GHG EMISSIONS FROM OIL SANDS TAILINGS PONDS:

Overview and modelling based on fermentable substrates

PART I: REVIEW OF THE TAILINGS PONDS FACTS AND PRACTICES

Zvonko Burkus*, Justin Wheler and Shan Pletcher

PART II: MODELLING OF GHG EMISSIONS FROM TAILINGS PONDS BASED ON FERMENTABLE SUBSTRATES

Zvonko Burkus

Alberta Environment and Sustainable Resource Development (AESRD)

* Zvonko Burkus, Ph.D.
Mine Water Policy Specialist
Land Policy (oil sands)
Alberta Environment & SRD

zvonko.burkus@gov.ab.ca
Tel 780-643-0811
Fax 780-422-4192
10th floor, Oxbridge Place
9820 - 106 St.
Edmonton, AB, T5J 2J6
Canada

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REPORT SUMMARY

Surface mining of Alberta bitumen is probably the biggest mining operation in the world. It has a significant environmental footprint with about 840 km^2 total active footprint in 2012 and 895 km^2 in 2013 (Fig 1) (AESRD 2014). Of this area, tailings ponds covered 239.3 km^2 in 2013 including dykes, berms and beaches. Reclaimed tailings areas covered about 19.2 km^2 leaving 220.1 km^2 in active pond structures. However only 88.5 km^2 is covered with process-affected water within ponds, which is about 40.2% of the total pond surface area, or 9.9% of the total active footprint that includes cleared, disturbed and other categories.

Extraction and upgrading/refining of mined bitumen are energy intensive operations that require significant fuel consumption resulting in emissions of greenhouse gases (GHG) – carbon dioxide, methane and nitrous oxide. Emissions of nitrous oxide are production/machinery related, originating mostly from combustion processes such as diesel fuel burning in heavy trucks. Nitrous oxide emissions were considered as insignificant in GHG emissions from tailings ponds.

The less understood part of GHG emissions from surface mining operations is methane and carbon dioxide production from fluid tailings ponds, primarily as a result of microbial biodegradation/fermentation of lost diluent. The diluent originates in froth treatment tailings that also contain significant concentrations of residual bitumen, and associated heavy minerals that contain pyrite whose potential oxidation may be a cause of carbon dioxide emissions.

The quantity of the lost diluent and its historical changes and future projections are not well understood by general public and academia despite data provided by the operators and regulators. In Part I, this paper will explain past, current and future practices that affect greenhouse gas (GHG) emissions from tailings ponds and present a few facts that contrast with assumptions commonly made in literature regarding fugitive emissions from oil sands mines.

Part I demonstrates that due to the diversity of operations and project history, it is not accurate to assess industry average GHG intensity from tailing ponds based on the measurement of one project and one point in time, and assume that it is applicable to others. Both directly measured historic data such as diluent losses and GHG reports made by companies as well as companies' tailings management plans are now available. Those reports take into account the unique facility processes, the variety of current and future tailing treatment technologies applied, and Closure and Reclamation Scenarios expected.

Part I also shows that current measurement of emissions from ponds using flux chambers is better than high level estimates. Fugitive GHG measurements are continuously improving in terms of frequency and coverage of sampling campaigns and accuracy of the instruments, but still have uncertainties especially when projected forward in time. Historically, GHG emissions intensity from oil sands has decreased and it still has a potential to decrease further.

Part II proposes a Base GHG Model for calculating future GHG emissions. This modelling effort presents a different approach to calculate GHG emissions from ponds based on fermentable substrates with a focus on diluent, which has been shown to be the most bioavailable part of tailings. It shows how it may be possible to decrease emissions by affecting fermentation

pathways and applying processing or treatment technologies. Different scenarios based on the Base GHG Model show potential pathways toward lowering the Alberta bitumen GHG profile.

This modelling approach, as compared to the published literature is more realistic, and allows easy adjustment due to changing technologies. The Model could work together with the current measurement and reporting system to address potential time and place sampling bias of local GHG measuring campaigns. It may also help to quantify future GHG emissions. Initial application of the Model conservatively shows **total average GHG (CO_2+CH_4) fugitive emissions intensity from ponds to be below 1.0 g CO_2eq/MJ** bitumen produced, and distinguishes emissions from different producers based on the type of diluent and the associated carbon content and physical behavior such as volatility and solubility in water. The Model also demonstrates the influence of applied or potential tailing technologies on changing GHG profiles.

The Base GHG Model will need further validation and adjustment for ensuing technological changes. Its simplicity almost guarantees further application, but its application in the field and by regulators still needs to be determined.

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Caroline Bampfylde provided the most recent readings for land disturbed and pond surfaces as well as Figure 1 (Copyright Government of Alberta 2014).

DISCLAIMER

The proposed model in this publication has not been used or adopted by Alberta Environment and Sustainable Resource Development (AESRD) for any official regulatory purpose or policy development. It is only one of the tools that, after successful validation, might be used in combination with other methods to evaluate future area fugitive emissions from oil sands tailings ponds.

The Base GHG Model or its derivatives cannot be used for any commercial purpose without written permission of Dr. Zvonko Burkus.

PART I: Review of the Tailings Ponds and Practices

1 INTRODUCTION

As the production of bitumen from Alberta oil sands grows in terms of both production and environmental footprint (Fig 1), so does the negative attention from some NGOs and even from the scientific community. One of the main points in those critiques is that oil sands create excessive greenhouse gas (GHG) emissions. It is impossible to say that emissions from bitumen are low due to the nature of bitumen extraction operations. The most recent study by Jacobs Consultancy (2012) compared life-cycle GHG emissions from Alberta bitumen to other oils in the world including both light and heavy oils.

The Jacobs Consultancy (2012) analysis of bitumen production and refining shows that bitumen GHG profile is similar to other heavy oils such as Maya, or Venezuela's Bachaquero except for one small detail – fugitive emissions. Those emissions were taken from Yeh et al. (2010) at their face value and require a thorough analysis.

Canada is one of rare jurisdictions that have publically accessible, third party verified data on GHG and other emissions from large emitters. There are provincial and federal reporting programs, *Specified Gas Reporting Regulation* (Government of Alberta 2004) and Greenhouse Gas Reporting Program, respectively.

To shed light on the situation, Part I of this paper will discuss a few aspects of bitumen production related to fugitive GHG-s:

1) Review of existing literature on pond emissions
2) Origin and history of pond methane emissions
3) Types of tailings and tailing processing technologies
4) Overview of mine plans and closure and reclamation plans
5) Provincial and Federal GHG measuring and reporting system
6) Discussion of emissions measurement uncertainty

2 LITERATURE REVIEW

Reports on emissions in peer reviewed literature started with the Holowenko et al. (2000) publication with further research and publications described in Section 2. This section covers literature that went far enough to calculate intensity of GHG emissions or describe some important details about oil sands.

Yeh et al. (2010) is the most cited peer reviewed report on methane emissions from tailings ponds. Its underlying assumptions are based on another peer reviewed paper, Holowenko et al. (2000), which reports measured methane emissions from Syncrude Canada Ltd. (Syncrude) MLSB pond (Mildred Lake Settling Basin) in 1998. Based on those measurements, Yeh et al. (2010) assumed 15 years lag time in methane bubbling and about 35 years of intensive bubbling, which are potentially reasonable assumptions for Syncrude's diluent. One should have in mind

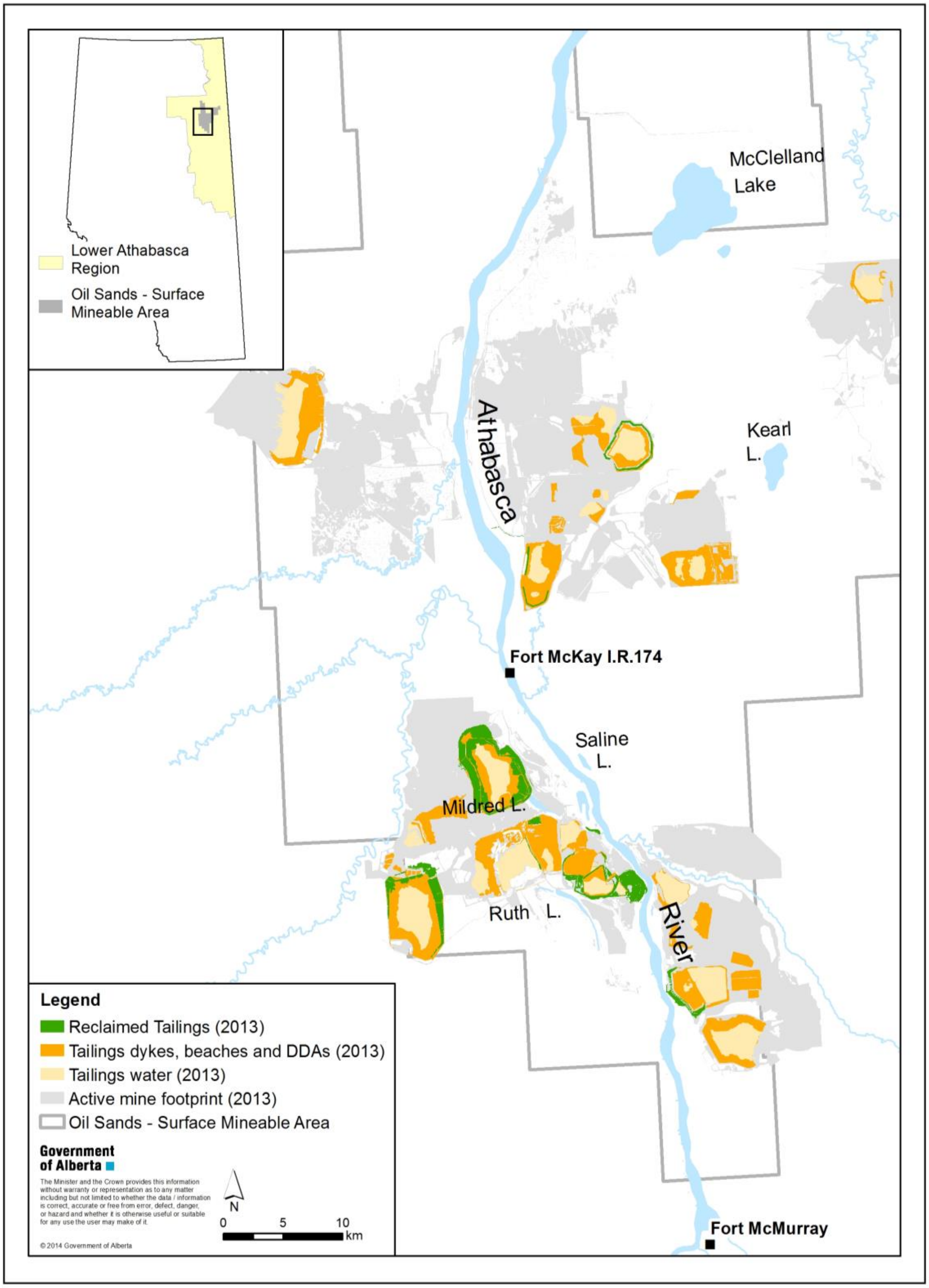

Figure 1. Map © of oil sands surface mines and tailing ponds north of Fort McMurray.

that currently this pond receives froth treatment tailings (FTT) from Aurora North mine and all FTT are deposited (beached) on the south shore of the MLSB basin.

The following assumptions are not consistent with current knowledge of the industry. Yeh et al. (2010) assumed that at the end of mining, 25% of Syncrude's lease will be occupied by fluid ponds and all of them will be bubbling at the same rate. Their estimate of GHG emissions intensity applied to all oil sands mines was 2.6 g CO_2eq/MJ of bitumen. However, Syncrude has additional working ponds (Table 1) that do not contain FTT, none of which are intensively bubbling. The only spot where some reduced bubbling appeared is Base Mine Lake (BML) due to transfer of some MFT (mature fine tailings) from the froth-receiving MLSB to BML. Yeh et al. (2010) also included relatively high estimated loss of carbon from salvaged organic matter at the level of ~1.2 g CO_2eq /MJ, which brings the total CH_4 emissions estimate to 3.8 g CO_2 eq /MJ of bitumen. GHG-s from organic matter need separate validation and are not discussed in this paper.

The insight into pond sizes and types (Table 2) shows that water surface area is often below 50% of the total pond surface area that also includes dykes, berms and beaches. Dykes and beaches, although made of tailings sand, are not a significant source of CH_4 emissions since they contain minimal lost bitumen and practically no diluent. Thus these surfaces should have been taken out of assumptions made by Yeh et al. (2010), so that correct active pond surface could be taken into account.

Jacobs Consultancy was contracted by Alberta Department of Energy to produce a study titled *EU pathway study: Life cycle assessment of crude oils in a European context* (Jacobs Consultancy 2012). Jacobs used the same assumptions about GHG fugitive emissions from Yeh et al (2010), as described previously. The study did not take into account any other public source of GHG intensity estimates such as facility reported measurement data or mine modelling calculations although they were available at the time.

TECK Resources submitted a mine application in 2011 (TECK 2011a) for its Frontier project. They estimated that from the overall mine GHG emissions, 60% of GHG will be coming from stacks, 20% from mine fleet, 15% from mine face and only 5% from tailings areas based on the total CH_4 emissions of 112.9 t/day and projected bitumen production of 310.5 Kbbl/day.

TECK predicted that total fugitive CH_4 emissions (mine face + tailings) will be 1.49 g CO_2eq/MJ assuming 25 as global-warming potential (GWP) multiplication factor for methane, or 1.25 g CO_2eq/MJ if this factor is 21. Pond CH_4 emissions are predicted to be roughly ¼ of these values. TECK plans to start the project in 2021 and use light paraffinic diluent.

TECK (2011a) also assumed that 50% of the solvent lost to the pond will be lost as volatile organic compounds (VOC-s). From the other 50% of carbon that reaches pond, methane production will be 21% by weight based on TECK's internal Clearstone (2011) reference.

An update to TECK estimated future emissions was prepared in the Supplemental Information Response (TECK 2013). The maximum GHG emissions were estimated about 214 Kt of CO_2 e in 2052 using 21 as GWP factor for methane.

TECK (2011b) also serves as a source of data about other oil sands mines. In TECK (2011b) report, Table 3A-90 shows that majority of diluent (>60%) in Suncor Energy Inc. (Suncor) ponds is composed of light hydrocarbons (C_5 to C_8) in addition to about 20% of heavier fractions (C_9 to C_{16}) and about 5 to10% BTEX. This diluent composition is used to correspond to N8 naphtha in the Base GHG Model (PART II, Table 1) as a light naphtha diluent.

Data for Syncrude diluent (Table 3A-91) depict about 86% of C_9 to C_{16} fraction, 3 to 4% of BTEX and about 5% of light (C_5 to C_8) fraction. Paraffinic producers (Table 3A-92) have diluent with ~95% of C_5 to C_8 fraction; thus C_6 is a good conservative representative of that diluent. Shell Canada Energy (Shell) plans to use the diluent that is a mix of C_5 and C_6 with the density of 0.645 to 0.655 g/cm^3 (15^{o}C) due to the presence of pentane. It is significantly less than we assumed in this study (0.685 g/cm^3).

