6 APPENDIX I - VENT EMISSION MONITORING SYSTEM

A custom continuous vent emission monitoring system was designed and constructed to study the evaporation losses from an underground gasoline storage tank.

6.1 Site Description

6.1.1 General

The selected monitoring site is a retail gasoline station located in northwest Calgary. It was constructed in 2008 and sells three grades of gasoline (i.e., regular, midgrade and premium) plus diesel. There are three underground fuel storage tanks located at the site; one each for regular gasoline, premium gasoline and diesel, respectively. Midgrade gasoline is blended inline using regular and premium gasoline, and therefore, is not stored as a separate product.

The normal business hours of the station are 6:00 AM to 10:00 PM, seven days a week. The regular gasoline tank was selected for monitoring to ensure a good mix of both high-activity periods and static periods, and also allow a reasonable number of tank filling events to be monitored.

A schematic drawing showing the general site layout is presented in Figure 4.

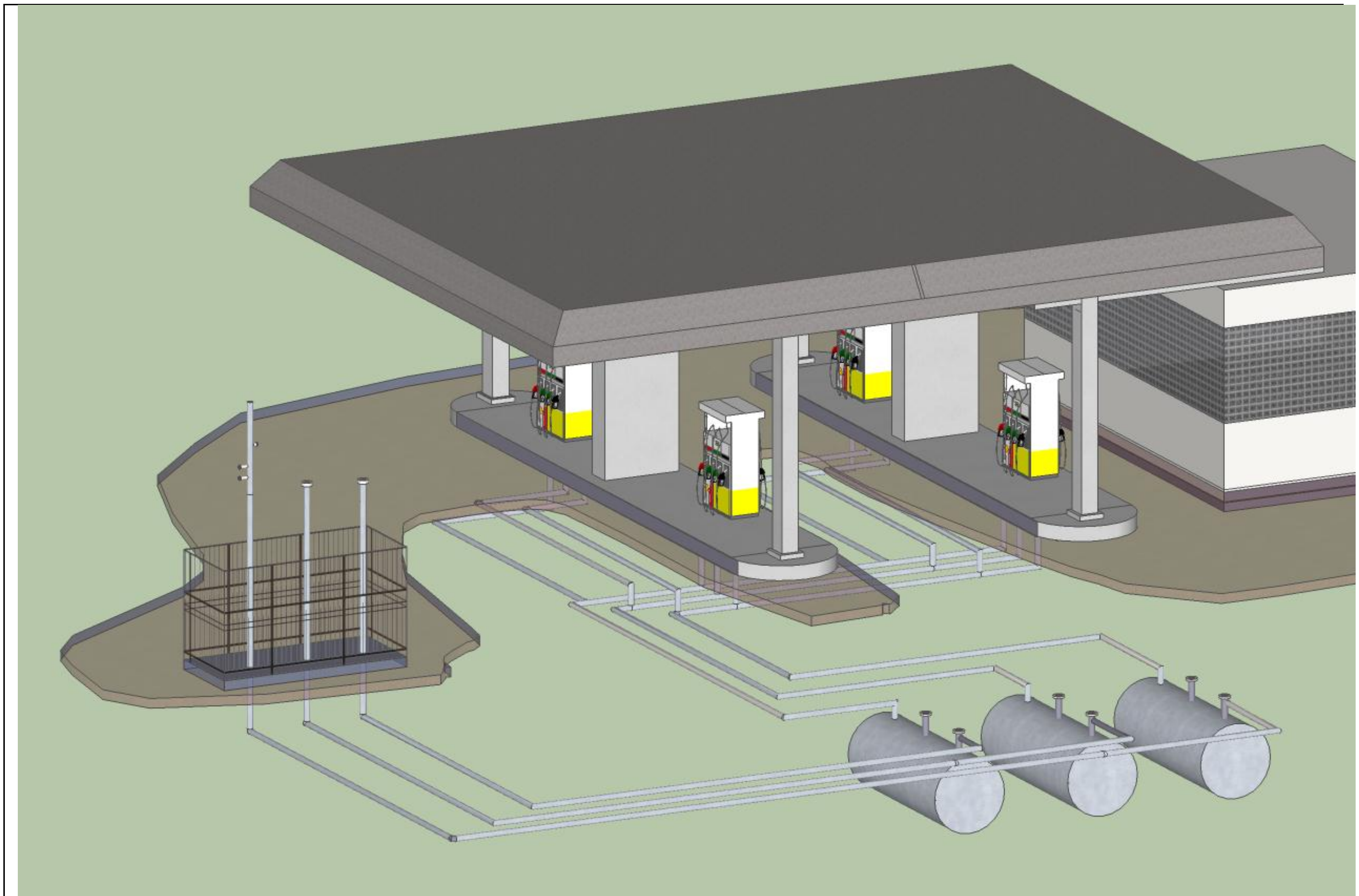


Figure 4: Schematic drawing showing the general layout of the host facility.

6.1.2 Tank

Each tank at the site featured three connections: one for the fuel line leading to the dispensers, one for use by the fuel delivery truck when filling the tank and one connected to a vent stack located at the edge of the site. A schematic diagram showing a typical side view of a tank is presented in Figure 5. The vent stack features a weather cap at the top but, otherwise is free venting (i.e., the tank is not equipped with a pressure-vacuum valve or breather). Except during the brief period of time when a fuel delivery truck is connecting to, or disconnecting from, the fill connection on the tank, the only way for air to get into the tank, and for air and fuel vapours to leave the tank, is through the dedicated vent stack.

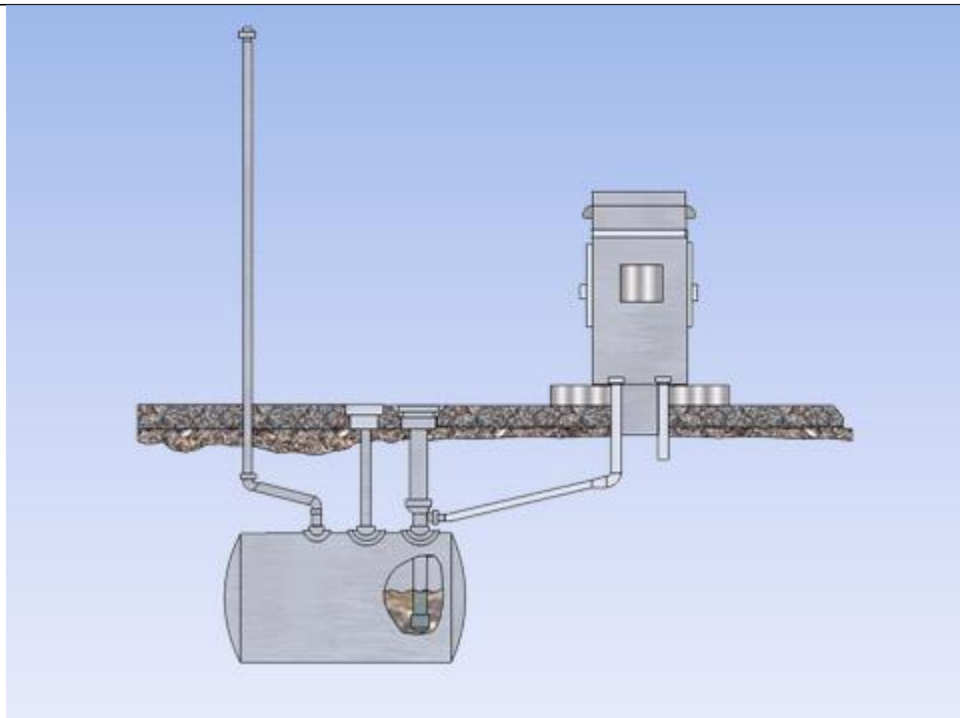


Figure 5: Schematic diagram showing a side view of a typical underground storage tank.

The regular gasoline tank was a 100,000 L horizontal underground double-walled fiberglass tank manufactured by ZCL. An engineering drawing of the tank is presented in Figure 6.

6.1.3 Fuel Dispossessors

The site has five 2008 Wayne Ovation Dispensers (4 gasoline/1 diesel). It is possible to have 8 customers filling with regular fuel at the same time. The dispensers are rated for 38 L/min. The rate can change depending on the quantity of customers filling at the same time, and the individual dispenser filter conditions. The operator's standard is to provide at least 35 L/min of flow to each dispenser.

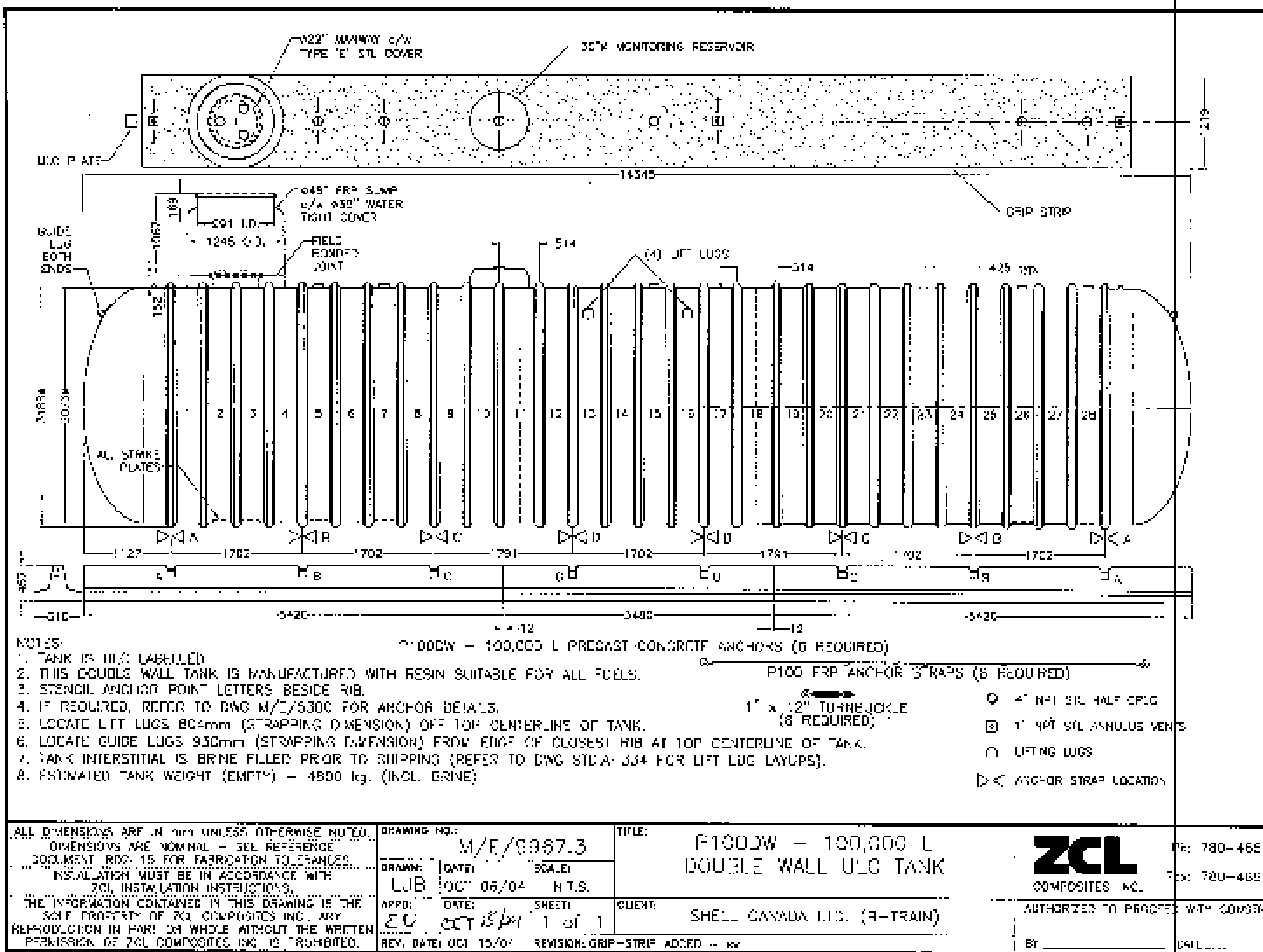


Figure 6: Design drawing of the monitored underground gasoline storage tank.

6.2 Automatic Tank Gauging System

Each tank at the site was equipped with an automatic tank gauging and leak detection system manufactured by The Veeder-Root Company. A piping and instrumentation diagram of the system is provided in Figure 7. This system monitors both the liquid level and the temperature of the stored liquid, and communicates with a backroom control and data acquisition system (i.e., Veeder-Root TLS-350R). A photograph of the backroom hardware is presented in Figure 8.

