 (1)	**24**	**64,600**	**10**	**1**	**18,000**
2004	**71**	**250,000**	**25**	**3**	**66,000**
2005	**24**	**80,000**	**10**	**3**	**21,000**
2006	**31**	**57,617**	**11**	**0**	**9,820**

(1) from October 15

The table shows that both the number and the severity of the unauthorized releases during the fenceline monitoring years were significantly improved when compared to 2004.

VII. ON-GOING EMISSION REDUCTION PROGRAMS

As a result of the fenceline monitoring program, several facilities have initiated on-going programs to further identify and reduce emissions.

- **BASF** – The facility is participating in a voluntary pilot project to evaluate the application of gas imaging technology to improve VOC leak detection.
- **Chemtura** – The facility plans to continue to use the procedures and experiences gained from the fenceline monitoring program to identify and correct releases as they may occur.
- **Enterprise** – Besides the improvements to the flare air blower mentioned earlier in this report, the facility also modified the procedure for recharging a treater. The procedure now requires that the vessel be depressured more slowly in order to not slug propane and propylene to the flare.
- **ExxonMobil Chemical Plant and Refinery** – The facilities have worked with barge fleet companies and independent surveyors to modify the procedures to provide closed hatch sampling and gauging of marine vessels. Also, due to the success in locating emission sources during strike responses, an infra-red camera has been purchased and its use will be incorporated into daily operations for finding leaks and emissions.
- **ExxonMobil Plastics** – Plans include the following: 1) replace several pumps in VOC service due to their poor leak history; 2) continue root-cause investigations and reliability efforts to reduce flaring events and accidental releases; 3) transition to the HAWK in lieu of Method 21 as the technology matures.
- **ExxonMobil Polyolefins** – Plans include the following: 1) continue reliability efforts to reduce flaring events and accidental releases; 2) evaluate the feasibility of routing streams to the oxidizer that are currently going to the flare.
- **Lion** – The facility plans to continue using the GC to identify and mitigate excess emissions of 1,3-Butadiene, styrene and acrylonitrile as they may occur within the plant.
- **Placid** – As stated earlier in this report, Placid is proposing to install vent collection and treatment on 13 VOC tanks.
- **Plantation** – The facility intends to continue with current operational practices in order to maintain the emission reductions described in Section VI of this report.
- **Shell** – The facility has joined an industry sub-group that will study emissions associated with port activities.
- **Syngenta** – The facility plans to continue with programs for monitoring cooling towers and tank roof tops for VOC emissions. Additionally, the facility plans to continue to use the procedures and experiences gained from the fenceline monitoring program to identify and correct releases as they may occur.
- **Williams** – Plans include the following: 1) upgrade control valve bodies to a lower emission design type; 2) conduct post-turnaround leak surveys of the facility with the HAWK; 3) move plant turn-arounds to outside of the ozone season.

VIII. CONCLUSIONS

Following are conclusions from the program.

- The program had a significant positive impact on both the number of strikes at the LDEQ monitors and on the number and severity of HRVOC RQs being reported to LDEQ.
- Facilities that performed the Environmental Audit are properly accounting for HRVOC emission sources. While some individual fugitive emissions locations were found missing from the LDAR program, the number was very small when compared to the total number of components that are being monitored.
- Floating roof tanks, both internal and external, that vent directly to the atmosphere are a very significant source of VOC emissions. The mechanical seals, if not maintained properly, allow vapors to escape and whenever the roof is landed on its legs for any reason, the vapors that accumulate beneath the roof are vented through the relief valve as the tank is re-filled. The facilities in the program that have a large number of floating roof tanks had higher monitor set points and many more strikes than the other facilities. Although the stored liquids contain only small amounts of HRVOC, all of the chemicals are ozone precursors and have the capability of forming ozone, albeit at a slower rate.
- Flares appear to be emitting some unburned compounds, including HRVOC, that could be more than what is estimated by flare manufacturers, at least under some conditions. Many strikes were attributed to flares. Also, due to the height of the flares, some of the unburned emissions may not be picked up by the monitors on the fenceline.
- Many strikes were attributed to loading and unloading operations. Regulations for these operations need to be reviewed to determine if revisions are needed.
- While only a few of the strike samples contained significant amounts of HRVOC, many of the samples showed low levels of HRVOC, especially ethylene and propylene. A separate study[1] by EPA showed that the ethylene and propylene in the atmosphere at the Capitol and Bayou Plaquemine monitoring stations has increased in the period of 2001-2005 over the period of 1996-2000. Reduction of HRVOC may be necessary to bring the area into attainment with the 8-hour ozone standard and should be considered.
- Facilities that installed GCs instead of a canister system were much more successful in finding the likely source. This was due to the fact that the GC provided near-real-time speciation and the response team was able to immediately search for the emission source in the areas of the plant that contained the chemicals that showed up on the GC rather than randomly checking the whole plant.
- Where the monitors were located on the fencelines, higher set points were needed to keep the number of strikes in range. These monitors also had a lot higher level of activity and it was easier to locate the potential source.
- The fenceline program demonstrated that GCs in a trigger mode are viable options for transient emission monitoring.
- Meteorological instrumentation, especially wind direction monitors, needs to be checked for accuracy on a routine basis.

1 *M. Sather and K Cavender, Trends analysis of ambient 8 hour ozone and precursor monitoring data in the south central U.S., Journal of Environmental Monitoring, 2007, 9, 143-150.*

IX. APPENDICES

Appendices can be found in the complete report that is available in the EDMS System using document ID numbers 35879695 through 35879709