Siddique et al. (2011) calculated the potentially fermentable materials ($<C_{19}$ fraction) from bitumen to be ~4,560 t a year for the Syncrude Mildred Lake (ML) project. They overestimated MFT loss since the total volume of MFT in the MLSB (Mildred Lake Settling Basin) was misunderstood as annual production. It is relatively easy to estimate bitumen loss as roughly 9-10 % of the production. Average Syncrude production was almost 380,000 bbl/day in 2011 (AER 2013), which would result in about 35,000 bbl/day of bitumen lost to tailings with annual loss of about 12.8 million bbl, or roughly 2 Mt, assuming a bitumen density of 1.0 (1 bbl = 159 L). The presence of 0.04% of $<C_{19}$ would mean the loss of ~800 t vs. ~4,560 t assumed by Siddique et al (2011). This means that Siddique et al. (2011) overestimated the $<C_{19}$ portion of annual bitumen loss by more than 5 times. The actual loss of bitumen as the difference between mined and produced was even less than this estimate (AER 2013).

Siddique et al. (2011) used Roberts (2002) work and established the CH_4:CO_2 ratio for GHG production from short aliphatic hydrocarbons (Eq. 4 to 6, Part II). The theoretical maximum of CO_2 production as part of GHG gasses is 42% to 46% (w/w) when originating from the C_6 to C_{16} aliphatic hydrocarbons, with the rest 54% to 58% becoming CH_4.

Siddique et al. (2011) also measured fermentation of nC_{14}, nC_{16} and nC_{18} (linear hydrocarbons) to be 80 to 84% of the theoretical maximum that was established by Roberts (2002). Siddique et al. (2006) reported that nC_6 was more resistant to methanogenesis than longer, i.e. nC_{10} molecules.

Previous calculations (Siddique et al. 2006) show that 77 to 79% of short chain alkanes were transformed into methane, while Zengler et al. (1999) measured only 64% of methane from the nC_{16} carbons added to an enrichment culture.

While Siddique et al. (2011) added pure straight chain alkanes that could be free, emulsified or attached to the surface of clays and bitumen, it is expected that natural $<C_{19}$ fraction will contain iso-forms and be present at or below the bitumen surface due to its hydrophobicity. Thus, even present $<C_{19}$ fraction may not be bioavailable and bacterial access to such material warrants further research. Natural fractions present in ore deposit below the mine surface could be also fermented and liberated as methane, but over a significantly longer time period.

Brandt (2012) discussed different models that evaluate LCA (Life-Cycle Assessment) of GHG emissions from different oils. He found GHGenius as the best model for calculating industry's GHG average because it also covers other emissions such as fugitive and land use. He also recommended that

> *Future work in oil sands GHG emissions should move toward modelling the emissions of specific process configurations. For example, models should be used to model emissions by project and compare those modelled emissions to reported emissions estimates.*

which is exactly what this paper is trying to do in Part II. Interestingly, Brandt (2012) acknowledges the existence of reported emissions estimates, but those were not mentioned in Yeh et al. (2010).

The Nodelcorp report (Nodelcorp 2005) prepared for TOTAL Joslyn mine is a less known report based on some measurements and engineering calculations. In this report the sum of mine face, tailing and overburden dump emissions are 291,438 t/year of CO_2eq. These emissions are equivalent to ~1.31 g CO_2 eq/MJ assuming 6,100 MJ/bbl of bitumen, which is far less than the 3.8 g/MJ CO_2 eq assumed by Yeh et al. (2010).

Third party measurements of pond emissions reported through Alberta's *Specified Gas Emitters Regulation*, *Specified Gas Reporting Regulation*, and Canada's Greenhouse Gas Emissions Reporting Program (GHGRP), or engineering estimates do not appear to be considered by literature reviewed.

Alberta Environment and Sustainable Resource Development (AESRD) data from an industry report (Syncrude 2012) show that the ratio of GHG emissions of methane from mine face, ponds and other fugitive sources is roughly 50:40:10, respectively, but the only producers with significant reported methane emissions are Suncor and Syncrude. Canadian Natural Resources Ltd. (CNRL) has a young mine, while Shell uses paraffinic diluent whose propensity to create methanogenic emissions in ponds is not well understood. Recent research found delays in biodegradation of most iso-paraffins due to longer acclimation by indigenous microbes, but almost no recalcitrance (Siddique, personal comm.).

The data for Syncrude, that were taken to represent the whole industry by Yeh et al. (2010), are submitted to the GHGRP and can be found via a direct Environment Canada link http://www.ec.gc.ca/ges-ghg/donnees-data/index.cfm?do=facility_info&lang=en&ghg_id=G10187&year=2012

The total Syncrude methane CO_2 eq emissions in 2010 were 627,410 t for both Mildred Lake and Aurora North projects using a GWP of 21. Divided over 20.3 Mm^3 of bitumen production (AER 2013, ST 39 report), CH_4 CO_2 eq turns out to be about 0.81 g/MJ if 21 is used for methane GHG effect, or 0.96 g CO_2e/MJ with the factor of 25.

These measurements are also reported to the Alberta provincial Single Window Information Management System (SWIM), which combines Federal and Provincial reporting of GHG-s. Since they are based on true measurement in the field, usually by Clearstone Engineering, they are far more reliable than any estimate based on past emissions applied to future closure and reclamation scenarios.

AER (2010) limits diluent loss to 4 volumes per 1,000 volumes of produced bitumen. This rule was made in the 2002 to 2004 period and applied on ongoing basis. Newer mines, as shown in Part II of this publication, usually take 2 to 3 years to stabilize technology and achieve such diluent loss. Diluent loss as well as bitumen mined and produced are reported by each company and published in the AER's ST 39 or ST 43 statistical series reports.

3 WHY PONDS BUBBLE?

Holowenko et al. (2000) performed field measurements on the Mildred Lake Settling Basin (MLSB) on Syncrude site in 1997/1998. They measured emissions of methane as ~12 g/m^2 but have not assumed that all the surface of MLSB pond was bubbling. Thus even at that time they calculated methane emissions to be ~6 g/m^2 of pond surface. They found out that diluent is the main source and cause of bacterial fermentation of residual hydrocarbons. They also discovered the role of sulfate depletion in the delayed timing of methane emissions.

Other references (Siddique et al. 2007, 2008, 2011) addressed the part of diluent that can be fermented by methanogens and found significant delay in degradation of more complex or longer-chain hydrocarbons. Methane production from n-alkanes and BTEX was modelled, but there was no attempt to express that as GHG intensity in CO_2eq/MJ of bitumen, although such a procedure could be fairly straightforward.

Guo (2009) provided some history of the MLSB pond and specified that fermentation, temperature and densification rates increased in 1994 and later. Part of the reason for the visible onset of methanogenesis was the change in tailings discharge practices. In 1994 warm tailings were discharged mostly on the south side keeping temperature higher and constant. Froth Treatment Tailings (FTT) are the warmest tailings produced. This event speeded up the onset of intensive bubbling but it only affected the timing of bubbling. In different terms, if tailings would be colder, gas production would be delayed. Guo (2009) had access to original Syncrude measurement of the gas content in deeper layers of MFT. He also reported that gas contents at both the South and North sides of the MLSB were lower in 2000 and 2002 than in 1999. Holowenko et al. (2000) took samples in summers of 1997 and 1998 when bubbling was more intensive. This change clearly demonstrates variability in gas production, implying that historical measurements from one pond cannot be extrapolated to other ponds and producers or even to the same producer over time.

Guo (2009) also reported a change in the pH of MFT from 1992 to 2003 with the deeper layers changing from pH = 8.6 to pH = 7.8, which was attributed to CO_2 dissolution. Indeed, the south station measured an increase in HCO_3^- ion from 720 mg/L to 1,600 mg/L over 1991 to 2003. Sulfate concentration at the same station decreased from ~40 mg/L in 1985 to ~20 mg/L in 1995, or lower in deeper layers. Chloride increased over the same period. Part of the reason for chloride increase could be more brackish ore supply and/or continuous recycling. Naphtha content at the south station also decreased from 1996 to 2002 meaning that the Holowenko et al.

(2000) measurements actually covered the period of higher naphtha concentrations in the MLSB and higher potential for bubbling. It also demonstrated the need for the time component in the understanding and measurement of GHG emissions.

Different types of tailings have different composition. As shown by Holowenko et al. (2000), Fedorak et al. (2002, 2003) and Siddique et al. (2006, 2008, 2011), the main reason for the fermentation is lost diluent. Diluent is not present everywhere, in every type of tailings or in every pond. This contradicts Yeh et al. (2010) assumptions that extrapolated the Syncrude data to all ponds in the oil sands.

3.1 Facts about Ponds

Froth treatment tailings (FTT) carry lost diluent which is fermented by microorganisms into GHG-s. These tailings are also called TSRU (tailing solvent recovery unit) or NRU (naphtha recovery unit) tailings by different producers. It is not an intention of this paper to give detailed descriptions of the types of tailings, but it is important to state that only ponds that receive FTT (Table 1) will undergo intensive bubbling. In Syncrude's case that pond is Mildred Lake Settling Basin (MLSB). It was activated in 1978 and receives FTT from both mines – Aurora North (AN) mine and Mildred Lake. Thus ponds at Aurora North receive no FTT and do not have intensive bubbling, contrary to assumptions by Yeh et al. (2010). Similarly, all FTT from the Shell Jackpine project are deposited at the Muskeg River Mine (MRM).

Pond sizes (Table 2) show that pond water surface in 2008 were approximately 63.4 km^2, or slightly less than 50% of total pond surface that includes dykes, berms and beaches. Dykes and beaches, even if made of tailings sand would be a negligible source of emissions since they contain minimal lost bitumen and practically no diluent. Thus these surfaces should have been taken out of assumptions made by Yeh et al. (2010). **Pond water surface areas** on the Syncrude site were not measured, but assumed to be equal to the pond areas and that bubbling surfaces will cover about 25% of the total lease.

If this surface were used, then the Yeh et al. (2010) number for pond methane CO_2eq intensity would be ~1.37 g CO_2eq/MJ, which, although improperly derived from emissions prior to 2000, is a much more realistic number. Syncrude (2011a) submits facility data as part of the compliance report under the *Specified Gas Emitters Regulation*. The 2011 report indicates that 41% of the MLSB water surface area is actively bubbling, which represents 14% of total pond water surface area on the both Syncrude mines.

Due to differences in diluent chemical composition and deposition practices, the results from one producer cannot be extrapolated to other producers. As shown in Table 1, Syncrude, Shell and CNRL beach their FTT, while Suncor (2010) uses subaqueous deposition to reduce VOC emissions. Suncor is also currently using thin lift deposition to dry mature fine tailings (MFT) from its ponds. This encourages evaporation and aerobic decomposition of residual diluent. MFT was dried on a few hundred hectares in 2012 as part of Suncor's tailing reduction operation – TRO.

Table 1. Ponds and their fluid tailing content as of June 2012.
Sourced from Tailings Management plans at AER (2014) website (former ERCB), and 2011 Reclamation and Closure Plans.

Company	Mine	Pond	Type of tailings	Comment
Syncrude	Mildred Lake	MLSB (ETF)*	FTT, FFT/MFT, S	FTT beached
		SWSS	MFT, S	
		West-in-pit (BML)	MFT	Material from MLSB and EIP
		East-In-Pit	CT, MFT	Off spec to BML, deposition ended
		SWIP	CT, MFT	
		NMSP	CT, MFT, S	New pond in pit
	Aurora North	ETF	FFT/MFT, S	Froth sent to Mildred Lake
		East Pit	FFT/MFT, S, CT	Froth sent to Mildred Lake
Suncor	Millennium &NSE	Pond 1	In reclamation*	MFT pumped to other ponds
		Pond 1A	OSPW, MFT	Old MFT, receives water from 2/3
		Pond 2/3*	FTT	Subaqueous deposition
		Pond 5	CT	Off spec dried on beaches - TRO
		Pond 6	CT	Off spec dried on beaches - TRO
		Pond 7	CT	A lot of MFT and off-spec CT
		Pond 8A	CT, MFT	Beaches used for TRO
		Pond 8B	MFT	Accepts TRO leachate, will be mined
Shell	MRM	ETF*	MFT, TT, FTT, WT	FTT beached, interlayered with TT and S
		Cell 1*	FTT, MFT, WT	In-pit
	Jackpine	ETF	TT, MFT, S	Froth sent to Muskeg River Mine
CNRL	Horizon	ETF*	MFT, FTT, S	FTT beached
Imperial	Kearl	ETF*	MFT, FTT, S	Start in late 2012, FTT beached

* Ponds receiving or received FTT, thus bubbling or prone to bubbling and GHG emissions

ETF ─ external tailing facility

NA ─ not applicable

CT ─ composite tailings

TT ─ thickened tailings

FTT ─ froth treatment tailings

FFT/MFT ─ fresh Fluid Fine Tailings to consolidate into MFT
WT – whole tailings

S – Sand, sometimes denoted as CST ─ coarse sandy tailings, or SCT ─ straight coarse tailings
MRM – Muskeg River Mine
OSPW – Oil Sands Process-affected Water

Table 2. Examples of approximate process water vs. total pond surfaces.
From AESRD (2013) data; in square kilometres.

Pond	Water surface	Pond area	Water vs. pond	MSL Area
	km^2	km^2	%	km^2
Syncrude				440.4 [1]
BML	7.26	8.1	89.6	
MLSB	9.54	28	34.1	
SWSS	8.35	30	27.8	
AN-ETF	5.36	12.3	43.6	
Suncor				220.9
STP	8.74	23.51 [2]	37.2	
Pond 8A	1.15	4.98	23.1	
Pond 8B	7.15	8.39	85.2	
Shell MRM ETF	3.70	13.16	28.1	123.3
CNRL ETF	8.8	25 [3]	41.9	186.6

MSL – mineral surface lease

[1] Includes both Mildred Lake and Aurora North mines

[2] Suncor TRO Application 2010

[3] Pond area at full size

4 TAILINGS AND TECHNOLOGIES

More detailed reviews of tailing types and technologies are described by BGC (2010) and Sobkowicz (2012). This short overview relates to tailing types and technologies from the composition and handling point of view that may influence the creation of methane and/or CO_2.

4.1 Types of Original Tailings

FTT – Froth Treatment Tailings, as already described in Section 3.1, are high in hydrocarbons and diluent, thus represent the main source of fermentable materials as well as VOC-s in surface mines. In addition, they are the main source of BTEX and poly-aromatic hydrocarbons (PAH-s) as well as heavy minerals. Some of those minerals are pyrite and siderite, which can oxidize in aerobic conditions and contribute to CO_2 emissions. Although these indirect inorganic emissions are not the focus of this review, they warrant further investigation.

CST – Coarse Sandy Tailings are composed mostly of silica sand and are depleted in bitumen (labeled "**S**" in Table 1). They are also called cyclone underflow since they are a heavy fraction that sinks during and after bitumen flotation process. This stream does not contain diluent and should not be a significant source of emissions. It is either beached or used to construct dykes or to make engineered tailings (CT). Due to low toxicity to plants, CST can also be used for reclamation as subsoil material. CST does not have significant buffering capacity and cannot neutralize acidity except for process water in pores that is used for pipeline transportation and hydraulic deposition. Once this pore water is drained or replaced by rain, the buffering ability of this tailing stream is insignificant.

FFT –Fluid Fine Tailings are fresh tailings coming out from the extraction usually containing 8 to 15% solids, which are mostly silt and clays. Original FFT do not contain diluent, but do contain most of the residual bitumen.

FFT may also contain a significant amount of other minerals such as siderite, dolomite etc. that provide significant buffering to acidification, but also a potential for inorganic CO_2 emissions. In the extraction unit they are called middlings. The term is sometimes used interchangeably with MFT (Syncrude). Recently, there is a desire to use only the term FT – fluid tailings for simplicity. If deposited into the same pond with FTT, FT may contain diluent. FT may be also created after settling of FTT when they contain diluent and elevated pyritic minerals.

