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TECHNICAL REPORT

Convective Evaporation Losses From Underground Storage Tanks

PREPARED FOR

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EXECUTIVE SUMMARY

This report is presented as part of a multi-year study being conducted in cooperation with Carleton University to develop improved algorithms for estimating average and instantaneous emissions from petroleum storage tanks. Given that the work is still in progress, the results presented herein are preliminary and are subject to change.

The need for improvements to the methods used to estimate evaporation losses from storage tanks has been identified by both industry and regulators, and is seen as particularly important in Alberta given the predicted rapid expansion of the oil production sector and downstream oil transportation system in the coming decades. If successful, such methodological improvements are expected to ultimately lead to new verifiable, practical and implementable strategies for managing tank emissions, which would directly and indirectly benefit a broad range of stakeholders, domestically and internationally, including federal, provincial or regional air quality administrators and operators of storage tank farms throughout the upstream oil and gas industry and downstream refined products distribution sector. Moreover, federal and provincial regulators, as well as industry operators, would be equipped with more representative data concerning the quantification of fugitive inorganic compound (IOC), volatile organic compound (VOC), odour, and greenhouse gas (GHG) emissions from liquid storage tanks.

The focus herein is evaporation losses from fixed-roof storage tanks. A review of the existing American Petroleum Institute (API) algorithms for estimating evaporation losses from this type of tank has been conducted and specific unaccounted for effects have been identified. To help evaluate the significance of the emission contributions from these unaccounted for effects, a detailed monitoring program has been conducted on an underground gasoline storage tank at a retail gasoline station. The preliminary monitoring results and initial recommendations for enhancement of the existing evaporation loss algorithm for fixed-roof tanks are presented.

Background

The potential for odour and benzene emissions from storage tanks has been a matter of particular concern at recent hearings for pipeline terminals and upgrader developments, and poses a significant challenge for the proponents of these developments in trying to determine the required level of vapour control. As well, regulators are challenged in trying to understand discrepancies between recent Differential Absorption LIDAR (DIAL) and ambient air monitoring results, which suggest that storage losses are being understated using current estimation methods. To adequately assess receptor impacts, it is necessary to be able to predict both average emissions as well as instantaneous emission rates as a function of meteorological conditions and tank activities. The current US Environmental Protection Agency (EPA) TANKS software program for estimating evaporation losses from storage tanks is limited to estimating only average emissions. API specifically recommends that its evaporation loss correlations not be used to size vapour control systems. Some of the key issues and limitations concerning the current API evaporation loss correlations include the following:

• Companies are tending to estimate their emissions based on the assumption that their tanks, and any floating roofs and the seals on the floating roofs, are in good condition.

Guidelines are needed to help users properly assess the condition of their tank for the purpose of estimating emissions.

- There are questions as to whether the existing algorithms adequately account for all the effects that contribute to evaporation losses from storage tanks. At a minimum, the completeness of the current algorithms and the reasonableness of the assumptions inherent in these algorithms needs to be assessed and verified against appropriate measurement results.
- Vapour analyses for speciation of the estimated emissions are rarely available. Therefore the vapour composition is usually estimated based on Raoult's law and the liquid analysis. While liquid analyses are much more available than vapour analyses, they normally do not provide concentrations of the critical odorants which ultimately occur in the product vapours, namely: H₂S and other reduced sulphur compounds. The sulphur content of the liquid product is a parameter which is usually known; however, assuming the sulphur is all present as H₂S greatly overstates actual H₂S concentrations. Alternatively, in some Environmental Impact Assessments (EIA's) the authors have chosen, in the absence of any data, to set H₂S concentrations to zero which is equally wrong. A reliable means of estimating H₂S and mercaptan concentrations based on the sulphur content of the product and the type of product (e.g., light, medium, or heavy oil) is therefore needed.

Between 2006 and 2030, marketable production of Alberta's Oil Sands sector is expected to increase 444% from 1.126 million to 5 million barrels per day. This growth will contribute to increased shipments of product to market as well as increased shipments of diluents to heavy oil and crude bitumen production sites. Furthermore, conventional hydrocarbon liquid production is becoming more sour and odorous as companies are exploiting progressively deeper reserves, and the development of pipeline terminals and upgraders is expanding into more populated and industrially developed areas where air quality issues will be more challenging to manage. The corresponding growth in required delivery and storage infrastructure will result in significantly increased emissions from liquid storage tanks, which are currently very difficult to monitor and In advance of spiking production, it is essential to seek practical solutions for control. quantifying heavy oil storage tank emissions, which are necessary to affect a range of operational and infrastructure based mitigation strategies. Being able to accurately assess average and instantaneous emissions from storage tanks will assist companies in selecting the right vapour controls and determining the maximum allowable headspace concentrations of pollutants to avoid offsite odours and health risk impacts. The latter information can then be used to develop headspace monitoring programs as a proactive means of tracking the performance of floating roofs and identifying tanks in need of repair in advance of any air quality exceedances.