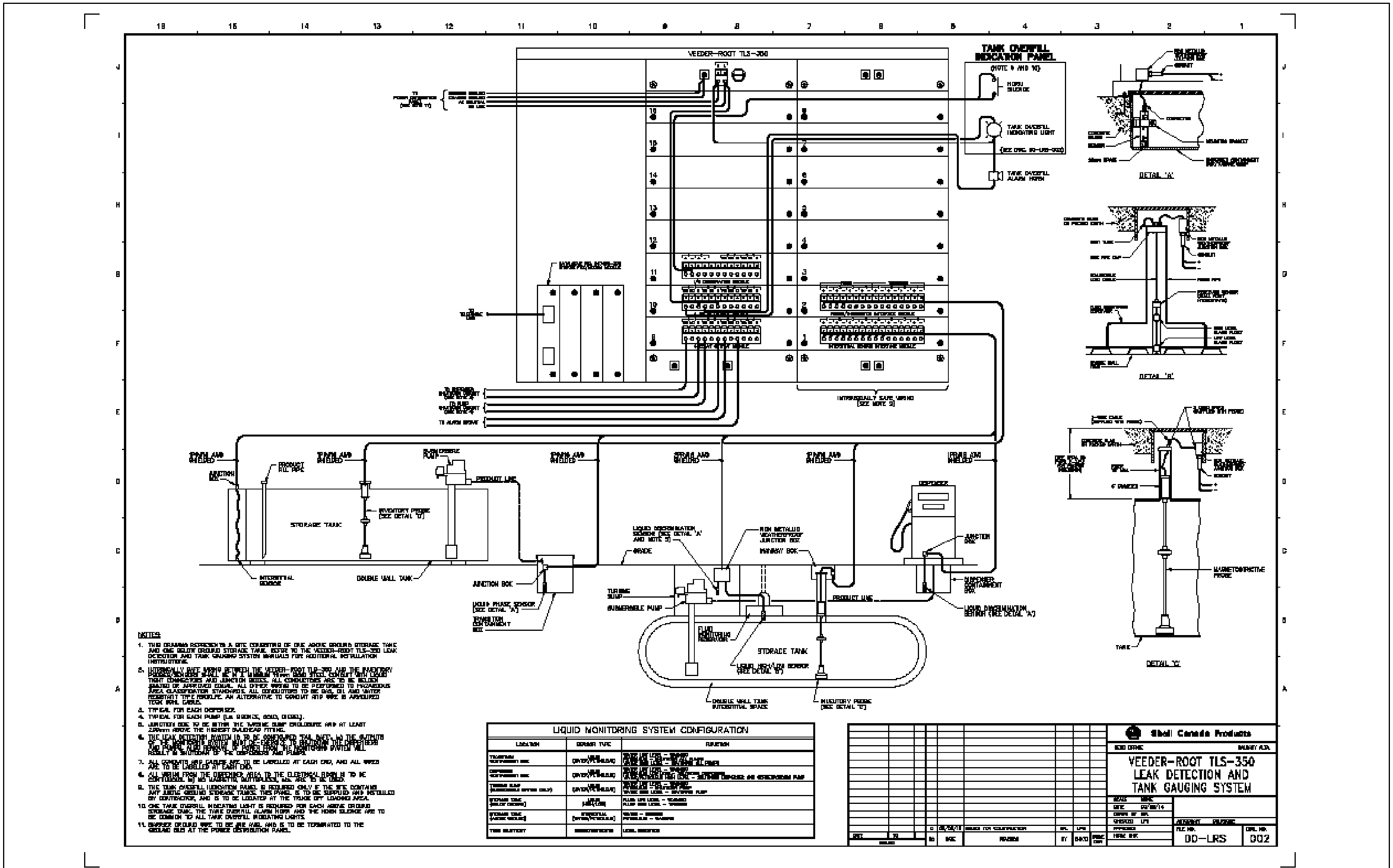


Figure 7: A piping and instrumentation diagram of the Veeder-Root automatic tank gauging and leak detection system.

Figure 8: Photograph of the backroom control and data acquisition system for the Veeder-Root automatic tank gauging and leak detection system.

A laptop computer with a wireless communications card and a copy of Veeder-Root's "Inform" software was installed to poll the Veeder-Root console and log results (the laptop is shown in Figure 8). The Veeder-Root console did not have any communication ports available to connect to the Field Laptop. Consequently, an appropriate serial port card was installed to facilitate these communications. The Inform software was set to poll and log the data from the Veeder-Root console once every 2 minutes which was the greatest polling rate that could be achieved.

6.3 Vent Emission Monitoring System

6.3.1 Parameters Monitored

The vent emissions monitoring system was designed to monitor the seven parameters listed in Table 2, namely: ambient temperature, barometric pressure, vent gas hydrocarbon concentration, vent gas oxygen concentration, relative humidity, vent gas exit velocity and vent gas exit temperature. Additionally, as noted in Section 6.2, the tank liquid level and temperature measured by the Veeder-Root automatic gauging system were also logged. Collectively, this information allows a complete mass balance to be performed, all key environmental and activity factors affecting the instantaneous and cumulative evaporation losses to be monitored and their effects on the emissions rate to be trended.

Table 2: Summary of the parameters monitored by the VEMS and the specifications of these devices.

Parameter	Device	Manufacturer	Model	Operating Range	Accuracy	Output Rate
Ambient Temperature	Relative Humidity/Temperature Probe	RM Young	Model 41382VC/VF	±0.3°C	-50 to +50°C	10 Second Time Constant
Barometric Pressure	Barometer	RM Young	61302V	500 to 1100 hPa	±0.3 hPa rms over -50°C to +60°C	1.8 Hz to 1 per minute.
Hydrocarbon (HC) Concentration	IR Gas Sensor (Calibrated to Butane)	Sensor Electronics Corp.	SEC Signature HC PGA	±5% of reading or ±3% of full scale. Repeatability of ±2%	0 to 20 % by volume.	N/A
Oxygen Concentration	Electrochemical Gas Sensor	Sensor Electronics Corp.	SEC3000	±5%	0 to 25% by volume.	N/A
Relative Humidity	Relative Humidity/Temperature Probe	RM Young		±2%	0 to 100%	10 Second Response Time
Vent Gas Exit Velocity	Clamp-on Ultrasonic Flow Meter	Siemens	SITRANS FUG1010 IP65 Nema 4X	0 to 50 m/s	±0.5% to 1.0% of flow for 2 NPS up to 48 NPS Pipe.	1 Hz to one per 1.2 hours.
Vent Gas Temperature	Type-T Thermocouple (Unshielded, Fast Responding) 3.17 mm Sensor Diameter	WIKA	TC10-0-1-NCZ5FS-1-DSZZK-010-919-2-P-00400-ZZ	±1°C or 1.5% (whichever is greater)	-200 to 370°C	N/A

6.3.1.1 Ambient Temperature

The ambient temperature was measured in close proximity to the monitoring equipment on the vent stack (see Figure 9). The thermocouple was protected by a radiation shield to avoid interference due to solar radiation.

Figure 9: Photograph showing the ambient temperature and relative humidity sensor.

6.3.1.2 Barometric Pressure

The barometer was installed inside the control panel of the VEMS. A ventilation hole was drilled in the panel to allow communication between the barometer and the outside atmosphere.

6.3.1.3 Vent Gas Hydrocarbon Concentration

The hydrocarbon sensor was mounted on the side of the vent stack near the outlet and was only wetted to the flow to avoid any potential interference or impedance of the flow in the vent pipe. An infrared hydrocarbon sensor was chose because of its low energy demands and resistance to fouling or deactivation due to prolonged exposure to elevated hydrocarbon concentrations. The sensor was equipped with a heater element to allow it to perform in cold weather.

The hydrocarbon sensor was factory calibrated to butane as this was expected to offer the most accurate response to gasoline vapours. Nonetheless, it is recognized that in a multi-component application where the sensor may have different sensitivities to different components, the readings should be considered as being more qualitative than quantitative. For the purposes of this study, the data from the hydrocarbon sensor were primarily used to observe trends in the hydrocarbon concentrations and were not actually used to calculate emission rates. The more reliable estimates of the hydrocarbon content of the vent gas were determined using the methods described in Sections 6.3.1.4 and 6.3.1.6.

6.3.1.4 Vent Gas Oxygen Concentration

Like the hydrocarbon sensor, the oxygen sensor was mounted on the vent stack and only wetted to the flow to avoid any potential flow interference. As well, it was equipped with both an insulating kit and a heater element to allow it to function properly in cold weather.

The selected oxygen sensor is reported to be resistant to any interference or cross sensitivities in the presence of hydrocarbon vapours. Consequently, the readings from this sensor were considered to be more reliable and quantitative than the readings from the hydrocarbon sensor discussed in Section 6.3.1.3.

The hydrocarbon vapour content of the vent gas was calculated from the oxygen sensor readings using the following relation:

$$\boldsymbol{x = \frac{O_{2A} - O_{2V}}{O_{2A}}} \qquad \textbf{Equation 24}$$

Where,

x = mole fraction of gasoline vapour in the vent gas, kmole/kmole
O_{2A} = oxygen concentration in the ambient air, mol %
O_{2V} = oxygen concentration in the vent gas, mol%

The oxygen sensor indicated oxygen concentrations in the ambient air of 20.72 mol% which is slightly less than the normally expected value of 20.8 mol% for air. The value of O_{2A} was set to 20.72 mol% for the purpose of calculating the hydrocarbon vapour content of the vent gas.

6.3.1.5 Relative Humidity

The relative humidity of the ambient air is not a critical parameter for determining the hydrocarbon emission rate from the tank vent; however, it was considered to be useful in detecting periods when frost formation was occurring which might affect the flow characteristics and possibly cause fouling of the gas sensors.

6.3.1.6 Vent Gas Exit Velocity and Sound Velocity

Knowing the vent exit velocity and whether the flow is into or out of the vent is critical to determining the instantaneous and average emission rates. A non-intrusive clamp-on transit-time ultrasonic gas flow meter was selected for this purpose because of the following factors:

- Good sensitivity and accuracy, as well as a wide operating range.
- Does not cause any flow interference.
- Operates over a wider range of flow velocities than most other technologies.
- Is composition independent (i.e., the measured flow velocity does not need to be corrected to account for the composition of the vent gas).
- Provides flow direction.
- Resistant to fouling and tolerant of some aerosols being present in the flow.

Moreover, in addition to measuring flow velocity, transit-time ultrasonic gas flow meters also measure the speed of sound in the interrogated gas. The speed of sound can be used to back-calculate the molecular weight of the gas stream and, from that result, determine the vapour content of the vented air-vapour mixture. The speed of sound in a perfect gas may be calculated using the following relation:

$$\boldsymbol{a = \sqrt{\frac{1000\gamma R T_V}{M}}} \qquad \textbf{Equation 25}$$

Where,

a	=	speed of sound in the vent gas, m/s
γ	=	specific heat ratio, 1.4 (for air) dimensionless
R	=	ideal gas constant, 8.3145 kPa m^3/kg-mole °K
T_V	=	exit temperature of the vent gas, °K
M	=	molecular weight of the vent gas, kg/kmole

The specific heat ratio is relatively insensitive to changes in temperature and is very similar in value for both air hydrocarbon vapours (i.e., 1.4 versus 1.3). Thus, it is a reasonable approximation to treat the specific heat ratio as a constant.

Knowing the speed of sound in the vent gas, the equation for sound velocity may be re-written to calculate the molecular weight of the vent gas as follows:

$$\boldsymbol{M = \frac{1000\gamma R T_V}{a^2}} \qquad \textbf{Equation 26}$$

Knowing the molecular weight of the vent gas as well as the molecular weight for air and gasoline vapours, the following relation may be used to estimate the mole fraction of gasoline vapour in the vent gas:

$$x = \frac{M - M_A}{M_V - M_A}$$ **Equation 27**

Where,

x	=	mole fraction of gasoline vapour in the vent gas, kmole/kmole
M_A	=	molecular weight of air, 28.966 kg/kmole
M_V	=	molecular weight of the regular gasoline vapor at the host facility, 64.563 kg/kmole

Calculation of the vapour content in this manner provides and independent means of verifying the results of both the oxygen and hydrocarbon sensors.

6.3.1.7 Vent Gas Exit Temperature.

A Type-T thermocouple was selected to measure the vent gas exit temperature due to its superior performance over the anticipated range of temperatures. The thermocouple was installed near the vent outlet and was inserted part way into the vent pipe but without a thermowell to ensure fast response and to minimize any flow restrictions. The element on the selected thermocouple was only 3.7 mm in diameter and restricted the available flow area by less than 5%.

6.3.2 Vents Stack

Rather than modify the existing vent stack, a custom stack was designed and temporarily installed for the duration of the monitoring program. Mechanical drawings of the vent stack are presented in Figures 10 and 8 and show the exact positioning of all the stack mounted sensors.

6.3.3 VEMS Control Panel and Communication System

The overall VEMS was designed as a standalone system which features a solar panel and batteries for power, a data logging unit and a wireless communications system for secure remote access via the internet. Currently, the VEMS is polling and logging the readings from all of the VEMS sensors and measurement devices once every 8 seconds.