MFT - Mature Fine Tailings are created from FFT after 2 to 3 years of settling and consolidation. They carry a significant percentage of bitumen that is, on a solids basis, often comparable with bitumen ore. MFT have 25 to 40% solids with 30% assumed for accounting purposes in industry reports, and also sometimes expressed as 370 kg of solids per cubic metre. Depending on the chemical composition of the pond, MFT may differ in composition from FFT; i.e. reduction processes create sulphidic minerals such as FeS that may re-oxidize if exposed to air. Microbial processes in these tailings can significantly change both mineral and pore water composition, sometimes resulting in the production of gases such as H_2S, CO_2, CH_4 and others that may reach surface of ponds if created in sufficient quantities. MFT may also originate from froth tailings. Such MFT has different composition – more diluent and more oxidation-prone minerals.

WT – Whole Tails, both cyclone overflow and underflow tailings are combined and beached. This process is applied by Shell. The chemical composition is a combination of CST and FFT.

4.2 Engineered Tailings

These are the tailings that underwent some type of treatment aside from natural processes, very often combined with the addition of coagulants or other additives.

- **TT – Thickened Tailings** are made in the plant by treating FFT with coagulants and/or flocculants in large thickeners that may also act as water clarifiers. Their main purpose is to recycle warm water and its embedded energy for extraction, resulting in energy savings. Shell and a few other producers (i.e. CNRL Horizon, Imperial Kearl) are building or planning to install thickeners. Such plants should naturally have lower GHG emissions due to energy saved. Thickeners also have an ability to recover a small amount of additional bitumen, contributing to lower overall GHG intensity due to higher bitumen capture. Flocculants, when used, however represent potential fermentable material that can be digested by bacteria and may increase GHG emissions.
- **CT – Composite Tailings** are a mix of CST and MFT with the addition of coagulants such as lime or gypsum as a source of clay-binding calcium. Segregated (off spec) material behaves like MFT but usually has higher sand to fines ratio. Flue gas desulphurization (FGD) gypsum, which is a mix of calcium and magnesium sulfate, is the most common coagulant used for these tailings. Shell plans to use alum (aluminum

sulfate) instead of FGD gypsum. Alum is an acidic salt that may change buffering capacity of tailings. If MFT used is related to a pond with residual diluent where FTT are disposed, then some methanogenic potential from these tailings may exist once the sulfate reduction is finished. (Fedorak et al. 2003). Reduction processes may significantly change the chemical composition of these tailings. They are usually deposited in-pit with almost no potential for re-oxidation.

- **NST – Non-Segregating Tailings** are a mix of CST (sand) and TT. It is expected to have lower segregation than CT and a higher density. As fresh middlings are used for TT (no diluent), methanogenic potential is minimal except for the microbial action on flocculant as potentially fermentable material. Use of gypsum or alum as coagulant may change methanogenic potential through sulphate reduction processes.

4.3 Tailing Processing Technologies

In addition to processes described for Engineered Tailings, fluid tailings may be treated with additional processes in order to reduce their inventory.

Drying – there is more than one technique to dry tailings**.** Either MFT or TT may be used for this purpose. Thus there are different names for dried tailings that depend on the company. It has been called TLD or thin-lift drying; AFD – atmospheric fines drying, TRO – tailing reduction operation, while the acronym MFTD is used for dried MFT. Tailings are usually treated with polymers; deposited layers are 15 to 50 cm thick and left to desiccate and then dry. Drying creates cracking and significant volatilization of residual light hydrocarbons as well as aerobic conditions for MFT that was stored anaerobically in the tailings ponds. After 15 to 20 days (or longer if wet weather or thicker layers) a next layer may be deposited over the old one.

Shell's AFD process may employ thicker deposits (~ 1m) that may use amphi-rollers – tractors that partially float on deposited MFT or TT and rework the surface while creating draining channels and re-aeration of tailings. AFD still awaits large scale application and optimization. Drainage water is recycled to the extraction water loop.

Centrifugation – although it may start commercial operation soon, technology is not perfected yet. MFT is the only material to be centrifuged although there were some tests done on FTT. It may be expected that additional bitumen recovery could be a focus in the future development. Centrifuged tailings containing >50% solids (ideally over 55%) are also deposited in relatively thin layers (0.5 to 1.0 m) to further drain and dry in aerobic conditions. Centrate is returned to the pond. Recently, Syncrude tested medium deep centrifuge cake deposition that started as a 2 m deep deposit. This type of centrifuge cake is less aerobic and needs a detailed GHG assessment. A recently approved demonstration project will use up to 30 m in-pit deposition of the centrifuge cake. Despite some aeration, this type of deposition should be assumed to be anaerobic with some questions about long term biodegradation of the polymers used. Methanogenic potential will depend on origin of MFT (mixed with FTT or not), but the evolution of methane from this dense deposit and potential depletion by methanovores in upper layers warrant future research.

Rim-ditching is a fluid tailings treatment borrowed from the Florida phosphate industry that produces phosphogypsum as tailing byproduct. In oil sands, it is also called advanced dewatering. MFT is treated with polymer and deposited in 5 to 10 m layers. Polymer addition results in quick dewatering of one part of entrained water. Edges of the deposit are ditched with a hoe to enhance dewatering. This technology is being piloted on the Syncrude site.

Co-mingling with overburden is new/old technology that was tested on the Syncrude site 25 years ago (Lord personal comm.). The current pilot on the Syncrude site uses Clearwater clays as sorbent that can bind water from MFT or centrifuge cake. No additive is used so far, but MFT may carry residual diluent. After short exposure to air, the MFT/clay mix could be deposited in deep layers, preferably in-pit. High solids content (~68%) with low permeability clays may slow down GHG gas evolution to the point that it may be hard to predict if it will reach the atmosphere or be transformed in the reclamation layer above the clays. Sulphate in pore water would delay and change methanogenic potential. The technology is limited to mines that have significant amount of Clearwater clays in their overburden, mostly on the West side of the Athabasca River such as Syncrude ML, CNRL Horizon and Suncor, while Aurora North does not have significant amounts of this material. There may be some potential to use other materials for mixing with fluid tailings such as Pleistocene sand if available in sufficient quantities.

Retorting of the ore is a process of roasting at high temperatures in order to distill and crack hydrocarbons within bitumen. As previously piloted, it may result in elimination of fluid tailings and technically zero diluent loss. The process would also allow for earlier reclamation due to potential for dry stacking of such sandy tailings in pit. However, even this process will result in the creation of a potentially smaller end pit lakes (EPL), but without fluid tailings.

If applied to ore, froth, or FTT, retorting would significantly cut GHG emissions from ponds due to complete recovery of diluent with potential to reduce processing GHG-s as well. It would also remove most of toxic BTEX and PAH-s from residual tailings. Potential increase in plant GHG-s would be offset by higher synthetic fuel yields, pipeline building and pumping and further refining steps.

5 OVERVIEW OF MINING AND CLOSURE AND RECLAMATION PLANS

The end of mining will mean the creation of the end pit lakes (EPL-s) that are sometimes also called end of mine lakes (Suncor 2011). Depending on the final scenario presented in Table 3, the majority of these ponds, 24 of 32 end pit lakes, will not contain any significant amount of unprocessed MFT, meaning that there will be no artificially added fermentable materials that could incite methanogenic bubbling. Furthermore, five of these projects (Fort Hills, Muskeg River, Jackpine, Frontier and Joslyn) should not have any MFT in the EPL-s (AER 2014), thus making predictions about CH_4 emissions based on surface areas as done in Yeh et al. (2010)

extremely unreliable. The potential Shell Pierre River project was not accounted for in this analysis because it may undergo substantial changes. As discussed in individual C&R plans further in this paper, most of this EPL size includes significant littoral areas that do not contain any MFT, again making overestimates about active bubbling surfaces.

Table 3. The number of EPL-s with MFT or with OSPW only.

Company / Project	**Mining period**	**End-of-mine Volume of MFT**	**MFT in EPL-s**	**Number of EPL-s**	**Number of EPL-s with MFT**	
		Mm^3	Mm^3		**yes**	**no**
Suncor						
Millennium + North Steepbank mines	1967 to 2033	75 [3]	75	6	2	4
Fort Hills	2016 to 2068	31	0	3	0	3
Syncrude						
Mildred Lake	1978 to 2034	187	187	1	1	0
BML*	1995 to 2013	204	130	1	1*	0
Aurora North	2000 to 2038	215	215	1	1	0
Aurora South	2022 to 2050	48	48	1	1	0
Shell						
Muskeg River Expansion	2002 to 2055	70[1]	0	2	0	2
Jackpine Expansion	2010 to 2050	49	0	4	0	4
CNRL Horizon	2008 to 2048	177	177	4	1	3
Imperial Kearl	2013 to 2055	66	66	4	1	3
Total E&P Joslyn North	2019 to 2036	4.6	0	1	0	1
TECK Frontier	2021 to 2057	15	0	4	0	4
SUM				32	8	24

*Initial volume of 204 Mm^3, Syncrude expects BML to consolidate to ~130 Mm^3. The pond is a demonstration project for water capped EPL-s.

[1] Tailing management plan (2012) shows 142 Mm^3 but lower number proposed during different presentations to AESRD

[2] Imperial (2011) plans to separate and process FTT, final EPL devoid of diluent

[3] Potential MFT in Pond 1A not accounted

Fluid tailings can be intensively processed by using different technologies such as CT/NST, thickeners, centrifuges, atmospheric drying, etc. While the primary purpose of some of those technologies is to recover energy, almost all of them are designed to handle fluid tailings in more aerobic conditions, which may change fermentation pathways of available substrates resulting in more CO_2 instead of methane in deep ponds with MFT covered with OSPW.

Two of the new projects, Imperial Kearl and Total Joslyn, proposed the segregation of FTT from the rest of the fluid tailings. Potential emissions from separately processed tailings are impossible to predict at this time, but it can be said with great certainty that MFT at the Kearl project EPL-s should not have high methanogenic potential because of the potential absence of diluent.

It should be kept in mind that Closure and Reclamation (C&R) Plans may be changed significantly toward the end of mining also affecting the number of planned EPL-s.

The **Syncrude (2011b)** C&R plan document reveals two EPL-s at the Mildred Lake site, both containing MFT. Base Mine Lake and North Mine Lake will have an area of 732 ha and 878 ha, respectively, or 1,610 ha in total pond area vs. 24,649 ha in all landscape units at ML. Aurora North's West Pit Lake, which may be named Sutherland Lake at the time of closure (Syncrude 2011), should have a surface area of 1,588 ha vs. 10,216 ha in all landscape units at AN (Table 3-2 in Syncrude 2011b). That leaves water surfaces sum for Syncrude at 3,198 ha vs. the sum of 34,865 ha in reclaimed areas or 9.2% of the footprint. Without accounting for the fact that Aurora North will not be an intensively bubbling lake (no froth tails disposed), this again demonstrates that the assumption made by Yeh et al. (2010) which assumed 25% of the total lease area would be actively bubbling ponds, overestimates emissions by at least a factor of 2.5.

The **Suncor Millennium** mine situation is similar to Syncrude. Their closure and reclamation plan (Suncor 2011) shows that there may be only one major surface water body – Millennium Pit Lake with potentially 75 Mm^3 of MFT (not FTT), and few smaller end-of-mine lakes (Table 3). Those are Pond 7, Pond 1A, and two smaller lakes in the area of today's Pond 6. Pond 1A may contain residual material from FTT currently stored in Pond 2/3 that should undergo dry landscape reclamation. Suncor's Pond 1 (347 ha) was drained in 2010 and underwent dry reclamation and was renamed Wapisiw Lookout. Current Pond 6 and 8A will have similar destiny, while Pond 8B will be drained and mined through, but the Millennium Pit Lake will be created in the final pit depression roughly in the same place.

The Millennium Pit Lake should occupy ~840 ha vs. 22,090 ha in total development footprint or ~3.8% of the lease. Some previous plans show these surfaces to be somewhat larger, 1,037 ha, which would represent about 4.7% of the lease area. Pond 1A will be included in this larger surface and may contain significant amount of lost diluent potentially transferred from Pond 2/3, while Millennium Pit Lake may have some smaller amounts due to material transfers. Pond 2/3 is supposed to be dry reclaimed. Again it shows how overestimated GHG emissions can be on assumed future wet surfaces without basing GHG calculations on the current scenarios.

Suncor Fort Hills project is a Suncor-led joint venture inherited from the Petro-Canada merger. This facility is approved but not currently scheduled for construction. C&R plans (Fort Hills 2011) envision no fluid tailings in the final landscape. The C&R plan predicts that water surfaces in the end of mining for the 3 EPL-s should be 6.21 km^2 for East Pit Lake, 3.7 km^2 for Southwest Pit Lake and 5.4 km^2 for West Pit Lake, or 15.31 km^2 in total vs. 127.58 km^2 for the total project closure area, or about 12%. On the other hand this project predicts no MFT in EPL-s, thus no significant emissions from EPL-s, while, during mining, the volumes of MFT that include FTT will be significantly suppressed to about 31 Mm^3. Fort Hills project plans to achieve such state by drying its fluid tailings in aerobic conditions. Due to this approach it is obvious that the Yeh et al. (2010) assumption that GHG-s should be calculated based on EPL-s' surface becomes impractical for the estimation of GHG intensity from tailings ponds or areas.

Shell Muskeg River Mine project C&R plans underwent some changes so that the new version of reclamation and closure plan was submitted to AESRD in the end of December 2012 (Shell

MRM 2012). According to that plan, EPL-s will be about 713 ha including about 357 ha in the form of shallow littoral areas. This is about 5.8% of the total lease area.

These C&R plans were significantly changed from previous submissions when Shell planned >170 Mm^3 of fluid tailings deposited in one EPL. The change resulted in zero MFT in the bottom of EPL-s, thus eliminating the main source of methanogenic materials. Once more this demonstrates that basing the estimate of GHG emissions based on the ratio of EPL end mine footprint is not consistent with current plans.

Shell Jackpine project also underwent significant changes in its most recent Closure and Reclamation plans (Shell Jackpine 2011), which now show no MFT in the aqueous landscape. Interestingly, MFT is planned to be used for reclamation to support constructed wetlands as relatively impervious material that can serve as an aquiclude. Total EPL surfaces are projected to be 1,198 ha or 15.7% of the total disturbance area of 7,564 ha.

Submitted applications for the Jackpine Expansion project stick to zero MFT commitment in EPL-s. It also contains four EPL-s as approved by the Joint Review Panel. Shell Jackpine (2011) C&R plan also contains about 276 ha of constructed wetlands in the final landscape plus 214 ha of littoral wetlands on the outskirts of EPL-s.

CNRL Horizon plans to increase production of bitumen over time to 270,000 bbl/day with about 177 Mm^3 of MFT left at the end of mining. CNRL's (2011b) closure and reclamation plan proposes two bigger and two smaller EPL-s for the reclaimed landscape. The total area of EPL is approximately 2,900 ha, which includes about 730 ha of littoral zones. The total EPL area is 15.5% of the 18,662 ha of disturbed surface (Table 3). Only one of these lakes, named PL1 in the submission, is supposed to contain MFT. This lake represents only 7.3% of the future disturbed area, or even less if littoral area of 380 ha containing no MFT is deducted. The project also envisages three relatively big wetlands with 1,260 ha in total surface. These wetlands should not contain any fluid tailings or other potentially fermentable materials.

TECK (2011a) Frontier project also plans for zero MFT in the final landscape. At closure, there are four proposed pit lakes with the total surface of 2,558 ha or 8.7% of the 29,335 ha of total disturbance. Other shallow littoral areas encompass 451 ha (1.5%). Other types of wetlands include 5,572 ha or 19% of the total site disturbance but are not expected to contain any material with fermentable substrates such as diluent. This project also plans to dry MFT from Froth Tailings, thus providing mostly aerobic conditions for diluent fermentation during operation.