Specific Effects Not Accounted for by the Current Evaporation Loss Algorithms

The API evaporation loss algorithms used in the US EPA's TANKS program account for the following potential evaporation loss mechanisms:

• Working losses – when the liquid level decreases in a fixed-roof tank, ambient air is drawn into the tank which changes the degree of vapour saturation in the vapour space. This change then promotes the evaporation of further product from the exposed surface of the stored liquid. The air-vapour mixture that develops in the vapour space is physically displaced into

the atmosphere when the liquid level subsequently rises. Floating roof tanks have greatly reduced working losses as the stored liquid is covered by the floating roof and only the residual product left clinging to the tank wall and the surface of any support columns which penetrate the floating roof gets exposed to the atmosphere and is available for evaporation.

• **Standing or breathing losses** – for fixed-roof tanks, API attribute these emissions strictly to diurnal temperature changes. When the temperature drops, the vapours in the vapour space of the tank contract allowing more ambient air to enter the tank which thereby changes the vapour saturation level resulting in more product evaporation. When the temperature rises, the vapours in the tank vapour space expand resulting in some of the vapours being physically displaced to the atmosphere. For floating roof tanks, an additional contribution occurs as a result of enhanced evaporation losses around the perimeter seals and deck fittings due to wind effects.

Four potentially noteworthy effects, which are not accounted for by the current evaporation loss algorithms and which apply to fixed-roof storage tanks are as follows:

- Vapour Growth Due to Product Evaporation When liquid is removed from a freeventing tank it causes an equal volume of air to be drawn into the tank, which then causes some product to evaporate into the vapours space due to the change in vapour saturation conditions. This evaporation then causes an equal number of moles of the existing air-vapor mixture to be displaced from the tank.
- **Temperature Differences Between the Ambient Air and the Tank Vapour Space** If cool air (i.e., relative to the temperature of the tank vapour space) is drawn into the tank, it will cause subsequent air-vapor displacement as it warms (i.e., due to heat transfer from the stored liquid). If warm air is drawn into the tank it will cause more air to be drawn into the tank as it cools.
- **Convective Mixing** The existing algorithms for fixed-roof storage tanks assume a vertical concentration gradient occurs in the vapour space, with the greatest concentration of vapours occurring near the liquid surface and the lowest concentration of vapours occurring at the top of the tank vapour space. The algorithm increases the magnitude of the gradient at the liquid surface with increases in the vapour pressure of the stored product and the amount of outage (i.e., the vertical distance from the liquid surface to the top of the tank). If the liquid product is cooler than the vapour space and the ambient air, then a positive temperature gradient will occur (i.e., temperature increases in moving upwards from the liquid surface, resulting in a negative concentration gradient). Well mixed conditions would be expected to occur in heated tanks and where the product is warm relative to the vapour space and ambient air, causing natural convective mixing.
- Wind Scavenging Effects Ventilation of a free-venting fixed-roof tank due to wind effects and possible thermal effects will contribute to the displacement of air-vapour mixture from the vapour space by the incoming fresh ambient air and, thereby, will contribute to increased evaporation losses.

The data from a winter tank testing program conducted by Clearstone Engineering Ltd and Carleton University in 2009 show that sustained convective mixing can develop in the vapour space of both fixed roof and floating roof tanks, which contributes to increased emissions. Additionally, unpublished data for underground gasoline storage tanks (a type of fixed-roof

storage tank) shows that evaporation losses are actually appreciably greater in the winter, when the ground is warm relative to the ambient air, than in the summer when the opposite occurs. During the summer conditions the vapour space tends to become stratified which helps to impede evaporation losses.

Monitoring Program

The primary aim of the monitoring program has been to better document the evaporation loss mechanisms that occur under winter conditions when convective mixing effects would be expected to occur, and thereby, allow the development of updated algorithms to account for this behaviour.

An underground gasoline storage tank was selected for this work because it represents a wellbehaved and well-instrumented system (i.e., it has continuous liquid-level and product temperature monitoring data available) and was convenient to access. The emissions monitoring system comprises a clamp-on ultrasonic flow meter and an array of gas sensors on the vent from a tank to continuously monitor the vapour flow rate leaving the tank. Additionally, the system closely monitors the local ambient conditions and the exit vent gas temperature.

The principle outcomes of this work include:

- Compilation of detailed measurement results showing the emission characteristics of an underground storage tank during winter conditions, and showing that this behaviour departs dramatically from corresponding predictions by the US EPA TANKS evaporation loss model.
- Development of a refined algorithm for more accurately estimating average and instantaneous emission rates from storage tanks.
- Field demonstration of a system for continuous measurement of evaporations losses from an underground storage tank.