Several photographs of the VEMS are presented in Figures 12 and 13 below. A diagram depicting the VEMS communication features is presented in Figure 14.

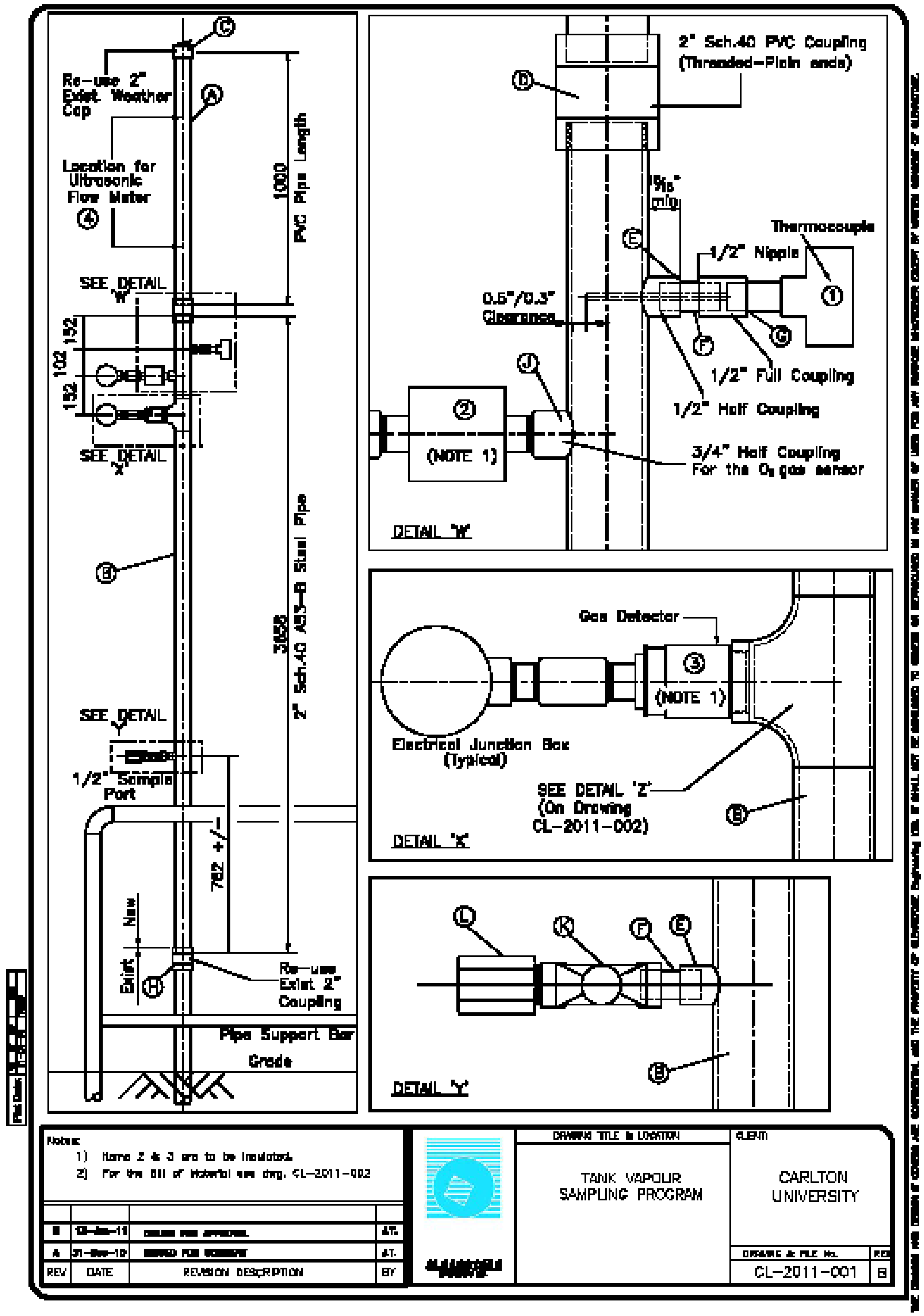
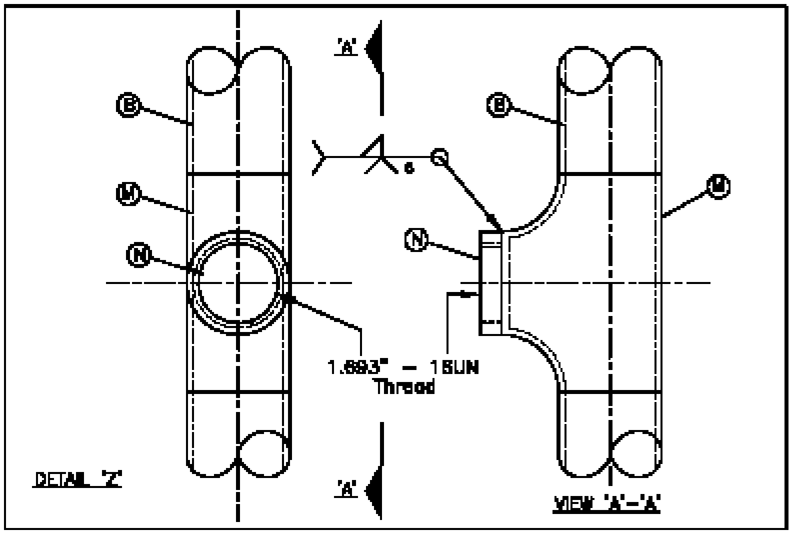


Figure 10: Mechanical drawing (Part 1) of the custom vent stack assembly.



Bill of Material			
Item	Qty	Size	Description
A	3'-0"	2"Sch.40	PVC Pipe, PBE Length T.B.D.
B	12'-0"	2"Sch.40	Steel Pipe - A53-B, TBE Length T.B.D.
C	1	2"	Weather Cap - Re-use Exist Cap.
D	1	2"Sch.40	PVC Coupling NPT/Socket ends
E	2	1/2" NPT	Half Coupling 2000# A-105
F	2	1/2" x 1.6" Lg.	A106 Sch.80 Nipple NPT both ends
G	1	1/2" NPT	Full Coupling 2000# A-105
H	1	2"	Full Coupling 2000# A-105 - Existing
J	1	3/4" NPT	Half Coupling 2000# A-105
K	1	1/2" NPT	WKM (Or equal) 600# Ball Valve A105
L	1	1/2" NPT	Solid Hex.Hd.Plug (Long) 6000# A105
M	1	2"	Straight Tee Sch.40 BW ASTM A-234 Gr.WPB
N	1	-	2.375" Dia.X 0.5" thick solid steel plate c/w drilled & tapped 1.693" -16 UN thread.

Item	Qty	Connection	Instrumentation	Supplier
1	1	1/2" NPT	TC10 Industrial Thermocouple Assembly TC10-0-I-NG25F9-1-0922X-0101-3181-2-P-00400-ZZ 017 [illegible]	
2	1	3/4" NPT	SEC Signature Process Gas Analyzer O_2 Sensor P/N 142-0648	SENSOR ELECTRONICS Corp.
3	1	1.693" Thread	SEC Signature Gas Detector HC SEC 3000 Sensor	SENSOR ELECTRONICS Corp.
4	1	-	Ultrasonic Flow Meter T.B.D.	

Notes:

REV	DATE	REVISION DESCRIPTION	BY
A	15-Jan-11	ISSUED FOR APPROVAL	AT.

DRAWING TITLE & LOCATION: TANK VAPOUR SAMPLING PROGRAM

CLIENT: CARLTON UNIVERSITY

DRAWING & FILE No.: CL-2011-002 REV: A

Figure 11: Mechanical drawing (Part 2) of the custom vent stack assembly.

Figure 12: Photograph showing the temporary solar-powered vent emission monitoring system (VEMS) installed to monitor evaporation losses from an underground gasoline storage tank.

Figure 13: Photograph showing a different view of the temporary solar-powered vent emission monitoring system (VEMS) installed to monitor evaporation losses from an underground gasoline storage tank.

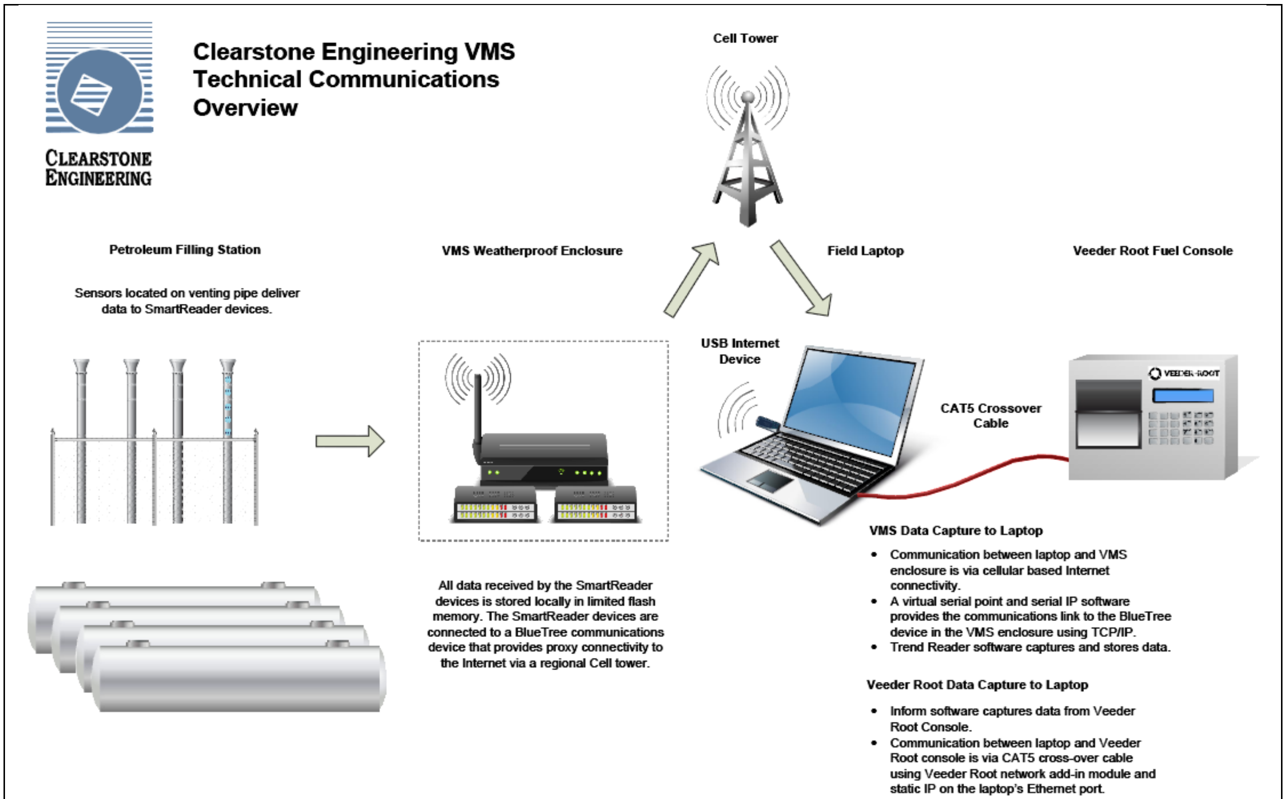


Figure 14: A flow diagram depicting the design of the secure communications system used to remotely access the VEMS results.

7 APPENDIX II – DETAILED VEMS RESULTS

The VEMS was installed at the host site and activated on 14 February 2011. Data acquisition for polling and capturing information from the Veeder-Root console did not become functional until 24 February 2011. There were some initial problems with the vent gas temperature sensor which did not get resolved until 9 March 2011. Figures 15 to 25 present graphs showing the trends in different calculated and measured parameters based on data compiled by the VEMS and Veeder-Root automatic tank gauging system during the period of 6 to 29 March 2011.

Figure 15 shows the calculated density of the vent gas and ambient air as well as the liquid inventory in the tank. The densities were calculated based on the measured temperatures and vent gas oxygen content (as described in Section 6.3.1.6 using Equation 26). The vapour molecular weight was taken to be 64.563 based on a detailed analysis of the actual fuel vapours (see Section 8). The molecular weight of air was taken to be 28.966.

The plateaus in the fuel inventory curve are where there are no regular fuel sales occurring at the site (i.e., between 10:00 PM and 6:00 AM each day), the downward sloping portions of the curve reflect periods when regular fuel sales are occurring (i.e., between 6:00 AM and 10:00 PM each day), and the large vertical breaks in the curve occur when fuel is being delivered to the site. This same fuel inventory curve is shown in most of the subsequent graphs presented in this section as it allows the reader to easily see what activity is occurring at the site and how it may be affecting the other plotted parameters.