Total E&P Joslyn joint venture project proposed one pit lake in its 2010 submission (Total Joslyn 2010). This is the smallest mining project in the region with the shortest life span – only about 20 years with the maximum capacity about 100,000 bbl/day of diluted bitumen based on paraffinic process. Processing of MFT is based on deeper TT deposits, but it is not clear if they should be deposited as multilayers. There should be one pit lake in the end containing about 15 Mm^3 of OSPW but without MFT, similar to Fort Hills, Jackpine and TECK Frontier projects (Table 3). The final surface of the Pit Lake is 230 ha or 3.3% of the total disturbance of 6,980 ha. The most recent amendment envisions a larger pit lake, but the project was also recently shelved by Total E&P.

Considering no MFT in the EPL, short life time of the mine and use of very volatile diluent that is predominantly pentane, it seems that none of the assumptions made by Yeh et al. (2010) will be applicable to this project.

Companies depict littoral areas in lakes as wetland areas, and newer Closure and Reclamation plans show increases in wetlands. Littoral areas should cover 10 to 30% of EPL area and provide more aerobic conditions for the faster reclamation of oil sands process-affected water (OSPW). In order to ensure viability of littoral areas, they will be devoid of MFT. Bottoms of littoral areas covered with organic-rich soils, which should enhance reclamation (CEMA 2012). No significant amount of diluent should be present in these areas, thus probably creating less methanogenic (bubbling) surfaces.

The majority of companies plan to dilute OSPW in EPL-s with river water after mine closure. Thus the final volume and area covered are much larger than the initial volume and area of tailings immediately after the end of mining, which may result in overestimation of GHG generating areas. A deeper water column would create less aerobic conditions for degradation of diluent (more methane) and slower remediation of sediments.

It is also important to note as stated before that C&R plans can be changed or adjusted with time, thus the above discussion reflects only approved plans submitted between 2010 and 2012.

Thus, a 'one size fits all' approach for the estimation of the pond GHG emissions does not reflect the best available information. A situation described in previous projects, demonstrates a need for a different type of approach for the estimation of intensity of GHG emissions from tailings ponds. One alternative approach is proposed in the Part II of this paper where mine-specific attributes are used for the calculation of expected life cycle fugitive emissions.

6 PROVINCIAL AND FEDERAL REPORTING SYSTEMS

Information about Alberta oil sands can be found at the AESRD website http://esrd.alberta.ca/focus/default.aspx with the additional information about Provincial GHG regulations at http://esrd.alberta.ca/focus/alberta-and-climate-change/regulating-greenhouse-gas-emissions/default.aspx.

SGRR and GHGRP – Alberta's *Specified Gas Reporting Regulation* came into force in 2003 with Environment Canada's Greenhouse Gas Reporting Program (http://www.ec.gc.ca/ges-ghg/default.asp?lang=En&n=040E378D-1) following one year later. These regulations require all large final emitters of greenhouse gases to report their annual emissions. The original Alberta threshold for reporting was 100,000 tonnes CO_2eq per year (AESRD 2007), which was lowered to 50,000 tonnes CO_2eq/year in 2010. Oil sands surface mines have been required to report since the beginning of these programs. Carbon dioxide, methane, nitrous oxide and high global warming potential emissions are reported by source category but currently published only as totals (i.e. methane emissions from combustion, transportation, fugitive sources, including mine face, ponds and spot sources such as tank farms, or pipeline leaks, are summed all in one number).

SGER – Alberta's *Specified Gas Emitters Regulation* was established in 2007 and requires the reporting of emissions and production from all large final emitters (facilities emitting greater than 100,000 tonnes CO_2eq/year) that have operated for more than three years, and places mandatory intensity based emissions reduction targets on these facilities. Information submitted under the SGER must first be verified by a third party and signed off by a certifying official for the company. AESRD technical staff then conducts an internal review of the data, as well as hires auditors to re-verify a portion of facility submissions. Facilities are required to submit detailed quantification methodology and provide any additional information deemed necessary to review the compliance submission. This detailed information provides significant insight into the emissions sources at large final emitters.

Methane and CO_2 emissions from tailings ponds and mine faces are both currently quantified using emissions flux chamber surveys, which measure both the surface flux and the composition of the gases being emitted from the surface. These measurements have been conducted periodically over time at all oil sands surface mines. Since 2013, facilities have been required to conduct annual surveys and follow standard guidance to determine the spatial coverage of sampling in quantifying emissions from area fugitive sources. Historically, the sampling has been conducted at the discretion of the measurement professionals. All three mines subject to the SGER in 2011 (Syncrude, Shell, and Suncor) conducted flux surveys of their mines and tailings ponds. The summarized results of these measurement campaigns are shown in Table 4, as submitted to AESRD through the SGER. Until recently GWP for methane was 21, but it was updated to 25 in March of 2014 as can be seen in Specified Gas Reporting Standard (Government of Alberta 2014).

Table 4. Fugitive GHG emissions and GHG emissions from ponds as measured in 2011 flux survey.
Note that as per the SGER in 2011 the Methane GWP = 21.

Company	**CH_4**	**CO_2**	**Total GHG CO_2 eq**	**GHG Intensity[1]**	**Total GHG/L diluent**
	t/y	t/y	t	g CO_2 eq/MJ bitumen	Kg CO_2 eq/L diluent
Suncor mines+upgrader					
Emissions from ponds	5,813	164,948	287,026	0.45	4.48
Total fugitive	6,469	167,810	309,953	0.48	4.84
Syncrude ML + AN					
Emissions from ponds	26,803	224,500	787,366	1.01	10.6
Total fugitive	42,223	305,573	1,192,354	1.53	16.1
Shell MRM + JP					
Emissions from ponds	322	32,862	39,616	0.08	1.00
Total fugitive	2,486	127,243	179,448	0.38	4.51

[1] 1 bbl bitumen =159 L, contains 6100 MJ; production from AER (2013), Table 6 Part II

These data show that both carbon dioxide and methane emissions are generated in tailings ponds, but that these emissions vary significantly from facility to facility due to variability in diluent types and amounts lost to the ponds, pond age, other carbon sources lost to the ponds (such as glycol, citrate, etc.). Tailings ponds at active mine sites are very dynamic systems with varying compositions within the ponds, as well as varying types of materials being deposited in different parts of the ponds over time. As mentioned above, the key difference in the context of greenhouse gas emissions is that not all ponds contain FTT. The management of the ponds can also involve pumping water out for reuse or pumping the tailings from pond to pond for operational reasons. As a consequence, there is also significant variation in emissions between ponds and even within ponds at a given site.

Table 5 shows the examples of 2011 and 2012 emissions from ponds and dedicated disposal area

Table 5. Examples of GHG-s from ponds and DDA-s in 2011 and 2012.
Data adopted from Small et al. (2014) and Suncor (2013). Methane GWP = 21.

Company	**Mine**	**Pond**	**CO_2**	**CH_4**	**CO_{2eq}**
			(t/ha/y)	(t/ha/y)	(t/ha/y)
Syncrude[1]	Mildred Lake	MLSB (ETF)*	52.9	26.2	603.5
		SWSS	10.9	0.04	11.8
		BML	88.1	3.3	157.8
		East-In-Pit	23.3	0.06	24.5
	Aurora North	ETF	31.6	0.004	31.6
		East Pit	497.9	0.13	500.6
Suncor [2]	Millennium &NSE	Pond 2/3*	59.7	9.5	258.1
		Pond 6	3.7	0.04	4.6
		Pond 7	4.5	0.03	5.1
		Pond 5/6	92.9	0.63	106.2
	TRO DDA panels [3]	Pond 8A North	55.6	0.34	62.7
		Pond 8A South	52.3	0.33	59.1
		DDA1-panel A	37.0	0.25	42.3
		DDA1-panel B	50.5	0.34	57.5
		DDA1-panel C	38.6	0.26	44.0
Shell [4]	MRM	ETF*	4.6	0.09	6.2
		Cell 1*	156.7	0.48	166.8
		AFD Panel	20.8	0.19	24.7
	Jackpine	ETF-sand cell	35.4	0.55	46.9
CNRL [5]	Horizon	ETF*	30.3	0.29	36.3

* Ponds receiving or received FTT, thus bubbling or prone to bubbling and higher methane & GHG emissions

ETF – external tailing facility, Imperial Kearl was not operational in 2011. Suncor Pond 1 reclaimed in 2010

[1] Syncrude (2012)

[2] Suncor (2012)

[3] Suncor (2013)

[4] Chamberland, personal comm. (2012)

[5] CNRL (2011a)

(DDA). It highlights the variability in emissions rates. Aurora North high CO_2 emissions may not be related to diluent presence (since froth is pipelined to MLSB) and need further attention. It is obvious that Shells fugitive GHG emissions are dominated by CO_2. While there is no straight answer 'why', it is worth noting that Shell's diluent is of light type with much higher volatility and water solubility (PART II, Table 3). In addition, tailing management practices such as beaching may be contributing to CH_4 vs. CO_2 ratio.

It can be concluded that Provincial and Federal monitoring and reporting systems have established a reliable source of information on GHG emissions from tailings in oil sands mining.

6.1 Measurement of Pond GHG and VOC Emissions

Although not the focus of this paper, it is worth mentioning that a few methods have been used, but the most standard is the use of flux chamber equipped with gas purge and connected to either sampling apparatus or field GC-MS for the in-situ determination of gases. The description of flux chamber can be found at CAPP (2014). An inherent weakness of this method is not in the method itself but in environmental conditions during measurements. For example, while methane generation (by bacteria) is expected to be relatively constant, a few factors tend to release more gases from the tailings ponds such as lake inversion, pumping of the pond content, storms or a sudden drop in atmospheric pressure (Barr-Deltares 2008), but the chambers are usually not deployed during such weather events.

A review of other GHG monitoring methods was conducted by Hashisho et al. (2012). Besides measurements of VOC-s and GHG-s, some of the methods may also be applied to measure Reduced Sulphur Compounds (RSC), some of which have been indicated as potential odour contributors. Work is ongoing to test and evaluate alternative monitoring techniques to supplement or replace the emissions flux chamber, which can help improve the understanding of pond processes driving emissions.

7 DISCUSSION AND RECOMMENDATIONS

Part I of this paper served to highlight mine variability in bitumen extraction and potential confusion about the most accurate way to account for GHG emissions from surface mining projects. In short, variety of information can be summarized as:

1. Mining started in 1967, while first GHG measurements were made in late 1990's, with some GHG emissions projections going 50 years in the future. There was a significant time delay in intensive bubbling. At this time, time delay of intensive current or future GHG emissions cannot be assessed.
2. Production practices and even diluent composition and quantity lost to ponds have changed over time, and play a role in the variability of measurement.
3. Previous measurements are just one slice in time that cannot be extrapolated to future GHG emissions.

4. FTT are a source of fermentable diluent that is the main source of GHG-s.
5. Some ponds receive froth tails and some even double dose of froth tailings with diluent from 2 mines, while others are devoid of froth treatment tailings as a carrier of fermentable diluent.
6. Changing pond chemistry (pH, ions, temperature…) may delay or trigger methane formation.
7. According to the most recent C&R plans, the majority of EPL-s will not have MFT.
8. Changing AER rules lowered diluent loss to ≤4/1,000 bbl of produced bitumen.
9. Use of lighter diluents, i.e. pentane vs. naphtha, creates less methane due to higher volatility and less carbon available, thereby confounding estimates of GHG-s.
10. Branched hydrocarbons found in residual diluent and/or bitumen may not ferment completely or their biodegradation may be significantly delayed.
11. Changing tailings treatment technologies create tailing deposits with different characteristics. Most of them result in significantly changed chemistry that modifies the fermentation pathways toward more CO_2 production (CT/NST), or in significantly higher aeration providing oxygen for aerobic degradation.
12. Aerobic deposits have a GHG potential different from water-capped MFT in BML and from other deep tailings deposits.
13. Other smaller sources of GHG-s from additives or aerobic oxidation of minerals warrant more detailed investigation.

Provincial and Federal regulations (SGRR and GHGRP) have resulted in valuable sources of GHG information. Emissions of other released compounds are also reported through the National Pollutant Release Inventory. Reported emissions are based on measurements and verified by regulators.

All those factors raise the question about the most appropriate way to estimate emissions for both the currently operating mines, and future projects like Total Joslyn, Shell Jackpine Expansion and TECK Frontier that may have no fluid tailings in the EPL-s. All these projects plan to use advanced technologies that involve some kind of concentration of fluid tailings, i.e. by centrifugation, and actively process them in mostly aerobic conditions due to spreading in thin lifts and drying.

While all those technologies may not influence the mass of diluent lost, they can certainly change the destiny of lost diluent towards evaporation and aerobic fermentation, which would drastically cut the amount of hydrocarbons available for methanogenesis and their GHG effect. One of the primary options to decrease GHG-s from ponds, which will be dissected in the Part II, is to further reduce diluent losses.

One option to address the quantification challenges is to propose another method for the calculation of methane emission intensity from tailings ponds. Since a plethora of publications show that the lost diluent is the main cause of bubbling in tailings ponds, Part II proposes the first Base GHG Model for the calculation of GHG emission intensity (methane plus CO_2) from tailings ponds based on fermentable substrates.

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PART II: Modeling of GHG emissions from Tailing Ponds based on Fermentable Substrates

1 BASE GHG MODEL DEVELOPMENT

In order to decrease uncertainty related to the estimation of GHG emissions from tailing ponds as a result of using industrial scale assumptions as in Yeh et al (2010), and measurement of GHG and other fugitive fluxes as assessed by the flux chamber or other measurements, there was a need to develop a model of GHG emissions based on fermentable substrates found in some tailings. This Base GHG Model is based on a few assumptions that need to be validated through the field measurements, but those measurements will be less dependent on time and location of the measurements while providing data for the adjustment of model assumptions.

The Base GHG Model aims to express GHG intensity of biogenic gasses per unit of energy in mined bitumen. Rejected or low grade ore is not taken into account. Since it was already shown in multiple papers that the overwhelming majority of fermentable substrate is lost diluent (Holowenko et al. 2000, Siddique et al. 2006, 2007, 2008, 2011), the model will focus on diluent source, historical practices in tailing deposition and physical and biochemical characteristics and fate of diluent. Although fermentation kinetics of diluent components can be fitted to zero and first order reactions (Siddique et al. 2008), such an approach may not be necessary to calculate the lifecycle GHG intensity from tailings ponds.