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LIST OF ACRYNOMS

API	-	American Petroleum Institute
AUPRF	-	Alberta Upstream Petroleum Research Fund
BII	-	Broad Industry Initiative
CAPP	-	Canadian Association of Petroleum Producers
ERCB	-	Energy Resources Conservation Board
GHG	-	Greenhouse Gas
IOC	-	Inorganic Compound
NPS	-	Nominal Pipe Size
NRCan	-	Natural Resources Canada
PERD	-	Program of Energy Research and Development
PTAC	-	Petroleum Technology Alliance Canada
RVP	-	Reid Vapour Pressure
SEPAC	-	Small Explorers and Producers Association of Canada
US EPA	-	U.S. Environmental Protection Agency
UPAIRI	-	Upstream Petroleum Air Issues Research Initiative
VEMS	-	Vent Emission Monitoring System
VOC	-	Volatile Organic Compound

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1 INTRODUCTION

Gaseous emissions from liquid storage tanks are a significant source of fugitive IOC, VOC, odour and GHG emissions that are usually quantifiable only through modelling. Variations in tank design, operating conditions, and liquid properties add to the challenge. US EPA's AP-42 air pollutant emission factor compendium outlines the standard modelling approach commonly used to estimate storage tank emissions. This approach attributes gaseous releases from storage tanks to three main mechanisms: working losses (i.e., where the tank liquid level is changed, pushing out gases from the head space); breathing losses (i.e., where temperature and pressure changes lead to expansion and venting of gases in the tank); and flashing losses (i.e., where gas dissolved in the product readily volatilizes or boils off when the product is brought from pressurized conditions to stock tank conditions). The AP-42 calculation procedure relies on the combination of standard emissions factors and the output of the previously described models to generate an average emissions estimate, typically on an annual basis. However, the instantaneous emissions may vary substantially in time and may deviate significantly from the estimated average emissions.

The work documented in this report has been conducted to help refine the existing algorithms used to estimate working and standing losses from fixed-roof storage tanks. Section 2.0 provides a review of the current algorithm and documents standing loss mechanisms not accounted for by these algorithms. Analytical models for the unaccounted for effects are then presented.

Section 3 provides an overview of the evaporation losses from an underground gasoline storage tank measured during winter conditions using a custom continuous vent emission monitoring system (VEMS). The VEMS was designed to be able to monitor both standing and working losses. Details of the VEMS are presented in Appendix I (Section 6). Presentation and discussion of the detailed monitoring results is provided in Appendix II (Section 7). Appendix II (Section 8) presents detailed laboratory analyses of the product vapours.

The conclusions and recommendations of this study are presented in Section 4. All references cited are listed in Section 5.

2 EVAPORATION LOSS ALGORITHM

2.1 <u>Current API Algorithm for Fixed-Roof Tanks</u>

API calculates total losses from fixed roof tanks as the sum of the standing storage loss and working loss:

 $L_T = L_S + L_W \qquad \qquad \text{Equation 1}$

where:

2.1.1 <u>Standing Storage Loss</u>

The standing storage loss, L_s , is the loss of stock vapours due to tank vapour space breathing. For fixed-roof tanks standing storage losses are estimated using the following equation:

 $L_S = 365 V_V W_V K_E K_S$ Equation 2

where:

Ls	=	standing storage loss, kg/y
V_V	=	vapour space volume, m ³
W_V	=	stock vapour density, kg/m ³
K _E	=	vapour space expansion factor, dimensionless
Ks	=	vented vapour saturation factor, dimensionless
365	=	constant, the number of daily events in a year, $(year)^{-1}$

For underground horizontal tanks, US EPA states in AP-42 that no breathing or standing storage losses occur ($L_S = 0$) because the insulating nature of the earth limits the diurnal temperature change.

2.1.1.1 Vapour Space Expansion Factor

The calculation of the vapour space expansion factor, K_E , depends upon the properties of the liquid in the tank and the breather vent settings. If the tank location and tank color and condition are known, K_E is calculated using the following equation:

$$K_E = 0.00324 \Delta T_V = 0.00324 [0.72(T_{AX} - T_{AN}) + 1.37 \alpha I]$$
 Equation 3

where:

K _E	=	vapour space expansion factor, dimensionless
ΔT_V	=	daily vapour temperature range, °K
T _{AX}	=	daily maximum ambient temperature, °K
T_{AN}	=	daily minimum ambient temperature, °K

α	=	tank paint solar absorptance, dimensionless
Ι	=	daily total solar insolation on a horizontal surface, MJ/(m ² d)
0.003	324 =	constant, (°K) ⁻¹
0.72	=	constant, dimensionless
1.37	=	constant, (°K m ² d)/MJ

If the tank location is unknown, a value of K_E may be calculated using typical meteorological conditions. For the lower 48 states, the U.S. EPA suggests using a daily solar insolation value of 15.6 MJ/(m²d), a daily range of ambient temperature of 11.7°K, a daily minimum ambient temperature of 263.1 °K, and a tank paint solar absorptance is 0.17 for white paint in good condition. Use of these values gives a K_E value of 0.04.