In looking at the air and vent gas density curves it is interesting to see that the vent gas density rapidly approaches that of the ambient air at the start of the business day when fuel sales are occurring and remains so until the end of the business day when the vent gas density rapidly increases again. For the vent gas density near the top of the stack to be greater than the density of the ambient air, the pressure inside the tank has to be greater than the barometric pressure. This situation would occur when the tank is being filled, but more importantly, when vapour growth is occurring in the tank due to warming of the gas and due to evaporation of liquid product.

Figure 16 presents a graph showing the measured emission rate of hydrocarbon vapour from the tank vent as a function of the ambient temperature. There is no clear trend in the data, which means the evaporation rate is largely independent of the ambient temperature for the range of temperatures considered.

Figure 17 presents a graph showing the hydrocarbon emission rate from the tank vent plotted as a function of time. The emission rate is expressed in terms of the volume (Litres) of liquid fuel evaporated per hour. The greatest emission rates occur during the inactive periods and during the relatively brief periods when the tank is receiving a load of fuel. The latter emission rates are, by far, the greatest. Figure 18 show the same data using a greatly reduced evaporation rate scale to allow better depiction of the differences between evaporation rates during normal dispensing (active) and inactive periods.

Figure 19 shows the measured and calculated concentrations of hydrocarbon vapour in the vent gas. The hydrocarbon concentration determined from the vent gas sound velocity is calculated using Equation 26 presented in Section 6.3.1.6. The value determined from the vent gas oxygen measurements is calculated using Equation 23 presented in Section 6.3.1.4. The vent gas hydrocarbon concentration indicated by the hydrocarbon (HC) sensor ranges up to about 15 percent, the values calculated based on the measured vent gas sound velocity range up to between 45 and 60 percent and the values calculated based on the measured oxygen concentrations range up to between 45 and 55 percent. In comparison, the saturation level of the gasoline vapours in air was determined under controlled laboratory conditions to be approximately 24.2 percent at -3°C and 34.4 percent at +15°C (i.e., see the laboratory results presented in Section 8). Use of the API RVP correlation results in vapour concentrations of 30.2 to 32.8 percent at -3°C and 57.1 to 61.6 percent at 15°C (see Section 8). The laboratory values are expected to be most accurate, which means that the O_2 and speed-of-sound based vapour concentrations both over state the maximum possible vapour concentrations. Notwithstanding this, it is noteworthy that vapour concentrations determined from the O_2 and sound speed data agree much better with the estimates determined using the API RVP correlation. To resolve this apparent discrepancy, the vapours in the vent stack need to be sampled, analysed and the results then compared to the vapour concentrations determined from the O_2 and sound speed readings at the time of the sampling. Samples of the gasoline in the tank should also be collected at that time and submitted to a laboratory for accurate determination of the RVP. In any case, given that the O_2 and sound speed are based on completely different technologies and are in close agreement with each other, this suggests they may at least provide a reasonable indication of the trend in the vapour concentrations. Figure 20 shows a similar graph of measured and calculated vent gas oxygen concentrations. Here, the oxygen concentration calculated from the hydrocarbon sensor data result in poor agreement with the O_2 data.

Figure 21 presents a graph of barometric pressure plotted as a function of time. The values range from 87 kPa to about 89.5 kPa. This amounts to only about a 3% difference between the two limits. Thus, the barometric pressure was relatively stable.

Figure 22 presents a graph showing the ambient air relative humidity as a function of time. The values range from about 22 to 95 percent with the greater values tending to occur during the warmer periods (i.e., when snow would be melting).

A graph of showing the temperature of the ambient air, vent gas and the fuel in the underground tank as a function of time is presented in Figure 23. The fuel temperature is quite stable with slight discontinuities occurring when shipments of fuel are received. The fuel temperature ranges from -5 to about 0°C. The ambient air and vent gas temperatures agree closely when the ambient air temperature is greater than that of the product fuel. When the ambient air temperature is less than the product temperature, the vent gas temperature is noticeably warmer than the ambient air, which indicates a reasonable flow of vent gas is occurring from the tank at these times.

The vent gas exit velocity is plotted as a function of time in Figure 24. The velocity scale has been reduced to provide better resolution of the day-to-day values. This truncates the high exit velocities that occur during a fuel delivery. Overall, the average flow is positive. The positive day-to-day values tend to range between 0 and 1 to 1.5 m/s, while the day-to-day negative flows range between 0 and -2 to -2.5 m/s. The larger range of the negative values likely reflects the range in instantaneous sales rates at the site.

Figure 25 presents a graph showing the vent gas sound velocity presented as a function of time. There are clear variations in the sound velocity with activity levels at the site. The very low sound velocity values that appear as outliers in the first part of the graph correspond to a period of colder weather and actually only occur at the very start and end of the activity periods. It is speculated that condensation and/or the formation of ice crystals is occurring in the vent stack at these times.

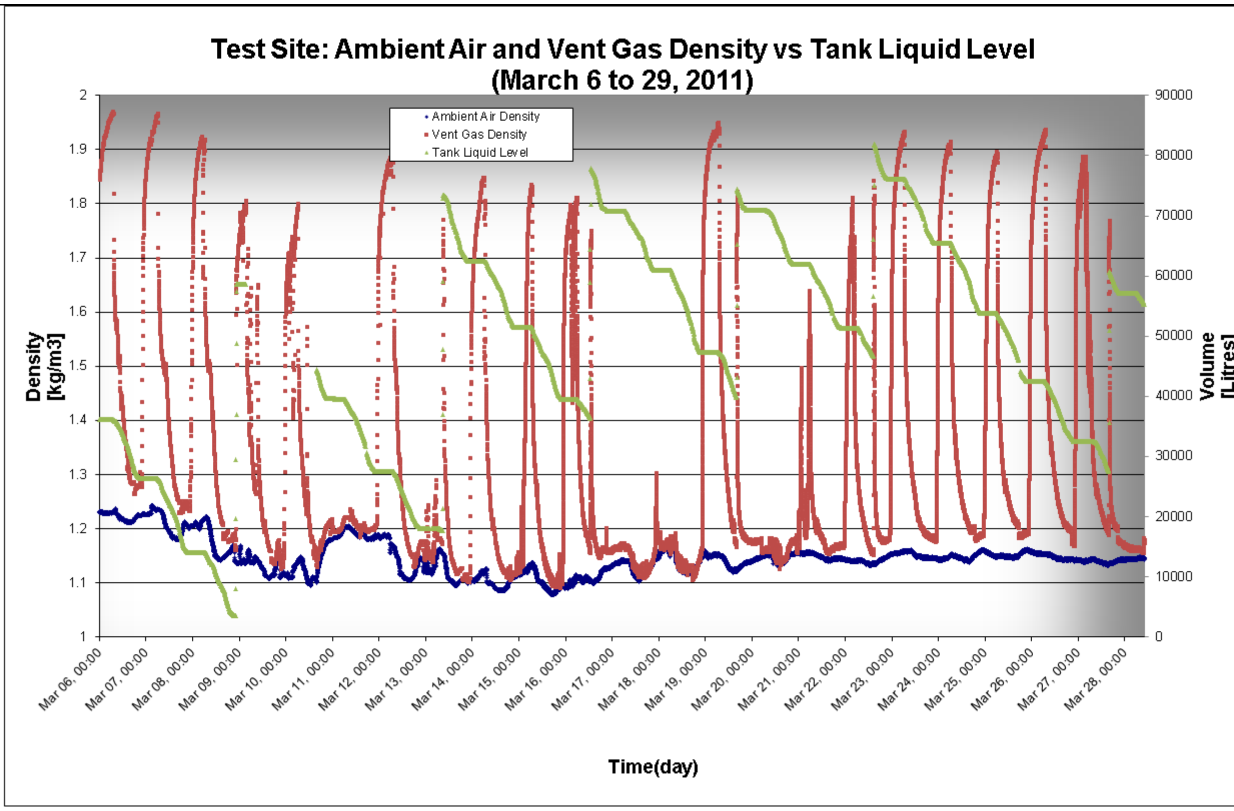


Figure 15: Graph showing the vent gas and ambient air densities, as well as the tank liquid level, as a function of time from 6 to 28 March 2011.

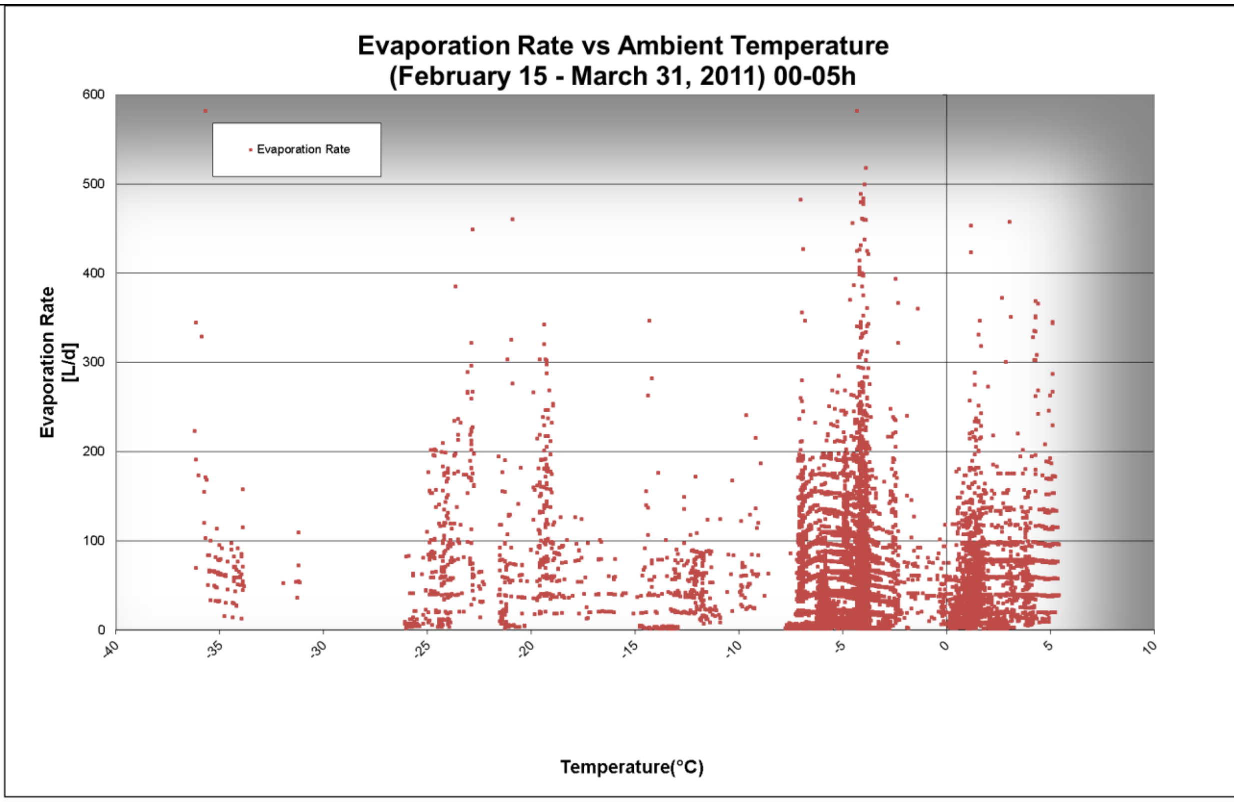


Figure 16: Graph showing the measured evaporation rate as a function of the ambient temperature during the period of 6 to 28 March 2011.