The amount and type of lost diluent is more or less known. The Alberta Energy Regulator – AER (formerly ERCB) limits that volume to 0.4% volume of diluent per volume of produced bitumen. Diluent losses are reported to AER and can be found on the AER website in the ST 39 publications. Both lost diluent and bitumen produced are reported in m^3. Lost diluent is initially present only in froth treatment tailings (FTT) as already discussed in Part I. The further destiny of diluent in FTT is mostly known in general, and can be summarized in equation (1) based on present and available carbon. Diluent CO_2eq intensity per MJ for methane can be calculated starting from the diluent entering ponds, different successive aerobic and anaerobic fermentation losses and methanogenic mass balance as shown in equation 1:

$$D_{CH4e} = 159 \text{ x } 0.004_{DVLF} \text{ x } SG_{dil} \text{ x } C\%_{dil} \text{ x } VF_{voc} \text{ x } AnF \text{ x } SRBF \text{ x } CH_4\,mF \text{ x } MEF \text{ x } 16/12 \text{ x } 25 / 6100 \qquad \text{(Eq.1)}$$

While CO_2 emissions were calculated from the difference in mass of carbon that entered the pond, and mass of carbon that was fermented into methane as:

$$D_{CO2e} = \{(159 \text{ x } 0.004_{DVLF} \text{ x } SG_{dil} \text{ x } C\%_{dil} \text{ x } VF_{voc}) – (159 \text{ x } 0.004_{DVLF} \text{ x } SG_{dil} \text{ x } C\%_{dil} \text{ x } VF_{voc} \text{ x } AnF \text{ x } SRBF \text{ x } CH_4\,mF \text{ x } MEF)\} \text{ x } 44/12 \text{ x } 1/6100 \qquad \text{(Eq. 2)}$$

In equations 1 and 2 the factors and values used are:

159 = volume of 1barrel (bbl) in litres

0.004 = maximum diluent volumetric loss factor (DVLF) allowed by AER

SG_{dil} = specific gravity of diluent

$C\%_{dil}$ = % of carbon in diluent

VF_{voc} = volatility factor – represents diluent that is left after VOC-s are emitted

AnF = anaerobic/aerobic split factor; conservatively taken as 0.9 (90%) for these calculations

SRBF = 0.9, factor represents available diluent carbon left after losses to other fermentations such as sulphur reduction

CH_4 mF = molar factor for $CO_2 : CH_4$ split in methanogenic fermentation

MEF = methane efficiency factor, conservatively assumed as 0.9 (90%) in this case

16/12 = weight correction from available carbon to methane

25 = CO_2 equivalent for methane GHG effect, previously 21 in Alberta

6100 = Mega Joules (MJ) of energy assumed to be contained per bbl of bitumen

44/12 = Weight correction for available carbon to CO_2

Total Diluent GHG intensity in g CO_2eq/MJ was calculated as the sum of these 2 equations

$$D_{GHGe} = \text{Eq. (1)} + \text{Eq. (2)} \qquad \text{(Eq. 3)}$$

The assumptions for the listed factors used for the initial calculations in this model are presented in Table 1, and are somewhat different for the mines using naphtha vs. mines with paraffinic diluent. For Excel calculations, the model was simplified by relating mass of carbon at each step as described later in Table 4.

SG_{dil} and $C\%_{dil}$ are the inherent properties of diluent used. For this paper we assumed somewhat idealized composition of diluent (Table 1), because it is relatively hard to find out exact values for diluents used or planned to be used by companies. Table 2 represents real properties of the diluent, but the composition is not idealized since real diluents have abundant presence of iso-forms of alkanes and aromatics. The data are obtained from companies directly, i.e. as MSDS, or from regulatory submissions to AESRD.

To make those calculations easier to understand, it is necessary to describe the destiny of lost diluent through the explanation of loss factors.

DVLF (diluent volumetric loss factor) is the factor that can significantly influence methane production calculations. Thus, it is necessary to describe how that loss occurs.

Hot froth treatment tailings (FTT) are pumped to the tailings ponds and their deposition is carried out mostly in two ways – beached on the edges of the ponds or deposited sub-aqueously into separate ponds as described in Table 1 of Part I. Beaching hot FTT creates more VOC-s whose destiny may ultimately lead to greenhouse gas emissions but is beyond the scope of this model and paper. Beaching of paraffinic diluent probably creates more VOC-s due to the lower boiling point and higher water solubility (Table 3). Although FTT may lose some energy, beached FTT will still be warm and entrain some air (oxygen) by the time they reach the recipient pond. During beaching, it is not expected that the evaporation of all hydrocarbons will be uniform – lighter ones are more volatile. Thus we assumed a bit higher density than ideal for residual diluent meaning higher carbon content.

Table 1. Assumptions for the Base GHG Model calculations of organic carbon entering methanogenesis by diluent type.

Parameter	**Paraffinic (P)**	**Naphtha (N8) light**	**Naphtha (N10) heavy**
Empirical formula of proxy molecule	C_6H_{14}	C_8H_{18}	$C_{10}H_{22}$
Molar mass (approximate)	86	114	142
Carbon %	83.72	84.21	84.51
Density, Kg/m^3 (SG_{dil})	655	703	(730*) 780
Volatilized (1 - VF_{VOC})	40%	35%	30%
Aerobic fermentation in pond (1 - AnF)	10%	10%	10%
Loss to other fermentations (1 - SRBF)	10%	10%	10%
CO_2 : CH_4 molar ratio	1.25 : 4.75	1.75 : 6.25	2.25 : 7.75
Methane from theoretical maximum (MEF)	90%	90%	90%

* density of pure n-decane

Table 2. Type and properties of diluent used by companies.

Company	**Diluent**	**Specific Gravity**[1]	**Average molecular weight**	**Flash point**	**Log Kow**	**Solubility in water**
		Kg/m^3		^{o}C		mg/L
Syncrude	naphtha	760	NA	-2	NA	NA
Suncor	sour naphtha	770 to 800	NA	-5 to -10	NA	NA
Shell MRM	paraffinic	645 to 655	NA	NA	NA	NA
CNRL	naphtha	730	106 (C_7 to C_8)	-6	NA	NA
Imperial	paraffinic	NA	NA	NA	NA	NA

NA – not available but necessary for modelling and validation of individual mines

[1] same numerical value is expressed for g/L or kg/m^3

Kow – octanol-water partitioning coefficient

Table 3. Physical properties of modelled hydrocarbons.

Hydrocarbon	**Formula**	**Spec. Gravity**	**Boiling point**	**Vapor pressure**	**Flash Point**	**Log Kow**	**Solub. in water,**
		Kg/m^3	**^{o}C**	**Pa**	**^{o}C**		**mg/L**
Pentane	C_5H_{12}	626	36	57,900	-49	3.255	40
Hexane (P)	C_6H14	654.8	68.5	17,600	-26	3.764	9.5
Octane (N8)	C_8H_{18}	703	125.5	1,470	13	4.783	7
Decane (N10)[1]	$C_{10}H_{22}$	730	174	195	46	5.802	0.037
Toluene	C_7H_8	867	110.6	3,786	4	2.73	520
Xylene[2]	C_8H_{10}	870	~140	933 to 1,200	17 to 30	3.16	198

[1] Although practically insoluble in water, the presence of lighter hydrocarbons may increase its volatility
[2] Few isomers present, average numbers

Total volatility (average) of diluent was calculated to be 40.1% by Cenovus (2010). Thus, for this exercise, it was applied to paraffinic diluent only, while we were more conservative for naphtha-type diluents and assumed volatility loss to be 35% for light naphtha (N8) and 30% for heavy naphtha (N10).

After entering a pond together with tailings, diluent partitions onto solids and bitumen as described by Kasperski et al. (2010) and Afara et al. (2010). They showed that higher bitumen in MFT binds more diluent and that naphtha loss was about 30% in laboratory conditions (no beaching), confirming the value of our volatility factor (VF_{voc}).

In that partitioning, partly soluble light hydrocarbons like pentane and hexane would create equilibrium between fraction soluble in OSPW and fraction adsorbed onto clays and bitumen in tailings. The oil slick present on the majority of FTT ponds could adsorb soluble diluent (due to partitioning) and enhance its volatilization from the pond surface, thus increasing volatile losses.

AnF factor describes the amount of carbon (hydrocarbons) that remains in lower parts of ponds and is available for anaerobic fermentations that include production of methane. Ponds have both aerobic and anaerobic areas. Areas of deeper anaerobic layers are apparently bigger, but fresh fluid tailings are deposited in more aerated surface layers. Sub-aerial deposition such as beaching contributes to aeration and aerobic processes.

Working ponds are expected to have established microcosms with the aerobic layer at the top and completely anaerobic layer below with MFT expected to be completely anoxic. The more diluent that FTT carries, the more reduced the conditions in the pond will be.

Turbulent warm FTT will carry some dissolved oxygen and entrapped air bubbles. FFT are also expected to entrain some air. Due to high organics, dissolved oxygen (DO) further from the tailing outlet is expected to be very low. Besides DO, the main mechanism that will determine the amount of diluent carried into the anoxic layer is partitioning (Afara et al. 2010). As both FTT and FFT contain bitumen, it is expected that the lost diluent will partition mostly onto the bitumen with a smaller amount deposited onto other organic material and clays. Regardless of this ratio, for this exercise we will conservatively assume that 90% of the diluent was carried into the anaerobic part of the pond toward methanogens – the true amount needs to be measured in a research project.

It should not be forgotten that wave action on pond surfaces also creates entrainment of air in addition to oxygen diffusion. Despite that, we assumed only about 10% loss to aerobic fermentations regardless of diluent type or pond shape and exposure to wind.

SRBF factor was named after sulfate reducing bacteria (SRB) as supposedly the main fermenter group in anaerobic processes. First, hydrocarbons need to be degraded to smaller more digestible molecules. Spormann and Widdel (2000), and Fedorak et al. (2000) proposed that hydrocarbons need to be degraded to acetate with β-oxidation as the main mechanism. During biodegradation of hydrocarbons, methanogenesis is the last process to happen. While methanogenesis may happen concurrently with other processes, there are other hydrocarbon degradation pathways that provide more energy to bacteria. The main one discussed in Holowenko et al. (2000) and Salloum et al. (2002) is sulfate reduction. Fedorak et al. (2003) proposed 20 mg/L of sulfate as approximate depleted concentration when SRB may be outcompeted by methanogenic bacteria. Sulfate reduction may consume some acetate and create carbon dioxide or carbonate as proposed by Salloum et al. (2002) (in their Eq. 1), resulting in pH and bicarbonate increase in ponds as a result of acetate and hydrogen depletion, which also results in reduced methane formation. Hydrogen depletion could also be responsible for subdued methane formation (Siddique et al. 2011) in addition to the anaerobic methane oxidation with sulfate (Spormann and Widdel 2000; Fedorak et al. 2003). We assumed that only 10% of anaerobic hydrocarbon was lost in these processes, which results in SRBF factor = 0.9 in the Base GHG Model.

Other higher energy pathways such as nitrate reduction were assumed within the SRBF factor.

CH_4mF is methane molar factor that describes the ratio between CO_2 and CH_4 produced during methanogenesis as related to total moles of carbon since methane is not the only gas produced. Alkanes are fermented into these two gasses in a ratio that was described by Spormann and Widdel (2000) and Siddique et al. (2006, 2011). For example, 1 mol of decane $C_{10}H_{18}$ would ideally create 7.75 mol of CH_4 and 2.25 mol CO_2 (Eq. 4) from 10 moles of carbon.

The theoretical maximums for the methane production from short aliphatic hydrocarbons were derived from Roberts (2002) and presented in Siddique et al (2006).

$$C_{10}H_{22} + 4.5\ H_2O \rightarrow 2.25\ CO_2 + 7.75CH_4 \qquad \text{(Eq. 4)}$$

$$C_8H_{18} + 3.5\ H_2O \rightarrow 1.75\ CO_2 + 6.25\ CH_4 \qquad \text{(Eq. 5)}$$

$$C_6H_{14} + 2.5\ H_2O \rightarrow 1.25\ CO_2 + 4.75\ CH_4 \qquad \text{(Eq. 6)}$$

The weight ratio of CO_2 and CH_4 production from decane in Eq. 4 is 44.4% of carbon dioxide vs. 55.6% methane. nC_6 to nC_{18} hydrocarbons produce 42 to 46% CO_2 if 100% of the hydrocarbon molecule is consumed into these two gasses. But methanogenesis is not an ideal reaction.

MEF is the methane efficiency factor that accounts for a lower efficiency of methane formation. Siddique et al. (2011) injected different pure alkanes into active MFT that had already biodegraded its diluent, reactivated it and found the emissions from “spent” MFT to be 80 to 84% of the theoretical maximum after 54 weeks of measurement. Previously, Siddique et al. (2006) measured the emissions of methane from short chain n-alkanes to be 77 to 79% of the same theoretical maximum, while the rest of carbon could go to biomass synthesis.

Zengler et al. (1999) injected nC_{16} into ditch mud and measured methane emissions to be only 64% of the maximum. Part of the loss was ascribed to handling, but a part was attributed to sulfate reduction bacteria that consumed available hydrogen from acetate formation, thus confirming the assumption that part of the available hydrocarbon will be consumed by other processes before methanogenesis can start.

Siddique et al. (2007) measured the gas evolved from BTEX and naphtha after addition to activated tailings under more ideal lab conditions and found only 15 to 23% of whole naphtha was metabolized. We will assume that 100% of naphtha or paraffinic diluent is biodegradable.

Thus our 0.9 factor (90%) for methanogenic efficiency is assumed to be fairly conservative.

Straight alkane chains are easier to digest through β-oxidation. Branched molecules will create more of the recalcitrant material. Still, for these calculations in the Base GHG Model we will assume that the yield of methane is 90% of the degradable fraction of diluent. The rest of carbon that entered ponds, after losses to VOC-s, is not considered as recalcitrant at all, but completely turned into CO_2. Validation of the model could introduce an additional factor as bioavailability of hydrocarbons.

Another potential reaction that can change the $CH_4 : CO_2$ ratio in a pond is the establishment of methanotrophs. Holowenko et al. (2000) mentioned that these consortia can utilize methane and deplete water of oxygen impacting the viability of the ecosystem. It is not known how much methane is potentially utilized by methanotrophs in the ponds and especially under the ice when gases are at least partially blocked from escaping to the atmosphere. For the sake of this Base GHG Model, we do not account for methane losses to other processes such as methane oxidation, which is a conservative assumption.

The additional fermentable hydrocarbon is contained in bitumen. Siddique et al. (2011) assumed that bitumen contains about 0.04% of $<C_{19}$ hydrocarbons and demonstrated that despite a lag, these hydrocarbons can create methane emissions in laboratory conditions. These emissions could be expected to be apparent once all the consumable substrate from lost diluent is spent. Thus there would be slow bubbling from MFT capped EPL-s long after the end of mining even in the absence of fresh diluent input. The timing and intensity of such gas formation will also depend on the presence of other factors like concentration of sulfate, amendments (polymers), available bitumen surface etc., which is hard to predict at this time since none of the mines have finished operation. However, for this exercise this source of emissions was excluded since the quantity and bioavailability of these hydrocarbons is much lower than the volume of fermentable materials in lost diluent.

2 BASE GHG MODEL CALCULATIONS AND RESULTS

The summary of calculations from this Base GHG Model is presented in Table 4. For modelling simplicity three diluents were evaluated as theoretical representatives: paraffinic (P); Light naphtha (N8); and heavy naphtha (N10). Pure linear hexane, octane and decane were used as P, N8 and N10, respectively, for calculations. Some values and assumptions for diluent properties are listed in the Table 1.

Table 4 shows calculated total CO_2eq emissions intensity from ponds based on fermentable diluent and Eq. (1 to 3). The volume of lost diluent (step 2) is assumed to be 4 vol./1,000 vol. of bitumen as regulated by AER, while recent real losses are lower as shown later in Tables 6 and 7. From diluent density (step 4) and carbon content in diluent (step 6), the mass of carbon lost per bbl of bitumen is given in step 7. After deducting volatility losses of 30 to 40% (step 8), carbon entering the pond and available for biological fermentation is given in step 9. 10% of this carbon is lost to aerobic fermentations (steps 10 to 11), and an additional 10% to fermentation other than methanogenesis (step 12) such as sulfate reduction, physiological functions, etc.