When the liquid stock has a true vapour pressure greater than 0.6895 kPa, a more accurate estimate of the vapour space expansion factor, K_E , is obtained by the following equation (Note: if K_E is less than zero, standing storage losses will not occur):

 $K_E = \frac{\Delta T_V}{T_{LA}} + \frac{\Delta P_V - \Delta P_B}{P_A - P_{VA}} > 0 \qquad \text{Equation 4}$

where:

ΔT_V	=	daily vapour temperature range, °K;
ΔP_V	=	daily vapour pressure range, kPa;
ΔP_B	=	breather vent pressure setting range, kPa;
PA	=	atmospheric pressure, kPa
P _{VA}	=	vapour pressure at daily average liquid surface temperature
T_{LA}	=	daily average liquid surface temperature, °K;

Notes:

1. The daily vapour temperature range, ΔT_V , is calculated using the following equation:

$$\Delta T_{\rm V} = 0.556(0.72 \,\Delta T_{\rm A} + 1.37 \,\alpha \, {\rm I})$$
 Equation 5

where:

ΔT_V	=	daily vapour temperature range, °K
ΔT_A	=	daily ambient temperature range, °K;
α	=	tank paint solar absorptance, dimensionless;
Ι	=	daily total solar insolation factor, MJ/m ² d;

2. The daily vapour pressure range, ΔP_V , can be calculated using the following equation:

$$\Delta P_{\rm V} = P_{\rm VX} - P_{\rm VN} \qquad \text{Equation 6}$$

where:

$\Delta P_{\rm V}$	=	daily vapour pressure range, kPa
P _{VX}	=	vapour pressure at the daily maximum liquid surface temperature, kPa;
P_{VN}	=	vapour pressure at the daily minimum liquid surface temperature, kPa;

The following method can be used as an alternate means of calculating ΔP_V for petroleum liquids:

$$\Delta \boldsymbol{P}_{V} = \frac{0.50BP_{VA}\Delta T_{V}}{T_{LA}^{2}} \quad \text{Equation 7}$$

where:

$\Delta P_{\rm V}$	=	daily vapour pressure range, kPa
В	=	constant in the vapour pressure equation (see Table 7.1-5 in Section 7 of AP-42), °K;
P _{VA}	=	vapour pressure at the daily average liquid surface temperature, kPa
T _{LA}	=	daily average liquid surface temperature, °K;
ΔT_V	=	daily vapour temperature range, °K;

3. The breather vent pressure setting range, ΔP_B , is calculated using the following equation:

$$\Delta P_{B} = P_{BP} - P_{BV}$$
 Equation 8

where:

$\Delta P_{\rm B}$	=	breather vent pressure setting range, kPag
P_{BP}	=	breather vent pressure setting, kPag
P _{BV}	=	breather vent vacuum setting, kPag

If specific information on the breather vent pressure setting and vacuum setting is not available, the method assumes 0.207 kPag for P_{BP} and -0.207 kPag for P_{BV} as typical values. If the fixed roof tank is of bolted or riveted construction in which the roof or shell plates are not vapour tight, the method assumes that $\Delta P_B = 0$, even if a breather vent is used.

4. The daily ambient temperature range, ΔT_A , is calculated using the following equation:

$\Delta T_{\rm A} = T_{\rm AX} - T_{\rm AN} \qquad \mbox{Equation 9}$

where:

ΔT_A	=	daily ambient temperature range, °K
T _{AX}	=	daily maximum ambient temperature, °K
T_{AN}	=	daily minimum ambient temperature, °K

5. The vapour pressures associated with daily maximum and minimum liquid surface temperature, P_{VX} and P_{VN}, respectively, are calculated by substituting the corresponding temperatures, T_{LX} and T_{LN} , into the vapour pressure function.

2.1.1.2 Vapour Space Outage

The vapour space outage, H_{VO} is the height of a cylinder of tank diameter, D, whose volume is equivalent to the vapour space volume of a fixed roof tank, including the volume under the cone or dome roof. The vapour space outage, HVO, is estimated from the following equation:

> $H_{VO} = H_S - H_L + H_{RO}$ **Equation 10**

where:

H _{VO}	=	vapour space outage, m; use $\pi D/8$ for horizontal tanks
Hs	=	tank shell height, m
H_L	=	liquid height, m
H _{RO}	=	roof outage, m.

2.1.1.3 Vented Vapour Saturation Factor

The vented vapour saturation factor, K_s, is calculated using the following equation:

$$K_S = \frac{1}{1 + 0.0252 P_{VA} H_{VO}}$$
 Equation 11

where:

Ks	=	vented vapour saturation factor, dimensionless
P _{VA}	=	vapour pressure at daily average liquid surface temperature, kPa;
H_{VO}	=	vapour space outage, m,
0.0252	=	constant, (kPa-m) ⁻¹

Inherent in the above relation for K_S is an assumption there is a vertical concentration gradient (or stratification) in the vapour space.