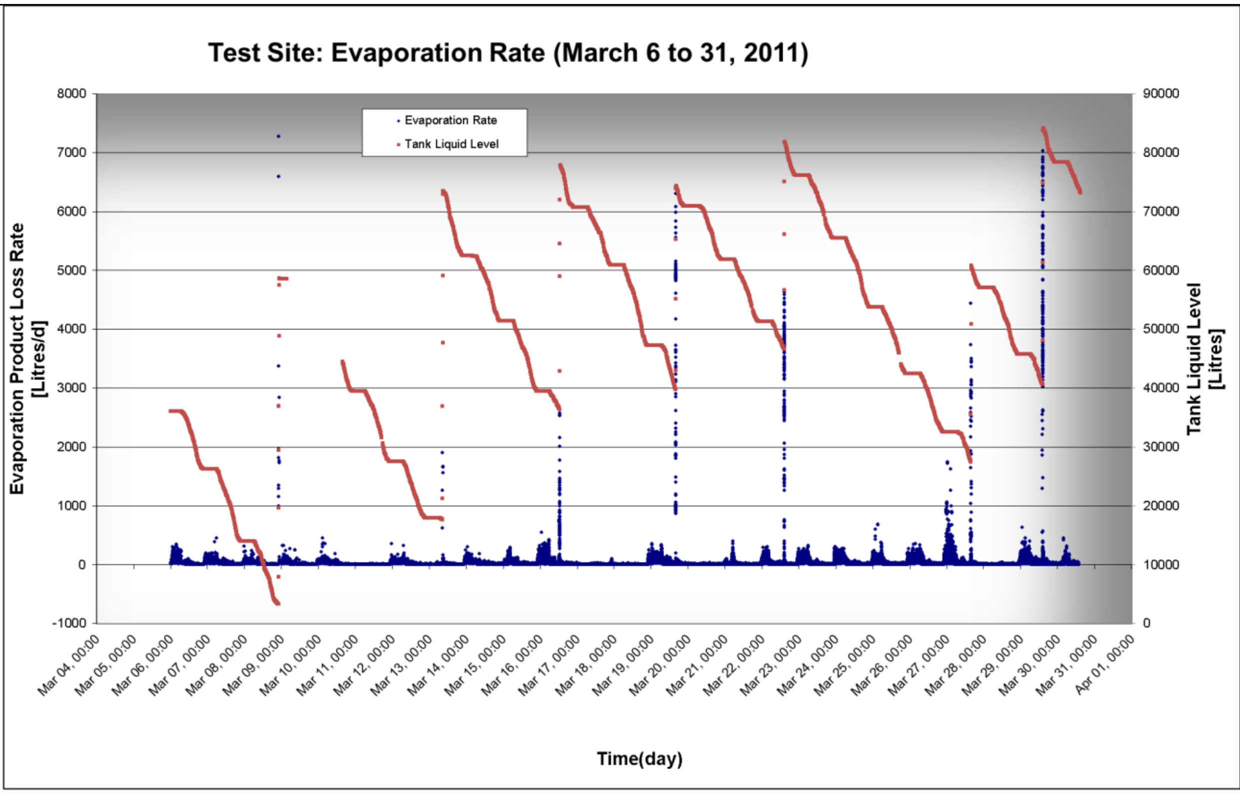


Figure 17: Graph showing the measured evaporation rate as a function of time from 6 to 28 March 2011.

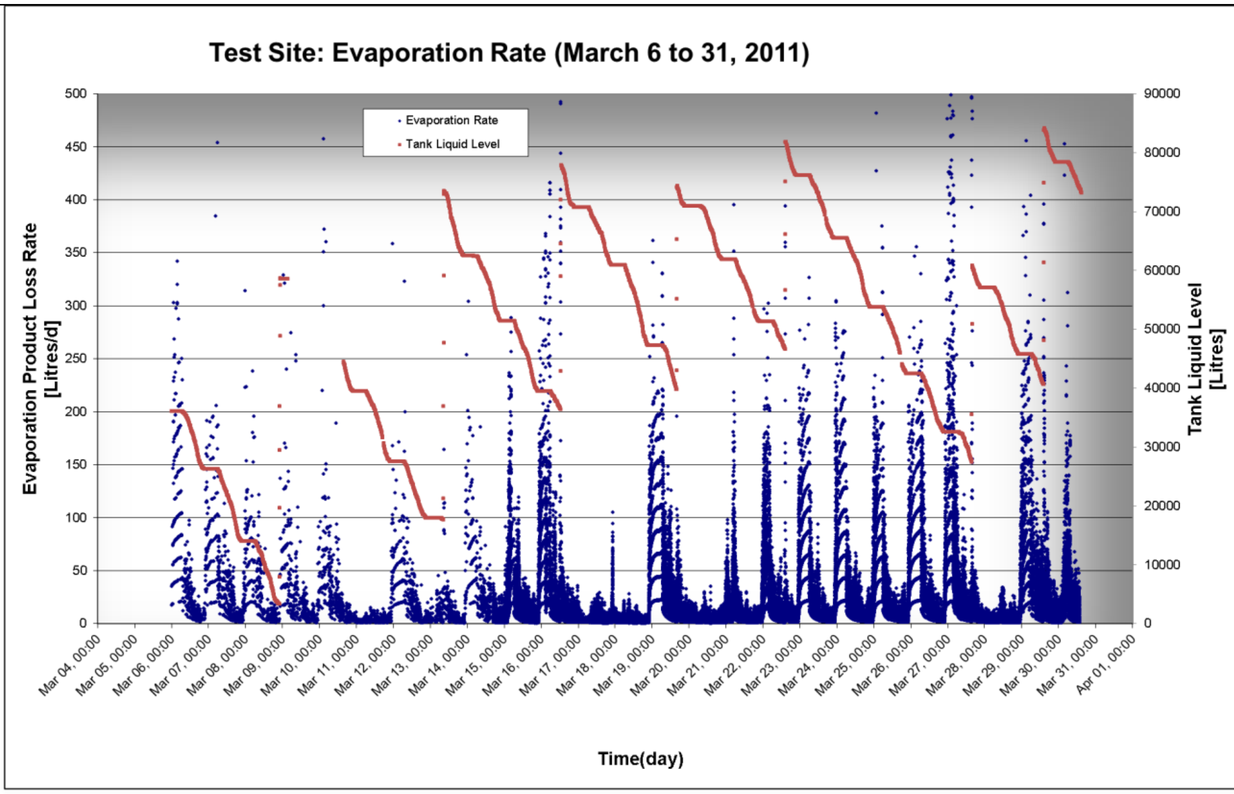


Figure 18: Graph showing the measured evaporation rate as a function of time for the period of 6 to 28 March 2011 at a greater degree of resolution.

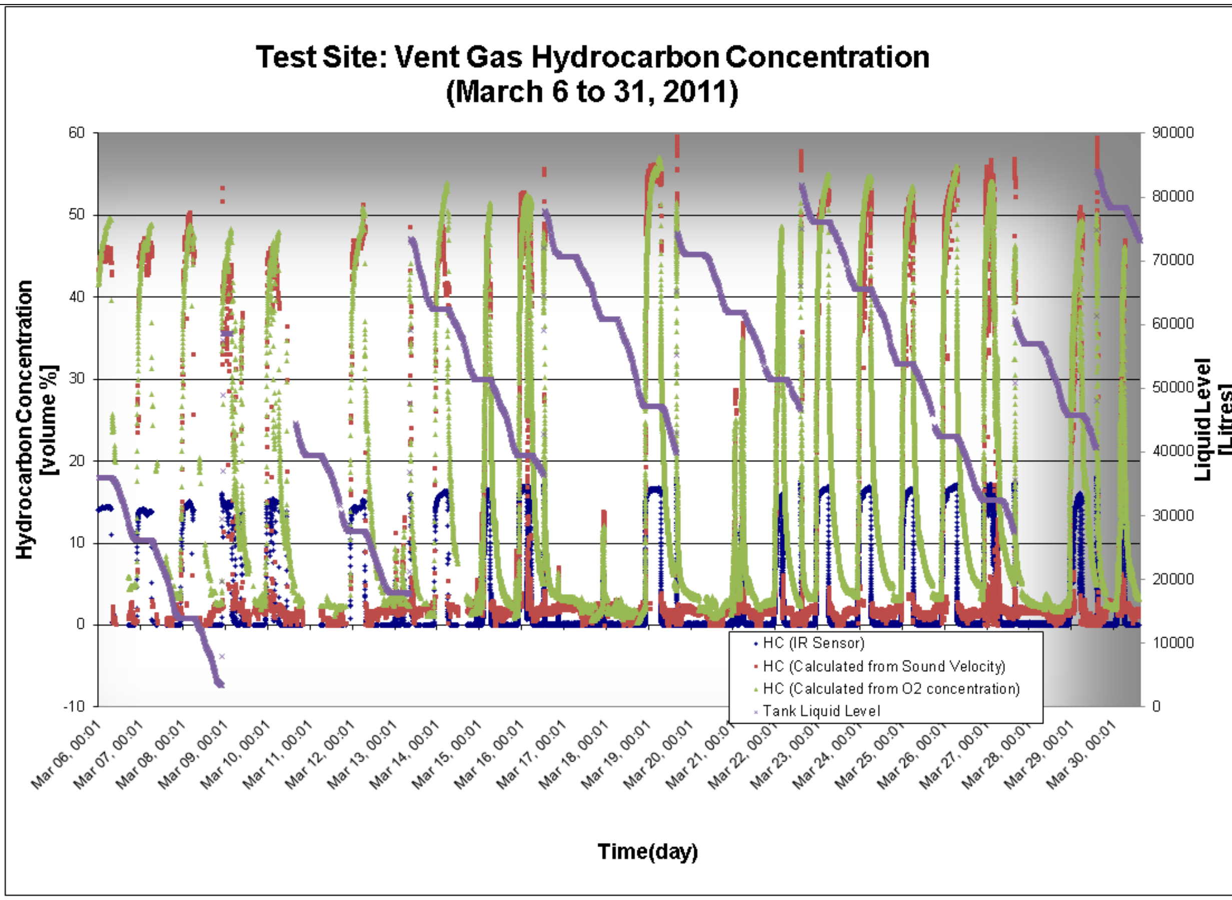


Figure 19: Graph showing the vent gas hydrocarbon concentration as a function of time from 6 to 31 March 2011. Both the measured and backcalculated values are presented.

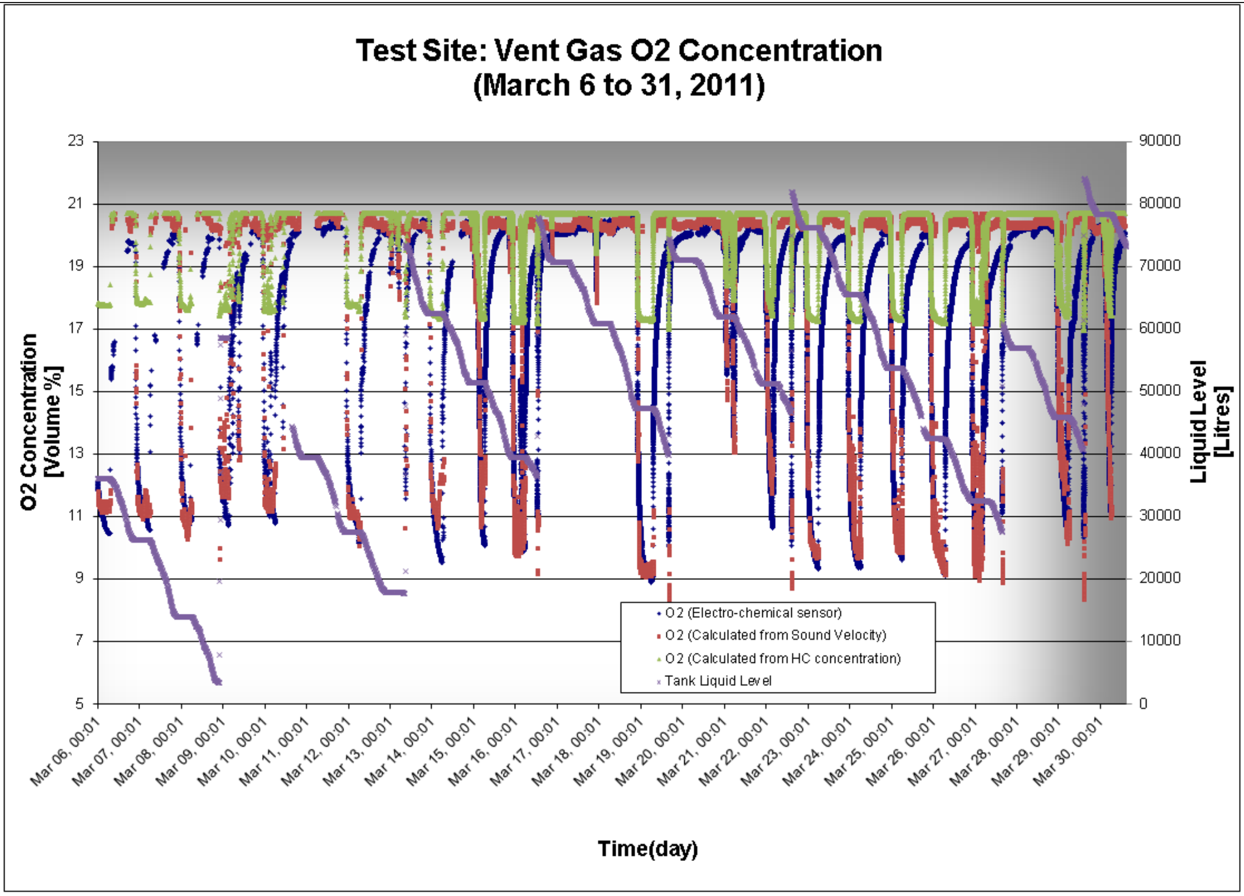


Figure 20: Graph showing the vent gas oxygen concentration as a function of time from 6 to 31 March 2011. Both the measured and backcalculated values are presented.