The mass of fermentable carbon available for methanogenic processes, after all the losses is presented in step 13, which is roughly 48 to 56% of initial theoretical carbon. Methanogenesis also creates a small amount of CO_2 in molar terms but almost 50% by weight. After deduction for created CO_2 in steps 14 to 15, and 10% deduction for methanogenesis efficiency (step 16) carbon mass emitted as methane is presented in step 17. After correction from carbon to methane (16/12) and multiplication with methane global warming potential CO_2eq factor of 25 (step 18), the amount of methane CO_2eq emissions produced from different diluents varies from 4,210 to 5,527 g CO_2eq per barrel of bitumen (step 19). If factor 21 is used those amounts would be proportionally smaller as compared in Table 6 for different emission scenarios. Emission intensity is calculated by dividing step 19 with 6,100 MJ/bbl (step 20) resulting in 0.69 to 0.91 g CO_2eq/MJ of methane fugitive emissions (step 21), which is 3 to 4 times less than estimated by Yeh et al. (2010). It also demonstrates the need for individual assessments of pond emissions.

All non-methanogenic carbon that entered the pond (step 22) can be assumed to become CO_2 (steps 23 to 26), resulting in **total conservative fugitive emissions intensity estimates in the range of 0.75 to 0.98 g CO_2eq/MJ** (step 27) depending on the type of diluent, without any accounting for recalcitrant carbon or other possible fermentation pathways.

Factors used can be different from the proposed ones, but we were very conservative in the characterization of losses and diluent properties. An error greater than 10% higher is not expected, while any treatment of MFT that could result in different fermentation factors would significantly decrease methane emissions as discussed later in different scenarios (section 4).

Theoretical boundaries for emissions may be generally driven by assumptions that all material is transferred either into CH_4 or CO_2. If all the lost diluent would be fermented, then that would be DVLF = 0.4% from 1 bbl or 0.636 L. Such volume contains 364.74 g of pure carbon in paraffinic diluent (P) or 419.22 g of carbon in N10 naphtha. If all of that carbon would undergo

Table 4. Base GHG Model factors and results from step by step model calculations of GHG emissions intensity from lost diluent.
Values in the table rounded from Excel calculations.

			Diluent		
Step	Parameter and unit	**Multiplier factor**	Paraffinic (P)	Naphtha (N8) light	Naphtha (N10) heavy
	Proxy molecule →		C_6H_{14}	C_8H_{18}	$C_{10}H_{22}$
1	1 barrel of bitumen, L		159	159	159
2	Diluent loss to tailings, DVLF	0.004	0.004	0.004	0.004
3	Volume of diluent lost, L		0.636	0.636	0.636
4	Density, g/L	variable	685[1]	703	780*
5	Weight of diluent lost, g		435.66	447.108	496.08
6	Carbon mass ratio in diluent	variable	72/86	96/114	120/142
7	Carbon weight in lost dil. g		**364.74**	**376.51**	**419.22**
8	VF_{voc} – volatility factor	variable	0.6	0.65	0.7
9	Carbon left in pond , g		**218.84**	**244.73**	**293.46**
10	AnF (anaerobic-aerobic split)	0.9	0.9	0.9	0.9
11	Carbon for anaerobic processes, g		196.96	220.26	264.11
12	SRBF (10% loss to other fermentations)	0.9	0.9	0.9	0.9
13	Carbon in methanogenesis, g		**177.26**	**198.23**	**237.70**
14	CH_4 molar part of carbon	variable	4.75 : 6	6.25 : 8	7.75 : 10
15	Carbon available for methane, g		140.33	154.87	184.22
16	MEF – methane efficiency	0.9	0.9	0.9	0.9
17	Carbon emitted as methane, g		**126.30**	**139.38**	**165.80**
18	CO_2eq factors	16/12 x 25	16/12 x 25	16/12 x 25	16/12 x 25
19	Methane CO_2eq, g/bbl		4,210.0	4,646.1	5,526.5
20	Factor per MJ energy	1/6,100	1/6,100	1/6,100	1/6,100
21	**Methane CO_2 eq/MJ, g**		**0.69**	**0.76**	**0.91**
22	Carbon available for CO_2, g (step 9 minus step 17)		**92.54**	**105.35**	**127.66**
23	Carbon to carbon dioxide	44/12	44/12	44/12	44/12
24	CO_2 (from step 22), g		339.3	386.3	468.1
25	Factor per MJ energy	1/6,100	1/6,100	1/6,100	1/6,100
26	**CO_2/MJ (from step 24)**		**0.056**	**0.063**	**0.077**
27	**Total pond GHG emissions intensity CO_2eq/MJ, g**		**0.75**	**0.83**	**0.98**

* Heavy naphtha – assumed heavier than pure decane whose density is 730 g/L

[1] Real density on Shell site is 0.645 to 0.655 meaning it is a mix of pentane and hexane

Multiplication factors are in red; values in bold are: **Black** – mass of carbon, **Green** – methane GHG intensity, **Brown** – CO_2 intensity, **Blue** – Total GHG intensity methanogenesis without any losses to VOC-s, aerobic processes, SRB, or methane inefficiency (VF = AnF = SRBF = MEF = 1 in Eq. 1 to 3)), and with CO_2 as a co-product (CH_4mF calculated from Eq. 4, 6,), that would be 288.8 g and 324.9 g of carbon in methane respectively from P and N10 diluents. Taking into account carbon ratio in methane (16/12) and methane GHG effect (x 25 GWP factor), those masses represent a theoretical maximum methane emissions of 9,625 g of CO_2eq for paraffinic and 10,830 g of CO_2eq for naphtha N10 type diluent. The remaining 76.0 g and 94.3 g of carbon can be assumed to be released as CO_2 from P and N10 diluents respectively. This gives total theoretical maximum greenhouse gas emissions per barrel of bitumen of 9,904 g and 11,176 g CO_2eq respectively from P and N10 diluents. Results for N8 are between P and N10 values.

If N10 diluent would have lower density, 730 g/L instead of 780g/L used), values for methane emissions would be proportionally lower.

Assuming 6,100 MJ/bbl of bitumen, methane emissions would translate into a theoretical maximum of 1.578 g and 1.775 g of CO_2eq/MJ from P and N10 diluent. Total CO_2eq values take into account CO_2 as a by-product of methane production resulting in 1.624 and 1.832 g of CO_2eq/MJ from P and N10 naphtha, respectively, or still significantly less than assumed by Jacobs Consultancy (2012) and Yeh et al. (2010) that calculated emissions to be on average 2.61 g of CO_2eq as methane emissions. These GHG emissions need to be adjusted for the volatility of diluent.

Correct modelling of theoretical GHG maximum should deduct volatilized diluent (30 to 40% of N10 and P diluents, respectively), which would result in the more realistic upper theoretical boundary of 0.947 g of CO_2eq/MJ for P diluent, and 1.242 g of CO_2eq/MJ for N10 as methane emissions when all the diluent that reaches pond is fermented into CH_4 and CO_2 without any other fermentation or losses.

The lower boundary is the minimum emissions if all carbon in diluent would become CO_2 without any methane produced, which is 0.22 and 0.25 g CO_2/MJ for paraffinic and N10 diluent respectively. These values are 0.13 and 0.18 g, respectively, if only the diluent that enters a pond and can be fermented is taken into account, with volatilized diluent deducted (30% and 40%, respectively for N10 and P) since VOCs are not recognized as GHG-s. If the density of diluent is lower than assumed or some carbon remains in the pond these values would be reduced proportionately.

Although both upper and lower boundaries are practically impossible, these numbers give a range of emissions expected from tailings ponds. Lower diluent losses than 0.4% would further suppress CO_2 and CH_4 emissions and could be a pathway for emissions reduction.

Any diluent lost to tailings will also be lost to the environment resulting in potential odors, or be lost in other fermentations as previously described.

The weight ratio of methane vs. sum of CH_4+CO_2 in the Base GHG Model gas mix is 32.1 to 33.2%. The weight of methane vs. weight of lost P diluent is 38.7% and 44.6% for N10, while Clearstone (2011) predicted methane to be 21% of the solvent lost to the pond, indicating three possibilities: either much higher bio-fermentation into other gasses or products, lower total fermentability or much higher volatilization. On the other hand, our numbers are more conservative.

Such losses may be quite possible due to branched hydrocarbons that are resistant to fermentation plus the presence of sulphate and sulphur-rich compounds that may change fermentation pathways resulting in more CO_2 and less methane. There is also a strong possibility that losses of available carbon to aerobic fermentations and to SRB-type processes are much higher in the ponds than in our Base GHG Model. This is despite the fact that that CO_2 is much more soluble in water than methane and in deep MFT layers where hydrostatic pressure is much higher, it may be much more present as solute in water or in bitumen.

3 DISCUSSION OF BASE GHG MODEL

3.1 Comparison with Published Data

GHG emission numbers reported through the GHGRP seem to be within our calculations of methane emissions from ponds. As discussed in Part I, Syncrude emission intensity is 0.96 g/MJ CO_2eq (recalculated using x 25 factor) as reported by GHGRP for 2010 confirming that any measurement is better than unsubstantiated assumptions published earlier. That calculation also demonstrates that the values for CH_4 emissions calculated in this Base GHG Model are very conservative and at about the same or higher than reported GHG emissions.

Recently, Syncrude's loss of diluent is less than 4 volume units per 1,000 volumes of bitumen (Table 7), with significant production of sulfate rich CT tailings that can change fermentation pathways.

Diluent variants such as sour naphtha used by Suncor until recently may affect model estimates. Biodegradation of such diluent probably results in significant production of reduced sulphur compounds (RSC) that potentially create odors, but are not classified as GHG-s (e.g., benzothiophenes). Thus the GHG impact per MJ of energy on the Suncor Millennium project is probably somewhat less than calculated as N8 & N10 diluents. Biodegradation pathways of hydrocarbons rich in nitrogen and sulphur warrant further research.

Holowenko et al. (2000) reported 60 to 80% of the flux gas from tailing ponds to be methane with total emissions of about 12 g/m^2 per day from the active zone only. They also assumed 40-60% of the MLSB water surface, not the entire pond, to be an active bubbling zone. The pond surface was about 12 km^2 at that time while entire pond was 28 km^2 that includes beaches, dykes and berms.

Taking into account the surface area of 9.27 km^2 in 2008, 50% active surface, 12 g/day of methane from the active surface and bitumen production of 350 Kbbl/day, Syncrude CO_2eq emissions can be calculated as approximately 0.55 g/MJ (CH_4 factor 21; 6,100 MJ/bbl), or 0.65 g for methane CO_2eq (GWP factor 25). Using total pond surface of 28 km^2, as was done by Yeh et al. (2010), would boost this number to 1.97 g/MJ CO_2eq. Thus, it can be concluded that the measurements by Holowenko et al. (2000) could be in the realistic range of emissions and very close to our model numbers. Methane emissions in 2000 or earlier could be somewhat higher due to higher historic diluent loss prior to 2000. Holowenko et al. (2000) also found that CH_4 emissions from real MFT were produced from less than 1% of total carbon in MLSB.

They also reported that the rate of methanogenesis was dependent on temperature, but the amount of methane created was essentially the same after longer holding periods (516 days) meaning that over time all the lost diluent would be eventually transformed into GHG-s regardless of observed rate.

The Nodelcorp (2005) estimate also seems to be very close to GHG emissions from our Base GHG Model with 1.3 g CO_2eq/MJ vs. 3.8 g CO_2eq/MJ assumed by Yeh et al. (2010). Both numbers include emissions from landforms.

Siddique et al. (2007) found that only 15 to 23% of naphtha was metabolized by methanogenic bacteria in MFT despite the stimulation by a methanogenic medium. After 46 weeks, iso-paraffins and naphthenes were largely unchanged demonstrating either significant lag phase in fermentation, or partial or complete recalcitrance of branched hydrocarbons.

Siddique et al. (2008) produced a kinetic model for the production of methane. Again, there was an assumption made that 25% of the MLSB volume is methanogenic. The model estimated CH_4 production to be 8.9 to 400 million L, while Holowenko et al. (2000) estimates ~101 million L. Thus the Siddique et al. (2008) model can underestimate or overestimate CH_4 production. However, the results yield some valuable conclusions. Larger n-alkanes were degraded preferentially to shorter ones (C_{10}>C_6). Using 80% yield of methane fitted well with experimental numbers. One should keep in mind that hydrocarbons were added into old MFT that already went through original fermentation so that sulfate reduction and other pre-methanogenic fermentations were minimized. The model also successfully predicted the degradation of BTEX.

However, when real naphtha was used, less methane was produced. Siddique et al. (2008) concluded that only about 30% of naphtha is readily biodegradable despite using trace minerals and vitamins to enhance microbial processes. One metric ton of naphtha was estimated to produce ~280 m^3 of methane, meaning that only about 150 kg of carbon would partition into methane (15% by weight), which is almost 3 times less than our model results for N10 diluent that predicts 165.8 g of carbon in methane from 496.08 g of diluent or 44.6%. The results from Siddique et al. (2008) fit well with Clearstone (2011) measurements that also show much smaller methane evolution from ponds with 21% of methane evolved related to the diluent loss. However Clearstone measurements do not account for time lag between diluent loss and active fermentation, nor do they show the current GHG footprint of lost diluent.

Guo (2009), as discussed in Part I, provided some history of the MLSB pond and specified that fermentation, temperature and densification rates increased in 1994 and later. Part of the reason for the rapid onset of methanogenesis was the change in tailings discharge practices. In 1994 warm tailings were discharged mostly on the south side keeping temperature higher and constant.

FTT are the warmest tailings for any producer. This event could speed up the onset of bubbling. On the other hand, if tailings would be colder, gas production would be slower. If such slower methane emission was measured it would show much lower intensity just because of when and how the measurement was undertaken. This Base GHG Model eliminates such variability. Guo (2009) had access to original Syncrude measurement of the gas content in deeper layers of MFT. He also reported that gas content at both South and North side of the MLSB was lower in 2000 and 2002 than in 1999. Holowenko et al. (2000) took samples in summers of 1997 and 1998. This change clearly demonstrates variability in gas production that cannot be extrapolated to other ponds and producers or even to the same producer over time.

Guo (2009) also reported a change in the pH of MFT with the deeper layers changing pH over 1992 to 2003 from pH 8.6 to pH 7.8, which was attributed to CO_2 dissolution. Indeed, the south station measured increase in HCO_3^- ion from 720 mg/L to 1,600 mg/L over 1991 to 2003. Sulfate concentration at the same station decreased from ~40 mg/L in 1985 to ~20 mg/L in 1995, or lower in deeper layers. Chloride increased over the same period. Part of the reason for chloride increase could be more brackish ore supply and/or continuous recycling. Naphtha content at the south station also decreased in the period 1996 to 2002 meaning that Holowenko et al. (2000) measurements actually covered the period of higher naphtha concentrations in the MLSB and higher potential for bubbling. It also demonstrated the need for the control of time component in the measurement of GHG emissions.

3.2 Comparison of Base GHG Model Emissions with Measured Values

Table 5 shows methane and CO_2 emissions intensity calculated from our model compared with measured values for 2011 that were reported to the Climate Change Secretariat (AESRD) through the SGRR program.

Table 5. Comparison of measured and reported vs. Model pond intensity and total GHG emissions in 2011.

Company	**Model**			**Total CO_2eq**	
	CO_2	CH_4*	$\sum CO_2 + CH_4$	Model	Reported
	g CO_2eq/MJ	g CO_2eq/MJ	g CO_2eq/MJ	Kt	Kt
Shell	0.043	0.447	0.49	145	39.6
Suncor	0.063	0.636	0.699	448	287
Syncrude	0.068	0.675	0.743	580	787
CNRL	0.078	0.773	0.850	206	NA

* GWP factor in 2011 for methane (x 21) was used;
NA-not available

The values were calculated using data for diluent loss and bitumen production from ST39 reports (AER 2013), as shown in Tables 6 and 7. For modelling purpose, the Base GHG Model steps from Table 4 were adjusted to include real diluent loss (Table 8) and real diluent density in Table 2.