2.1.1.4 Stock Vapour Density

The density of the vapour is calculated using the following equation:

$$W_V = \frac{M_V P_{VA}}{RT_{LA}}$$
 Equation 12

where:

vapour density, kg/m³ W_V =

vapour molecular weight, kg/kg-mole; M_V =

R	=	the ideal gas constant, 8.3145 kPa m ³ /kg-mole °K
P _{VA}	=	vapour pressure at daily average liquid surface temperature, kPa
T_{LA}	=	daily average liquid surface temperature, °K

2.1.2 Working Loss

The working loss, L_W , is the loss of stock vapours due to tank filling or emptying operations. Fixed-roof tank working losses can be estimated using the relation:

$$L_W = 0.000414 M_V P_{VA} Q K_N K_P$$
 Equation 13

where:

L_{W}	=	working loss, kg/y
M_V	=	vapour molecular weight, kg/kg-mole
P _{VA}	=	vapour pressure at daily average liquid surface temperature, kPa
Q	=	annual net throughput (tank capacity [m ³] times annual turnover rate), m ³ /y
K _N	=	working loss turnover (saturation) factor, dimensionless
	=	for turnovers >36, $K_N = (180 + N)/6N$
	=	for turnovers \leq 36, K _N = 1
Ν	=	number of turnovers per year, dimensionless
K _P	=	working loss product factor, dimensionless
	=	for crude oils $K_P = 0.75$
	=	for all other organic liquids, $K_P = 1$

Inherent in the above working loss relation is an assumption that the volume of air drawn into the tank during withdrawals is at the same temperature as the liquid surface or is initially warmer that the liquid surface and eventually cools down to the liquid surface temperature. If the incoming air is colder than the surface of the stored liquid then as it warms through contact with the liquid, it will cause physical displacement of air-vapour mixture in the vapour space. For example, if the product is heated or the ambient air is cold (e.g., due to winter or cold weather conditions), it is conceivable that a temperature difference of 30°C or more could exist between the incoming air and the liquid surface. For a tank containing a liquid with a surface temperature of 10°C this could result in emissions being underestimated by a factor of up to [(273.15+10)/(273.15-20)-1] = 0.119 or about 11.2%. For at tank heated to 80°C with air coming in -30°C, the emissions would be understated by a factor of up to [(273.15+80)/(273.15-30)-1] = 1.452 or about 45.2%.

Furthermore, when fresh air is drawn into the vapour space of a tank it changes the degree of saturation in the vapour space causing more product to evaporate. The addition of product vapours to the vapour space will cause physical displacement of an equal number of moles of air-vapour mixture. The working loss equation, as currently posed, only accounts for the physical displacement of a volume of air-vapour mixture equal to the tank capacity times the annual turnover rate.

The working loss turnover (saturation) factor implies that a reasonable amount of time is required for air drawn into the tank to become saturated with vapours, and for annual turnovers of more than 36 that the

entrained air will not reach saturated conditions. This assumes there is little or no natural convection in the vapour space of the tank other than that caused by changes in the liquid level.

The basis for the working loss product factor is not clear; however, it serves, depending on the type of stored product, to further reduce the calculated degree of saturation.

A variation of the working loss equation presented by API that accounts for the vent setting may be written as follows (the above comments concerning inherent assumptions still apply):

$$L_W = QK_N K_P W_V K_B$$
 Equation 14

where:

L_W	=	working loss, kg/y
Q	=	annual net throughput (tank capacity $[m^3]$ times annual turnover rate), m^3/y
K _N	=	working loss turnover (saturation) factor, dimensionless
	=	(180 + N)/6N, for turnovers > 36
	=	1.0, for turnovers ≤ 36
Ν	=	number of turnovers per year, dimensionless
K _P	=	working loss product factor, dimensionless
	=	0.75 for crude oils
	=	1.0 for all other organic liquids
W_V	=	vapour density, kg/m^3 ,
K _B	=	vent setting correction factor, dimensionless
	=	for open vents and for a vent setting range up to ± 0.207 kPa, K _B = 1

The vent setting correction factor accounts for any reduction in emissions due to the condensation of vapours prior to the opening of the vent. This correction factor will only affect the calculation if the vent settings are greater than ± 0.207 kPa (0.03 psi).

2.1.2.1 Vent Setting Correction Factor

When the breather vent settings are greater than the typical values of \pm 0.207 kPa (0.03 psi), and the condition expressed in following equation is met,

$$K_N\left[\frac{P_{BP}+P_A}{P_I+P_A}\right] > 1.0$$
 Equation 15

Then the value of K_N is determined using the following equation:

$$K_B = \begin{bmatrix} \frac{P_I + P_A}{K_N} - P_{VA} \\ P_{BP} + P_A - P_{VA} \end{bmatrix}$$
 Equation 16

where:

K_B	=	vent setting correction factor, dimensionless
PI	=	pressure of the vapour space at normal operating conditions, kPa

 P_I is an actual pressure reading (the gauge pressure). If the tank is held at atmospheric pressure (not under a vacuum or held at a steady pressure) P_I would be 0.

PA	=	atmospheric pressure, kPa
K _N	=	working loss turnover (saturation) factor (dimensionless)
	=	(180 + N)/6N, for turnovers > 36
	=	1.0, for turnovers ≤ 36
P _{VA}	=	vapour pressure at the daily average liquid surface temperature, kPa
P _{BP}	=	breather vent pressure setting, kPa.