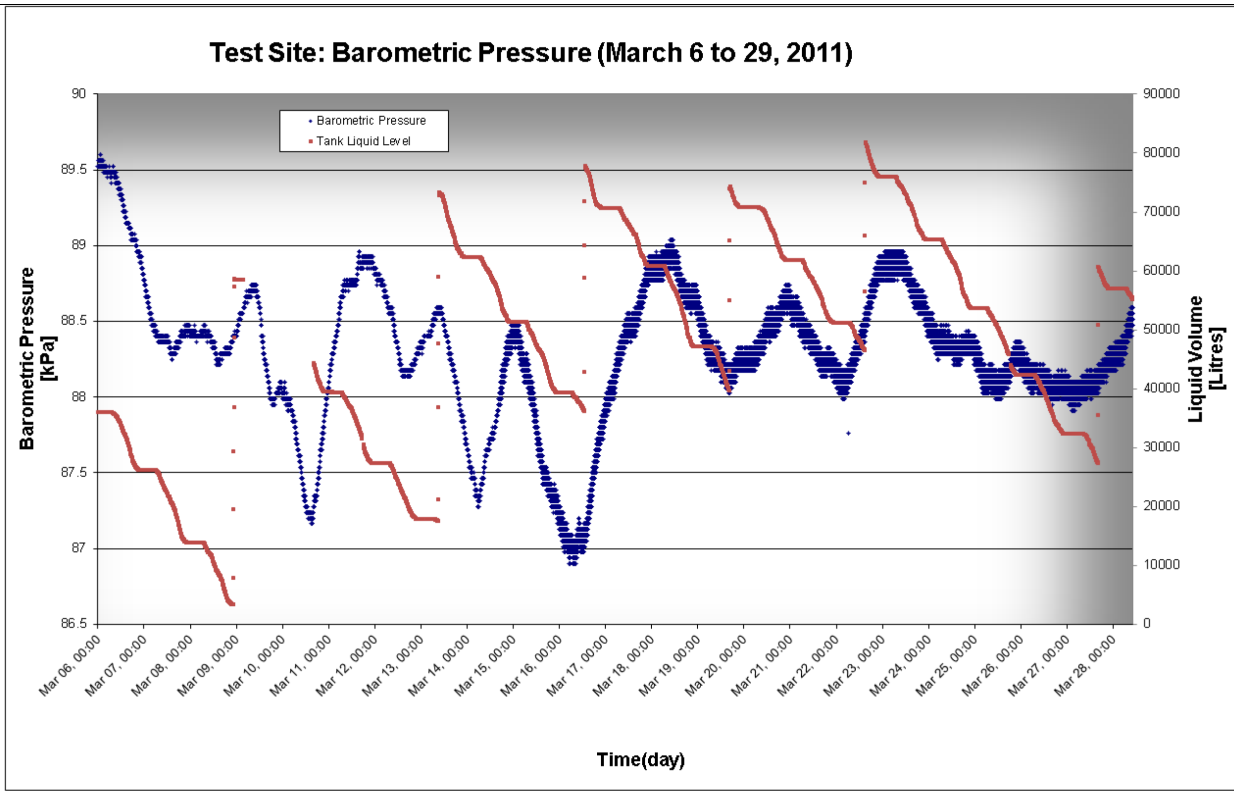


Figure 21: Graph showing the barometric pressure as a function of time from 6 to 28 March 2011.

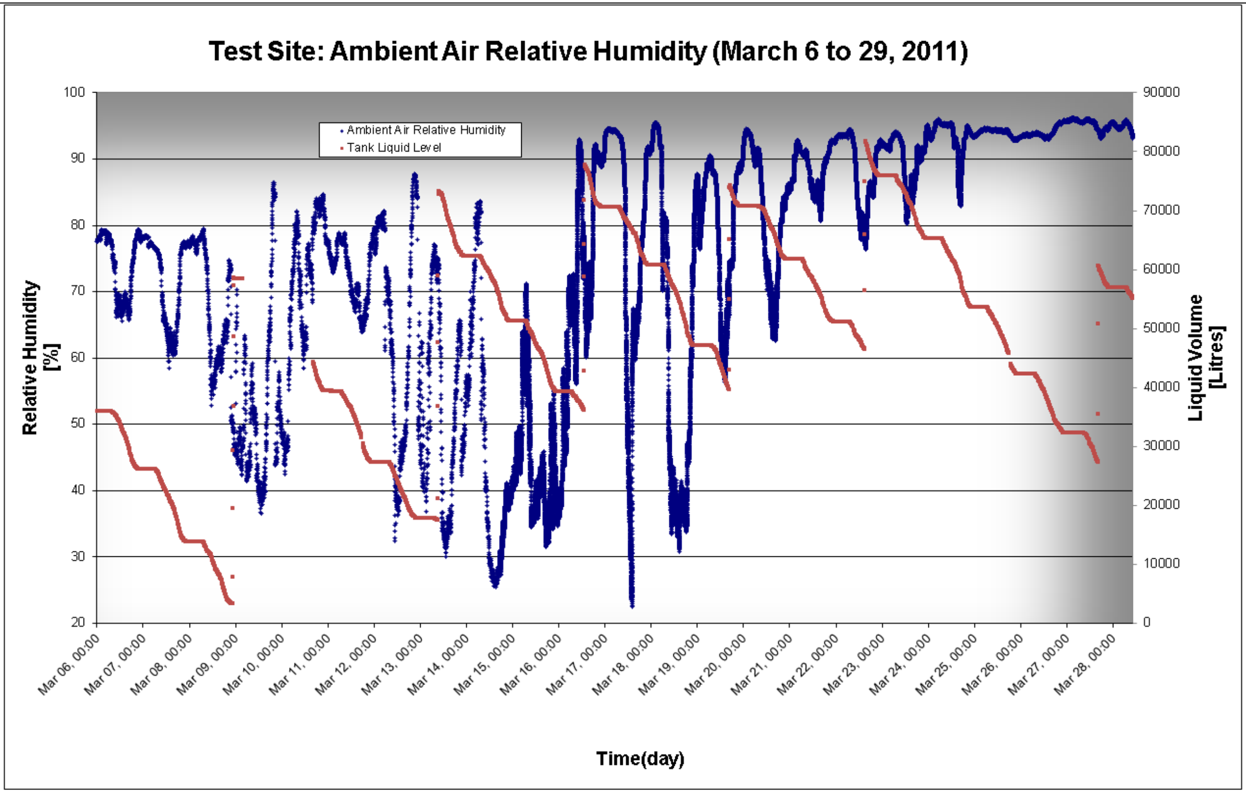


Figure 22: Graph showing the ambient air relative humidity as a function of time from 6 to 28 March 2011.

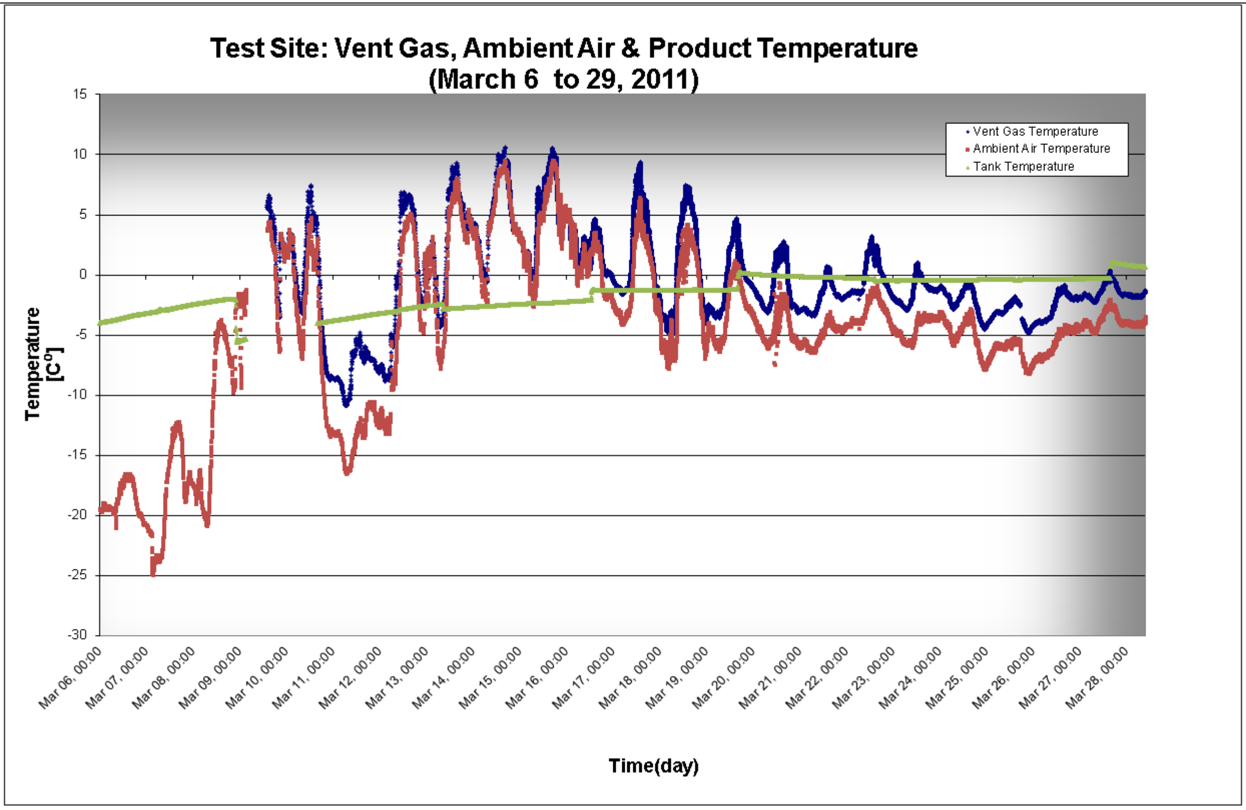


Figure 23: Graph showing the ambient air, vent gas and tank temperatures as a function of time from 6 to 28 March 2011.

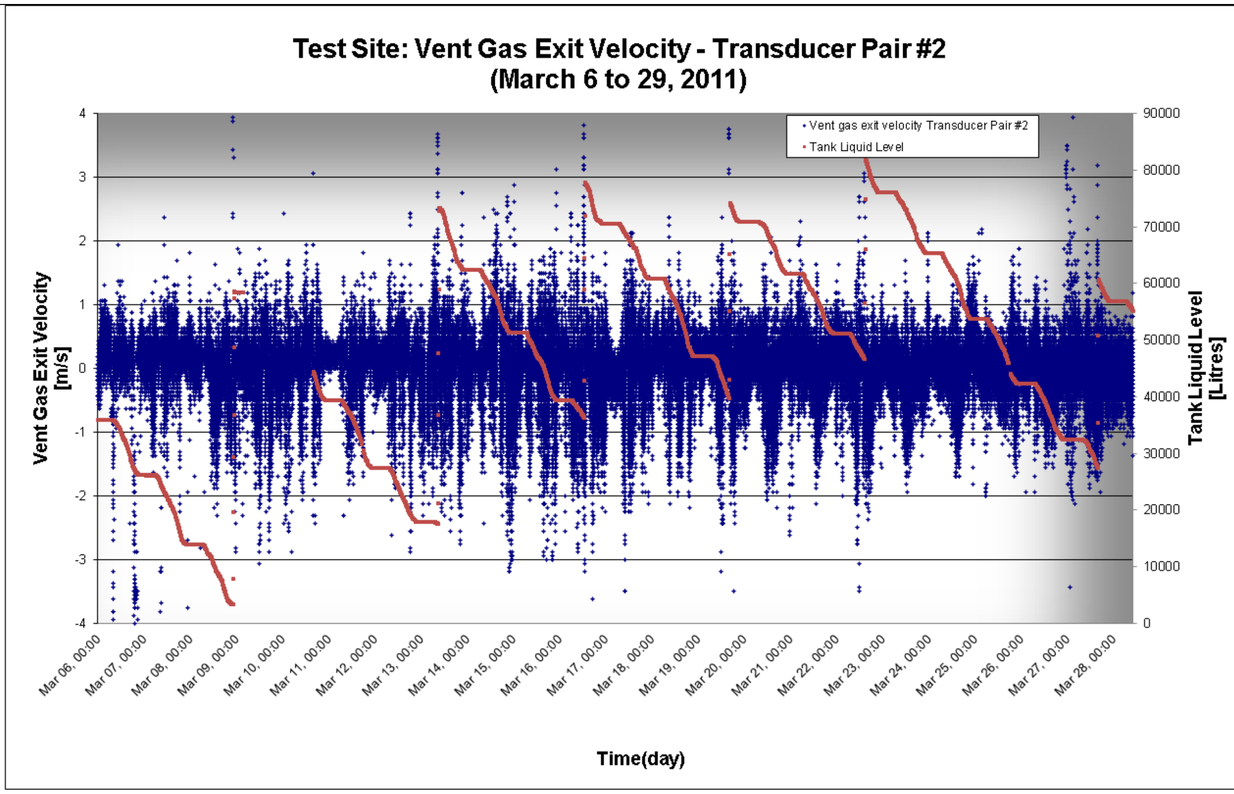


Figure 24: Graph showing the vent gas exit velocity as a function of time from 6 to 28 March 2011.