Results clearly depict that the difference between Model emissions and reported measured values are much smaller than between the Model and Yeh et al. (2010) values, thus confirming the applicability of the Model as a conservative estimate of GHG emissions from tailings ponds. The highest emission intensity could be at the CNRL site predominantly due to the higher diluent loss (Table 7) combined with carbon-rich naphtha diluent, while emissions at Shell were ~42% lower due to much lower diluent loss (both volume and mass), and less carbon-rich diluent (mix of pentane and hexane). Such a big difference also shows a need for a site specific approach instead of assuming the same emission factor derived from assumed pond areas.

The Model was conservative assuming that all lost diluent was fermented either into methane or carbon dioxide. Potential recalcitrance of some hydrocarbons, mineralization of carbon or production of other metabolic products and biomass can offset the fermentability of hydrocarbons from lost diluent.

It may be hard to determine if measured emissions originate from diluent loss in 2011, from 2010, or from a combination of any previous year with the influence of SO_4 reduction and recalcitrance of individual hydrocarbons. This Base GHG Model has an ability to eliminate such measurement uncertainty and estimate the total GHG emissions regardless of their dynamics.

4 OTHER POTENTIAL SCENARIOS

The Base GHG Model tells us where GHG emissions could be, but not where they really are, where they were in the past, or where they could be in the future. Table 8 lists 16 different scenarios for the modelling of CH_4 emissions. Scenarios 1 to 5 depict recent or historical emissions, while scenarios 6 to 16 look into future pathways that may decrease the emissions through lower diluent loss (scenarios 6 to 8), more aerobic conditions – aeration (scenarios 9 to 11) or optimized scenarios (12 to 16) when the combination of changes leads to significantly lower emissions.

Scenarios 1 to 3 estimate recent methane emissions using the 5-year (2008 to 2012) average diluent loss for three major producers (Table 7). CNRL emissions were omitted since they were struggling with production problems in a manner similar to older companies some time ago, although they achieved significantly lower diluent loss in 2012 of only 2.42 bbl/1,000 bbl of produced bitumen. Both factors for methane annual GHG effect, 21 and 25, were used since they create significant difference and Model results are shown in Table 8.

Scenarios 1 to 3 show that after taking the average diluent loss for the period 2008 to 2012, the CO_2eq/MJ for methane is even lower than estimated in the Base GHG Model with the estimated range of 0.47 to 0.66 g CO2eq/MJ for different diluents (producers) when factor 21 is used, or 0.56 to 0.79 g CO2eq/MJ when methane GWP multiplier of 25 is used.

Table 6. Bitumen production and diluent losses (m^3) from 2008 to 2012 from the ST 39 reports to the AER.

Company	**2008**		**2009**		**2010**		**2011**		**2012**	
	Diluent	Bitumen	Diluent	Bitumen	Diluent	Bitumen	Diluent	Bitumen	Diluent	Bitumen
Syncrude	74,912	20,079,406	58,614	19,644,050	80,279	20,291,019	74,184	20,354,891	61,493	19,532,894
Suncor	47,594	14,359,705	49,803	16,798,837	53,334	15,437,844	64,036	16,699,348	56,090	15,489,880
Shell	31,160	7,830,752	22,921	8,096,945	24,910	7,713,594	39,793	12,240,782	38,770	13,103,311
CNRL	2,719	55,114	57,701	3,603,553	26,564	6,310,747	11,820	2,759,757	14,459	5,985,672
Σ	156,385	42,324,977	189,039	48,143,385	185,087	49,753,204	189,833	52,054,778	170,812	54,111,757

Shell Albian (MRM) includes deliveries from Jackpine (JP).
Shell MRM shows significant metering differences (>100%) due to diluent use for pipeline transport.
All numbers are from ST-39 2008 to 2012 reports from the AER website accessible at http://aer.ca/data-and-publications/statistical-reports/st39

Table 7. Recent diluent volumetric loss (DVLF) per 1,000 units of bitumen volume (ST 39, AER 2013) calculated from Table 6.

Company	**2008**	**2009**	**2010**	**2011**	**2012**	**Average '08 to '12**
Syncrude	3.73	2.98	3.96	3.64	3.15	3.50
Suncor	3.31	2.96	3.45	3.83	3.62	3.44
Shell	3.98	2.83	3.23	3.25	2.96	3.22
CNRL	49.33	16.01	4.21	4.28	2.42	3.51 [1]
Weighted average[2]	3.69	3.93	3.72	3.65	3.16	**3.62**

[1] 2010 to 2012 average since CNRL Horizon is a new mine; average is 6.05 for the whole 2008-2012 period.

[2] Calculated from the sum in Table 6. Not applicable to Model since there is no average diluent.

Table 8. Different scenarios for methane CO_2eq/MJ from changing Model assumptions. Only factors different from Base GHG Model in Table 4 are presented. Values in the table rounded from Excel calculations. Factors in bold varied from Base Model.

Scenario	**Diluent**	**DVLF**	**VF_{voc}**	**AnF**	**SRBF**		**CH_4 g CO_2eq/MJ**	
No.	**2008 to 2012 average diluent losses**						**x 21**	**x 25**
1	P	**0.00322**	0.60	0.9	0.9		0.466	0.555
2	N8	**0.00344**	0.65	0.9	0.9		0.550	0.655
3	N10	**0.00350**	0.70	0.9	0.9		0.666	0.792
	Possible higher historical diluent losses							
4	P	**0.006**	0.60	0.9	0.9		0.87	1.035
5	N10	**0.006**	0.70	0.9	0.9		1.142	1.359
	Potential future lower methane CO_2eq emissions							
		Lower diluent loss						
6	N10	**0.002**	0.70	0.9	0.9		0.381	0.453
7	N10	**0.001**	0.70	0.9	0.9		0.190	0.226
8	P	**0.002**	0.60	0.9	0.9		0.290	0.345
		More aeration						
9	N10	0.004	0.70	**0.5**	0.9		0.423	0.503
10	P	0.004	0.60	**0.5**	0.9		0.322	0.383
11	P	**0.002**	0.60	**0.5**	0.9		0.161	0.192
		Optimized scenarios						
12	P	**0.002**	0.60	**0.2**	**0.7**		0.050	0.060
13	N10	**0.002**	0.70	**0.2**	**0.7**		0.066	0.078
14	P	**0.001**	0.60	**0.2**	**0.7**		0.025	0.030
15	N10	**0.001**	0.70	**0.2**	**0.7**		0.033	0.039
16	N10	0.004	0.70	**0.2**	**0.2**		0.038	0.045

Average industry methane emissions intensity for the same 2008-2012 period, adjusted for production and individual mine diluent losses, could be calculated as 0.58 and 0.69 g CO_2eq/MJ for the methane GWP factors 21 and 25, respectively, or 0.62 and 0.74 CO_2eq/MJ when CNRL is taken into account with high startup emissions.

All further scenarios in Table 8 used only P and N10 diluent estimates in order to show the range of numbers.

Higher historical losses (Table 9) show where and why emissions could have been in late 1990-s when Holowenko et al. (2000) performed measurements on MLSB. 50% higher diluent loss (6 vs. 4 volumes per 1,000 bbl of bitumen) would cause 50% higher emissions, which could be even higher if time delay is accounted for. Scenarios 4 and 5 show methane GHG in the range of 1.035 g CO_2eq/MJ for P diluent, to 1.36 g CO_2eq/MJ for heavy N10 diluent. Shell Muskeg River Mine was not operational at that time, so the value for P diluent is only theoretical. Still it depicts potential emissions intensity at the start of mining or diluent accumulation for later emissions. Had Yeh et al. (2000) used the true water surface for the derivation of bubbling areas, 1.36 g CO_2eq/MJ would be quite close to their estimate of CH_4 emissions as discussed previously.

Scenarios 6 to 16 demonstrate where potential methane GHG intensity could be if there is significant change in operational practices reflected in lower diluent volumetric loss – lower DVLF factor – or there is a change in technology for FTT treatment that decreases the supply of hydrocarbon available for methanogenesis reflected in more aerobic conditions.

With greater recovery of diluent (Scenarios 6 to 8), potential CH_4 GHG intensity would decrease proportionally to the maximum of 0.453 g CO_2eq/MJ if diluent loss would be 2/1,000 volumes (scenario 6), or half of that value (scenario 7) if allowed naphtha loss would be only 1/1,000 vol. of bitumen.

Lighter diluent (Scenario 8) would create even lower emissions than naphtha N10 diluent.

Stimulation of aerobic processes was assessed by lowering AnF factor from 0.9 to 0.5 and presented in scenarios 9 to 11. It would have an effect similar to lowering diluent loss to tailings (scenarios 6 to 8) even if diluent loss stays in the similar range as it is today. Thin lift aerobic deposition of MFT as already proposed by Shell as their AFD tailings technology, or Suncor in the TRO process, could be additionally enhanced by aerating MFT, which of course needs to be tested in the field.

Maximum lowering of methane emissions can be achieved if there are multiple approaches. Optimized Scenarios 12 to 16 present options to simultaneously lower diluent loss (lower DVLF), increase pond aeration (lower AnF) and modify chemistry (lower SRBF) in order to decrease the supply of fermentable substrates to methanogenic bacteria. These measures would push methane intensity from tailings ponds below 0.1 g CO_2eq/MJ, but lowering SRBF may result in higher RSC emissions, depending on the chemicals applied.

Scenario 16 demonstrates that minimization of methane GHG effect can be also achieved even with today's diluent loss of ~4/1,000 bbl but with intensive aeration and chemical treatment that could stimulate other fermentations prior to potential methanogenesis. In that scenario, CH_4 emissions could be below 0.05 g CO_2eq/MJ even for the heavy carbon rich N10 diluent.

Intensive aerobic processes could also increase volatile losses, but that potential change in hydrocarbon availability was neglected in this exercise.

Table 9. Historical volumetric diluent loss per 1,000 units of bitumen volume from ST 43 (AER 2008).

Company	**1967 to 1995**	**1996**	**1997**	**1998**	**1999**	**2000**	**2001**	**2002**	**2003**	**2004**	**2005**	**2006**	**2007**
Suncor	8.89	7.97	5.76	5.38	5.55	6.71	6.90	5.11	5.31	3.61	3.00	3.57	3.66
Syncrude	8.27	5.19	5.42	5.51	4.58	5.79	5.90	3.95	3.86	4.03	3.66	3.11	3.52
Shell	-	-	-	-	-	-	-	-	16.99	8.93	8.08	5.23	4.20

It can be concluded that changing tailing technologies and advances in understanding of fermentation processes would lead to significant lowering of methanogenic GHG emissions from oil sands mining operations.

Brandt (2012) recommended the use of ERCB (now AER) data series for the calibration of the models. In our case, AER's data series (ST 39 and ST43) are the basis for the development and application of this model.

4.1 Other Fermentable Substrates

One may ask if bitumen hydrocarbons are fermentable in addition to lost diluent. Strausz et al. (2010) performed detailed analysis of Athabasca hydrocarbons and found only about 0.04% of acyclic saturates with maximum $C_n = 19$, and 1.68% of monocyclic with $C_{n\ max} = 18$. The question is bio-availability of these two fractions. If they were easily fermentable they would be already gone over millions years of geological storage. Thus, these "lighter" natural fractions could be neglected as candidates for fermentation for the development of the Model. In addition, it would be hard to say whether these fractions are fermented more than in natural bitumen deposits, but could be a part of future validation modelling and research.

Not to be neglected, biodegradation of naphthenic acids was established by Herman et al. (1994) and Han et al. (2009). Although present at the ppm level in water they may be significant contributor over time, while their partitioning onto solids needs yet to be clarified.

Much more serious candidates for microbial fermentation are citrate (previously used by Shell), demulsifiers, and lost glycol and deicing agents. Annual use of glycol and de-icing agents was 539 and 309 m^3 respectively (Shell 2012), and as such can be neglected as a significant contributor to GHG when compared to 35,391 m^3 of lost diluent. Glycol is partially collected (138 m^3), while a good portion is probably evaporated from engines as a coolant.

Citrate was used by Shell for water softening and as an extraction additive. Citrates are completely soluble and represent a desirable substrate for microbial processes. Since it is oxygen rich compound it can be assumed that all of the citrate is fermented quickly while the slurry is warm and aerobic. Thus, assuming that all 4,380 t used was pure citrate (MW $C_6H_5O_7^{3-}$ = 189 g/mol) and not other forms such as tri-sodium citrate or hydrated forms of salts, the use of citrate would produce at most 6,118.1 t of CO_2 if completely fermented to CO_2 only. It is safe to assume that citrate would be a preferred substrate for other metabolic functions, but whatever the number it pales in comparison to methanogenic losses from diluent fermentation. Recently, citrate use may have been discontinued.

Demulsifiers are used to separate bitumen from water and impurities. Their use is limited compared to diluent losses – i.e. Syncrude used 1,217.6 m^3 of demulsifier (Syncrude 2014), but due to affinity to bitumen it is counted that most of it, 97.9% is gone to the upgrader or refineries with bitumen, while a small portion (252 m^3) is lost to ponds with FTT and fermented. Due to a very small loss compared with diluent loss, demulsifier loss is neglected for the Base GHG

Model, but it is relatively easy to add it for the real accounting of fermentable materials transformation into GHG-s.

5 MODEL VALIDATION AND FUTURE GHG PROJECTIONS

5.1 Model Validation and Application

The Base GHG Model is a good start for future development and validation. Once the true volatile losses of diluent are verified (VF_{VOC}), it may be easier to establish fermentation pathway ratios, such as the aerobic – anaerobic ratio, than to organize complicated measurement campaigns, especially in the future when the number of ponds and tailing deposits increases. Such experiments can be done in the lab or pilots since some difference in lab/pilot measurements vs. field should not create huge changes in the value of SRB or MEF factors. The determination of aerobic-anaerobic ratio(AnF) in ponds may be a bigger challenge due to varying pond shape, depth, MFT interface depth, wind direction, redox processes, etc.

Further Base GHG Model development, validation and application will be important for the oil sands industry and regulators. During validation some of the main foci could be:

- Confirmation of true total diluent loss through the measurements of light and fermentable hydrocarbons in the FTT stream
- Adjustment of factors to reflect:
    - Real diluent composition with % of carbon closer to true values,
    - Methane : CO_2 ratio due to difference in hydrocarbons – i.e. cyclic and aromatic fuels have less hydrogen
    - SRBF factor may highly depend on CT or NST production on site or subsequent exposure of MFT to air
- Other sources of fermentable carbons with residual bitumen as the primary source
- Additives that may contribute to GHG-s or change fermentation pathways,
- Indirect CO_2 emissions such as pyrite oxidation and buffering, etc.

5.2 Model vs. New Oil Sands Projects

As one can see from the modelling of GHG emissions, paraffinic diluent, due to lower specific gravity and higher volatility, would produce lower GHG emissions from the methanogenic fermentation. All new projects proposed by the oil sands companies are based on this process.

Imperial Kearl (full capacity ~345 Kbbl/day) started operation in 2013, Fort Hills (~190 Kbbl/day) may start in ~2016 (Fort Hills 2011), Joslyn (~100 Kbbl/day) although currently shelved may be opened later. Shell’s Jackpine Expansion (~300 Kbbl/day) should achieve full capacity ~2020. After 2021, when TECK Frontier project is planned to start (277 Kbbl/day) the majority of bitumen production could be from the paraffinic process decreasing the average GHG emissions from the mined bitumen.

That fact, combined with the today's regulated diluent loss of 4/1,000 vol. would contribute to the lowering of future GHG emissions intensity by at least 20% compared with today's measured fugitives from the tailing ponds. Lowering of diluent loss also has economic benefits since diluent is about twice as expensive as bitumen. Some new projects may also look into further processing of the froth treatment tailings such as gasification of hydrocarbons. Such a process would virtually eliminate methane production in ponds and may be viable if there is significant increase in the price of natural gas.