2.2 Modified Algorithm for Fixed-Roof Storage Tanks

Figure 1 presents a schematic diagram of a free-venting underground storage tank. The ambient temperature, T_A , is assumed to be different than the temperature in the vapour space, T_V . Immediately before the withdrawal of liquid from the tank, the number of moles of air and product vapours in the vapour space of the tank may be determined using the relation:

$$n_V = \frac{P_A V_V}{R T_V}$$
 Equation 17

Where:

n_V	=	number of moles of air-vapour mixture in the vapours space immediately before removal
		of an incremental volume of liquid, kmoles
PA	=	ambient pressure, kPa
Vv	=	volume of the vapour space in the tank, m ³
R	=	the ideal gas constant, 8.3145 kPa m ³ /kg-mole °K
T_V	=	temperature of the air-vapour mixture in the vapour space, °K

Immediately after an incremental volume, ΔV , of liquid is removed from the tank, the number of moles of air-vapour mixture in the vapour space will be as follows:

$$n'_V = n_V + n_A = \frac{P_A}{R} \left[\frac{V_V}{T_V} + \frac{\Delta V}{T_A} \right]$$
 Equation 18

Where:

- n'_V = number of moles of air-vapour mixture in the vapour space immediately following the incremental volume of product removal, kmoles
- n_V = number of moles of air-vapour mixture in the vapours space immediately before removal of an incremental volume of vapour, kmoles



Figure 1: Schematic diagram of a tank showing the mass inflows and outflows.

n_A	=	number of moles of ambient air drawn into the tank due to the incremental volume of
		liquid removal, kmoles
PA	=	ambient pressure, kPa
V_V	=	volume of the vapour space in the tank immediately before the removal of the incremental volume of liquid, m ³
ΔV	=	volume of the incremental amount of liquid removed from the tank, m ³
R	=	the ideal gas constant, 8.3145 kPa m ³ /kg-mole °K
T_A	=	temperature of the ambient air which enters the tank, °K
$T_{\rm V}$	=	temperature of the air-vapour mixture in the vapour space prior to the air ingress, °K

The input of an incremental amount of ambient air to the tank changes the temperature of the vapour space and the degree of vapour saturation in the vapour space. These changes cause some of the stored liquid to evaporate and for some exchange of heat with the stored liquid until an approximate state of equilibrium is achieved. If the available volume of the vapour space is neglected, the number of moles of air-vapour mixture resulting from this process may be determined using the following relation:

$$n_V'' = n_V + \Delta n_A + \Delta n_V = \frac{P_A V_V}{RT_V} + \frac{P_A \Delta V}{RT_A} \left(\frac{1}{1 - xK_S}\right)$$
 Equation 19

Where:

n_V'' = number of moles of air-vapour mixture at equilibrium following the incremental volume of liquid removal, kmole
x = mole fraction of vapours in the air-vapour mixture at saturation conditions, kmole/kmole
K_S = vented vapour saturation factor, dimensionless

 $\Delta V = volume of the incremental amount of liquid removed from the tank, m³$

However, the total moles of gas that the can be held in the enlarged vapour space at atmospheric pressure is:

$$n_{max} = \frac{P_A(V_V + \Delta V)}{RT_V}$$
 Equation 20

The difference between this amount and the amount given by n_V'' is approximately equal to the air-vapour mixture displaced from the tank due to thermal and evaporative vapour growth. Thus, the emissions of product vapour may be estimated using the following relation:

$$n_{S} = n_{V}^{\prime\prime} - n_{max} = \frac{P_{A}\Delta V}{RT_{A}} \left(\frac{1}{1 - xK_{S}}\right) - \frac{P_{A}\Delta V}{RT_{V}}$$
 Equation 21

Where:

 $n_{\rm S}$ = standing storage losses due to thermal and evaporative growth, kmole

This equation may be expressed in the form of a standing loss equation as follows:

$$L_{S} = \frac{P_{A}M_{V}Q}{R} \left[\frac{1}{T_{A}} \left(\frac{1}{1 - xK_{S}} \right) - \frac{1}{T_{V}} \right]$$
 Equation 22

Where,

Ls	=	standing storage loss, kg/y
$\mathbf{P}_{\mathbf{A}}$	=	ambient pressure, kPa
$M_{\rm V}$	=	vapour molecular weight, kg/kg-mole;
Q	=	annual net throughput (tank capacity $[m^3]$ times annual turnover rate), m^3/y
R	=	the ideal gas constant, 8.3145 kPa m ³ /kg-mole °K
Х	=	mole fraction of vapours in the air-vapour mixture at saturation conditions, kmole/kmole
Ks	=	vented vapour saturation factor, dimensionless
T_A	=	temperature of the ambient air which enters the tank, °K
T_V	=	temperature of the air-vapour mixture in the vapour space prior to the air ingress, °K

A further refinement of Equation 22 could be made to account for possible vapour condensation effects as the vapours change temperature in passing through the vent system. This will be evaluated as part of the next phase of this study.