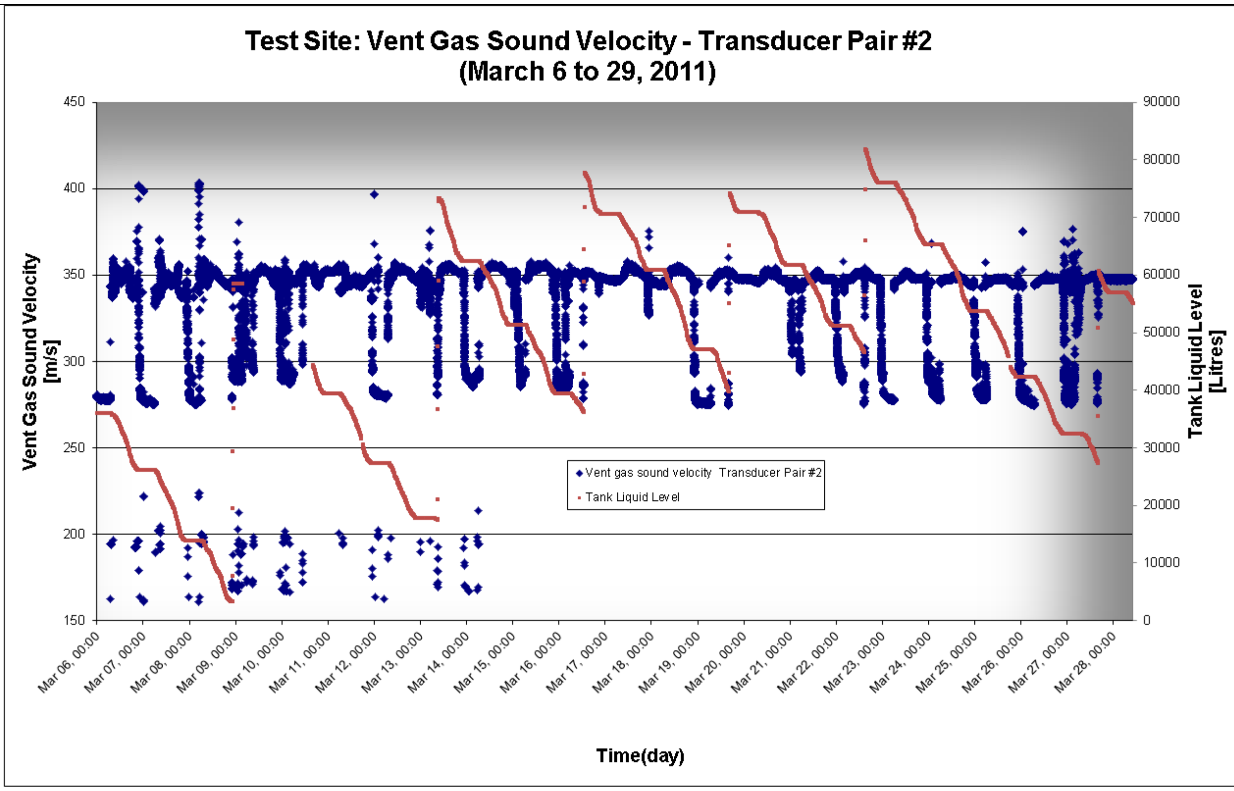


Figure 25: Graph showing the vent gas sound velocity as a function of time from 6 to 28 March 2011.

8 APPENDIX III – GASOLINE VAPOUR ANALYSIS

Detailed vapour speciation profiles were developed for the gasoline in the monitored tank by collecting samples of the stored gasoline and subsequently using these samples to create vapour samples under controlled laboratory conditions. The vapour saturation level and the molecular weight of the gasoline vapours at -3°C and +15°C are presented in Table 3. As would be expected, both the vapor saturation level and molecular weight increase with the product temperature; although, the impact of temperature on the molecular weight is very slight (i.e., less than 1 percent) for the values considered.

Table 3: Vapour saturation and molecular weight at -3°C and +15°C as measured for gasoline taken from the monitored underground storage tank (March 17, 2011).

Temperature (°C)	Vapor Saturation Level (Mol Fraction)	Vapour Molecular Weight (Air-Free)
-3	0.2420	64.563
15	0.3436	64.967

The detailed composition profiles are presented in Table 4 on both an air-in and air-free basis. A total of 64 different substances were detected in the vapours (i.e., on an air-free basis).

The basic methodology involved completely filling 40 mL glass sample containers with gasoline in the field and then in the laboratory, a vapour space was created by replacing 20 mL of liquid from each sample container with purified air. The air was allowed to come into equilibrium with the sample at controlled temperatures of -3°C and +15°C, to reflect typical winter and summer product temperatures in the underground storage tank, respectively. Each vapour sample was analyzed for a full range of hydrocarbons and reduced sulphur compounds as well as for CO_2. O_2 and N_2.

This headspace analysis technique was designed to avoid the potential for interferences due to emissions by upwind sources. The analyses were performed by Alberta Research Council at their laboratory in Vegerville. Four different sets of analyses were performed on each sample.

The local barometric pressure at the Vegreville laboratory was 93 kPa and local barometric pressure in Calgary is about 88.5 kPa.

Tests were performed to determine if vigorous agitation of the gasoline and air mixture for 1 minute would affect the vapour content of the air-vapour mixture in the headspace created in the sample container. Analyses of the headspace mixture immediately before the agitation agreed well (i.e., within ±5%) with the values obtained 1 minute and 4 minutes after the agitation, thus indicating that saturated conditions had been achieved in all three instances.

The exact Reid vapour pressure (RVP) of the gasoline was not available but was reported by the fuel supplier to be in the range of 100 to 107 kPa in March. Based on use of the API RVP correlation and an assumed ASTM distillation slope of 3.0 °F/%, the true vapor pressure of the gasoline at -3°C would be 28.1 to 30.5 kPa, and at 15°C would be 53.1 to 57.3 kPa. Accordingly, the calculated vapor saturation level of the gasoline at -3°C would be a mol fraction of 0.302 to 0.328 and at 15°C would be a mol fraction of 0.571 to 0.616. The reason for the large discrepancy between the calculated and measured saturation levels is not clear, but it is likely due to a lower than expected fuel RVP (possibly due to weathering of the fuel between the time it's RVP was measured at the refinery and when it was sampled at the retail gasoline station) and potential weaknesses in the API RVP correlation.

8.1 Inerts

The analysis for inerts determined concentrations of N_2, O_2, CO_2 and CO in the gas samples. The analyses were performed by gas chromatography with thermal conductivity detection (GC/TCD). The minimum detection limit for this method was 50 ppm for CO_2 and 100 ppm for the other inerts.

8.2 Reduced Sulphur Compounds (RSCs)

Analyses for sulphur gases were performed by gas chromatography with sulphur chemiluminescence detection (GC/SCD). The minimum detection limit of this method was 1-ppb. The specific sulphur compounds targeted by the analysis are summarized in Table 5. No non-target sulphur compounds were detected by the analysis.

8.3 C_1 through C_4 Gases

The analyses for lighter VOCs were done by gas chromatography with flame ionization detection (GC/FID). The minimum detection limit for individual compounds was 50 ppb. The target compounds are summarized in Table 6.

8.4 C_5 through C_{12+} Gases

Analyses for the heavier VOCs in gas samples were done by mass spectroscopy (GC/MS) with cryogenic focusing to provide a minimum detection limit of 10 $\mu g/m^3$. For liquid samples, a purge and trap GC/MS analysis was performed for compounds in the C_5 to C_{12} range and a solvent extraction GC/MS analysis was done for compounds heavier than C_{12}. The GC/MS was operated in full scan (or total ion) mode. In this operating mode the substance type denoted by each chromatographic peak is determined based on the best match quality achieved with the available entries in the instrument's mass spectral library. Additionally, the instrument was calibrated using a calibration standard of selected target compounds (see Table 7), and therefore provided exact matches where these substances occurred in the collected samples.

Table 4: Detailed vapour speciation profiles measured for gasoline collected from the monitored underground storage tank (March 17, 2011).

Substance	CAS Number	Mol Formula	Mol Weight	As Sampled at -3°C (Air In)		As Sampled at -3°C (Air In)		As Sampled at -3°C (Air Free)		As Sampled at -3°C (Air Free)	
				Mol Fraction	Mass Fraction	Mol Fraction	Mass Fraction	Mol Fraction	Mass Fraction	Mol Fraction	Mass Fraction
1,2,3-Trimethylbenzene	526-73-8	C9H12	120	0.0000305	0.0000966	0.0000331	0.0000946	0.0001261	0.0002281	0.0000964	0.0001724
1,2,4-Trimethylbenzene	95-63-6	C9H12	120	0.0001235	0.0003909	0.0001411	0.0004032	0.0005103	0.0009235	0.0004106	0.0007343
1,3,5-Trimethylbenzene	108-67-8	C9H12	120	0.0000373	0.0001179	0.0000442	0.0001263	0.0001540	0.0002786	0.0001286	0.0002300
1-Butanol, 3-methyl- (impure)	123-51-3	C5H12O	88	0.0000158	0.0000368	0.0000179	0.0000375	0.0000654	0.0000868	0.0000521	0.0000683
1-Butene	106-98-9	C4H8	56	0.0002787	0.0004116	0.0002752	0.0003670	0.0011515	0.0009725	0.0008009	0.0006684
1-Decanol, 2-hexyl-	2425-77-6	C16H34O	242	0.0000322	0.0002055	0.0000441	0.0002540	0.0001330	0.0004855	0.0001283	0.0004626
1-Octene	111-66-0	C8H16	112	0.0000796	0.0002351	0.0001061	0.0002830	0.0003289	0.0005555	0.0003088	0.0005154
2,2-Dimethylbutane	75-83-2	C6H14	86	0.0011929	0.0027058	0.0022153	0.0045377	0.0049289	0.0063922	0.0064478	0.0082637
2,3-Dimethylbutane	79-29-8	C6H14	86	0.0018791	0.0042623	0.0029732	0.0060901	0.0077642	0.0100692	0.0086536	0.0110908
2,3-Dimethylpentane	565-59-3	C7H16	100	0.0005447	0.0014367	0.0009934	0.0023661	0.0022507	0.0033941	0.0028913	0.0043089
2-Methylheptane	592-27-8	C8H18	114	0.0002090	0.0006285	0.0002996	0.0008136	0.0008637	0.0014847	0.0008722	0.0014817
2-Methylhexane	591-76-4	C7H16	100	0.0016152	0.0042601	0.0026700	0.0063595	0.0066737	0.0100639	0.0077713	0.0115814
2-Methylpentane	107-83-5	C6H14	86	0.0087410	0.0198269	0.0142245	0.0291371	0.0361165	0.0468387	0.0414017	0.0530620
3-Methylheptane	589-81-1	C8H18	114	0.0005226	0.0015712	0.0009188	0.0024947	0.0021591	0.0037118	0.0026741	0.0045431
3-Methylhexane	589-34-4	C7H16	100	0.0016996	0.0044828	0.0029348	0.0069902	0.0070227	0.0105901	0.0085420	0.0127299
3-Methylpentane	96-14-0	C6H14	86	0.0049617	0.0112544	0.0084531	0.0173151	0.0205009	0.0265872	0.0246035	0.0315327
Benzene	71-43-2	C6H6	78	0.0006239	0.0012835	0.0011170	0.0020751	0.0025779	0.0030322	0.0032511	0.0037791
Butane	106-97-8	C4H10	58	0.0816040	0.1248342	0.1088992	0.1504397	0.3371750	0.2949057	0.3169608	0.2739680
Carbon dioxide	124-38-9	CO2	44	0.0002322	0.0002695	0.0001632	0.0001711	0.0009596	0.0006367	0.0004751	0.0003115
cis-2-Butene	590-18-1	C4H8	56	0.0002639	0.0003898	0.0002518	0.0003359	0.0010905	0.0009209	0.0007330	0.0006117
cis-2-Pentene	627-20-3	C5H10	70	0.0000589	0.0001088	0.0000780	0.0001301	0.0002434	0.0002569	0.0002270	0.0002368
Cyclohexane	110-82-7	C6H12	84	0.0003748	0.0008303	0.0006261	0.0012527	0.0015485	0.0019615	0.0018224	0.0022813
Cyclohexane, (1-hexyltetradecyl)-	4443-60-1	C26H52	364	0.0000338	0.0003243	0.0000311	0.0002699	0.0001396	0.0007662	0.0000906	0.0004915