5.3 Change in Tailing Treatment Technologies

Almost complete recovery or transformation of lost diluent into CO_2 instead of methane is not impossible. As new technologies are developed, there are two possible tested pathways:

1. Processing of FTT and recovery of lost diluent in the range of at least 70 to 90%. One such technology was piloted by Titanium Corporation (http://www.titaniumcorporation.com/) with the original goal of the recovery of heavy minerals.
2. Thin lift deposition of MFT or TT. Tailing are mixed with a polymer and spread on the beach or inside specially designed cells in 30 to 100 cm layers. Centrifuge cake could be also dried in a similar way.

   This approach creates aerobic conditions and any diluent will partially evaporate and/or be fermented and mostly transformed into CO_2. Such a scenario represents minimized GHG emissions intensity from tailings. The results of Air Emissions Monitoring Programs were presented in Suncor (2012). Table 6 in that document shows that MFT tailings in pond 6 were measured to emit 16.9 $\mu g/m^2 \cdot s$ of methane, while the emissions from the DDA at that pond were 71% lower despite higher solids content, confirming that aerobic deposition of diluent-rich tailings results in lower CH_4 emissions.

   Methane emission numbers from previous calculations from fresh FFT that is dried, after assuming similar volatility as in Table 4, show that the amount of carbon from P and N10 diluent in tailings spread in thin layers will be 218.8 g/bbl and 293.5 g/bbl of bitumen, respectively. Complete transformation of this carbon into CO_2 emissions will result in 0.132 CO_2/MJ and 0.176 g CO_2/MJ for P and N10 diluent, respectively. Such emissions should be considered to be almost negligible even if volatile diluent is taken into account.

Other technologies that were already piloted or may be developed soon would encompass retorting of some sort, either of bitumen ore, froth or of FTT (EPI 2013). In such cases there would be no diluent used or lost to tailing ponds and thus no significant methane emissions from any ponds. Retorting of ore, if economically feasible, would increase recovery of bitumen while not having fluid tailings created at all. Emissions would be mostly CO_2 and, if combined with hydrocracking, could result in significant reduction of total CO_2 GHG emissions from surface mining or its intensity per barrel of produced fuel. Some of these technologies may have the ability to reduce even legacy tailings.

6 KNOWLEDGE AND RESEARCH GAPS

From the aforementioned it seems that there are two pathways to lower fugitive GHG emissions from ponds or MFT:

1. Avoid or decrease the loss of diluent
2. Decrease methanogenesis from legacy MFT by changing fermentation pathways or applied tailing treatment technology

Segregation and treatment of diluent enriched froth tails may be the best approach to control future methanogenic emissions although other technologies that enhance fermentations other than methanogenic should not be neglected.

Due to partitioning of diluent to bitumen, bitumen removal from legacy MFT is another option that could have multiple environmental, but also economic benefits. In addition such a scenario would allow for more certain remediation and reclamation of tailing ponds.

Additional research that would enhance the knowledge around GHG emissions from tailings could be in the following areas:

- Real VOC losses, from ponds and from a project.
- Environmental destiny of VOC-s (from ponds and beaches) as odors and GHG-s, and optimization of management methods.
- Current quantities of diluent in legacy MFT with specific focus on submerged bitumen-rich tailing interface.
- Partitioning of diluents and other pollutants in ponds.
- Biodegradation of residual bitumen and other hydrocarbons including naphthenic acids, including long-term studies.
- Life cycle of methane including its biodegradation by methanotrophs and contribution to anoxic conditions under ice (DO depletion).
- Mineralization of CO_2, especially in deeper layers and when MFT is treated *in-situ* as e.g., Suncor Pond 5.
- Solubility of generated gasses with pressure increase in pond depths
- Indirect inorganic GHG emissions from oxidation of tailing minerals (e.g., pyrite (Siddique et al. 2014), and siderite).
- Other lost carbon such as soil stockpiles, CO_2 from soil reaction with sulphur from stockpiles etc.
- CO_2 liberated from acid rains through buffering processes.
- Nitrate addition to remediate ponds.
- Aerobic treatments – aeration or advanced oxidation.

MFT quality if potentially placed in an EPL is an issue that may need to be considered. There are few potential scenarios for EPL content, some of which were discussed in the Tailing Roadmap and Action Plan (Sobkowicz 2012):

- MFT that contains FTT. This scenario has few options that are related to type of diluent. The worst case scenario comes from combining froth from different mines into one pond, resulting in increased concentrations of bitumen and diluent. Paraffinic treatment would also add additional rejected asphalthene into such future lake sediment.

- Regular MFT from middling without FTT residue. Such scenario happens when FTT are shipped to another pond, i.e. from Aurora North to Mildred Lake, or when FTT are segregated as proposed for Imperial Kearl and Total Joslyn mines.
- MFT depleted from hydrocarbons – preferred to previous two options. Additional technology is applied to remove lost bitumen during or after mining. Solid % not significantly changed.
- Concentrated or condensed MFT at the bottom of EPL with the purpose to decrease the volume and seal pond bottom. Such dense MFT that is produced for example by centrifugation may be also covered by additional sand or overburden to decrease flux of contaminants. A variant of this scenario would include removal of bitumen.

7 CONCLUSIONS

Both Part I and Part II of this overview and Model demonstrate that current information, and to a degree measurement practices, are a kind of educated guessing when it comes to methanogenic lifecycle emissions intensity from tailing ponds and total fugitive emission intensity per MJ of energy in produced bitumen. Measurements being reported through SGRR are much closer to the realistic values, but cannot provide some long-term answers. Based on lag time in fermentation, and information on the mechanics of froth tailings transfer and deposition on Syncrude MLSB pond, it can be said that:

- Three events worked together to boost bubbling in MLSB in the late 1990-s – high historic diluent loss (>8 vol./1,000 vol. of bitumen), sulfate depletion in deeper layers, and higher temperature of discharged tailings.
- Measurement of emissions at one point in time and one place or project cannot be extrapolated to future emissions.
- Due to changing regulations and technologies, lower future emissions may be expected.
- Less than half of the diluent that reaches the pond is or will become methane.
- Diluent in a pond also undergoes other processes that decrease availability for the creation of methane.
- A site-specific and pond-specific approach to emission modelling is necessary due to differences in losses and type of diluent at this time, and differences in tailing treatment technologies in the future.
- The time component for the regulation and modelling of GHG emissions is important. The onset and duration of each year emissions based on the previous year diluent loss needs to be established. It can be individualized to each project in order to avoid uncertainty and expensive post-mining measurements and reporting.

The Base GHG Model shows that:

- GHG emissions from one site or one producer cannot be universally applied to all oil sands mines.
- Emissions of CH_4 from current diluent losses are far lower (< 1.0 g CO_2eq) than reported elsewhere, i.e. in Yeh et al. (2010), while historically they were higher proportionally to lost diluent.
- Lighter diluents create less methane due to lower carbon mass and higher volatility.
- Aerobic biodegradation and/or aerobic tailing treatments significantly decrease generation of methane.
- Other anaerobic microbial processes such as sulphate reduction contribute to diluent depletion in tailings ponds. They may also result in significant creation of reduced sulphur compounds, depending on chemistry of tailings.

Newer technologies and tailings treatments have potential and are expected to significantly lower fugitive GHG emissions from bitumen in tailings ponds. Production of CT or NST, if using sulfate, may decrease available substrates due to SRB activity, while aerobic MFT treatments will result in transformation of available carbon mostly to CO_2.

Current CH_4 emissions, as measured, are probably the consequences of previously higher diluent loss and the delay in the fermentation of hydrocarbons. At present it is hard to evaluate the time of that delay, which has to be considered for the evaluation of fugitive emissions after the end of mining.

Provincial and Federal GHG reporting systems are valuable sources of information about GHG-s and other released compounds. They are based on measurements and verified by third parties and regulators. In combination with SGRR, the Model could provide more transparent picture of state of the environment.

Further validation and development of this Model seems to be reasonable, which, with its inherent flexibility, results in a more realistic estimate of true GHG emissions from tailing ponds and their potential changes in the future. It pinpoints potential future trends in lowering GHG emissions from oil sands.

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9 ACRONYMS AND GLOSSARY

AER	Alberta Energy Regulator; formerly Energy Resources Conservation Board or ERCB
AESRD	Alberta Environment and Sustainable Resource Development, the Ministry
AFD	atmospheric fines drying, drying MFT in up to 1 m layers, may be mixed with flocculant
AI-EES	Alberta Innovates – Energy and Environment Solutions, Provincial arms-length research funding agency http://ai-ees.ca
Aliphatic	composed of linear or branched carbon chains, not cyclic or aromatic
AN	Aurora North, Syncrude's oil sands mining project north-east of Mildred Lake
Aquiclude	impermeable area underlying or overlying a water body,
bbl	barrel of bitumen, traditional unit for volume of petroleum, approximately 159 liters
BML	Base Mine Lake, also known as West-In-Pit, former mine pit
BTEX	a mix of aromatic hydrocarbons mostly containing benzene, toluene, ethyl-benzene and xylene isomers
C&R	closure and reclamation
CAPP	Canadian Association of Petroleum Producers
CEMA	Cumulative Environmental Management Association
Centrate	watery residue after centrifugation and production of paste from MFT or FFT
CH_4	methane

C_n	Hydrocarbon with n number of carbon atoms, e.g. C_5 is pentane with 5 carbon atoms
CNRL	Canadian Natural Resources Limited, an oil sands company with its Horizon mine about 70 km north of Fort McMurray, has an upgrader on site
CST	Coarse Sandy Tailings, contain >90% sand in solids, may be used for reclamation, also SCT or S
CO_2	carbon dioxide
CO_2eq	carbon dioxide equivalent, a measure of global warming potential (GWP) of a gas obtained after multiplication of its mass by a factor, i.e. 21 or 25 for methane
CT	composite tailings, made of sand mix with fines (MFT) and coagulant (e.g. FGD)
Diluent	hydrocarbon mix used for separation of bitumen from solids and water
DO	dissolved oxygen, usually in water expressed in mg/L
EML	end-of-mine-lake, used interchangeably with EPL by some companies
EPL	end pit lake, mining hole filled with water and potentially with tailings and/or overburden
Eq.	equation
ERCB	former Energy Resources Conservation Board, now AER http://www.aer.ca/
ETF	External tailing facility, a tailing storage pond outside of mining area and above ground level
FFT	fine fluid tailings from production, contain ~6 to15% solids, mostly clay
FGD	Flue gas desulphurization, capturing and neutralizing gasses from the upgrader in oil sands
FTT	Froth Treatment Tailings obtained after mixing of bitumen froth with diluent in order to separate hydrocarbons from water and solids; rich in residual diluent
GC-MS	gas chromatography-mass spectrometry – analytical technique used for chemical analysis of some organic compounds
GHG	Greenhouse gas
GHGRP	Greenhouse Gas Reporting Program
GWP	Global Warming Potential, factor showing warming potency compared to CO_2
H_2S	hydrogen sulfide, toxic gas created by the reduction of sulfate in tailings ponds
ha	hectare, one hundred are, metric unit for area, 100 by 100 metres
HCO_3^-	hydrogen bicarbonate ion, created by dissolution of CO_2 in water, especially under pressure

JP or JPM	Jackpine Mine, Shell's 300 Kbbl/day oil sands mining project adjacent to MRM
Kbbl	one thousand barrels
Kg	kilogram, metric unit for mass, one thousand grams, roughly the weight of 1 L of water
Kow	partitioning coefficient for solubility of a compound between water and octanol, usual logarithmic in value
Kt	Kiloton, one thousand tonnes (metric)
LCA	life-cycle assessment or analysis
Log	logarithmic value of the number
m^2	square metre
MFT	mature fine tailings, aged clay-rich tailings (FFT) approximately with 30+% solids (processing sludge)
MFTD	drying of MFT, same as AFD or TRO
mg	milligram, one thousandth of a gram
MJ	megajoule, a measure of contained energy
ML	Mildred Lake – the name of Syncrude's original bitumen mining project
MLSB	Mildred Lake Settling Basin, a settling pond that received most attention
Mm^3	million cubic metres
MRM	Muskeg River Mine, Shell's bitumen mining project
MSL	mineral surface lease, area leased by the Province to a company
N8	light naphtha, a type of diluent used by oil sands industry
N10	heavy naphtha, diluent with longer hydrocarbons than N8, thus having higher specific density and carbon content
NA	not applicable
nC_5	pentane with the carbon atoms in straight chain configuration (not branched)
NGO	Non-Government Organizations
NPRI	National Pollutant Register Inventory
NRU	naphtha recovery unit, same as TSRU
NST	non-segregating tailings, a mix of sand with TT
OSPW	Oil sands process-affected water, sometimes called process-affected water or PAW
P	Paraffinic, diluent composed of pentane-hexane mix
PAH	poly-aromatic hydrocarbons, composed of fused benzene rings, usually toxic, some carcinogenic, heavily regulated at very low levels, mostly insoluble in water

pH	physical unit for acidity or basicity of solution; pH<7 the solution is acidic, pH~7 solution is neutral and at pH>7 solution is alkaline
Pond	tailing storage structure, usually made of earth and with some water in the middle
Recalcitrant	resistant to chemical change or microbial action
RSC	Reduced sulphur compounds, usually smelly or toxic sulphur-rich chemicals, e.g. H_2S or benzothiphene
S	Sand, sandy tailings; sometimes denoted as CST or SCT
SCT	straight coarse tailings
SGER	*Specified Gas Emitters Regulation*, Alberta's program for lowering GHG emissions
SGRR	*Specified Gas Reporting Regulation*
Shell	Shell Canada Limited. A part of the Dutch energy company with 2 operating oil sands mines, Muskeg River Mine (MRM) and Jackpine. 3rd project, Pierre River, currently on hold. Shell's upgrader is located beside Edmonton, AB
SIR	Supplemental Information Request, Regulator's request for additional information
SO_4	sulfate, anion in water that can be reduced to H_2S by bacteria
SRB	Sulphur Reducing Bacteria can transform SO_4 to elemental S or H_2S to gain energy
ST39, ST43	statistical series about bitumen and energy production and consumption published by AER, see references for links
STP	South Tailings Pond, Suncor's tailing storage pond south of Millennium mine
Suncor	Suncor Energy Inc., a Canadian company with few oil sands projects, Millennium mine is operational with an upgrader on site, while Fort Hills is approved
SWIM	provincial Single Window Information Management system
SWSS	South-West Sand Storage, Syncrude's tailings pond
Syncrude	Syncrude Canada Ltd., a joint venture company with Mildred Lake and Aurora North operational oil sands mines with an upgrader at Mildred Lake, Aurora South mine delayed
t/y	tonnes per year (metric)
TECK	TECK Resources – a mining company that submitted application for the Frontier oil sands mine
Thickener	large bowl shaped vessel with conical bottom used to recover water and concentrate solids in tailings such as FFT in oil sands
TLD	thin lift drying, another name for treating/drying MFT, same as TRO or AFD

TRO	Tailing Reduction Operation, Suncor's MFT drying technology (project)
TOTAL	Total Joslyn, an oil sands mining project by French Total E&P, north of Fort McMurray. Currently on hold due to economics (Sept 2014).
TSRU	tailing solvent recovery unit, recovery of solvent (diluent) from fresh FTT
TT	thickened tailings, produced within thickeners from FFT, should contain 30 to 50% solids and coagulant and/or flocculant
WT	whole tailings, obtained by mixing back SCT and FFT
VOC	volatile organic compound(s), usually evaporate easier than water