3 OVERVIEW OF THE MONITORING RESULTS

The atmospheric emissions from an underground storage tank were continuously monitored for a 6-week period beginning on 14 February 2011. The monitoring was conducted using a custom vent emission monitoring system (VEMS) designed to detect and measure hydrocarbon emissions from the tank during both active and inactive periods without affecting the vent behavior. Additionally, a temporary data logging system was installed to retrieve and log data from the automatic liquid level gauging system which existed on the monitored tank. Wireless communications were used to remotely access the VEMS and tank data acquisition systems via a secure Internet connection. The data from the automatic gauging system were logged once every 8 seconds throughout most of the monitoring period. The data from the automatic gauging system were logged once every 2 minutes which was the greatest polling frequency achievable.

A detailed description of the VEMS is provided in Appendix I (Section 6.0) and the detailed monitoring results are presented in a series of graphs in Appendix II (Section 7.0). Overall, the VEMS performed well and was able to measure the emissions during periods when the tank was inactive, when gasoline was being dispensed and when gasoline deliveries were being received.

Table 1 presents a summary of the total measured emissions that occurred each day during the monitoring period, and compares these results to the values that would be estimated using the current API algorithm for a free-venting fixed roof storage tank, and to the values that would be estimated by assuming saturated conditions in the vapour space (due to convective mixing effects) for the purpose of calculating working losses, and using Equation 22 to estimate the standing losses. Two sets of measured values are presented: "Measured Emissions" and "Corrected Measured Emissions". The "Measured Emissions" were determined by applying the following relation to the relevant measurement data:

$$m = \sum x \frac{P_A M_V}{RT_V} V_V \Delta t$$
 Equation 23

Where,

т	=	mass of gasoline vapour emitted on a given day, kg
x	=	mole fraction of gasoline vapour in the vented gas as determined from the oxygen
		readings (see Section 6.3.1.4), kmole/kmole
P_A	=	measured barometric pressure, kPa
M_V	=	measured molecular weight of the gasoline vapours at -3°C, kg/kmole
	=	64.563 kg/kmole (see Table 3 in Section 8: Appendix III – Gasoline Vapour Analysis)
R	=	ideal gas constant, 8.3145 kPa m ³ /kg-mole °K
T_V	=	measured exit vent gas temperature, °K
V_V	=	measured exit vent gas velocity for periods when the velocity is positive (i.e., flow is out of
		the vent stack), m/s
∆t	=	time step between each set of readings on a given day, s

The "Corrected Measured Emissions" were determined using the same relation as the "Measured Emissions" (i.e., Equation 23) except the value of x was set to 0.2420 (see Table 3 in Section 8: Appendix III – Gasoline Vapour Analysis) for all cases where the measured value of x was determined to be greater than 0.2420 (i.e., the saturation level of gasoline vapours in the tank vapour space).

For the time period considered (31 days), the measured hydrocarbon emissions totaled 595 kg and the corrected value totaled 405 kg. In comparison, the API algorithm for fixed-roof storage tanks estimated a total of 186 kg (only 31 percent of the totaled measurement result and 46 percent of the totaled corrected values), and this amount is attributed strictly to working losses. The modified algorithm estimated 501 kg (84 percent of the measured value and 124 percent of the corrected value); 200 kg was estimated to be due to working losses and 301 kg was estimated to be due to standing losses. The fact the modified algorithm overestimates the amount of emissions when compared to the corrected measurement results may be due to condensing of some of the vapours as they flow through the vent system and encounter temperatures colder than in the tank vapour space. Condensation effects would tend to be most important during standing periods in cold weather. The high velocities that occur during filling of the underground tank (e.g., > 30 m/s) would reduce the potential cooling of the vent gas and may be sufficient to entrain any aerosols that may form.

As discussed in Section 2, the existing API correlations are based on an inherent assumption that stratified conditions exist in the vapour space of a fixed-roof storage tank, except during periods when the tank is being filled. During the filling periods, the air-vapour mixture physically displaced from the tank is assumed to be saturated or nearly saturated with vapours from the stored liquid. A factor is used to decrease the degree of saturation as a function of annual turnovers for tanks that have greater than 36 turnovers per year. Based on the sales volume during the monitoring period and the capacity of the tank (100,000 L), the annual number of turnovers the tank experiences is 39.5. During standing or inactive periods, API assumes a negative vertical vapour concentration gradient (i.e., the vapour concentration decreases with the vertical distance above the liquid surface), and the average degree of saturation in the vapour space is decreased with increasing vapour pressure of the product and the amount of vertical outage. Moreover, for the specific case of underground storage losses API assumes no breathing or standing losses due to the stable temperature of the ground. This scenario is depicted in Figure 2 and is perhaps most reflective of summer conditions when there would be a positive vertical temperature gradient, which would contribute to stratification in the vapour space.

The developed algorithm assumes there is perfect convective mixing in the vapour space which results in saturated vapour conditions (see Figure 3). Furthermore, the modified algorithm allows for the impact of vapour growth due to both thermal effects (i.e., temperature differences between air entering the tank and the stored product) and the displacement of gases from the vapour space as product evaporates. It is clear, based on the reasonable agreement between the measurements and the proposed estimation technique, that these effects can be readily accounted for and the existing algorithms can be easily adapted for this purpose.