Table 4: Detailed vapour speciation profiles measured for gasoline collected from the monitored underground storage tank (March 17, 2011).											
Substance	**CAS Number**	**Mol Formula**	**Mol Weight**	**As Sampled at -3°C (Air In)**		**As Sampled at -3°C (Air In)**		**As Sampled at -3°C (Air Free)**		**As Sampled at -3°C (Air Free)**	
				Mol Fraction	**Mass Fraction**	**Mol Fraction**	**Mass Fraction**	**Mol Fraction**	**Mass Fraction**	**Mol Fraction**	**Mass Fraction**
Cyclohexane, 1,2-dimethyl- (cis/trans) $	583-57-3	C8H16	112	0.0000419	0.0001238	0.0000000	0.0000000	0.0001732	0.0002925	0.0000000	0.0000000
Cyclopentane	287-92-3	C5H10	70	0.0015202	0.0028066	0.0025418	0.0042378	0.0062811	0.0066303	0.0073980	0.0077176
Cyclopentane, 1,2-dimethyl-, trans-	822-50-4	C7H14	98	0.0000869	0.0002246	0.0000000	0.0000000	0.0003590	0.0005305	0.0000000	0.0000000
Cyclopentane, ethyl-	1640-89-7	C7H14	98	0.0000368	0.0000952	0.0000561	0.0001309	0.0001522	0.0002250	0.0001632	0.0002384
Cyclopropane, 1,2-dimethyl-, cis-	930-18-7	C5H10	70	0.0000497	0.0000918	0.0000000	0.0000000	0.0002054	0.0002169	0.0000000	0.0000000
Ethane	74-84-0	C2H6	30	0.0000734	0.0000581	0.0000725	0.0000518	0.0003032	0.0001371	0.0002111	0.0000944
Ethyl benzene	100-41-4	C8H10	106	0.0001731	0.0004840	0.0002239	0.0005652	0.0007154	0.0011435	0.0006516	0.0010293
Ethyl mercaptan	75-08-1	C2H6S	62	0.0000019	0.0000030	0.0000026	0.0000039	0.0000077	0.0000072	0.0000077	0.0000071
Heptane	142-82-5	C7H16	100	0.0008825	0.0023277	0.0015041	0.0035824	0.0036465	0.0054990	0.0043777	0.0065240
Heptane, 2,2,3,4,6,6-hexamethyl-	62108-32-1	C13H28	184	0.0000385	0.0001870	0.0000625	0.0002739	0.0001592	0.0004418	0.0001819	0.0004988
Heptane, 4-methyl-	589-53-7	C8H18	114	0.0000735	0.0002209	0.0001019	0.0002767	0.0003036	0.0005219	0.0002966	0.0005039
Hexane	110-54-3	C6H14	86	0.0047189	0.0107037	0.0078118	0.0160015	0.0194977	0.0252861	0.0227370	0.0291406
Hexane, 2,3-dimethyl-	584-94-1	C8H18	114	0.0001668	0.0005015	0.0003206	0.0008706	0.0006892	0.0011848	0.0009332	0.0015855
Hexane, 2,4-dimethyl-	589-43-5	C8H18	114	0.0000954	0.0002869	0.0001352	0.0003672	0.0003943	0.0006779	0.0003937	0.0006688
Isobutane	75-28-5	C4H10	58	0.0544730	0.0833305	0.0734545	0.1014743	0.2250741	0.1968581	0.2137958	0.1847964
Isobutylene	115-11-7	C4H8	56	0.0002090	0.0003087	0.0003055	0.0004075	0.0008637	0.0007293	0.0008891	0.0007420
Isopentane	78-78-4	C5H12	72	0.0488779	0.0928196	0.0714724	0.1225690	0.2019561	0.2192750	0.2080268	0.2232122
Isopropyl mercaptan	75-33-2	C3H8S	76	0.0000015	0.0000030	0.0000021	0.0000038	0.0000063	0.0000072	0.0000061	0.0000070
m,p-Xylene	108-38-3 / 106-42-3	C8H10	106	0.0007316	0.0020453	0.0009211	0.0023255	0.0030228	0.0048319	0.0026809	0.0042350
Methane	74-82-8	CH4	16	0.0002396	0.0001011	0.0001947	0.0000742	0.0009902	0.0002389	0.0005667	0.0001351
Methyl mercaptan	74-93-1	CH4S	48	0.0000001	0.0000001	0.0000001	0.0000001	0.0000002	0.0000001	0.0000002	0.0000001
Methylcyclohexane	108-87-2	C7H14	98	0.0002407	0.0006221	0.0004174	0.0009743	0.0009945	0.0014697	0.0012149	0.0017743

Table 4: Detailed vapour speciation profiles measured for gasoline collected from the monitored underground storage tank (March 17, 2011).											
Substance	**CAS Number**	**Mol Formula**	**Mol Weight**	**As Sampled at -3°C (Air In)**		**As Sampled at -3°C (Air In)**		**As Sampled at -3°C (Air Free)**		**As Sampled at -3°C (Air Free)**	
				Mol Fraction	**Mass Fraction**	**Mol Fraction**	**Mass Fraction**	**Mol Fraction**	**Mass Fraction**	**Mol Fraction**	**Mass Fraction**
Methylcyclopentane	96-37-7	C6H12	84	0.0025759	0.0057068	0.0044422	0.0088878	0.0106430	0.0134817	0.0129296	0.0161856
m-Ethyltoluene	620-14-4	C9H12	120	0.0000900	0.0002850	0.0001021	0.0002919	0.0003721	0.0006733	0.0002973	0.0005316
Nitrogen	7727-37-9	N2	28	0.5975142	0.4412662	0.5188454	0.3460235	0.0000000	0.0000000	0.0000000	0.0000000
Nonanal	124-19-6	C9H18O	142	0.0000343	0.0001285	0.0000000	0.0000000	0.0001418	0.0003036	0.0000000	0.0000000
Nonane, 2-methyl-	871-83-0	C10H22	142	0.0000647	0.0002424	0.0000000	0.0000000	0.0002674	0.0005726	0.0000000	0.0000000
n-Propylbenzene	103-65-1	C9H12	120	0.0000272	0.0000862	0.0000343	0.0000980	0.0001125	0.0002036	0.0000998	0.0001784
Octane	111-65-9	C8H18	114	0.0001425	0.0004285	0.0001761	0.0004780	0.0005889	0.0010123	0.0005124	0.0008706
o-Ethyltoluene	611-14-3	C9H12	120	0.0000303	0.0000959	0.0000346	0.0000990	0.0001252	0.0002265	0.0001008	0.0001802
Oxygen	7782-44-7	O2	32	0.1604632	0.1354315	0.1375815	0.1048623	0.0000000	0.0000000	0.0000000	0.0000000
o-Xylene	95-47-6	C8H10	106	0.0002650	0.0007408	0.0003358	0.0008478	0.0010948	0.0017501	0.0009774	0.0015439
Pentane	109-66-0	C5H12	72	0.0177354	0.0336797	0.0268167	0.0459884	0.0732799	0.0795642	0.0780525	0.0837501
Pentane, 3,3-dimethyl-	562-49-2	C7H16	100	0.0001520	0.0004009	0.0002518	0.0005998	0.0006281	0.0009472	0.0007330	0.0010924
p-Ethyltoluene	622-96-8	C9H12	120	0.0000410	0.0001296	0.0000588	0.0001680	0.0001692	0.0003063	0.0001710	0.0003059
Propane	74-98-6	C3H8	44	0.0021853	0.0025360	0.0027516	0.0028837	0.0090291	0.0059910	0.0080089	0.0052516
Propyl mercaptan	107-03-9	C3H8S	76	0.0000004	0.0000008	0.0000006	0.0000010	0.0000017	0.0000020	0.0000017	0.0000019
Propylene	115-07-1	C3H6	42	0.0000044	0.0000049	0.0002114	0.0002114	0.0000183	0.0000116	0.0006152	0.0003851
Thiophene	110-02-1	C4H4S	84	0.0000002	0.0000004	0.0000002	0.0000004	0.0000007	0.0000009	0.0000006	0.0000007
Toluene	108-88-3	C7H8	92	0.0002206	0.0005354	0.0003603	0.0007895	0.0009116	0.0012648	0.0010486	0.0014377
trans-2-Butene	624-64-6	C4H8	56	0.0004297	0.0006346	0.0007229	0.0009642	0.0017753	0.0014992	0.0021040	0.0017559
trans-2-Pentene	646-04-8	C5H10	70	0.0001004	0.0001854	0.0001621	0.0002702	0.0004148	0.0004379	0.0004717	0.0004921
Undecane, 2,8-dimethyl-	17301-25-6	C13H28	184	0.0000353	0.0001711	0.0000000	0.0000000	0.0001457	0.0004042	0.0000000	0.0000000
TOTAL				1.0000000	1.0000000	1.0000000	1.0000000	1.0000000	1.0000000	1.0000000	1.0000000

Table 5: Listing of the target reduced sulphur compounds (RSCs).	
CAS Number	**Substance Name**
638-02-8	2,5-Dimethyl Thiophene
872-55-9	2-Ethyl Thiophene
554-14-3	2-Methyl Thiophene
616-44-4	3-Methyl Thiophene
592-88-1	Allyl Sulphide
109-79-5	Butyl Mercaptan
544-40-1	Butyl Sulphide
75-15-0	Carbon Disulphide
463-58-1	Carbonyl Sulphide
624-92-0	Dimethyl Disulphide
75-18-3	Dimethyl Sulphide
3658-80-8	Dimethyl Trisulphide
75-08-1	Ethyl Mercaptan
352-93-2	Ethyl Sulphide
111-31-9	Hexyl Mercaptan
7783-06-4	Hydrogen Sulphide
75-33-2	Isopropyl Mercaptan
74-93-1	Methyl Mercaptan
107-03-9	Propyl Mercaptan
7446-09-5	Sulphur Dioxide
110-02-1/513-44-0 and 513-53-1	Thiophene/*iso* and *sec* Butyl Mercaptan
110-66-7	*n* Amyl Mercaptan
1679—09-0	*tert* Amyl Mercaptan
75-66-1	*tert* Butyl Mercaptan

Table 6: Listing of the target substances in the C_1 to C_4 range.	
CAS Number	**Substance Name**
106-99-0	1,3-Butadiene
106-98-9	1-Butene
74-86-2	Acetylene
106-97-8	Butane
74-84-0	Ethane
107-00-6	Ethylacetylene
74-85-1	Ethylene
75-28-5	Isobutane
115-11-7	Isobutylene
74-82-8	Methane
74-98-6	Propane
115-07-1	Propylene
74-99-7	Propyne
590-18-1	Cis-2-Butene
624-64-6	Trans-2-Butene

Table 7: Listing of the target substances in the C_5 to C_{12+} range.	
CAS Number	**Substance Name**
630-20-6	1,1,1,2-Tetrachloroethane
71-55-6	1,1,1-Trichloroethane
79-34-5	1,1,2,2-Tetrachloroethane
79-00-5	1,1,2-Trichloroethane
75-34-3	1,1-Dichloroethane
75-35-4	1,1-Dichloroethylene
563-58-6	1,1-Dichloropropylene
87-61-6	1,2,3-Trichlorobenzene
96-18-4	1,2,3-Trichloropropane
120-82-1	1,2,4-Trichlorobenzene
95-63-6	1,2,4-Trimethylbenzene
96-12-8	1,2-Dibromo-3-chloropropane
106-93-4	1,2-Dibromoethane
95-50-1	1,2-Dichlorobenzene
107-06-2	1,2-Dichloroethane
78-87-5	1,2-Dichloropropane
108-67-8	1,3,5-Trimethylbenzene
541-73-1	1,3-Dichlorobenzene
142-28-9	1,3-Dichloropropane
106-46-7	1,4-Dichlorobenzene
594-20-7	2,2-Dichloropropane
110-75-8	2-Chloroethoxyethylene
95-49-8	2-Chlorotoluene
106-43-4	4-Chlorotoluene
71-43-2	Benzene
108-86-1	Bromobenzene
75-27-4	Bromodichloromethane
75-25-2	Bromoform
74-83-9	Bromomethane
56-23-5	Carbon tetrachloride
108-90-7	Chlorobenzene
75-00-3	Chloroethane
67-66-3	Chloroform
124-48-1	Dibromochloromethane
74-95-3	Dibromomethane
100-41-4	Ethyl benzene
87-68-3	Hexachlorobutadiene
98-82-8	Isopropylbenzene (Cumene)
1634-04-4	MTBE
75-09-2	Methylene chloride
91-20-3	Naphthalene
100-42-5	Styrene

Table 7: Listing of the target substances in the C_5 to C_{12+} range.	
CAS Number	**Substance Name**
127-18-4	Tetrachloroethylene
108-88-3	Toluene
79-01-6	Trichloroethylene
75-69-4	Trichlorofluoromethane
75-01-4	Vinyl chloride
156-59-2	cis-1,2-Dichloroethylene
10061-01-5	cis-1,3-Dichloropropylene
108-38-3 / 106-42-3	m,p-Xylene
104-51-8	n-Butylbenzene
103-65-1	n-Propylbenzene
95-47-6	o-Xylene
99-87-6	p-Isopropyltoluene
135-98-8	sec-Butylbenzene
98-06-6	tert-Butylbenzene
156-60-5	trans-1,2-Dichloroethylene
10061-02-6	trans-1,3-Dichloropropylene