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3/6/2011 0 10,118.70 -18.75 -3.60 32.62 20.25 0.00 0.00 0.00 0.00 10.44 1	10.44										
3/7/2011 0 12,536.10 -18.33 -2.84 18.64 14.28 0.00 0.00 0.00 0.00 12.95 1	12.95										
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Table 1: Comparison of measured and estimated evaporation losses for an underground gasoline storage tank.												
Date	Delivery	Sales	Average	Average	Measured	Corrected	API Emissions			Modified Algorithm		
	(Litres)	(Litres)	Ambient	Product	Emissions	Measured	Working	Standing	Total	Working	Standing	Total
			Temperature	Temperature	(kg)	Emissions	Losses	Losses		Losses	Losses	
			(°C)	(°C)		(kg)	(kg)	(kg)	(kg)	(kg)	(kg)	(kg)
3/26/2011	0	10,009.30	-5.60	-0.37	17.90	10.50	0.00	0.00	0.00	0.00	8.85	8.85
3/27/2011	33500	9,244.90	-3.67	0.10	21.92	13.64	19.20	0.00	19.20	20.73	7.99	28.72
Total	321,194.00	330,394.40			595.45	404.96	185.50	0.00	185.50	200.29	300.80	501.09





4 <u>CONCLUSIONS AND RECOMMENDATIONS</u>

4.1 Conclusions

- (1) A standalone vent emissions monitoring system (VEMS) has been developed and deployed to continuously measure the evaporation losses from an underground gasoline storage tank at a retail gasoline station during both active and inactive periods under winter conditions. The purpose of the monitoring was to develop a better understanding of the mechanisms contributing to these emissions. In particular, it was known that evaporation losses from underground gasoline storage tanks are greater in the winter than in the summer, which is not predicted by current evaporation loss estimation methods. The monitoring results indicate that during winter conditions, natural convective mixing occurs in the tank vapour space due to the negative vertical temperature gradient.
- (2) The current practice of assuming zero standing losses from underground storage tanks is invalid in these circumstances as the monitoring results show significant evaporation losses during cold weather standing periods. A modification to the existing algorithm has been proposed to estimate the amount of emissions in these situations. The results show good agreement with the measurement results; although, further refinements may be warranted to account for condensation effects in vent system and possibly the volume of the vent line. A comparison of the results using the current evaporation loss algorithm with the proposed enhancement shows that the current method may be underestimating the actual emissions by a factor of 2 or more. The proposed modification agrees to within 23 percent of the corrected measurement results.
- (3) Clear indications of the presence of breathing losses during standing periods include the following: positive vapour flow from the vent stack (see Figures 17 and 18 in Appendix II), near saturated vapour conditions at the top of the vent stack compared to extremely low values during product dispensing periods (i.e., when ambient air is being drawn into the tank) (see Figure 19 in Appendix II), and warmer than ambient temperatures in the vent stack than during product dispensing periods (see Figure 23 in Appendix II).
- (4) While strong indications of convective mixing have been shown to exist during winter conditions, it is reasonable to expect that this would occur in all tanks (underground and aboveground) wherever the stored product is warm relative to the ambient air. Situations where this may happen include heated storage tanks and tanks which receive hot product (e.g., from a hot process or source, heated pipeline or a pipeline where the product becomes heated due to friction losses). This also raises questions as to whether standing losses may be greater than currently thought for fuel tanks on mobile sources.

4.2 <u>Recommendations</u>

- (1) It is recommended that monitoring of the underground gasoline storage tank be continued to verify and quantify evaporation losses during all four seasons, and to determine when the transmission from a convective vapour space to a stratified vapour space occurs. Additionally, the learnings from this work should be extended to potentially improve the algorithms used to estimate evaporation losses from other types of storage tanks (e.g., heated aboveground tanks and floating roof tanks).
- (2) Indications are that the hydrocarbon vapour concentrations determined from the VEMS O₂ and sound speed data overstate the actual hydrocarbon vapour content of the vent gas (see Section 7),

and that the actual RVP of the gasoline is less than the values reported by the fuel supplier (possibly due to product weathering during upstream handling and transportation) (see Section 8). To resolve these apparent discrepancies, the vapours in the vent stack need to be sampled, analysed and the results compared to the vapour concentrations determined from the O_2 , sound speed and RVP data readings at the time of the sampling. Based on this information, a strategy for more accurately monitoring hydrocarbon vapour concentrations in the vent gas should be devised.

- (3) The importance of vapour condensation in the vent system should be evaluated for situations where the vent gas cools in passing through the vent system (e.g., for buried underground tanks during the winter).
- (4) The VEMS should be applied to continuously monitor emissions from a well-behaved aboveground fixed-roof tank for which accurate liquid-level monitoring data are available.
- (5) A system for continuously monitoring the conditions in both internal and external floating roof storage tanks should be devised.
- (6) Based on an improved understanding of the mechanisms contributing to evaporation losses from storage tanks, efforts should be undertaken to develop improved emissions management strategies for these sources.

5 <u>REFERENCES CITED</u>

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